A new high-pressure equation of state for metals

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Abstract. A new theory is developed for metals which permits calculation of the free energy, pressure, and bulk modulus and its pressure derivatives as a function of the relative volume. With free energy, not only attractive and repulsive lattice energy, but also the Fermi energy, exchange, and correlation energies of the electrons are accounted for. The theory exhibits a certain analogy to the statistical theories. The overestimation of electron density near the nucleus has been overcome by a quantum-mechanical theory by Goodisman, the result of which is used in the present theory. The computational expenditure, however, is reasonable also for the purpose of practical high-pressure research. Five well-known quantities serve as input parameters: atomic change, valency, atomic volume, bulk modulus and its first derivative with respect to pressure for vanishing pressure. The curves calculated from the new 'MY' equation of state are compared with high-compression data of twenty metals. For seventeen metals good or very good agreement is obtained, for three, a reasonable agreement is obtained.

1 Introduction

In experimental high-pressure physics and in geophysics it is common to use equations of state which are either completely empirical or are based on assumptions which do not permit any large extrapolation beyond the pressure range that is experimentally feasible. One case in point here is the equation developed by Prieto and Renero (1982). It is mainly based on the empirical linear relationship between shock velocity and particle velocity. This approach is completely legitimate. However, if equations of state are to be applied also to pressure ranges where there is no certainty as to the validity of the previously mentioned relation, the physical foundation of the new equation of state should reach to a greater depth. In this case, the main difficulty is to confine the computational expenditure to reasonable proportions: strictly speaking, we would have to solve the Schrödinger equation for a multiparticle problem. This, as is well known, is not possible. For pressures above 100 Mbar, occurring, for example, in stars, the Thomas–Fermi (TF) theory can be used, all the more so as it can be shown (Lieb 1981) that results of the TF theory in the large-nuclear-charge limit merge with those of quantum theory. The physical applicability of the statistical theories for atoms and molecules extends far beyond our problem. The TF energy functional is

$$E_{\text{TF}} = -\int \mu(x')V(x')\mathrm{d}x' + D'(\mu,\mu) + U' + \tfrac{3}{5}\gamma_{\text{p}}\int \mu^{5/3}(x')\mathrm{d}x', \qquad (1)$$

where μ is the electron density, x' the location, $\mathrm{d}x'$ the volume differential, V a *slowly* varying potential in which the electrons are moving; the constant γ_{p} is given by

$$\gamma_{\text{p}} = \frac{1}{8}\left(\frac{3}{\pi}\right)^{2/3}\frac{h^2}{m}, \qquad (2)$$

where m is the electron mass and h is Planck's constant. The first term on the right-hand side of equation (1) is the potential energy of the electrons in the field generated by the atomic nuclei. The second term, $D'(\mu,\mu)$, is the energy of the classical

Coulomb interaction between electrons; U' is the repulsive electrostatic energy of the nuclei. The fourth term (Fermi term) expresses the kinetic energy of the electrons. The TF theory has now been extended and improved several times (see, for example, March 1974). With metals, it is important to screen the nonclassical electron–electron interactions. Therefore, the exchange energy $-(0.916/r_s)$Ry is used to account for the mutual repulsion of electrons having the same spin. The Seitz radius r_s is the mean interelectronic spacing expressed in Bohr radii. The interpolation formula of Wigner (1934, 1938) is used for taking the correlation energy per electron, E_{corr}, into account:

$$E_{corr}/\text{Ry} = \frac{-0.88}{r_s + 7.8}. \tag{3}$$

Perrot (1979) has shown how a zero-temperature equation of state of metals can be derived from the TF and related theories. As was to be expected, the computational expenditure was very high. According to Perrot, the results are reliable only for very high compressions, for example, in the case of the TF Dirac model for $x \leqslant 0.02$ in lithium, $x \leqslant 0.05$ in beryllium and aluminium, and $x \leqslant 0.1$ in copper, where x is a relative volume given by the ratio of the zero-pressure mass density to the mass density. Consequently, we have adopted a middle-course approach which will be described below.

