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Cohesion in d-State Metals at High Pressures

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A description of the d-band structure in which the pseudopotential theory is combined with the muffin-tin orbital theory serves for the calculation of the cohesive properties of d-state metals. The coupling of free-electron states and local, non-overlapping d-states is also taken into account. On this basis, two new models are developed. In both the models, it is assumed that the ratio of nearest-neighbour separation to the atomic radius is independent of the pressure. In the first model (MB), the additional condition is that a redistribution of electrons between the two outer shells, which are not completely filled, is permissible. In the second model (MC), the requirement is that for elements with a filled d-shell the theoretical bulk modulus at vanishing pressure is exactly equal to the experimental bulk modulus at vanishing pressure and that the pressure exactly vanishes for the zero-pressure volume. In a comparison with various kinds of measured values, MC proves to be particularly successful for all d-state metals except Sc, Ti, and Nb. In both the models, the initial pressure derivative of the bulk modulus is not an input parameter, but can be predicted.

Eine Beschreibung der d-Band-Struktur, in der die Pseudopotentialtheorie mit der „muffin-tin“-Orbitaltheorie kombiniert wird, wird für die Berechnung der Kohäsionseigenschaften von Übergangsmetallen benutzt. Die Kopplung der Zustände freier Elektronen und lokaler, nichtüberlappender d-Zustände wird ebenfalls berücksichtigt. Auf dieser Grundlage werden zwei neue Modelle entwickelt. In beiden Modellen wird angenommen, daß das Verhältnis des Abstandes nächster Nachbarn zum Atomradius unabhängig vom Druck ist. Im ersten Modell (MB) ist die zusätzliche Bedingung, daß eine Umverteilung der Elektronen zwischen den beiden äußeren Schalen, die nicht vollständig gefüllt sind, erlaubt ist. Im zweiten Modell (MC) ist die Forderung, daß für Elemente mit einer gefüllten d-Schale der theoretische Kompressionsmodul bei verschwindendem Druck dem experimentellen Kompressionsmodul bei verschwindendem Druck exakt gleich ist und daß der Druck für das Nulldruckvolumen exakt verschwindet. In einem Vergleich mit verschiedenen Arten von Meßwerten zeigt sich MC als besonders erfolgreich für alle Übergangsmetalle außer Sc, Ti und Nb. In beiden Modellen ist die Ableitung des Kompressionsmoduls nach dem Anfangsdruck kein einzugebender Parameter, sondern kann vorhergesagt werden.

1. Introduction

Quite diverse methods are used for calculating the pressure p , the bulk modulus B , and other cohesion-related variables for d-state metals. Migault's method [1, 2], for example, is well suited for practical high-pressure research. He obtains the equation of state from a Morse potential and from a formula for the dependence of the Grüneisenparameter γ on the relative volume x ,

$$\gamma = \frac{3j - 4}{6} - \frac{x}{2} \frac{d^2(px^j)/dx^2}{d(px^j)/dx}.$$

For $j = 0$ the Grüneisen parameter is obtained according to Slater [3], for $j = 2/3$ according to Dugdale and McDonald [4], and for $j = 4/3$ according to Vashchenko and Zubarev [5]. Whereas the constants of the Morse potential follow from conditions

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at vanishing pressure, Migault introduced j as material-specific parameter. He determined it in such a way that for each individual metal the theoretical Hugoniot curves run in an optimum way through the measuring points. In [6] the method has been somewhat generalized. The Birch-Murnaghan equation of state is widely used. It involves the determination of the zero-pressure bulk modulus B_0 and the initial pressure derivative of the bulk modulus B_1 through the fitting of the theoretical curve to the experimental pressure–volume data. Thus, e.g., Heinz and Jeanloz [7] determined B_0 and B_1 from room-temperature static-compression data of gold.

Unlike the authors of these semi-empirical papers, other authors have attempted to derive the afore-mentioned variables from first principles. Principally, it would be necessary to solve a relativistic extension of the Schrödinger equation for a multi-particle problem. This is practically impossible, so that one has to rely on approximations. For pressures above 10 TPa, successes have been achieved by means of statistical Thomas-Fermi-Dirac (TFD) models. By introducing a new correction of the gradient of the local electron density, Perrot [8, 9], with a great deal of numerical work, calculated the equation of state for a few metals with filled lower electron shells, with the TFD proving to be reliable for $x \leq 0.02$ in lithium, $x \leq 0.05$ in beryllium and aluminium, and $x \leq 0.1$ in copper. Unfortunately, these calculations cannot be applied in geophysics because the pressures in the earth only reach to a maximum of 363.85 GPa, so that the relative volume x is much greater, and iron, nickel, and other metals with only partially filled d-shells are assumed to be present in the earth's core. Moruzzi et al. [10] self-consistently calculated the energy bands, among other things also for d-band metals. The zero-pressure variables such as the cohesive energy and bulk modulus obtained as a result, at least for 4d-metals, are very close to the measured values. Computational expenditure, however, is very high, so that the idea to repeat these calculations for high pressures appears to be hardly attractive. On the other hand, attempts should also be made in geophysics and astrophysics as well as in applied high-pressure research to do away with the semi-empirical methods mentioned in the beginning and to provide theory with a more solid physical foundation to improve extrapolatability. It is also not our goal to fit the theory with free parameters to facilitate adaptation to a theory, but to calculate them from theory with the help of well-known inputparameters. Due to the envisaged geophysical application, the theory should be a unified theory for all d-state metals.

