Experimentally, the Grüneisen coefficient $\gamma_G \equiv V(\delta P/\delta E)_V$ is found at not too high temperatures to depend only on the volume according to a function which is characteristic of the material. A good first-order estimate of the thermal energy along the Hugoniot can be obtained directly from the shape of the Hugoniot in the P-V plane. The usual steady-state conservation conditions across a shock front imply that the change in total internal energy in shock compression is equal to the area of the triangle formed by the initial state, the shock state, and the $P = 0$ line in the P-V plane. On the other hand, the gain in lattice potential energy is approximately the internal energy gain along the isentrope through the initial point which, in turn, is simply the area under the isentrope, or approximately the area under the Hugoniot. Thus the thermal shock energy is approximately the area between the Hugoniot and a straight line connecting the initial and final states, independent of the precise form of the equation of state. In the range where the solid has a constant molar specific heat of $3R$, an approximate shock temperature is thereby determined. However, to evaluate the thermal pressure arising from this thermal energy at any particular density along the Hugoniot, additional information is required in the form of an estimate of Grüneisen's γ_G for the material at that volume.

Rice's estimate of $\gamma_G(V)$ along the Hugoniot was apparently based on the then most extensive high-pressure thermodynamic data on alkali metals, which was the work on Na by Beecroft and Swenson[5]. In their analysis of the behavior of the compressibility along different isotherms, the latter authors concluded that their low-pressure data could be represented most economically by an isothermal compressibility which was independent of temperature. This assumption, applied to the adiabatic compressibility and combined with the Mie–Grüneisen equation of state, predicts a simple, explicit volume dependence for γ_G which is independent of the shape of the zero-degree isotherm,

$$\gamma_G(V) = \frac{V/V_0}{(\gamma_0 + 1)/\gamma_0 - V/V_0} \tag{1}$$

where $\gamma_0 \equiv \gamma_G(V_0)$. This volume dependence for Na is shown in Fig. 5 where γ_G is seen to decrease to very small values at high compression. By thus legislating γ_G to be small, Rice's calculated zero-degree isotherm is forced to be close to the Hugoniot at high compression, as shown in Figs. 1–4. However, as we shall argue below, such small values of γ are not to be expected for these alkali metals on the basis of conventional theories for the thermal properties. Moreover, Monfort and Swenson[6] have more recently concluded that the analysis of the static Na data was faulty on the basis of a comparison with newer ultrasonic data.

Since a complete theory of the thermal equation of state of metallic solids is not available, it has been necessary in interpreting shock data to resort to rather crude approximate phenomenological theories for calculating the volume dependence of the Grüneisen coefficient, γ_G. A brief review of these theories is therefore useful in order to clarify our reasons for using them in the analysis of the alkali metal data.

The thermal properties of the monatomic metallic solids are thought to consist of two independent additive components arising from thermal excitations of lattice vibrational modes and electrons. The electronic component is generally negligible at pressures below 100 kbar and will be ignored (see below). In theories for the lattice component, γ_G is related to the shape of the zero-degree isotherm $P_0(V)$. By making simplifying approximations in standard models of the thermal behavior of solids, a single formula for γ_G can be obtained.

$$\gamma_G = \frac{t-2}{3} - \frac{1}{2}\frac{d \ln\left[d(P_0 V^{2t/3})/dV\right]}{d \ln V} \tag{2}$$

from the Debye, lattice dynamic, and Einstein (or 'free volume') models for $t = 0$, 1 and 2,

Fig. 5. Various estimates of the volume dependence of γ_G. DM, Dugdale–MacDonald formula, $t = 1$; FV, free-volume, $t = 2$; R, Rice's form; TF, Thomas–Fermi model; Swenson, thermal data of [5]; IG, ideal gas value of $\frac{2}{3}$.

respectively. These cases are identified with Slater (SL) and Dugdale and MacDonald (DM) who first derived the cases $t = 0$ and 1 respectively, and the case $t = 2$ is denoted here as the free-volume (FV) approximation[10]. When combined with the Mie–Grüneisen equation for the energy $E_H(V)$ and pressure $P_H(V)$ along the Hugoniot, i.e.

$$\gamma_G = V \frac{P_H(V) - P_0(V)}{E_H(V) - E_0(V)}. \qquad (3)$$

Equation (2) can be numerically solved to obtain $P_0(V)$ and $\gamma_G(V)$.

In spite of the approximations involved, this approach has proved very useful in obtaining $\gamma_G(V)$ and $P_0(V)$ from shock data on the monatomic solids. The calculated behavior of $P_0(V)$ is nearly identical in typical solids for the SL, DM and FV approximations and, as noted previously, in agreement with static X-ray compression data on the less compressible solids. The similarity in the calculated

functions $P_0(V)$ is, in turn, a result of the fact that calculated values of $\gamma_G(V)$ for the different forms of equation (2) differ usually by decreasing amounts with increasing compression. This is illustrated in Fig. 5 where the DM and FV values of γ_G for Na are compared as functions of volume. The largest differences occur near $P_0(V_0) = 0$ where it can be shown directly from equation (2) that for the DM and FV formulas $\gamma_G(V_0)$ is respectively $\frac{1}{3}$ and $\frac{2}{3}$ less than its value according to the Slater formula. However, at low pressures and small compressions where these differences in γ are largest, the Hugoniot and the isentrope through the initial state can only differ by very small amounts (of third order in the compression). At higher compressions, the differences between the calculated γ are small enough to result in nearly the same thermal pressure corrections. Tables 1–4 present the results of the DM calculation for Li, Na, K and Rb, using the experimental data of Rice. The calculated