APPLICATION OF THE FOURTH-ORDER ANGAROMONIC THEORY TO THE PREDICTION OF EQUATIONS OF STATE AT HIGH COMPRESSIONS AND TEMPERATURES

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The fourth-order anharmonic theory is the extension of the ordinary theory of lattice dynamics into the regime of finite strain. Exhaustive numerical applications of the theory at high pressure are made, yielding predictions for density, temperature, and elastic moduli of seventeen solids under shock compression. The theory describes well most of the density data to compressions (\(\Delta \rho / \rho\))\text{max} which are generally in accord with expectation (0.38), with some notable exceptions. The data at high shock temperatures (or initially porosity samples) are considerably fewer; the theoretical predictions are generally accurate. Elastic moduli data in the shock state are fewer yet; the theory gives less satisfactory predictions.

The geophysical interest in these results is that the total elasticity (density, thermal expansivity, and elastic velocities of solids under upper mantle conditions can be described within a unified theoretical framework. With our present knowledge, it is preferable to use the predictions of the cubic model. This uncertainty is shown to include also the predictions of the Eulierian formulation of finite strain theory.

1. Introduction

Whenever an empirical or semi-empirical equation is used to fit pressure-volume (\(P-V\)) data for condensed media over a large range of compressions it has been customary to evaluate the constants of the equation using data from specific density and ultrasonic measurements at very modest pressures (rather than to fit the equation over the entire compression range) (ANDERSON, 1965). If the equation of state is based upon it Taylor expansion (as are, for example, the Murnaghan equation, and the Lagrangian and the Eulerian finite strain equations), then it becomes simply an extrapolation formula \(P(V,V_0)\), and automatically describes the data within some radius of convergence (\(\Delta P/V\))\text{max} outside of which its predictions become progressively poorer. For geophysicists the important questions to be answered by the use of such equations is (1) whether this limit (\(\Delta P/V\))\text{max} is a safely large number, and (2) whether it can be identified even in the absence of complete high-pressure data so that the general reliability of the predictions can be estimated. The answers to

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the first question may be difficult in cases where available data extend over a limited range of compression accessible only to shock waves, where the uncertainty of the Hugoniot-isothermal correction has previously obscured the point of divergence. In the complete absence of high-\(P\) data, the limit (\(\Delta P/V\))\text{max} is unknown, as the truncated Taylor expansion contains no information at all about the neglected terms.

Both of these problems are avoided by the fourth-order anharmonic equation of state (LEIBFRIED and LEWIS, 1961; THOMSEN, 1970). The Hugoniot-isothermal correction to shock data is well-defined, although the Grüneisen parameter must be specified as a function of volume only (and not temperatures) within the limits of the fourth-order approximation. Furthermore, since the theory describes the entire \(P-V-T\) space in a unified way, the predictions at high \(P\) are related to those at high \(T\). In particular, an estimate is provided for the limiting compression (\(\Delta P/V\))\text{max} through the following argument. The theory reduces, at zero pressure, to the ordinary theory of lattice dynamics, which is generally adequate to describe most solids to temperatures approaching their melting points. For many solids, the lattice vibration/amplitude approaches \(\frac{1}{2}\) the lattice spacing at these temperatures (GILVARRY, 1958). This a fourth-order truncation of the Taylor
expansion of the lattice potential (which describes anharmonic effects to second order) is generally adequate for such vibrational displacements. One may then expect the fourth-order theory to be adequate for homogeneous strains of the same order, or for volumetric compression of $(\Delta V/V)_{volumetric} = 0.3$ or 0.2.

The present paper is intended to test the validity of this estimate exhaustively, that is, for all cubic solids for which the necessary data (or most of it) exists. The data required are shock and/or static compression data to high pressure, X-ray data on lattice parameters, specific heat ($C_p$) and thermal expansivity ($\alpha$) data, and ultrasonic data on incompressibility ($K'$), and its $P$ and $T$ derivatives. In addition, the solid must remain in the initial crystal structure, to appropriately high pressures. These requirements narrow the list of available tests to seventeen: 5 alkali metals, 3 transition metals, aluminum, 8 alkali halides and 2 oxides.

Since the theory is a fourth-order one, in contrast to most other semi-empirical equations (which have only three adjustable parameters), it is necessary to evaluate the fourth-order parameter (A in eq. (1) below) by ultrasonic data for the second pressure derivative of the adiabatic incompressibility, $(\partial^2 K'/\partial P^2)_S$. This datum is only available for a few solids; for the others on our list we have estimated it in various ways, based on analogy with the known values, on atomic models, or by fitting to shock data at low pressures. The procedures are described in detail below; the uncertainty in this parameter is one of the points of discussion in the final section.

