

Two Equations of State for Metals, Halides, and Oxides

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(With 6 figures)

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Summary

An isothermal equation of state is derived for metals; the mean kinetic energy, the exchange and correlation energies of the electrons as well as a quantum-statistical correction also being taken into account. This equation of state, which has proven its worth for 20 studied metals, has been simplified such that the only input parameters which still have to be known are the initial bulk modulus and the initial pressure derivative of the bulk modulus. Let the simplified equation of state be designated as MZ. The pressure—volume curves of MZ and of two other proven equations of state were compared with isothermal experimental high-compression data of 13 halides and oxides and of 20 metals. Compared with the other two equations, the approximation of the measured values achieved through MZ was not only better for the metals, where an improvement had to be expected after all, but also for most of the non-metallic compounds under investigation. The paper also reports on a study of the melting temperature as a function of pressure.

Zusammenfassung

Eine isotherme Zustandsgleichung für Metalle wird hergeleitet. Dabei sind auch die mittlere kinetische Energie, die Austausch- und die Korrelationsenergie der Elektronen sowie eine quantenstatistische Korrektur berücksichtigt. Diese Zustandsgleichung, die sich für 20 untersuchte Metalle bewährt hat, wurde so vereinfacht, daß als Eingangsparameter nur noch die Nulldruck-Inkompressibilität und die Druckableitung der Inkompressibilität bei Nulldruck bekannt sein müssen. Die vereinfachte Zustandsgleichung heiße MZ. Die Druck-Volumen-Kurven von MZ und zweier anderer bewährter Zustandsgleichungen wurden mit isothermen Hochdruckmeßdaten von 13 Halogeniden und Oxiden und von 20 Metallen verglichen. Nicht nur für die Metalle, wo dies ja nach Herleitung zu erwarten war, sondern auch für die meisten untersuchten nichtmetallischen Verbindungen war die Approximation der Meßwerte durch MZ besser als die durch die anderen zwei Gleichungen. Auch über eine Untersuchung der Abhängigkeit der Schmelztemperatur vom Druck wird berichtet.

1. Introduction

The relationship between the pressure p , volume V and temperature T is highly significant for practical high-pressure research. However, the equations of state are also important in planetary physics, where attempts are made to deduce the chemical constitution of the planets from the density models. Here, three obstacles have to be overcome: Firstly, the density distribution in the planet must be known with sufficient accuracy. This can be the case only where a network of seismometers has recorded a sufficient number of seismic events. Secondly, reliable equations of state are

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required in order to determine which chemical models are realistic at all. Thirdly, knowledge on abundances of the elements are needed from cosmochemistry in order to limit the number of possible chemical elements and compounds. Thereby, the number of models is also strongly reduced.

In the present paper we want to consider the second point, whose importance, however, goes far beyond the field of geophysics. In some cases, the equations of state used are based on considerations from the mechanics of continua and from thermodynamics, but very often they are purely empirical. An equation frequently used is that by BIRCH-MURNAGHAN (BIRCH [11]):

$$p = \frac{3}{2} \kappa_0 (x^{-7/3} - x^{-5/3}) \left[1 + \frac{3}{4} (4 - \kappa_1) (1 - x^{-2/3}) \right], \quad (1)$$

where x is the relative volume or, expressed in another way, the ratio of the zero-pressure density ρ_0 to the density ρ ; κ_0 denotes the initial bulk modulus and κ_1 the initial pressure derivative of the bulk modulus. The BIRCH-MURNAGHAN equation has been developed from a truncated expansion of the HELMHOLTZ free energy as a polynomial series in EULERIAN strain. The corresponding series in LAGRANGIAN strain converges less strongly. ULLMANN and PAN'KOV [45] generalized the BIRCH-MURNAGHAN equation and found their equation M1:

$$p = \frac{3\kappa_0}{\kappa_1 - 2} (x^{(1-2\kappa_1)/3} - x^{-(1+\kappa_1)/3}). \quad (2)$$

For $\kappa_1 = 4$, M1 merges into the abridged BIRCH-MURNAGHAN equation. Since the quantity κ_1 lies in the proximity of 4 for a few geophysically relevant materials (e.g., for Fe(ϵ), FeO, MgO), it is not astonishing that both equations yield similarly good results in respect of the Earth. Isothermal high-compression data of many elements and compounds are better approximated by equation (2) than by (1). This has been shown by ULLMANN and PAN'KOV [45] and by WALZER et al. [52].

2. Development of the equation of state MY and comparison with experimental high-compression data

Though the above two equations of state give a good approximation of the isothermal high-compression data, the approximation is by no means ideal. Therefore, we want to derive two new equations of state and verify them with the help of measured data. The first new equation, called MY, applies to metals. It was derived primarily to apply it to the metallic cores of the planets. The second new equation, MZ, is above all valid for halides and oxides.

Let us derive equation MY from an interatomic potential. In their Section 4, STACEY et al. [42] give a good survey of older suggestions of this kind. Our statement is to be more realistic from the point of view of solid state physics. Thereby, it is hoped that, given a very good approximation of the measured values is achieved, it will also become possible to extrapolate to regions which are not yet accessible to static high-compression experiments. STACEY et al. [42] and WALZER [49] have shown that equation (2) can be derived also from a LENNARD-JONES potential and the pertinent free energy

$$\Phi = \frac{A_1}{x^{m/3}} - \frac{B_1}{x^{n/3}}. \quad (3)$$

We have to deal with the case $m = 2n$. The quantities A_1 and B_1 are constants. However, the metallic bond is certainly too complex as to be simply expressed by a repulsive and an attractive term of the potential. Yet, the statistical theories apply to higher compressions than reached in planets. The central pressure of Saturn amounts to about $6 \times 10^{11} \text{ N m}^{-2}$, that of Jupiter to $30 \times 10^{11} \text{ N m}^{-2}$. This means that in all planets (even the largest ones) the shell structure of the atoms still plays a part, and the THOMAS-FERMI (TF) theory is not applicable. On the other hand, the expansions of the TF theory may indicate which expression for the HELMHOLTZ free energy is realistic. GOODISMAN [23], MARCH [35] and LIEB [32] have given reviews of the stages of these expansions. Already the functional for the TF theory contains, in addition to the potential between electrons and nuclei, the classical potential between the electrons and the potential between the nuclei, the kinetic energy of the electrons. Thus, the latter will have to be additionally considered in our statement. The expansion of the TF theory performed by DIRAC [17] amounts, in fact, to a consideration of the exchange energy of the electrons. We define this exchange energy after SEITZ [40] by $-(0.916/r_s)$ Ryd, thereby accounting for the mutual repulsion of electrons having the same spin; r_s is the mean interelectronic spacing, expressed in BOHR units. GOMBÁS [22] as well as HOHENBERG and KOHN [28] generalized the TF-DIRAC theory to account for correlation effects. We use for this purpose the interpolation formula by WIGNER [54], [55]:

$$E_{\text{corr}} = \frac{-0.88}{r_s + 7.8} \text{ Ryd} . \quad (4)$$

Now, let us assume that the HELMHOLTZ free energy is the sum of individual terms:

$$\Phi = \Phi_i + \Phi_0 + \Phi_t + \Phi_e . \quad (5)$$

Φ_i is the interaction free energy, for which we use an LJ potential; Φ_0 is the zero-point free energy, which will be neglected below. Let the thermal free energy be expressed by