Andersen (see [12]), also basing on the density functional formalism [11], has developed his atomic sphere approximation (ASA). Pettifor [13] showed that the calculation of the cohesive properties is largely independent of the details of the band structure computed by means of ASA. Harrison and coworkers [14, 15] also have shown that a separation of the electronic states into local, non-overlapping d-states and free-electron states is possible, with coupling between them being taken into account. A good introduction is given by Pettifor [16]. In the following, basing on the considerations of the quoted authors, we develop two new models, which are related to one another, some simple and plausible additional assumptions being newly introduced. The models will be compared with measured values. The parameters will not be fitted.

2. Theory

Let the number of valence electrons per ion be Z , that of d-electrons Z_d , and that of nearly free s-electrons Z_s . In this case

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

Inspired by [17 to 19], we regard Z_s and Z_d as variables of the atomic volume Ω , which is a function of the pressure p , so that we may cover the transfer of electrons from s to d bands caused by the pressure as well as the occasional reverse transfer,

$$Z_s(\Omega) = \left(Z_s^0 - Z_s^{0'} \Omega_0 + Z_s^{0''} \frac{\Omega_0^2}{2} \right) + (Z_s^{0'} - Z_s^{0''} \Omega_0) \Omega + \dots, \quad (2)$$

where Ω_0 is the atomic volume at zero-pressure, and

$$Z_s^0 = Z_s(\Omega_0), \quad Z_s^{0'} = \left. \frac{dZ_s(\Omega)}{d\Omega} \right|_{\Omega=\Omega_0} \quad \text{and} \quad Z_s^{0''} = \left. \frac{d^2Z_s(\Omega)}{d\Omega^2} \right|_{\Omega=\Omega_0}. \quad (3)$$

At first, we calculate the share E_b to the total energy per ion occurring due to the coupling that broadens the d-states into bands. Using the approximation of the density of d-states according to Friedel [20], we get

$$E_b = -\frac{W_d}{20} Z_d(10 - Z_d). \quad (4)$$

The bandwidth is

$$W_d = \left[\frac{12}{N_a} \right]^{1/2} \left(\sum_i \sum_{j+i} V_D^2(r_{ij}) \right)^{1/2} \quad (5)$$

with

$$V_D \equiv \left(\frac{1}{5} \sum_m V_{ddm}^2(r) \right)^{1/2}. \quad (6)$$

The coupling between the local non-overlapping d-states and the free electron states is expressed by

$$V_{ddm} = \langle d' | H | d \rangle = \frac{2m}{\hbar^2} \sum_{\mathbf{k}} \frac{\langle d' | \Delta | \mathbf{k} \rangle \langle \mathbf{k} | \Delta | d \rangle}{k_d^2 - k^2}. \quad (7)$$

To obtain δV , a muffin-tin potential is assumed. For the hybridization potential [21] we have

$$\Delta = \delta V - \langle d | \delta V | d \rangle. \quad (8)$$

The plane wave is defined by

$$|\mathbf{k}\rangle = \Omega^{-1/2} \sum_l (2l+1) i^l j_l(kr) \left[\frac{4\pi}{2l+1} \right]^{1/2} Y_l^0(\theta_2, \Phi_2) e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (9)$$

The d-states are expressed by

$$|d\rangle = R_2(r) Y_2^m(\theta_1, \Phi_1). \quad (10)$$

\mathbf{r}_j is the position vector of the atom, m the mass, and e the electric charge of the electron, R_2 is the radial d-state wave function, Y_1^0 and Y_2^m are spherical harmonics, $\theta_1, \theta_2, \Phi_1, \Phi_2$ are angular coordinates, r is the interionic distance, N_a the number of atoms, \hbar Planck's constant divided by 2π .

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

with

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

We now introduce two assumptions. First, we assume that the ratio of the nearest-neighbour separation to the atomic radius remains a constant, K , also at rising pressure. Secondly, we assume that $Z_s^{0''}$ and corresponding constants obtained from higher

derivatives, vanish. We take into account that

$$(12)^{1/2} \left[\frac{\eta_{dd0}^2 + 2\eta_{dd1}^2 + 2\eta_{dd2}^2}{5} \right]^{1/2} = 30.9 \quad (13)$$

and, to facilitate the formulation, we introduce the following three material-dependent constants:

$$\begin{aligned} a &= Z_s^0 - Z_s^{0'} \Omega_0, \\ b &= Z_s^{0'}, \\ c &= Z - Z_s^0 + Z_s^{0'} \Omega_0. \end{aligned} \quad (14)$$

Thus, the band-broadening share to the energy is

$$E_b = - (30.9) n^{1/2} \frac{\hbar^2}{2m} \frac{r_d^3}{K^5} \left(\frac{4\pi}{3} \right)^{5/3} (c - b\Omega) \left[1 - \frac{c - b\Omega}{10} \right] \Omega^{-5/3}; \quad (15)$$

n is the number of nearest neighbours of an atom, r_d the d-state radius of the free atom obtained from [21]. There, it had been calculated through fitting to the bandwidths given in [22].

