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## **Elastic and Bonding Properties of Transition Metals**

By

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A theory linking the nearly-free-electron theory to d-band broadening and hybridization effects is further developed in such a way that a model, called MA, for the energy, the pressure  $p$ , the bulk modulus and its derivatives with respect to pressure as a function of the relative volume  $x$  is created. The theoretical values of MA are compared with all known experimental data for transition metals. For predictions of the relative volume as a function of pressure as well as for the predictions of the first derivative of the bulk modulus with respect to pressure at zero pressure significant improvements are obtained. The approximation of measured values in the  $p$ - $x$  plot is very good for most transition metals, in particular for iron, too, and good for the other metals.

Eine Theorie, die die Theorie der fast freien Elektronen mit der der d-Bandspreizung und der Hybridisation verbindet, wird so weiterentwickelt, daß ein Modell, genannt MA, für die Energie, den Druck  $p$ , den Kompressionsmodul und seine Druckableitungen als Funktion des relativen Volumens  $x$  entsteht. Die theoretischen Werte von MA werden mit allen bekannten Meßdaten von Übergangsmetallen verglichen. Dabei ergeben sich sowohl für die Voraussagen des relativen Volumens als Funktion des Druckes als auch für die der ersten Druckableitung des Kompressionsmoduls bei Nulldruck erhebliche Verbesserungen. Für die meisten Übergangsmetalle werden die Meßwerte im  $p$ - $x$ -Diagramm sehr gut approximiert. Das gilt insbesondere für Eisen. Auch für die anderen stellt MA eine gute Näherung dar.

### **1. Introduction**

In principle, it is possible to compute the elastic and bonding properties of transition metals from a relativistic generalization of the Schrödinger equation. Since a solution of the Schrödinger equation is possible only for very simple cases, a number of approximation methods have been developed. However, for the zero-pressure bulk modulus, its first derivative with respect to pressure and for the equation of state, these methods yield theoretical values constituting a rather poor approximation of measured values. Therefore, empirical and semi-empirical equations of state are used to the present day in applied high-pressure research, in geophysics and astrophysics. It is the objective of this paper to modify the afore-mentioned methods such as to make the density of transition metals so well predictable as a function of pressure that the user may renounce empirical methods. Wigner and Seitz [1] studied the bonding in monovalent sodium. Studies on polyvalent metals were published only much later. The reason for this was, first, the necessity to self-consistently compute the potential in the Schrödinger equation not only in dependence on the ion core, but also on the Coulomb field of the valence electrons. The existence of spin follows from the relativistic quantum mechanics. Therefore, secondly, exchange and correlation terms had to be introduced. This was done by the local density functional formalism by Kohn et al. [2, 3]. Moruzzi et al. [4, 5] applied it to 3d and 4d metals. Using self-consistent

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energy band calculations, they were able to compute very well the Wigner-Seitz radius, the cohesive energy, and the zero-pressure bulk modulus of the 4d transition metals.

Andersen [6, 7], basing his studies on the local density functional formalism, found the atomic sphere approximation and the related muffin-tin orbital theory. From the linear superposition of the muffin-tin orbitals, a solution of the Schrödinger equation is obtained. Pettifor [8, 9] used the atomic sphere approximation for calculating the band structure of the transition metals. Many details of this structure proved to be immaterial for the calculation of the bonding forces. The pseudopotential theory [10, 11] shows a possibility for reaching a separation between free-electron-like and d-like states. Harrison and Froyen [12] combined the pseudopotential theory with the muffin-tin orbital theory. As a result, in a similar way as Pettifor [8], they achieved a significant simplification of the theory of d-band structure of transition metals. Harrison and Wills, basing their work on this, developed a theory of the binding energy of simple metals [13] and of transition metals [14]. These theories are very promising. Yet, the agreement between the theoretical and experimental values is not sufficient for further practical application. Therefore, we shall further develop this theory, laying particular emphasis on the comparison with experimental values. For a further familiarization with this field, the following three review articles are recommended: [15, 16, 17].

