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COMPARISON OF SOME EQUATION-OF-STATE THEORIES BY USING EXPERIMENTAL HIGH-COMPRESSION DATA [*1]

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Three theories that are of importance for planetary physics are examined by establishing whether the curves in the pressure–density diagram which have been calculated from the appropriate equations of state satisfactorily describe the dynamic and static data obtained for cubic solids. For this purpose, the fourth-order anharmonic theory derived from lattice dynamics, a theory based on the Eulerian formulation of finite strain, and a new theory as outlined in Section 2 have been compared. It is found that the new theory yields results that show the best agreement with the measured values.

1. Introduction

It is an essential prerequisite for planetary physics to have good equations for the description of pressure–volume data for materials subject to high pressure in order to permit reliable extrapolations in the high-pressure regions which hardly lend themselves for experiments. It is the objective of the present paper to compare a new theory by Ullmann with the fourth-order anharmonic theory by Leibfried and Ludwig (1961) and Thomsen (1970), and with a theory based on the fourth-order Eulerian formulation of finite strain in respect of its suitability for the description of empirical shock and static compression data. To avoid any subjective selection of observation data, we consciously confine ourselves to the compression data of 17 cubic solids that have been used by Ahrens and Thomsen (1972) in their thought-provoking paper.

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2. The new theory

We consider a macroscopic body which is assumed to be a physically-homogeneous thermodynamic system. Thus, an equilibrium state of this body can be represented by the pressure P, the volume V and the entropy S, each of these state variables depending on the two others. In the initial state of the body let P, V, S take the values $0, V_0, S_0$, respectively. Hence, using the volumetric contraction $x \equiv V/V_0$, the equation of state of the body may be written in the general form of:

$$P = -y'(x)(\partial/\partial y)Y(y, S)$$

where $Y(y, S)$ stands for the strain energy, measured per volume V_0 of the uncompressed body, as a function of S and a dimensionless variable y depending on x. We note that, necessarily, $y(x) < 0$, $dy/dx \equiv y'(x) > 0$ and $Y(y, S) > 0$ for $x < 1$ and, without loss of generality, $y(1) = 0, y'(1) = 1$ and $Y(0, S_0) = 0$. Besides, we observe that $Y(y, S)$ simultaneously means the internal energy of the body in the equilibrium state $\{P, V, S\}$, measured per volume V_0.

The functions $Y(y, S)$ and $y(x)$ are assumed to be continuously differentiable with respect to y and x,

respectively, as many times as required. So the bulk modulus $\kappa = k(P, S)$ is continuously differentiable with respect to P up to any order required. For further convenience we put:

$$\kappa_0 \equiv k(0, S_0)\,,$$

$$\kappa_n \equiv \kappa_0^{n-1}(\partial^n/\partial P^n)k(0, S_0)$$

and

$$Y_{n+2} \equiv \kappa_0^{-1}(\partial^{n+2}/\partial y^{n+2})\,Y(0, S_0)$$

for $n = 1, ..., N+1$, where the integer N is arbitrarily fixed. In particular:

$$(\partial/\partial y)\,Y(0, S_0) = 0 \quad \text{and} \quad (\partial^2/\partial y^2)\,Y(0, S_0) = \kappa_0$$

Then, if $y(x)$ is chosen, Y_{n+2} proves to be a polynomial in the n material parameters $\kappa_1, ..., \kappa_n$. Attention is now confined to adiabatic changes of the body so that $S = S_0$. Using Taylor's theorem, we thus have:

$$Y(y, S) = \tfrac{1}{2}\kappa_0 y^2\left[1 + 2\sum_{n=1}^{N}\frac{Y_{n+2}}{(n+2)!}\,y^n\right] + R_{N+3} \qquad (1)$$

where R_{N+3} is the remainder and $Y_{n+2} = Y_{n+2}(\kappa_1, ..., \kappa_n)$ as remarked.

For instance, the function $y = (\frac{3}{2})(1 - x^{-2/3})$ helps to obtain:

$$P \approx \tfrac{3}{2}\kappa_0(x^{-7/3} - x^{-5/3})\left[1 + \sum_{n=1}^{N}(\tfrac{3}{2})^n\frac{Y_{n+2}}{(n+1)!}\right.$$
$$\left.\times\,(1 - x^{-2/3})^n\right] \qquad (2)$$

which is Birch's (1947, 1952) approximation of the equation of state. In particular:

$$Y_3 = 4 - \kappa_1$$

and

$$Y_4 = \tfrac{35}{9} + (3 - \kappa_1)(4 - \kappa_1) + \kappa_2$$

Further, from $y = 3(1 - x^{-1/3})$ we obtain:

$$P \approx 3\kappa_0(x^{-5/3} - x^{-4/3})$$
$$\times\left[1 + \sum_{n=1}^{N} 3^n\frac{Y_{n+2}}{(n+1)!}\,(1 - x^{-1/3})^n\right] \qquad (3)$$

which comes close to Bardeen's (1938) approximation of the equation of state for the alkali metals. Here, in particular:

$$Y_3 = 3 - \kappa_1$$

and

$$Y_4 = \tfrac{20}{9} + (2 - \kappa_1)(3 - \kappa_1) + \kappa_2$$

Finally, the "Lagrange finite-strain scalar":

$$y = \tfrac{3}{2}(x^{2/3} - 1)$$

used by Thomsen (1970, 1972) leads to:

$$P \approx \tfrac{3}{2}\kappa_0(x^{-1/3} - x^{1/3})$$
$$\times\left[1 + \sum_{n=1}^{N}(\tfrac{3}{2})^n\frac{Y_{n+2}}{(n+1)!}\,(x^{2/3} - 1)^n\right] \qquad (4)$$

which, however, is unsuitable as shown by Pan'kov and Ullmann (1975). Instead the Bardeen and, above all, the Birch equation has proved its worth for gaining information on the compressional behaviour of substances geophysically relevant.