2. The fourth-order anharmonic equation of state

If the crystal potential energy of a lattice of cubic symmetry is Taylor-expanded in terms of atomic displacements from an initial (e.g. equilibrium) configuration, and if the expansion is truncated to fourth order, transformed to rotationally invariant form and specialized to isotropic compressions it can be written (Tosi and Muñoz, 1970) in the form

$$
\phi(V) = \frac{\tilde{K}P}{2!} \eta^2 - \frac{27}{31} \tilde{e} \eta^\gamma + \frac{81}{43} \tilde{a} \eta^\delta$,\tag{1}
$$

where $\eta$ is a Lagrangian finite strain scalar, related to the volumetric compression $V/V_0$ by

$$
\eta = \left[ (V/V_0)^3 - 1 \right]$.\tag{2}
$$

The constants $\tilde{K}, \tilde{P}, \tilde{e}, \tilde{a}$ (and $\gamma, \delta$ introduced below) have straightforward interpretations as properties of the initial configuration, which is taken conventionally to be that of the static lattice at zero pressure. Thus $\tilde{P}$ is the specific volume of this state, $\tilde{K}$ its incompressibility, etc.

This same expansion, fourth-order truncation and transformation, along with second-order perturbation theory, were previously used by Lehmert and Ludwig (1961) to discuss the vibrational effects in the equation of state. They showed that this approximation was both necessary and sufficient for the "thermal equation of state" of $MIV, T$ to be "quasi-harmonic" in form. In other words, the "quasi-harmonic" Mie-Grüneisen equation

$$
P(V, T) = -\frac{\delta \phi}{\delta V} + \frac{\gamma(V)}{V} U_s(V, T)$\tag{3}
$$
is true only to fourth-order in atomic displacements; if higher-order terms are important in the potential, then additional terms must appear in the equation of state. Tosi and Muñoz (1970) argued that in view of this restriction, the functions $\gamma(V)$ and $\chi(V)$ in eq. (3) are uniquely determined, as Taylor expansions truncated at the appropriate order. In particular, the Grüneisen parameter $\gamma(V)$ exists only in the fourth-order anharmonic approximation (and then only at high $T$, or when all mode gammas are equal); its only functional form consistent with this approximation is

$$
\gamma(V) = (V/V_0)^{(3 + 3\sigma_0)} \tag{4}
$$

where the constants $3$ and $\sigma_0$ were mentioned previously. Then the pressure (3) may be written out explicitly as

$$
P(V, T) = -\frac{3}{2} \kappa(V/V_0)^3 \left( \eta - \frac{1}{3} \eta^2 + \frac{\eta^3}{3} \right) + (C_v(V/V_0)^{\gamma(V)} - (3 + 3\sigma)(1 - 1/3\kappa_0(T))$.\tag{5}
$$

This is the equation which we test against isostructural compression data in the next section. $C_v$ is the vibrational energy of the lattice in the harmonic approximation, and evaluated at the static volume $V_0$, $C_v$ is the corresponding specific heat. The quantity $U_s(V, T)$ in eq. (3) is

$$
U_s(V, T) = U_s(T) [1 - 3\eta(1 - TC_v(U_s))$.\tag{6}
$$

We have calculated $C_v(T)$ and $C_v(U_s)$ using the Debye vibrational model, with Debye temperature $\theta_D$ chosen...
so as to yield the observed value of $C_p$ at ambient conditions. While not entirely consistent, this procedure seems satisfactory for the present purpose; however, a higher-order anharmonic theory would probably require a more sophisticated vibrational model.

The six disposable constants in eqs. (5), $\hat{a}_p, \hat{b}_p, \hat{c}_p, A, \delta$, are related to six experimental data, $V_0, K_b^0, K_s^0, K_s^0, x_0, (\hat{a}_p/T)_p$ respectively. Here the subscript zero indicates a measurement under standard conditions, typically but not necessarily chosen as $P = 0, T = 300 \text{ K}$. The prime indicates a pressure derivative, e.g. $K_s' = (\partial K_s/\partial P)_T$, etc. The evaluation of the six constants requires the simultaneous solution of six nonlinear equations, which is seen done iteratively, after a scheme of THOMSEN (1972).

