
Calculations of the Hugoniot pressure and pressure derivative of the bulk modulus for transition metals

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Abstract. A bonding theory for transition metals has been derived which permits good to very good predictions for the energy, static pressure, Hugoniot pressure, bulk modulus, and its pressure derivative with respect to their dependence on the relative volume. The d band structure has been expressed through a combination of the transition-metal pseudopotential theory and the muffin-tin orbital theory. The nearly free s electrons contribute four terms to the energy: kinetic energy, exchange energy, a Madelung term, and its pseudopotential correction. Three further assumptions are made: the ratio of the nearest-neighbour separation to the atomic radius remains constant for each pressure; at least for elements with full d shells the pressure must exactly disappear at zero-pressure volume; and at least for elements with full d shells the calculated and the experimental bulk modulus must be in exact agreement at vanishing pressure. The essential aspect of this theory, called MC theory, is that it is applicable in a unified manner to all transition metals. In addition to seven well-known microphysical input parameters, two macrophysical input parameters are required.

1 Introduction

In practical high-pressure research, in geophysics and astrophysics, it is common practice to use three-parameter approximations for the Hugoniot and also for the isothermal equation of state. Usually these equations of state are substantiated through thermodynamic considerations, while some are even purely empirical. In most cases, the zero-pressure density, ρ_0 , the initial bulk modulus, B_0 , and the pressure derivative of the bulk modulus, B_1 , at vanishing pressure are used as input parameters. Pan'kov and Ullmann (1979) and Stacey et al (1981) have drawn up a systematic list of commonly used equations of state of this type. Such equations are also frequently used for metals. Thus, for example, Fisher et al (1974) have employed the second order Birch-Murnaghan equation for estimating B_1 from shock wave data. Only a slight dependence on the pressure was obtained, so that the equation was applicable. The most uncertain variable in the aforementioned type of equations is B_1 . Therefore, my intention will not be to employ B_1 as an input parameter, but to use very exactly known constants from atomic physics instead. Moreover, a more precise analysis of the bonding and cohesive forces would be desirable. On the other hand, there are quite a number of theoretical physical papers on the electron theory of metals. Good surveys on this subject were written, for example, by Harrison (1980), Mackintosh and Andersen (1980), and Pettifor (1983), and edited by Ziesche and Lehmann (1983). The original papers on the electron theory of metals, however, rarely get as far as macrophysical variables, such as pressure, density, bulk modulus, and their derivatives, Grüneisen parameter, etc. Where these variables were calculated with good accuracy there was a great deal of computer work involved (eg Moruzzi et al 1978). Where considerable simplifications have been made (eg Wills and Harrison 1983), the tendencies of the variables in the Periodic Table are well represented in qualitative terms, but the accuracy of the prediction is too low for practical purposes.

It is the objective of the present paper to close the gap between theoretical physics and practical high-pressure research in relation to transition metals, with only moderate amount of computation. Frequently, theories are verified with the help

of only a few examples, in which cases the approximation may be very good (see, for example, Lin and Li 1983). Here however, a unified theory is preferred, i.e. the main objective is not the greatest accuracy of the approximation of the measured values for *a few* materials, but the good approximation of several macrophysical observable variables for, if possible, all transition metals with the help of *one* equation of state. In the same spirit, an earlier paper on metals (Walzer 1984a) showed analogies to the Thomas–Fermi theory with allowance for the exchange energy of the nearly free electrons made through an expression stemming from the Hartree–Fock theory. No allowance had been made in that paper for the strong attractive force of the partially filled d band. This force, however, is essential for the bonding of transition metals. Another approach will be adopted here also with regard to the nearly free electrons.

In principle, the Hugoniot pressure and pressure derivative of the bulk modulus as well as other macrophysical variables can nowadays be derived from quantum mechanics. Starting from the one-electron approximation, self-consistent band calculations can be made by using, eg, the density-functional formalism introduced by Hohenberg and Kohn (1964). Exchange and correlation are represented here as a function of electron density. The total energy reaches its minimum for the true electron density. From the band structure thus calculated many properties can be derived: elastic parameters and bonding structure, phonon spectra and Grüneisen parameter, melting temperatures and phase diagrams. Fermi surfaces, de Haas–van-Alphen effect, densities of states, electronic heat capacity, x-ray diffraction, electron–phonon coupling, electric and thermal conductivities and many other ones. Since these band structure calculations are too tedious for practical applications, for example in geophysics, use is made here of the finding by Pettifor (1977) and Wills and Harrison (1983), who, using different approaches, had shown that a separation between nearly free sp electrons and d-like states yields meaningful results. Harrison and Froyen (1980) derived earlier simplified expressions for the d band structure from the pseudopotential theory and muffin-tin orbital theory. Walzer (1984b) tried to derive the static pressure p as a function of the relative volume x for transition metals and was successful chiefly for transition metals with a nearly full d shell. The theory presented here is a combination of Wills and Harrison’s (1983) and Walzer’s (1984b) approaches. It has also been possible to use in this paper much more comprehensive material from observations for verification.

2 Theory

Let the number of d electrons be Z_d . If we want to calculate the d band broadening portion, E_b , of the total energy per ion, we can estimate the density of d states per ion after Friedel (1969) and obtain

$$E_b = -\frac{1}{20}W_d Z_d(10 - Z_d), \quad (1)$$

where W_d is the bandwidth. To be able to calculate the bandwidth, we can, after Wills and Harrison (1983), express the connection between local nonoverlapping d states and the orthogonalized plane waves by a hybridization matrix element $\langle \mathbf{k} | \Delta | d \rangle$, where Δ is a hybridization term in the Hamiltonian. Δ is spherically symmetric around the nucleus:

$$\Delta = \delta V - \langle d | \delta V | d \rangle;$$

δV is the difference between the bulk potential and the potential of the free atom. The plane wave is defined by the equation:

$$|\mathbf{k}\rangle = \Omega^{-1/2} \sum_l (2l+1) i^l j_l(kr) \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_l^0(\theta_2, \phi_2) \exp(i\mathbf{k} \cdot \mathbf{r}_j) \quad (2)$$

where Ω is the volume of the system, r_i the position vector of the atom, Y_l^0 the spherical harmonic, and θ_2 and ϕ_2 are angular coordinates. The $|k\rangle$ are orthogonal to the core states and d states.

$$|d\rangle = R_2(r) Y_2^m(\theta_1, \phi_1) \quad (3)$$

defines the atomic d states. R_2 is the radial d state wave function. The bandwidth is obtained from

$$W_d = \left(\frac{12}{N_a} \right)^{1/2} \left| \sum_i \sum_{j \neq i} V_D^2(r_{ij}) \right|^{1/2}, \quad V_D \equiv \left[\frac{1}{5} \sum_m V_{ddm}^2(r) \right]^{1/2} \quad (4)$$

with

$$V_{ddm} = \frac{2m}{\hbar^2} \sum_k \frac{\langle d' | \Delta | k \rangle \langle k | \Delta | d \rangle}{k_d^2 - k^2} \quad (5)$$

or

$$V_{ddm} = \frac{\hbar^4}{m^2} \left(\frac{r_d}{r_0} \right)^3 \sum_k \frac{k^4 Y_2^{m*}(\theta_k, \phi_k) Y_2^m(\theta_k, \phi_k)}{(-\hbar^2 k^2 / 2m)} \exp(i\mathbf{k} \cdot \mathbf{d}) \quad (6)$$

with $\mathbf{k} \cdot \mathbf{d} = kd \cos \theta_k$ and

$$V_D(r) = \frac{\hbar^2 r_d^3}{m r^5} \left[\frac{1}{5} (\eta_{dd0}^2 + 2\eta_{dd1}^2 + 2\eta_{dd2}^2) \right]^{1/2}. \quad (7)$$

r_d is the d state radius stemming from free-atom calculations. The numerical values for it are taken from Harrison and Froyen (1980, table 1). They obtained the r_d values by fitting the bandwidths given by Andersen and Jepsen (1977) using the atomic-sphere approximation. m is the electron mass, \hbar is Planck's constant divided by 2π , r is the interionic distance, N_a the number of atoms, n the coordination number. r_0 is the radius of the atomic volume $\Omega_0 = \frac{4}{3}\pi r_0^3$. We have

$$\eta_{dd0} = -\frac{45}{\pi}, \quad \eta_{dd1} = \frac{30}{\pi}, \quad \eta_{dd2} = -\frac{15}{2\pi}. \quad (8)$$

This is a result which, in a somewhat different form, has been obtained by Andersen (1973) from his atomic sphere approximation.

