

## Theoretical study of structural energy, phonon spectra, and elastic constants of Rh and Ir

N SINGH

Department of Physics, M D University, Rohtak 124 001, India

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**Abstract.** The transition metal pair potential (TMPP) is used to study band structure energy of Rh and Ir. Both metals are found to be most stable in fcc structure down to atomic volume  $0.5V_0$ . The pressure at  $0.5V_0$  is found to be 5.235 Mbar and 9.216 Mbar in Rh and Ir, respectively. The TMPP is also used to study other properties of these metals like cohesive energy, phonon frequencies at observed volume. The bulk moduli and elastic constants of these metals at observed volume are calculated by including the volume contribution.

**Keywords.** Structural energy; phonon spectrum; elastic constants.

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### 1. Introduction

The pressure of several megabar is needed to derive phase transformation in transition metals. For example, a solid-solid phase transformation of Mo was found in a shock compression experiment [1] at a pressure of 2.1 Mbar and a temperature of 4100 K. Rhodium and iridium possess unusual mechanical properties and can bear high stresses at normal temperature. For example, they are characterized by brittle failure of single crystals, which occurs after a long-range of plastic deformation. The phonon spectra of these metals exhibit Kohn anomalies. Recently, Sigalas and Papaconstantopoulos [2] have used many-body alloy Hamiltonian method [MBAH] to study the total energy and elastic constants of several transition metals including Rh and Ir. The total energy is calculated as a function of atomic volume for fcc, bcc and hcp structures of Rh. It is found that Rh stabilizes in fcc phase at observed atomic volume. Greenberg *et al* [3], in a specific case of Ir, found that the contribution of three-body interaction to the lattice properties turns out to be small. Several versions of the interatomic potentials were proposed by them. A final choice for the potential could not be made owing to insufficient experimental information, particularly lack of data on phonon spectra. Over the past 40 years, phonon spectra of crystals have been obtained by neutron-scattering experiments for a wide class of systems, ranging from metals to semiconductors, insulators to alloys. The notable exceptions are the fcc transition metals Rh and Ir, despite their technological importance in many catalytic

applications. Recently, detailed investigations of phonon spectra for Rh have been presented by Eichler *et al* [4]. Experimental [5] information of phonon spectra for bulk Ir was available at a few wave vectors along  $[100]T$  and  $[110]T_1$  directions only. Very recently, Heid *et al* [6] have reported the experimental results of phonon frequencies of Ir along symmetry directions alongwith their theoretical results. The Animalu–Heine model potential and modified Animalu–Heine model potential have been used by Ivanov *et al* [5] and Katsnelson *et al* [7] to study the mechanical properties and phonon spectra of Rh and Ir theoretically. In order to interpret the results of complex structures of transition metals and rare-earths, it is still desirable to have simple methods of general applicability which are easy to handle and can reproduce the results of most of their properties close to the experimental values. In the present paper, we have chosen to study the structural energy of Rh and Ir using the TMPP, because sufficient experimental [4–6] information of phonon spectra and mechanical properties of these metals is available now in the literature.

The paper has been divided into four sections. In §1, a brief introduction of the paper is given. Section 2 is used to describe the necessary formalism in brief. In §3 the calculations and results, effective pair potential (TMPP), structural energy, cohesive energy, bulk modulus, elastic constants, Cauchy ratio and phonon spectra are presented. Finally, we summarize the results in §4.

## 2. Theory

Considering the non-interacting band model for  $s$ - and  $d$ -electrons, the ion-ion interaction for transition metals is written as the sum of  $s$ - $s$  contribution,  $d$ - $d$  repulsive and  $d$ - $d$  attractive contributions as follows [8]:

$$V_{\text{eff}}(r) = [V_{FE}(r) + V_d(r) + V_{dd}(r)] \exp(-\pi k_B T r / \hbar v_F), \quad (1)$$

where  $V_{FE}$  is obtained in second-order perturbation theory using the Heine–Abarenkov [9] model potential and a rational dielectric function [10]. A part of bandstructure contribution obtained in this way exactly cancels the ion-ion Coulomb contribution. The final expression for  $V_{FE}(r)$  comes out to be [11]

$$V_{FE}(r) = \frac{Z_s^2 e^2}{r} \sum_{n=1}^3 A_n \cos(k_n r + \alpha_n) \exp(-\lambda_n r), \quad (2)$$