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

where k is BOLTZMANN's constant, T the temperature, N' the number of atoms, h is the PLANCK quantum of action, and ν_i denotes the frequency. Hence, the statement for the HELMHOLTZ free energy of metals is

$$\Phi = a \left(\frac{A}{x^{2n/3}} - \frac{2B}{x^{n/3}} \right) + b \left(\frac{C}{r_{s0}^2 x^{2/3}} - \frac{D}{r_{s0} x^{1/3}} - \frac{E}{r_{s0} x^{1/3} + F} \right) + \Phi_t , \quad (7)$$

r_{s0} being the mean interelectronic spacing at zero pressure. In the following, the free parameters a , b and n will be replaced by well-known macrophysical quantities specific of the material. The terms on the right-hand side mean, respectively, repulsive and attractive lattice term, FERMI free energy of the electrons, exchange and correlation term of the electrons, thermal term. The relative volume x can also be expressed by $x = r_s^3/r_{s0}^3$. A and B result from the geometry of the crystal lattice. For fcc lattices, we have $A = 1.0110$ and $B = 1.2045$, account being taken of the influences of the atoms up to the third shell of neighbours around a fixed atom (HIRSCHFELDER et al.

[27]). $C-F$ have been taken from WIGNER [54]. We have

$$\begin{aligned} C &= 2.21 \text{ Ryd} \cdot (\text{BOHR unit})^2, & E &= 0.88 \text{ Ryd} \cdot \text{BOHR unit}, \\ D &= 0.916 \text{ Ryd} \cdot \text{BOHR unit}, & F &= 7.8 \text{ BOHR units}. \end{aligned}$$

The material constant r_{s0} is expressed in BOHR units by the following relationship:

$$r_{s0} = [3v_0/(4\pi w a_1^3)]^{1/3}, \quad (8)$$

where v_0 is the atomic volume in 10^{-30} m^3 units. For metals, we used the values from GÓRZECKI's [24] Table 1. w is the valency, a_1 is the first BOHR radius for hydrogen, expressed in units of 10^{-10} m . Thus, $a_1 = 0.529 177 06$.

We calculate the pressure in the temporary form p^* with the help of the thermodynamic relation $p^* = -(\partial\Phi/\partial x)_T$ and obtain the temporary form of the new equation of state for metals:

$$\begin{aligned} p^* &= -\frac{\partial\Phi}{\partial x} = -r_{s0}^3 \frac{\partial\Phi}{\partial y} = r_{s0}^3 \left\{ \frac{2n}{3} a \left[\frac{Ar_{s0}^{2n}}{y^{2n/3+1}} - \frac{Br_{s0}^n}{y^{n/3+1}} \right] + \right. \\ &\quad \left. + \frac{1}{3} b \left[\frac{2C}{y^{5/3}} - \frac{D}{y^{4/3}} - \frac{E}{(y^{1/3} + F)^2 y^{2/3}} \right] \right\}. \end{aligned} \quad (9)$$

In this equation, the substitution $y^{1/3} = r_{s0}x^{1/3}$ applies.

The (temporary) bulk modulus κ is calculated from equation (9):

$$\begin{aligned} \kappa &= -x \frac{\partial p^*}{\partial x} = -y \frac{\partial p^*}{\partial y} = r_{s0}^3 \left\{ \frac{2n}{3} a \left[\frac{(2n/3 + 1) Ar_{s0}^{2n}}{y^{2n/3+1}} - \frac{(n/3 + 1) Br_{s0}^n}{y^{n/3+1}} \right] + \right. \\ &\quad \left. + \frac{2}{9} b \left[5Cy^{-5/3} - 2Dy^{-4/3} - E \frac{2 + Fy^{-1/3}}{(y^{1/3} + F)^3 y^{1/3}} \right] \right\}. \end{aligned} \quad (10)$$

From this, we obtain

$$\begin{aligned} -x \frac{\partial \kappa}{\partial x} &= -y \frac{\partial \kappa}{\partial y} = r_{s0}^3 \left\{ \frac{2n}{3} a \left[\frac{(2n/3 + 1)^2 Ar_{s0}^{2n}}{y^{2n/3+1}} - \frac{(n/3 + 1)^2 Br_{s0}^n}{y^{n/3+1}} \right] + \right. \\ &\quad \left. + \frac{2}{27} b \left[25Cy^{-5/3} - 8Dy^{-4/3} - \right. \right. \\ &\quad \left. \left. - E \frac{Fy^{-1/3}(1 + Fy^{-1/3}) + (2 + Fy^{-1/3})(4 + Fy^{-1/3})}{(y^{1/3} + F)^4} \right] \right\}. \end{aligned} \quad (11)$$

For zero pressure, the following equation follows from $\partial\kappa/\partial p^* = (-x \partial\kappa/\partial x) \kappa^{-1}$:

$$\left(-x \frac{\partial \kappa}{\partial x} \right) \Big|_{x=1} = \kappa_0 \kappa_1. \quad (12)$$