In the following we assume that the ratio of the nearest-neighbour separation to the atomic radius remains a constant, K , even for the case where the crystal is compressed. Furthermore, we only take into account the interaction of nearest neighbours.

Thus, because

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

we obtain the bandwidth term of the total energy

$$E_b = -Z_d \left(1 - \frac{1}{10} Z_d \right) \times 30.9 n^{1/2} \frac{\hbar^2}{2m} \frac{r_d^3}{K^5} \left(\frac{4}{3}\pi \right)^{5/3} \Omega_0^{-5/3}. \quad (9)$$

By means of

$$E_b \equiv -k_4 \Omega_0^{-5/3}. \quad (10)$$

we define the constant k_4 .

Another contribution to the total energy is made by the coupling between empty d states and occupied plane-wave states and the coupling between occupied d states

and empty plane-wave states. This hybridization shift share in the energy is

$$\delta E_{\text{hs}} = Z_d \sum_{|\mathbf{k}| > k_F} \frac{|\langle \mathbf{k} | \Delta | d \rangle|^2}{(E_d - E_{\mathbf{k}})} - (10 - Z_d) \sum_{|\mathbf{k}| < k_F} \frac{|\langle \mathbf{k} | \Delta | d \rangle|^2}{(E_d - E_{\mathbf{k}})}, \quad (11)$$

with $k_F = r_0^{-1} (\frac{2}{3} \pi Z_s)^{1/3}$, Z_s being the number of nearly free s electrons. The contribution to the total energy expressing the shift in the d band centre is

$$E_c = Z_d n (11.40) \frac{\hbar^2 r_d^6}{m K^8} (\frac{4}{3} \pi)^{8/3} \Omega_0^{-8/3} \equiv k_5 \Omega_0^{-8/3}. \quad (12)$$

The electrons of the outer shell are treated as a uniform electron gas. The true potential in the Schrödinger equation is replaced by an empty-core pseudopotential. For practical calculation, the radius of the core, r_c , is taken from Harrison (1980). The energy of the free-electron-like states is

$$E_{\text{fe}} = \frac{3}{10} Z_s \frac{\hbar^2}{m} k_F^2 - \frac{3}{4\pi} Z_s e^2 k_F - \frac{Z_s^2 e^2 \alpha k_F}{(18\pi Z_s)^{1/3}} + \frac{2}{3\pi} Z_s e^2 r_c^2 k_F^3. \quad (13)$$

e is the electron charge, $\alpha = 1.8$ is to be fixed in our calculations. The first term on the right-hand side of equation (13) represents the mean kinetic energy of the nearly free electrons, the second the exchange energy, which is a result of Pauli's exclusion principle, the third is the Madelung energy, while the fourth is a correction of the Madelung term, which is required because the true potential in the Schrödinger equation is replaced by the pseudopotential. From equation (13) we get

$$E_{\text{fe}} = k_1 \Omega_0^{-2/3} - k_2 \Omega_0^{-1/3} + k_3 \Omega_0^{-1}, \quad (14)$$

with

$$k_1 = 2.210 \frac{\hbar^2}{2m} Z_s^{5/3} (\frac{4}{3} \pi)^{2/3}, \quad (15)$$

$$k_2 = \frac{1}{2} e^2 [0.916 Z_s^{4/3} + \alpha Z_s^2] (\frac{4}{3} \pi)^{1/3}, \quad (16)$$

$$k_3 = 2\pi e^2 r_c^2 Z_s^2. \quad (17)$$

Magnetic contributions to the total energy of the 3d metals are important (Eastman et al 1979; Hasegawa and Pettifor 1983). Allowance for them could be made through local-spin-density calculations. However, we shall not do this and take them generally into account in the constants b_n and c_n still to be introduced. As concerns iron, we are mainly interested in the non-magnetic ϵ -phase because of the envisaged application of the theory to the Earth's core. By adding up the individual portions, we get for the energy

$$E = k_1 \Omega^{-2/3} - k_2 \Omega^{-1/3} + k_3 \Omega^{-1} - b_n k_4 \Omega^{-5/3} + c_n k_5 \Omega^{-8/3}, \quad (18)$$

with b_n and c_n still having to be specified. As has been shown, the values for k_1 to k_5 can be calculated from atom-physical variables and are individually fixed for each transition metal. From equation (18) follows the equation of state

$$p = \frac{2}{3} k_1 \Omega^{-5/3} - \frac{1}{3} k_2 \Omega^{-4/3} + k_3 \Omega^{-2} - \frac{5}{3} b_n k_4 \Omega^{-8/3} + \frac{8}{3} c_n k_5 \Omega^{-11/3}. \quad (19)$$

The bulk modulus, B , can be calculated from the static pressure p by means of $B = -\Omega \partial p / \partial \Omega$.

$$B = \frac{10}{9} k_1 \Omega^{-5/3} - \frac{4}{9} k_2 \Omega^{-4/3} + 2k_3 \Omega^{-2} - \frac{40}{9} b_n k_4 \Omega^{-8/3} + \frac{88}{9} c_n k_5 \Omega^{-11/3}. \quad (20)$$

We define the relative volume $x = \Omega / \Omega_0$, which will be largely used for comparing the theory with the measured values. If we demand that for vanishing pressure

actually $x = 1$, a trivial requirement that has to be satisfied, and that the theoretical zero-pressure bulk modulus, B_0 , is in conformity with the experimental zero-pressure bulk modulus, $B_{0,ex}$, which can be quite precisely determined, *one* of the possibilities for fixing b_n and c_n is obtained. The model thus produced will be designated MA. If, on the other hand, one holds the view that all essential factors have already been covered with the enumerated energy portions, one can take $b_n = c_n = 1$. The model thus created will be designated WH. A compromise model is created if one assumes that the model WH applies to $Z_d \leq 2$ while the model MA applies to $Z_d = 10$ (ie to materials consisting of atoms with a full d shell), and that the transition between these extreme models takes place in a linear manner. The last requirement is expressed by the statement

$$b_n = \frac{1}{Z_d} [(c_1 Z_d - c_2) b_{MA} + (c_3 - c_4 Z_d) b_{WH}] \quad (21)$$

and by a similar statement for c_n . From this follow

$$b_n = \frac{1}{4Z_d} [(5Z_d - 10) b_{MA} + 10 - Z_d] \quad (22)$$

and

$$c_n = \frac{1}{4Z_d} [(5Z_d - 10) c_{MA} + 10 - Z_d]. \quad (23)$$

Model C (abbreviated MC) is defined through equations (18), (22), and (23). We use the variable

$$-\Omega \frac{\partial B}{\partial \Omega} = \frac{59}{27} k_1 \Omega^{-5/3} - \frac{16}{27} k_2 \Omega^{-4/3} + 4k_3 \Omega^{-2} - \frac{320}{27} b_n k_4 \Omega^{-8/3} + \frac{968}{27} c_n k_5 \Omega^{-11/3} \quad (24)$$

for calculating the pressure derivative of the bulk modulus at zero pressure:

$$B_1 = \frac{1}{B(\Omega_0)} \left(-\Omega \frac{\partial B}{\partial \Omega} \right)_{\Omega = \Omega_0} \quad (25)$$

$x^{1/3}$ is the ratio of a certain length in the metal body under pressure to the same length at vanishing pressure. We use

$$x^{1/3} = \frac{1 + \gamma_0^{-1}}{1 + \gamma^{-1}} \quad (26)$$

and the following expression for the Hugoniot pressure p_H

$$p_H = \frac{p(\Omega) + [\gamma(\Omega)/\Omega][E_0 - E(\Omega)]}{1 - \frac{1}{2}\gamma(\Omega)[(\Omega_0/\Omega) - 1]}, \quad (27)$$

where γ is the Grüneisen parameter, and γ_0 the Grüneisen parameter at zero pressure.

