

## Volume variation of nuclear Grüneisen parameter for equation of state studies

B K GODWAL

Neutron Physics Division, Bhabha Atomic Research Centre,  
Trombay, Bombay 400 085, India

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**Abstract.** The method of first principle pseudopotential is used to simulate the volume variation of nuclear Grüneisen parameter. The elements Al and Be, for which Neal's experimental data exist are investigated. The nuclear Grüneisen obtained from the details of phonon frequencies are in better agreement with the experimental data as compared to those obtained from approximate Slater and Dugdale-MacDonald methods, often used in shock wave studies.

**Keywords.** Grüneisen parameter; equation of state; phonon frequencies; volume variation; first principle pseudopotential.

### 1. Introduction

Knowledge of the volume dependence of nuclear Grüneisen parameter  $\gamma(V)$  is vital for relating the shock Hugoniot to the zero-degree isotherm. It is also useful in describing states off principal Hugoniot. In the equation of state studies a model (Zel'dovich and Raizer 1967; McMahan and Ross 1977; Godwal *et al* 1979) is often used in which the total internal energy and pressure at a given volume  $V$  and temperature  $T$  are divided into two terms (neglecting the electronic thermal contribution)

$$E = E_c + E_T, \quad (1)$$

$$P = -(\partial E_c / \partial V) + \gamma E_{T/V} = P_c + P_T \quad (2)$$

The two terms in (2) arise from the compression of the cold body (*i.e.* at 0°K) and the thermal motion of the ions (nuclei),  $\gamma$  the nuclear Grüneisen parameter, is related to phonon frequencies,  $\nu_s$ , through the relation

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

where  $\langle \rangle$  means average overall normal modes.

The commonly used formulations to calculate the volume variation of  $\gamma$  are those of Slater (1939), Landau and Stanyakovich (1945), Dugdale and MacDonald (1953), Rice *et al* (1958) and the free volume approximation. For these

$$f(V) = \frac{t-2}{3} - \frac{V}{2} \frac{\partial^2 (P_c V^{2t/3})}{\partial V^2} \Big/ \frac{\partial (P_c V^{2t/3})}{\partial V}, \quad (4)$$

where  $t=0$  corresponds to the Slater theory,  $t=1$  to Dugdale MacDonald theory, and  $t=2$  to the free volume theory. The  $\gamma(V)$  obtained from Slater model is based on the Debye approximation for the lattice vibration spectrum while in the Dugdale-MacDonald relation all the force constants have the same volume dependence and hence  $\gamma$ 's evaluated using it may not have the true volume dependence. However for most metals the Dugdale-MacDonald model is adequate, while for aluminium, the Slater formula works better (Godwal *et al* 1979). In this paper we have used the first principle pseudopotential method to derive  $\gamma(V)$ 's from the details of phonon frequencies. These  $\gamma(V)$  calculations are made upto the compression of  $\sim 0.5$  which is achieved experimentally using shocks.

## 2. Method of calculation

The pseudopotential approach to lattice dynamics has been adequately discussed in literature (Joshi and Rajagopal 1968) and does not warrant any repetition here. The phonon frequencies required in (3) for the evaluation of  $\gamma(V)$  were obtained from the usual secular equation (Gilat *et al* 1969).

$$|D_{\alpha\beta}(kk', \mathbf{q}) - \nu^2 I| = 0. \quad (5)$$

Within the small core approximation, the dynamical matrix  $D$  has two contributions (Kay and Reissland 1976),  $D_{\alpha\beta}^c(kk', \mathbf{q})$  the direct ion-ion coulomb interaction and  $D^E(kk', \mathbf{q})$  that due to the conduction electrons ( $k, k'$  are ionic labels within a unit cell,  $\alpha, \beta$  are the cartesian directions and  $\mathbf{q}$  is the wave vector).  $D^E$  involves the pseudopotential experienced by an electron due to the ion and involves the form factor computed with the pseudopotential. We have neglected the contribution to the dynamical matrix from ion core repulsions which is negligible because the size of the core is very much smaller than the nearest neighbour distance (at least for Al and Be; also see Herring and Hill 1940). In our calculations, the ionic charges and the parameters of bare pseudopotential are frozen and then phonon frequencies are computed for different (hydrostatically compressed) volumes. The mode  $\gamma$ 's (one longitudinal and two transverse) was evaluated numerically at each of the 256 points in the Brillouin zone and the mean in (3) is found by simple averaging of all these  $\gamma$ 's.