To eliminate the unknown material constants a , b and n , we rearrange equations (9) to (11) to zero pressure and employ equation (12) so that these material-dependent constants can be expressed as functions of the initial bulk modulus κ_0 and the initial pressure derivative of the bulk modulus κ_1 . The values A to F are known. We get

$$a = U/n, \quad (13)$$

$$b = GU, \quad (14)$$

$$n = K + [K^2 - M + N\kappa_1]^{1/2}, \quad (15)$$

where

$$U = \frac{3}{2} \kappa_0 [(2n/3 + 1) A - (n/3 + 1) B + GH]^{-1} \quad (16)$$

and

$$G = 2 (B - A) \left[\frac{2C}{r_{s0}^2} - \frac{D}{r_{s0}} - \frac{Er_{s0}}{(r_{s0} + F)^2} \right], \quad (17)$$

$$H = \frac{1}{3} \left[5Cr_{s0}^{-2} - 2Dr_{s0}^{-1} - Er_{s0} \frac{2r_{s0} + F}{(r_{s0} + F)^3} \right], \quad (18)$$

$$I = \frac{1}{9} \left[25Cr_{s0}^{-2} - 8Dr_{s0}^{-1} - Er_{s0} \frac{F(r_{s0} + F) + (2r_{s0} + F)(4r_{s0} + F)}{(r_{s0} + F)^4} \right], \quad (19)$$

$$J = (4A - B)/9, \quad (20)$$

$$K = L(\kappa_1 - 2)/2, \quad (21)$$

$$L = (2A - B)/3J, \quad (22)$$

$$M = (A - B + GI)/J, \quad (23)$$

$$N = (A - B + GH)/J. \quad (24)$$

It has already been pointed out above that our theory shows a certain loose analogy to the TF-DIRAC-GOMBÁS (TFDG) theory. Up to now, those corrections of the TF theory have been included which can be explicitly expressed in x . In the statistical theories mentioned, the electron density for the region close to the nucleus has been overrated. GOODISMAN [23] eliminated this shortcoming by complementing the TFDG theory through quantum-statistical calculations. The joining has been done in a non-arbitrary manner. All parameters have been determined. This expansion gives also a good approximation of various experimental results which have nothing to do with our compression problem.

We employ the final result of GOODISMAN's theory by multiplying equation (9) by f_0 :

$$f_0 = \frac{0.72Z^{7/3} - 0.24Z^2 + 0.43Z^{5/3}}{0.7689Z^{7/3}}. \quad (25)$$

The new isothermal equation of state, called MY, is then defined by

$$p = f_0 \left\{ \frac{2}{3} na \left[\frac{A}{x^{2n/3+1}} - \frac{B}{x^{n/3+1}} \right] + \frac{1}{3} br_{s0}^3 \left[\frac{2C}{y^{5/3}} - \frac{D}{y^{4/3}} - \frac{E}{(y^{1/3} + F)^2 y^{2/3}} \right] \right\}. \quad (26)$$

Z is the nuclear charge. The following substitution applies:

$$y^{1/3} = r_{s0} x^{1/3}. \quad (27)$$

In practice, equations (8), (13) to (24), (25) and (27) must be substituted in equation (26) if we want to calculate the pressure p as a function of the relative volume x for metals. Naturally, κ also changes by the factor f_0 . The calculation of the pressure is completely straightforward: The constants A to F and a_1 follow from theoretical calculations. The computational expenditure required for the application of equation (26), i.e., of MY, is reasonable also for equation-of-state practitioners. For the ma-

terial concerned, only five well-known quantities have to be substituted: atomic charge Z , valency w , atomic volume v_0 , initial bulk modulus κ_0 and the initial pressure derivative of the bulk modulus κ_1 .

The curves calculated from the new equation of state MY were compared with the isothermal high-compression data for 20 metals (WALZER [51]). The result is to be briefly indicated here: For Li, Na, Mg, Ca, Fe, Ni, Cu, Zn, Rb, Mo, Pd, Ag, Cd, In, Sn, Au and Pb, the experimental values show good to excellent agreement with the curves calculated by means of MY; for K, V and Nb, there is mediocre agreement. Compared to the equations of state (1) and (2), marked improvements were achieved except for K.

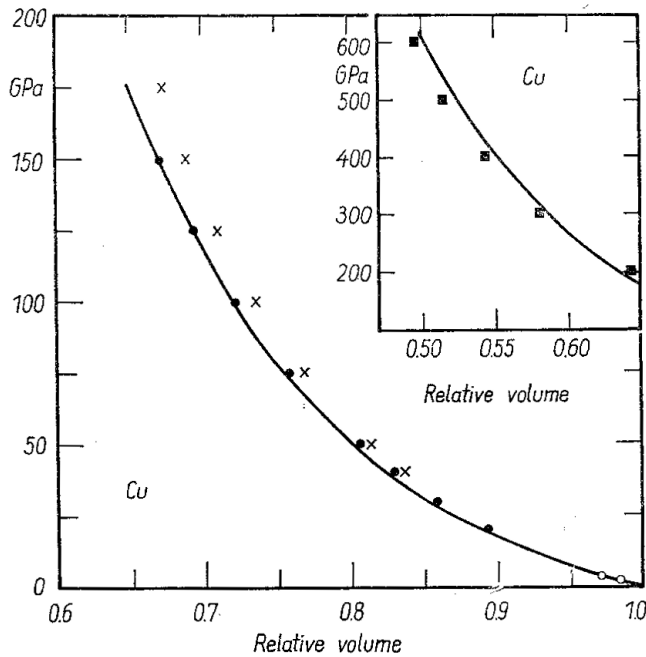


Fig. 1. Pressure versus relative volume plot for copper; ——— calculated through MY

Fig. 1 gives an example for the good agreement of the curves obtained with the aid of equation (26) with the isothermal measured data. For copper, e.g., the following material constants were used in the equation of state MY: $Z = 29$, $w = 2$, $v_0 = 11.81 \times 10^{-30} \text{ m}^3$, $\kappa_0 = 1.33 \times 10^{11} \text{ N m}^{-2}$, $\kappa_1 = 5.65$. The last two numerical values have been taken from BARSCH and CHANG [7], [8]. The representation of the experimental values in Fig. 1 and Figs. 3—6 is based on the one employed by ULLMANN and PAN'KOV [45], who collected the data from literature. Crosses generally indicate HUGONIOT data (here, smoothed ones after CARTER et al. [15]). Yet, not these have to be directly compared with the theoretical (isothermal) curves of MY, but the isothermal measured points: Solid squares represent the zero isothermal values according to AL'TSHULER et al. [2], full circles give the room isotherm after CARTER et al. [15], and open circles denote the static data after VAIDYA and KENNEDY [46].

