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EQUATION OF STATE, BINDING ENERGIES, BULK MODULUS AND GRÜNEISEN CONSTANTS OF 3d, 4d AND 5d TRANSITION METALS

J. K. BARIA, P. N. GAJJAR and A. R. JANI

Department of Physics, Sardar Patel University, Vallabh Vidyanagar - 388120, India
E-mail address: jay_baria@yahoo.com

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A model pseudopotential, depending on an effective core radius but otherwise parameter free, is proposed to study the equation of state by incorporating the s-d hybridization effects. A new criterion for the selection of the exchange and correlation effects is also put forward. The equations of state for Cu, Ta, Mo, W and Pt have been studied up to the pressure of 1000 GPa. The binding energy, pressure, bulk modulus and frequency-independent Grüneisen constant as functions of volume for transition metals are calculated. The theoretical results are compared with available experimental results. The successful application to 27 metals has confirmed our formalism.

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1. *Introduction*

Equation of state (EOS) namely, the relationship between pressure, volume and temperature, i.e. the (P, V, T) relation, are of immense importance to theoreticians as well as experimentalists. In theoretical physics, they provide a test to the theoretical models of cohesion and predict the onset of phase transition (insulator to metal, valence transition, solid to liquid, stable crystal structure, etc.). They are also used as pressure calibration in high-pressure experiments and are needed to relate the measured pressure variation of some physical quantity (e.g. elastic constants, transport properties, specific heat, etc.) to the calculated volume variation. It has been discovered that d-electrons play a crucial role in determining the stable structure of not only the transition metals but also of the lanthanides, alkaline-earth and group II-B metals. For the transition metals from left to right across the periodic table, the trend seems to be hcp $\rightarrow$ bcc $\rightarrow$ hcp $\rightarrow$ fcc sequence of structures

[1,2], and for lanthanides it is hcp → Sm-type → dhcp → fcc [3,4]. In the case of alkaline earth metals, the trend explained by the presence of d-electrons includes the hcp → fcc → bcc sequence observed with increasing atomic numbers [5,6] that can be studied using energy–volume relation and equation of state. In astrophysics the, EOS is used to unravel the mysteries of evolution of stellar bodies like white dwarfs, neutron stars and black holes while in geophysics it helps to understand the structure of the Earth. The range of the pressure interior of the Earth is ≤ 350 GPa.

Various experimental techniques were used to study the EOS under high pressure. The data by Bridgman [7] using the piston cylinder method were the first to be reported and the pressure range was about 5–10 GPa (static). In a similar way Vaidya and Kennedy [8] made careful measurement up to about 4.5 GPa. Drickmer [9] extended the pressure range up to 20–30 GPa using a supported anvil device. In the early seventies, the range of static pressure EOS has been extended to over 100 GPa using diamond anvil devices [10,11]. The development of dynamic shock wave techniques using chemical explosives increased the pressure range to 50 GPa [12,13]. Since then a number of techniques (e.g. lasers [14], electron guns [15], underground nuclear explosions [16]) have been developed for generating controlled dynamic high pressures, whose limit is 10 TPa.

While studying EOS theoretically, the major difficulty arises from the question how to incorporate correctly the structurally complicated inter-particle interactions of the many-body problem. Previously, many authors [17–25] have studied the EOS using different techniques such as the tight-binding total-energy classical cell model [21], the generalized pseudopotential theory [22], Debye-Grüneisen theory [23], recent classical mean-field model [24], linearised augmented plane-wave method with both the local density and generalized gradient approximation [25] and model pseudopotential methods [17–20].

In the present work, we have studied the EOS for all d-band metals using our newly proposed pseudopotential. The EOS of Cu, Ta, Mo, W and Pt have been studied up to a pressure of 1000 GPa, for Rh, Ni, Co and Pd the pressure range is up to 55 GPa and for Au, Ag, Fe, V, Y, Zr, Nb and Ti up to a pressure 5 GPa. We have also calculated the binding energy, bulk modulus and the frequency-independent Grüneisen constants of all 3d, 4d and 5d elements.

2. *Model potential and its form factor*

In the last four decades, effective local pseudopotentials have been frequently used in the calculation of metallic properties of simple metals [26–38], noble metals [39–44] and transition metals [45–49]. The model potential of Kulshrestha et al. [41] for noble metals depends on two radii, r_c, the core radius and r_m, the ionic radius, where the r_c is calculated by making use of an empirical relation [41]. This effective potential is repulsive in the region $0 < r < r_c$ and attractive for $r_c < r < r_m$. They applied it to calculate the phonon dispersion of Cu, Ag and Au, which led to satisfactory results. The agreement for other properties, like binding energy, liquid metal resistivity, is rather poor and shows variations of 23–67% from experimental values. Nand et al. [42] proposed a model pseudopotential for Ni, which is local and contains one parameter. They applied it to the phonon dispersion of Ni, which is reasonably well represented. However, we have checked that with the same parameter it could not produce other properties of the metals, such as binding energies, elastic constants and bulk moduli (it deviates about 11–49% from the experimental values). Idrees et al. [44] proposed a phenomenological but single parameter model potential for the noble metals Cu, Ag and Au. This potential is repulsive from zero to r_{m} (core radius), attractive and constant in the region $r = r_{\mathrm{m}}$ to $r = r_{\mathrm{w}}$ (Wigner-Seitz radius), and purely Coulombic beyond r_{w}. They used it to calculate the binding energy, liquid metal resistivity, thermoelectric power, elastic constants and band gap, which are in better agreement with experimental results but have not reported lattice dynamical study and related properties of these metals.