It can be shown (see Ullmann and Pan'kov, 1976) that the coefficients Y_{n+2}, $n = 1, ..., N$, in eq. 1 vanish by introducing y as a function of x and the N parameters $\kappa_1, ..., \kappa_N$, written $y = \varphi_N(x; \kappa_1, ..., \kappa_N)$, which satisfies the N initial conditions:

$$y_2 = -\tfrac{1}{3}(1 + \kappa_1) \qquad (5)$$

and, in case of $1 < n \leqslant N$:

$$y_{n+1} = \frac{1}{n+2}\left[X_{n+2} - \sum_{k=2}^{[\frac{n+2}{2}]} l_k\binom{n+2}{k}y_k y_{n+2-k}\right], \qquad (6)$$

where for convenience $(\partial^m/\partial x^m)\varphi_N(1; \kappa_1, ..., \kappa_N)$ is denoted by y_m. As usual $[\frac{n+2}{2}]$ stands for the greatest integer not greater than $(n+2)/2$. The symbol l_k is defined by the rule: $l_k = 1$ for $k < (n+2)/2$, $l_k = 1/2$ for $k = (n+2)/2$. The quantity X_{n+2} depends on $\kappa_1, ..., \kappa_n$, so it may be compared to $Y_{n+2} = Y_{n+2}(\kappa_1, ..., \kappa_n)$ and is identical with it, if y in eq. 1 is replaced by $x - 1$. In particular:

$$X_4 = (1 + \kappa_1)(2 + \kappa_1) + \kappa_2 \qquad (7)$$

$$X_5 = -(1 + \kappa_1)(2 + \kappa_1)(3 + \kappa_1)$$
$$- 2(3 + 2\kappa_1)\kappa_2 - \kappa_3 \qquad (8)$$

Consequently, formula (1) can be reduced to:

$$Y(y, S) = (1/2)\kappa_0 y^2 + R_{N+3}$$

We see that the strain energy $Y(y, S)$ is approximately a pure quadratic function of $y = \varphi_N(x; \kappa_1, ..., \kappa_N)$ if $|R_{N+3}|$ is negligibly small in comparison with the term $(1/2)\kappa_0 y^2$. Since the physical quantity R_{N+3} is incalculable by exact mathematical procedure or by assessment based upon very general conditions, the validity of $|R_{N+3}| << (1/2)\kappa_0 y^2$ can be learned only on using data. Hence, returning no strong argument, we suppose that the remainder R_{N+3} sufficiently approximates $\kappa_0 Y_{N+3} y^{N+3}/(N+3)!$ and, in place of eq. 1, write:

$$Y(y, S) \approx \tfrac{1}{2}\kappa_0 y^2 \left[1 + \frac{2}{(N+3)!}\, Y_{N+3} y^{N+1}\right] \qquad (9)$$

From the initial conditions for the function $y = \varphi_N(x; \kappa_1, ..., \kappa_N)$ it follows in addition that:

$$Y_{N+3} = X_{N+3} - \sum_{k=1}^{[\frac{N+3}{2}]} l_k \binom{N+3}{k} y_k y_{N+3-k} \qquad (10)$$

where X_{N+3} is a polynomial in $\kappa_1, ..., \kappa_N$ and κ_{N+1} (see above). Therefore, if $Y_{N+3} \approx 0$ then an approximate relation between κ_{N+1} and $\kappa_1, ..., \kappa_N$ comes true. For instance, in the case of $N = 1$ we have:

$$Y_4 = \tfrac{1}{3}(1 + \kappa_1)(5 + 2\kappa_1) + \kappa_2 - 4\frac{\partial^3}{\partial x^3}\varphi_1(1; \kappa_1) \qquad (11)$$

and in the case of $N = 2$:

$$Y_5 = -\tfrac{1}{18}(1 + \kappa_1)(83 + 55\kappa_1 + 8\kappa_1^2) - \tfrac{1}{6}(31 + 19\kappa_1)\kappa_2 - \kappa_3 - 5\frac{\partial^4}{\partial x^4}\varphi_2(1; \kappa_1, \kappa_2) \qquad (12)$$

In order to obtain a form of y leading to a suitable expression for this variable in the concrete, N subsidiary quantities $u_1, ..., u_N$ are now introduced, where u_n is to be a function of $\kappa_1, ..., \kappa_n$, i.e. $u_n = u_n(\kappa_1, ..., \kappa_n)$ $(n = 1, ..., N)$. Thus we write $y = f_N(x; u_1, ..., u_N)$. Practically, only a few values for κ_2 reliable to some extent are available, and we are furthermore wanting information on κ_3 gained from experimental values. Compared to it, almost all the data required for the determination of κ_1 are reliable at the very least for our purpose. It is hardly necessary to note that κ_0 does not give rise to objections. It is, therefore, expedient to confine our attention to the two cases that N takes the values 1 and 2, respectively. We must now turn to the question how to decide in the concrete on the function $f_1(x; u_1)$, since an infinite set of such functions having the same properties characterizing $f_1(x; u_1)$ are available. Being concerned with it, we refer to the two approximations (2) and (3) which are closely connected with the well-known equations named after Birch and Bardeen. We are of the opinion that the mathematical expression of $f_1(x; u_1)$ must prove to be most simple and, in particular, the approximation:

$$P \approx -\kappa_0 y \frac{\partial y}{\partial x}\left[1 + \frac{1}{(N+2)!}\, Y_{N+3} y^{N+1}\right] \qquad (13)$$

resulting from eq. 9 in the case of $N = 1$ has to be true to the type of equations, which are used by preference even now.