## 3. Results and discussions

For applying the above procedure to Al, we employed Ashcroft's empty core pseudopotential with core radius  $r_A = 1.12$  a.u. and  $V = 110.6$  a.u. (Godwal *et al* 1979) to com-

pute  $F_N(q)$ , the normalised energy wave number characteristic. A comparison of such computed  $\gamma$  values with the experimental measurements of Neal (1976) is shown in figure 1. Also shown are the  $\gamma$ 's computed from theoretically-computed (Godwal *et al* 1979) zero degree isotherm through Slater's formula. It may be seen that though the precision of the experimental data (these are difficult experiments to do) is not high, the  $\gamma$ 's calculated more rigorously from theory are in better agreement with the experimental data than those calculated from the Slater model. The Slater's  $\gamma$ 's were also used by Al'tshuler *et al* (1960) to reduce their shock Hugoniot to zero degree isotherm.

For the metal Be, Neal (1979) observed from his experimental data that  $\gamma$  attains a value of 1.8 when extrapolated to  $V/V_0 = 1.0$ . This value is however different from the thermodynamic ( $\gamma_{\text{thermo}}$ ) value of 1.1 which is obtained using (Sheard 1958)

$$\gamma_{\text{thermo}} = \frac{\alpha \beta^T V}{C_V}, \quad (6)$$

$\beta^T$  is the isothermal bulk modulus and  $\alpha$  is the volume coefficient of thermal expansion,  $V$  the specific volume and  $C_V$  is the lattice heat capacity at constant volume. At high

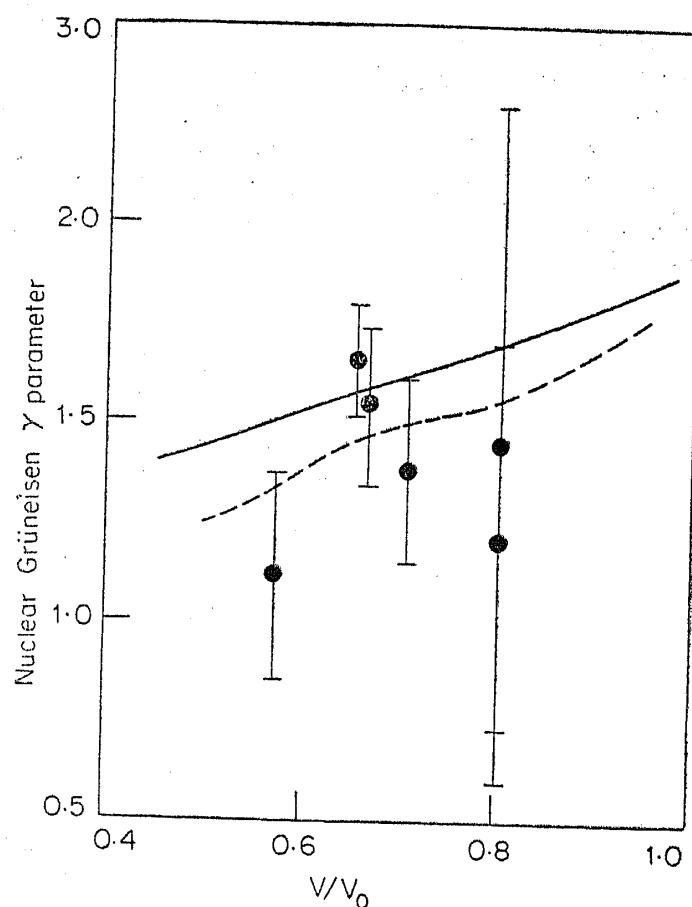


Figure 1. Variation of nuclear Grüneisen parameter with volume for Al. The dashed curve is computed from the details of phonon frequencies and the solid curve is obtained using Slater's model. Neal's experimental points ( $\times$ ) are also shown with the error bars.

temperatures ( $T \geq 1/3 T_{\text{Debye}}$ )  $\gamma_{\text{thermo}}$  becomes equal to  $\gamma$ . However there is still very good agreement between  $\gamma$  (at  $V/V_0 = 1.0$ ) and  $\gamma_{\text{thermo}}$  for many elements, as discussed in detail by Rice *et al* (1958). But for Be this discrepancy between two  $\gamma$ 's ( $\gamma$  and  $\gamma_{\text{thermo}}$ ) might, in some way, be due to difficulties in establishing a thermodynamic value for a material that has exhibited the shock anisotropic effects. For most part, however, it is the result of phase change (Neal 1979). Be undergoes a hcp-bcc phase transition (under shock) at a pressure of  $\approx 90$  kbar. However our recent studies (Godwal *et al* 1981) have shown that  $\gamma(V)$  is insensitive to structural changes (the potential however was kept fixed). The insensitivity of  $\gamma(V)$  to structural changes is also supported by Welch *et al* (1978) on the basis of their molecular dynamical calculations.

