

PHONON DISPERSION IN EQUIATOMIC BINARY ALLOYS

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The computations of the phonon dispersion curves (PDC) of four equiatomic K based binary alloys viz. $K_{0.5}Li_{0.5}$, $K_{0.5}Na_{0.5}$, $K_{0.5}Rb_{0.5}$ and $K_{0.5}Cs_{0.5}$ to second order in local model potential is discussed in terms of real-space sum of Born von Karman central force constants. Instead of the concentration average of the force constants of metallic Li, Na, K, Rb and Cs, the pseudo-alloy-atom (PAA) is adopted to compute directly the force constants of four equiatomic K-based binary alloys. The exchange and correlation functions due to Hartree (H) and Ichimaru-Utsumi (IU) are used to investigate influence of screening effects. The phonon frequencies of four equiatomic K-based binary alloys in the longitudinal branch are more sensitive to the exchange and correlation effects in comparison with the transverse branches. While, the frequencies in the longitudinal branch are suppressed due to IU-screening function than the frequencies due to static H-screening function.

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1. Introduction

The $A_{1-X}B_X$ ($A=K$; $B=Li, Na, Rb, Cs$) 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 $K_{0.5}Li_{0.5}$, $K_{0.5}Na_{0.5}$, $K_{0.5}Rb_{0.5}$ and $K_{0.5}Cs_{0.5}$ systems since the lattice dynamics of the pure alkalis have been investigated in detail. But the work on the comprehensive study of static and vibrational properties their binary alloys is almost negligible [1-9]. Only Soma *et al.* [7] have studied the phonon dispersion curves of for $Cs_{0.7}K_{0.3}$, $Cs_{0.3}K_{0.7}$, $Cs_{0.7}Rb_{0.3}$, $Cs_{0.3}Rb_{0.7}$ and $Rb_{0.71}Cs_{0.29}$ alloys. Very recently Gajjar *et al.* [4] have studied the lattice dynamics of bcc $Cs_{0.3}K_{0.7}$ alloy. Experimentally, Kamitakahara and Copley [8] have studied the lattice dynamics of $Rb_{1-X}K_X$ alloys with $X=0.06, 0.18$ and 0.29 by neutron scattering. Vora and co-workers [1, 2] have reported the static and vibrational properties of equiatomic Na-based binary alloys using model potential formalism. Very recently, Gajjar *et al.* [3] have studied the lattice dynamics of bcc $Cs_{0.3}K_{0.7}$ alloy. Recently, Chushak and Baumketner [9] have reported the dynamical properties of liquid $Cs_{0.3}K_{0.7}$ alloy. For the interatomic interaction, they have used an ancient empty core model [9] and generated phonon dispersion curves of the liquid alloy. So we have decided to work on four equiatomic K-based binary alloys i.e. $K_{0.5}Li_{0.5}$, $K_{0.5}Na_{0.5}$, $K_{0.5}Rb_{0.5}$ and $K_{0.5}Cs_{0.5}$. By treating the K based binary alloys as a pseudo-alloy-atom (PAA), real space sum analysis [1, 2] is used to compute phonon dispersion relation along three major symmetry directions. Well recognized linear model potential of Gajjar *et al.* [10, 11] is used to describe the electron-ion interaction for the pseudo-alloy-atom of K-based four binary alloys. For the first time an advanced and more recent local field correlation function due to Ichimaru-Utsumi (IU) [12] 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 [13].

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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 $D_{\alpha\beta}(\mathbf{q})$ is the dynamical matrix in which the force between two ions depends only upon the distance between them is given by,

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

here $\phi(r)$ is the interionic pair potential, r_α and r_β are the 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,

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

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.

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

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

Where F (q) is the energy wave number characteristic given by

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

With Ω_0 , $V_b(q)$, $\varepsilon_H(q)$, 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 is given by [10, 11]

$$V(q) = \frac{-8\pi Z}{\Omega_0 q^2} \left(\cos(qr_c) - \frac{(qr_c)^2}{(1 + (qr_c)^2)} \right). \quad (7)$$

here, Z, Ω_o and r_c are the valence, atomic volume and parameter of the model potential of four equiatomic K-based binary alloys, respectively.

