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COHESION IN TRANSITION METALS UNDER HIGH PRESSURES

Uwe Walzer [1)]

A bonding theory for transition metals has been derived up to a computing program. The theory permits good to very good predictions for the total energy, static pressure, Hugoniot pressure, bulk modulus and its pressure derivative as a function of the relative volume. A combination of the pseudopotential theory 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, nonoverlapping d-states is also taken into account. The nearly free s-electrons contribute four terms to the energy: kinetic energy, exchange energy, a Madelung term, and its pseudopotential correction. On this basis, two new models are developed. In both models, it is assumed that the ratio K of nearest-neighbor separation to the atomic radius is independent of the pressure p. In the first model (MB) [15], 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) [14], the requirement is that for elements with a full 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 very successful for all d-state metals except Sc, Ti and Nb. In both models, the initial pressure derivative B_1 of the bulk modulus is not an input parameter, but can be predicted. The theories are applicable in a unified manner to all transition metals.

Below, only the final results for the two equations of state will be given. For the calculation of the static pressure p as a function of the volume Ω, we have, according to model B:

$$
\begin{aligned}
p = {} & -c_1 \tfrac{5}{3} b(a\Omega^{-1} + b)^{2/3} + c_1 \tfrac{2}{3} (a\Omega^{-1} + b)^{5/3} + c_2 \tfrac{4}{3} b(a\Omega^{-1} + b)^{1/3} - \\
& - c_2 \tfrac{1}{3} (a\Omega^{-1} + b)^{4/3} + 2b(a + b\Omega)\,(c_3\Omega^{-1/3} - c_4\Omega^{-1}) - \\
& - (a + b\Omega)^2\,(c_3 \tfrac{1}{3} \Omega^{-4/3} - c_4\Omega^{-2}) - \\
& - c_5 \left[1 - \tfrac{c - b\Omega}{10}\right] (\tfrac{5}{3} c\Omega^{-8/3} - \tfrac{2}{3} b\Omega^{-5/3}) + \\
& + c_5 \tfrac{1}{10} b(c - b\Omega)\Omega^{-5/3} + c_6\,(\tfrac{8}{3} c\Omega^{-11/3} - \tfrac{5}{3} b\Omega^{-8/3}) \qquad (1)
\end{aligned}
$$

with

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$$c_1 \equiv (2.210)\,\frac{\hbar^2}{2m}\,(\tfrac{4\pi}{3})^{2/3}\ ; \qquad c_4 \equiv 2\pi e^2 r_c^2\ ;$$

$$c_2 \equiv (0.916)\,\frac{e^2}{2}\,(\tfrac{4\pi}{3})^{1/3}\ ; \qquad c_5 \equiv (30.9)n^{1/2}\,\frac{\hbar^2}{2m}\,\frac{r_d^3}{K^5}\,(\tfrac{4\pi}{3})^{5/3}\ ;$$

$$c_3 \equiv \frac{e^2}{2}\,\alpha\,(\tfrac{4\pi}{3})^{1/3}\ ; \qquad c_6 \equiv (11.40)n\,\frac{\hbar^2}{m}\,\frac{r_d^6}{K^8}\,(\tfrac{4\pi}{3})^{8/3}\ . \qquad (2)$$

$\hbar$ is the Planck quantum of action, divided by 2π, e is the charge and m the mass of the electron, $\alpha = 1.8$ is fixed, r_c is the Ashcroft empty-core radius, r_d is the d-state radius of the free atom, n is the number of nearest neighbors of an atom. The three parameters a, b and c denote

$$a = Z_s^o - Z_s^{o'}\Omega_o\ , \quad b = Z_s^{o'}\ , \quad c = Z - Z_s^o + Z_s^{o'}\Omega_o \qquad (3)$$

where Z_s^o is the number of s-electrons at vanishing pressure, $Z_s^{o'}$ the volume derivative of the number of s-electrons at vanishing pressure and Ω_o the volume at zero-pressure. Higher derivatives were equated to zero. However, according to model C,

$$p = \tfrac{2}{3}\,k_1\Omega^{-5/3} - \tfrac{1}{3}\,k_2\Omega^{-4/3} + k_3\Omega^{-2} - \tfrac{5}{3}\,b_n k_4\Omega^{-8/3} + \tfrac{8}{3}\,c_n k_5\Omega^{-11/3} \qquad (4)$$

