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Abstract

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THE GRÜNEISEN PARAMETER FOR NaCl AT HIGH PRESSURES

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The dependence of the pressure P on the volume x ($x = v/v_0$ is the relative volume, v_0 the specific volume under normal conditions) has been studied experimentally by Bridgman ([1]) under static conditions up to pressures of $\sim 10^5$ bar. In recent years a dynamic method of compressing solids by means of strong shock waves has been developed, and shock adiabats (Hugoniot adiabats) have been experimentally determined for many metals ([2,4]), as well as for NaCl ([10]), at considerably higher pressures.

The shock adiabat in principle makes it possible to determine the equation of state. The Hugoniot adiabat (3) contains two unknown functions of volume: $P_0(x)$, the potential pressure, and $\gamma(x)$, the Grüneisen parameter; therefore, in determining the equation of state from the shock adiabat, one usually assumes some functional relation between γ and P_0. On the other hand, an independent determination of $P_0(x)$ makes it possible, from the experimental shock adiabat, to investigate the behavior of the Grüneisen parameter at high pressures. Such an investigation is carried out below for NaCl. It was found that the experimental γ is described very well by the Landau-Slater formula, normalized at $x = 1$ (at $P = 0$).

We write the free energy of the crystal in the form

$$F(x,T) = \Phi(x) + \theta f\left(\frac{\theta}{T}\right), \tag{1}$$

where T is the absolute temperature and θ is the characteristic temperature. Here $\Phi(x)$ is the potential part of the free energy, depending only on the volume. The second term in (1) is due to phonons. For $\theta f(\theta/T)$, interpolation formulas of Debye, Einstein, or their combinations ([3]) are widely used.

From the definition of the pressure $P = -\rho_0(\partial F/\partial x)_T$ and the equation of the Hugoniot adiabat

$$E_H - E_0 = \frac{P_H}{2\rho_0}(1-x), \tag{2}$$

which relates the pressure P_H in the shock wave to the energy of the body E_H subjected to this pressure, we obtain the desired equation expressing P_H as a function of the Grüneisen parameter γ and the potential pressure P_0:

$$P_H = \frac{1}{1 - \dfrac{\gamma(1-x)}{2x}} \left\{ P_0 + \frac{\rho_0 \gamma}{x}(E_0 - \Phi) \right\}. \tag{3}$$

Here, as in (2), E_0 is the energy per unit mass of the crystal ahead of the shock-wave front, $P_0 = -\rho_0(\partial\Phi/\partial x)$, $\gamma = -\partial \ln\theta/\partial \ln x$. The expression (3) for P_H contains two unknown functions Φ (or P_0) and γ, which determine the equation of state of the solid.

For Φ, various expressions have previously been proposed ([5,6]). In our view, the most rational is to specify Φ in the form of the Born–Mayer potential

$$\Phi = \frac{3}{\rho_0}\left(\frac{A}{b} e^{b(1-x^{1/3})} - K x^{-1/3}\right), \qquad P_0 = A x^{-2/3} e^{b(1-x^{1/3})} - K x^{-4/3}, \tag{4}$$

where A, b, K are numerical parameters determined from experiment ([7,8]).

Further, from (1) it follows that γ is related to the thermodynamic characteristics of the crystal by the relation

$$\gamma = \frac{\alpha x}{\rho_0 c_v \beta}, \tag{5}$$

where $\alpha = \frac{1}{x}\left(\frac{\partial x}{\partial T}\right)_P$ is the coefficient of thermal expansion, $\beta = -\frac{1}{x}\left(\frac{\partial x}{\partial p}\right)_T$ is the coefficient of volume compressibility, and c_v is the heat capacity per unit mass.

Since the dependence of c_v, β, and α on volume has not been studied experimentally, it is not possible to determine the Grüneisen parameter at high pressures with the aid of (5). It is usually assumed that the Grüneisen parameter is related to the potential pressure P_0 either by the Landau–Slater formula ([11,12])

$$\gamma_1 = -\frac{x}{2}\frac{d^2 P_0/dx^2}{dP_0/dx} - \frac{2}{3}, \tag{6}$$

or by the Dugdale–MacDonald formula ([13])

$$\gamma_2 = -\frac{x}{2}\frac{d^2(P_0 x^{2/3})/dx^2}{d(P_0 x^{2/3})/dx} - \frac{1}{3}. \tag{7}$$

Both expressions (6) and (7) have not been tested experimentally; however, in the Debye theory (6) has a simple physical meaning and corresponds to a constant Poisson ratio, while (7) gives γ at $P = 0$ that agrees better with thermodynamic values (5) for metals.