The coupling between occupied d-states and empty plane wave states and the coupling between empty d-states and occupied plane-wave states gives rise to a hybridization shift,

$$\delta E_{hs} = Z_d \sum_{|\mathbf{k}| > k_F} \frac{|\langle \mathbf{k} | \Delta | d \rangle|^2}{E_d - E_{\mathbf{k}}} - (10 - Z_d) \sum_{|\mathbf{k}| < k_F} \frac{|\langle \mathbf{k} | \Delta | d \rangle|^2}{E_d - E_{\mathbf{k}}}. \quad (16)$$

We go along with the argumentation used by Wills and Harrison [15], but on account of our modified assumptions we achieve a different result for the energy share E_c defining the shift of the d-band centre,

$$E_c = (11.40) n \frac{\hbar^2}{m} \frac{r_d^6}{K^8} \left(\frac{4\pi}{3} \right)^{8/3} (c - b\Omega) \Omega^{-8/3}. \quad (17)$$

This energy portion expresses the non-orthogonality of d-like states. k_F is defined by

$$k_F = r_0^{-1} \left(\frac{9\pi Z_s}{4} \right)^{1/3} \quad \text{and} \quad \Omega_0 = \frac{4\pi r_0^3}{3}. \quad (18)$$

The free-electron-like states are dealt with by means of the pseudopotential method [14], with r_c being the Ashcroft empty-core radius and r_0 the atomic radius of [15]. The energy portion of the s-electrons is

$$E_{re} = \frac{3}{10} Z_s \frac{\hbar^2}{m} k_F^2 - \frac{3}{4\pi} Z_s e^2 k_F - \frac{Z_s^2 e^2 \alpha k_F}{(18\pi Z_s)^{1/3}} + \frac{2}{3\pi} Z_s e^2 r_c^2 k_F^3. \quad (19)$$

Now, we convert the terms on the right-hand side of (19) in accordance with our assumptions. The first term is the mean kinetic energy of a uniform electron gas. It is

$$E_1 = (2.210) \frac{\hbar^2}{2m} \left(\frac{4\pi}{3} \right)^{2/3} (a + b\Omega)^{5/3} \Omega^{-2/3}. \quad (20)$$

The second term is the exchange energy and looks as follows:

$$E_2 = -(0.916) \frac{e^2}{2} \left(\frac{4\pi}{3} \right)^{1/3} (a + b\Omega)^{4/3} \Omega^{-1/3}. \quad (21)$$

The Madelung energy is defined by the third term, with $\alpha = 1.8$ being consistently assumed for all transition metals. It is

$$E_3 = -\frac{e^2}{2} \alpha \left(\frac{4\pi}{3}\right)^{1/3} (a + b\Omega)^2 \Omega^{-1/3}. \quad (22)$$

Since the true potential in the Schrödinger equation had been replaced by the pseudo-potential, a correction to the Madelung energy is required. The fourth term thus created looks as follows:

$$E_4 = 2\pi e^2 r_c^2 (a + b\Omega)^2 \Omega^{-1}. \quad (23)$$

From (15), (17), and (20) to (23), the total energy per ion is obtained,

$$E = c_1(a + b\Omega)^{5/3} \Omega^{-2/3} - c_2(a + b\Omega)^{4/3} \Omega^{-1/3} - c_3(a + b\Omega)^2 \Omega^{-1/3} + \\ + c_4(a + b\Omega)^2 \Omega^{-1} - c_5(c - b\Omega) \left[1 - \frac{c - b\Omega}{10}\right] \Omega^{-5/3} + c_6(c - b\Omega) \Omega^{-8/3} \quad (24)$$

with

$$c_1 = (2.210) \frac{\hbar^2}{2m} \left(\frac{4\pi}{3}\right)^{2/3}, \\ c_2 = (0.916) \frac{e^2}{2} \left(\frac{4\pi}{3}\right)^{1/3}, \\ c_3 = \frac{e^2}{2} \alpha \left(\frac{4\pi}{3}\right)^{1/3}, \\ c_4 = 2\pi e^2 r_c^2, \\ c_5 = (30.9) n^{1/2} \frac{\hbar^2}{2m} \frac{r_d^3}{K^5} \left(\frac{4\pi}{3}\right)^{5/3}, \\ c_6 = (11.40) n \frac{\hbar^2}{m} \frac{r_d^6}{K^8} \left(\frac{4\pi}{3}\right)^{8/3}. \quad (25)$$

The equation of state — solved for static pressure — obtained from this is

$$p = -c_1 \frac{5}{3} b(a\Omega^{-1} + b)^{2/3} + c_1 \frac{2}{3} (a\Omega^{-1} + b)^{5/3} + c_2 \frac{4}{3} b(a\Omega^{-1} + b)^{1/3} - \\ - c_2 \frac{1}{3} (a\Omega^{-1} + b)^{4/3} + 2b(a + b\Omega) (c_3 \Omega^{-1/3} - c_4 \Omega^{-1}) - \\ - (a + b\Omega)^2 \left(c_3 \frac{1}{3} \Omega^{-4/3} - c_4 \Omega^{-2}\right) - \\ - c_5 \left[1 - \frac{c - b\Omega}{10}\right] \left(\frac{5}{3} c \Omega^{-8/3} - \frac{2}{3} b \Omega^{-5/3}\right) + \\ + c_5 \frac{1}{10} b(c - b\Omega) \Omega^{-5/3} + c_6 \left(\frac{8}{3} c \Omega^{-11/3} - \frac{5}{3} b \Omega^{-8/3}\right). \quad (26)$$