2 Development of the new MY equation of state

The following considerations are based on the experience gained from statistical theories. For the potential energy, however, a Lennard-Jones–Devonshire (LJD) potential is used. Then, the free energy Φ is given by

$$\Phi = \Phi_i + \Phi_0 + \Phi_t + \Phi_e, \tag{4}$$

where Φ_i is the interaction free energy, for which a LJD potential is assumed. The zero-point free energy, Φ_0, is given by

$$\Phi_0 = \frac{1}{2} \sum_{i=1}^{3N'} h\nu_i, \tag{5}$$

the thermal free energy, Φ_t, by

$$\Phi_t = kT \sum_{i=1}^{3N'} \ln\left[1 - \exp\left(\frac{-h\nu_i}{kT}\right)\right], \tag{6}$$

where ν_i is the frequency, N' the number of atoms, k Boltzmann's constant, T the temperature; Φ_e is the free energy of the free electrons. At first, the temperature dependence and the zero-point energy will be neglected. Hence, in the following an isothermal equation of state will be developed. The Helmholtz free energy is given by

$$\Phi = a\left(\frac{A}{x^{2n/3}} - \frac{2B}{x^{n/3}}\right) + b\left(\frac{C}{r_{s,0}^2 x^{2/3}} - \frac{D}{r_{s,0} x^{1/3}} - \frac{E}{r_{s,0} x^{1/3} + F}\right), \tag{7}$$

where

$A = 1.0110, \quad B = 1.2045, \quad C = 2.21$ Ry,

$D = 0.916$ Ry, $\quad E = 0.88$ Ry, $\quad F = 7.8$.

The relative volume x can also be expressed by $x = r_s^3/r_{s,0}^3$, where $r_{s,0}$ is the value of r_s at vanishing pressure. $r_{s,0}$ is a material constant and is calculated from the expression

$$r_{s,0} = \left(\frac{3v_0}{4\pi w a_1^3}\right)^{1/3}, \tag{8}$$

where a_1 is the first Bohr radius for hydrogen, expressed in units of 10^{-10} m, hence $a_1 = 0.52917706$; v_0 is the atomic volume in units of 10^{-30} m^3, which can be found, for example, in table 1 of Górecki (1979); w is the valency; a, b, and n in equation (7) are also material parameters which subsequently are replaced by quantities that are better suited for macrophysical measurements, while the quantities A–F follow from theory and have identical numerical values for all metals. The constants A and B result from the geometric arrangement of the atoms in the crystal lattice. The numerical values specified are for fcc lattices (see Hirschfelder et al 1954), with atoms having been taken into account up to the third shell of neighbours around a fixed atom. We also take these numerical values for other lattices, especially since increasing pressures probably will ultimately create the closest packing for all metals. Values of the constants C–F have been taken from Wigner (1934). The five terms on the right-hand side of equation (7) have the following significance: (i), (ii) repulsive and attractive lattice terms; (iii) Fermi free energy of the electrons; (iv) exchange energy of the electrons, which follows from Hartree-Fock calculations; (v) correlation energy of the electrons as formulated by Wigner. Using the thermodynamic relation $p = -(\partial\Phi/\partial x)_T$, where p is pressure, and the substitution $y^{1/3} = r_{s,0}x^{1/3}$, the following equation results from equation (7)

$$p = -\frac{\partial\Phi}{\partial x} = -r_{s,0}^3 \frac{\partial\Phi}{\partial y} = r_{s,0}^3 \left[\tfrac{2}{3}na\left(\frac{Ar_{s,0}^{2n}}{y^{(2n/3)+1}} - \frac{Br_{s,0}^n}{y^{(n/3)+1}} \right) \right. $$
$$\left. + \tfrac{1}{3}b\left(\frac{2C}{y^{5/3}} - \frac{D}{y^{4/3}} - \frac{E}{(y^{1/3}+F)^2 y^{2/3}} \right) \right]. \tag{9}$$

Equation (9) is the temporary form of the new equation of state for metals. From this equation the bulk modulus κ is computed, where $\kappa = -x\partial p/\partial x = -y\partial p/\partial y$:

$$\kappa = r_{s,0}^3 \left\{ \tfrac{2}{3}na\left[\frac{(\tfrac{2}{3}n+1)Ar_{s,0}^{2n}}{y^{(2n/3)+1}} - \frac{(\tfrac{1}{3}n+1)Br_{s,0}^n}{y^{(n/3)+1}} \right] \right. $$
$$\left. + \tfrac{2}{9}b\left[5Cy^{-5/3} - 2Dy^{-4/3} - E\frac{2+Fy^{-1/3}}{(y^{1/3}+F)^3 y^{1/3}} \right] \right\}. \tag{10}$$

From this we obtain

$$-x\frac{\partial\kappa}{\partial x} = -y\frac{\partial\kappa}{\partial y} = r_{s,0}^3 \left\{ \tfrac{2}{3}na\left[\frac{(\tfrac{2}{3}n+1)^2 Ar_{s,0}^{2n}}{y^{(2n/3)+1}} - \frac{(\tfrac{1}{3}n+1)^2 Br_{s,0}^n}{y^{(n/3)+1}} \right] + \tfrac{2}{27}b\left[25Cy^{-5/3} \right. \right. $$
$$\left. \left. - 8Dy^{-4/3} - E\frac{Fy^{-1/3}(1+Fy^{-1/3})+(2+Fy^{-1/3})(4+Fy^{-1/3})}{(y^{1/3}+F)^4} \right] \right\}. \tag{11}$$