## 2. Theory

For the purpose of simplification, we neglect the redistribution of electrons to the two external, not fully filled shells. The number  $Z$  of valence electrons per ion results from the sum of free  $s$  electrons and of the  $d$  electrons,

$$Z = Z_s + Z_d. \quad (1)$$

We treat the outer electron shell as a uniform electron gas under the influence of an empty-core pseudopotential of radius  $r_c$  (see [16]). The energy per ion for the free-electron-like states is

$$E_{fe} = \frac{3}{10} Z_s \frac{\hbar^2}{m} k_F^2 - \frac{3}{4\pi} Z_s e^2 k_F - \frac{Z_s^2 e^2 \alpha k_F}{(18\pi Z_s)^{1/3}} + \frac{2}{3\pi} Z_s e^2 r_c^2 k_F^3. \quad (2)$$

For the radius  $r_0$  of the atomic volume  $\Omega_0$  we have

$$r_0 = k_F^{-1} (9\pi Z_s / 4)^{1/3} \quad \text{and} \quad \Omega_0 = 4\pi r_0^3 / 3. \quad (3)$$

Thus, from (2) we get

$$E_{fe} = k_1 \Omega_0^{-2/3} - k_2 \Omega_0^{-1/3} + k_3 \Omega_0^{-1} \quad (4)$$

with

$$k_1 = 2.210 \frac{\hbar^2}{2m} Z_s^{5/3} \left( \frac{4\pi}{3} \right)^{2/3}, \quad (5)$$

$$k_2 = \frac{e^2}{2} [0.916 Z_s^{4/3} + \alpha Z_s^2] \left( \frac{4\pi}{3} \right)^{1/3}, \quad (6)$$

$$k_3 = 2\pi e^2 r_c^2 Z_s^2. \quad (7)$$

The first term of (2) defines the mean kinetic energy of free electrons, the second one the exchange energy, the third term is the Madelung energy, the assumption we are making from now on being  $\alpha = 1.8$ . The fourth summand is a correction term for the Madelung energy which is introduced on account of the empty-core pseudopotential.

$e$  is the electron charge,  $m$  the electron mass, and  $\hbar$  Planck's quantum of action divided by  $2\pi$ .

When dealing with the coupling which broadens the d states into bands, we calculate the energy  $E_b$  according to Friedel [18], the bandwidth  $W_d$  according to Harrison and coworkers [12, 14, 16], introducing, however, a first (differing) hypothesis.

$$E_b = -\frac{1}{2} Z_d (1 - Z_d/10) W_d, \quad (8)$$

$$W_d = \left[ \frac{12}{N_a} \right]^{1/2} \left( \sum_i \sum_{j \neq i} V_{bd}^2(r_{ij}) \right)^{1/2} \quad \text{and} \quad V_D \equiv \left( \frac{1}{5} \sum_m V_{ddm}^2(r) \right)^{1/2}. \quad (9)$$

$$V_{ddm} = \sum_{\mathbf{k}} \frac{\langle d' | \Delta | \mathbf{k} \rangle \langle \mathbf{k} | \Delta | d \rangle}{E_d - E_{\mathbf{k}}} \quad (10)$$

is an expression for the coupling between the local nonoverlapping d states and the orthogonalized plane waves.  $\Delta$  is a hybridization term in the Hamiltonian. The plane wave can be expressed as follows (Schiff [19]):

$$|\mathbf{k}\rangle = \Omega^{-1/2} \sum_l (2l+1) i^l j_l(kr) [4\pi/(2l+1)]^{1/2} Y_l^0(\theta_2, \Phi_2) e^{i\mathbf{k}\cdot\mathbf{r}_j}.$$

$\mathbf{r}_j$  is the position vector. The atomic d states are expressed by  $|d\rangle = R_2(r) Y_2^m(\theta_1, \Phi_1)$ , where  $R_2$  is the radial d-state wave function. It is known [12] that

$$V_D(r) = \frac{\hbar^2 r_d^3}{m r^5} [(\eta_{dd0}^2 + 2\eta_{dd1}^2 + 2\eta_{dd2}^2)/5]^{1/2} \quad (11)$$

with

$$\eta_{dd0} = -\frac{45}{\pi}, \quad \eta_{dd1} = \frac{30}{\pi}, \quad \eta_{dd2} = -\frac{15}{2\pi}. \quad (12)$$