If conversion into the Hugoniot pressure p_H is necessary, we use

$$p_H = \left\{ p(\Omega) + \frac{\gamma(\Omega)}{\Omega} [E_0 - E(\Omega)] \right\} \left[1 - \frac{\gamma(\Omega)}{2} \left(\frac{\Omega_0}{\Omega} - 1 \right) \right]^{-1}. \quad (27)$$

To calculate the volume dependence of the bulk modulus B , the following formula, following from (26), is used:

$$\begin{aligned} B = & c_1 \frac{10}{9} a \Omega^{-1} [(a\Omega^{-1} + b)^{2/3} - b(a\Omega^{-1} + b)^{-1/3}] - c_2 \frac{4}{9} a \Omega^{-1} [(a\Omega^{-1} + b)^{1/3} - \\ & - b(a\Omega^{-1} + b)^{-2/3}] - \frac{10}{9} b^2 c_3 \Omega^{2/3} + \frac{4}{9} a b c_3 \Omega^{-1/3} - \frac{4}{9} a^2 c_3 \Omega^{-4/3} + \\ & + 2a^2 c_4 \Omega^{-2} + \frac{1}{3} b c c_5 \Omega^{-5/3} - \frac{2}{15} b^2 c_5 \Omega^{-2/3} - \\ & - c_6 \frac{1}{9} (10 - c + b\Omega) (4c\Omega^{-8/3} - b\Omega^{-5/3}) + \frac{88}{9} c c_6 \Omega^{-11/3} - \frac{40}{9} b c_6 \Omega^{-8/3}. \end{aligned} \quad (28)$$

In semi-empirical theories of the cohesive properties, the initial pressure derivative of the bulk modulus B_1 frequently serves as an input parameter. It can be experimentally determined, but only within wide error limits, or it is created there only by fitting the theoretical curves to the measured values. According to the theory presented here, B_1 can be advantageously theoretically calculated,

$$B_1 = \frac{1}{B(\Omega_0)} \left(-\Omega \frac{\partial B}{\partial \Omega} \right)_{\Omega=\Omega_0}, \quad (29)$$

with

$$\begin{aligned} -\Omega \frac{\partial B}{\partial \Omega} = & c_1 \frac{10}{9} a \Omega^{-1} \left[(a\Omega^{-1} + b)^{2/3} + (a\Omega^{-1} + b)^{-1/3} \left(\frac{2}{3} a\Omega^{-1} - b \right) + \right. \\ & \left. + \frac{1}{3} a b (a\Omega^{-1} + b)^{-4/3} \Omega^{-1} \right] - \\ & - c_2 \frac{4}{9} a \Omega^{-1} \left[(a\Omega^{-1} + b)^{1/3} + (a\Omega^{-1} + b)^{-2/3} \left(\frac{1}{3} a\Omega^{-1} - b \right) + \right. \\ & \left. + \frac{2}{3} a b (a\Omega^{-1} + b)^{-5/3} \Omega^{-1} \right] + \\ & + \frac{4}{27} c_3 (5b^2 \Omega^{2/3} + a b \Omega^{-1/3} - 4a^2 \Omega^{-4/3}) + 4c_4 a^2 \Omega^{-2} + \\ & + c_5 \left(b c \Omega^{-5/3} - \frac{1}{5} b^2 \Omega^{-2/3} \right) - c_6 \frac{1}{9} (10 - c + b\Omega) \times \\ & \times \left(\frac{32}{3} c \Omega^{-8/3} - \frac{5}{3} b \Omega^{-5/3} \right) + c_6 \frac{1}{27} (968c\Omega^{-11/3} - 320b\Omega^{-8/3}). \end{aligned} \quad (30)$$

A considerable difficulty in the numerical calculation of $E(x)$, $p(x)$, $B(x)$, B_1 (with $x \equiv \Omega/\Omega_0$) stems from the fact that, because of (14), two unknown parameters are still contained in the constants a , b , and c , namely Z_s^0 and Z_s^0 . They are to be defined by the following two conditions: First, the theoretical $B(\Omega_0)$ must equal the experimental bulk modulus $B_{0,ex}$ at vanishing pressure. Secondly, with $\Omega = \Omega_0$, the pressure p should vanish exactly.

The model described up to this point is designated MB. Due to the just mentioned procedure for the determination of Z_s^0 and Z_s^0 , a very long computation time is required. Although the results are much better than those of a modified Wills-Harrison model (WH in [23]), they are just of medium quality as concerns the coincidence of the theo-

retical with the observed pressures. This becomes obvious in a comparison of the dash-dotted MB curves in Fig. 1 and 2 with the experimental points. Therefore, but above all, because of the time-consuming computational procedure, the model has been simplified and modified: We neglect the redistribution of electrons, i.e., we take $b = 0$ and introduce two constants b_n and c_n , which still have to be specified. In these circumstances, (15), (17), and (20) to (23) yield the following total energy per ion:

$$E = k_1 \Omega^{-2/3} - k_2 \Omega^{-1/3} + k_3 \Omega^{-1} - b_n k_4 \Omega^{-5/3} + c_n k_5 \Omega^{-8/3} \quad (31)$$

with

$$\begin{aligned} k_1 &\equiv (2.210) \frac{\hbar^2}{2m} Z_s^{5/3} \left(\frac{4\pi}{3}\right)^{2/3}, \\ k_2 &\equiv \frac{e^2}{2} [(0.916) Z_s^{4/3} + \alpha Z_s^2] \left(\frac{4\pi}{3}\right)^{1/3}, \\ k_3 &\equiv 2\pi e^2 r_c^2 Z_s^2, \\ k_4 &\equiv Z_d \left(1 - \frac{Z_d}{10}\right) (30.9) n^{1/2} \frac{\hbar^2}{2m} \frac{r_d^3}{K^5} \left(\frac{4\pi}{3}\right)^{5/3}, \\ k_5 &\equiv Z_n (11.40) \frac{\hbar^2}{m} \frac{r_d^6}{K^8} \left(\frac{4\pi}{3}\right)^{8/3}. \end{aligned} \quad (32)$$

