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Theoretical Investigations of Lattice Dynamics and Dynamical Elastic Constants of $Rh_{0.6}Pd_{0.4}$ and $Rh_{0.2}Pd_{0.8}$ Binary Alloys Using Transition Metal Pseudopotential

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The experimental and theoretical studies of various properties of transition metals alloys are important in the material science research. Inspired by such fact, in the present communication we have carried out theoretical studies of lattice dynamics and dynamical elastic constants of $Rh_{0.6}Pd_{0.4}$ and $Rh_{0.2}Pd_{0.8}$ using transition metal pseudopotential. The form of the pseudopotential used in the present calculation is directly derived from generalized pseudopotential theory (GPT) and no phenomenology was used to construct pseudopotential in real space. The pseudopotential was found to be successful for the study of static, dynamic and transport properties of many transition metals. In absence of any experimental and theoretical studies first time we are presenting theoretical results of phonon dispersion for both the alloys which may be considered as prediction. Due to unavailability of experimental results, presently computed elastic constants are comparable with those studied recently by using Exact Muffin-Tin Orbitals method within the Perdew-Burke-Ernzerhof exchange-correlation approximation. Encouraged by present approach, we would like to extend it further for the remaining binary alloys of transition metals alloys.

Keywords: Pseudopotential, Transition metals alloys, Binary alloys, Elastic constant.

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1. INTRODUCTION

Pseudopotential method in its numerous forms (local and non-local) have done tremendous job for calculating large number of static, dynamic and electronic properties of metals, liquid metals, metallic glasses and metallic alloys with good degree of success [1].

In condensed matter physics, wide range of theoretical studies of transition metals and transition metal alloys have been carried out. The main focus is to investigate structural, mechanical, elastic, thermodynamic and electronic properties of transition metals and their metallic binary and ternary alloys [2]. The reason for such interest is due to unusual electronic and mechanical behavior of transition metals. Thus, transition metals and their alloys require different treatment due to the presence of *d*-electrons in pseudopotential formalism. Transition metal series possesses several interesting properties such as a high melting and boiling points, high electrical and thermal conductivity, hardness, malleability, or the optical and magnetic behavior [2]. The theoretical and experimental studies of various physical properties of transition metals alloys are important in many areas of science and technology. These alloys have broad applications in micro electronic industry, in nuclear reactors, in medical devices and metallurgy [2].

In the present paper, we have studied theoretically Rh-Pd based binary alloys within the framework of pseudopotential theory. We have studied phonon frequencies in symmetry directions and dynamical elastic constants (C_{11}, C_{12} and C_{44}) for Rh_xPd_{1-x} with $x = 0.6$ and 0.2. For the present calculation, we have used pseudopotential proposed by Pandya et al. [3] for the transition metals. They have derived form of the pseudopotential directly from generalized pseudopotential theory due to Harrison and no phenomenology was used for the pseudopotential in real space. Such pseudopotential was successfully used to investigate large number of static, dynamical and electronic properties of empty *d*-band metals (Ca, Sr and Ba), partly filled *d*-band metals (Cu, Ag and Au) and *d*-band metals (Pd, Pt, Ni, Rh, Ir, Fe and Co) [3-6]. During literature survey, we have found that the complete theoretical studies of physical properties of 4*d* transition metals alloys using pseudopotential theory and first principles method are very scanty. Even experimental studies of lattice dynamics and elastic constants of many single crystals 4*d* transition metals binary alloys have not been carried out yet. In such circumstances, theoretical investigations of many properties of such alloys serve as a good prediction.

This paper is divided into three main sections. Section 2 is devoted to mathematical formulation which are used in the present calculations. We present our computed results in graphical and tabulated manner in section 3. The results are presented and discussed in section 3. Section 4 is concluded with some remarks.