$r$  is the interionic distance,  $N_a$  the number of atoms,  $n$  the coordination number,  $d$  the nearest-neighbor separation. We now introduce the hypothesis that the ratio of the nearest-neighbor separation to the atomic radius remains a constant  $K$  also in the case of compression of the crystal. Moreover, we use only the interaction exerted by the nearest neighbors, thus obtaining

$$E_b = -Z_d \left( 1 - \frac{Z_d}{10} \right) (30.9) n^{1/2} \frac{\hbar^2 r_d^3}{2m K^5} \left( \frac{4\pi}{3} \right)^{5/3} \Omega_0^{-5/3} \quad (13)$$

because

$$30.9 = (12)^{1/2} [(\eta_{dd0}^2 + 2\eta_{dd1}^2 + 2\eta_{dd2}^2)/5]^{1/2}.$$

We define a constant  $k_d$ ,

$$E_b = -k_d \Omega_0^{-5/3}, \quad (14)$$

$r_d$  is the d-state radius applicable to the free atom. We take the  $r_d$  from [12] which are adapted to the bandwidths given by Andersen and Jepsen [20]. For  $r_0$  and  $r_c$ , we take the values from [14], with the core-radius  $r_c$  being so adapted that the correct atomic volume at zero pressure is obtained. In addition to the afore-mentioned energy contributions, a small contribution  $E_c$  is added which describes the shift in the d-band center. The procedure in which it has been derived is found in the paper by Wills and Harrison [14].

It is a consequence of the nonorthogonality of d-like states. In our hypothesis, it is

$$E_c = Z_d n (11.40) \frac{\hbar^2 r_d^6}{m K^5} \left( \frac{4\pi}{3} \right)^{8/3} \Omega_0^{-8/3} \equiv k_s \Omega_0^{-8/3}. \quad (15)$$

Magnetic effects, making a contribution above all to the energy of the 3d metals [21, 22], as well as spin-orbit coupling are not directly taken into account by us. Instead, we use the following expression for the energy

$$E = k_1 \Omega^{-2/3} - k_2 \Omega^{-1/3} + k_3 \Omega^{-1} - b k_4 \Omega^{-5/3} + c k_5 \Omega^{-8/3}. \quad (16)$$

From this, we obtain the new equation of state

$$p = k_1 \frac{2}{3} \Omega^{-5/3} - k_2 \Omega^{-4/3} + k_3 \Omega^{-2} - b k_4 \frac{5}{3} \Omega^{-8/3} + c k_5 \frac{8}{3} \Omega^{-11/3}. \quad (17)$$

From the pressure  $p$ , the bulk modulus  $B$  is calculated

$$B = k_1 \frac{10}{9} \Omega^{-5/3} - k_2 \frac{4}{9} \Omega^{-4/3} + k_3 2 \Omega^{-2} - b k_4 \frac{40}{9} \Omega^{-8/3} + c k_5 \frac{88}{9} \Omega^{-11/3}. \quad (18)$$

One point each of the curve is fixed in (17) and (18): We postulate that for the atomic volume  $\Omega = \Omega_0$  at vanishing pressure  $p = 0$  really follows from (17) and that the