The above studies indicate that for a successful application, proper cancellation within the core is required. In the present article, we propose a local form of a pseudopotential, which includes in a simple parametric way all features dictated by the physics of the situation. Particularly in noble, transition and actinide metals, the filled d- and f-bands tend to push the outer states up in energy. This effect, called "hybridization", would require a repulsive term in the model potential. Hence, in r-space, inside the core radius the model potential is a combination of repulsive and attractive terms (i.e. the corresponding cancellation within the core region). Beyond the core radius, the model potential is Coulombic in nature. In real space, the potential is of the form,

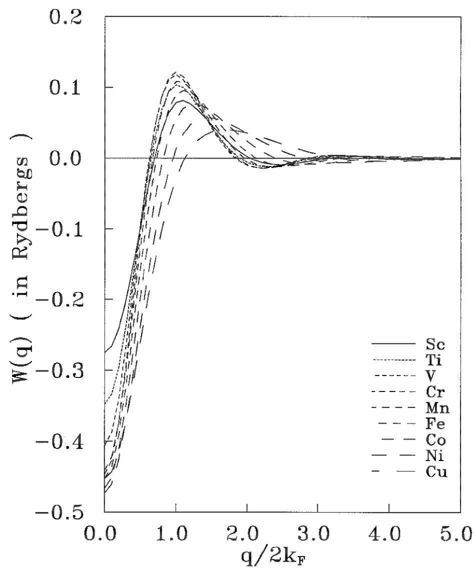
$$\begin{aligned} W(r) &= -\frac{2Zr}{r_{\mathrm{c}}^2}[2 - \mathrm{e}^{1-r/r_{\mathrm{c}}}], \quad r < r_{\mathrm{c}}, \\ &= -\frac{2Z}{r}, \qquad\qquad\qquad r > r_{\mathrm{c}}. \end{aligned} \tag{1}$$

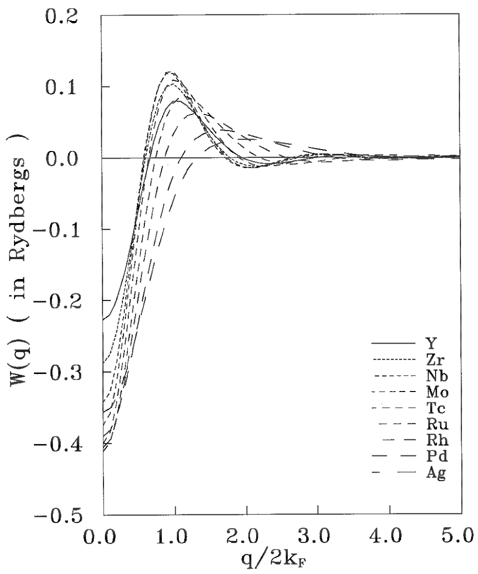
In the wave-number space (**q**-space) the potential (in Rydberg) takes the form,

$$\begin{aligned} W_{\mathrm{B}}(q) = & -\frac{8\pi Z}{\Omega_0 q^2}\left\{\frac{4(\cos qr_{\mathrm{c}} - 1)}{q^2 r_{\mathrm{c}}^2} + \frac{4\sin qr_{\mathrm{c}}}{qr_{\mathrm{c}}} + \frac{\sin qr_{\mathrm{c}}}{(1+q^2r_{\mathrm{c}}^2)^3}[5qr_{\mathrm{c}} \right. \\ & -4q^3r_{\mathrm{c}}^3 - q^5r_{\mathrm{c}}^5] + \frac{\cos qr_{\mathrm{c}}}{(1+q^2r_{\mathrm{c}}^2)^3}[11q^2r_{\mathrm{c}}^2 + 4q^4r_{\mathrm{c}}^4 + q^6r_{\mathrm{c}}^6] \\ & \left. + \frac{2\mathrm{e}q^2r_{\mathrm{c}}^2(q^2r_{\mathrm{c}}^2 - 3)}{(1+q^2r_{\mathrm{c}}^2)^3} - \cos qr_{\mathrm{c}}\right\}, \end{aligned} \tag{2}$$

where Z is the valency, Ω_0 the volume per ion, $\mathbf{q}$ the wave vector and e the base of natural logarithms. It is evident that the potential contains only one parameter, r_c, and exhibits a varying cancellation within the core region. This cancellation effect is crucial for transition metals. In addition, the potential is continuous at r_{c} and decreases as $r \to 0$ for $r < r_{\mathrm{c}}$ which is essential for any pseudopotential.

In the pseudopotential formalism, it is necessary that the potential parameter can be determined properly. In the present work, we have calculated the potential parameter from the zero pressure condition. The advantage of this method is that the potential does not bear any constraint due to a fitting procedure with the experimentally observed physical property. Hence, this potential could be visualized as a parameter-free potential in the sense that the parameter is not determined by fitting it with any experimentally observed physical property of the system.





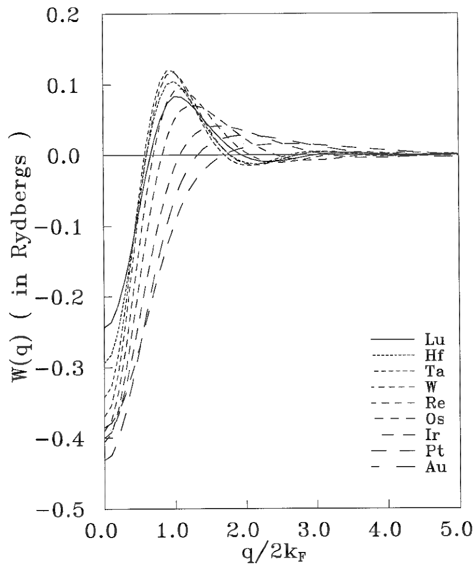


Fig. 1 (upper left). Form factors of Sc, Ti, V, Cr, Mn, Fe, Co, Ni *and* Cu.

Fig. 2 (upper right). Form factors of Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd *and* Ag.

Fig. 3 (left). Form factors of Lu, Hf, Ta, W, Re, Os, Ir, Pt *and* Au.

A number of dielectric functions [50–59] has been tried to obtain the screened form factor of the pseudopotential, but there is no unique way of selecting a proper screening function. It is well known that Taylor's [57] screening function is best justified at high densities while Vashishta and Singwi's [56] screening function at low densities. The Ichimaru and Utsumi [58] screening function accurately reproduces the Monte Carlo results as well as those of microscopic calculations. The latter also satisfies the self-consistency conditions in the compressibility sum rule and short-range correlations. A notable feature in this function is its logarithmic singularity at $q = 2k_\mathrm{F}$ and the accompanying peak at $q = 1.94k_\mathrm{F}$. The screening function of Sarkar et al. [59] is also derived in the same fashion as that of Ichimaru and Utsumi [58] and it is latest one. In the present study, a new criterion on the selection of a proper screening function is investigated. The energy-volume relation has been studied for all transition metals using different screening functions. Finally, the screening function which gives the lowest energy, namely the Taylor's [57], is adopted for further calculations. We then used this particular combination of r_c and this screening function to calculate the EOS, binding energy, bulk modulus and Grüneisen constants of all transition metals. The screened model potentials for all transition metals in **q**-space are shown in Figs. 1–3. The curves have been drawn using Hartree's [55] static dielectric function along with the exchange and correlation effects of Taylor's [57] screening function. It is seen that all pseudopotential curves lie below the horizontal axis for small q-values and give the required limiting value of the pseudopotential, i.e., $W(q) \to -2/3E_\mathrm{F}$ as $q \to 0$. The typical range of $q_0/(2k_\mathrm{F})$ for all transition metals by present formfactor is found between $0.5807 \le q_0/(2k_\mathrm{F}) \le 1.7021$, and the formfactors are free from unnecessary oscillations at high q-values, which is highly desirable for any pseudopotential formalism.