For calculating Hugoniot compression curves, we first write the Rankine-Hugoniot energy conservation equation,$$
U - U_0 = \frac{1}{2} P_p (V_0 - V),
$$
where $U$ is the internal energy. In the present approximation, this is
$$
U_i = U_0 + \hat{a}_p (V_i) - \hat{b}_p (V_i - V),
$$
which can be substituted directly into eq. (3) yielding the Hugoniot pressure
$$
P_p (V_i) = \left[ \frac{\hat{a}_p}{V_i - \hat{b}_p} + \frac{\hat{a}_p}{V_i - \hat{b}_p} \right] \times (1 - 1) (V_i - V).$$

3. Calculations and results

The values of the constants in eqs. (1)-5 were calculated for the seventeen solids, on the basis of the data shown in table 1. The calculated values of the constants are given in table 2. The high-pressure predictions are then compared with experimental data; this comparison is shown graphically for the solids in figs. 1-17. The essential information yielded by the comparison is the point in compression, $(\Delta V)/V_{obs}$, where the theory becomes inadequate, and where the data begin to trend away from the theoretical curve. This point cannot be chosen unambiguously in general due to scatter and discontinuity in the data. Also, the formal uncertainty in the theoretical curve becomes rather large, due to the large amount of data (each with its own uncertainty) required to generate the constants. Rather than attempting to do the comparison rigorously, we have adjusted slightly the thermal derivatives of table 1 (within the experimenters' stated uncertainties) so as to optimize the agreement of the theoretically predicted values by comparing eq. (5) with high-temperature data. We then accepted the resulting constants (table 2) as exact and determined the $(\Delta V)/V_{obs}$ by inspection, with a nominal criterion for agreement between theory and data of 1/2%. The resulting values for $(\Delta V)/V_{obs}$ are given in table 3.

Also given in table 3 for the metals are the compressions $(\Delta V)/V_{obs}$, which is the point where the Hugoniot crosses the fusion curve. It is significant that these compressions are smaller (except for AI) than the corresponding limits of adequacy $(\Delta V)/V_{obs}$ of the theory. This means that in general the theory appears to describe well the properties of the metals up to their melting points. The theory describes part of the liquid regime as well as a result of the generally small differences in compressibility between solid and liquid (a limitation on this similarity is discussed below in the case of copper). A similar statement cannot be made for the non-metals under study, as reliable estimates of the melting curve are not generally available.

Also given in table 3 are the values of the product $K_b K_s$ (as measured, calculated or inferred, according to the notes in the table). This non-dimensional number is roughly a constant (except for NaCl, cf. the discussion below wherever it has been measured, its value being in the range $-4$ to $-11$). The gross constancy of this parameter serves as a criterion for "reasonableness" of the values found, for other solids, by calculating from the atomic model or by fitting to low-temperature data. The criterion is not a strong one for the metals, as the parameter has been measured for only one metal, and the haldies cannot be expected to yield much information which is relevant to the metals. However, it does serve as a basis for discussion.

The figures also show room-temperature isotherms labelled $T_0$, which are calculated from the fourth-order Eulerian formulation of finite strain (cf. e.g. BACON and CRANCE, 1977):

$$P (V, T_0) = \frac{3K_b}{V_0} (V/V_0)^{-5} (1 - \frac{T_0}{T} e^{1} + \frac{1}{4} e^{2}),$$