If, however, P_0 and P_H are known from independent measurements, then (3) makes it possible to determine γ from these quantities

$$\gamma = \frac{P_H - P_0}{\frac{\rho_0}{x}(E_0 - \Phi) + \frac{P_H(1-x)}{2x}}. \tag{8}$$

The shock adiabat (P_H) for NaCl was obtained in ([10]), and the parameters in (4) for P_0 were calculated from Bridgman' s static data up to 10^5 bar in ([6]):

$$A = 0.965 \cdot 10^5 \text{ bar}, \qquad b = 9.69, \qquad K = 1.053 \cdot 10^5 \text{ bar}, \qquad \rho_0 = 2.167. \tag{9}$$

The values (9) should be regarded as quite reliable, since at a pressure of $\sim 10^5$ bar the volume of NaCl changes by approximately 20%, which, say, for metals of the Cu type would correspond to pressures of $\sim 3 \cdot 10^5$ bar. We also note that the theoretical three-member Born–Mayer potential for NaCl ([9]) agrees well with (4), (9)*. We now proceed to the calculations.

From the condition $P = 0$ at $x = 1$, using (1), we obtain:

$$E_0 = \Phi(1) + \frac{1}{\gamma_0}\frac{\partial \Phi}{\partial x}\bigg|_{x=1}, \qquad \gamma_0 = \frac{\alpha}{\rho_0 c_v \beta}\bigg|_{x=1} = 1.55, \tag{10}$$

which, for a given Φ, determines the initial energy E_0 and does not depend on the particular form of $f(\theta/T)$. In the Debye approximation

$$E_0 = \Phi(1) + \frac{R\nu}{\mu}\left[\frac{9}{8}\theta_0 + 3T_0 D\left(\frac{\theta_0}{T_0}\right)\right],$$

* In ([10]), when comparing the described potential with experiment, the authors used only the quoted value of b, while for A and K they took theoretical values, which is inconsistent.

where R is the gas constant; ν is the number of atoms in the molecule; μ is the molecular weight; $\theta_0 = 299°\text{K}$ is the characteristic Debye temperature; T_0 is the temperature ahead of the shock-wave front; $D(\theta_0/T_0)$ is the Debye function. For NaCl with parameters (9), both expressions give coincident values of E_0.

The γ calculated from (8), with the experimental values P_H from (10), are shown in Fig. 1,a. The large scatter of the points is due to experimental errors.

It is increased by the fact that the thermal pressure $P_T \sim \gamma$ amounts to only $10 \div 16\%$ of P_H. Smoothing these values by the least-squares method, from formula (13) we obtain for the Grüneisen parameter the values shown by curve 1.

The Grüneisen parameters γ_1 (6) and γ_2 (7), calculated with the constants (9), are shown respectively in Fig. 1,2 and 1,3. It is seen from the graph that under a parallel shift 2 practically coincides with 1; therefore we shall determine γ by the expression

$$\gamma = \gamma_1 + \delta, \tag{11}$$

where the constant δ is determined from the condition that γ (11) coincide with γ_0 (10) at $P = 0$, i.e.

$$\delta = \gamma_0 - \gamma_1(1). \tag{12}$$

The γ normalized in this way are shown in Fig. 1,4, and the corresponding shock adiabat (3) in Fig. 1,5. Line 6 corresponds to the pressure P_0.

Fig. 1. Shock adiabat and Grüneisen parameter.
1 –averaged values of experimental γ at the specified values of the parameters (9); 2 –γ_1 according to Landau-Slater; 3 –γ_2 according to Dugdale and MacDonald; 4 –γ normalized by formula (11); 5 –theoretical shock adiabat (3) with parameters (9); 6 –potential pressure P_0; a –experimental γ according to formula (8); b –experimental values P_H from (10)

Comparing curves 1 and 4, we note that δ decreases somewhat with decreasing x, but since this decrease is insignificant, it may be neglected.

The theoretical shock adiabats (3), calculated with unnormalized γ_1, unnormalized and normalized γ_2, lie appreciably above the experimental points (10).

In (11) enters γ, which is determined through the derivatives of P_0 with respect to x (6), and since P_0, in turn, depends on the same parameters A, b, K as does Φ (4), actually three parameters A, b, K enter the shock-adiabat equation (3) instead of the two unknown functions γ and Φ. In this case (11) takes the form

$$\gamma = \frac{1}{6} - \frac{A\left(b^2 x^{1/3} + 2b + 2x^{-1/3}\right) e^{b(1-x^{1/3})} - 12Kx^{-1}}{A\left(b + 2x^{-1/3}\right) e^{b(1-x^{1/3})} - 4Kx^{-1}} + \delta. \tag{13}$$

Taking advantage of this circumstance, on the basis of only the experimental data [10], by formulas (3), (12), and (13), the following values of the parameters were obtained by the method of least squares:

$$A = 0.800 \cdot 10^5 \text{ bar}, \qquad b = 10.66, \qquad K = 0.889 \cdot 10^5 \text{ bar}, \tag{14}$$

and although they differ from (9), the agreement with Bridgman' s data remains quite satisfactory.

Thus, it follows from the experimental data that the Grüneisen parameter should be determined by means of the Landau–Slater formula, normalized to the thermodynamic γ_0 under normal conditions.

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Note: Figure translations are in progress. See original paper for figures.