0°K isotherms are also plotted in Figs. 1–4 and are seen to be in close agreement with the Russian calculations. A constant specific heat of $3R$ has been assumed, and the 298°K isotherm $P_{DM}(298°)$ has been calculated for comparison with Bridgman data. The differences between this isotherm and that for the SL and FV approximations are indicated in Table 5 in the range 50–100 kbar. The discrepancy between Bridgman's isotherm and $P_{DM}(298°)$ is also tabulated and is seen to be an order of magnitude larger. Therefore, the three approximations for the lattice γ_G expressed by equation (2) show the same large inconsistency with Bridgman's compression data.

numbers of the solid metallic elements[11]. The best average fit is obtained for the DM approximation where it was found that over a range of thermodynamic values from 1 to 3, γ_G was fit on the average to ±10 per cent using shock wave data[10]. The fit is somewhat better when ultrasonically measured values of the pressure variation of compressibility are used. For certain groups of elements it is, however, possible to get better fits for the other values of t, and a reasonable recipe for analyzing the shock data for these cases is to use the value of t in equation (2) which produces the zero pressure agreement with thermodynamic data. The FV formula gives best agreement for the alkali metals as can

Table 5. Comparison of values of γ_G and $P(298°)$ isotherm calculated in SL, DM and FV approximation from shock data. Differences from the DM 298°K isotherm are shown for SL and FV as well as Bridgman data in the range of densities corresponding to shock pressures from 50 to 100 kbar

Mat.	γ_G^*	γ_{SL}	γ_{DM}	γ_{FV}	P_{FV}-P_{DM}	P_{DM}-P_{SL}	P_{BR}-P_{DM}
					(kbar at 298°)		
Li	0·81	1·541	1·208	0·975	1–3	1–2	8–16
Na	1·17	1·817	1·484	1·151	1–3	1–3	10–24
K	1·23†	1·719	1·386	1·053	2–4	1–3	11–30
Rb	1·06	1·797	1·464	1·131	2–5	1–3	19–39

*Thermodynamic data in [3].

†Varies from 1·05–1·23, depending on thermal expansion coefficient.

In their reduction of Hugoniot data, the Russian group has also made use of the DM equation in a somewhat different way. The DM form of equation (2) is integrated, assuming γ_G has the form

$$\gamma_G(V) = \tfrac{2}{3} + \left[\gamma_G(V_0) - \tfrac{2}{3}\right]\left(\frac{V}{V_0}\right)^M$$

and the value of M is chosen which predicts a Hugoniot in best agreement with the data.

Use of equation (2) is further justified by the significant correlation of calculated γ_G at zero pressure with thermodynamic values of $V(\partial P/\partial E)_V$ over the whole range of atomic

be seen in Table 5. In addition, shock wave data on metals, together with the above theory, show γ_G initially decreasing with compression at a rate which is consistent with rates derived from the variation of melting temperature with pressure or the temperature dependence of the elastic constants[12] where such data exist.

The mathematical reason for the similarity of the solutions of the various equations (2) for γ_G is as follows: When $P_0(V)$ varies as V^{-n}, then equation (2) shows that $\gamma_G = \tfrac{1}{2}(n-\tfrac{1}{3})$ independent of t. On the other hand, there is an increasing tendency for the pressure along the experimental 0°K isotherm

to have a power law dependence of volume, as is seen when the *P-V* experimental isotherms are displayed in a ln − ln plot. This volume dependence is also observed in a Thomas–Fermi equation of state for the zero-degree isotherm of the elements[13] at high compression. In the latter theory, the pressure of the atomic electron gas slowly approaches a volume dependence of $V^{-5/3}$ in the limit of high compression for which equation (2) implies γ_G, the ideal gas value → $\frac{2}{3}$. In a more correct calculation of the lattice modes in a Thomas–Fermi picture[14], γ_0 decreases very slowly with volume from values ~1 at normal densities to a high compression limit of $\frac{1}{2}$. The results of this calculation for γ_G are also shown in Fig. 5 for comparison with the other estimates of γ_G. Thus all theories predict γ_G to be considerably above the value Rice has used in the vicinity of two-fold compression.

The closeness of the Thomas–Fermi estimate to the thermodynamic γ_G reflects the similarity of the Thomas–Fermi model of the Na atom in a solid to the Bardeen–Fuchs force model which is used to explain many normal properties of the alkali metals[7, 8]. The Russian group also find the 0°K isotherm calculated from the Bardeen model in close agreement with the isotherm obtained from shock data on Na and K. When the compression becomes sufficient to cause additional energy bands of the alkali atoms to overlap, a more complicated behavior than shown by either the Bardeen model or the TF curve in Fig. 5 can be expected. Such effects are presumably already present at normal density in other metals exhibiting larger values of γ, such as the noble metals. In these other metals, the interatomic forces, both attractive and repulsive, depend on higher powers of the interatomic spacing. However, all compression data on the alkali metals are smoothly varying and show no evidence of new force laws. Also, the systematics of changes of electronic configuration with pressure which are shown by nearby elements in the periodic table[15] do not indicate such a change in these alkali metals in the range of compressions discussed here.

There is an additional thermal component of the equation of state arising from electronic excitation in the solid which, however, plays a minor role in the data below 100 kbar. This component was introduced by the Russian authors[4] mainly because of its importance at much higher pressures. A free electron model for electronic pressure P_e suggests a value of $\frac{2}{3}$ for $V(dP_e/dE_e)$. However, this value is so close to the lattice values of the alkali metals that the net change in the thermodynamic γ is entirely negligible below 100 kbar.

In our analysis, there remains a possible source of error which is currently under investigation. It arises from the fact that all measured Hugoniot points in Figs. 1–4 for the alkali metals are actually above the melting line. A more complicated equation of state is therefore necessary to account for the heat of fusion and the additional temperature dependence of thermodynamic quantities in the liquid state. In the past, such corrections have not proved significant, but their importance for the compressible materials should be checked.

On the basis of these arguments, the 298° isotherm obtained from shock wave data for the alkali metals should be reliable to ~5 per cent. In view of the much larger disagreement with static data and the scatter in Bridgman data, it appears desirable to recheck the static compression data for the alkali metals, particularly above 40 kbar, by improved or different techniques to see if unexpected thermal behavior does exist below 100 kbar, or if unexpected systematic errors are present in the shock wave data.

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