where

$$e = -\left[ (V/V_0)^{-3} - 1 \right].$$
The table below contains data used for the calculations of the constants in eqs. (1)-(5) from Burdick and Chang (1967), except as noted. The prime indicates $(200^0/191)P_0$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$P_0$ (cm$^2 $g$^{-1}$)</th>
<th>$K'$ (kb)</th>
<th>$K''$ (kb)</th>
<th>$a_1$ ($10^{-19}$ cm$^2$ g$^{-1}$)</th>
<th>$(191^0/200)P_0$ $a_1$ (kb)</th>
<th>$C''$ (c.g.s. $-$ K)</th>
</tr>
</thead>
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<tr>
<td>Li</td>
<td>1.872</td>
<td>120.0</td>
<td>3.69</td>
<td>-0.0157</td>
<td>13.98</td>
<td>-0.121</td>
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<tr>
<td>Na</td>
<td>1.051</td>
<td>69.9</td>
<td>3.79</td>
<td>-0.0022</td>
<td>20.79</td>
<td>-0.0139</td>
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<tr>
<td>K</td>
<td>1.175</td>
<td>33.3</td>
<td>3.93</td>
<td>-0.0195</td>
<td>22.20</td>
<td>-0.0127</td>
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<td>Ca</td>
<td>0.1119</td>
<td>139.7</td>
<td>3.60</td>
<td>-0.00565</td>
<td>3.46</td>
<td>-0.0255</td>
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<td>Ag</td>
<td>0.09854</td>
<td>103.0</td>
<td>6.29</td>
<td>-0.00579</td>
<td>7.36</td>
<td>-0.0199</td>
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<td>Au</td>
<td>0.08181</td>
<td>123.0</td>
<td>6.82</td>
<td>-0.01107</td>
<td>4.23</td>
<td>-0.0296</td>
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<td>Al</td>
<td>0.37078</td>
<td>764.0</td>
<td>4.90</td>
<td>-0.06067</td>
<td>6.78</td>
<td>-0.1642</td>
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<td>LiF</td>
<td>0.3791</td>
<td>969.3</td>
<td>5.12</td>
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<td>9.96</td>
<td>-0.254</td>
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<td>NaF</td>
<td>0.3473</td>
<td>482.0</td>
<td>5.19</td>
<td>-0.0464</td>
<td>9.81</td>
<td>-0.178</td>
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<td>NaCl</td>
<td>0.46211</td>
<td>252.1</td>
<td>5.29</td>
<td>-0.0359</td>
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<tr>
<td>NaBr</td>
<td>0.3123</td>
<td>208.3</td>
<td>5.29</td>
<td>-0.0777</td>
<td>12.6</td>
<td>-0.1050</td>
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<tr>
<td>NaI</td>
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<td>162.2</td>
<td>5.48</td>
<td>-0.0361</td>
<td>15.77</td>
<td>-0.0773</td>
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<tr>
<td>CaF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2608</td>
<td>181.35</td>
<td>5.78</td>
<td>-0.0403</td>
<td>13.89</td>
<td>-0.1021</td>
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<tr>
<td>CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2444</td>
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<td>CaBr&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>12.153</td>
<td>-0.0660</td>
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<td>BaF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2251</td>
<td>175.76</td>
<td>4.27</td>
<td>-0.00147</td>
<td>4.05</td>
<td>-0.199</td>
</tr>
</tbody>
</table>

$K''$ and $K''$ are calculated using the atomic model $A$ of Thomsen (1972),$^a$ Speidel et al. (1972),$^b$ Speidel (1972),$^c$ Speidel (1969),$^d$ and Anderson et al. (1968),$^e$ Burdick and Shaw (1967),$^f$ and Juhlin et al. (1955).$^g$

$^a$ Calculated from $(K'' P'')$ using the atomic model $A$ of Thomsen (1972),$^h$ Speidel et al. (1972),$^i$ Speidel (1972),$^j$ Speidel (1969),$^k$ Anderson et al. (1968),$^l$ Burdick and Shaw (1967),$^m$ and Juhlin et al. (1955).$^n$

$^b$ Dedicated to fitting low pressure shock data.$^o$

$^c$ Fitted to the model.$^p$

$^d$ From the assumption that $K''$ and $K''$ are calculated using the atomic model $A$ of Thomsen (1972),$^q$ Speidel et al. (1972),$^r$ Speidel (1972),$^s$ Speidel (1969),$^t$ Anderson et al. (1968),$^u$ Burdick and Shaw (1967),$^v$ and Juhlin et al. (1955).$w$

$^e$ Not possible to rigorously define a Grüneisen parameter, or to calculate a Hugoniot without making additional, inconsistent assumptions. Because a thermal pressure has not been added to the Eulerian isotherm, one must remember while comparing these curves with shock data, to mentally add a thermal pressure correction of approximately the size of the difference between the Hugoniot (H) and isotherm (I) curves of the (La-grannerian) anharmonic theory. Since the procedure allows comparison of the Lagrangian and the Eulerian pressure-volume curves, it provides some measure of the inherent ambiguity of the finite-strain approach. This test is not a rigorous one, as the values of $K''$ used in eq. (9c) is obtained from the Lagrangian fit to the shock wave data in cases where the appropriate ultrasonic data are lacking. However, this inconsistency is not serious, since the Eulerian $P$–$V$ curves are inherently less sensitive to the value of $K''$ than are the corresponding Lagrangian curves.

3.1. Litheum

Fig. 1. Diagram that shows the theoretical Hugoniot apparently agrees well with shock data up to $(51(V/E)_{max}$
Fig. 1. In all of figs. 1-21, the curve H is the Hugoniot in the fourth-order anharmonic theory (eq. 8) and the curve T is the corresponding isentropic (eq. 5). P is the isotherm of the fourth-order B粘ian fluid with equation (9). The sources of the data are indicated by numbers which refer to the list below. Open symbols are elastic compression data; filled symbols are shock data.


Fig. 2. See fig. 1.

Fig. 3. See fig. 1.

Fig. 4. See fig. 1.

Fig. 5. See fig. 1.

Fig. 6. See fig. 1.