3. Calculation of the melting temperature as a function of pressure for metals

In the calculation of the $p(x)$ curves by means of the equation of state MY, we consciously did not exhaust all possibilities. The numerical values taken for the con-

stants A and B were those for fcc lattices for all metals. That is to say, the differences in the crystal lattices of the metals were ignored in order to facilitate the convenient applicability of MY to the metallic cores of the planets. Nevertheless, agreement with the experimental data was astonishingly good. On the basis of this approach, we shall attempt now to calculate the dependence of the melting temperature T_m on the pressure p . STACEY and IRVINE [43], [44] found for close-packed materials that LINDEMANN's melting law

$$\frac{d \ln T_m}{dp} = \frac{2(\gamma - 1/3)}{\alpha} \quad (28)$$

applies. γ is the GRÜNEISEN constant, whose dependence on pressure and volume can be represented in such a way (see, e.g., MIGAULT et al. [36]):

$$\gamma = \frac{3j - 4}{6} - \frac{V}{2} \frac{d^2(pV^j)/dV^2}{d(pV^j)/dV} \quad (29)$$

It can be shown that for densest spherical packings $j = 4/3$, and we find the VASHCHENKO-ZUBAREV formula

$$\gamma = \frac{\frac{1}{2} \frac{d\alpha}{dp} - \frac{5}{6} + \frac{2}{9} \frac{p}{\alpha}}{1 - \frac{4}{3} \frac{p}{\alpha}} \quad (30)$$

BRENNAN and STACEY [14] proved that this applies also to non-central atomic forces.

Now, $T_m(p)$ was calculated from the equations (26), (28) and (30) and compared with measured data. The results were definitely differing. It turned out that the simplification mentioned was not favourable for calculating the melting temperature. Fig. 2 presents examples for good and bad agreement achieved with the experimental data. The solid lines follow from our theory. In Fig. 2a, the dashed lines indicate, according to MIGAULT et al. [36], the theoretical values given by these authors for various j , while the black squares indicate the measured values. In Fig. 2b, the upper dashed line represents the melting line according to the vacancy-mechanism theory of GÓRECKI [24], while the open circles represent the experimental results obtained by KENNEDY et al. [30]. In the calculation of the continuous melting lines, the following

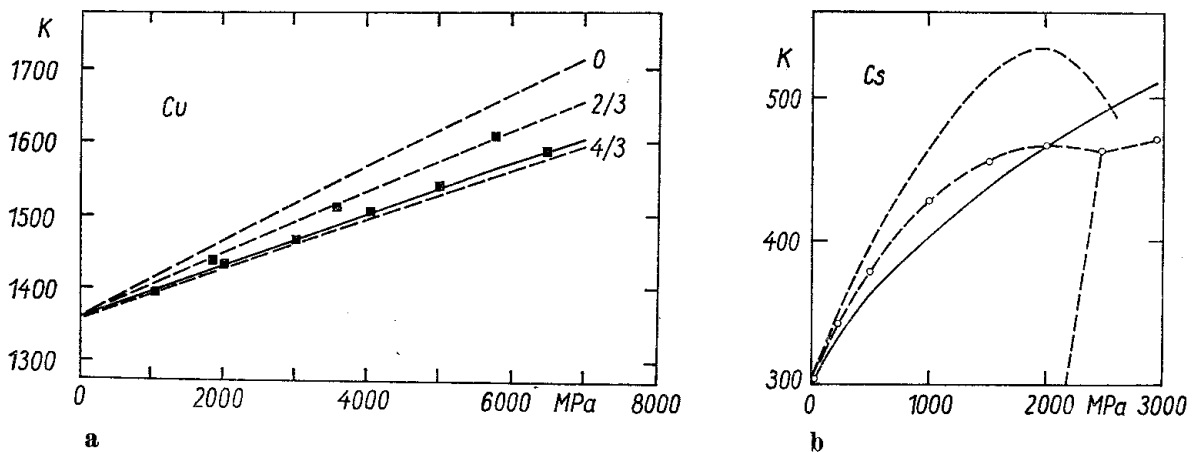


Fig. 2. Melting temperature versus pressure plot for copper (a) and cesium (b)

material constants were used for Cs: $Z = 55$, $w = 1$, $v_0 = 115.17 \times 10^{-30} \text{ m}^3$, $\kappa_0 = 17.9 \times 10^8 \text{ N m}^{-2}$, $\kappa_1 = 3.17$, $T_{m0} = 301.8 \text{ K}$. For Cu, we took additionally $T_{m0} = 1356 \text{ K}$. The melting temperatures at zero pressure T_{m0} were taken from GSCHNEIDNER [25], κ_0 and κ_1 for Cs from GUINAN and STEINBERG [26].

Table 1. Some numerical values of the 20 metals examined with the help of MY. Z : atomic number, w : valency, v_0 : atomic volume after GÓRECKI [24] (* calculated with the help of the numerical values of GSCHNEIDNER's [25] Table 7, ** calculated from $v_0 = 11.77 \times 10^{-30} \text{ m}^3$ of Fe(α)); r_{s0} : mean interelectronic spacing at zero pressure, f_0 : a quantum-statistical quantity

Element	Z	w	$v_0 [10^{-30} \text{ m}^3]$	r_{s0}	f_0
Pb	82	2	30.33	2.901685	0.894186
Au	79	1	16.96	3.011929	0.894033
Sn(w)	50	4	27.07*	2.217408	0.892882
In	49	3	26.12*	2.411682	0.892868
Cd	48	2	21.58	2.590458	0.892858
Ag	47	1	17.06	3.017837	0.892851
Pd	46	2	14.72	2.280318	0.892849
Mo	42	4	15.58	1.844471	0.892891
Nb	41	5	17.98	1.796012	0.892916
Rb	37	1	92.67	5.304965	0.893096
Zn	30	2	15.24	2.306859	0.893872
Cu	29	2	11.81	2.118895	0.894054
Ni	28	2	10.94	2.065532	0.894261
Fe(ϵ)	26	2	10.81**	2.057318	0.894762
V	23	3	13.88	1.953405	0.895794
Ca	20	2	43.48	3.271819	0.897312
K	19	1	75.31	4.950552	0.897969
Mg	12	2	23.27	2.656388	0.906761
Na	11	1	39.50	3.992410	0.909121
Li	3	1	21.61	3.265285	0.988836

Table 2. Material parameters employed; data compiled by ULLMANN and PAN'KOV [45]

Material	$\kappa_0 [10^8 \text{ N m}^{-2}]$	κ_1	Figs.	Origin of the data
NH ₄ Cl	176.7	8.21	3a	GARLAND and RENARD [20]
NH ₄ Br	158.6	7.66	3b	GARLAND and YARNELL [21]
AgCl	417.4	7.00	3c	LOJE and SCHUELE [33]
AgBr	377.7	7.49	3d	
LiF	665.7	5.24	4a	ANDERSON [5]
NaCl	237.5	5.35	4b	ROBERTS and SMITH [39]
NaBr	192.0	5.3	4c	ROBERTS and SMITH [39], BARSCH and CHANG [8]
NaI	162.2	5.48	4d	BARSCH and SHULL [10]
CsCl	167.4	5.98	5a	BARSCH and CHANG [9]
CsBr	143.4	5.95	5b	
CsI	118.9	5.93	5c	
MgO	1599	4.25	6a	ANDERSON et al. [6]
CaO	1049	5.26	6b	

4. Development of the equation of state MZ and comparison with experimental high-compression data obtained for halides and oxides

Equation MZ cannot be derived irrespective of MY. Actually, it is only a modification of MY which makes it possible to try out MZ for *each* material, provided that κ_0 and κ_1 are known and experimental data for the comparison are available. This simplification of MY facilitates the application.