where the amplitude  $A_n$  and the phase  $\alpha_n$  are defined as

$$A_n = 2d_n |\hat{v}(q_n)|^2, \quad (3)$$

and

$$\alpha_n = \delta_n + 2 \arg \hat{v}(q_n), \quad (4)$$

respectively. The modulus of normalized Heine–Abarenkov [9] model potential,

$$\hat{v}(q_n) = D \sin q_n r_c / q_n r_c + (1 - D) \cos q_n r_c,$$

where  $D$  and  $r_c$  are potential parameters, is defined as

$$|\hat{v}(q_n)| = \left[ \frac{D^2}{2(k_n^2 + \lambda_n^2)r_c^2} (\cosh 2\lambda_n r_c - \cos 2k_n r_c) + \frac{(1-D)^2}{2} (\cosh 2\lambda_n r_c + \cos 2k_n r_c) + \frac{D(1-D)}{(k_n^2 + \lambda_n^2)r_c} (\lambda_n \sinh 2\lambda_n r_c + k_n \sin 2k_n r_c) \right]^{1/2}, \quad (5)$$

and

$$\arg \hat{v}(q_n) = \tan^{-1} \times \left[ \frac{[D/((k_n^2 + \lambda_n^2)r_c)](k_n \tanh \lambda_n r_c - \lambda_n \tan k_n r_c) - (1-D) \tanh \lambda_n r_c \tan k_n r_c}{[D/((k_n^2 + \lambda_n^2)r_c)](\lambda_n \tanh \lambda_n r_c + k_n \tan k_n r_c) + (1-D)} \right]. \quad (6)$$

The parameters  $k_n$ ,  $\lambda_n$ ,  $d_n$  and  $\delta_n$  are functions [11] of the electron radius  $r_s \cdot q_n = k_n + i\lambda_n$  is the pole of the inverse dielectric function. For detail derivations of  $V_d(r)$  and  $V_{dd}(r)$ , we refer the paper of Wills and Harrison [8] (hereafter referred as WH). The final analytical expressions of attractive and repulsive  $d$ - $d$  contributions are defined as

$$V_d(r) = -Z_d \left[ 1 - \frac{Z_d}{10} \right] \left[ \frac{12}{n} \right]^{1/2} \frac{28.1 \hbar^2 r_d^3}{\pi m r^5}, \quad (7)$$

and

$$V_{dd}(r) = Z_d \frac{225 \hbar^2 r_d^6}{\pi^2 m r^8}, \quad (8)$$

respectively. Here  $r_d$ ,  $Z_d$  and  $n$  are the  $d$ -state radius, number of  $d$ -electrons in the  $d$ -band and coordination number, respectively. The temperature dependence in effective ion-ion interaction has been included through damping factor,  $\exp(-\pi k_B \text{Tr}/\hbar v_F)$ , obtained by Takanaka and Yamamoto [12]. Here  $v_F = \hbar k_F/m$  is the Fermi velocity and  $k_B$  is the Boltzmann constant.

Using the interionic potential,  $V_{\text{eff}}(r)$ , the radial  $K_r$  and tangential  $K_t$  force constants are given by

$$K_r = \frac{d^2 V_{\text{eff}}(r)}{dr^2} = K_r^{FE} + K_r^d + K_r^{dd}, \quad (9)$$

and

$$K_t = \frac{1}{r} \frac{dV_{\text{eff}}(r)}{dr}, = K_t + K_t^d + K_t^{dd}, \quad (10)$$

where

$$K_r^{FE} = \frac{Z_s^2 e^2}{r^3} \sum_{n=1}^3 A_n \cos(k_n r + \alpha_n) \exp(-\tilde{\lambda}_n r) \times [2 + 2\tilde{\lambda}_n r + \tilde{\lambda}_n^2 r^2 - k_n^2 r^2 + 2k_n r(1 + \tilde{\lambda}_n r) \tan(k_n r + \alpha_n)], \quad (11a)$$

$$K_r^d = V_d(r) \left[ \frac{30}{r^2} + \frac{10y}{r} + y^2 \right] \exp(-yr), \quad (11b)$$

$$K_r^{dd} = V_{dd}(r) \left[ \frac{72}{r^2} + \frac{16y}{r} + y^2 \right] \exp(-yr), \quad (11c)$$

and

$$K_t^{FE} = \frac{Z_s^2 e^2}{r^3} \sum_{n=1}^3 A_n \cos(k_n r + \alpha_n) \exp(-\tilde{\lambda}_n r) \times [1 + \tilde{\lambda}_n r + k_n r \tan(k_n r + \alpha_n)], \quad (12a)$$

$$K_t^d = -V_d(r) \left[ \frac{5}{r^2} + \frac{y}{r} \right] \exp(-yr), \quad (12b)$$

$$K_t^{dd} = -V_{dd}(r) \left[ \frac{8}{r^2} + \frac{y}{r} \right] \exp(-yr), \quad (12c)$$

with

$$y = \frac{\pi k_B T}{\hbar v_F}, \quad (13)$$

and

$$\tilde{\lambda}_n = \lambda_n + y. \quad (14)$$

Using  $K_r$  and  $K_t$ , the interionic force constant  $K_{\alpha\beta}$  is defined as

$$K_{\alpha\beta}(r) = \frac{d^2 V_{\text{eff}}(r)}{dr_\alpha dr_\beta} = \left[ \delta_{\alpha\beta} - \frac{r_\alpha r_\beta}{r^2} \right] K_t + \frac{r_\alpha r_\beta}{r} K_r. \quad (15)$$

Here  $\alpha$  and  $\beta$  are cartesian components  $x, y, z$ . The dynamical matrix

$$D_{\alpha\beta}(q) = \sum_l K_{\alpha\beta}(r_l) [1 - \exp(-iq \cdot r_l)], \quad (16)$$

is used to calculate the phonon frequencies.