2. THEORY

To obtain the vibrational frequency $\omega_{\vec{q},\lambda}$ for $\vec{q},\lambda$ mode, one essentially requires to diagonalize the dynamical matrix for different values of $\vec{q}$ (for more details see [5]). The total dynamical matrix $D_{\alpha\beta}(\vec{q})$ is made up of three contributions: one coulombic contribution $D^{c}_{\alpha\beta}(\vec{q})$, second electronic contribution $D^{E}_{\alpha\beta}(\vec{q})$ and third repulsive contributions $D^{R}_{\alpha\beta}(\vec{q})$.

The coulombic contribution is given as

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$$D^{c}_{\alpha\beta}(\vec{q}) = \frac{2}{M}\begin{bmatrix} \sum_Q G_1(|\vec{Q}+\vec{q}|)\,(\vec{Q}+\vec{q})_\alpha(\vec{Q}+\vec{q})_\beta - \\ \sum'_Q G_1(|\vec{Q}|)Q_\alpha Q_\beta + \\ \sum'_R\{ \phi'_1(R)\delta_{\alpha\beta} \\ +2\phi''_1(R)R_\alpha R_\beta(1-\cos(\vec{q}\cdot\vec{R}))\} \end{bmatrix} \quad (2.1)$$

The expressions for $G_1(|\vec{Q}|)$, $\phi'_1(R)$ and $\phi''_1(R)$ are given in reference [5].

The electronic contribution is given by,

$$D^{2}_{\alpha\beta}(\vec{q}) = \frac{2}{M}\begin{bmatrix} \sum_Q F(|\vec{Q}+\vec{q}|)(\vec{Q}+\vec{q})_\alpha(\vec{Q}+\vec{q})_\beta \\ -\sum'_Q F(|\vec{Q}|)\,Q_\alpha Q_\beta \end{bmatrix} \quad (2.2)$$

$$D^{3}_{\alpha\beta}(\vec{q}) = \frac{6\Omega}{M}\sum_{\vec{Q}_1,\vec{Q}_2,\vec{Q}_3}\begin{bmatrix} (\vec{q}+\vec{Q}_1)_\alpha(\vec{q}+\vec{Q}_2)_\beta \times \\ \Gamma^{(3)}(\vec{q}+\vec{Q}_1,-\vec{q}-\vec{Q}_2,\vec{Q}_3) \\ \times V_{ion}(|\vec{q}+\vec{Q}_1|) \\ V_{ion}(-|\vec{q}+\vec{Q}_2|) \\ V_{ion}(|\vec{Q}_3|) \\ \times \Delta(\vec{Q}_1-\vec{Q}_2+\vec{Q}_3) \end{bmatrix} \quad (2.3)$$

Here, $F(Q)$ is an energy wave number characteristic [5]. The $F(Q)$ contains bare-ion pseudopotential $v_{ion}(q)$, static dielectric function $H(Q) - 1$ and exchange and correlation function $Y(Q)$. Here, we have used $Y(Q)$ due to Taylor [6]. The expression for repulsive contribution $D^{R}_{\alpha\beta}(\vec{q})$ is taken from [5]. $D^{E}_{\alpha\beta}(\vec{q})$ contains pseudopotential. In the present study, we have used pseudopotential proposed by Pandya et al. [3] which has following form in the q-space.

$$v_{ion}(q) = \frac{1}{\Omega}\left[-\frac{8\pi Z^*}{q^2}\cos(qr_c) + \frac{\beta}{\left[1+q^2r_d^2\right]^4}\right]. \quad (2.4)$$

Here, Z^* is the effective valency, Ω is atomic volume, r_c is core radius, r_d is the radius of d-electrons and β is a hybridization parameter.

In the next section, we discussed method to determine three pseudopotential parameters (r_c, r_d and β) along with two Born-Mayer type parameters (α_B and γ_B).

