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Abstract

Full Text

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THE EFFECT OF PRESSURE ON ANHARMONICITY

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1. A review of work on the influence of anharmonicity on the thermodynamic parameters of crystals at normal pressures has been given by Leibfried and Ludwig ([1]). We are interested in the question of the behavior of these parameters on the shock adiabat, i.e., under conditions of increasing pressures and temperatures. To this end, the influence of high pressures on anharmonicity and on the Grüneisen parameter in ionic and van der Waals crystals, i.e., in substances whose forces may with good reason be regarded as central and known, has been investigated in detail. The investigation was carried out for the classical limiting case, since at high pressures the shock adiabat lies in the region of high temperatures $T > \theta$, where T is the temperature and θ is the Debye temperature. The calculations themselves, as can be seen from ([1]), are quite cumbersome; therefore, below we give certain results that are of interest for the analysis of the high-temperature portion of the shock adiabat.

2. The mean square of the frequency is expressed in terms of the interaction potential between particles $\varphi_{\mu\nu}$ in the following way ([1]):

$$\overline{\omega^2} = \frac{1}{3sN}\sum_{\mathbf{k},\lambda}\omega^2(\mathbf{k},\lambda) = \sum_{\mathbf{h}\mu\nu}{}' \frac{1}{M_\nu}\Delta\varphi_{\mu\nu}\left(\mathbf{R}^{\mathbf{h}\mu\nu}\right). \tag{1}$$

Relation (1) is completely exact, and no assumptions are required for its derivation except pair interaction and central forces. In (1) the following notation is used:
$\mathbf{R}^{\mathbf{h}\mu\nu} = \mathbf{R}^{\mathbf{m}\mu} - \mathbf{R}^{\mathbf{n}\nu}$ is the vector distance between the $\binom{\mathbf{m}}{\mu}$ and $\binom{\mathbf{n}}{\nu}$ particles; $\mathbf{m}$ and $\mathbf{n}$ are vector integer indices of the elementary cells; μ and ν are scalar indices numbering the particles in the elementary cell; s is the number of particles in the elementary cell; N is the number of elementary cells in the crystal; M_ν is the mass of the ν-th particle; $\mathbf{k}$ is the wave vector; λ is the index numbering the phonon branches and the phonon polarization; $\varphi_{\mu\nu}\left(\mathbf{R}^{\mathbf{h}\mu\nu}\right)$ is the interaction potential between the μ and ν particles located at a distance $\mathbf{R}^{\mathbf{h}\mu\nu}$; Δ is the Laplace differential operator, the Laplacian; the prime on the sum means that the point $\mathbf{h} = 0,\ \mu = \nu$ is excluded from the summation (self-energy).

For cubic crystals the Grüneisen parameter is a scalar and can be approximately determined by the formula*

$$\gamma = -\frac{1}{2}\frac{d\ln\overline{\omega^2}}{d\ln x} = -\frac{1}{6}\left\{\sum{}' \frac{R^2(Q\Delta\varphi)}{M_\nu}\right\}\left\{\sum{}' \frac{\Delta\varphi}{M_\nu}\right\}^{-1}, \tag{2}$$

* The general expression for the Grüneisen parameter has the form

$$\gamma = -\frac{1}{3Ns}\sum_{\mathbf{k},\lambda}\frac{d\ln\omega(\mathbf{k},\lambda)}{d\ln x}.$$

Below we shall compare γ, determined with the aid of various approximate theoretical formulas. Accordingly, the terms "high-frequency"or "low-frequency" γ, etc., will be used.

where, for convenience, indices analogous to (1) have been omitted from the summation signs and from φ; $O = 2\dfrac{d}{dR^2} = \dfrac{1}{R}\dfrac{d}{dR}$ is the differential operator introduced into the theory of crystal lattices by Born; R is the scalar distance between particles; $x = V/V_0$ is the relative volume.

In order to determine γ in (2) completely, it is necessary to choose an interaction potential. Considering NaCl, the interaction potential between a pair of ions $\mu, \nu (= 1, 2 \text{ or } +, -)$ with charges $\pm e$, separated by a distance R, will be chosen in the form

$$\varphi_{\mu\nu} = (-1)^{\mu+\nu}\frac{e}{l_0}y^{-1}\left(\frac{l}{R}\right) + \left\{A_{\mu\nu}e^{-x_{\mu\nu}y} - A_m^{\mu\nu}y^{-m}\left(\frac{l}{R}\right)^m - A_{m_1}^{\mu\nu}y^{-m_1}\left(\frac{l}{R}\right)^{m_1}\right\}, \tag{3}$$

where l_0 is the shortest distance between unlike ions at $p = T = 0$; l_{10} denotes the shortest distance between like ions under the same conditions; in the braces the first term describes exponential repulsion, and the two following terms the van der Waals attraction ($m = 6,\ m_1 = 8$). The van der Waals attraction plays a comparatively small role and is not taken into account at first. The repulsive potential is determined by means of [2,3]