The bulk modulus ( $B$ ) can be obtained by differentiating the total energy of the metal twice and finally we get [13, 14]

$$B = V \frac{\partial^2}{\partial V^2} \left( \frac{1}{2} \sum_{i \neq 0} V_{\text{eff}}(r_i) \right) + \Delta_{bs}. \quad (17)$$

The volume contribution  $\Delta_{bs}$  to  $B$  arises from the volume dependence of the bandstructure part of energy  $\sum_q V_{bs}(q)$ . The analytical expression of  $\Delta_{bs}$  comes out to be

$$\Delta_{bs} = V \left( 2 \frac{\partial^2}{\partial V_0 \partial V_{osc}} + \frac{\partial^2}{\partial V_{osc}^2} \right) \sum_q V_{bs}(q). \quad (18)$$

$\partial/\partial V_0$  operates on explicit volume term while  $\partial/\partial V_{osc}$  operates on volume dependence of the dielectric function  $\epsilon(q)$  only.

The elastic constants for cubic crystals in long-wavelength limit [15]  $\bar{C}_{11}$ ,  $\bar{C}_{12}$  and  $\bar{C}_{44}$  can be obtained easily once the force constants are known. By including volume-dependent contribution,  $\Delta_{bs}$ , we can get the elastic moduli using the following relations:

$$C_{11} = \bar{C}_{11} + \Delta_{bs}, \quad (19a)$$

$$C_{12} = \bar{C}_{12} + \Delta_{bs}, \quad (19b)$$

$$C_{44} = \bar{C}_{44}. \quad (19c)$$

It is to be noted that  $C_{44}$  remains unaffected by volume forces, because it involves only homogeneous strain at constant volume [13,14].

The effective potential defined by (1) is short ranged and it is fitted to a Gaussian expansion of the form

$$V_{\text{eff}}(r) = \frac{Z_s^2 e^2}{r} \sum_i C_i \exp(-\beta_i r), \quad (20)$$

by least square fitting method. Fitted values of  $C_i$  and  $\beta_i$  are given in table 1. The maximum deviation in the fitted values of the effective potential at a few points up to  $r = 3.7\pi/k_F$  is found to be 1.0 mRy for both the metals. Here  $k_F$  is Fermi-wave vector.

### 3. Calculations and results

There is a large overlap between electron densities of core and valence electrons in transition metals. Therefore, it is very difficult to distinguish between conduction and core

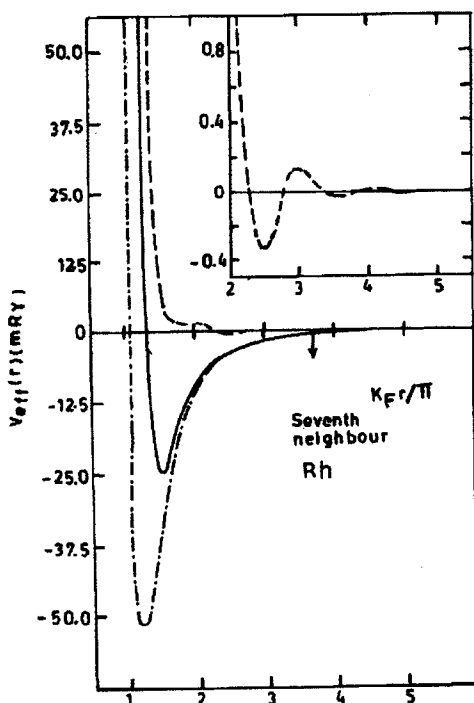
**Table 1.** Coefficient ( $C_i$ ) in Ry and exponential decays ( $\beta_i$ ) in a.u.<sup>-1</sup> for effective pair potentials.