3 Comparison of the theory with experimental results

We now want to use various experimental variables for the verification of MC, namely the Hugoniot pressure, p_H , the bulk modulus, B , the pressure derivative of the bulk modulus at zero pressure, B_1 , etc. It is the main purpose of this paper to show that the MC theory really yields numerical values which are applicable in high-pressure research, and that a unified approach applies to all transition metals. Therefore it is important to make a comparison with all accessible experimental $p_H(x)$ values. The comparison with the experimental data for static pressure $p(x)$ is of a comparable quality (Walzer 1987). For each transition metal nine input parameters, listed in

table 1, are required for the calculation of the theoretical curves or numerical values among them, the radius of the atomic volume, r_0 , the core radius, r_c , and the d state radius, r_d , the origin of which has already been mentioned. Also required are the nearest-neighbour separation, d , and $B_{0,ex}$, the experimental isothermal bulk modulus at vanishing pressure. These two variables have been taken from Kittel (1970). Then follows the zero-pressure Grüneisen parameter γ_0 given by Gschneidner (1964). n is the number of nearest-neighbour atoms after Leibfried and Breuer (1978) and Schulze (1967). Z_s is the number of electrons per ion in the free-electron-like state, and Z_d is the number of d band electrons according to Wills and Harrison (1983). Only $B_{0,ex}$ and γ_0 are macroscopic variables, γ_0 being needed only for the calculation of $\rho_H(x)$ and $\gamma(x)$. First, we shall compare in figure 1 the theoretical data with the observed Hugoniot data. Out of the twenty-seven transition metals, only for four—osmium, ruthenium, technetium, and manganese—no experimental values could be located, so that no comparison was possible in these cases. The other twenty-three transition metals are dealt with in the order of decreasing atomic weights. The approximation of the measured values through MC is very good for gold and iridium. The same is true of platinum for the range $0.7 \leq x \leq 1$; for higher compressions ($x < 0.7$), the approximation is good, but the theoretical Hugoniot values are somewhat too high. For rhenium, the agreement between theoretical values and measured values is very good in the interval $0.8 \leq x \leq 1$; and for tungsten in the interval $0.75 \leq x \leq 1$. For higher compressions, the theory is also good, but the theoretical Hugoniot pressure is a little bit overestimated. The approximation of the

Table 1. List of input parameters for MC.

Element	$\frac{r_0}{10^{-10} \text{ m}}$	$\frac{r_c}{10^{-10} \text{ m}}$	$\frac{r_d}{10^{-10} \text{ m}}$	$\frac{d}{10^{-10} \text{ m}}$	$\frac{B_{0,ex}}{\text{GPa}}$	γ_0	n	Z_s	Z_d
Sc	1.81	0.95	1.24	3.25	43.5	(1.03)	12	1.5	1.5
Ti	1.61	0.91	1.08	2.89	105.1	1.28	12	1.5	2.5
V	1.49	0.87	0.98	2.62	161.9	1.38	8	1.5	3.5
Cr	1.42	0.82	0.90	2.50	190.1	1.51	8	1.5	4.5
Mn	1.43	0.78	0.86	2.24	59.6	1.16	8	1.5	5.5
Fe	1.41	0.71	0.80	2.48	168.3	1.70	8	1.5	6.5
Co	1.39	0.62	0.76	2.50	191.4	1.95	12	1.5	7.5
Ni	1.38	0.53	0.71	2.49	186.0	1.83	12	1.5	8.5
Cu	1.41	0.46	0.67	2.56	137.0	1.96	12	1.5	9.5
Y	1.99	1.09	1.58	3.55	36.6	1.00	12	1.5	1.5
Zr	1.77	1.06	1.41	3.17	83.3	0.71	12	1.5	2.5
Nb	1.62	1.01	1.28	2.86	170.2	1.58	8	1.5	3.5
Mo	1.55	0.95	1.20	2.72	272.5	1.61	8	1.5	4.5
Tc	1.50	0.84	1.11	2.71	(297.0)	(2.61)	12	1.5	5.5
Ru	1.48	0.72	1.05	2.65	320.8	3.12	12	1.5	6.5
Rh	1.49	0.62	0.99	2.69	270.4	2.29	12	1.5	7.5
Pd	1.52	0.52	0.94	2.75	180.8	2.18	12	1.5	8.5
Ag	1.59	0.45	0.89	2.89	100.7	2.44	12	1.5	9.5
Lu	1.92	1.06	1.58	3.43	41.1	0.66	12	1.5	1.5
Hf	1.75	1.05	1.44	3.13	109.0	1.04	12	1.5	2.5
Ta	1.62	1.02	1.34	2.86	200.0	1.69	8	1.5	3.5
W	1.56	0.94	1.27	2.74	323.2	1.76	8	1.5	4.5
Re	1.52	0.79	1.20	2.74	372.0	2.59	12	1.5	5.5
Os	1.49	0.66	1.13	2.68	(418.0)	(2.02)	12	1.5	6.5
Ir	1.50	0.51	1.08	2.71	355.0	2.39	12	1.5	7.5
Pt	1.53	0.33	1.04	2.77	278.3	2.69	12	1.5	8.5
Au	1.59	0.40	1.01	2.88	173.2	3.06	12	2	9

experimental Hugoniot values of hafnium is good to very good, and for tantalum in the range $0.7 \leq x \leq 1$ very good. For $x < 0.7$ the approximation can be designated as good with tantalum. For the closely related elements lanthanum and lutetium, the following holds: observational values are known only for lanthanum, the complete set of input parameters only for lutetium. Therefore a partially illegitimate comparison has been made in the diagram; this comparison, however, showed good to very good coincidence. For silver, palladium and niobium the theory showed very good agreement with the measured values over the entire pressure range. For rhodium and molybdenum, this was the case for $0.75 \leq x \leq 1$; for $x < 0.75$, the theoretical p_H values are somewhat too high. The approximation of the measured values for zirconium and yttrium can be called good to very good. For reasons of clarity not all experimental values could be entered into one plot for copper. Agreement is very good over the entire measuring range. This was also the case in three further $p_H(x)$ diagrams not shown here. The same can be said of nickel. In the case of cobalt the measured values for $0.7 \leq x \leq 1$ are very well approximated; for $0.7 < x$, the theoretical Hugoniot values are somewhat too high. In the case of iron it should be noted that a bcc-hcp phase transition occurs at about 13 GPa and that the majority of the measured values belong to ϵ -Fe. The volume change at the transition point is approximately 5.1%. Therefore, the following recalculation was made: $0.949x(\alpha\text{-Fe}) = x(\epsilon\text{-Fe})$. Everywhere, the approximation of the measured values is very good, also for low α -Fe values, for which no curve has been plotted here. It is clear that iron is of particular importance for investigations of the Earth's core, in particular with regard to a few unsolved problems which relate to the nature of hydromagnetic convection in the outer core (Ullmann and Walzer 1980). The representation of the measured values by MC can be judged to be good to very good for chromium, the theoretical p_H values being somewhat too low. Vanadium is very well approximated for $0.6 \leq x \leq 1$ and well for $x < 0.6$. In the latter range the theoretical values are somewhat overestimated. The approximation of the measured values for titanium is good in the range $x < 0.6$ and moderate to bad for $0.6 \leq x \leq 1$. The approximation for scandium is bad, at least for practical purposes. Yet the curvature of the theoretical curves is also correct in the last two cases. Thus the result is that MC represents the Hugoniot values of the transition metals well to very well with the exception of the two elements which are situated in the left upper corner of the respective section of the Periodic Table.