In the long wavelength limit ($q \to 0$) dynamical elastic constant for fcc are obtained by using following set of equations [7].

$$C_{11} = \frac{1}{6a}\sum_n N(n)\left[x^2k^{(n)}_{xx} + y^2k^{(n)}_{yy} + z^2k^{(n)}_{zz}\right], \quad (2.5)$$

$$C_{44} = \frac{1}{12a}\sum_n N(n)\begin{bmatrix}(y^2+z^2)k^{(n)}_{xx} + (z^2+x^2)k^{(n)}_{yy} \\ +(x^2+y^2)k^{(n)}_{zz}\end{bmatrix}, \quad (2.6)$$

$$C_{12} + C_{44} = \frac{1}{3a}\sum_n N(n)\begin{bmatrix}yzk^{(n)}_{yz} + zxk^{(n)}_{zx} \\ +xyk^{(n)}_{xy}\end{bmatrix}, \quad (2.7)$$

where, a is lattice constant and $N(n)$ is the number of atoms at the n^{th} neighbor separation. In the present calculations, we have adopted the method used by Bhatia et al. [7] to compute tensor force constant ($K_{\alpha\beta}(R)$).

The bulk modulus is given by,

$$B = \frac{[C_{11}+2C_{12}]}{3}. \quad (2.8)$$

3. RESULTS AND DISCUSSION

In the present pseudopotential (2.4), we have five adjustable parameters namely r_c, r_d , β, α_B and γ_B. Following Pandya et al. [3], five parameters are reduced to three parameters (β, α_B and γ_B) in following manner. He has calculated r_c by using relation $r_c = 0.51R_aZ^{*-\frac{1}{3}}$.

Here, R_a is the radius of Wigner-Seitz sphere. Now, as in the atomic states, the wave functions of the d-electron are going beyond Wigner- Seitz radius by about 2 to 3 %, so they have consider to take $r_d = R_a$ [3]. Now pseudopotential contains only three adjustable parameters β, α_B and γ_B which are obtained from zero pressure condition and overall good agreement of calculated longitudinal phonon frequencies with experimental findings at (q, 0, 0) [6].The input parameters used in the calculation along with potential parameters are tabulated in Table 1.

Table 1 – Pseudopotential parameters along with input parameters (all are in a.u.)

	$Rh_{0.6}Pd_{0.4}$	$Rh_{0.2}Pd_{0.8}$
Z	1.94	1.98
M	104.426	105.942
Ω	95.502	98.034
$\boldsymbol{\beta}$	1.8198	2.4266
$\boldsymbol{r_c}$	1.15934	1.16158
$\boldsymbol{R_a}$	2.83516	2.86012
$\boldsymbol{\alpha_B}$	70	100
$\boldsymbol{\gamma_B}$	1.7	1.8

In the present calculation, for Pd we have used actual valency ($Z = 2$) and for Rh effective valency ($Z = 1.9$) as used by Antonov et al. [8]. The remaining input parameters including valency have been calculated for Rh-Pd binary alloys using simple combination rule.

Pandya et al. [3, 6] have studied phonon dispersion curves in symmetry directions for Pd and Rh with good degree of success (maximum deviation for both metals is within 10 %) [3, 6].

Elastic constants relate with stress and strain which can be studied by using two different approaches first one is static and another one is dynamic approach. We have adopted dynamic approach and calculated dynamical elastic constants C_{11}, C_{12}, C_{44} and bulk modulus B and compared with available theoretical results due to unavailability of experimental results tabulated in Table 2.

Computed results of C_{11}, C_{12}, C_{44} and bulk modulus B vary with theoretical results by 7.9, 4, 26 and 5.9 % for $Rh_{0.2}Pd_{0.8}$ respectively. Zoubi et al. [2] have calculated elastic constants and bulk modulus of both the alloys $Rh_{0.6}Pd_{0.4}$ and $Rh_{0.2}Pd_{0.8}$ using Exact Muffin-Tin Orbitals method within the Perdew-Burke-Ernzerhof exchange correlation approximation. For $Rh_{0.6}Pd_{0.4}$, the variation of C_{12} with theoretical result is only 0.6 % and the variation of C_{11} and bulk modulus B are 23 and 11 %.The maximum deviation of C_{44} is around 40 %. From the present study, we can conclude that our computed results using pseudopotential theory are in a good agreement with sophisticated first principles calculation.