Moreover, instead of taking the concentration average of pure metallic alkali elements, we have treated here $A_{1-x}B_x$ ($A=K$; $B=Li, Na, Rb, Cs$) as a pseudo-alloy-atom (PAA), which is more meaningful approach [10, 11]. Following definitions for the parameters of alloy $A_{1-x}B_x$ is adopted for making the computations of the phonon dispersion curves (PDC) of $K_{0.5}Li_{0.5}$, $K_{0.5}Na_{0.5}$, $K_{0.5}Rb_{0.5}$ and $K_{0.5}Cs_{0.5}$ alloys [1, 2].

$$r_c = (1 - X)r_{c(A)} + X r_{c(B)}, \quad (8)$$

$$Z = (1 - X)Z_{(A)} + X Z_{(B)}, \quad (9)$$

$$\Omega_o = (1 - X)\Omega_{o(A)} + X \Omega_{o(B)}, \quad (10)$$

$$M = (1 - X)M_{(A)} + X M_{(B)}, \quad (11)$$

$$k_F = (1 - X)k_{F(A)} + X k_{F(B)}. \quad (12)$$

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. 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.

3. Results and discussion

The input parameters viz. Z, Ω_o and k_F used in the present computations of the phonon dispersion curves (PDC) of equiatomic K based binary alloys are taken from [14]. The model potential parameter r_c (in atomic units) for Li, Na, K, Rb and Cs metals are taken as 0.7736, 1.2180, 1.4029, 1.7877 and 1.9106, respectively.

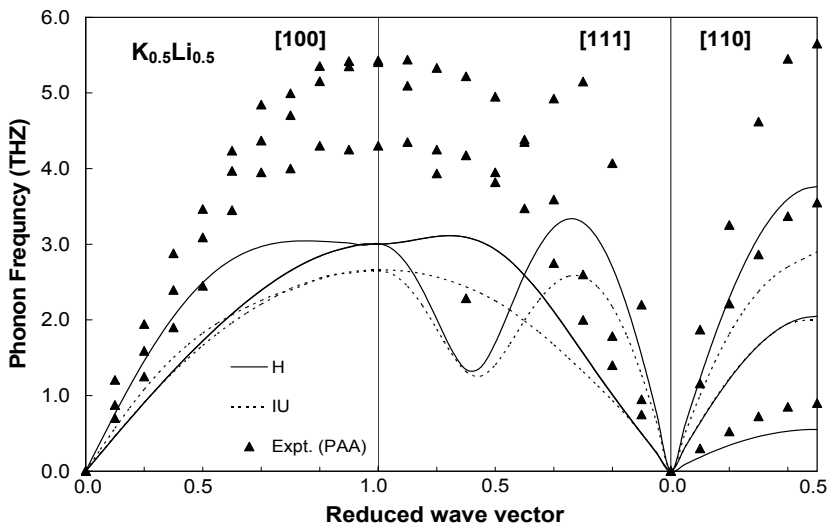


Fig. 1. Phonon dispersion curves of $K_{0.5}Li_{0.5}$ alloy.

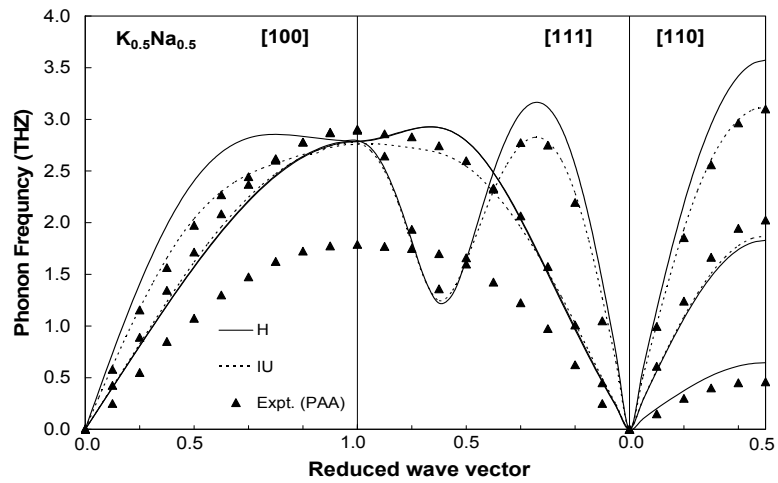


Fig. 2. Phonon dispersion curves of $K_{0.5}Na_{0.5}$ alloy.