3. *Theory*

As a first approximation to the electronic structure of transition metals with Z valence electrons per ion, we consider Z_d of these to be fixed in localized, non-overlapping d-states centred on each ion site with the relation

$$Z = Z_s + Z_d\,, \tag{3}$$

where Z_s is the number of free s-electrons per ion. For the transition metals, the total energy per ion is calculated using [46]

$$E_\mathrm{tot} = E_i + E_0 + E_1 + E_2 + E_b + E_c, \tag{4}$$

where $E_i = \alpha Z^2/r_\mathrm{a}$, α is the Madelung constant having the value 1.79175 for all transition metals, and r_a is the atomic radius.

$$E_0 = Z\left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s} - 0.115 + 0.031\ln r_s\right] \tag{5}$$

is the energy of a free electron gas, including the kinetic, exchange and correlation energies expressed with the standard parameter r_s.

$$E_1 = \lim_{q\to 0}\left[\frac{8\pi Z^2}{\Omega_0 q^2} + ZW_{\mathrm{B}}(q)\right] \tag{6}$$

is the average energy of the electron–ion interaction which with our model potential becomes

$$E_1 = \frac{8Z^2 r_c^2 k_{\mathrm{F}}^3}{3\pi}[6\mathrm{e}^{+1} - 16]. \tag{7}$$

The band structure energy

$$E_2 = \frac{\Omega_0}{16\pi}\sum{}' q^2 |W_{\mathrm{B}}(q)|^2 \frac{\varepsilon_{\mathrm{H}}(q)}{1 + [\varepsilon_{\mathrm{H}}(q) - 1][1 - f(q)]}. \tag{8}$$

The prime on the summation sign excludes the $q = 0$ term. Summation over nearest neighbors in reciprocal space is taken to achieve proper convergence in the fcc phase. $\varepsilon_{\mathrm{H}}(q)$ is the Hartree static dielectric function and $f(q)$ is the exchange and correlation term due to Taylor [57].

$$E_b = -30.9\frac{Z_d(10 - Z_d)}{10} n^{1/2} \frac{r_d^3}{d^5}. \tag{9}$$

The above equation is due to the coupling that broadens the d-states into bands due to Wills and Harrison [46].

$$E_c = 11.40 Z_d n \frac{r_d^6}{K^8}\left(\frac{4\pi}{3}\right)^{8/3} \Omega_0^{-8/3}. \tag{10}$$

Here E_c describes the shift of the d-band center [46]. The volume Ω_0 and the Fermi radius are given by the following relation

$$\Omega_0 = \frac{4\pi r_a^3}{3} \qquad \text{and} \qquad k_{\mathrm{F}} = \left(\frac{3\pi^2 Z_s}{\Omega_0}\right)^{1/3}. \tag{11}$$

Here, n is the coordination number, d the nearest neighbor separation, r_d is the d-state radius applicable to the free atom and r_a is the Wigner-Seitz radius. Then the pressure P is given by

$$P = -\frac{\mathrm{d}E}{\mathrm{d}\Omega_0}. \tag{12}$$

From the pressure P, the bulk modulus is obtained as [46,47]

$$B = -\Omega_0 \frac{\mathrm{d}P}{\mathrm{d}\Omega_0}. \tag{13}$$

The following relation determines the frequency-independent Grüneisen constant [46]

$$\gamma = -\frac{1}{2}\frac{\Omega_0}{B}\frac{\mathrm{d}B}{\mathrm{d}\Omega_0}. \tag{14}$$

4. Results and discussion

The input data such as coordination number, nearest neighbor distance, d-state radius, Wigner-Seitz radius and atomic valence are taken from Refs. [46], [47] and [60]. We have calculated the potential parameter r_c using the zero pressure condition which is tabulated in the Table 1. With these values of r_c and the Taylor's screening function, we have calculated the value of the binding energies of the transi-

TABLE 1(a). Various contributions to the binding energy at zero pressure.

	r_c (a.u.)	Various contributions to the total energy in Ry					
		E_i	E_0	E_1	E_2	E_b	E_c
Sc	2.278138	-1.17827	-0.21022	0.54172	-0.11331	-0.20082	0.03354
Ti	2.182266	-1.32465	-0.17485	0.70625	-0.14704	-0.35092	0.06241
V	2.086584	-1.43131	-0.14150	0.81455	-0.16128	-0.42418	0.07127
Cr	1.967013	-1.50186	-0.11595	0.83634	-0.15636	-0.45190	0.08001
Mn	1.870366	-1.49136	-0.11993	0.74035	-0.13017	-0.68272	0.17918
Fe	1.702500	-1.51251	-0.11185	0.63995	-0.09411	-0.30365	0.06077
Co	1.485970	-1.53432	-0.10327	0.50886	-0.04980	-0.25245	0.07251
Ni	1.269247	-1.54544	-0.9879	0.37943	-0.02232	-0.14280	0.05641
Cu	1.081773	-1.51251	-0.11185	0.26737	-0.02604	-0.03892	0.03566
Y	2.613985	-1.07168	-0.22832	0.53660	-0.13356	-0.26717	0.07083
Zr	2.543297	-1.20489	-0.20469	0.72191	-0.17286	-0.49185	0.14751
Nb	2.423815	-1.31644	-0.17715	0.85523	-0.18734	-0.60978	0.17550
Mo	2.382264	-1.37592	-0.15961	0.86260	-0.18097	-0.70259	0.22893
Tc	2.014131	-1.42177	-0.14474	0.74396	-0.14248	-0.69363	0.27071
Ru	1.726644	-1.44098	-0.13816	0.56920	-0.08004	-0.60360	0.27419
Rh	1.485504	-1.43131	-0.14150	0.41289	-0.03317	-0.38690	0.19717
Pd	1.204740	-1.40307	-0.15095	0.25580	-0.02448	-0.20170	0.13726
Ag	1.075202	-1.34131	-0.17066	0.17801	-0.05021	-0.04975	0.07429
Lu	2.542542	-1.11077	-0.22244	0.56532	-0.13715	-0.31729	0.09325
Hf	2.519295	-1.21866	-0.20167	0.73291	-0.17356	-0.55825	0.18526
Ta	2.538271	-1.31647	-0.17714	0.87130	-0.19044	-0.69960	0.23101
W	2.371332	-1.36710	-0.16234	0.82814	-0.17444	-0.80288	0.30336
Re	1.894193	-1.40307	-0.15095	0.63230	-0.10816	-0.82955	0.39582
Os	1.580087	-1.43131	-0.14150	0.46708	-0.04762	-0.71126	0.38938
Ir	1.221598	-1.42177	-0.14474	0.27363	-0.02223	-0.48402	0.31319
Pt	0.787344	-1.39390	-0.15392	0.10713	-0.12110	-0.26343	0.23756
Au	0.954561	-2.38455	-0.16737	0.24938	-0.17841	-0.14081	0.15452