Table 1  
List of input parameters of the theoretical models

element	$B_{0,\text{ex}}$ (100 MPa)	$r_0$ ( $10^{-10}$ m)	$r_c$ ( $10^{-10}$ m)	$r_d$ ( $10^{-10}$ m)	$d$ ( $10^{-10}$ m)	$n$	$Z_s$	$Z_d$
Sc	435	1.81	0.95	1.24	3.25	12	1.5	1.5
Ti	1051	1.61	0.91	1.08	2.89	12	1.5	2.5
V	1619	1.49	0.87	0.98	2.62	8	1.5	3.5
Cr	1901	1.42	0.82	0.90	2.50	8	1.5	4.5
Mn	596	1.43	0.78	0.86	2.24	8	1.5	5.5
Fe	1683	1.41	0.71	0.80	2.48	8	1.5	6.5
Co	1914	1.39	0.62	0.76	2.50	12	1.5	7.5
Ni	1860	1.38	0.53	0.71	2.49	12	1.5	8.5
Cu	1370	1.41	0.46	0.67	2.56	12	1.5	9.5
Y	366	1.99	1.09	1.58	3.55	12	1.5	1.5
Zr	833	1.77	1.06	1.41	3.17	12	1.5	2.5
Nb	1702	1.62	1.01	1.28	2.86	8	1.5	3.5
Mo	2725	1.55	0.95	1.20	2.72	8	1.5	4.5
Tc	(2970)	1.50	0.84	1.11	2.71	12	1.5	5.5
Ru	3208	1.48	0.72	1.05	2.65	12	1.5	6.5
Rh	2704	1.49	0.62	0.99	2.69	12	1.5	7.5
Pd	1808	1.52	0.52	0.94	2.75	12	1.5	8.5
Ag	1007	1.59	0.45	0.89	2.89	12	1.5	9.5
Lu	411	1.92	1.06	1.58	3.43	12	1.5	1.5
Hf	1090	1.75	1.05	1.44	3.13	12	1.5	2.5
Ta	2000	1.62	1.02	1.34	2.86	8	1.5	3.5
W	3232	1.56	0.94	1.27	2.74	8	1.5	4.5
Re	3720	1.52	0.79	1.20	2.74	12	1.5	5.5
Os	(4180)	1.49	0.66	1.13	2.68	12	1.5	6.5
Ir	3550	1.50	0.51	1.08	2.71	12	1.5	7.5
Pt	2783	1.53	0.33	1.04	2.77	12	1.5	8.5
Au	1732	1.59	0.40	1.01	2.88	12	2	9

experimental zero-pressure bulk modulus  $B_{0,\text{ex}}$  equals the theoretical zero-pressure bulk modulus  $B_0$ . From these two assumptions,  $b$  and  $c$  have been calculated.

From

$$-\Omega \frac{\partial B}{\partial \Omega} = k_1 \frac{50}{27} \Omega^{-5/3} - k_2 \frac{16}{27} \Omega^{-4/3} + k_3 4\Omega^{-2} - bk_4 \frac{320}{27} \Omega^{-8/3} + ck_5 \frac{968}{27} \Omega^{-11/3} \quad (19)$$

the pressure derivative of the bulk modulus at vanishing pressure is formed,

$$B_1 = \frac{1}{B(\Omega_0)} \left( -\Omega \frac{\partial B}{\partial \Omega} \right)_{\Omega=\Omega_0}. \quad (20)$$

The model proposed here for the behavior of transition metals under high pressure, i.e., (16) to (20) will be hereafter called model A (abbreviated MA). If we assume that  $b$  and  $c$  equal unity, we obtain a modified Wills-Harrison model (abbreviated WH).

### 3. Comparison of the Theory with Experimental Results

By comparing the curves  $p(\Omega)$  and  $B(\Omega)$  with measured values, the theory can be tested for its applicability to transition metals at  $\Omega \neq \Omega_0$ . Another test can be performed by comparing  $B_1$  with observed data.

Table I shows the well known input parameters. There are eight for each of the metals, seven of which having a microphysical nature. The only macroscopic input parameter is  $B_{0,\text{ex}}$ , the experimental isothermal bulk modulus at vanishing pressure according to [23], which parameter is given in the second column. The following columns contain the radius of the atomic volume  $r_0$  and the pseudopotential core radius  $r_c$ , both taken from [14], the d-state radius  $r_d$  according to [12], the nearest neighbor separation  $d$  according to [23],  $n$  the number of nearest neighbors in equilibrium according to [24, 25],  $Z_s$  the number of electrons per ion being in the free-electron-like states, and  $Z_d$  which is the number of electrons in the d-band according to [14].