Table 1, which summarizes a few numerical values for the 20 metals investigated with the aid of MY, is our starting point. The basic idea in the formation of MZ is to substitute mean values for some of the input parameters of MY. The mean values of r_{s0} and f_0 are 2.80076 and 0.900209, respectively. The major portion of the scattering around the latter value is caused by the smaller Z -values. A number of oxides occur-

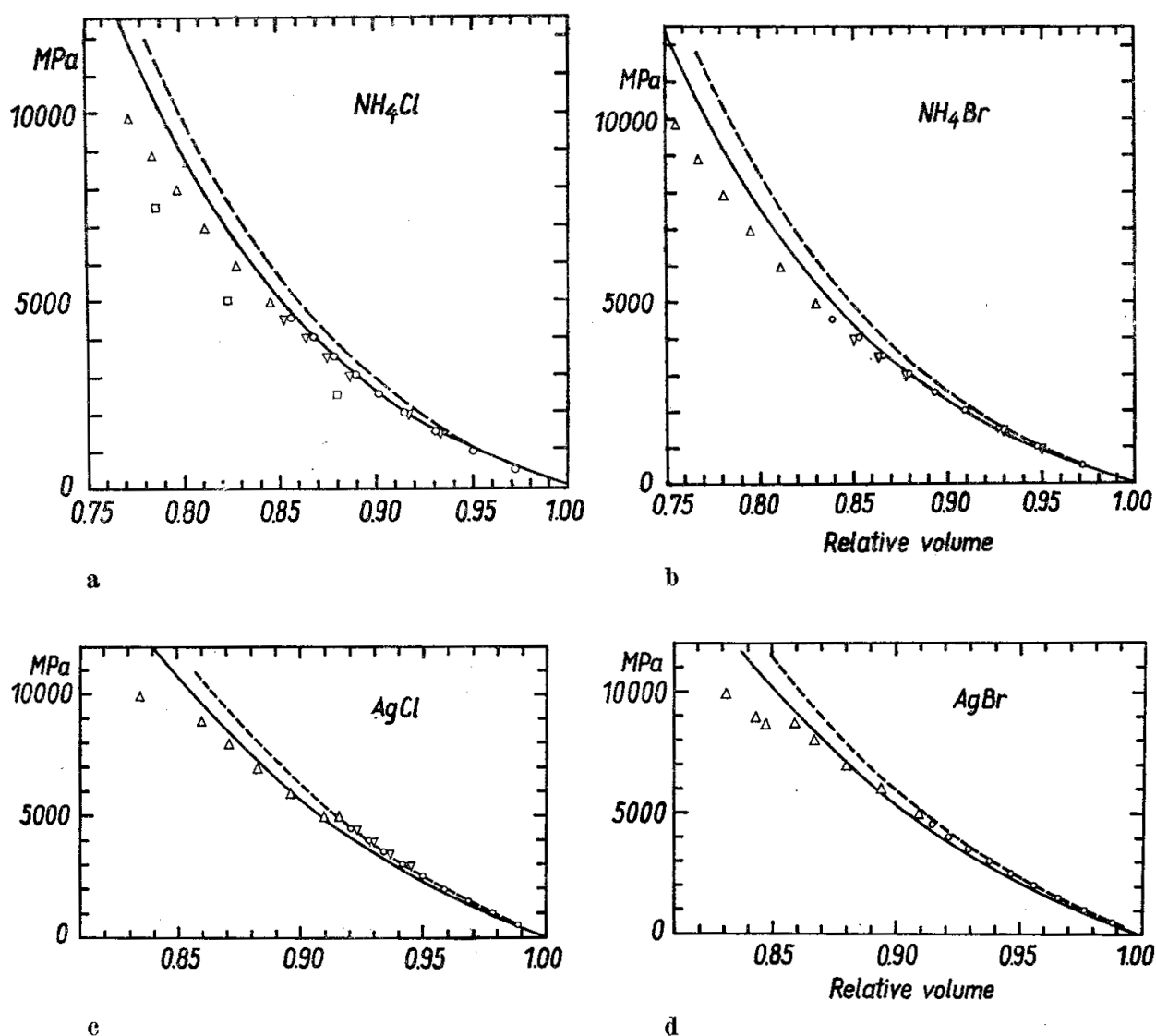
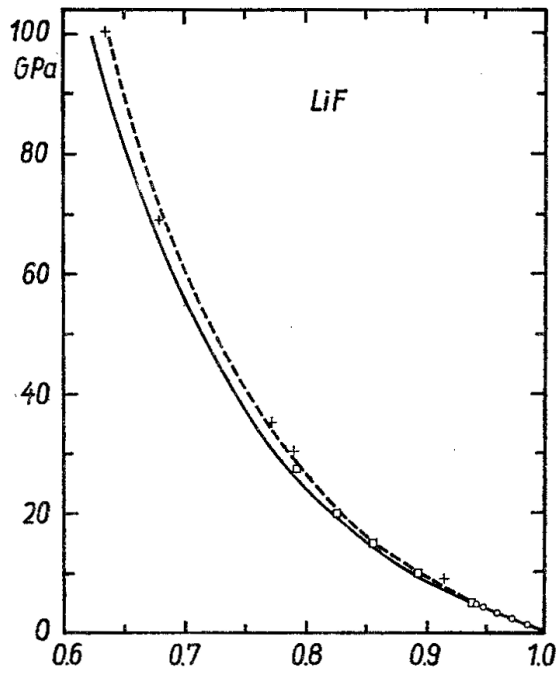
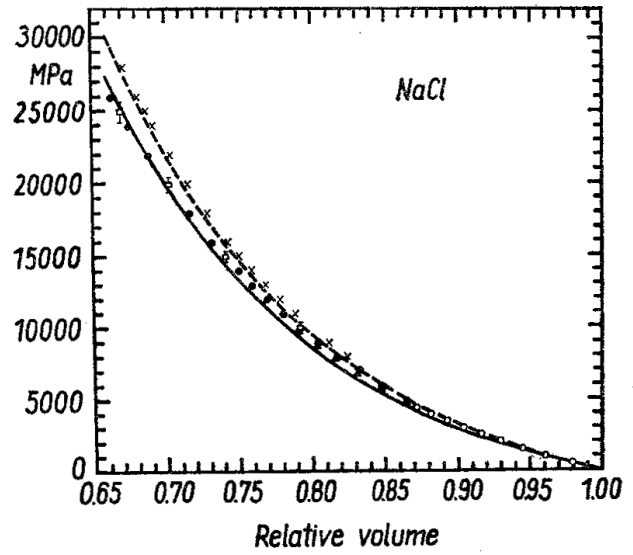