TABLE 1(b). The values of the binding energy at zero pressure. The values in parenthesis are the deviation (in %) from the experimental results.

Element	r_c (a.u.)	Total energy in Ry			
		Present work	Exp. [60]	Others [47]	Others [48]
Sc	2.278138	-1.12736(0.07)	-1.1265	-0.8907(20)	
Ti	2.182266	-1.22879(0.49)	-1.2349	-0.9524(23)	
V	2.086584	-1.27245(0.51)	-1.2790	-0.9780(30)	
Cr	1.967013	-1.30937(6.82)	-1.2257	-1.0183(16)	
Mn	1.870366	-1.50464(26.97)	-1.1850	-1.2393(4)	
Fe	1.702500	-1.32140(1.24)	-1.3381	-1.0919(18)	
Co	1.485970	-1.35847(0.00)	-1.3585	-1.1725(13)	
Ni	1.269247	-1.37351(0.90)	-1.3612	-1.2147(10)	-1.074(21)
Cu	1.081773	-1.38629(3.64)	-1.3376	-1.2249(8.4)	-1.102(17)
Y	2.613985	-1.09331(4.64)	-1.1466	-0.8408(26)	
Zr	2.543297	-1.20487(11.51)	-1.3561	-0.9077(33)	
Nb	2.423815	-1.26007(12.75)	-1.4443	-0.9443(34)	
Mo	2.382264	-1.32757(8.85)	-1.4566	-1.0149(30)	
Tc	2.014131	-1.38795(4.48)	-1.4531	- 1.1125(23)	
Ru	1.726644	-1.41940(4.08)	-1.4799	-1.2066(18)	
Rh	1.485504	-1.38281(3.11)	-1.4273	-1.2169(15)	
Pd	1.204740	-1.38713(7.49)	-1.4995	-1.2138(19)	-1.0250 (31)
Ag	1.075202	-1.35903(3.94)	-1.3075	-1.1793(10)	-1.0992 (15)
Lu	2.542542	-1.12908(-)	-	-0.8715	
Hf	2.519295	-1.23396(11.39)	-1.3926	-0.9356(32)	
Ta	2.538271	-1.28134(9.05)	-1.1749	-0.9616(18)	
W	2.371332	-1.37526(10.80)	-1.2411	-1.0693(14)	
Re	1.894193	-1.46362(9.61)	-1.6193	-1.2234(24)	
Os	1.580087	-1.47522(14.14)	-1.7183	-1.2938(24)	
Ir	1.221598	-1.48593(-)-	-1.3318		
Pt	0.787344	-1.58766(0.40)	-1.5940	-1.3357(16)	-1.017(36)
Au	0.954561	-2.46660(20.30)	-2.0498	-2.1087(3)	-1.985(3)

tion metals (3d, 4d and 5d elements). For comparison, the experimental values are taken from Ref. [60] as given in Ref. [45]. We have found significant contributions of band-structure part in the total energy of 1.49% for Ir and 14.87% for Nb and for other metals it varies in-between. The effect of the free-electron part also plays important role in the total energy calculation. The deviations of the present results for the binding energies of Sc, Ti, V, Fe, Co, Ni, Cu, Y, Tc, Ru, Rh, Ag and Pt are less than 5% from the experimental values. For Mn and Au we find large discrepancies, while the deviations for rest of the transition metals are below 15%. No experimental data are available for Lu and Ir. The reason for the discrepancy between the calculated and experimental values of the binding energy of Y, Zr and

Hf may be due to the hcp equilibrium structure [6]. Note that in the investigation of Singh [48], the maximum discrepancy is of the order of 36%.

The EOS of all transition metals is shown in Figs. 4–9. Our results of pressure-volume relation for Cu and Ta (Fig. 4) are extremely good and deviate little from