$$A_{\mu\nu} = \xi C_{\mu\nu} B \exp\left\{\frac{r_\mu + r_\nu}{\rho}\right\}\exp\left\{-\frac{l_{\mu\nu}}{\rho}\right\}, \tag{4}$$

where r_- and r_+ are the ionic radii; the Pauling coefficients are $C_{+-} = 1,\ C_{--} = 0.75,\ C_{++} = 1.25$. The factor $\xi \sim 1$ is chosen so that the pressure at $T = 0,\ y = l_0/l = 1$ vanishes.* The values of the remaining constants [3] are

$$\begin{gathered} r_- = 1.81\cdot 10^{-8}\text{ cm}, \quad r_+ = 0.98\cdot 10^{-8}\text{ cm}, \quad \rho = 0.345\cdot 10^{-8}\text{ cm}, \\ B = 0.23\cdot 10^{-12}\text{ erg}, \quad e = 4.8025\cdot 10^{-10}\text{ CGSE}, \quad l_0 = 2.81\cdot 10^{-8}\text{ cm}, \\ x = \frac{l_{0+-}}{\rho} = \frac{l_0}{\rho}, \quad x_1 = \frac{l_{0--}}{\rho} = \frac{l_{10}}{\rho}, \quad z_1 = 1.748, \quad z = 6, \quad \bar{z} = 12. \end{gathered} \tag{5}$$

In (5) z_1 is the Madelung constant; z and $\bar{z}$ are the numbers of nearest and next-nearest neighbors. With the aid of (3)–(5), the Grüneisen parameter (2) takes the form

$$\gamma = \frac{xy\left(1-\frac{2}{xy}-\frac{2}{x^2y^2}\right)A_{+-}e^{-xy} + \frac{\bar{z}}{z}x_1y\left(1-\frac{2}{x_1y}-\frac{2}{x_1^2y^2}\right)A_{Me}^{-x_1y}}{6\left\{\left(1-\frac{2}{xy}\right)A_{+-}e^{-xy} + \frac{\bar{z}}{z}\left(1-\frac{2}{x_1y}\right)A_{Me}^{-x_1y}\right\}}, \tag{6}$$

$$A_M = M\left(\frac{A_{--}}{M_-} + \frac{A_{++}}{M_+}\right), \qquad M = \frac{M_+M_-}{M_+ + M_-}. \tag{7}$$

Since in (2) and (6) the Coulomb terms make no contribution, calculations were carried out taking into account the van der Waals forces between unlike ions. The quantities A_m and A_{m_1} were chosen, in accordance with Mayer' s estimates (see [2]), equal to

$$A_6 = \frac{C}{z_6^{+-}l_0^{16}}, \qquad A_8 = \frac{D}{z_8^{+-}l_0^{18}}, \qquad C = 1.8\cdot 10^{-56}\text{ erg}\cdot\text{cm}^6, \quad D = 1.8\cdot 10^{-74}\text{ erg}\cdot\text{cm}^8, \tag{8}$$

where the lattice sum is denoted by z_n^{+-},

$$z_n^{+-} = \sum_{\text{h}}\left(\frac{l}{R_{12}^{\text{h}}}\right), \qquad z_6^{+-} = 6.595, \quad z_8^{+-} = 6.146, \quad z_{10}^{+-} = 6.041. \tag{9}$$

* In reality it should be equal to the zero-point-vibration pressure with the opposite sign. Since the latter is small, this is immaterial for our purposes.

Let us introduce the notation

$$\Delta\gamma_{\text{zn}} = -\frac{m(m-1)}{\chi^2}\frac{z_{m+2}^{+-}}{z}A_m y^{-(m+2)} - \frac{m_1(m_1-1)}{\chi^2}\frac{z_{m_1+2}^{+-}}{z}A_{m_1}y^{-(m_1+2)},$$

$$\Delta\gamma_{\text{ch}} = -\frac{(m+2)m(m-1)}{\chi^2}\frac{z_{m+2}^{+-}}{z}A_m y^{-(m+2)} - \frac{(m_1+2)m_1(m_1-1)}{\chi^2}\frac{z_{m_1+2}^{+-}}{z}A_{m_1}y^{-(m_1+2)}; \tag{10}$$

Figure 1

Figure 1: Figure 1

then the formula for the Grüneisen parameter (2), taking into account the van der Waals forces, takes the form

$$\gamma = \frac{\chi y\left(1-\frac{2}{\chi y}-\frac{2}{\chi^2 y^2}\right)A_{+-}e^{-\chi y}+\frac{\bar{z}}{z}\chi_1 y\left(1-\frac{2}{\chi_1 y}-\frac{2}{\chi_1^2 y^2}\right)A_M e^{-\chi_1 y}+\Delta\gamma_{\text{ch}}}{6\left\{\left(1-\frac{2}{\chi y}\right)A_{+-}e^{-\chi y}+\frac{\bar{z}}{z}\left(1-\frac{2}{\chi_1 y}\right)A_M e^{-\chi_1 y}+\Delta\gamma_{\text{zn}}\right\}}. \tag{11}$$

In Fig. 1 the Grüneisen parameter is shown, calculated according to (6), (11); according to (6), but taking into account repulsion only between nearest unlike neighbors, and the parameters corresponding to the Bridgman data ([4]); the experimental γ, determined in ([5]). For comparison, the Grüneisen parameters for NaCl are also given there, calculated by the known Landau-Slater and Dugdale-MacDonald formulas ([5]). The Grüneisen parameter determined by formula (2) ((6), (11)) may be regarded as the "high-frequency parameter" of Grüneisen, since the mean-square frequency (1) is determined mainly by high frequencies. It differs appreciably from the "low-frequency parameter"of Grüneisen, for which γ according to Landau-Slater may be adopted. Both types of γ differ from the experimental γ.