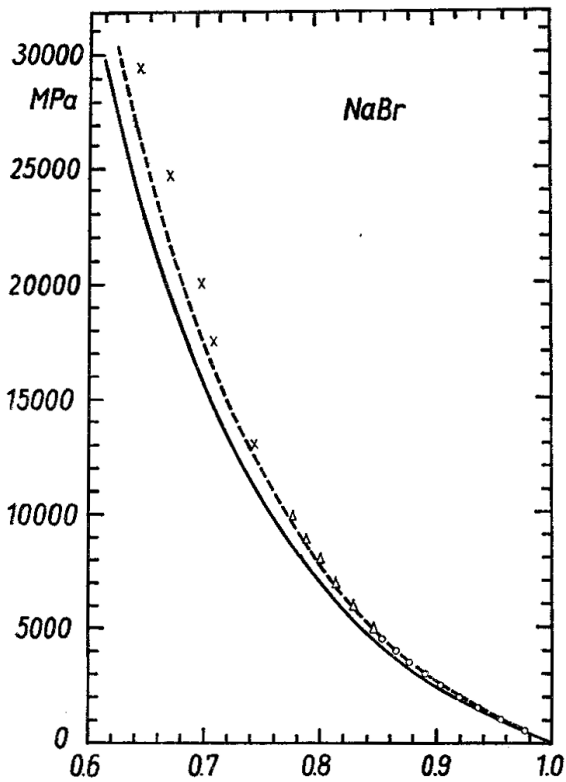
Fig. 3. Pressure versus relative volume plot for NH_4Cl (a), NH_4Br (b), AgCl (c) and AgBr (d). — calculated with the aid of the new equation of state MZ, ---- for comparison; the dashed curve has been determined by means of equation M1 by ULLMANN and PAN'KOV [45], which is a generalization of BIRCH's equation of state (1). Table 3 shows the sources of the experimental data. Only the more compact symbols should be used in comparing the two isothermal equations of state, not the crosses, as they represent HUGONIOT data



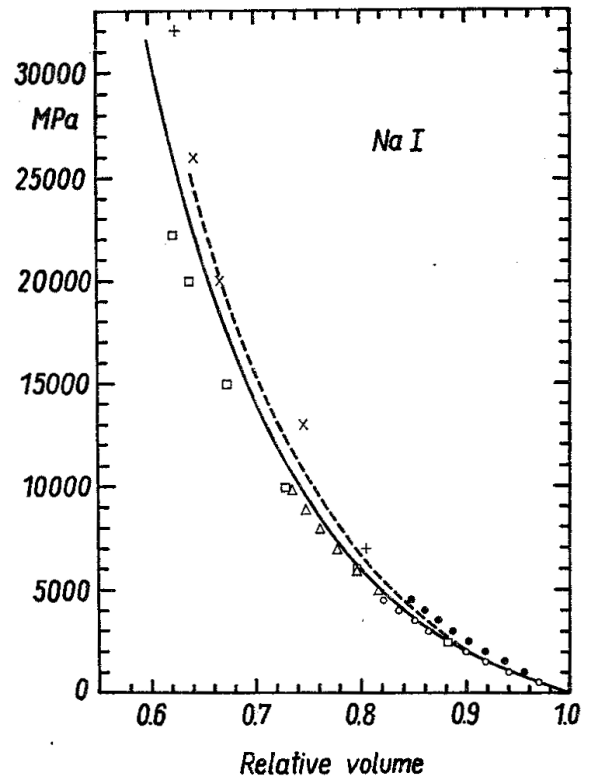
a



b



c



d

Fig. 4. Pressure versus relative volume plot for LiF (a), NaCl (b), NaBr (c) and NaI (d) (for the legend see Fig. 3)

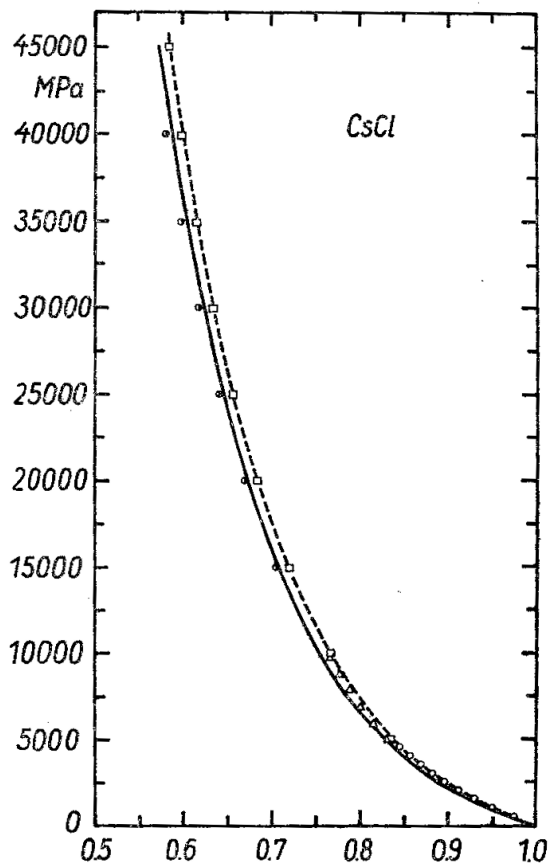
ring in the Earth's mantle have mean atomic weights in g/mole amounting to about 20: MgO, 20.16; SiO₂, 20.03; Al₂O₃, 20.39; Na₂O, 20.66 (BIRCH [12]; SHANKLAND [41]). For $Z = 20$ we have $f_0 = 0.897312$. This f_0 -value approximates the mean value and even more a modified mean value which is created when the lightest materials are omitted, which, after all, show the greatest deviations from the mean value. Moreover, numerical experiments show that w has only little influence on $p(x)$. Therefore, we define: The equation of state MZ is deduced from MY by specifying $r_{s0} = 2.80076$, $Z = 20$ and $w = 1$ for all materials.