Let the bulk modulus at vanishing pressure be denoted by κ_0, its derivative with respect to pressure at zero pressure by κ_1. Thus, $\kappa_0 \equiv \kappa|_{x=1}$ and $\kappa_1 \equiv \partial\kappa/\partial p|_{x=1}$. It should be noted that

$$\frac{\partial\kappa}{\partial p} = -\frac{x}{\kappa}\frac{\partial\kappa}{\partial x}. \tag{12}$$

For $x = 1$, we have $y = r_{s,0}^3$. Moreover, from equations (9)–(12) we obtain

$$b = Gna, \tag{13}$$

with

$$G = 2(B-A)\left[\frac{2C}{r_{s,0}^2} - \frac{D}{r_{s,0}} - \frac{Er_{s,0}}{(r_{s,0}+F)^2} \right]^{-1}; $$

$$\tfrac{3}{2}\kappa_0 = na[(\tfrac{2}{3}n+1)A - (\tfrac{1}{3}n+1)B] + Hb, \tag{14}$$

where

$$H = \tfrac{1}{3}\left[5Cr_{s,0}^{-2} - 2Dr_{s,0}^{-1} - Er_{s,0}\,\frac{2r_{s,0}+F}{(r_{s,0}+F)^3}\right],$$

as well as

$$\tfrac{3}{2}\kappa_0\kappa_1 = na[(\tfrac{2}{3}n+1)^2A - (\tfrac{1}{3}n+1)^2B] + Ib, \tag{15}$$

with

$$I = \tfrac{1}{9}\left[25Cr_{s,0}^{-2} - 8Dr_{s,0}^{-1} - Er_{s,0}\,\frac{F(r_{s,0}+F)+(2r_{s,0}+F)(4r_{s,0}+F)}{(r_{s,0}+F)^4}\right].$$

The constants κ_0 and κ_1 have been measured for many metals. Therefore, equations (13)–(15) are used for eliminating the unknown material constants a, b, and n from the equation of state (9):

$$a = U(\kappa_0)/n, \tag{16}$$

$$b = GU(\kappa_0), \tag{17}$$

with

$$U(\kappa_0) = \tfrac{3}{2}\kappa_0[(\tfrac{2}{3}n+1)A - (\tfrac{1}{3}n+1)B + GH]^{-1}, \tag{18}$$

and

$$n = K(\kappa_1) + [K^2(\kappa_1) - M + N\kappa_1]^{\frac{1}{2}}, \tag{19}$$

with

$$J = (4A-B)/9, \qquad K(\kappa_1) = \tfrac{1}{2}L(\kappa_1 - 2).$$

$$L = (2A-B)/3J, \qquad M = (A-B+GI)/J, \qquad N = (A-B+GH)/J.$$

The theory presented here has been constructed in analogy to the TF and related theories. Those corrections of the TF theory that can be *directly* expressed in terms of x by our theory have already been accounted for. But the statistical theories for atoms and molecules give only a rough approximation to the electron density because the assumptions of the theory are no longer satisfied at very small and very large distances from the nucleus. Von Weizsäcker's (1935) kinetic-energy correction provided the correct behaviour of the electron density for very small and very large distances from the nucleus. In that case, a term

$$\delta \int [(\nabla\mu^{\frac{1}{2}})(x')]^2\,dx'$$

has to be added to the right-hand side of equation (1), with

$$\delta = \frac{A'h^2}{8\pi^2 m}.$$

According to Lieb (1981), $A' = 0.186$ is the most favourable numerical value. This additional theory has been modified by various authors, Hohenberg and Kohn (1964) having taken a very systematic approach. However, these theories, too, have some shortcomings. To overcome them and to avoid an overestimation of the electron density near the nucleus, Goodisman (1970) connected a quantum-mechanical electron density for the region near the nucleus to the electron densities given by the statistical model. This extension of the theory approximates very well to various experimental results, for example, the diamagnetic shielding and the diamagnetic susceptibility. We take into account the final formulae of Goodisman's theory.