Consequently, we consider the case of $N = 1$ with the function

$$y = f_1(x; u_1) = \frac{1}{u_1}(x^{u_1} - 1) \qquad (14)$$

From this, using eqs. 5–7 and 11, we obtain:

$$u_1 = \tfrac{1}{3}(2 - \kappa_1), \qquad \kappa_1 > 2 \qquad (15)$$

and

$$Y_4 = -(1/9)(1 + \kappa_1)(1 - 2\kappa_1) + \kappa_2$$

Evidently, $Y_4 \approx 0$ is equivalent to:

$$\kappa_2 \approx \tfrac{1}{9}(1 + \kappa_1)(1 - 2\kappa_1) \qquad (16)$$

which proves to be true for different substances relevant to planetary physics (see Ullmann and Pan'kov, 1976). Thus, from eq. 13 for $N = 1$:

$$P \approx -\frac{3\kappa_0}{2 - \kappa_1}(x^{1/3 - 2/3\kappa_1} - x^{-1/3 - 1/3\kappa_1}) \qquad (17)$$

which is equivalent to Birch's standard equation in the case of $\kappa_1 = 4$ and can be recognized as the shortened form of Bardeen's equation when $\kappa_1 = 3$. Moreover, supposing $Y_4 \approx 0$, we have $\kappa_3 \approx -35/9$ from eq. 2 for $\kappa_1 = 4$ and $\kappa_2 \approx -20/9$ from eq. 3 for $\kappa_1 = 3$ as immediately results from eq. 16.

Since eq. 17 provides rather satisfying information, the use of the case $N = 2$ can be understood only for a desirable extension of the hitherto existing information volume. It is obvious that the correlations of the two cases must be governed by the associated func-

tions $f_1(x;u_1)$ and $f_2(x;u_1,u_2)$ for the variable y. Turning our attention to the case of $N=2$, we shall only deal with some main results. For details see Ullmann and Pan'kov (1976). The variable y is now expressed as:

$$y = f_2(x;u_1,u_2) = f_1(x;u_1)\exp[u_2(1-x+\ln x)] \tag{18}$$

which evidently agrees with eq. 14 for $u_2 = 0$. From this, using eqs. 5–8 and 12, it follows that

$$u_2 = \tfrac{1}{12}[\tfrac{1}{9}(1+\kappa_1)(1-2\kappa_1)-\kappa_2] \tag{19}$$

and

$$Y_5 = \tfrac{1}{27}(1+\kappa_1)(3+\kappa_1)(1-2\kappa_1) - \tfrac{1}{3}(3+7\kappa_1)\kappa_2 - \kappa_3 \tag{20}$$

Hence, in view of eq. 13 with $N=2$:

$$P \approx -\frac{\kappa_0}{u_1}(x^{2u_1-1}-x^{u_1-1}) \times\left[1+\frac{u_2}{u_1}(1-x)(1-x^{-u_1})\right]\Lambda(x;\kappa_1,\kappa_2,\kappa_3) \tag{21}$$

where

$$\Lambda(x;\kappa_1,\kappa_2,\kappa_3) = \exp[2u_2(1-x+\ln x)] + \tfrac{1}{3}Y_5\left(\frac{x^{u_1}-1}{2u_1}\right)^3 \times \exp[5u_2(1-x+\ln x)] \tag{22}$$

If eq. 19 comes true so that u_2 is very small, taken absolutely, and $\kappa_3 \approx -2\kappa_1\kappa_2$ is supposed to be reliable, then we have $Y_5 \approx 0$, and eq. 21 reduces to eq. 17. Since values of κ_3 resulting from laboratory experiments solely are, at present, not yet available, we are thrown back upon possibly reliable conjectures connected with this problem. Therefore, the assumption of $\kappa_3 \approx -2\kappa_1\kappa_2$ seems to be rather speculative. The reason why we nevertheless make reference to it is that the same relation arises from quite another theoretical aspect due to our modification of Keane's (1954) treatment, which recently gives rise to discussion. This modification will be dealt with in a separate paper.

3. Other theories

Two approximations of the equation of state of the new theory are used: eq. 17 has been denoted by model *1*, and eq. 21 with $Y_5 = 0$ by model *2*. The theoretical reference curves have been taken from Ahrens and Thomsen (1972). From lattice-theoretical considerations the fourth-order anharmonic equation of state was derived, which is written as follows for isothermal compression data:

$$P = -3\hat{K}(V/\hat{V})^{-1/3}\{\eta - \tfrac{3}{2}\Gamma\eta^2 + \tfrac{3}{2}\Lambda\eta^3\} + (\hat{U}_S/\hat{V})(V/\hat{V})^{-1/3}[\hat{\gamma} + 3\eta\{\lambda - \hat{\gamma}^2(1 - T\hat{C}_V/\hat{U}_S)\}] \tag{23}$$

where $\hat{V}$, $\hat{K}$, Γ, $\hat{\Lambda}$, $\hat{\gamma}$, λ are constants and $\hat{U}_S$ and $\hat{C}_V$ functions of temperature, and where:

$$\eta = \tfrac{1}{2}[(V/\hat{V})^{2/3} - 1] \tag{24}$$

The curves of this isothermal equation of state (23) of the Lagrangeian anharmonic theory are denoted in the figures by *T*, the Hugoniot curves of this theory by *H*. According to Ahrens and Thomsen (1972), the illustrations show the room-temperature isotherm curves T_E, for which the Eulerian formulation of finite strain (see Barsch and Chang, 1971) have been used. The corresponding equation of state is:

$$P = -3\kappa_0 x^{-5/3}[\epsilon - \tfrac{3}{2}\Gamma_E\epsilon^2 + \tfrac{3}{2}\Lambda_E\epsilon^3] \tag{25}$$

where

$$\epsilon = -\tfrac{1}{2}(x^{-2/3} - 1) \tag{26}$$

$$\Gamma_E = \kappa_1 - 4 \tag{27}$$

$$\Lambda_E = \kappa_2 + \kappa_1(\kappa_1 - 7) + \tfrac{143}{9} \tag{28}$$

Eqs. 2 and 25 can be identified. We, however, have repeated the notation of Barsch and Chang (1971) here.