Fig. 7. See fig. 1.
well in excess of the value (0.3–0.2) given by the simple argument above. The theory also agrees with the isothermal data of Bridgman below 40 kb (and the recent confirmation of this work by Vaidya et al., 1971). The disagreement with Bridgman’s (1949) data is apparently real; similar differences have been noted elsewhere (cf. Vaidya and Kennedy, 1971). The possibility of a phase change near 50 kb is eliminated by the absence of any anomalies in the electrical resistance (Bridgman, 1952).

This confirmation of the theoretical expectation is reassuring; however, one notes that the important third-order parameter $\Gamma$ (corresponding to $K_3$) has been evaluated by a guess, and the less important fourth-order parameter $\Delta$ has been evaluated by fitting the equation to the static data (at $\Delta V/V_0 < 0.12$). Hence the agreement at high pressure is perhaps fortuitous. However, the guess on $\Gamma$ is unlikely to be seriously in error since Li is similar in crystal structure and electronic configuration to Na and K, which form the basis
of the guess. Furthermore, the deduced value of \( K_a K_b^* \) is slightly higher than the measured value in Na, so \( A \) is probably fairly accurate also. Note that with this choice of parameters, the Eulerian isotherm is clearly in disagreement with the data.

3.2. Sodium

For sodium there is a clear disagreement between the static data at low \( P \) and the shock data starting at slightly higher \( P \), the required difference (due to thermal pressure) between these two data sets does not appear. The anharmonic theory shows good agreement with the shock data, within its estimated range of adequacy, and the Eulerian isotherm also can be said to agree with these data. The static data cited, however, are in distinctly better agreement with theory than is an older data set of Bridgman.

3.3. Potassium

Here is an ambiguous case. The anharmonic theory fits well the shock data up to quite large compressions, but disagrees with the static data. Thus one or both of the data sets are wrong, or the thermal pressure term of the theory is wrong. Since the theory was designed expressly to cope with thermal effects, this last possibility is not a wrong one. However, the Eulerian isotherm does reproduce precisely the static data, and could also describe the shock data if a suitable Grüneisen parameter were assumed (i.e. one which decreased rapidly with increasing \( P \)). The resolution of this ambiguity must await further experiment.

3.4. Copper

The theory describes well the compression of copper down to \( Y/V_o \approx 0.74 \), at which point the data become ambiguous. That of McQueen et al. (1970) trend
smoothly away from the theoretical Hugoniot, while that due to BERCER and FOLQUIGNON (1964) and to AL’TSULEK et al. (1958) remain close to the theoretical curve until \( V/V_0 \approx 0.68 \), at which point they appear to jump discontinuously. The sense of this jump leads one to look for an interpretation in terms of melting, and in fact the pressure at this point is in precise agreement with the calculated point of intersection of Hugoniot and melting curve (table 3). The critical pressure (1.5 Mb) is in satisfactory agreement with a calculated value of 1.33 Mb by McQUEEN et al. (1971). The discontinuity here (of real) is larger than one would expect as a result of melting (much larger than is apparent in Li, K, Ag, for example) and this interpretation is quite uncertain. We note that the Eulerian isotherm appears to be too high until the “discontinuity” in the data is reached.

3.5. Silver

The theory does not unexpectedly well here, whereas the Eulerian isotherm is far too high.

3.6. Gold, aluminium and lithium fluoride

The theory does quite well in these cases, but the Eulerian curve may do even better, if an appropriate \( \gamma \) is assumed.

3.7. Sodium fluoride

For NaF, the Hugoniot data diverge from the amharmonic Hugoniot at surprisingly small compressions. It is interesting to note that the data point at \( P = 302 \) kb lies at very large compressions; it is possible that this point lies in the B2 (CuCl) phase. Such a possibility was apparently not noticed by the original experimenters (cf. CHRISTIAN, 1956), perhaps because without the theoretical curves in the figure, the point is not ob-

Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>( V_0 ) (Mb)</th>
<th>( \delta V/V_{\text{mol}} )</th>
<th>( \delta V/V_{\text{mol}} )</th>
</tr>
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<tbody>
<tr>
<td>Li</td>
<td>-1.83</td>
<td>0.37</td>
<td>0.27</td>
</tr>
<tr>
<td>Na</td>
<td>-3.89</td>
<td>0.28</td>
<td>0.26</td>
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<tr>
<td>K</td>
<td>-9.00</td>
<td>0.3</td>
<td>0.21</td>
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<tr>
<td>Cs</td>
<td>-8.09</td>
<td>0.32</td>
<td>0.32</td>
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<td>Ag</td>
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<td>0.29</td>
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<tr>
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<td>0.13</td>
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<tr>
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<td>RbCl</td>
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<td>BeO</td>
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atomic calculation appears in general to give results which range from slightly more negative than the corresponding experimental values to considerably more negative.) Because of the difficulty in experimentally determining $K'_c$, further measurements seem to be desirable.