Further comparisons of the MC theory with observational results follow. In the first column of table 3 all transition metals are given. In the second column, the initial first derivative of the bulk modulus with respect to pressure is listed. Considerable uncertainty exists in regard of the variable $B_{1,ex}$, but it serves in many equations of state as an input parameter; this, naturally leads to a considerable uncertainty in the plots of $p_H(x)$, $p(x)$, etc. In contrast to this, we are able to calculate theoretically B_1 . The third column shows the theoretical B_1 values of a modified Wills-Harrison theory, the fourth the theoretical B_1 values of our MC theory. The observational variables $B_{1,ex}$ are much better approximated by MC than by WH. The fifth column shows how many times the experimental zero-pressure bulk modulus $B_{0,ex}$ is greater than the theoretical one according to WH. The same ratio for MC is shown in the sixth column. Here, too, the approximation of the measured values by MC is significantly better, in particular for d state metals with nearly full d shells. In the seventh column, the Hugoniot pressure is listed for all transition metals according to MC; this pressure leads to a decrease in the volume by one quarter of the original volume. Finally, the last two columns contain a list of the constants b_n and c_n that can be calculated with the help of the MC theory.

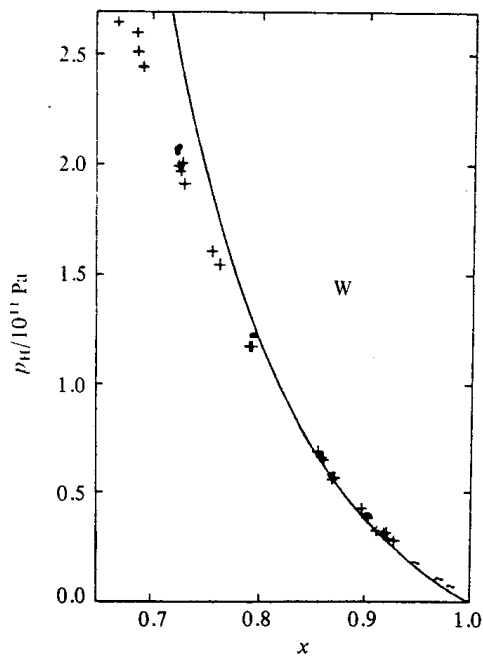
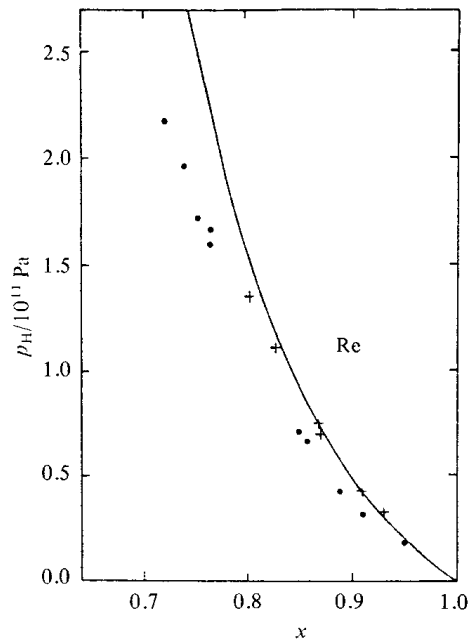
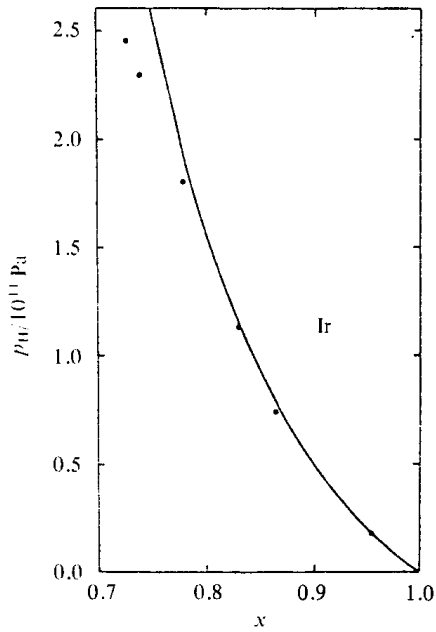
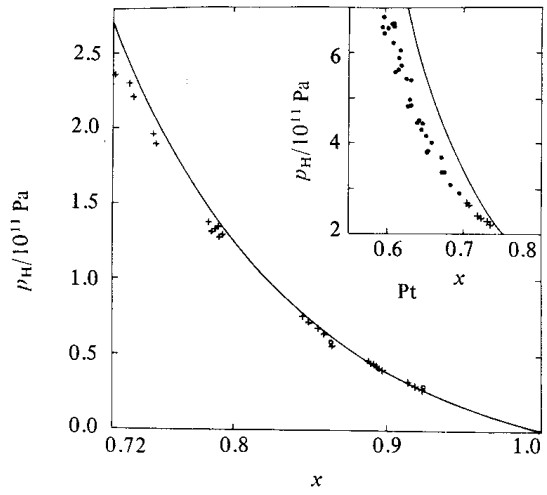
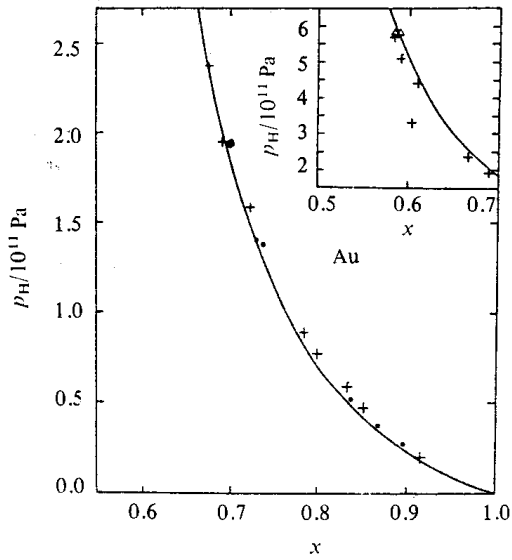


Figure 1. Hugoniot pressure, p_H , plotted against relative volume, x . For the symbols and origin of the experimental values, see table 2. The solid curves define the theoretical values which have been calculated by means of MC.