4. The estimation of the Hugoniot pressure

The available experimental data required for testing the new theory are, mainly, shock-compression data. Therefore, in order to obtain the theoretical Hugoniot the pressure from our models must be corrected by adding the thermal pressure (the difference between the Hugoniot and the isotherm or adiabat curves). It

has been customary to describe the Hugoniot curves with the help of the Mie-Grüneisen equation of state and the Rankine-Hugoniot conservation laws. Using our models together with the Mie-Grüneisen equation we would point out that the special problems concerning their mutual consistency may be essential (Thomsen, 1969; Thomsen and O.L. Anderson, 1971). Here, at least, we regard the equations of our models as possible extrapolated formulae describing the compressional behaviour of solids within some radius of convergence $x = x_{\min}$.

For convenience, model *1* is primarily used to compute the isentrope starting from the initial point $P = 0$, $T = 300$ K. The adiabatic values of the parameters κ_0 and κ_1 listed in Table I are based on the data of Ahrens and Thomsen (1972). The value of κ_1 (adiabatic–adiabatic pressure derivative of the bulk modulus) was obtained by the transformation of $(\partial\kappa_S/\partial P)_T$ to $(\partial\kappa_S/\partial P)_S$. Furthermore, for periclase we have used the value of $(\partial\kappa_S/\partial P)_T \approx 4.25$ (see Mao, 1974).

From the Mie-Grüneisen equation and the Rankine-Hugoniot energy-conservation equation we obtain – as usually – the Hugoniot pressure:

$$P_H = \frac{P(x, S_0) - \frac{\gamma}{x} Y(y, S_0)}{1 - \frac{\gamma}{2x}(1 - x)} \tag{29}$$

where $P(x, S_0)$ and $Y(y, S_0)$ are the corresponding adiabatic expressions for which model *1* is used. For the estimation of the Grüneisen parameter γ as a function of volume we use the simple formula (O.L. Anderson, 1974):

$$\gamma = \gamma_0 x^q \tag{30}$$

where γ_0 denotes the value of γ at $x = 1$.

The value of q is computed by means of the thermodynamical expression (O.L. Anderson, 1974):

$$q = \delta\frac{\kappa_S}{\kappa_T} - \left(\frac{\partial\kappa_S}{\partial P}\right)_T + 1 + \gamma_0 \tag{31}$$

where

$$\delta = -\frac{1}{\alpha\kappa_S}\left(\frac{\partial\kappa_S}{\partial T}\right)_P$$

is the Anderson-Grüneisen parameter and all values are referred to the ambient conditions. The values q based on the same data as in Ahrens and Thomsen (1972) are given in Table I. Some of the estimated q seem to be questionable such as in the cases of Li, K, Ag and BeO. The value for NaCl is in good agreement with the experimental result from Boehler et al. (1977).

The uncertainty in the problem of the Grüneisen parameter (O.L. Anderson and Mulargia, 1977) is essential for any estimation of the thermal pressure and, therefore, for the conclusions on the quality of theories of compression. Nevertheless, the possible deviations of the theory from the Hugoniot data can tentatively be estimated since the thermal pressure correction is usually of the order 10–20% in P at high compression. That corresponds to 2–4% in x.

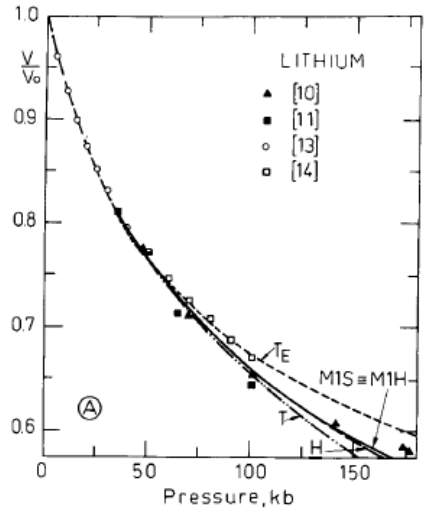
TABLE I

Material parameters employed

Material	κ_0 (kbar)	κ_1	γ_0	q
Li	120.0	3.33	0.88	5.8
Na	69.9	3.60	1.22	1.1
K	33.3	3.80	1.13	0.05
Cu	1369.7	5.49	1.98	1.2
Ag	1036.0	6.15	2.34	0.6
Au	1726.0	6.27	2.95	1.7
Al	764.0	4.46	2.13	1.8
LiF	696.3	4.95	1.63	1.2
NaF	482.0	5.02	1.51	1.2
NaCl	252.1	5.05	1.63	1.1
NaBr	208.3	5.04	1.61	1.6
NaI	162.2	5.25	1.74	0.8
CsCl	181.3	5.44	2.02	1.6
CsBr	156.0	5.53	1.68	1.9
CsI	126.2	5.49	1.69	1.5
MgO	1628.0	4.21	1.53	1.1
BeO	2186.0	5.31	1.26	not used