Rh		Ir	
$C_i$ (Ry)	$\beta_i$ (a.u. <sup>-1</sup> )	$C_i$ (Ry)	$\beta_i$ (a.u. <sup>-1</sup> )
162036.2	2.360963	150521.4	2.216420
-109133.2	1.799754	-129898.8	1.715583
75433.2	1.449932	89521.91	1.406388
-64080.44	1.210825	-157460.7	1.129895
34255.43	1.147245	126846.1	1.107453
-31.84	0.549197	-36.75	0.521604
4.77	0.401874	2.07	0.291697

electrons clearly in  $d$ -band metals. In this paper, the calculations for Rh and Ir are done by considering the configurations  $4d^7 5s^2$  and  $5d^7 6s^2$ , respectively. The atomic radius  $r_0$  at equilibrium is calculated from the observed [16] atomic volume. The atomic radius at  $T = 0$  K is extrapolated using the linear expansion coefficient data given in [17].  $d$ -electron orbital radii  $r_d$  for these metals are taken from [8]. In this paper  $r_d$  will not be considered as a fitting parameter as it is obtained by WH by using  $d$ -band width of the respective transition metal. The potential [9] parameters  $D$  and  $r_c$  are determined by fitting the elastic constant ( $C_{44}$ ) and bulk modulus ( $B$ ). The values of ( $D, r_c$ ) so obtained are found to be (0.40 a.u., 1.723 a.u.) and (0.13 a.u., 1.565 a.u.) for Rh and Ir, respectively.

### 3.1 Effective pair potential

The effective pair potentials calculated for Rh and Ir using (1) are shown in figures 1 and 2, respectively. The values of  $s$ - and  $d$ -electron contributions to  $V_{\text{eff}}(r)$  at equilibrium are found to be (5.62 mRy and  $-30.62$  mRy) and (6.0 mRy and  $-37.0$  mRy) in Rh and Ir, respectively. The  $d$ -electron contribution is found 5.5 times more than the  $s$ -electron contribution at the equilibrium position in both the metals. The magnitude of oscillatory part due to  $s$ -electron is very small and hardly shows any structure in the total effective potential. The depth of the potential well increases and the equilibrium position of the



**Figure 1.**  $V_{\text{eff}}(r)$  vs  $r$  for Rh. Dashed, dot-dashed and solid lines represent the contribution due to  $s$ -electrons,  $d$ -electrons and sum of the two contributions, respectively. In the inset the  $s$ -electron contributions is shown on a magnified scale.

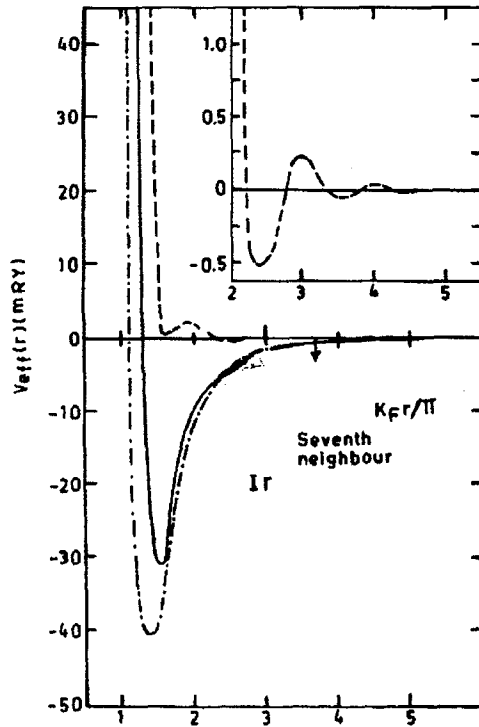
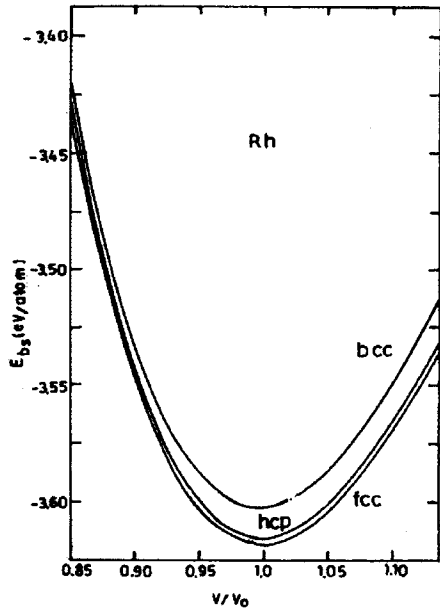


Figure 2.  $V_{\text{eff}}(r)$  vs.  $r$  for Ir. The rest of the legend is the same as that of figure 1.

