Electronic Grüneisen parameter in the shock Hugoniot equation of state of aluminum

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The shock Hugoniot equation of state for aluminum has been computed, using the pseudopotential method. The nuclear Grüneisen parameters, used in evaluating the ionic vibration contributions, have been derived from phonon frequencies. The computed electronic Grüneisen-parameter values depart considerably from the value 0.5, used often in analyzing shock-compression experiments. This leads to different Hugoniot temperatures compared with those derived by Al'tshuler *et al.*, although the P-V curve is in good agreement with their experimental results.

I. INTRODUCTION

For the interpretation of experimental shock P-V data for metals, especially for deriving the 0 °K isotherm, a model[1] is often used in which the total internal energy and pressure at a given volume V and temperature T are divided into three terms:

$$E = E_c + E_T + E_e , \tag{1}$$

$$P = -\left(\frac{\partial E_c}{\partial V}\right) + \frac{\gamma E_T}{V} + \frac{\gamma_e E_e}{V} . \tag{2}$$

The three terms describe the compression of the cold body (i.e., at 0 °K), the thermal motion of ions (nuclei), and the thermal excitations of electrons. γ and γ_e are the nuclear and electronic Grüneisen parameters and are functions of both V and T. While the volume variation of γ is often simulated by the Slater or Dugdale-Macdonald relation, a fixed value of 0.5 is employed for γ_e. The latter is based on the fact that for the limiting cases of very high temperatures or very large densities, the free-electron limit applies for which $E_e \sim T^2$ and $\gamma_e = \frac{2}{3}$, while for the infinite atom case $\gamma_e = \frac{1}{3}$ (see Gilvarry[2] and Latter[3]). Because densities and temperatures achieved in laboratory shock experiments are in between these limits, a mean of $\gamma_e = 0.5$ has been adopted for all metals (Al'tshuler *et al.*[4]). However, the values of γ_e for some of the metals, as determined from electronic thermal expansion measurements,[5] are

Al	1.8	Ni	2.0
Cu	0.7	Pt	2.3
Pb	1.7	Ta	1.3.

For the alloy $Pd_{0.95}Rh_{0.05}$, γ_e is as high as 3.9 (Fawcett[6]). These suggest values of γ_e higher than 0.5 at shock compressions where the electronic excitation contributions become significant. In this paper, we have attempted to examine this problem for the metal aluminum. We have evaluated all the three contributions in Eq. (2) by first-principle methods. Aluminum has been chosen because, for this metal, the experimental data are available up to 2.5 Mbars[7,8]—the region in which the contribution from the thermal electronic term becomes important. Also, there is discrepany between two sets of reported measurements on aluminum (see Fig. 1) at high pressures and we wanted to see whether this discrepancy can be resolved from our theoretical calculations.

The 0 °K equation of state of Al was earlier computed by Friedli and Ashcroft[9] using the pseudopotential technique, but they limited the compari-

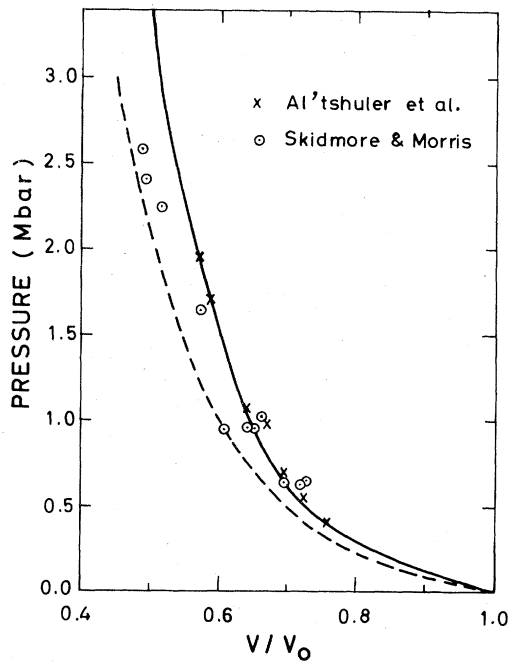

FIG. 1. Comparison of calculated Hugoniot (——) for aluminum with the experimental data of Al'tshuler *et al.* (Ref. 7) and Skidmore and Morris (Ref. 8). The zero-degree Kelvin isotherm is shown as ----.