5. Discussion

In Fig. 1A–Q two curves have been computed and drawn, the lower curve being the isentrope *M1S* and the upper curve being the shock adiabat *M1H* which we computed using both model *1* and the Mie-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M1S ≡ M1H
T
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0.6
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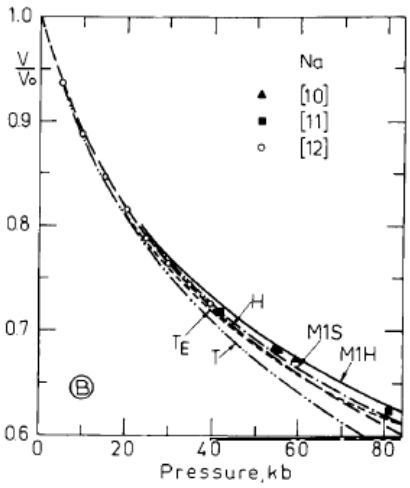
50
100
150
Pressure, kb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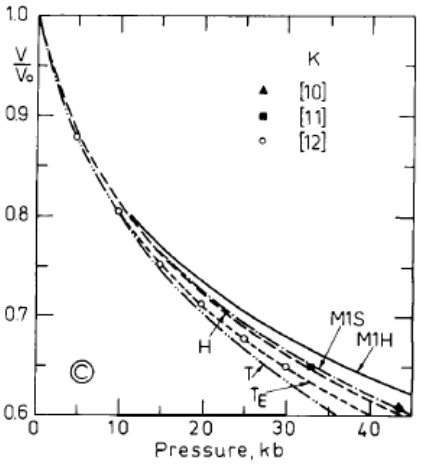
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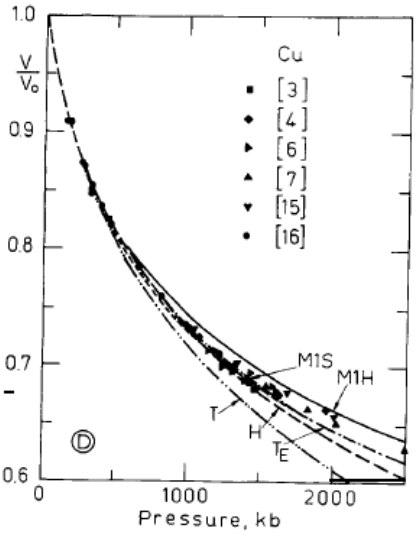
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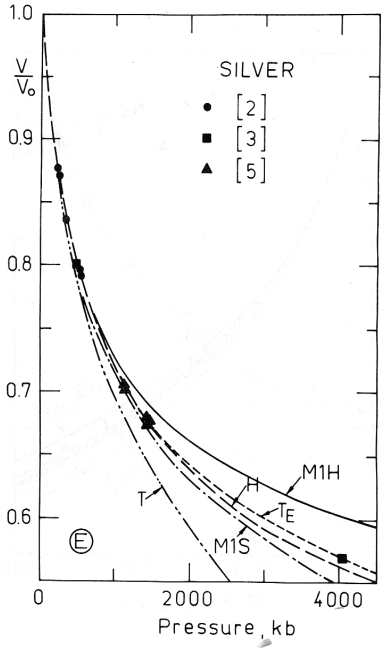