The lattice dynamics for this metal at normal pressure is described in detail by Sahni and Venkatraman (1969) within the framework of the local pseudopotential approximation for the hexagonal phase. We used their four-parameter pseudopotential obtained from measured phonon dispersion curves. However the  $\gamma(V)$ 's computed using this did not show the correct volume variation. Hence we decided to derive the pseudopotential. We took the shock-reduced zero degree isotherm of Rice *et al* (1958) and varied the core radius in empty core pseudopotential to reproduce it ( $\gamma_A = 0.552$  a.u. for  $V = 54.75$  a.u.)

In figure 2 we display the volume variation of  $\gamma(V)$  obtained using the derived pseudopotential. Also shown are the  $\gamma(V)$ 's computed using the Slater and Dugdale-MacDonald methods. It is seen that  $\gamma(V)$  values evaluated from phonon frequencies agree well with the experimental data of Neal (1979) at high compressions. The extrapolated value of  $\gamma(V)$  to  $V/V_0 = 1.0$  from the phonon dispersion, the Slater and the Dugdale-MacDonald methods are respectively 1.4, 1.3 and 0.98. The first of these three values is closest to the experimental value of 1.8. This is also different from the thermodynamic value of 1.1.

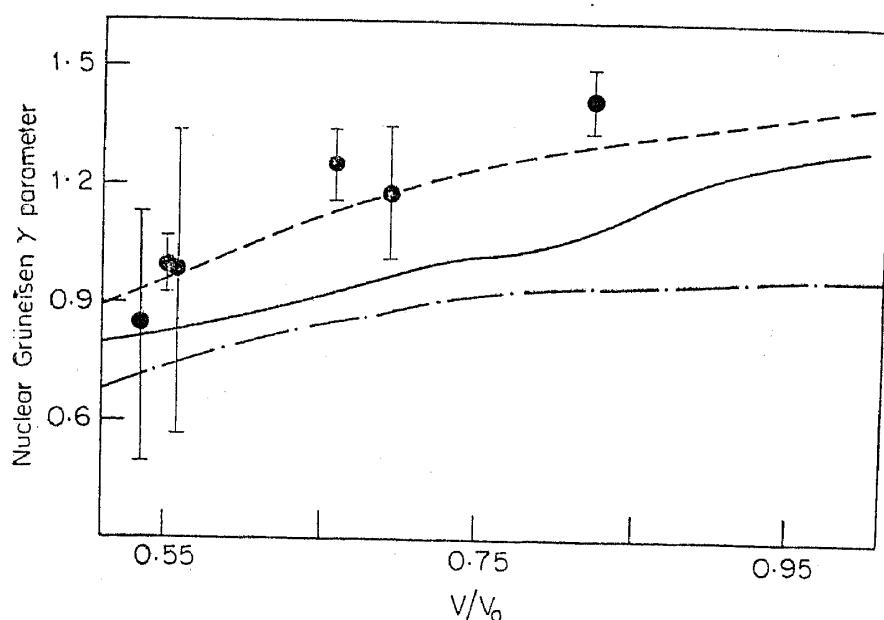


Figure 2. Variation of nuclear Grüneisen parameter with volume for Be. The dashed (—) curve is obtained from phonon frequencies while (—) and (—·—) are respectively computed using Slater and Dugdale-MacDonald methods. Neal's experimental points (×) are also shown with error bars.

In conclusion on the basis of our investigations for two metals Al and Be we find that volume variation of  $\gamma$ 's computed from phonon frequencies are in better agreement with the experimental data as compared to the  $\gamma$ 's evaluated from other approximate methods. We therefore feel that similar calculations should be done for other metals also. For Be the disagreement between the experimental and thermodynamic values of  $\gamma(V_0)$  is attributed to the fact that there is a change in the pseudopotential on hcp-bcc phase transition.

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