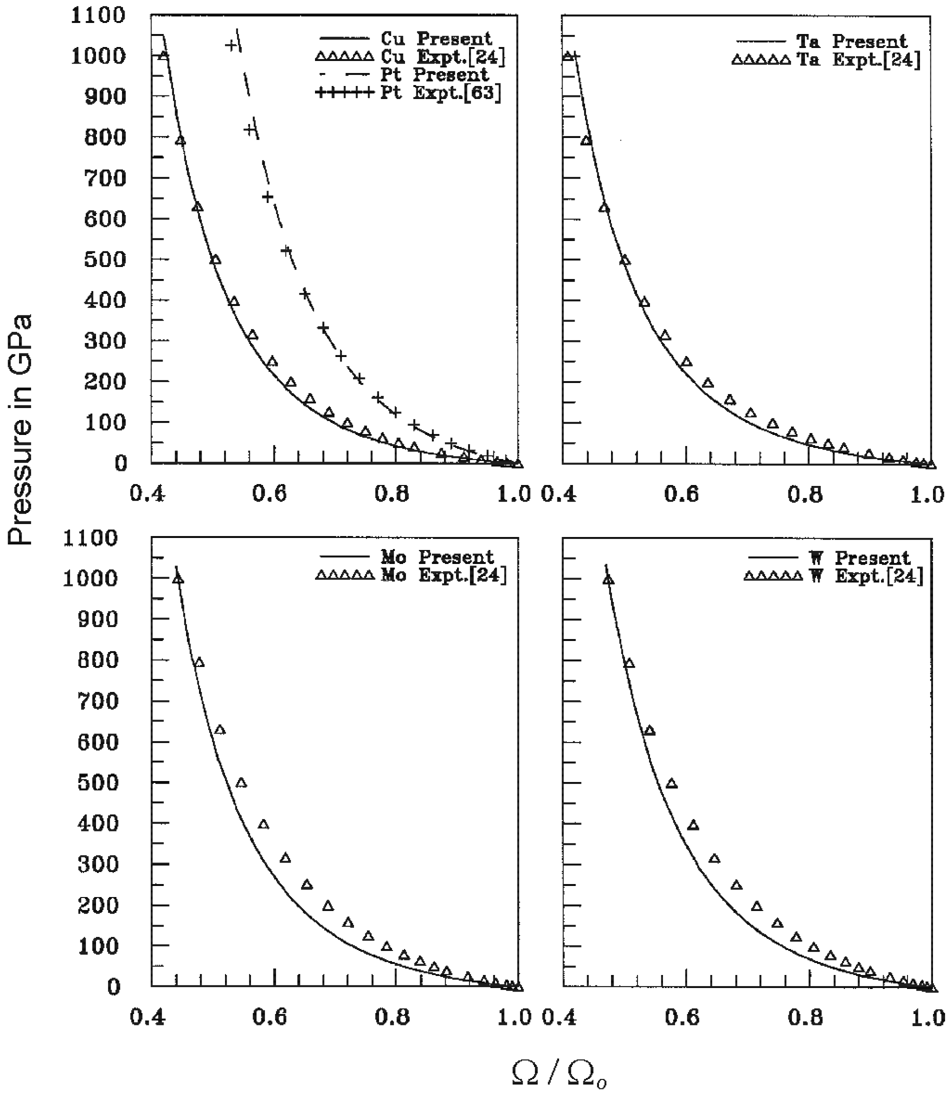


Fig. 4. Pressure–volume relations of Cu, Pt, Ta, Mo *and* W *up to 1000* GPa.

experimental findings above 1000 GPa. For Mo and W (Fig. 4) the values deviate at intermediate pressure and agree well above 700 GPa for Mo and above 800 GPa for W. We have also compared the theoretical 300 K isotherm [61] for platinum (Fig. 4) and found excellent agreement up to 500 GPa and small deviation at high

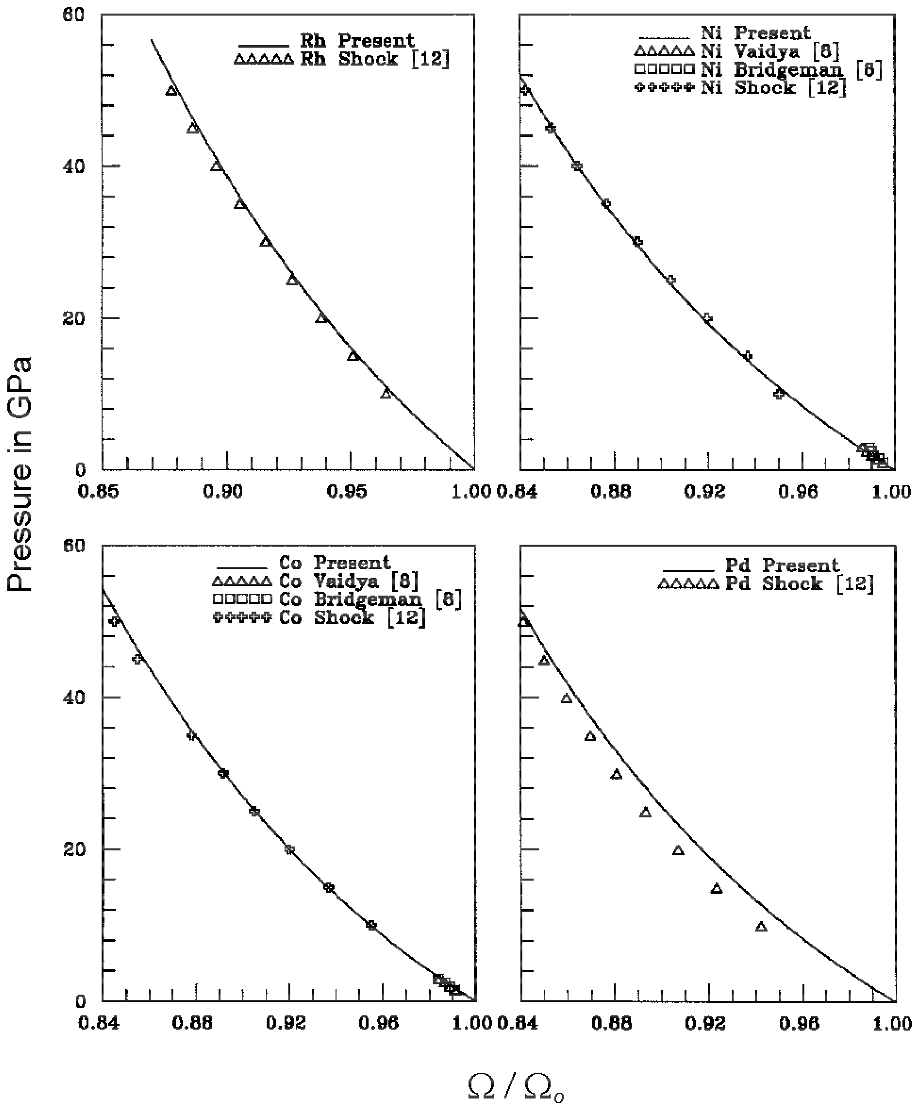


Fig. 5. Pressure–volume relations of Rh, Ni, Co *and* Pd *up to 55* GPa.

pressure. The results of Rh and Pd (Fig. 5) deviate a little while for Ni and Co (Fig. 5) excellent agreement with the experimental results is found. The results of Au, Ag, Fe, V, Y, Zr, Nb and Ti (Figs. 6 and 7) are found in extremely good agreement with the experimental findings.