The exchange term and the Madelung term have been combined here into the second term on the right-hand side of (31). The equation of state is

$$p = \frac{5}{3} k_1 \Omega^{-5/3} - \frac{1}{3} k_2 \Omega^{-4/3} + k_3 \Omega^{-2} - \frac{5}{3} b_n k_4 \Omega^{-8/3} + \frac{8}{3} c_n k_5 \Omega^{-11/3}. \quad (33)$$

The volume dependence of the bulk modulus is calculated from

$$B = \frac{10}{9} k_1 \Omega^{-5/3} - \frac{4}{9} k_2 \Omega^{-4/3} + 2k_3 \Omega^{-2} - \frac{40}{9} b_n k_4 \Omega^{-8/3} + \frac{88}{9} c_n k_5 \Omega^{-11/3}. \quad (34)$$

The initial pressure derivative of the bulk modulus is determined by means of (29), where, however,

$$\begin{aligned} -\Omega \frac{\partial B}{\partial \Omega} &= \frac{50}{27} k_1 \Omega^{-5/3} - \frac{16}{27} k_2 \Omega^{-4/3} + 4k_3 \Omega^{-2} - \frac{320}{27} b_n k_4 \Omega^{-8/3} + \\ &+ \frac{968}{27} c_n k_5 \Omega^{-11/3} \end{aligned} \quad (35)$$

applies. One obtains *one* possible determination of b_n and c_n by demanding that for $\Omega = \Omega_0$ the pressure is really exactly vanishing and that for $\Omega = \Omega_0$ the theoretical bulk modulus exactly coincides with the experimental bulk modulus. The model thus established is designated MA. It is applicable to materials with full d-shells, i.e. to $Z_d = 10$. If no additions have to be made to the enumerated energy portions, we take $b_n = c_n = 1$. The model WH thus established is applicable to $Z_d \leq 2$. The transition between these two extreme models is assumed to take place in a linear way, i.e.

$$b_n = Z_d^{-1} [(C_1 Z_d - C_2) b_{MA} + (C_3 - C_4 Z_d) b_{WH}]. \quad (36)$$

An analogous formula applies to c_n , with C_1 to C_4 being determined by the boundary conditions. From this the two factors are derived as follows:

$$b_n = (4Z_d)^{-1} [(5Z_d - 10) b_{MA} + 10 - Z_d], \quad (37)$$

$$c_n = (4Z_d)^{-1} [(5Z_d - 10) c_{MA} + 10 - Z_d]. \quad (38)$$

Model C (abbreviated MC) is defined by (31), (37), and (38). In the following, the usefulness of the described theory for the approximation and extrapolation of experimental data is shown.

3. Comparison of the Theoretical Data with Experimental Results

The theoretical predictions of the models MB and MC will now be verified with the help of the measuring data for various physical parameters. Table 1 contains the input parameters used. The first column gives the d-state metal examined. The next columns contain the radius r_0 of the atomic volume, the pseudopotential core radius r_c , and the d-state radius r_d , which have already been mentioned in the previous section. The fifth column contains the nearest-neighbour separation d , the sixth one gives $B_{0,ex}$, the experimental isothermal bulk modulus at vanishing pressure. These two parameters are taken from [24]. The last three columns contain the coordination number n according to [25, 26], the number of s-electrons Z_s , and the number of electrons in the d-band Z_d according to [15]. For MB, only the sum of Z_s and Z_d is used. In Fig. 1 and 2, isothermal and Hugoniot data for silver are compared with MB (dash-dotted curve) and MC (full curve). Although MB constitutes a significant improvement over WH, the pressure values still are clearly too low. MC is already a good approximation, but here the pressures are still slightly underestimated, too. Since the computational expendi-