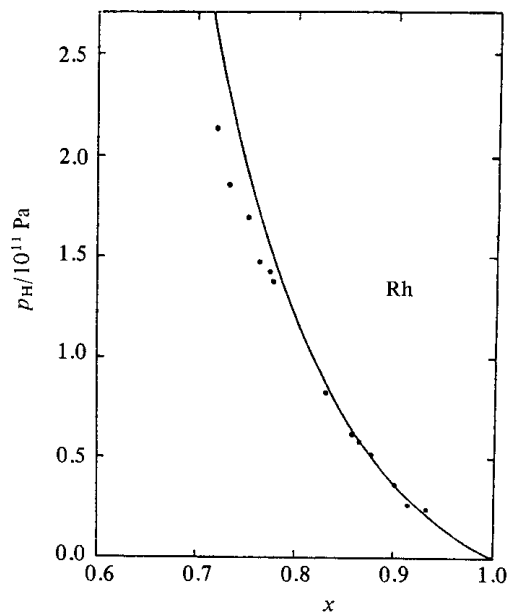
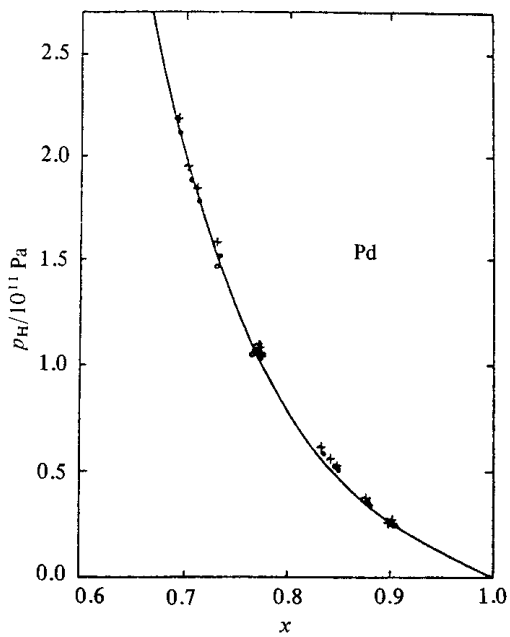
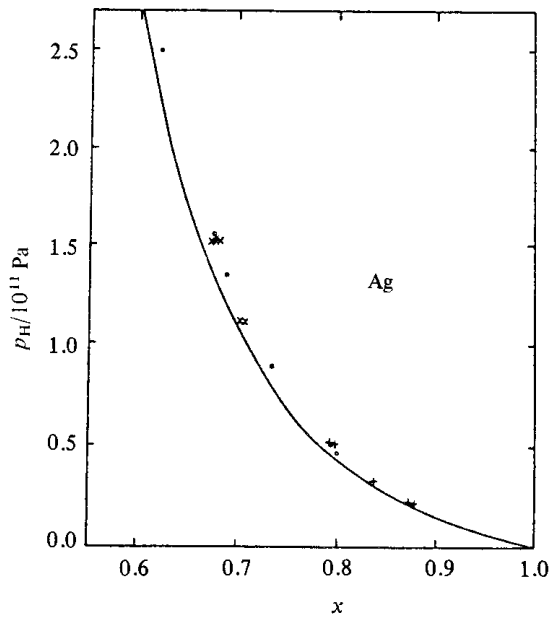
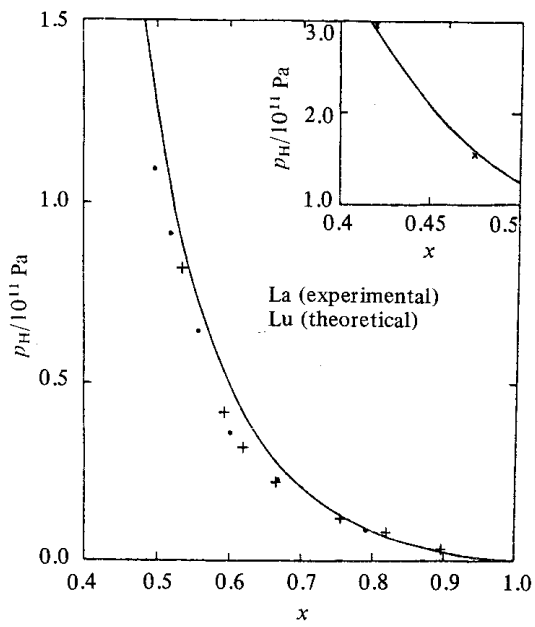
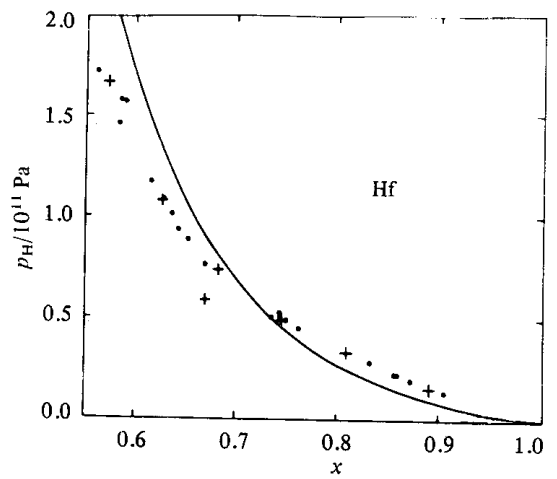
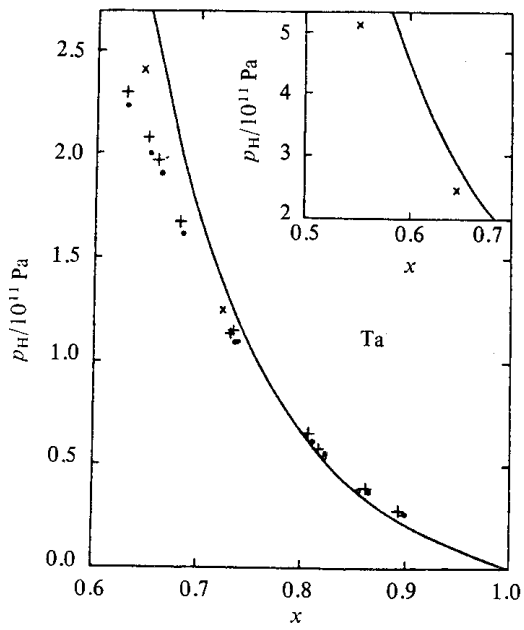


Figure 1 (continued)

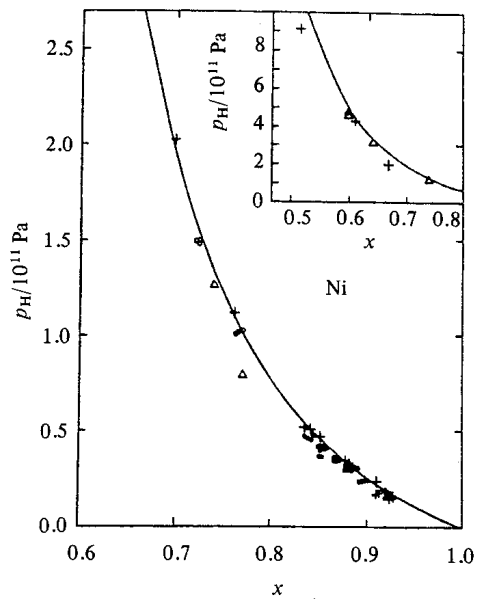
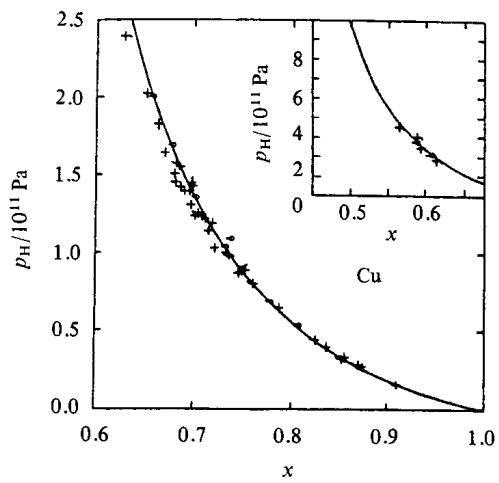
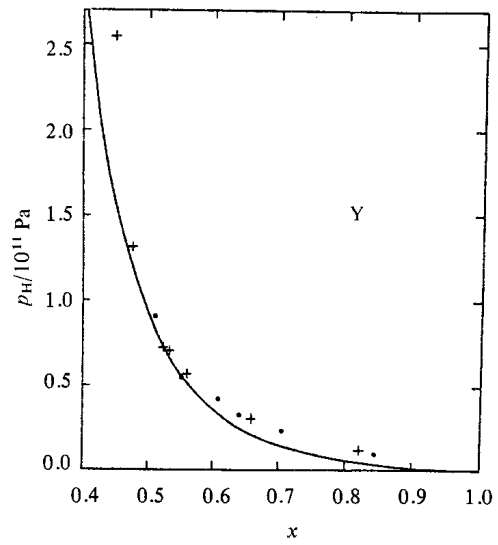
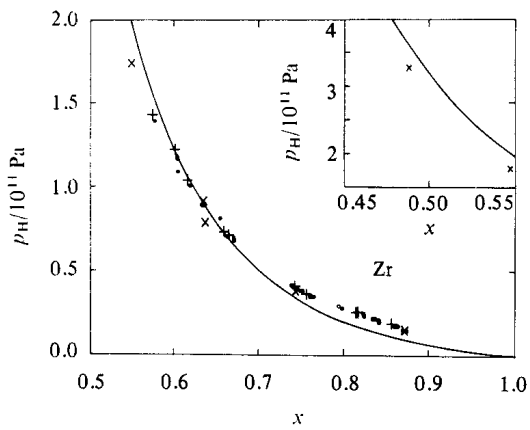
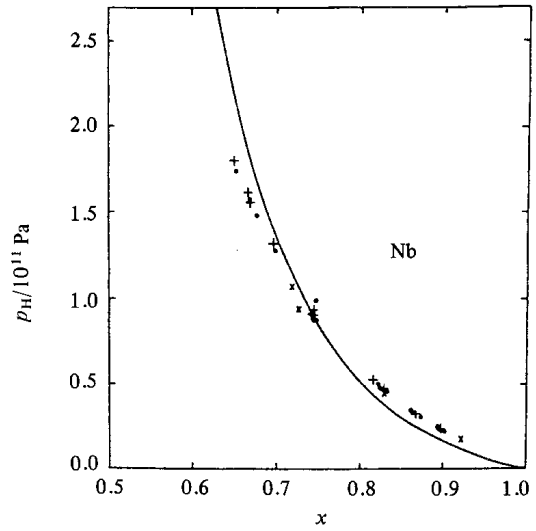
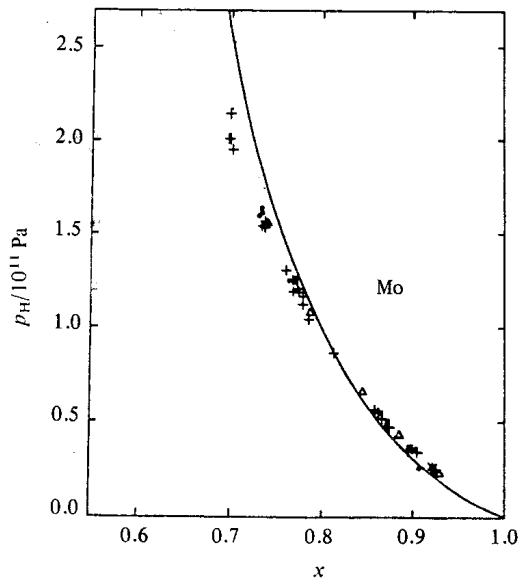