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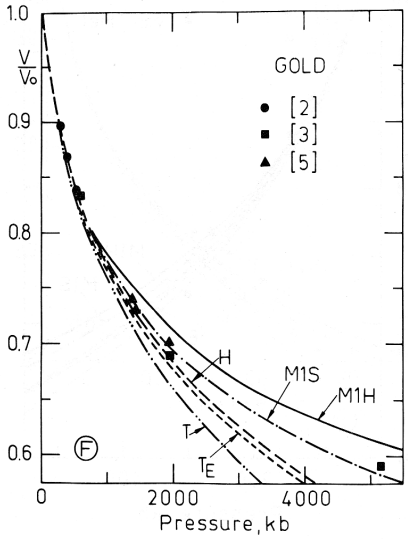
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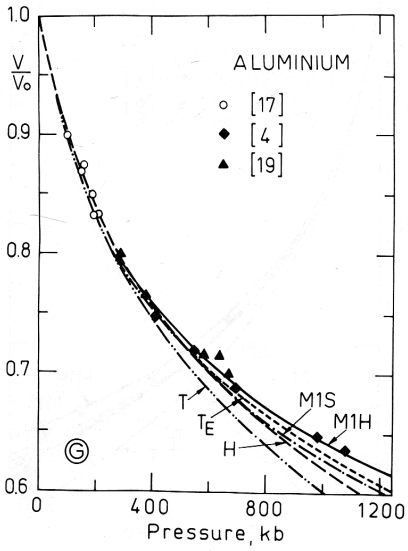
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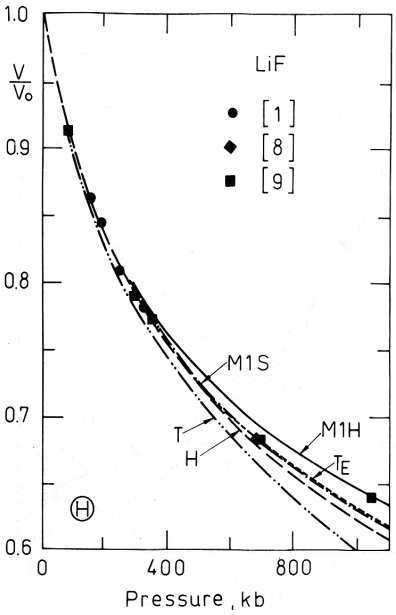
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0.7
0.6
LiF
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M1S
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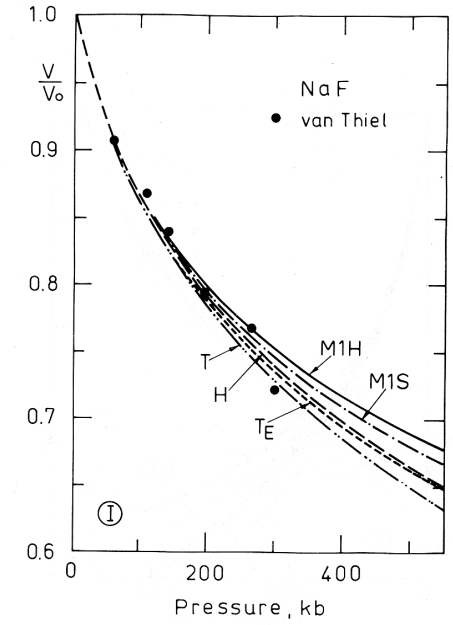
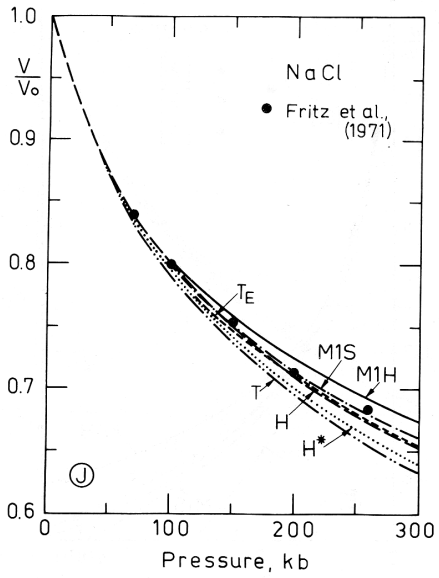
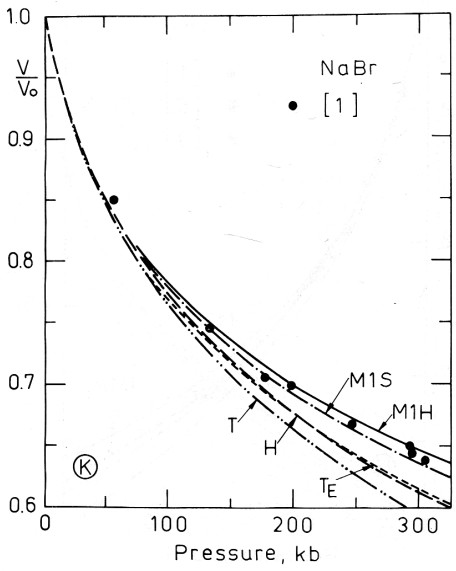
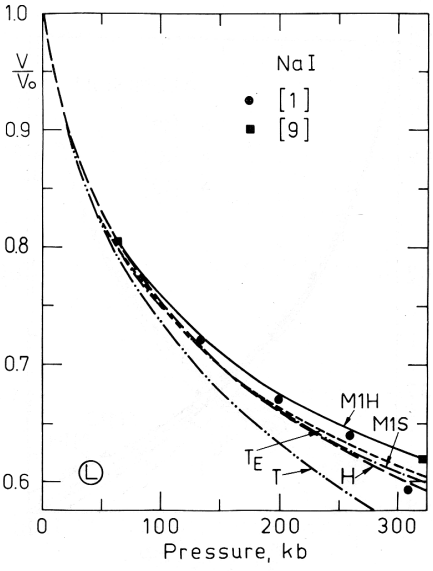
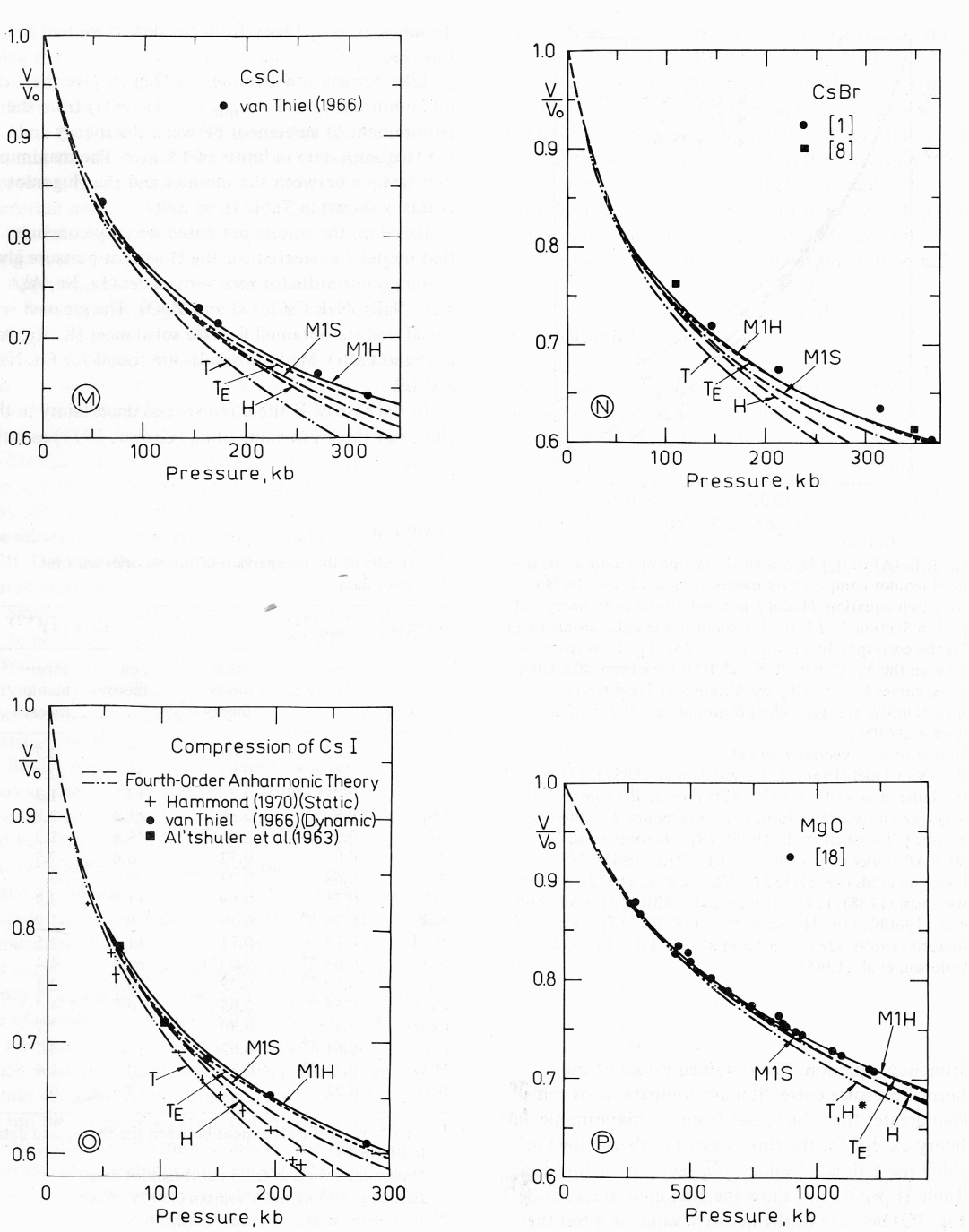
H
M1H
TE
Ⓗ
0
400
800
Pressure, kb