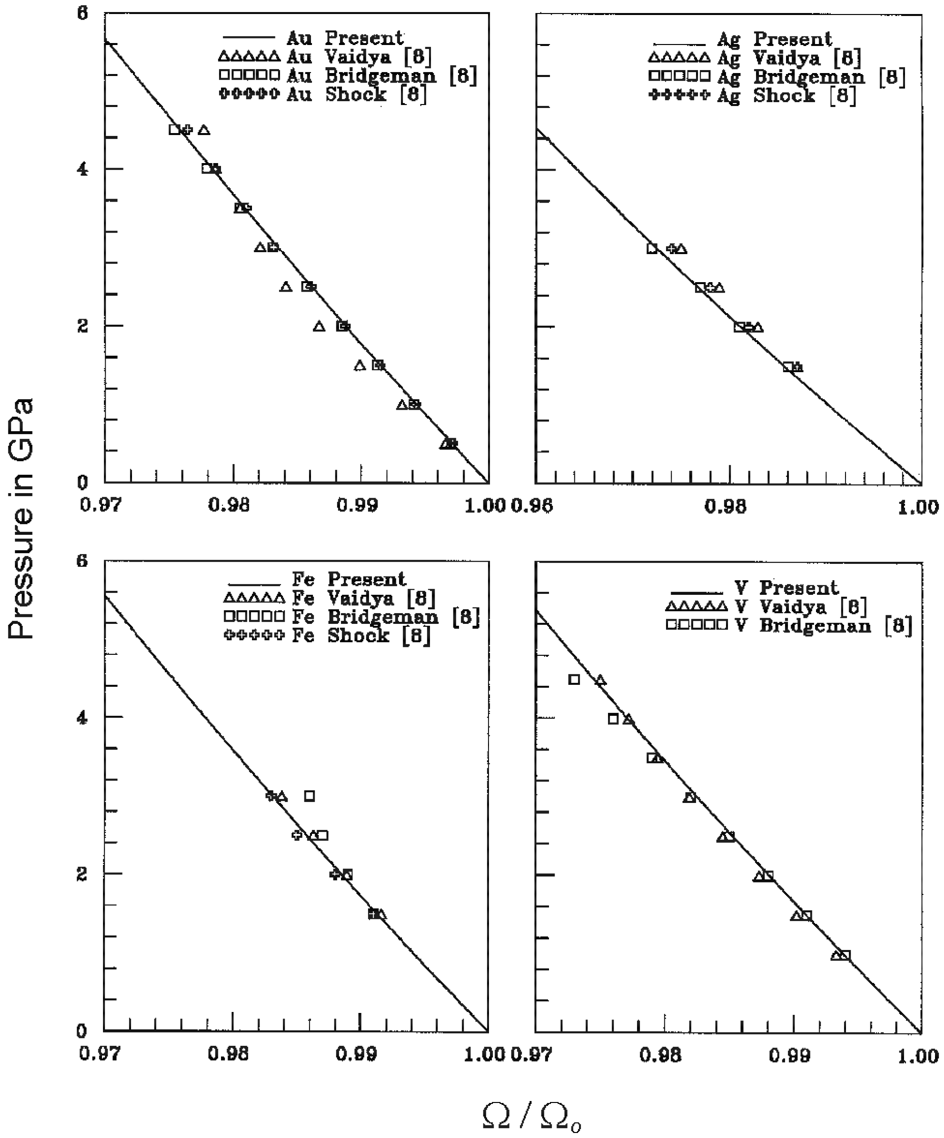


Fig. 6. Pressure–volume relations of Au, Ag, Fe *and* V *up to 4.5* GPa.

Soma et al. [18,19] have calculated the total crystal energy with the overlap potential energy given by Moriarty [5,22,45] and with the model potential of Kulshreshtha et al. [41]. Their pressure-volume relations of Cu and Ag are in good agreement with the experimental data while for Au disagreement is found above

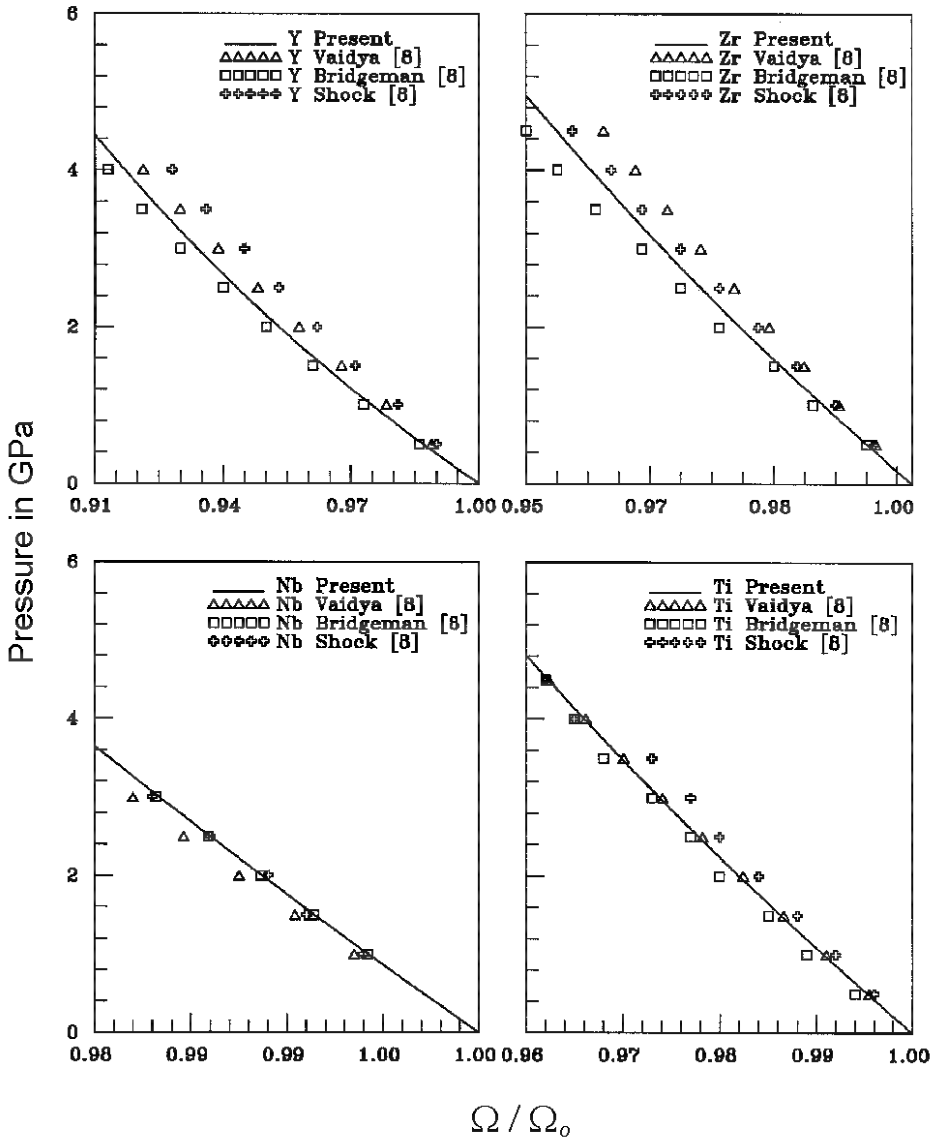
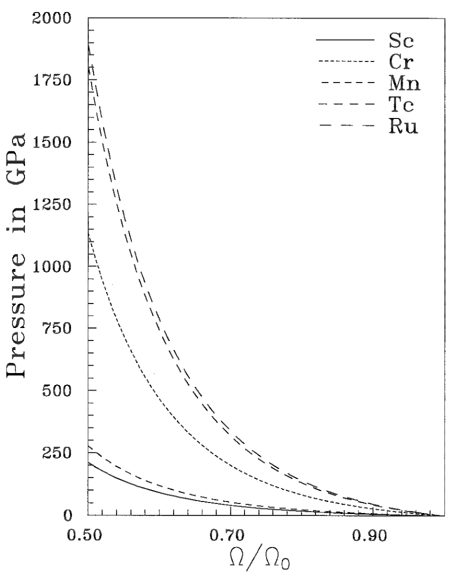


