

mediate temperatures. We see, for instance, that this approximation leaves γ independent of temperature. At high temperatures, γ is observed to be fairly constant, but below the Debye temperature it usually becomes temperature dependent.

The relationship of Thomsen's[1] equations to those derived here should be clarified. Thomsen's equation (40) is analogous to the present equation (32), in terms of η , truncated after the fourth order term. The only substantial difference is that the reference state has not been specified here, whereas Thomsen identified it with the stress-free rest configuration of the lattice. From the point of view of lattice dynamics, the latter is the natural reference state, but if the present equations are viewed as finite strain equations, in which thermal effects are (approximately) explicitly included, then the reference state is arbitrary (with the qualification that the approximation is poorer further from the rest state). Considerable convenience accrues in some applications from identifying the reference state as that at which experimental data are available, since Thomsen's[1] set of six simultaneous non-linear equations, relating his parameters to experimental quantities, is thereby avoided.

The expressions (24), (27) and (28) for γ given here have a certain arbitrariness. It would be possible, for instance, to expand them to the appropriate order in strain, or to do as Thomsen[1] did, i.e. by analogy to the pressure equation, to retain the factor arising from the volume differentiation and expand the remaining quotient. Thomsen's expression (43) for γ , apart from the reference state, is

$$\gamma = (V/V_0)^{2/3}(\gamma_0 + 3\lambda\eta), \quad (43)$$

where $\lambda = -(h' - g^2)/18$, which could be obtained from (27). In principle, there is no reason to prefer any of these forms over the others, but some trial calculations indicate that equations (24), (27) or (28) are less likely to give negative values of γ at large com-

pressions than (43) or its analogues. This may not be a sufficient criterion in some cases, however, since γ may approach zero near a phase change[14].

Thomsen's assertion[1], that the use of a fourth-order expansion in terms of η assures consistency with the expansion (3) of ϕ upon which the lattice dynamics is based can be seen to be incorrect. In fact, from (19) and (21), $\eta = e + \frac{1}{2}e^2$. Substitution of this relation into a fourth-order η expansion would yield up to eighth-order terms in e . Thus truncation of an e expansion at the fourth order would involve a different truncation error, and hence a different approximation.

Finally, some comments on the capabilities of the present theory. Thomsen[2, p. 367] pointed out that although this theory predicts that the elastic moduli (in the present case, K) are linear in T at high temperature and at constant *volume*, this does not imply linearity at constant *pressure*. Thus, measured non-linearity of elastic moduli with T , taken at zero pressure, does not imply that a higher-order thermal theory is required. However, Thomsen[1, p. 2009, 2010; 2, p. 370] goes on to claim that non-zero values of $(\partial^2 c_{\alpha\beta} / \partial P \partial T)$, where $c_{\alpha\beta}$ is an elastic modulus, do require a higher-order theory for their description. It has been argued here that the Mie-Grüneisen equation is valid at arbitrary volumes; therefore an arbitrary number of derivatives may be taken and the thermal contribution will be concluded, though it will still be $O(\delta^2)$. Thus, thermal contributions to all pressure derivatives of elastic moduli will result from this theory. Of course, the predicted *value* of the temperature coefficient may not agree with measured values, but the mere existence of a non-zero temperature coefficient is not sufficient grounds for requiring a higher order *thermal* theory.

5. ISENTROPES

The Mie-Grüneisen equation (17) can be regarded as giving the pressure either as a function of strain and temperature, or as a

function of strain and entropy. Thus an expression for the pressure along an isentrope can be obtained by expanding (17) in terms of strain at constant entropy. The temperature, or entropy, dependence of (17) is through U_q . From the result [3, p. 356] that

$$\left(\frac{\partial U_q}{\partial V}\right)_s = -\frac{\gamma}{V} U_q, \quad (44)$$

one can obtain the expansion of U_q in terms of e , for instance, at constant entropy:

$$U_q(e, S) = U_q^0 + \frac{1}{2}gU_q^0e + \frac{1}{8}(2h - g^2)U_q^0e^2 + \dots \quad (45)$$

The result of substituting (45) into (17) is an equation of exactly the same form as (31):

$$P(e, S) = -\frac{(1+e)^{-2}}{3V_0} (a_{0s} + a_{1s}e + a_{2s}e^2 + a_{3s}e^3 + \dots) \quad (46)$$

where the new coefficients are

$$a_{0s} = \phi_0^I + \frac{1}{2}gU_q^0, \quad (46a)$$

$$a_{1s} = \phi_0^{II} + \frac{1}{4}(2h - g^2)U_q^0, \quad (46b)$$

$$a_{2s} = \frac{1}{2}\phi_0^{III} + \dots, \quad (46c)$$

$$a_{3s} = \frac{1}{6}\phi_0^{IV} + \dots \quad (46d)$$

Analogous results are obtained for the equations in terms of η and E . Equations (46) thus give the pressure along an isentrope in terms of the same parameters (namely g , h , and the derivatives of ϕ) as (31) for an isotherm.

6. HUGONIOTS

In principle, it is possible to relate derivatives along a Hugoniot to isothermal derivatives in a manner similar to that of the previous section, but since these relations are more complicated, it is easier to obtain the Hugoniot pressure from the energy difference between it and some reference curve. Expressions for Hugoniots have been

given, for instance, by Thomsen[1] who related the Hugoniot to the static pressure $-(d\phi/dV)$, and, for example, Ahrens *et al.* [15] and McQueen *et al.* [16] who relate the Hugoniot to an isentrope. Since the latter method does not require the intermediate calculation of the derivatives of ϕ , and since the results of the last section can be used, it will be used here.

The Hugoniot equation derived here will be generalized to take account of possible initial porosity of the material or a phase change during the shock process. The term 'high pressure phase' will be taken here to include the compacted, non-porous material in the case of initial porosity.

Take the initial state of the material to be $P = 0$, $V = V'_0$, $T = T_0$, the $(P = 0, T = T_0)$ volume of the high pressure phase to be V_0 , and the final shocked state to be (P_h, V, T_h) . The Rankine-Hugoniot equations give, in this case,

$$U(V, T) - U(V'_0, T_0) = \frac{1}{2}P(V'_0 - V), \quad (47)$$

where U is the total internal energy, which, in the quasi-harmonic approximation, is $U = \bar{\phi} + U_q$. Define the transition energy E_t as

$$E_t = U(V_0, T_0) - U(V'_0, T_0). \quad (48)$$

E_t can be obtained from the enthalpy of phase change, if it is known. If there is no phase transition, i.e. if there is only a reduction of porosity, then this can be taken as zero (the surface energy of the pores can be neglected [17]).

If the pressure and temperature on the isentrope centered at $P = 0$, $V = V_0$ are P_s and T_s , respectively, at V , then, from (17)

$$P_h - P_s = \frac{\gamma}{V} [U_q(V, T_h) - U_q(V, T_s)]. \quad (49)$$

P_s can be calculated according to the previous section. From the identity

$$P = -\left(\frac{\partial U}{\partial V}\right)_s, \quad (50)$$