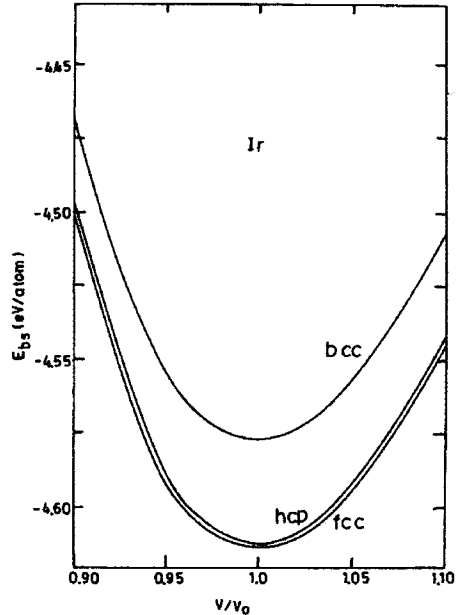
$V_{\text{eff}}(r)$  shifted away from the centre as we go from  $4d \rightarrow 5d$  metal.  $V_{\text{eff}}(r)$  decreases faster as we increase  $r$  beyond equilibrium position and becomes almost negligible around seventh nearest neighbour for both the metals. Thus the contribution up to seventh shell is found sufficient to achieve convergence while computing structural properties of the metals under consideration.

### 3.2 Bandstructure energy

In the present study of Rh and Ir the calculation is done for three crystal structures bcc, fcc and hcp for an ideal axial ratio  $c/a$  down to compressed atomic volume  $0.5V_0$ , where  $V_0$  is observed [16] atomic volume. The bandstructure energy  $[(1/2)\sum_i V_{\text{eff}}(r_i)]$  curves as function of atomic volume are shown in figures 3 and 4 for Rh and Ir, respectively. The fcc phase is found lowest in energy for both Rh and Ir. The present results for Rh are similar to those drawn by Sigalas and Papaconstantopoulos [2], as both calculations predict that Rh and Ir stabilize in fcc phase at all the atomic volumes considered so far. However, the calculated energy difference in the present case is considerably small for all volumes than the energy difference found by Sigalas and Papaconstantopoulos [2], this is because we have considered only the structural contributions to the energy. The augmented-plane wave (APW) and tight-binding (TB) methods used for calculating the total energy are certainly better than the first-principle method followed by us. It is to be noted that these authors



**Figure 3.** Bandstructure energy  $E_{bs} = 1/2 \sum_{i \neq 0} V_{\text{eff}}(r_i)$  for fcc, bcc and hcp structures of Rh as a function of atomic volume.  $V_0$  is the observed atomic volume.



**Figure 4.** Bandstructure energy  $E_{bs} = 1/2 \sum_{i \neq 0} V_{\text{eff}}(r_i)$  for fcc, bcc and hcp structures of Ir as a function of atomic volume.

considered the contributions up to third- and second-nearest-neighbours, while calculating the total energy for Rh and Ir, respectively. On the other hand, the bandstructure energy is calculated by us considering the contributions up to 7th nearest-neighbours for both Rh and Ir. The stability of the bcc and hcp lattice with respect to fcc lattice as a function of atomic volume is shown in figures 5(a) and 5(b) for Rh and Ir, respectively. The structural energy of hcp phase is found very close to the fcc phase over most of the volume range considered, which is most reasonable since the two structures have the same first- and second-nearest-neighbours distance.

### 3.3 Cohesive energy, bulk modulus, elastic constants and phonon frequencies

The force constants defined by (15) in the present paper combined with (2) given by Squires [18] are used to calculate the elastic constants of Rh and Ir. The TMPP defined by (1) and the effective pair potential obtained by WH are basically same. Therefore, we have compared the calculated results of elastic constants and bulk modulus with those obtained by WH in table 2. The cohesive energy is calculated by taking the sum of (i) the values obtained using (2) defined by Wills and Harrison [19] and (ii) the bandstructure energy  $[(1/2)\sum_i V_{\text{eff}}(r_i)]$  defined in the present paper. The calculated values of the cohesive energy are found to be 7.07 eV and 8.01 eV for Rh and Ir, respectively. The experimental [20]