3.9. Sodium bromide

For NaBr, the theory gives very poor agreement with experiment, while the Eularian curve appears to do considerably better.

3.10. Sodium iodide

The theory begins to fail near $(AV/V_O) \approx 0.25$, marginally in accord with expectations; the Eularian isotherm is much too high. As in the case of NaF, the data show a hint of a phase transition near 300 kbar, where a single Hugoniot point falls well below the trend of the data. A point reported by Al'tsuev et al. (1963) at slightly higher pressure does not show this effect, but one above 600 kbar (not shown) apparently does. This interpretation is in accord with the argument in the discussion of NaF above, and a calculation (Yavas, 1972) with the anharmonic theory that the transformation occurs at or below $P \approx 200$ kbar, $V/V_O \approx 0.57$ on the isotherm (or $V/V_O \approx 0.61$ on the Hugoniot) is given.

3.11. Cesium chloride and cesium bromide

CaCl and CsBr show rather poor agreement between the data and the anharmonic theory, with rather better agreement for the Eularian curves.

3.12. Cesium iodide

CaI is the only one of the solids in this study for which both shock and static data over large compressions exist and are described well by the anharmonic theory (cf., the discussions of Na and K above). The figure does show, however, that there is some inconsistency between the two data sets, the static data being anomalously low at $V/V_O \approx 0.78$, and perhaps at $V/V_O \approx 0.59$. However, uncertainty in the high-pressure X-ray data near 300 kbar stems both from the uncertainties in the NaCl isotherm (which was utilized as a pressure standard)

3.13. Magnesium oxide

For MgO, again the theory gives ambiguous results, due to uncertainty in the input data. Using the value of $K''_c = 4.27$ from table 1, the limit of adequacy of the theory is $(AV/V_O)_l \approx 0.24$, marginally within expectation. However, using other recent data for $K''_c$, the limit ranges from 0.30 ($K''_c = 4.5$) to 0.18 ($K''_c = 3.8$). The curve $H^*$ in fig. 16 is drawn using the latter value of $K''_c$. A critical discussion of the experimental situation has recently been published (Sears and Aksnes, 1972); until this is experimentally resolved, the calculations such as the present one will have little significance. The differences between the present isotherms for MgO and NaCl and those previously calculated (Thomsen, 1970) arise from differences in input, and cannot be discussed satisfactorily until these differences are resolved.


The anharmonic theory gives the appearance of describing very well the shock Hugoniot, but the value of $K''_c = 38$ (inferred from the data in the range $(AV/V_O < 0.25)$ is unreasonably large (negative). A more "reasonable" value would move the theoretical Hugoniot to pressures higher than the data, whereas the pattern established above indicates that the theory generally fails at high compression by falling below the data. Because the ultrasonic data of table 1 are based on a polycrystalline sample (rather than a single crystal), we suspect that these measurements may not reflect the intrinsic properties of the lattice, but may be contaminated by the effects of internal strain, etc. (Thomsen, 1972). Finally, it is interesting to speculate that the "anomalously low" Hugoniot point at $1.1$ Mb might indicate a phase change near this point.

4. Porous Hugoniot analysis

The Rankine-Hugoniot equation (7) may be made more general by replacing the reference volume $V_O$ with an arbitrary initial volume $V_i$; which may differ from $V_O$ because of initial porosity or heat. In this case, the continuum mechanics equations have the same structure, but the atomic free energy and hence the pressure have additional contributions due to the porosity (which vanishes due to the irreversible work done on it) or to the initial heat. We discuss here the applica-
tions of the theory to shock compression of initially porous, room temperature material, and we follow current practice of neglecting the surface contribution to the free energy.

It follows trivially from the Rankine-Hugoniot equation (7) that the Hugoniot $P_d(V)$ of a material with initial density $\rho_i$ is displaced from the Hugoniot $P_d(V)$ of the solid material by an amount

$$ P_d(V) - P_d(V) = P_d(V) \left[ \frac{\rho_i}{\rho_f} - 1 \right] \left[ \frac{V_f}{V_i} + 1 \right] - \rho_i $$

at each volume $V$. The derivation does not involve the $T$ independence of $\gamma$, so that eq. (10) is valid, independent of any assumptions on the equation of state. That is, $\gamma(V)$ in eq. (10) could be replaced by

$$ \gamma^n(V, T) = V \left( \frac{\partial P(V, T)}{\partial V} \right) \left( U(V, T) - \phi(V) \right), $$

where $\theta$ and $\phi$ are completely arbitrary. $\gamma^n$ is not equal to the quantity $\gamma(V) = V \left( \frac{\partial P(V, T)}{\partial V} \right) \left( \frac{1}{U(V, T)} - \frac{1}{\phi(V)} \right)$, which appears in eqs. (3) and (4) except within the fourth-order anharmonic approximation.