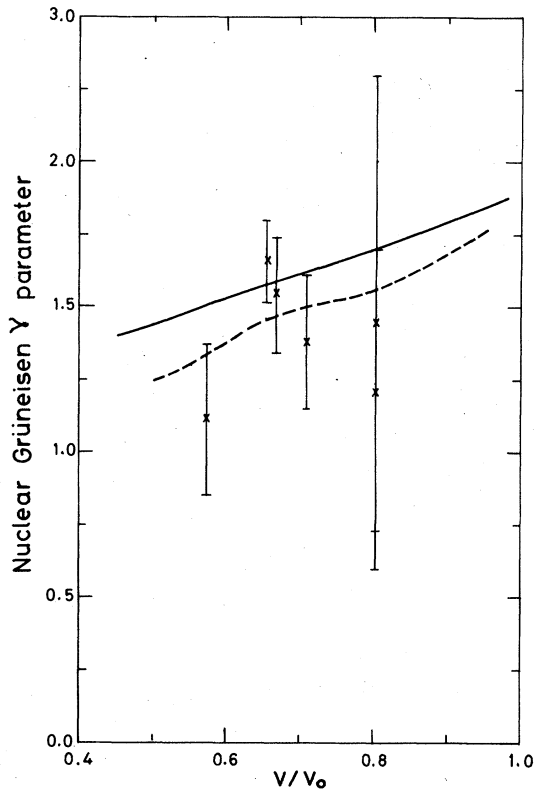

FIG. 2. Grüneisen γ's vs V/V_0 for aluminum. The points (×) with error bars are the experimental values taken from Neal (Ref. 13) and the two theoretical curves are (1) ----- computed from Eq. (3) and (2) ——computed from Slater's formula [Eq. (4)].

son of their results with the experimental data for two dilute alloys of aluminum up to 1.2 Mbars, a pressure value up to which the uncertainty arising from γ_e, mentioned above, is not of much importance.

II. CALCULATION PROCEDURE

For the 0 °K term, E_c, we have employed the expression for the total energy given by Heine and Weaire.[10] This is made up of the energy of the free-electron gas with exchange and correlation corrections, Madelung energy, and the pseudopotential band-structure energies up to second order. Our choice of the pseudopotential, its parameters, and the treatment of first-order band-structure energy is similar to that of Friedli and Ashcroft.[9] These calculations are for an ordered fcc lattice of Al. The effect of liquid disorder on melting (at $T=0.5$ eV and $V/V_0=0.6$ for Al) is ignored. This has been shown to be negligible for Na by Stroud and Ashcroft.[11] Also, experimentally no discernable change takes place in the compressibility of Al across the Hugoniot melting point.

We took $E_T=3kT$ (per atom) and the nuclear γ parameters were estimated as a function of volume from the phonon frequencies, ν, through the relation

$$\gamma(V)=\left\langle\frac{-d\ln\nu}{d\ln V}\right\rangle. \tag{3}$$

The phonon frequencies were computed by the procedure described by Gilat *et al.*[12] The normalized energy wave number characteristic required in these calculations at each volume was computed by employing the Ashcroft's pseudopotential form factors (as used for E_c above). The mode γ's (one longitudinal and two transverse) were evaluated numerically at each of the 256 points in the Brillouin zone and the mean in Eq. (3) found by simple averaging of all these γ's. A comparison of such computed γ values with the recent experimental measurements by Neal[13] is shown in Fig. 2. Also shown are the γ's computed from the 0 °K isotherm through the Slater's formula[14] [Eq. (4)], the method followed by Al'thshuler *et al.*[7] in their analysis of shock compression data:

$$\gamma(V)=-\frac{2}{3}-\frac{V}{2}\frac{\partial^2 P_c/\partial V^2}{\partial P_c/\partial V}. \tag{4}$$

It may be seen that the γ's, calculated more rigorously from theory, are in better agreement with the experimental data. It may be also noted that these do not display a smooth variation with volume like the Slater γ's. This is somewhat in accord with Neal's analysis.

E_e and P_e were computed from the expressions[15,16]

$$E_e=\sum_k \mathcal{E}_k(V)[n_k(T)-n_k(0)], \tag{5}$$

$$P_e=-\sum_k \frac{\partial \mathcal{E}_k(V)}{\partial V}[n_k(T)-n_k(0)], \tag{6}$$

where $\mathcal{E}_k(V)$ are the conduction-electron ground-state eigenvalues and $n_k(T)$ is the occupancy of any level, given by the Fermi-Dirac distribution function. $\mathcal{E}_k(V)$'s were evaluated by us, using the standard pseudopotential energy-band method. These were done at 2048 points in the Brillouin zone with 27 plane waves up to $\{220\}$.[17] The Hugoniot energy and pressure were then derived at each volume by an iteration procedure in which the temperature was varied so that Eqs. (1) and (2) (with P_e instead of the term $\gamma_e E_e/V$) and the Rankine Hugoniot energy relation were simultaneously satisfied. The temperature for which this happens is the Hugoniot temperature.