1.0
V/Vo
0.9
0.8
0.7
0.6
NaF
van Thiel
M1H
M1S
T
H
TE
Ⓘ
0
200
400
Pressure, kb


1.0
V/Vo
0.9
0.8
0.7
0.6
NaCl
Fritz et al., (1971)
TE
M1S
M1H
T
H
H*
Ⓙ
0
100
200
300
Pressure, kb


1.0
V/Vo
0.9
0.8
0.7
0.6
NaBr
[1]
M1S
M1H
T
H
TE
Ⓚ
0
100
200
300
Pressure, kb


1.0
V/Vo
0.9
0.8
0.7
0.6
NaI
[1]
[9]
M1H
M1S
TE
T
H
Ⓛ
0
100
200
300
Pressure, kb


CsCl
van Thiel (1966)
M1S
M1H
T
TE
H
Pressure, kb
CsBr
[1]
[8]
Compression of Cs I
Fourth-Order Anharmonic Theory
Hammond (1970)(Static)
van Thiel (1966)(Dynamic)
Al'tshuler et al.(1963)
MgO
[18]
T,H*

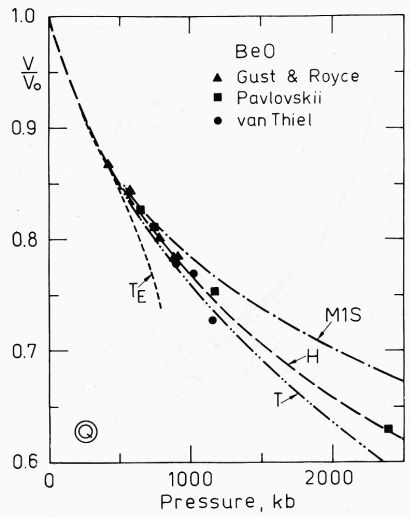


Fig. 1. In (A) to (Q) *M1S* is the isentrope of model *1*, *M1H* is the Hugoniot computed by means of model *1* and the Mie-Grüneisen equation. Model *1* is based on the new theory outlined in Section 2. *H* is the Hugoniot in the anharmonic theory, *T* is the corresponding isotherm (eq. 23). T_E stems from the Eulerian theory. Curves *M1S* and *M1H* have been calculated by us, curves *H*, *T* and T_E by Ahrens and Thomsen (1972). *Open symbols* are static compression data, *solid symbols* are shock-wave data.
Sources of the experimental data:
[*1*] = Van Thiel (1966); [*2*] = Walsh et al. (1957); [*3*] = Al'tshuler et al. (1958); [*4*] = Al'tshuler et al. (1960a); [*5*] = McQueen and Marsh (1960); [*6*] = Berger and Fauquignon (1964); [*7*] = Isbell et al. (1968); [*8*] = Kormer et al. (1965); [*9*] = Al'tshuler et al. (1963); [*10*] = Rice (1965); [*11*] = Bakanova et al. (1965); [*12*] = Vaidya et al. (1972); [*13*] = Bridgman (1938); [*14*] = Bridgman (1948); [*15*] = Al'tshuler et al. (1960b); [*16*] McQueen et al. (1970); [*17*] = Roy and Steward (1969); [*18*] = Carter et al. (1971); [*19*] = G.G. Anderson et al. (1965).

Grüneisen equation. The obtained values of the thermal pressure correction are comparable or somewhat greater than the values from the anharmonic theory except for the three cases Li, Ag and BeO in which the estimated values of q seem to be doubtful (Table I). We do not show the Hugoniot *M1H* for BeO (Fig. 1Q) because of the negative value of q but the deviation of our theory from the data is evident in this case.

Like Ahrens and Thomsen (1972) we give the minimum values of $x = x_{\min}$ (see Table II) from the requirement of agreement between the theory and the Hugoniot data in limits of 1% in x. The maximum x-difference between the theories and the Hugoniot points is shown in Table II, as well.

Based on the results presented we may conclude that model *1* corrected for the Hugoniot pressure gives rather good results for nine substances (Li, Na, Al, NaF, NaBr, NaI, CsCl, CsI and MgO). The greatest deviations are obtained for five substances (K, Ag, Au, BeO and CsBr). Medium results are found for Cu, NaCl and LiF.