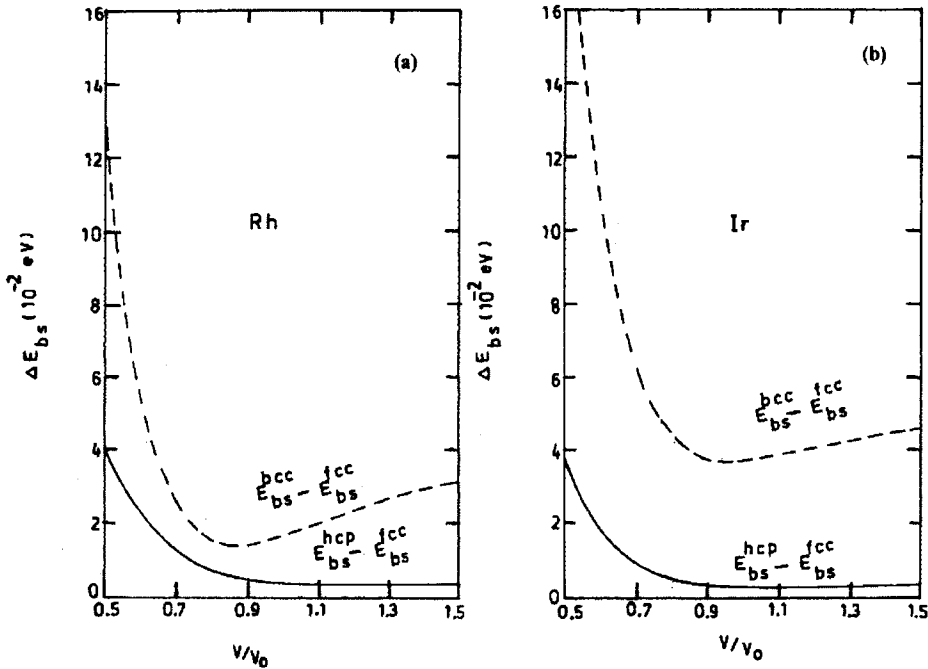


Figure 5. The bandstructure energy of bcc and hcp phase relative to fcc phase ( $E_{bs}^{bcc} - E_{bs}^{fcc}$ ) and ( $E_{bs}^{hcp} - E_{bs}^{fcc}$ ), respectively, as a function of atomic volume for Rh and Ir.

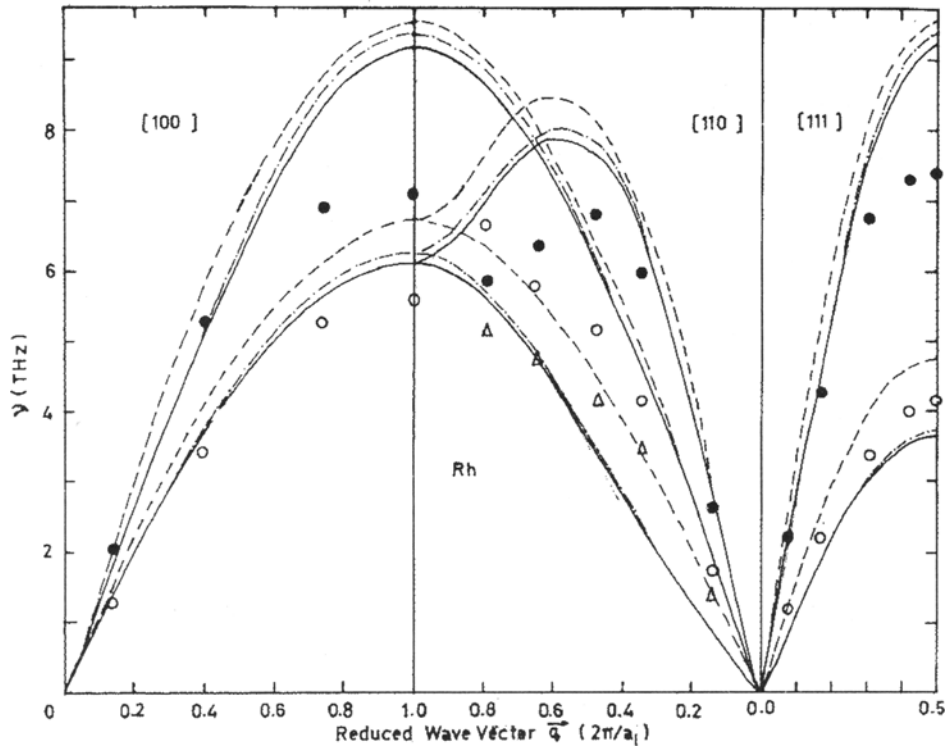
values of cohesive energy are 5.75 eV and 6.94 eV for Rh and Ir, respectively. The corresponding results obtained by WH are 8.24 eV and 8.03 eV. The volume contribution ( $\Delta_{bs}$ ) is found to be  $-0.282$  Mbar and  $-0.471$  Mbar for Rh and Ir, respectively. The calculated values of bulk modulus ( $B$ ) for Rh and Ir have been improved by 12% and 16%, respectively, by adding  $\Delta_{bs}$  to it. The TMPP yields overall better results for cohesive energy (except for Ir as the calculated value is found equal to that obtained by WH), bulk moduli and elastic constants for both the metals as compared to the results obtained by WH. This is because these authors have employed the Thomas–Fermi dielectric function for  $s$ -electron screening. Whereas in  $s$ -electron part of TMPP it is represented by the rational dielectric function, which includes the exchange and correlation corrections through its parameters as they are obtained by fitting it with Lindhard–Taylor [21] dielectric function by least square fitting method. Overall better agreement of our calculated results with the experimental [22] values shows that the rational dielectric function combined with two-parameter Heine–Abarenkov [9] model potential is a better choice over the one-parameter Ashcroft [23] model potential and Thomas–Fermi screening function to describe the  $s$ - $s$  interaction in TMPP. One should note that the TMPP obtained by WH has its own importance because of its simplicity and original character. We have also compared our results with the other available theoretical results [2, 6, 24–26] in table 2. The calculated results of bulk modulus for Rh and Ir are found to be 12% and 4% off, respectively, than the experimental values. But the corresponding results obtained in [2] are found 43% and 18% off than the experimental values. The calculated values of  $C_{11}$  for Rh are found almost 30% off using the