The pressure difference (10) due to the porosity is positive because the initial porosity allows the shock to deposit more thermal energy in the solid; we call it the "porosity pressure" for short. In the form (10) it can be used to test theoretical predictions of thermal pressure, completely independently of any theory for compression of the static lattice (by using data for the solid Hugoniot $P_d(V)$, rather than theory). Hence it provides a test of our form (4) for $\gamma(V)$ which is independent of our form (1) for $\phi(V)$.

We have applied this test in all cases where the relevant data are available, namely those of Cu, Al, NaCl and MgO. The comparison of theory with experiment is shown in figs. 18–20. For Cu and Al, the initial densities of individual samples varied slightly within each group of shots. A separate calculation was made for each shot and a minor correction was then applied so that each member of a group had effectively the same (mean) $\rho_i$. Some groups of shots were not analyzed at all because they happened to have initial densities which implied the near-vanishing of the denominator in eq. (10). Of course, the predictions of the theory are not reliable in these circumstances. Unfortunately, all of the data (Korman et al., 1965) for NaCl lay in this unusable regime of the theory, except for a single point (with $\rho_i = 1.43$) for which the observed "porosity pressure" at $V/V_d = 0.816$ was 76 kb (versus the theoretical value of 81 kb).

For Cu and MgO, the data show considerable scatter, but show a general agreement with the theory. However, for each group of samples, the cloud of points drifts (at high compression) to pressures higher than the corresponding theoretical curves. For Al, the theoretical curves lie distinctly above the clouds of data points.
A tentative explanation of these patterns is suggested by comparison of the calculated shock temperatures with the corresponding melting temperatures calculated using the formula of *Kraeft* and *Kennedy* (1966) and the melting point data cited in table 3. For Cu, the melting line is crossed by each porous Hugoniot at a point indicated by the slash on the corresponding theoretical curve (fig. 18). These points roughly correspond with the compressions where the theory begins to diverge from the cloud of data points. Furthermore, these compressions-at-melting are not sensitive to the assumed formula for melting, as the shock temperatures rise very steeply with increasing compression. For Al, all of the porous data are in the molten regime. We tentatively conclude that the theory describes adequately the thermal pressure everywhere in the solid part of the phase diagram of these three materials. This implies that the form \( \varphi(V) \) (eq. 4) is adequate to describe the data at least in the solid region. However, owing to the scatter in the data, it is not possible to reject other functional forms as incorrect.

5. Elastic moduli in the shocked state

The same approximation which leads to the equation of state (5) yields also the adiabatic elastic moduli as functions of specific volume and temperature (*Thomsen*, 1972):

\[
\begin{align*}
\varepsilon_0(V, T) & = E_0 \frac{\partial V}{\partial P} \left( \frac{1}{3} \varepsilon_0 + \varepsilon_0 \frac{\partial P}{\partial V} \right) \\
& - \left( \frac{\partial V}{\partial P} \right)^n \left( \frac{1}{3} \varepsilon_0 + \varepsilon_0 \frac{\partial P}{\partial V} \right) - P(V, T) \varepsilon_0
\end{align*}
\]

(11)

Here \( \varepsilon_0 \), \( \Gamma_0 \), \( A_0 \), and \( \lambda_0 \) are the stress equivalents of \( R \), \( \Gamma \), \( A \) and \( \lambda \), respectively. The subscripts 0, 1, 2, \ldots, 6 are Voigt notation for the tensor index pairs \( \phi_k \), where \( k = 1, 2, 3 \); etc., \( \phi \) is in the Kroncker delta \( \delta_{ij} \), and \( \delta_0 \) is defined by

\[
\delta_0 = \delta_0 = - \delta_0 \delta_0 + \delta_0 \delta_0 + \delta_0
\]

The constants appearing in eq. (11) were calculated routinely for all the materials in this study; those for Al and Cu are listed in table 4. The high \( P \), \( T \) predictions of the theory (11) can be compared with data (ALTHUELER et al., 1966b) for the bulk modulus \( K \) and the longitudinal modulus \( (K + \mu) \) in the shocked state along the Hugoniot \( (P_h, T_h) \). These moduli are related to the appropriate acoustic velocities by \( K = \rho C_L^2 \), etc. (rather than \( \rho \bar{C}^2 \) as in AlTHUELER et al., 1966b).