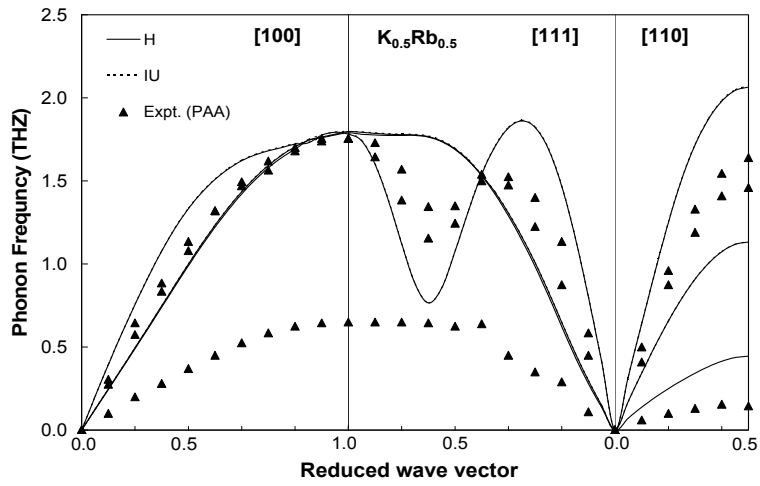


Fig. 3. Phonon dispersion curves of $K_{0.5}Rb_{0.5}$ alloy.

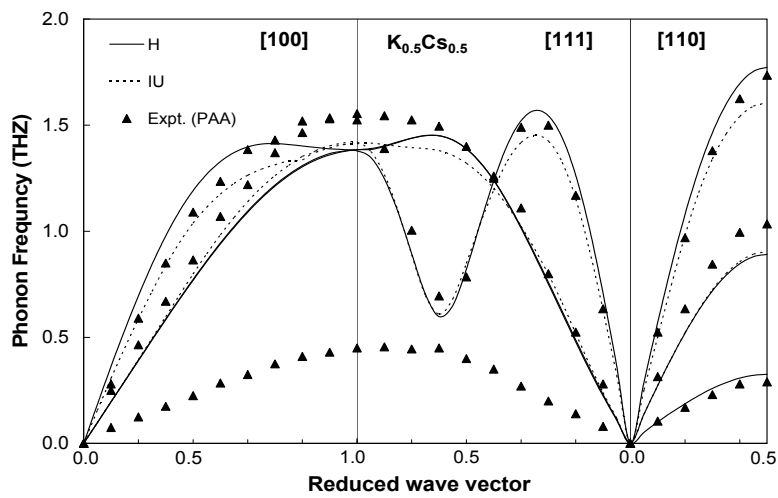


Fig. 4. Phonon dispersion curves of $K_{0.5}Cs_{0.5}$ alloy.

The phonon dispersion curves (PDC) of four equiatomic K-based binary alloys viz. $K_{0.5}Li_{0.5}$, $K_{0.5}Na_{0.5}$, $K_{0.5}Rb_{0.5}$ and $K_{0.5}Cs_{0.5}$ along [100], [110] and [111] directions of high symmetry, which are shown 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 frequencies in the longitudinal branch are suppressed due to IU-screening function than the frequencies due to static H-screening function. While in the transverse branch effect of exchange and correlation enhances slightly the phonon modes. It is found that at the zone boundaries of [100] and [111] directions, i.e., for the larger momentum transfer the effect of local field correlation is 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. Also, we observe that when we move from $K_{0.5}Li_{0.5}$ to $K_{0.5}Cs_{0.5}$ alloys, the phonon frequency decreases with increase in the average volume of the solid alloys. The phonon dispersion curves (PDC) are seen to be quite unsatisfactory except near the small k-regions ($k < 0.6$ or so) because of the average data of the pure metallic elements. For $K_{0.5}Li_{0.5}$, $K_{0.5}Na_{0.5}$, $K_{0.5}Rb_{0.5}$ and $K_{0.5}Cs_{0.5}$, present results deviate more from the experimental points. The results for equiatomic K-based alloys can be improved by fitting the parameters of the potential to the phonon frequency. But present study is independent of such fitting hence in some cases the discrepancy is observed. The experimental phonon frequencies of such alloys are not available, but the experimental values of phonon frequency are estimated from the pure metallic components [15-19], which are shown in Figures 1-4. This comparison favours and confirms our formulation of pseudo-alloy-atom (PAA) of four equiatomic K-based binary alloys. Also, 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 the solid binary alloys.

4. Conclusions

At the end, we conclude that the present form of the pseudo-alloy-atom (PAA) model is successful in explaining the phonon dispersion relation of equiatomic K-based binary alloys and hence it could be explored for predicting the behavior of other such solid solutions. The comparison of present theoretical findings with the estimated experimental data helps us to note that the binding of $A_{1-x}B_x$ ($A=K$; $B=Li, Na, Rb, Cs$) 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. Such study is under progress and the results will be reported in due course of the time. 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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