In Fig. 1 to 9, the theoretical curves obtained with the models MA (full curve) and WH (dashed curve) are compared with the measured points for all transition

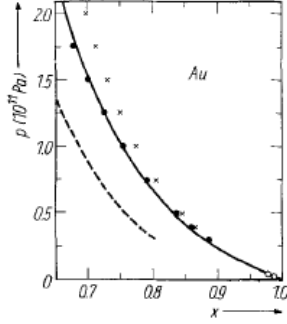


Fig. 1

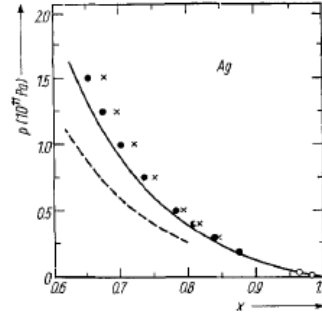


Fig. 2

Fig. 1. Gold. Comparison of equations of the state MA (full curve) and WH (dashed) with experimental data:  $\circ$  static data [27],  $\bullet$  room isotherm [28] calculated from Hugoniot data (crosses)  
Fig. 2. Silver. For text, see Fig. 1

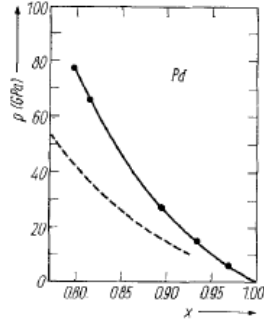


Fig. 3

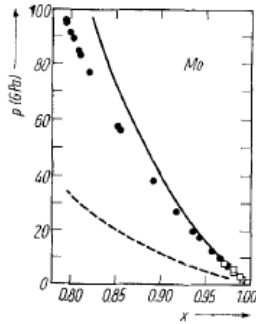


Fig. 4

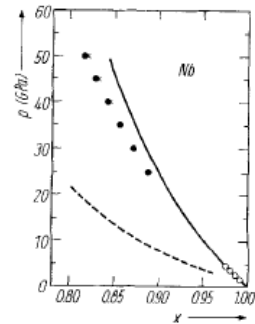


Fig. 5

Fig. 3. Palladium. For text, see Fig. 4

Fig. 4. Molybdenum. Comparison of the equations of state MA and WH with measured data. The experimental values are taken from Mao et al. [29] (293 K isothermal data, ●) and Li Chung Ming and Manghani [30] (□)

Fig. 5. Niobium. Comparison of the equations of state MA and WH with measured data: ○ static data [31]; Hugoniot data and room isotherms calculated from them have been taken from [32]

metals. For this purpose, the pressure  $p$  is plotted versus the relative volume  $x = \Omega/\Omega_0$ . Crosses denote Hugoniot data, insignificant for the comparison, from which room isotherms, in some cases also zero isotherms, have been calculated in literature. The knowledge we have of the compression comes from shock-wave data, X-ray investigations, and volumetric measurements. The graphic representation of the compared experimental results in Fig. 1, 2, 5, 6, 7, 8 a, and 9 is based on that used by

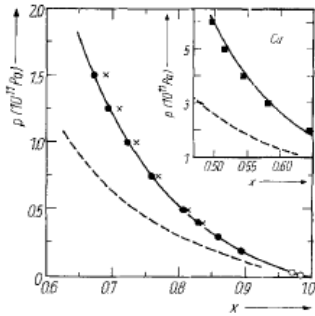


Fig. 6

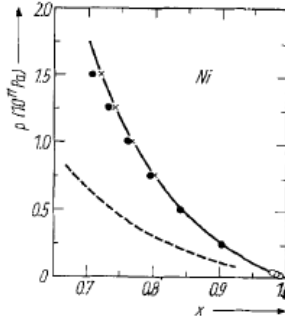


Fig. 7

Fig. 6. Copper. Comparison of the equations of state MA and WH with experimental data: ■ zero isotherm [33]. For further text, see Fig. 1

Fig. 7. Nickel. Comparison of the equations of state MA and WH with experimental data: × Hugoniot values, ● isotherms calculated from them according to [34], ○ static data according to [27]