The data are on polycrystalline samples, and so the shear moduli \( \mu \) must be calculated as a special average of the single-crystal moduli \( \varepsilon_{ij} \) and \( \varepsilon_{ij} \). The theory of *Kneubuh* (1967) for "perfectly disordered" aggregates was used for this purpose.

In fig. 21, the comparison of theory and experiment is shown graphically. The theoretical curves lie systemati-
cally lower than the data for the bulk modulus. This sort of behavior is expected at high compressions on the basis of the P-V curves in figs. 4 and 7, but it appears here even at the modest compressions where the slopes of theory and P-V data (figs. 4, 7) appear to coincide.

Also in fig. 21, one sees that the single datum for the longitudinal modulus is matched very closely by the theory. It is difficult to draw conclusions from this agreement, vis-a-vis the disagreement for $K'$ because the data point lies at smaller compression. We may speculate, however, that eq. (11) is valid for these materials for compressions $(\Delta V/V_{0,88}) \ll 0.2$.

6. Discussion

We conclude (from the results shown in table 3) that the fourth-order anharmonic theory is adequate to predict $P(V)$ for the metals to compressions of $(\Delta V/V_{0,88}) = 0.3$ as expected, and in a few cases to much greater compression. For ionic compounds, the maximum compression is generally smaller, and more erratic within each group of halides. The uncertainties associated with the two relevant equations, MgO and BeO, make generalizations for this class hazardous. Experimental resolution of the experimental uncertainties in the parameters $K_{\text{eff}}$ and $K_{\text{iso}}$ will eventually allow a more definitive test of the fourth-order theory for these classes of materials. The purely thermal contributions to the pressure seem to be well described for the metals up to their melting points and for MgO to temperatures almost three times the Debye temperature (figs. 18-20). Thus we probably know the extent of the defects in the equation of state of minerals better than we know the temperature profile in the Earth. However, the description of the free energy function as a function of temperature can be improved by using a more refined model for the specific heat (Kramers and Kaman, 1972). The elastic moduli are described well to compressions of perhaps 0.2, although the data are very limited (fig. 21).

On this basis, we conclude that the anharmonic theory is probably adequate to describe the elasticity of all cubic minerals in the Earth's upper mantle and transition zones (down to 1000-1500 km depth, depending on the compressibility). By elasticity we mean the pressure $P(V, T)$, the elastic velocities (through the elastic moduli $c_{ij}(V, T)$) and an appropriate averaging technique; cf. Kroner (1973), and the thermal expansivity $a(V, T)$. The extension of the theory to non-cubic materials should result in the extension of the conclusion to all the minerals of geophysical interest, although we have not made such an extension. At lower depths, most of the minerals are in phases which are unstable at zero pressure, and for which the considerable data required by the theory are not available now and probably will not be for some time into the future. For these minerals, it becomes more satisfactory to base a theory upon detailed assumptions on the inter-atomic forces for the static part of the free energy, and calculate only the thermal part by expansion methods (cf. e.g. Sammis, 1971). The present calculations offer hope that a fourth-order anharmonic treatment will suffice for this thermal part even in the lower mantle.

In the comparison of the fourth-order anharmonic (Lagrangean) theory with the Eulerian finite strain theory, we find that about half of the solids of this study are described better by the anharmonic theory, and the other half by the Eulerian theory. This is somewhat discouraging, as it implies that neither is suitable for geophysical predictions and interpretations at high compressions as may be found in the lower mantle. This conclusion is a numerical result of comparing the theories with data; it follows despite the fact that the coefficients of the Lagrangian strain formulation are typically much larger than those of the Eulerian formulation (typical numbers are $F = 5$, $F_0 = 1$ and $a = 0$, $a_0 = -5$). These data are not available to Bracchi (1947) when he concluded that, since the Eulerian formalism apparently converges faster than the Lagrangian, a treatment in terms of the former was "advantageous". In fact, we may conclude from the
present comparison with data that the higher-order terms of both formulations become negligible at reasonable strains, depending on the particular solid. The principal advantage of the Lagrangian formalism is that it allows treatment of the thermal (anharmonic) effects as in the elastic moduli within the same, unified framework.

From the viewpoint of this theoretical framework, the important experiments of the next few years will determine (1) the low-pressure single-crystal elasticity of the upper mantle materials with greater accuracy (especially in $\rho$) than is now available, (2) the low-pressure polycrystal elasticity of high-pressure phases and (3) the high-pressure elasticity of any mineral with presumably lower accuracy. The last two experimental areas will be critical for interpretation of the composition and mineralogy of the lower mantle.

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