Fig. 7. Pressure–volume relations of Y, Zr, Nb *and* Ti *up to 4.5* GPa.

3.3 GPa. Antonov et al. [20] have successfully studied phonon dispersion curves, phonon density of states, mode Grüneisen parameter and thermodynamic properties of Cu, Ag, Au, Ni, Pd, Pt, Co, Fe, Rh and Ir. They have also calculated the pressure-volume relation of Ni, Pd, Rh, Ir and Pt with great success but the rest of metals might give disagreement from experimental findings. Walzer [47] has also successfully calculated the bulk moduli of all 3d, 4d and 5d transition metals with two fitting parameters and the pressure-volume relation of nine transition metals, from which the PV relation of Mo, Nb and V deviate strongly from the experimental results. However, with the same parameters, his total energies deviate much from the experimental findings. Wang et al. [24] have also calculated Hugoniots and 293 K isotherms at pressures up to 1000 GPa for Al, Cu, Ta, Mo and W using the classical mean-field approach, and their results are excellent. But their method is intricate and time consuming. In the absence of experimental information on the pressure-volume relation for Sc, Cr, Mn, Tc, Ru, Lu, Hf, Re, Os and Ir (Figs. 8–9), our present results will serve as a very good reference for further comparisons either with theoretical or experimental data.



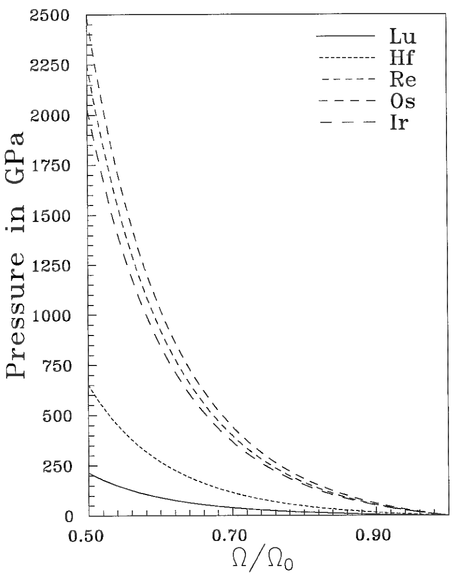


Fig. 8 (left). Pressure–volume relations of Sc, Cr, Mn, Tc *and* Ru *up to 2500* GPa.

Fig. 9. Pressure–volume relations of Lu, Hf, Re, Os *and* Ir *up to 2500* GPa.

In Table 2, we report the calculated values of the bulk moduli for all transition metals. The presently obtained theoretical values of the bulk moduli for all metals are in excellent agreement with the experimental values. Alhough the bulk modulus obtained by Wojciechowski [49] was calculated with the novel idea of a stabilized uniform metallic valence, we note here that our results are better than his [49].

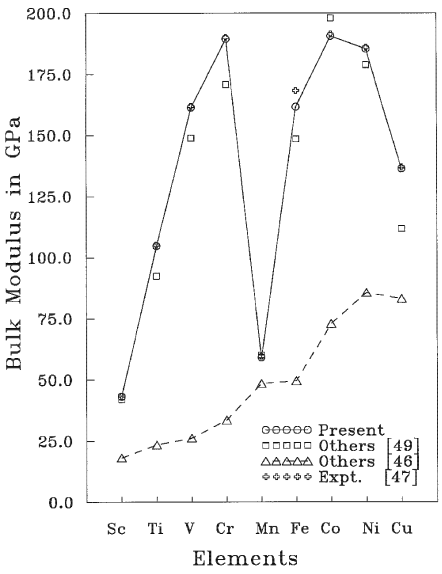
TABLE 2. The values of the bulk moduli in GPa.

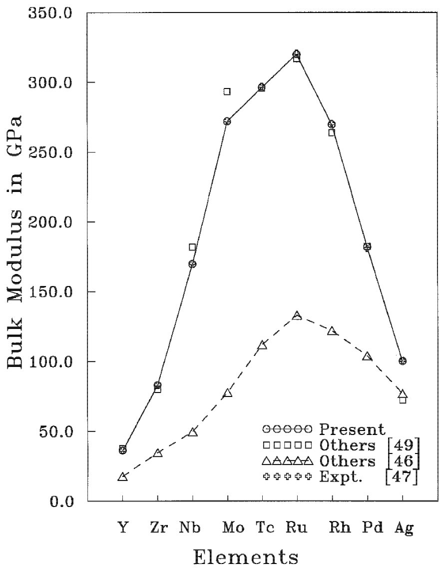
Element	Bulk modulus (GPa)			
	Present work	Exp. [47]	Others [46]	Others [49]
Sc	43.3	43.5	18.1	42.1
Ti	104.7	105.1	23.5	92.5
V	161.4	161.9	26.2	148.9
Cr	189.5	190.1	33.6	170.8
Mn	59.2	59.6	48.5	60.1
Fe	167.7	168.3	49.6	148.5
Co	190.7	191.4	73.0	198.0
Ni	185.4	186.0	85.7	178.6
Cu	136.4	137.0	83.3	111.8
Y	36.4	36.6	17.7	37.8
Zr	83.0	83.3	34.7	79.8
Nb	169.6	170.2	49.6	181.8
Mo	271.9	272.5	77.7	293.3
Tc	296.3	297.0	112.0	295.6
Ru	319.9	320.8	133.0	316.8
Rh	269.7	270.4	122.0	263.8
Pd	182.0	180.8	104.0	182.3
Ag	100.3	100.7	77.0	72.3
Lu	40.9	41.1	23.4	-
Hf	108.7	109.0	45.0	94.7
Ta	199.5	200.0	68.0	198.8
W	322.6	323.2	106.0	316.7
Re	371.2	372.0	166.0	388.1
Os	417.3	418.0	183.0	435.2
Ir	354.0	355.0	180.0	355.0
Pt	277.5	278.3	155.0	293.9
Au	172.5	173.2	166.0	153.0

The bulk moduli calculated by Wills and Harrison [46] are very poor. The present results of bulk moduli shown in Figs. 10–12 confirm the inverted parabolic trend as mentioned by Soderlind [62].