**Table 2.** Elastic constants ( $C_{ij}$  in Mbar), Cauchy ratio ( $C_{12}/C_{44}$ ), bulk modulus ( $B$  in Mbar) and volume contribution to  $B(\Delta_{b_s}$  in Mbar) of Rh and Ir at 300 K. Values written within parentheses are difference (in per cent) between theoretical values and experimental results.

		$C_{11}$	$C_{12}$	$C_{44}$	$C_{12}/C_{44}$	$B$
Rh	Expt. [22]	4.165	1.975	1.84	1.07	2.705
	Theor.	2.886(-30)	2.128(+8)	1.846(0)	1.15	2.381(-12)
	Wills and Harrison [8]	3.14(-25)	2.49(+26)	1.28(-30)	1.95	1.220(-55)
	Rose and Shore [24]	3.272(-21)	2.215(+12)	1.05(-43)	2.11	2.557(-5)
	Sigalas and Papaconstantopoulos [2]	5.554(+33)	3.044(+54)	2.09(+14)	1.46	3.881(+43)
	Söderlind <i>et al</i> [25]	3.97(-5)	1.71(-13)	1.96(+6)	0.87	2.463(-9)
	Cleri and Rosato [26]	3.92(-6)	2.37(+20)	1.99(+8)	1.19	2.89(+6)
	Eichler <i>et al</i> [4]	4.022(-3)	1.964(-1)	1.622(-12)		2.65(-2)
Ir	Expt. [22]	5.823	2.413	2.62	0.95	3.550
	Theor.	4.207(-28)	3.027(+25)	2.556(-3)	1.18	3.420(-4)
	Wills and Harrison [8]	4.17(-28)	3.24(+34)	1.75(-33)	1.86	1.80(-49)
	Rose and Shore [24]	4.136(-29)	2.769(+15)	1.326(-49)	2.09	3.233(-9)
	Sigalas and Papaconstantopoulos [2]	6.312(+8)	3.132(+30)	2.47(-6)	1.27	4.192(+18)
	Söderlind <i>et al</i> [25]	6.20(+6)	2.65(+10)	2.66(+2)	1.0	3.833(+8)
	Cleri and Rosato [26]	5.54(-5)	3.45(+43)	2.61(0)	1.32	4.15(+17)
	Heid <i>et al</i> [6]	6.67(+15)	2.82(+17)	2.55(-3)	1.11	4.11(+16)

two methods. The calculated results of  $C_{12}$ ,  $C_{44}$ , Cauchy ratio ( $C_{12}/C_{44}$ ) and bulk modulus ( $B$ ) are found closer to experimental values than those obtained by Sigalas and Papaconstantopoulos [2]. On the other hand, the tightbinding method [2] yields the value 6.312 Mbar for  $C_{11}$  in the case of Ir, which is much closer to the experimental [22] value 5.823 Mbar than our calculated value 4.207 Mbar. One of the reasons for getting 30–50% large values of  $C_{11}$ ,  $C_{12}$  and  $B$  in the case of Rh and 18–30% large values of  $B$  and  $C_{12}$  in the case of Ir might be that the parameters of the effective ion-ion interaction, used by Sigalas and Papaconstantopoulos [2] to calculate the elastic moduli, may not be accurate. Because the total energy, used to obtain the potential parameters by these authors, has been calculated for Rh and Ir by considering the contributions only up to second- and third-nearest neighbours.

The transition metal pair potential is also used to calculate the phonon spectra of Rh and Ir at observed volume. The calculated phonon spectra of these metals using (16) along with experimental [4, 6] values are shown in figures 6 and 7. The calculated values at Brillouin zone (BZ) boundary along longitudinal branches overestimate the experimental phonon frequencies at the maximum by 30% and 34% for Rh and Ir, respectively. However, the reasonably good agreement of the calculated values and experimental values of phonon frequencies is found along the transverse branches of the three symmetry directions for both Rh and Ir, except  $[111]T$  mode near BZ boundary, where the discrepancies between calculated and experimental values are found as much as 22% and 19% for Rh and Ir, respectively. The calculated phonon spectra do not show Kohn anomalies as we have considered Fermi surface as spherical. We have compared our calculated values of phonon frequencies of Rh and Ir in figures 6 and 7 with the theoretical values obtained by Ivanov *et al* [5] using Animalu–Heine model potential. The theoretical values obtained