Table 1
List of input parameters for MB and MC

element	r_0 (10^{-10} m)	r_c (10^{-10} m)	r_d (10^{-10} m)	d (10^{-10} m)	$B_{0,ex}$ (GPa)	n	Z_s	Z_d
Sc	1.81	0.95	1.24	3.25	43.5	12	1.5	1.5
Ti	1.61	0.91	1.08	2.89	105.1	12	1.5	2.5
V	1.49	0.87	0.98	2.62	161.9	8	1.5	3.5
Cr	1.42	0.82	0.90	2.50	190.1	8	1.5	4.5
Mn	1.43	0.78	0.86	2.24	59.6	8	1.5	5.5
Fe	1.41	0.71	0.80	2.48	168.3	8	1.5	6.5
Co	1.39	0.62	0.76	2.50	191.4	12	1.5	7.5
Ni	1.38	0.53	0.71	2.49	186.0	12	1.5	8.5
Cu	1.41	0.46	0.67	2.56	137.0	12	1.5	9.5
Y	1.99	1.09	1.58	3.55	36.6	12	1.5	1.5
Zr	1.77	1.06	1.41	3.17	83.3	12	1.5	2.5
Nb	1.62	1.01	1.28	2.86	170.2	8	1.5	3.5
Mo	1.55	0.95	1.20	2.72	272.5	8	1.5	4.5
Te	1.50	0.84	1.11	2.71	(297.0)	12	1.5	5.5
Ru	1.48	0.72	1.05	2.65	320.8	12	1.5	6.5
Rh	1.49	0.62	0.99	2.69	270.4	12	1.5	7.5
Pd	1.52	0.52	0.94	2.75	180.8	12	1.5	8.5
Ag	1.59	0.45	0.89	2.89	100.7	12	1.5	9.5
Lu	1.92	1.06	1.58	3.43	41.1	12	1.5	1.5
Hf	1.75	1.05	1.44	3.13	109.0	12	1.5	2.5
Ta	1.62	1.02	1.34	2.86	200.0	8	1.5	3.5
W	1.56	0.94	1.27	2.74	323.2	8	1.5	4.5
Re	1.52	0.79	1.20	2.74	372.0	12	1.5	5.5
Os	1.49	0.66	1.13	2.68	(418.0)	12	1.5	6.5
Ir	1.50	0.51	1.08	2.71	355.0	12	1.5	7.5
Pt	1.53	0.33	1.04	2.77	278.3	12	1.5	8.5
Au	1.59	0.40	1.01	2.88	173.2	12	2	9

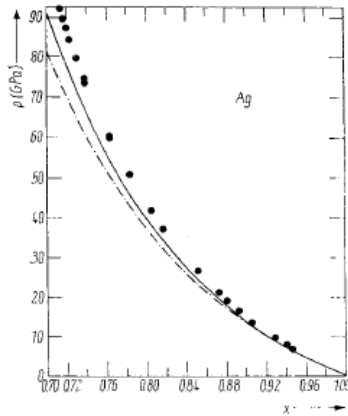


Fig. 1

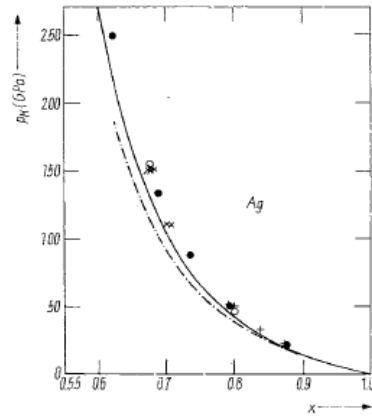


Fig. 2

Fig. 1. Pressure versus isothermal volume ratio x for silver. Solid circles designate the experimental values as reported by Mao et al. [27], the theoretical values according to MB are indicated by a dash-dotted line, and those obtained according to MC by a solid line

Fig. 2. Hugoniot pressure versus relative volume for silver. The measured values are marked \bullet [28], $+$ [29], \times [30], and \circ [31]. Theory MB is dash-dotted, theory MC continuous

ture for MB is extremely high, only MC has been computed for other materials. In Fig. 3 and 4, the predictions of MC are compared with the results of static compression experiments in a p - x plot for gold, α -iron, and ϵ -iron. In all cases, excellent agreement is achieved. The b.c.c.-h.c.p. phase transition for iron is allowed for by $0.949x(\text{Fe}(\alpha)) = x(\text{Fe}(\epsilon))$. Fig. 5 has been based on other experimental data. The approximation of the experimental data by MC (full curve) is very good for gold, palladium, molybdenum,

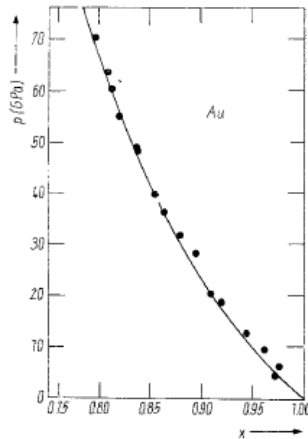


Fig. 3. Static pressure versus relative volume for gold. Measuring points according to Heinz and Jeanloz [7]. As in the following diagrams, the solid line represents MC

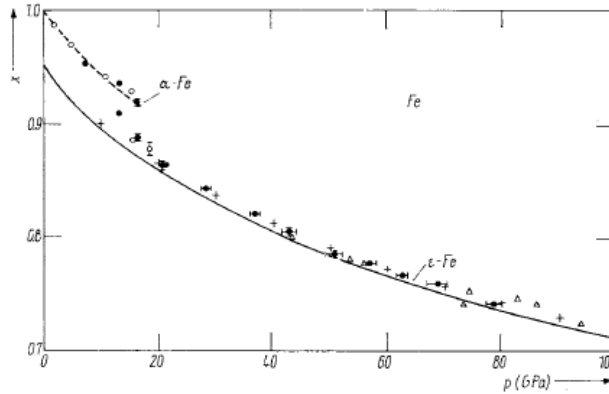


Fig. 4. Relative volume versus pressure for the b.c.c. and h.c.p. phases of iron. \circ are room-temperature static compression data for iron, with neon serving as a pressure-transmitting medium; \bullet the same, with argon serving as medium. The afore-mentioned data have been taken from Jephcoat et al. [32], \triangle from Mao and Bell [33], + from Brown and McQueen [34]