Figure 1 (continued)

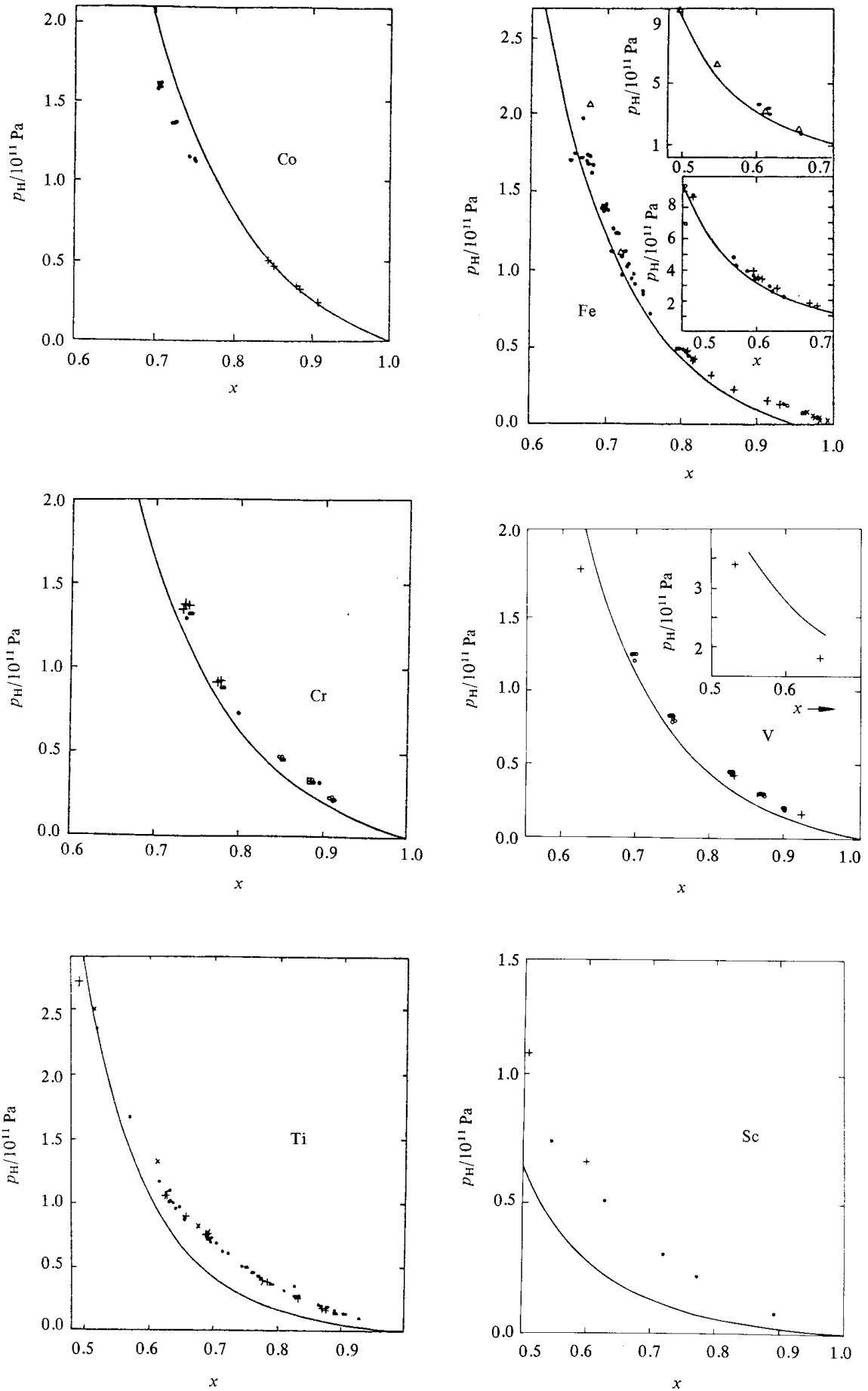


Figure 1 (continued)

Table 2. Explanation of symbols used in figure 1 and of the origin of the experimental Hugoniot data.

Metal	Symbol	Reference
Au	crosses	Van Thiel (1977) p 153
	solid circles	Walsh et al (1957)
	open circles	McQueen and Marsh (1960)
	modified crosses (⊕)	Al'tshuler et al (1958)
	open triangles	Jones et al (1966)
Pt	solid circles	Morgan (1974)
	crosses	McQueen and Marsh (1964)
	open circles	Walsh et al (1957)
	modified crosses (⊕)	McQueen et al (1970)
Ir	solid circles	McQueen et al (1970)
Re	solid circles and crosses	McQueen et al (1970)
W	crosses	McQueen et al (1970)
	Hugoniot value is located at centre point of a serpentine	Schmidt and Linde (1968)
Ta	open circles	McQueen and Marsh (1960)
	open circles	Walsh et al (1957)
	crosses	McQueen and Marsh (1964)
	diagonal crosses	Krupnikov et al (1963)
	solid circles	McQueen et al (1970)
Hf	crosses	Van Thiel (1977) p 255
	solid circles	McQueen et al (1970)
La	solid circles	Van Thiel (1977) p 278
	crosses	Al'tshuler et al (1967)
Ag	solid circles	Van Thiel (1977) p 149
	crosses	Walsh et al (1957)
	diagonal crosses	McQueen and Marsh (1960)
	open circles	Al'tshuler et al (1958)
Pd	crosses	Walsh et al (1957)
	modified crosses (⊕)	McQueen and Marsh (1964)
	open circles	Van Thiel (1977) p 203
	solid circles	McQueen et al (1970)
Rh	solid circles	McQueen et al (1970)
Mo	crosses	McQueen et al (1970)
	modified crosses (⊕)	Krupnikov et al (1963)
	open circles	McQueen and Marsh (1960)
	solid circles	Van Thiel (1977) p 221
	open triangles	Van Thiel (1977) p 217
	diagonal crosses	Walsh et al (1957)
Nb	open circles	Walsh et al (1957)
	crosses	McQueen and Marsh (1964)
	diagonal crosses	Al'tshuler et al (1967)
	solid circles	McQueen et al (1970)
Zr	open circles	Walsh et al (1957)
	crosses	McQueen and Marsh (1964)
	solid circles	McQueen et al (1970)
	diagonal crosses	Al'tshuler et al (1967)
Y	solid circles	Van Thiel (1977) p 260
	crosses	Al'tshuler et al (1967)

Table 2 (continued)