MZ gives good to excellent approximations of $p(x)$ for 17 of the 20 metals under study, while only mediocre approximations for 3 of them. This result is not astonishing, since the MY theory accounts better for the details of the metallic bond than earlier theories did, that were designed for equation-of-state practitioners, and since MZ is a simplified variant of MY. The main advantage of the equation of state MZ rests in its practical applicability to *any* material. As it is not a priori clear for non-metallic materials that MZ gives a better approximation of the experimental isothermal high-compression values than other good equations of state, it has to be proven through a comparison for each individual material. This is the principal objective of the present paper. Figs. 3–5 provide the comparison for all halides for which data are available. Fig. 6 shows two oxides that are geophysically relevant. The experimental data stem from volumetric measurements, shock-wave data and X-ray studies. The HUGONIOT pressure was estimated in the conventional manner by means of the MIE-GRÜNEISEN equation and the RANKINE-HUGONIOT conservation laws. This reformation of the measured values was performed either by the experimentalists listed in Table 3 themselves or by ULLMANN and PAN'KOV [45].

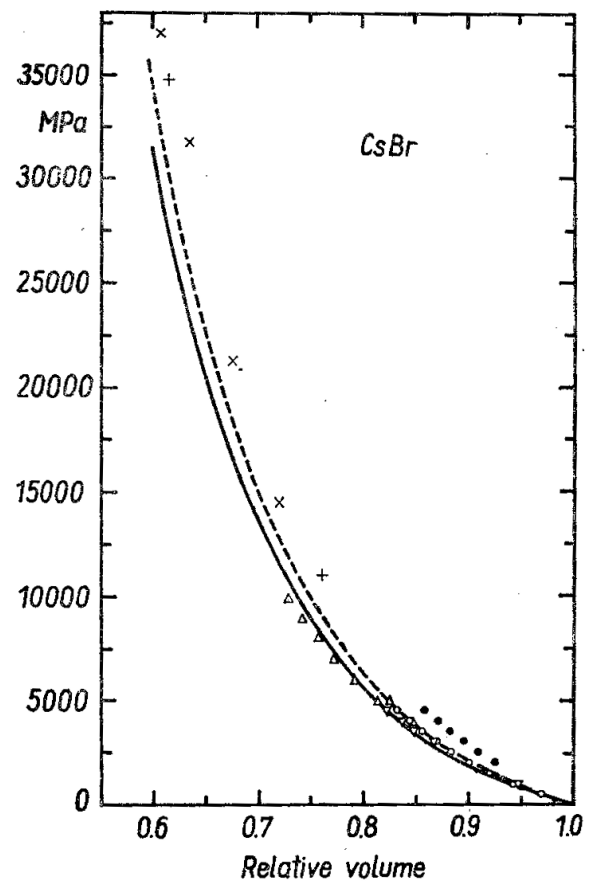
A view of Figs. 3–6 yields the following details: As to NH₄Cl and NH₄Br, the equation MZ gives a better approximation of the measured values than M1. With $0.85 \leq x \leq 1$, the experimental values lie on the curve of MZ, with $x < 0.85$, they are found below it. For AgCl and AgBr and $x < 0.91$, MZ is significantly better than M1. With lower compressions, where the curves lie anyway close to each other, M1 is somewhat better. For LiF, both curves are equally good. The HUGONIOT crosses do not count in the comparison, yet, since the isothermal values are positioned lower, they have to lie closer to MZ. With regard to NaCl, MZ coincides with the measured values, M1 lying markedly too high. NaBr is the only halide studied whose measured values coincide with M1, while MZ lies too low. For NaI, MZ is better than M1, but for higher compressions the measured values are lower than MZ. As to CsCl, both equations of state are equally good. In the case of CsBr and CsI, MZ shows significant improvements over M1. Regarding MgO, which is found in great quantities in the Earth, MZ gives a better approximation for $x < 0.6$, while for M1 this holds with $0.6 \leq x \leq 0.8$. However, in the latter range, both curves are almost equivalent, and for still lower compressions completely equivalent. Hence, as a whole, equation MZ is to be preferred for MgO; for CaO, the opposite applies.

5. Conclusions

The result, thus, is that from among the 13 compounds investigated only two (namely NaBr and CaO) are better represented by M1 than by MZ. The result is approximately the same for the BIRCH-MURNAGHAN equation (1).



a



b

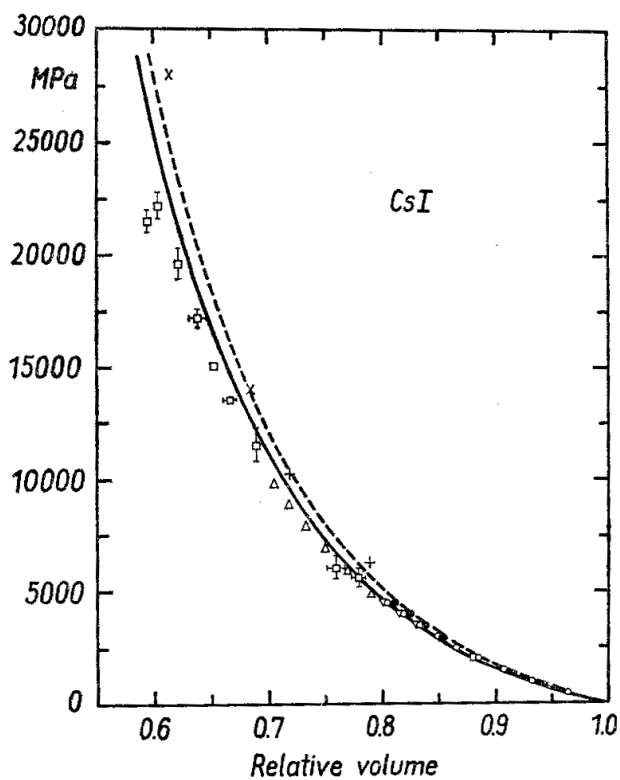


Fig. 5. Pressure versus relative volume plot for CsCl (a), CsBr (b) and CsI (c) (for the legend see Fig. 3)