In the case of K there is a special uncertainty in the choice of the input value of κ_0 (Grover, 1971) as well

TABLE II

The results of the comparison of the theories with the Hugoniot data

Materials	$x_{\min}$ (*1)		$\Delta x/x$ (%) (*2)	
	new theory	anharmonic theory *3	new theory	anharmonic theory
Li	0.63	0.63	−2.7	−2.7
Na	0.6–0.7	0.72	+1	−2.2
K	0.25–0.9	0.7	+3	−1.3
Cu	0.8 (?)	0.68	+1.4	−2.7
Ag	0.75		+5.8	−1.2
Au	0.8	0.72	+3.6	−7.5
Al	0.64	0.72	0.	−3
LiF	0.75	0.69	+1.5	−3.9
NaF	0.75 *4	0.79	0.	−1.7
NaCl	0.75	0.71	+1.2	−1.5
NaBr	0.64 *4	0.9 (?)	+0.8	−4.4
NaI	0.62 *4	0.75	+0.7	−2.3
CsCl	0.64 *4	0.85	0.	−4.7
CsBr	0.8	0.80	−4.5	−7.7
CsI	0.61 *4	0.67	0.	−3.7
MgO	0.71 *4	0.76	0.	−1.4
BeO	0.81		+7.6	0.

*1 At $x > x_{\min}$ the agreement between the theory and data is within 1%.
*2 Maximum deviation from the Hugoniot data.
*3 Given by Ahrens and Thomsen (1972).
*4 End of the data or a phase transition.

as in the estimated value of q as was noted previously. Using the value of $\kappa_0 \approx 30$ kbar and the more usual value of $q \approx 1$ would give the agreement of our theory with the data.

As to BeO Ahrens and Thomsen (1972) pointed out that the ultrasonic data seem to be incorrect. Moreover, they remarked the possibility of a phase transition near 1.1 Mbar (see Fig. 1Q). The value of κ_2 obtained by Ahrens and Thomsen (1972) by fitting the data at a lower pressure is also unreasonably small.

Applying model *1* to the substances with κ_1 values near 5 or more we must be careful as can be seen from the different results for alkali halides (see Table II). For metals with $\kappa_1 \lesssim 5$, however, model *1* systematically overestimates pressure-yielding curves which are very close to the Hugoniot data at $x \gtrsim 0.8$. It is obtained here for Cu, Au and Ag, and was shown earlier (Ullmann and Pan'kov, 1976) for other metals (Zn, Cd, Pb, Ni, Nb, Sn). In all such cases model *2* may successively be used by choosing, correspondingly, the values of κ_2 between approximately -10 and -20. Then the thermal pressure correction is estimated more or less satisfactorily.

Similar to model *1* in the cases of greater values of κ_1 some other equations of state used will give the deviations from the data. In particular, the Born-Mayer equation (Zharkov and Kalinin, 1971) and Born-Mie power equation will also overestimate the pressure values.

Birch's equation which is based only on the parameters κ_0 and κ_1 gives almost the same results as model *1* for the usual range of κ_1 between 3 and 6 (Ullmann and Pan'kov, 1976). The Eulerian curves T_E in Fig. 1A–Q representing the Birch isotherms were computed by Ahrens and Thomsen (1972) taking into account the term which includes the value of κ_2. They showed that the influence of this value is small but not negligible. In fact, the influence of some uncertainty in κ_2 for many cases may be compared with the uncertainty in the thermal pressure correction.

For the anharmonic theory the parameter κ_2 is much more important, but it is very difficult to obtain this value from ultrasonic measurements. If we use the values of κ_2 from the relation (16) of model *1* for the anharmonic theory, the results of both theories for the usual x-range ($x > 0.5$) will differ from each other by a value of 1–5% in x. The usual deviations of model *1* and the anharmonic theory from the data are in the opposite direction. Except for the cases of BeO, Au, NaF, NaBr and NaCl the values of κ_2 used by Ahrens and Thomsen are satisfied by relation (16) of model *1* in limits ±2. Therefore, we may approximately compare the results of both theories. However, due to the uncertainty in the choice of more correct values of κ_2 and in the Grüneisen parameter it is difficult to say which theory is to be preferred. The use of model *2* may bring almost the same results as the anharmonic theory.

6. Conclusions

The results of comparing model *1* with the Hugoniot data represented in Fig. 1A–Q and in Table II show that this model predicts the volume at high pressure (for $x \gtrsim 0.6$) with an error smaller than about 5%. Model *1* usually tends to overestimate the pressure values. In many cases the prediction of model *1* is better than 1% in x. Birch's equation of state, using the same values of κ_0 and κ_1, gives approx-

TABLE III

A comparison of experimental and theoretical data.

Material	Fig.	New theory (model *1*)	Anharmonic theory
Li	1A	×	×
Na	1B	×	
K	1C		×
Cu	1D	×	×
Ag	1E		×
Au	1F	× ?	× ?
Al	1G	×	
LiF	1H	×	×
NaF	1I	×	×
NaCl	1J	×	×
NaBr	1K	×	
NaI	1L	×	
CsCl	1M	×	
CsBr	1N	×	
CsI	1O	×	
MgO	1P	×	×
BeO	1Q		× ?

Crosses mean a good agreement of the corresponding curves with the Hugoniot data. For the static values of CsI the anharmonic theory gives agreeable results.

imately the same results. The curves of the anharmonic theory deviate from the Hugoniot data in the opposite direction on pressure and give an error of the same order. Although the choice of the preferable theory is difficult, we nevertheless would like to show by means of Table III which theory gives the best agreement with the Hugoniot data. For metals with $\kappa_1 \geq 5$ model *1* systematically deviates from the data at rather moderate pressures. The use of model *2* in these cases will give better results.

From the geophysical viewpoint it seems to be possible to apply different approximations for the equation of state to the substances which are relevant for the lower mantle where the value of κ_1 is near 4. Some advantage of model *1* and Birch's equation consists in not using the values of κ_2. We must, however, be careful about applying the different theories to the earth's core where κ_1 may be near 5 or more. Finally, we would also like to remark that up to now the accuracy of the current approximations for the equation of state is not sufficient to describe correctly the modern models of the earth from free-oscillation data. An important theoretical problem is the volume dependence of the Grüneisen parameter. However, without further accumulation and improvement of the experimental information on ultrasonic, static and shock-wave compression, it is difficult to test any reasonable equation-of-state theory.

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