Metal	Symbol	Reference
Cu	crosses	Van Thiel (1977) p 135/6
	modified crosses (+)	Van Thiel (1977) p 141
	modified crosses (+)	McQueen et al (1970)
	open circles	Walsh et al (1957)
	open circles with dash towards the left	Al'tshuler et al (1960)
Ni	crosses	Walsh et al (1957)
	open circles	McQueen and Marsh (1960)
	solid circles	Van Thiel (1977) p 162
	modified crosses (+)	Van Thiel (1977) p 163
	open triangles	Van Thiel (1977) p 164
Co	crosses	Walsh et al (1957)
	open circles	McQueen and Marsh (1960)
Fe	modified crosses (+) and open triangles	Van Thiel (1977) p 167
	diagonal crosses	Taylor and Rice (1963)
	downward pointing open semicircle	Skidmore and Morris (1962)
	solid circles	McQueen and Marsh (1960)
	open circles	Krupnikov et al (1963)
	modified crosses (+)	Al'tshuler et al (1960)
	Cr	open circles
crosses		McQueen and Marsh (1960)
solid circles		McQueen et al (1970)
V	solid circles	McQueen and Marsh (1960)
	crosses	Al'tshuler et al (1967)
	open circles	McQueen et al (1970)
Ti	open circles	Van Thiel (1977) p 243
	crosses	Walsh et al (1957)
	modified crosses (+)	McQueen and Marsh (1960)
	diagonal crosses	Krupnikov et al (1963)
	solid circles	McQueen et al (1970)
Sc	modified crosses (+)	Van Thiel (1977) p 249
	solid circles	Van Thiel (1977) p 258
	crosses	Al'tshuler et al (1967)

Figure 2 shows that the observational $B_{1,ex}$ values (dotted line) are situated much closer to B_1 calculated according to MC (solid line) than to B_1 calculated according to WH (broken line). Ramakrishnan et al (1978) have approximated their measured values for the Grüneisen parameter as a function of the relative volume x by $\gamma_R = \gamma_0 x^q$. Insofar as measured values for transition metals had been included, table 4 gives a comparison of Ramakrishnan's $\gamma_R(x)$ with the present $\gamma(x)$, which in view of the uncertainty of this variable can be designated as good. Figure 3 shows the systematic distribution of the Grüneisen parameter in the Periodic Table. The upper curves are for $x = 1$, and the lower ones for $x = 0.75$. For transition metals with nearly full d shells the decrease in the Grüneisen parameter through high pressure is significantly greater than for those metals with a small number of d electrons.

Table 3. A comparison of MC and WH models with observational results. The experimental values $B_{1,ex}$ have been taken from Steinberg (1982), except where indicated.

Element	$B_{1,ex}$	B_1		$B_{0,ex}/B_0$		p_H/GPa at $x = 0.75$ MC	b_n MC	c_n MC
		WH	MC	WH	MC			
Sc	2.0 ^a	1.432	1.432	2.427	2.427	8.922	1.000	1.000
Ti	4.37	0.814	2.045	5.030	2.506	26.810	1.268	1.961
V	4.26	0.609	3.451	6.173	1.637	70.366	1.652	3.427
Cr	4.89 ^a	0.709	4.325	5.513	1.334	103.568	1.797	3.806
Mn	5.0 ^b	3.502	4.474	-5.526	1.318	26.537	0.727	0.707
Fe	5.29	1.137	5.005	3.348	1.104	107.728	2.102	4.429
Fe(ϵ)						61.707		
Co	4.26 ^a	1.569	5.182	2.764	1.056	128.128	2.292	3.858
Ni	5.26	1.876	5.160	2.175	1.024	124.195	3.055	4.243
Cu	5.48	2.411	4.847	1.615	1.005	88.123	5.513	4.033
Y	2.0 ^a	2.182	2.182	2.143	2.143	9.763	1.000	1.000
Zr	4.11	2.340	3.219	2.290	1.731	32.576	1.147	1.310
Nb	4.06	1.628	4.020	3.326	1.481	85.782	1.522	2.128
Mo	4.50	1.612	4.765	3.507	1.279	161.196	1.832	2.592
Tc	unknown	2.232	5.285	2.480	1.139	205.595	1.820	2.300
Ru	6.61 ^a	2.402	5.497	2.312	1.083	237.341	1.963	2.329
Rh	4.50 ^a	2.314	5.529	2.262	1.049	193.327	2.339	2.650
Pd	5.42	2.826	5.377	1.716	1.019	126.547	2.482	2.352
Ag	6.12	3.313	4.899	1.369	1.004	66.603	3.149	1.939
Lu	3.2 ^c	2.762	2.762	1.784	1.784	13.707	1.000	1.000
Hf	3.95	2.399	3.290	2.314	1.742	43.928	1.167	1.317
Ta	3.79	1.994	4.215	2.742	1.418	106.634	1.511	1.950
W	4.33	1.901	4.865	3.070	1.260	196.053	1.823	2.362
Re	5.41	2.675	5.388	2.149	1.123	261.288	1.784	2.023
Os	3.4 ^b	2.727	5.581	2.031	1.073	295.715	2.045	2.174
Ir	4.83 ^a	2.790	5.628	1.948	1.042	258.715	2.285	2.238
Pt	5.18 ^a	2.946	5.583	1.768	1.020	205.433	2.822	2.260
Au	6.29	3.331	4.822	1.572	1.010	116.181	1.416	1.485

^a Taken from Guinan and Steinberg (1974)^b Taken from Gschneidner (1964)^c Estimated**Table 4.** A comparison of various approximations for the Grüneisen parameter of copper and α -iron. See text for further details.

x	Copper		Iron	
	γ_R	γ	γ_R	γ
1.000	2.008	1.960	1.664	1.700
0.975	1.942	1.912	1.639	1.662
0.950	1.876	1.865	1.614	1.624
0.925	1.810	1.818	1.588	1.587
0.900	1.745	1.772	1.562	1.550
0.875	1.681	1.727	1.536	1.514
0.850	1.618	1.683	1.509	1.478
0.825	1.555	1.639	1.483	1.442
0.800	1.492	1.595	1.455	1.407

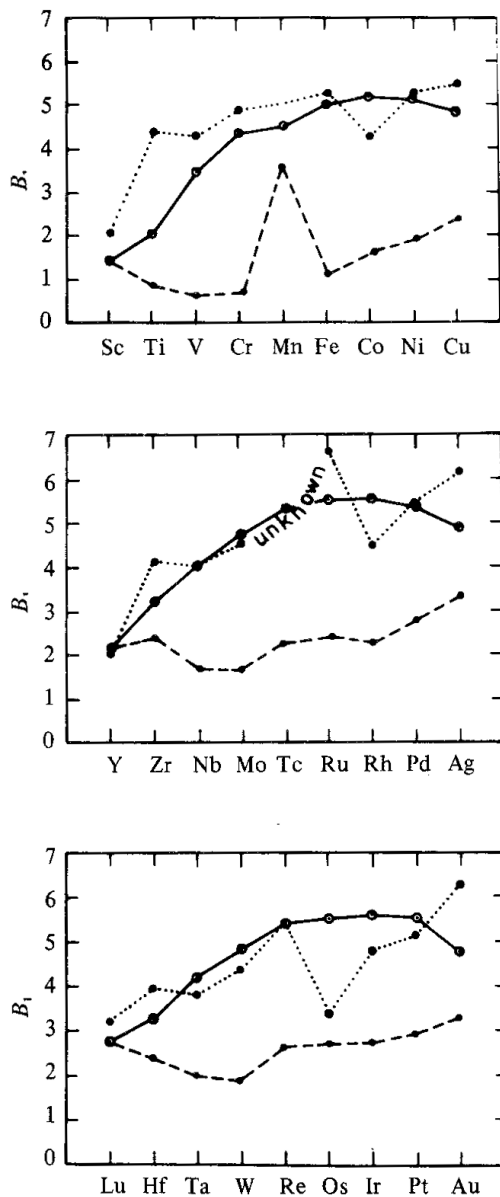


Figure 2. Initial pressure derivative of the bulk modulus, shown in the Periodic Table. The dotted lines connect the experimental data, broken lines the theoretical B_1 values according to WH, and the solid lines represent the theoretical B_1 values according to MC.