Hence it follows a factor f_0 for equation (9) is given by

$$f_0 = \frac{0.72Z^{7/3} - 0.24Z^2 + 0.43Z^{5/3}}{0.7689Z^{7/3}} \tag{20}$$

where Z is the nuclear charge. With $y^{1/3} = r_{s,0}x^{1/3}$, we obtain the following clear expression for the pressure, p:

$$p = f_0 \left\{ \frac{2}{3} na \left(\frac{A}{x^{(2n/3)+1}} - \frac{B}{x^{(n/3)+1}} \right) + \frac{1}{3} br_{s,0}^3 \left[\frac{2C}{y^{5/3}} - \frac{D}{y^{4/3}} - \frac{E}{(y^{1/3}+F)^2 y^{2/3}} \right] \right\} . \tag{21}$$

The new isothermal equation of state (21) is used together with the simple equations (8) and (13)–(20) to compute the pressure p in its dependence on the relative volume, x, for metals. The constants $A-F$ and a_1 are independent of the material and have been taken from basic theories; the following constants have to be individually inserted for each metal into the equations: the bulk modulus at vanishing pressure, κ_0, its derivative with respect to pressure at zero pressure, κ_1, the atomic volume, v_0, the valency, w, and the nuclear charge, Z. Since these material constants are known for most metals, equation (21) can conveniently be used for practical high-pressure studies and for planetary physics, too. Thus, it is the aim of this study to approximate, with the aid of a physically satisfactory theory, the experimental high-pressure values and, on account of the deeper physical penetration of the problem, to justify to a greater extent the confidence in extrapolation beyond the pressure range covered by measured values. An application of the results to the problem of the pressure dependence of the melting temperature and of the geophysical core paradox (Kennedy and Higgins 1973; Ullmann and Walzer 1980) also appears to be promising. The present theory is essentially a compromise between theoretical physics and the requirement of easy applicability. Incidentally, if the free energy, Φ, the bulk modulus, κ, or the quantity $-x\partial\kappa/\partial x$ are required for future computations, these quantities will, of course, have to be multiplied by f_0.

The present theory, denoted MY, has a certain connection with the MX equation-of-state theory (Walzer 1982). The resemblance is, however, only of a more formal kind. The new MY theory has a quantum-statistical correction. In the MX theory the mean interelectronic spacing $r_{s,0}$ is a constant. In the MY theory the quantity $r_{s,0}$ is computed individually for each metal; the author used Wigner's (1934) original values for the constants for $C-F$; the quantity K was introduced in another way. In the MX theory the quantities κ_0 and κ_1 serve as input; in the MY theory, however, we use five input constants. The MY theory applies only to metals; MX does so for all materials. The MY theory is found to approximate the experimental values better than MX.

3 Comparison with experimental data

Frequently, new equations of state are verified by their proponents only for few materials. Sometimes, there is every appearance that the material constants used in the theories have been derived from the measured values themselves that had been used for verification. In such circumstances, an excellent agreement of the measured values with the theoretical curves is not astonishing. Here, another approach has been chosen. For the test, all those metals were used for which the experimentally determined relative volume x is known to sufficiently high pressures. These data were taken from static volumetric measurements, shock-wave data, and x-ray studies. The symbols of the measured points shown in figures, the experimental methods, and the authors are listed in table 1. The material constants required for the calculation of the theoretical curves stem from other authors and are shown in table 2. In this way, the theory developed in the previous section and resulting in the new equation

of state MY has really been tested. Since the MY equation of state is an isothermal equation, it is not the Hugoniot data, represented by crosses, but the isothermal data that are decisive for the comparison with the curves. The latter are represented by circles, squares, and triangles. The figures have the same order as the materials in table 2; they have been arranged according to decreasing nuclear charge. A large number of the measured points to which we fitted our new theoretical curves has been taken from Ullmann and Pan'kov (1976). A number of the isotherms were computed in the usual way by means of the Mie–Grüneisen equation and of the Rankine– Hugoniot conservation law from experimental Hugoniot data. The formulae are given by Walzer et al (1979), for example.

Table 1. Explanation of the symbols of the experimental high-compression data used in figure 1.