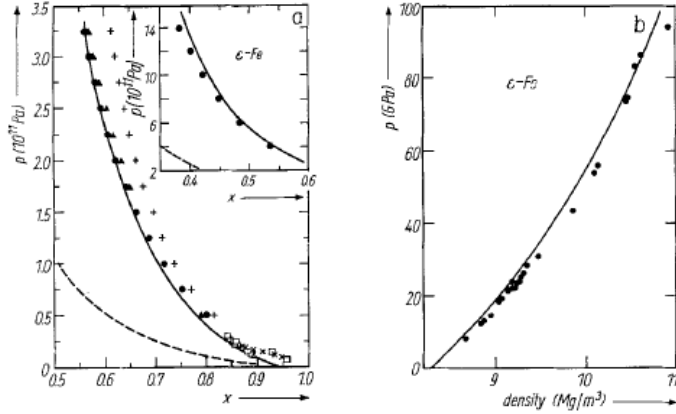


Fig. 8. Iron. Comparison of the equations of state MA and WH with experimental data. The curves are calculated for h.c.p. iron. The relative volume shown is  $\rho_0^{(x)}/\rho$  with  $\rho_0^{(x)}$  being the zero-pressure density for b.c.c. iron. The experimental data in a) have been taken from the following references: ● isotherms from Hugoniot data [36], ▲ isotherms from [34, 37], □ X-ray data from [38], × shock-wave data from [39], + smoothed Hugoniot data from [36]. The representation of 300 K isothermal experimental values in b) has been taken from [40], one value has been corrected according to the original work [35]

Ullmann and Pankov [26] who have compiled the numerical values from literature.

Since we have  $\rho_0^{(x)}/\rho_0^{(e)} = \frac{7.87}{8.36} = 0.9414$  for the ratio of the zero-pressure densities

of b.c.c. iron to h.c.p. iron, the  $p$ - $x$  curve for  $\epsilon$ -Fe begins only at  $x = 0.9414$ . When we look at Fig. 1 to 9, we see that MA yields a significant improvement in the approximation of the experimental data over WH. In particular, the excellent approximation obtained for iron shows good promise for an application in the study of the cores of the terrestrial planets. (Since the mantles of these planets are composed in a complex manner of silicates, oxides, and other materials, simpler equations of state will still have to be used for them. It is advisable to employ the model MZ [41], developed from [42] for this purpose.)

Table 2 shows a few further comparisons between the model WH and the new model MA, respectively, and observational results. In the first column, the element is

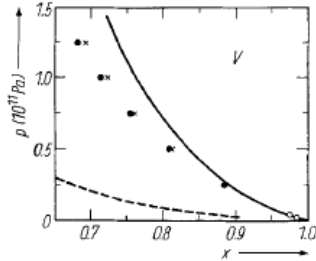


Fig. 9. Vanadium. Comparison of the equations of state MA and WH with experimental data: × and ● Hugoniot and room isotherm values calculated from them according to [34], ○ static data from [31]

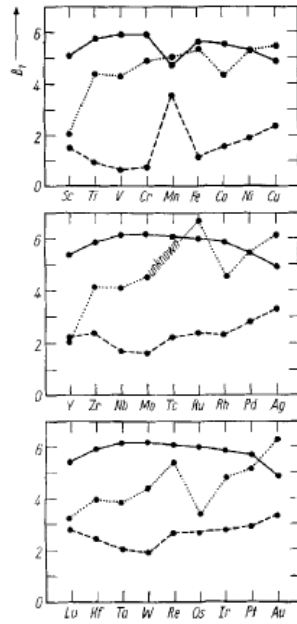


Fig. 10. The full line links the first derivatives of the bulk modulus with respect to pressure at vanishing pressure as predicted by MA, the dashed line the corresponding values as predicted by WH. The dotted line links the experimental values  $B_{1,ex}$ . An interesting paper on the systematics shown here has been written by Vohra et al. [46]