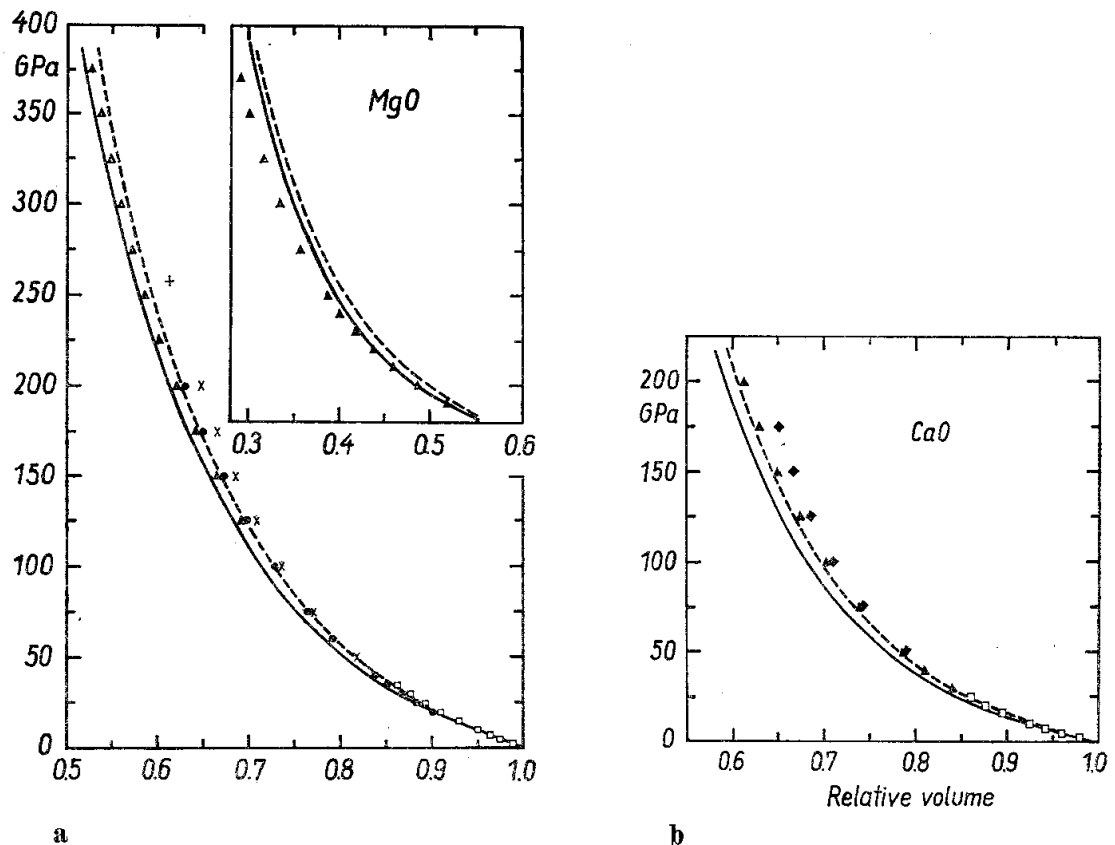


Fig. 6. Pressure versus relative volume plot for MgO (a) and CaO (b) (for the legend see Fig. 3)

Summing up, one can say that a new equation of state MY has been derived for metals. This equation has been simplified such that, now called MZ, it is principally applicable to all materials for which only the initial bulk modulus κ_0 and the initial pressure derivative of the bulk modulus κ_1 have to be known. With almost all of the 20 metals and 13 compounds examined, MY and MZ approximate the experimental isothermal data better than the equation of state MI by ULLMANN and PAN'KOV [45] and its special case, the equation of state Bi by BIRCH [11], which has a wide geophysical following. For reasons of clarity, the comparison with Bi has not been additionally shown in the figures. In most cases, MI is anyway an improvement in respect of Bi. The computational expenditure for Bi and MI, however, is lower than that for MY and MZ. Still, this is only a minor advantage, since MY and MZ can be calculated even with simple programmable desk computers. The essential advantage continues to be that, starting from the same input data, i.e., κ_0 and κ_1 , the equations of state MY and MZ give a better approximation of the experimental high-compression data than MI and Bi.

By the way, the equation of state MX (WALZER [49]) anticipates some features of MY. However, MY has a quantum-statistical correction. The interior of the theory is altered, too: In MX the mean interelectronic spacing r_{s0} is a constant. In MY the quantity r_{s0} is computed individually for each metal. In MY we used WIGNER's original constants for C to F . K is introduced differently. In MX the quantities κ_0 and κ_1 serve as input parameters, in MY five input constants were used, namely, the atomic charge, the valency, the atomic volume, κ_0 and κ_1 . MY and MZ approximate the experimental data better than MX does.

Table 3. Sources of the experimental values and legend of the symbols used in the drawings

Materials	Figs.	Symbols	References
NaCl, NaBr	4b 4c	open circles triangles crosses solid circles open squares	static data (VAIDYA and KENNEDY [47]) BRIDGMAN's data (BIRCH [13]) HUGONIOT (FRITZ et al. [19], WEAVER [53], VAN THIEL [48]) room isotherm, based on the HUGONIOT data men- tioned above X-ray data (PEREZ-ALBUERNE and DRICKAMER [38])
LiF, NaI, AgCl, AgBr, NH ₄ Cl, NH ₄ Br CsCl, CsBr, CsI	4a, d 3c, d 3a 3b 5a, b 5c	open circles open triangles, corner up solid circles lying crosses standing crosses open triangles, corner down open squares semisolid circles	static data (VAIDYA and KENNEDY [47]) BRIDGMAN's data (BIRCH [13]) isotherm from HUGONIOT data (KEELER [29]) HUGONIOT data (VAN THIEL [48]) HUGONIOT data (AL'TSHULER et al. [3], KORMER et al. [31]) BRIDGMAN's data (VAIDYA and KENNEDY [47]) X-ray data (PEREZ-ALBUERNE and DRICKAMER [38], HAMMOND's data quoted by MAO [34]) isotherm from the equation of state by DECKER [16])
MgO	6a	lying crosses solid circles solid triangles open squares standing crosses	smoothed HUGONIOT data (CARTER et al. [15]) room isotherm from HUGONIOT data (CARTER et al. [15]) room isotherm from HUGONIOT data (PAN'KOV and KALININ [37]) X-ray data (DRICKAMER et al. [18]) HUGONIOT data (AL'TSHULER [1]) and ceramic sample HUGONIOT data by McQUEEN and MARSH (BIRCH [13])
CaO	6b	open squares solid rhomb solid triangles	X-ray data (DRICKAMER et al. [18]) room isotherm computed by AL'TSHULER and SHARIPDZHANOV [4] room isotherm from HUGONIOT data (PAN'KOV and KALININ [37])

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