we see that

$$\Delta U \equiv U(V, T_s) - U(V_0, T_0)$$

$$= -\int_{V_0}^{V} P_s \, dV. \quad (51)$$

Thus for instance, if P_s is given in terms of e,

$$\Delta U = a_{0s}e + \tfrac{1}{2}a_{1s}e^2 + \tfrac{1}{3}a_{2s}e^3 + \tfrac{1}{4}a_{3s}e^4. \quad (52)$$

Eliminating $U_q(V, T_h)$ between (47) and (49), using (48) and noting that $\phi(V_0) = 0$, the final expression for the Hugoniot is

$$P_h\left[1 - \frac{\gamma}{2}\left(\frac{V_0'}{V} - 1\right)\right] = P_s - \frac{\gamma}{V}(\Delta U + E_t). \quad (53)$$

7. EQUATION OF STATE OF MgO

The elastic moduli of single-crystal MgO have been measured as a function of pressure and temperature by Spetzler[18]. The bulk modulus and its first pressure and temperature derivatives can be determined from such measurements. The parameters determined by Spetzler[18] are listed in Table 1, along with

Table 1. *Zero pressure elastic and thermodynamic data of magnesium oxide at* 300°K

ρ_0(g/cm³) [20]	3·584
K_{0T} (Mb) [18]	1·605
K_{0T}' [18]	3·89
$(\partial K_{0T}/\partial T)_P$ (Kb/°K) [18]	−0·272
α_0 (°K)⁻¹ [20]	$3·15 \times 10^{-5}$
C_V (erg/g°K) [21]	$9·25 \times 10^6$

the density, thermal expansion coefficient and specific heat of MgO, from the indicated sources.

These parameters were used in (34–41) to determine the parameters of the equations of state (32) and (33), in terms of η and E, respectively. Since the second pressure derivative of the bulk modulus, K'', is not given, only the third-order versions of these equations are determined in this way.

Using the 300°K isotherms given by (32)

and (33) the corresponding isentropes and Hugoniots were calculated according to the previous sections.

The fact that both the finite strain and the thermal parts of the equation of state are determined, so that Hugoniots can be calculated with reasonable accuracy, means, in effect, that extrapolations of the lower pressure data (specifically, the ultrasonic data) can be tested against Hugoniot data.

Carter et al.[19] have given data for a series of MgO Hugoniots, corresponding to different initial densities of the MgO samples. The lower initial density Hugoniots obtained by them are offset to higher pressures, and hence higher temperatures, than the single-crystal Hugoniot at the same density. These data thus provide a test of both the finite strain and the thermal parts of the present theory.

First, consider the finite strain part of the theory. In Fig. 1 are shown the single-crystal
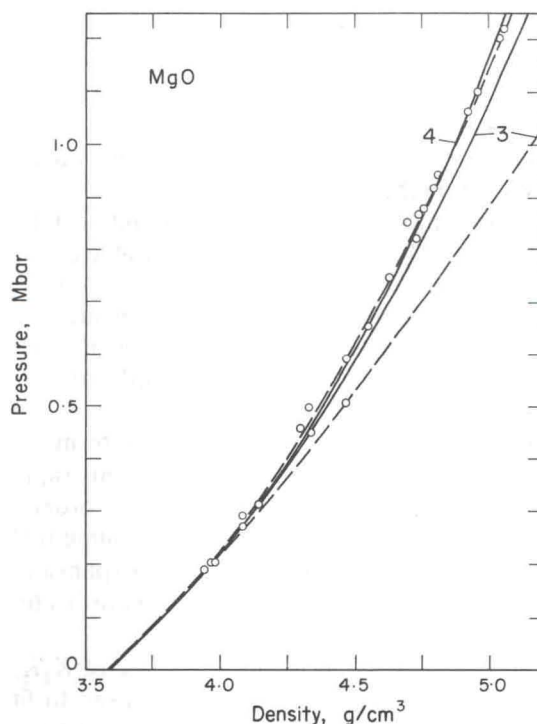

Fig. 1. Third- and fourth-order single-crystal MgO Hugoniots calculated in terms of E (solid) and η (dashed), compared with Hugoniot data of Carter *et al.*[19].

Hugoniot data of Carter *et al.*[19], along with the corresponding third-order Hugoniots calculated in terms of both the η and E strain measures. It can be seen that the 'E' Hugoniot is considerably closer to the data than the 'η' Hugoniot. This is an example of the empirical superiority of the 'E' equations which was, of course, pointed out by Birch [9, 10], and is the reason for the subsequent popularity of the 'Birch–Murnaghan' equation [11].

Also shown in Fig. 1 are fourth-order η and E Hugoniots in which K_0'' was determined by requiring a least-squares fit of the calculated curve to the data. The resulting values of $(K_0 K_0'')$ are given in Table 2. Clearly, the

Table 2. Values of $K_0 K_0''$ of MgO determined from Hugoniot data

Strain measure	$K_0 K_0''$
η	10·5
E	−1·1

fourth-order η and E Hugoniots fit equally well within the scatter of the data.

Comments on two important points can be made here. Firstly, it is clearly desirable to use an equation of state which involves the least number of disposable parameters, while still giving an acceptable representation of data. The greater success of the third-order E equation indicates faster convergence of the expansion in terms of E than that in terms of η. While there is no guarantee that this rapid convergence will continue to higher orders, it is certainly more reasonable to assume this about the E expansion than the η expansion, and E therefore appears to be a more useful strain measure than η.

The second point is that the value of $K_0 K_0''$ obtained depends on the equation used to fit the data (Table 2). It is, of course, a general property of truncated series expansions that the higher-order coefficients are less well

determined empirically, but it is one that seems to have received little notice in the context of finite strain expansions.

The thermal part of the equation of state will now be discussed. The volume dependence of γ resulting from equations (24, 27, 28, 43) is shown in Fig. 2. For the range of com-
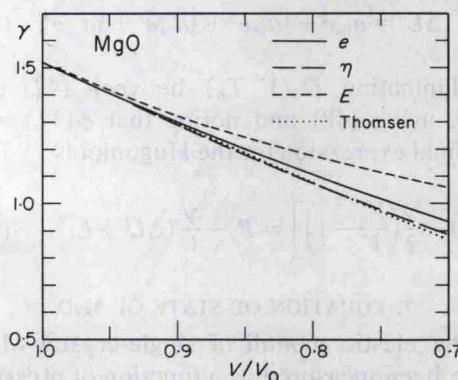

Fig. 2. Grüneisen parameter, γ, of MgO calculated from equations (24), (27) and (28), in terms of e, η and E, respectively, and from (43) given by Thomsen[1].

pressions, shown, the differences are not large. At larger compressions, γ given by (43) will be the first to become negative.

As mentioned previously, the Hugoniot data for different initial densities provide a test of the thermal part of the theory. The fourth-order E equations, with K_0'' evaluated from the single-crystal Hugoniot data (Table 2), were used to calculate the corresponding family of Hugoniots. These are compared with the data in Fig. 3. There is considerable scatter in the data but the separation of the various Hugoniots is quite apparent. The calculated Hugoniots reproduce this separation to within the scatter of the data. The fourth-order η equations would have yielded slightly smaller separations, as shown by the extrapolations of γ in Fig. 2, and would thus appear to be slightly less successful in explaining the data, but the evidence is marginal.

In conclusion, the finite strain extrapolations of the Mie–Grüneisen equation devel-