copper, nickel, α -iron, and ϵ -iron. In the case of vanadium, this is only so for high compressions, whereas for medium compressions and for niobium the theoretical curves of MC are too low. The estimations made according to WH are much too low in all cases. For iron, it has been shown that the bulk modulus, too, is very well approximated as a function of the relative volume by MC. The initial pressure derivative B_1 of the bulk modulus can be determined experimentally only with moderate accuracy. These values have been connected by the dotted line in Fig. 6. They have chiefly been taken from Steinberg [46], for scandium, chromium, cobalt, yttrium, ruthenium, rhodium, iridium, and platinum also from [47], and for manganese and osmium from [48]. The value for lutetium has been estimated. The values calculated according to WH have been connected by a dashed line, and the values calculated by means of MC by a continuous line. It turns out that the prediction possible with the help of MC is obviously considerably better. In Fig. 7, an analogous comparison for the zero-pressure bulk modulus B_0 is made. The signs have the same meaning as in Fig. 5. Here, too, MC is a practicable approximation. It should be noted here that also the prediction of Hugoniot pressures by MC is very good for all transition metals except scandium and titanium. Due to lack of space, however, it is not possible to show the comparisons in this paper.

4. Conclusions

Nowadays, it is possible to calculate the cohesive properties of d-state metals from the density functional formalism. However, there is a great deal of computation involved, and for various parameters only the tendency of the distribution in the Periodic Table is correctly indicated. Since it has been found that many details of the band structure are insignificant for cohesion, it has been possible to utilize a simplified theory with a separation of the free-electron states and local, non-overlapping d-states and coupling. From this theory, two models have been newly developed, a model MB with $s \rightarrow d$ electronic transfer and a model MC in which for metals with full d-shells

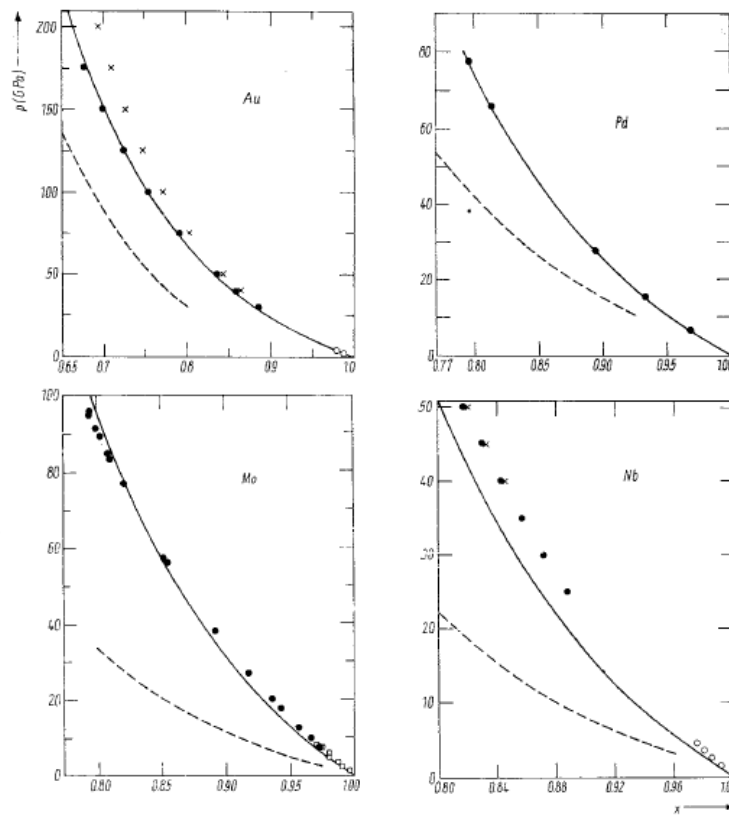


Fig. 5. Comparison of the equations of state MC (full curve) and modified Wills-Harrison (WH, dashed curve) with experimental data. For experimental values see the Table

Legend of symbols of Fig. 5

metal	symbol	reference
Au	●	room isotherm [35]
	×	Hugoniot data [35]
	○	static data [36]
Pd, Mo	●	293 K isothermal data [27]
	□	static data [37]
Nb	○	static data [36, 38]
	●	room isotherm [39]
	×	Hugoniot data [39]
Cu	■	zero isotherm [40]
	●	room isotherm [35]
	×	Hugoniot data [35]