III. RESULTS AND DISCUSSION

In Fig. 1, we compare our computed Hugoniot pressures with the data of Al'tshuler *et al.*[7] and

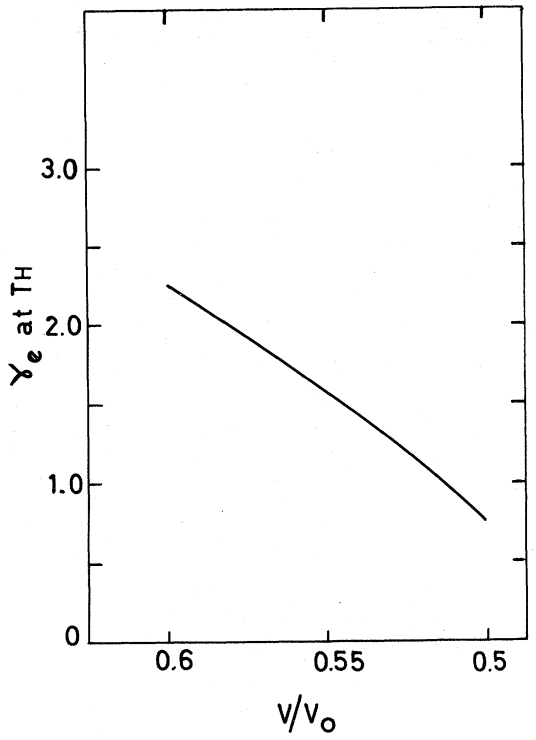

FIG. 3. γ_e at Hugoniot temperatures vs V/V_0 for aluminum.

of Skidmore and Morris.[8] Apart from the fact that there is more scatter in the latter data (this can be seen from the Fig. 1; some of their points even fall near the zero-degree isotherm), no reasons for the disagreement between the two experiments could be assigned by us. However, our curve is in very good agreement with the data of Al'tshuler *et al.*

The values of electronic Grüneisen parameter (now defined as $\gamma_e = VP_e/E_e$) as a function of V/V_0 at the corresponding shock temperature are plotted in Fig. 3. These values, as anticipated in the Introduction, differ considerably from the value 0.5. Consequently, the zero-degree isotherm and the Hugoniot temperatures obtained in our calculation should be different from those calculated by Al'tshuler *et al.*[7] as they used $\gamma_e = 0.5$ in their analysis. This is indeed found to be true, as illustrated in Fig. 4, where the two sets of shock temperatures are shown. Our values are consistently higher at larger compressions. Incidentally, it may be pointed out here that the theoretical values of γ_e are similar to those obtained by McMahan, Hord, and Ross[18] for metallic iodine.

The dependence of γ_e on temperature for a given compression is shown in Fig. 5. It is seen that γ_e decreases with temperature. Ultimately, in the limit of very high temperatures it is expected to reach its limiting Fermi-Dirac value of $\frac{2}{3}$. This general dependence of γ_e on both density and temperature is important where one has to do calculations for states not on the shock Hugoniot. Although these conclusions are drawn for aluminum, we expect these to hold for other simple metals also.

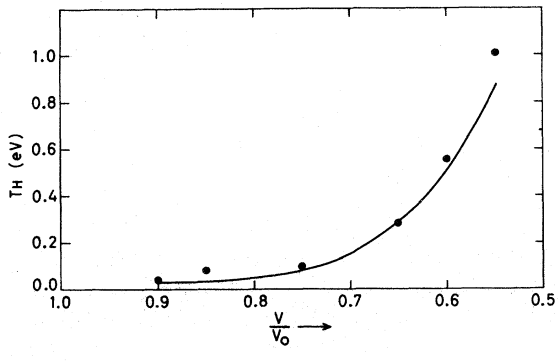

FIG. 4. Hugoniot temperatures vs V/V_0 for aluminum. Solid curve is taken from Al'tshuler *et al.* (Ref. 7) while solid points are from our calculations.

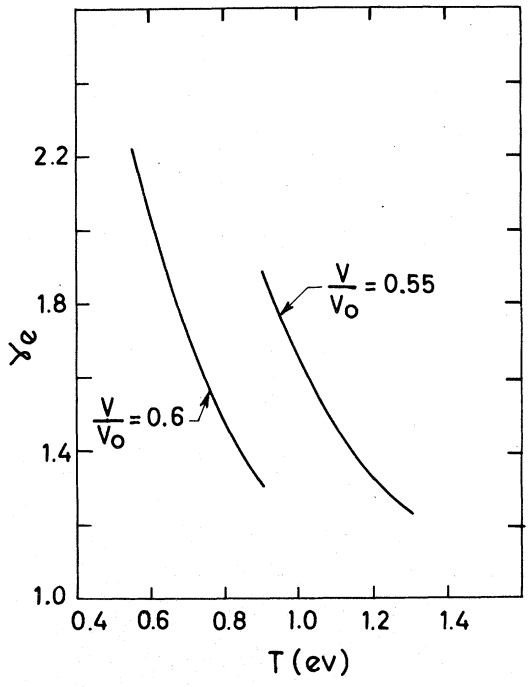

FIG. 5. γ_e vs temperature for $V/V_0 = 0.6$ and $V/V_0 = 0.55$ for aluminum .

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