Metal	Symbol	Source
Pd, Mo	solid circles	293 K isothermal data, Mao et al (1978)
	open squares	Ming and Manghnani (1978)
Rb, K, Na, Li	solid circles	room-temperature isotherm based on Hugoniot data reduction (Grover et al 1969)
	open circles	static data (Vaidya and Kennedy 1971)
	crosses	Rice et al (1958), Bakanova et al (1965), Carter et al (1971), Grover et al (1969)
	open triangles	Bridgman's data (quoted by Birch 1966)
Au, Ag, Cu, Ca, Mg	solid circles	room-temperature isotherm based on Hugoniot data reduction (Carter et al 1971)
	solid squares	zero-temperature isotherm (Al'tshuler et al 1962)
	open circles	static data (Vaidya and Kennedy 1970)
	crosses	Hugoniot data (Carter et al 1971)
	open triangles	Bridgman's data (quoted by Birch 1966)
Pb, Sn, Cd, Zn, Ni, V	open triangles, corner down	Bridgman's data (quoted by Vaidya and Kennedy 1970; Kennedy 1972)
	open triangles, corner up	Bridgman's data (quoted by Birch 1966)
	crosses (diagonal)	Hugoniot data (McQueen and Marsh 1960; Al'tshuler et al 1960)
	solid circles	room-temperature isotherm (McQueen and Marsh 1960)
	open circles	static data (Vaidya and Kennedy 1970, 1972)
	crosses (upright)	Hugoniot data (Al'tshuler et al 1962)
	solid squares	room-temperature isotherm based on the above Hugoniot data
In, Nb	crosses	Hugoniot data (Rice et al 1958)
	solid circles	room-temperature isotherm based on the above Hugoniot data
	open triangles	Bridgman's data (quoted by Birch 1966)
	open circles	static data (Vaidya and Kennedy 1970, 1972)
Fe	open circles	static data (Mao and Bell 1978)
	solid circles	isotherms from Hugoniot data (Takeuchi and Kanamori 1966)
	solid triangles	isotherms (McQueen and Marsh 1960; Pan'kov and Kalinin 1974)
	open squares	x-ray data (Takahashi et al 1968)
	crosses (diagonal)	shock-wave data (Bancroft et al 1956)
	crosses (upright)	smoothed Hugoniot data (Takeuchi and Kanamori 1966)

Table 2. List of material parameters used. Values of the atomic volume v_0 from Górecki (1979).

Element	Z	w	$v_0/10^{-30}\ \text{m}^3$	κ_0/kbar [a]	κ_1 [a]	Reference
Pb	82	2	30.33	419	5.72	16
Au	79	1	16.96	1664	5.2	7, 12, 14
Sn(w)	50	4	27.07 [b]	532	4.9	7, 8
In	49	3	26.12 [b]	392	6.0	15
Cd	48	2	21.58	457.9	6.77	2
Ag	47	1	17.06	1015	5.53	6, 13
Pd	46	2	14.72	1880	5.35	8
Mo	42	4	15.58	2610	4.4	8
Nb	41	5	17.98	1690	6.9	8
Rb	37	1	92.67	26.2	3.39	5
Zn	30	2	15.24	598	4.9	6, 7, 8
					6.4	
Cu	29	2	11.81	1330	5.65	12
Ni	28	2	10.94	1790	6.2	8
Fe(ϵ)	26	2	10.81 [c]	2060	4.0	11
V	23	3	13.88	1537	3.5	8, 9, 10
Ca	20	2	43.48	183	2.78	6, 7
K	19	1	75.31	31.2	3.85	4
Mg	12	2	23.27	344.2	4.16	2
Na	11	1	39.50	61.8	3.59	2, 3
Li	3	1	21.61	115	3.56	1

[a] Ullman and Pan'kov (1976); [b] computed from table 7 of Gschneidner (1964);
[c] from $v_0 = 11.77 \times 10^{-30}\ \text{m}^3$ for Fe(α).

References: 1, Day and Ruoff (1974); 2, Anderson (1966); 3, Ho and Ruoff (1968); 4, Smith and Smith (1965); 5, Grover (1971); 6, Vaidya and Kennedy (1970); 7, Ullmann and Pan'kov (1976); 8, Guinan and Steinberg (1974); 9, Bolef (1961); 10, Gschneidner (1964); 11, Takahashi et al (1968); 12, Barsch and Chang (1967); 13, Daniels and Smith (1958); 14, Carter et al (1971); 15, Voronov and Goncharova (1971); 16, Miller and Schuele (1969).