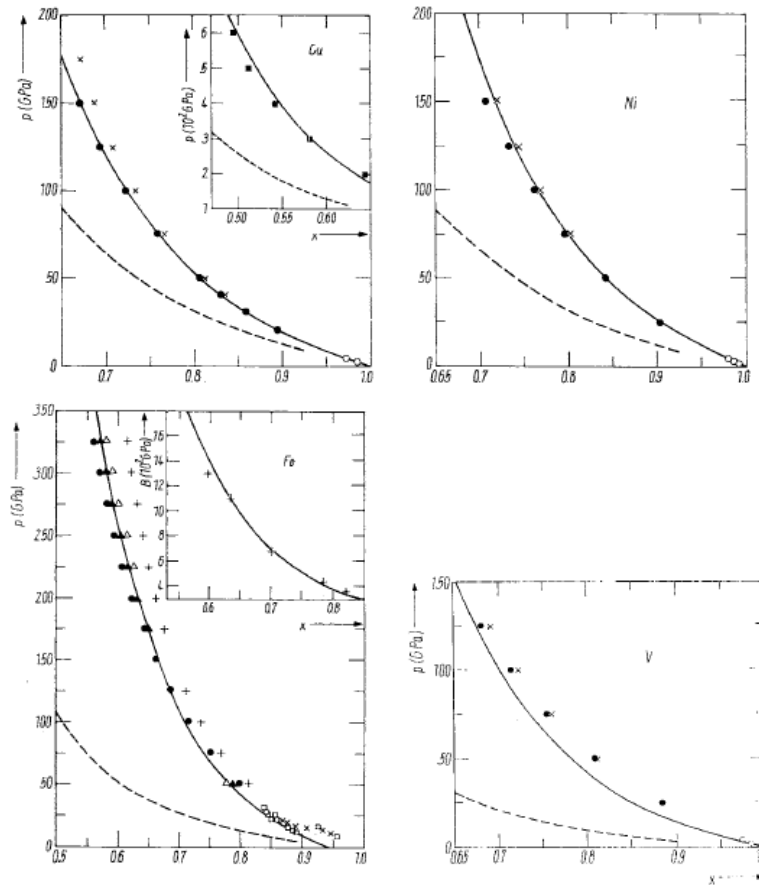


Fig. 5

Ni	○	static data [36, 38]
	●	isotherm [30]
	×	Hugoniot data [30]
Fe	●	isotherm [41]
	▲	isotherm [30, 42]
	□	X-ray data [43]
	+	smoothed Hugoniot data [41]
	×	shock-wave data [44]
	△	interpolated equation of state [45]
V	○	static data [36, 38]
	●	room isotherm [30]
	×	Hugoniot data [30]

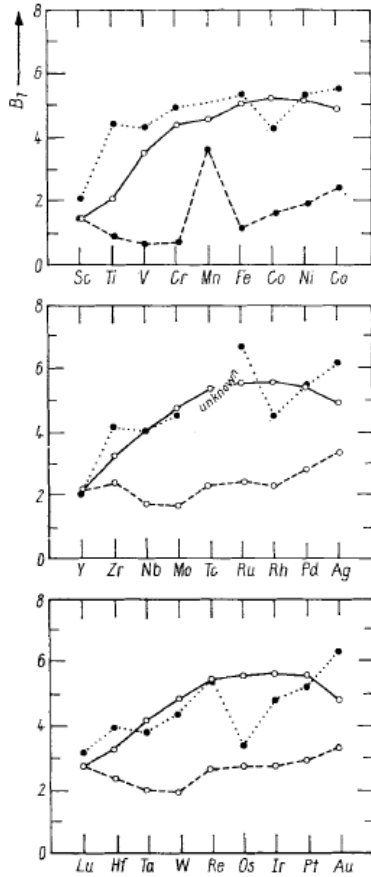


Fig. 6

Fig. 6. The initial pressure derivative of the bulk modulus. The full curve links the values predicted by means of MC, the dashed curve the theoretical values according to WH. The experimental values $B_{1,ex}$ are linked by a dotted line

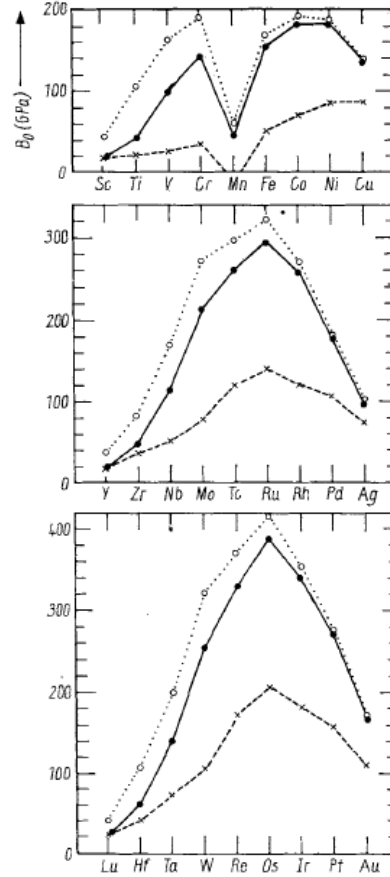


Fig. 7

Fig. 7. The bulk modulus at vanishing pressure. The solid curve links the theoretical predictions according to MC, the dashed curve those of WH. The experimental values $B_{0,ex}$ are linked by dotted lines

at zero pressure the bulk modulus and the zero-pressure volume have been fitted to the measured values, which are rather precisely known. MC gives very good predictions for all d-state metals, with the exception of three, and for these three the tendency of the predictions is correct with respect to the total energy, the static pressure, the Hugoniot pressure, and the bulk modulus, all of these parameters having been examined as functions of the relative volume. The numerical coincidence with experi-

mental results is so good that the predictions can also be used in practical high-pressure research, for investigations of the cores of the planets, and in astrophysics. As compared with semi-empirical methods, it is particularly convenient that the initial pressure derivative of the bulk modulus, which empirically is known only with a great degree of uncertainty, is not employed as an input parameter in MB and MC, but is theoretically calculated instead and yields good agreement in the Periodic-Table systematics of the measured values $B_{1,ex}$.

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