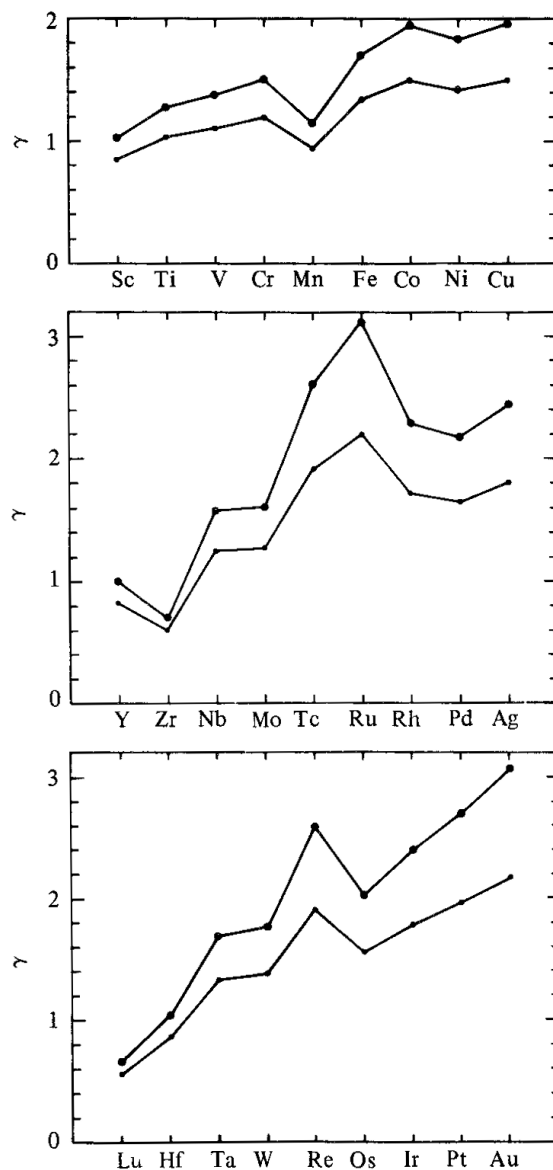


Figure 3. The Grüneisen parameter γ , represented in the Periodic Table. In each part of the diagram the upper curve represents the zero-pressure Grüneisen ratio, and the lower curve the Grüneisen ratio for $x = 0.75$.

4 Conclusions

A theory has been further developed, which yields very useful results for applied high-pressure research and for geophysics. The theory of d band broadening and of the shift of the d band centre is combined with that of the nearly free electrons. For transition metals with two d electrons it is assumed that the setup contains all energy portions. For those with full d shells it is assumed that the theoretical zero-pressure bulk modulus exactly conforms with the observational zero-pressure bulk modulus and that the pressure exactly vanishes for zero-pressure volume. The parameters b_n and c_n are fixed by these two additional requirements. In addition to this, the requirement was made that the transition between the two partial models in Z_d is linear. The agreement between the model thus created, MC with the measured Hugoniot data, static pressures, bulk moduli and their derivatives is good to very good for nearly all transition metals.

References

- Al'tshuler L V, Bakanova A A, Dudoladov I P, 1967 *Zh. Eksper. Teor. Fiz.* **53** 1967-1977
- Al'tshuler L V, Kormer S B, Brazhnik M I, Vladimirov L A, Funtikov A I, 1960 *Sov. Phys.-JETP* **11** 766
- Al'tshuler L V, Krupnikov K K, Brazhnik M I, 1958 *Sov. Phys.-JETP* **34** 614-619
- Andersen O K, 1973 *Solid State Commun.* **13** 133-136
- Andersen O K, Jepsen O, 1977 *Physica (Utrecht) B* **91** 317-328
- Eastman D E, Janak J F, Williams A R, Coleman R V, Wendin G, 1979 *J. Appl. Phys.* **50** 7423-7438
- Fisher E S, Manghnani M H, Katahara K W, 1974 in *Proceedings of the Fourth International Conference on High Pressure, Kyoto, Japan* (Kyoto: Physico-Chemical Society of Japan) pp 393-397
- Friedel J, 1969 in *The Physics of Metals* ed. J M Ziman (Cambridge: Cambridge University Press)
- Gschneidner K A Jr, 1964 *Solid State Physics* **16** 275-426
- Guinan M W, Steinberg D J, 1974 *J. Phys. Chem. Solids* **35** 1501-1512
- Harrison W A, 1980 *Electronic Structure and the Properties of Solids* (San Francisco, CA: Freeman)
- Harrison W A, Froyen S, 1980 *Phys. Rev. B* **21** 3214-3221
- Hasegawa H, Pettifor D G, 1983 *Phys. Rev. Lett.* **50** 130-133
- Hohenberg P, Kohn W, 1964 *Phys. Rev. Sect. B* **136** 864-871
- Jones A H, Isbell W M, Maiden C J, 1966 *J. Appl. Phys.* **37** 3493-3499
- Kittel C, 1970 *Introduction to Solid State Physics* fourth edition (New York: John Wiley)
- Krupnikov K K, Bakanova A A, Brazhnik M I, Trunin R F, 1963 *Sov. Phys.-JETP* **8** 205
- Leibfried G, Breuer N, 1978 *Point Defects in Metals* volume 1 *Introduction to the Theory* (Berlin: Springer)
- Lin Guang-Hai, Li Shu-Shan, 1983 *High Temp.-High Pressures* **15** 547-552
- Mackintosh A R, Andersen O K, 1980 in *Electrons at the Fermi Surface* ed. M Springford (Cambridge: Cambridge University Press) pp 149-224
- McQueen R G, Marsh S P, 1960 *J. Appl. Phys.* **31** 1253-1269
- McQueen R G, Marsh S P, 1964 Report GMX-6-566 Los Alamos Scientific Laboratory, Los Alamos, NM pp 51-62
- McQueen R G, Marsh S P, Taylor J W, Fritz J N, Carter W J, 1970 in *High Velocity Impact Phenomena* ed. R Kinslow (New York: Academic Press) pp 293-417
- Morgan J A, 1974 *High Temp.-High Pressures* **6** 195-201
- Moruzzi V L, Janak J F, Williams A R, 1978 *Calculated Electronic Properties of Metals* (New York: Pergamon Press)
- Pan'kov V L, Ullmann W, 1979 *Pure Appl. Geophys.* **117** 1001-1010
- Pettifor D G, 1977 *J. Phys. F* **7** 613
- Pettifor D G, 1983 in *Physical Metallurgy* 3rd edition, eds R W Cahn, P Haasen (Amsterdam: North-Holland), chapter 3
- Ramakrishnan J, Boehler R, Higgins G H, Kennedy G C, 1978 *J. Geophys. Res.* **83** 3535-3538
- Schmidt D N, Linde R K, 1968 Air Force W Laboratory Report AFWL-TR 68-33
- Schulze G E R, 1967 *Metallphysik* (Berlin: Akademie-Verlag)
- Skidmore I C, Morris E, 1962 *Thermodynamics of Nuclear Materials* (Vienna: International Atomic Energy Agency) p 173
- Stacey F D, Brennan B J, Irvine R D, 1981 *Geophys. Surv.* **4** 189-232
- Steinberg D J, 1982 *J. Phys. Chem. Solids* **43** 1173-1175
- Taylor J W, Rice M H, 1963 *J. Appl. Phys.* **34** 364-371
- Ullmann W, Walzer U, 1980 *Phys. Earth Planet Inter.* **22** 204-210
- Van Thiel M, 1977 (ed.) "Compendium of shock wave data" Report UCRL-50108, University of California, Lawrence Livermore Laboratory, Livermore, CA
- Walsh J M, Rice M H, McQueen R G, Yarger F L, 1957 *Phys. Rev.* **108** 169-216
- Walzer U, 1984a *High Temp.-High Pressures* **16** 335-346
- Walzer U, 1984b *Phys. Status Solidi B* **125** 55-64
- Walzer U, 1987 *Phys. Status Solidi B* **140** 377-391
- Wills J M, Harrison W A, 1983 *Phys. Rev. B* **28** 4363-4373
- Ziesche P, Lehmann G, 1983 (eds) *Ergebnisse in der Elektronentheorie der Metalle* (Berlin: Akademie-Verlag)