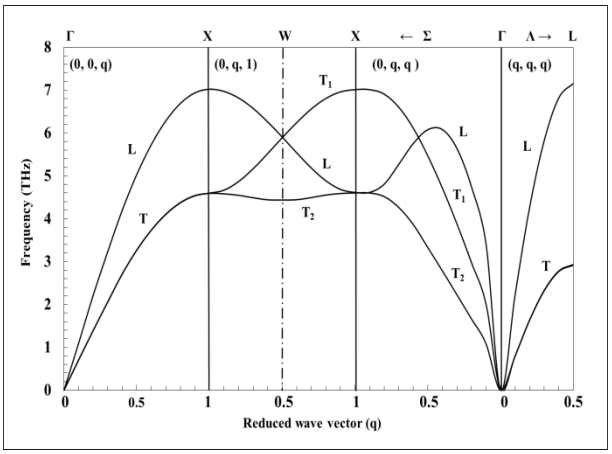

Fig. 1 – Phonon dispersion curves of $Rh_{0.2}Pd_{0.8}$ in symmetry directions

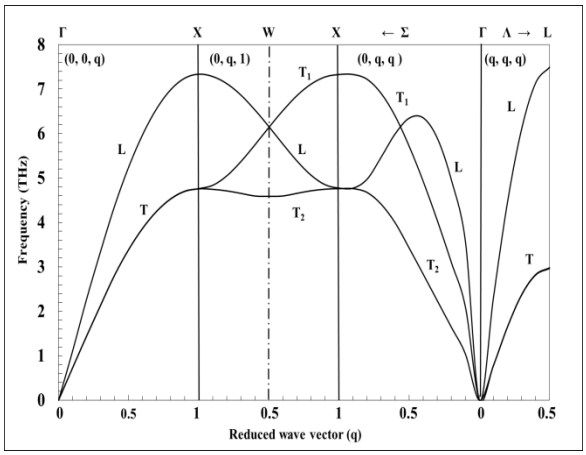

Fig. 2 – Phonon dispersion curves of $Rh_{0.6}Pd_{0.4}$ in symmetry directions

Table 2 – Dynamical elastic constants (C_{11}, C_{12} and C_{44}) and bulk modulus B for $Rh_{0.6}Pd_{0.4}$ and $Rh_{0.2}Pd_{0.8}$. All quantities are in 10^{12} dyne/cm^2

Alloy	$Rh_{0.6}Pd_{0.4}$		$Rh_{0.2}Pd_{0.8}$	
	Present	Other result [2]	Present	Other result [2]
C_{11}	2.66	3.46	2.43	2.64
C_{12}	2.03	2.05	1.85	1.93
C_{44}	1.06	1.83	0.96	1.30
B	2.24	2.52	2.04	2.17

In the next course of the calculation, we have studied phonon dispersion of both the alloys which are shown in Fig. 1 and Fig. 2, respectively. Both the alloys possess fcc structure. From both the graphs in absence of any neutron scattering data, our predicted dispersion curves are found to be correct because the special feature of the fcc structure is satisfied i.e. crossing of longitudinal (L) and transverse branch (T_1) of (0, q, 1) plane are found at wave vector $q = 2\pi/a$ (0, 0.5, 1). Such predicted phonon frequencies are helpful to understand many thermodynamic properties like thermal expansion, specific heats, Debye temperature, Debye Waller factor and melting temperature.

4. CONCLUSIONS

We, in the present communication, investigated lattice dynamics and dynamical elastic constants of 4d transition metal alloys Rh_xPd_{1-x} (with $x = 0.6$ and 0.2) using transition metal pseudopotential. The pseudopotential is directly extracted from generalized pseudopotential theory (GPT) and free from any kind of phenomenology. In absence of any experimental results, our computed results of elastic constants are comparable with those obtained by using highly sophisticated first principles method [2]. Moreover, in absence of any neutron scattering data for both the alloys, predicted phonon dispersion curves show special features of fcc structure. Such success will be helpful to understand many thermodynamic functions at extreme environment (at high temperature and high pressure) which is very useful in material research. Encouraged by such observation, we would like to extend such studies for remaining 4d transition metal binary alloys.

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