In Table 3, the theoretical values of the frequency-independent Grüneisen constants are compared with the experimental values reported by Wills and Harrison [46] and by Gschneidner Jr. [63]. Though Wills and Harrison [46] have estimated the Grüneisen constants using a fitting procedure, they failed to reproduce experiments. In this context, our results of the frequency-independent Grüneisen constants are better than the theoretical results by Wills and Harrison [46].

Comparison of the theoretical and experimental equation of state indicates that the present model is applicable for the statical calculations up to nearly 1000 GPa without renormalization of the parameters. The overall superiority in explaining binding energy, bulk modulus and frequency-independent Grüneisen constant also confirms the successful application of the present formulation. We believe that our simple pseudopotential model correctly reproduces the main features of the interatomic interactions in the transition metals. Investigations of surface properties, transport properties, magnetic properties, molecular dynamics and lattice dynamics, etc., are now in progress in order to establish the full range of applicability of this approach.





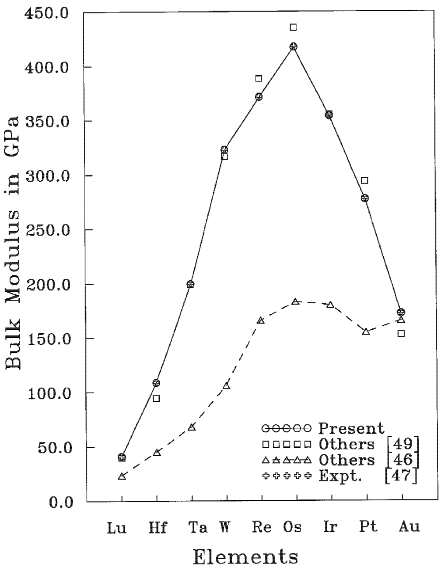


Fig. 10 (upper left). Bulk moduli of Sc, Ti, V, Cr, Mn, Fe, Co, Ni *and* Cu *(in* GPa*).*

Fig. 11 (upper right). Bulk moduli of Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd *and* Ag *(in* GPa*).*

Fig. 12 (left). Bulk moduli of Lu, Hf, Ta, W, Re, Os, Ir, Pt *and* Au *(in* GPa*).*

TABLE 3. The values of frequency-independent Grüneisen constants.

Element	Frequency-independent Grüneisen constants				
	Present work	Exp. [46]	Exp. [63]	Others [63]	Others [46]
Sc	2.04	-	-	1.17, 1.03	1.69
Ti	2.29	1.10	1.18	1.33, 1.28	1.84
V	2.36	1.27	1.05	1.55, 1.38	1.87
Cr	2.36	1.24	1.30	1.53, 1.51	1.98
Mn	1.89	1.95	2.07±0.86	1.28, 1.16	2.13
Fe	2.24	1.67	1.66±0.06	1.81, 1.70	1.93
Co	2.20	1.92	1.93±0.06	2.07, 1.95	2.09
Ni	2.12	1.84	1.88±0.08	2.00, 1.83	2.04
Cu	1.95	1.99	2.00±0.08	1.97, 1.96	1.97
Y	2.14	-	0.89	1.13, 1.00	2.16
Zr	2.34	0.83	0.83±0.06	0.82, 0.71	2.59
Nb	2.43	1.57	1.58±0.11	1.74, 1.58	2.76
Mo	2.46	1.59	1.60±0.08	1.65, 1.61	2.84
Tc	2.42	-	-	2.75, 2.61	2.81
Ru	2.39	2.60	-	3.25, 3.12	2.74
Rh	2.32	2.26	2.23±0.03	2.43, 2.29	2.60
Pd	2.19	2.24	2.28±0.10	2.47, 2.18	2.44
Ag	1.96	2.23	2.36±0.12	2.46, 2.44	2.24
Lu	2.15	-	-	0.75 , 0.6	2.32
Hf	2.38	-	1.15	1.07, 1.04	2.71
Ta	2.45	1.69	1.70±0.06	1.82, 1.69	2.87
W	2.46	1.71	1.68±0.06	1.78, 1.76	2.92
Re	2.43	2.61	-	2.66, 2.59	2.89
Os	2.41	1.78	-	2.02, 2.02	2.82
Ir	2.35	2.36	-	2.49, 2.39	2.72
Pt	2.28	2.71	2.56±0.12	2.92, 2.69	2.61
Au	1.94	2.91	3.04±0.04	3.09, 3.06	2.40

The main interest of the present investigation was to study the properties in the static limit and it is difficult to have certain parameters at desired temperature or continuous variation of such parameters (say lattice parameter) with temperature. However, incorporation of such effects (wherever possible) might throw additional light on the present study.

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JEDNADŽBE STANJA, ENERGIJE VEZANJA, VOLUMNI MODULI I GRÜNEISENOVE KONSTANTE 3d, 4d I 5d PRIJELAZNIH METALA

Uvodimo model potencijala koji ovisi o polumjeru efektivne sredice a ne o drugim parametrima radi proučavanja jednadžbe stanja s uključenim s-d efektima hibridizacije. Postavljamo također nov kriterij za odabir efekata izmjena i korelacija. Proučavamo jednadžbu stanja Cu, Ta, Mo, W i Pt za tlakove do 1000 GPa. Izračunavamo energije vezanja, tlak, volumne module i frekventno-neovisne Grüneisenove konstante. Ishodi računa uspoređuju se s eksperimentalnima za sve poznate podatke. Uspješna primjena našeg formalizma za 27 metala ga potvrđuje.