with

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

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

$$k_3 \equiv 2\pi e^2 r_c^2 Z_s^2\ ,$$

$$k_4 \equiv Z_d\,(1 - \frac{Z_d}{10})\,(30.9)\,n^{1/2}\,\frac{\hbar^2}{2m}\,\frac{r_d^3}{K^5}\,(\tfrac{4\pi}{3})^{5/3}\ ,$$

$$k_5 \equiv Z_d n\,(11.40)\,\frac{\hbar^2}{m}\,\frac{r_d^6}{K^8}\,(\tfrac{4\pi}{3})^{8/3} \qquad (5)$$

where Z_d is the number of d-electrons, Z_s that of the nearly free s-electrons. If the requirement is that, with equation (4), the pressure exactly vanishes for $\Omega = \Omega_o$ and that the theoretical bulk modulus is in precise agreement with the experimental bulk modulus, you obtain $b_n \equiv b_{MA}$ and $c_n \equiv c_{MA}$. If this obvious requirement is made only for elements with full d-shells, the equation of state for model C is obtained by using equation (4) with

$$b_n = (4Z_d)^{-1}[(5Z_d - 10)\,b_{MA} + 10 - Z_d] \qquad (6)$$

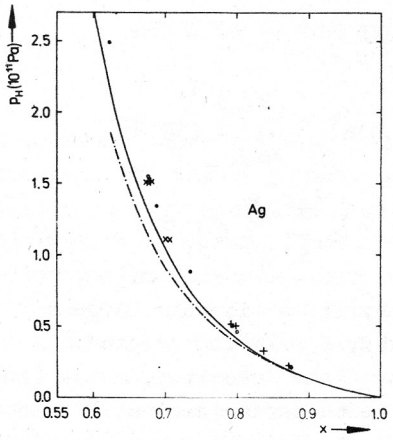

Fig. 1. Hugoniot pressure p_H versus relative volume x for silver. Theory MB is dash-dotted, theory MC continuous. The experimental values after [8] are solid circles, those after [9] upright crosses, those after [7] are oblique crosses and those after [1] empty circles.

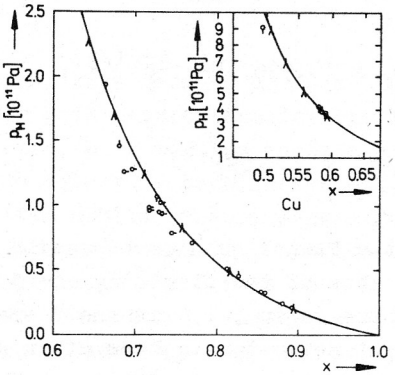

Fig. 3. Hugoniot pressure p_H versus relative volume for copper. The experimental values have been taken from [8]. The curve has been calculated according to the theory MC.

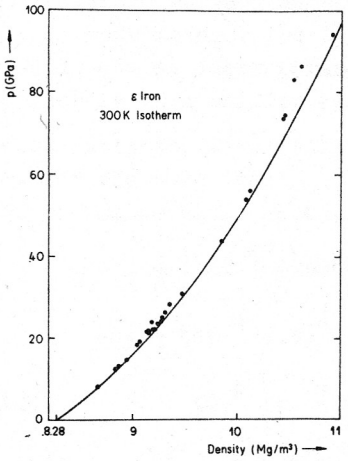

Fig. 2. Static high-pressure data p versus density for ε iron. The curve has been calculated according to theory MC. The solid circles represent expe-perimental results from [5] and [6] plotted after [2].

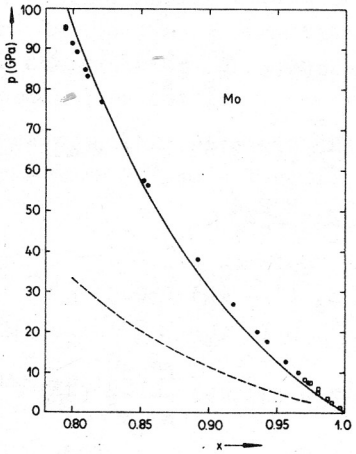

Fig. 4. Pressure p versus relative volume x. A comparision of the equations of state of MC (full curve) and of Wills and Harrison [16] (dashed curve) with experimental results for molybdenum. Full circles after [4], open squares after [3].

and

$$c_n = (4Z_d)^{-1} \left[(5Z_d - 10)\, c_{MA} + 10 - Z_d\right] . \qquad (7)$$

The formulas have been derived in [14] and [15]. These papers are developments based on [11] and [12]. It is to be expected that the new theories [14] and [15] are better suited than [10, 13] for deriving the pressure dependence of melting temperature. In the following, a comparison with measured data is to demonstrate the applicability of the theories.

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