given. Unless something else is specified, it is in the  $\alpha$ -phase. The second column shows by how many times the experimental zero-pressure bulk modulus is greater than the theoretical one according to WH. For MA, this ratio equals unity for all transition metals according to the construction of the model and, thus, is ideal. The experimental initial first derivative of the bulk modulus with respect to pressure, called  $B_{1,ex}$ , is given in the third column. The corresponding theoretical values  $B_1$  in the next two columns prove that MA gives a somewhat better approximation of the measured values than WH (see also Fig. 10). It is a large advantage of MA that, in contrast to the usual equations of state, it does not require  $B_{1,ex}$  as an input parameter, since this quantity is only insufficiently known for most materials. Unless specified otherwise, most  $B_{1,ex}$  values have been taken from Steinberg [43]. As Fig. 1 to 9 have shown that MA yields a realistic equation of state, the sixth column of Table 2 gives a view as to how the pressure values in the Periodic Table that are necessary for compressing the substance to  $x = 0.75$  change.

#### 4. Conclusions

A combination [12, 14] of the muffin-tin orbital theory and the transition-metal pseudopotential theory was used for formulating the d-band structure of transition metals. This permitted to write the total energy as a sum of the kinetic energy of the free electrons, the exchange energy, a Madelung term, and its pseudopotential correction as well as two terms representing band broadening and hybridization effects. Three assumptions were introduced:

- (i) The nearest-neighbor separation to atomic radius ratio is constant.
- (ii) At zero-pressure volume, the pressure has to vanish exactly.
- (iii) At zero-pressure volume, the experimental zero-pressure bulk modulus must be exactly obtained.



Table 2  
Supplementation of the comparison of the models MA and WH through experimental data. For an explanation, see text

element	$B_{0,ex}/B_0$ defined by WH	$B_{1,ex}$	$B_1$ defined by WH	$B_1$ defined by MA	$p$ (100 MPa) at $x = 0.75$ , defined by MA	$b$	$c$
Sc	2.427	2.0*)	1.432	5.111	269.92	1.846	4.190
Ti	5.030	4.37	0.814	5.736	707.07	2.071	4.844
V	6.173	4.26	0.609	5.913	1113.60	2.217	5.530
Cr	5.513	4.89*)	0.709	5.916	1308.37	2.148	5.041
Mn	5.526	5.0**)	3.502	4.724	355.79	0.657	0.632
Fe	3.348	5.29	1.137	5.606	1112.61	2.274	4.962
Fe( $\epsilon$ )					657.93		
Co	2.764	4.26*)	1.569	5.511	1246.95	2.409	4.118
Ni	2.175	5.26	1.876	5.311	1178.45	3.150	4.393
Cu	1.615	5.48	2.411	4.879	816.82	5.573	4.073
Y	2.143	2.0*)	2.182	5.354	234.33	1.567	2.399
Zr	2.290	4.11	2.340	5.858	568.82	1.590	2.240
Nb	3.326	4.06	1.628	6.093	1194.34	1.975	3.105
Mo	3.507	4.50	1.612	6.152	1922.75	2.197	3.293
Tc	2.480	unknown	2.232	6.070	2073.75	2.030	2.634
Ru	2.312	6.61*)	2.402	5.978	2212.19	2.113	2.536
Rh	2.262	4.50*)	2.314	5.822	1827.48	2.461	2.800
Pd	1.716	5.42	2.826	5.495	1171.02	2.550	2.415
Ag	1.369	6.12	3.313	4.920	602.45	3.178	1.951
Lu	1.784	3.2***)	2.762	5.372	263.95	1.396	1.881
Hf	2.314	3.95	2.399	5.962	752.75	1.670	2.269
Ta	2.742	3.79	1.994	6.140	1410.41	1.954	2.773
W	3.070	4.33	1.901	6.169	2282.98	2.185	2.962
Re	2.149	5.41	2.675	6.085	2598.37	1.986	2.286
Os	2.031	3.4**)	2.727	6.026	2896.00	2.207	2.357
Ir	1.948	4.83*)	2.790	5.886	2415.42	2.402	2.350
Pt	1.768	5.18*)	2.946	5.705	1849.06	2.906	2.318
Au	1.572	6.29	3.331	4.865	1027.17	1.428	1.498

\*) According to [44], \*\*) according to [45], \*\*\*) estimated.

The resulting model was tested using experimental compression data from nine transition metals, a significant numerical improvement of prediction being obtained.

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