Fig. 1. Dependence of the Grüneisen parameter of NaCl on the relative volume. 1 —experimental Grüneisen parameter ([5]); 2 —Grüneisen parameter determined by the Landau-Slater formula ([5]); 3 —Grüneisen parameter determined by the Dugdale-MacDonald formula ([5]); 4 —Grüneisen parameter determined by (6); 5 —Grüneisen parameter determined by (6), but taking into account repulsion only between nearest neighbors; 6 —Grüneisen parameter determined by (11) with account of van der Waals forces; 7 —the quantity G for NaCl.

We therefore come to the conclusion: the hope that the Grüneisen parameter "does not depend on frequency" (see the footnote on p. 302), as was assumed at the initial stages in the study of equations of state, must be abandoned. This makes the question of the experimental and theoretical investigation of γ at high pressures one of the principal ones. Let us note at once that the theoretical determination of γ promises to be very difficult, since the Grüneisen parameter is sensitive to the choice of the potential.

Item 3. In Fig. 1 the quantity G is presented

$$G = \frac{\mathcal{P}_\gamma}{\Gamma_1}, \qquad \gamma = \gamma^0(1+\Gamma_1), \qquad p_\Gamma = p_{\Gamma_0}(1+\mathcal{P}_\gamma),$$

$$\mathcal{P}_{\gamma} = \left\{1 - \frac{\gamma_0(1-x)}{2x}\right\}^{-1} \left(1 - \frac{p_0}{p_{\Gamma_0}}\right) \Gamma_1. \tag{12}$$

In (12), p_T and p_0 are, respectively, the theoretical shock adiabat and the zero isotherm; f_γ^0 is the error in the theoretical shock pressure caused by the error Γ_1 in the Grüneisen parameter γ^0 adopted in the calculation. We see that for such a "soft"substance as NaCl, $G \sim 0.2$ at $x = 0.6$ and $p_0 \sim 4{\cdot}10^5$ atm, and it increases comparatively slowly as x decreases. On the other hand, for such a poorly compressible substance as copper, at $x = 0.6$ ($p_0 > 2 \cdot 10^6$ atm), $G \sim 0.425$ and increases sharply as x decreases. Taking into account that electronic excitations in Cu, Ag, and Au make a relatively small contribution to the shock pressure, and that this contribution can be very well estimated theoretically, as well as the exponential decrease of the anharmonicity (see below), one may suppose that the shock adiabats of noble metals in the high-pressure region can be successfully used to investigate the Grüneisen parameter with the aid of experimental data.

Item 4. The contribution to the free energy F, proportional to T^2 due to anharmonicity, has the form (1)

$$F_{\text{an}} = F_3 + F_4, \qquad F_3 = -\frac{9}{4} s^3 N (kT)^2 P; \qquad F_4 = \frac{9}{8} s^2 N (kT)^2 Q, \tag{13}$$

where P is a quantity determined by the third-order term in the expansion of the potential energy Φ, and Q correspondingly by the fourth-order term. The main result of the calculations may be summarized by the formula

$$P,\ Q \sim e^{\kappa y}, \tag{14}$$

where κ is a certain average exponent in the repulsive potential; $y = x^{1/3}$ is the relative lattice constant. Qualitatively, result (14) may be obtained as follows:

$$P \sim \frac{\left|\Phi^{\text{III}}\right|^2}{(\bar{\omega}^2)^3}, \qquad Q \sim \frac{\Phi^{\text{IV}}}{(\bar{\omega}^2)^2}, \tag{15}$$

where Φ^{III}, Φ^{IV} are the third and fourth derivatives of the potential energy; $\bar{\omega}^2$ is the mean square frequency (1). $\bar{\omega}^2$ is proportional to the second derivative of the potential, Φ^{III} to the third derivative, and Φ^{IV} to the fourth derivative. However, already in the second derivative the exponential term becomes predominant, not to mention the higher derivatives. Hence (14) immediately follows. It follows from (14) that the anharmonicity of crystals with exponential repulsion decreases rapidly as the volume decreases. Connected with this is the fact that, if one introduces an "anharmonic analogue" of the Grüneisen parameter γ_a, it will be large:

$$\gamma_a = \left(\frac{\partial \ln F_{\text{an}}}{\partial \ln x}\right)_T \sim \frac{\kappa}{3}. \tag{16}$$

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CITED LITERATURE

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