4 Conclusions

For metals, a new equation of state has been devised which is based on a more precise analysis of the bonding forces. This theory, though developed in analogy to the statistical theories, yields, in contrast to them, realistic results not only for very high pressures, but also for medium pressures where the shell structure of the atoms is still evident. Thus, it might be expected that it is applicable to the metallic core of the earth and other planets, and also to material physics. The computational expenditure is much lower than for the TF and related theories, but higher than, for example, for the equation of state of Birch (1966). A comparison of the isothermal theoretical curves of the twenty metals studied with the measured data (see figure 1) yields good to excellent agreement for seventeen materials and moderate agreement for three. It must be noted that the Hugoniot data must not be taken into account when considering the fit. Because of the deeper physical reasoning involved in derivation of the MY equation there is hope that an extrapolation beyond the range covered by measured data is more justified than with other equations of state commonly used in practical materials research for high pressures. Only well-known quantities are required as material parameters, that is, nuclear charge, valency, atomic volume, bulk modulus at zero pressure, and its first derivative with respect to pressure at zero pressure.
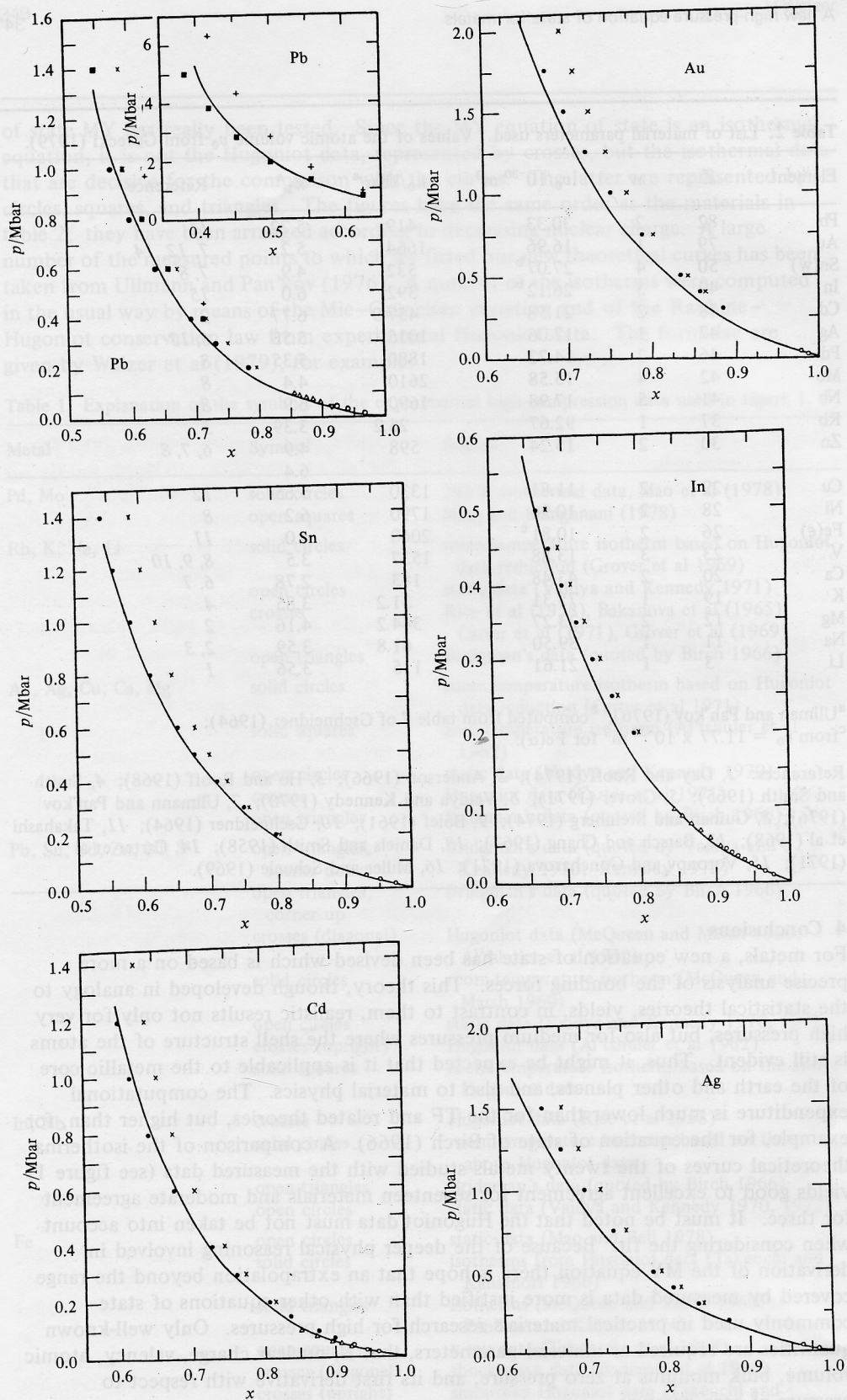
Figure 1. Pressure-relative volume plots for metals. The isotherms were computed by means of the new MY equation of state, use having been made of the material constants listed in table 2. The type and origin of the experimental data entered for comparison purposes are shown in table 1.
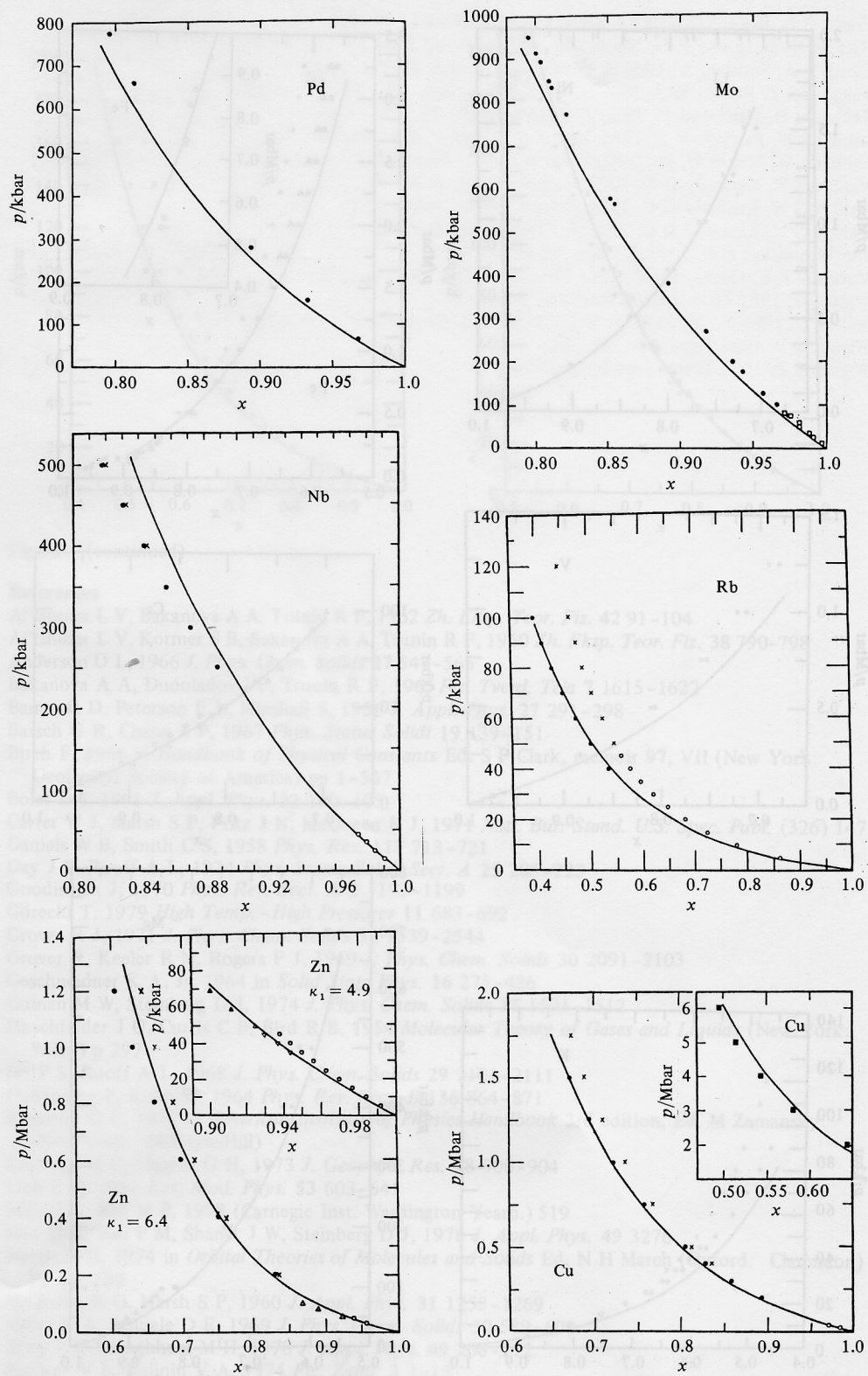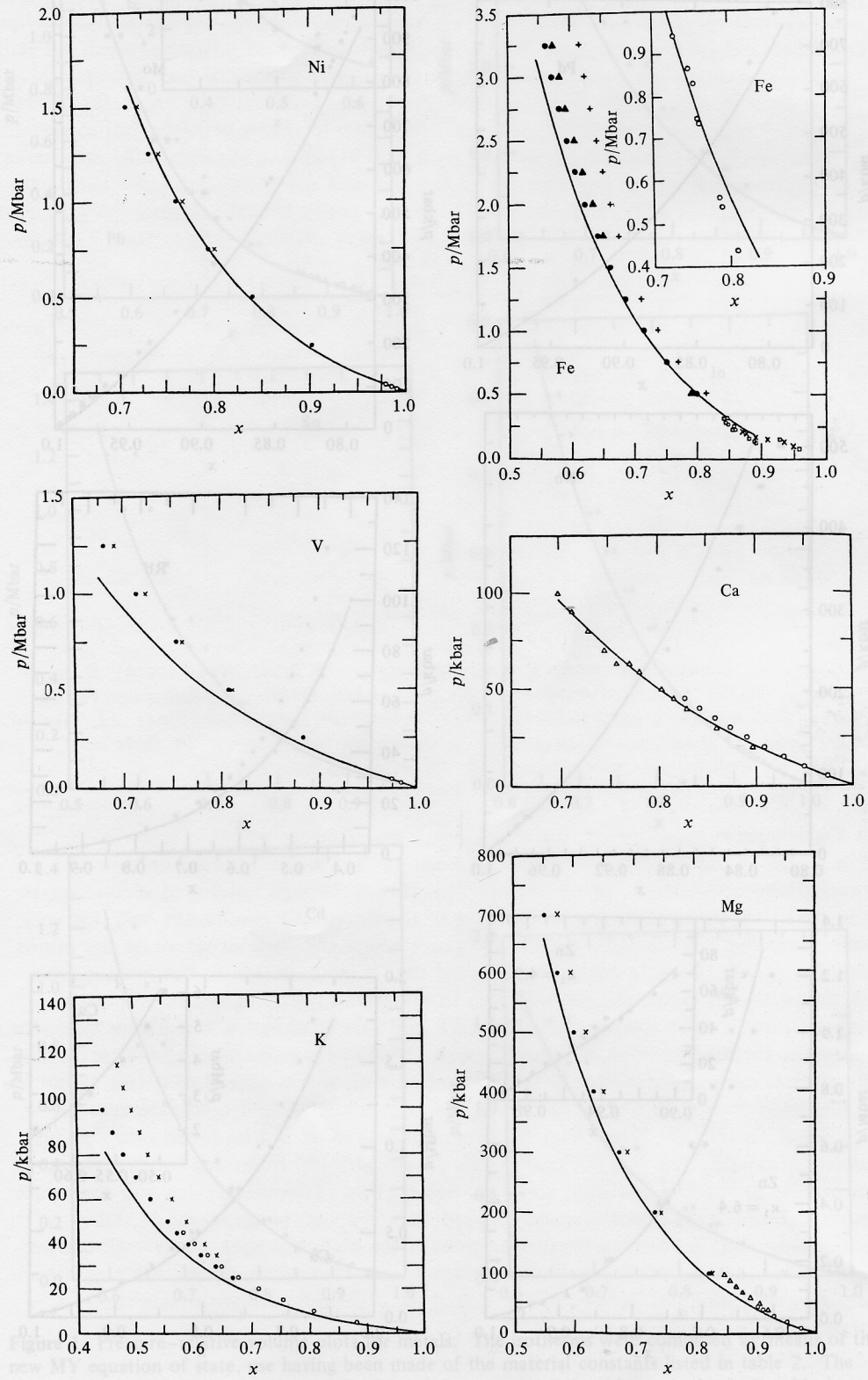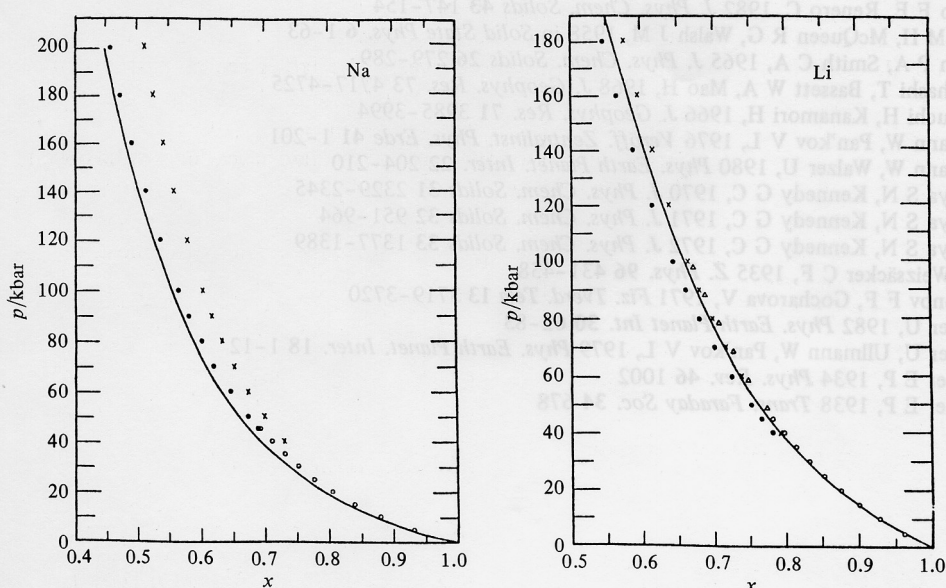
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