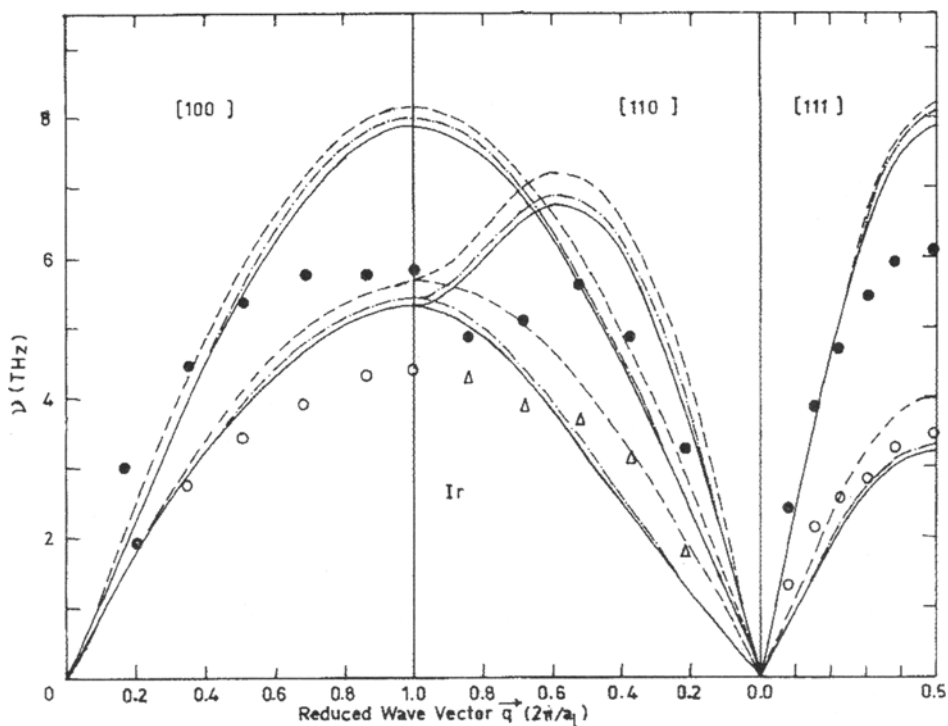


**Figure 6.** Phonon dispersion curves of Rh. Solid and dash-dot lines represent the present results obtained at 300 K and 0 K, respectively. Dashed lines represent the theoretical results obtained by Ivanov *et al* [5] at  $T = 0$  K. ●, ○ and Δ represent the experimental values due to Eichler *et al* [4] at room temperature.

by Ivanov *et al* [5] are found 5% higher than our calculated values for Rh and Ir because these authors have obtained the values of phonon spectra at  $T = 0$  K instead of 300 K. Our calculated values of phonon frequencies at  $T = 0$  K shown by dash-dot lines are found 2% higher than our calculated values at  $T = 300$  K.

#### 4. Conclusion

In summary, TMPP has been used to study the structural energy of  $4d$  and  $5d$  transition metals Rh and Ir. The  $d$ -electron contribution to effective potential is found dominating at the equilibrium position for both the metals. The calculated structural energy predicts that (i) fcc structure at observed volume is most stable for Rh and Ir, (ii) the fcc phase for both Rh and Ir is stable down to the atomic volume  $0.5V_0$ , i.e., no phase transformation takes place under pressure in both Rh and Ir. The pressure corresponding to atomic volume  $0.5V_0$  is found to be 5.235 Mbar and 9.216 Mbar for Rh and Ir respectively. At the high pressure



**Figure 7.** Phonon dispersion curves of Ir. Solid and dash-dot lines represent the present results obtained at 300 K and 0 K, respectively. Dashed lines represent the theoretical results obtained by Ivanov *et al* [5] at  $T = 0$  K. ●, ○ and Δ represent the experimental values due to Heid *et al* [6] at room temperature.

the  $p$ -band becomes broad and starts overlapping with  $s$ -band. Our predicted structural at high pressure may not be very accurate for both Rh and Ir, because the  $s$ - $p$  hybridization, which plays a significant role [27] in predicting phase transformation at high pressure, has been neglected in the present calculation of bandstructure energy. The volume contribution  $\Delta_{bs}$  is found quite significant for both the metals because it contributes 12–16% to  $B$  for Rh and Ir. The TMPP yields 30–34% higher values of oscillation modes near BZ boundary along longitudinal modes than the experimental values [4, 6] for Rh and Ir. However, our calculated and theoretical values of phonon frequencies obtained by Ivanov *et al* [5] along all the three symmetry directions are found to agree within 5% for both Rh and Ir, except [111] $T$  mode near BZ boundary.

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