CALCULATION OF THE GRÜNEISEN COEFFICIENT

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The analysis and interpretation of experimental data relating to the static and shock compression of solids, as well as a theoretical description of their behavior under pressure, is connected in an essential way with the determination of the Grüneisen coefficient. Calculation of the Grüneisen coefficient from equations of state or from shock adiabats is usually done with the aid of model representations for the bonding forces in the given material [1, 2]. It is desirable, when studying materials with a complicated internal structure, as in the case of alloys, composite materials, and rocks, to determine the Grüneisen coefficient independently of specified representations for the bonding forces. In this paper we calculate the Grüneisen coefficient from static and shock compression data directly without using specific physical models.

In obtaining expressions for the Grüneisen coefficient we employ formulas relating the first, second, and third derivatives of the shock adiabat $p_H(V)$ and the isentrope $p_S(V)$ at an equilibrium point V_0 (see [3, 4]):

$$p'_H(V_0) = p'_S(V_0), \quad p''_H(V_0) - p''_S(V_0); \tag{1}$$

$$p'''_H(V_0) + \frac{\gamma_0}{2V_0} p''_H(V_0) = p'''_S(V_0), \tag{2}$$

where γ_0 is the Grüneisen coefficient of the unperturbed material.

Our calculation of the quantity γ_0 is based on an expression which follows from Eqs. (1) and (2):

$$\gamma_0 = 2V_0 \left(\frac{p'''_S(V_0)}{p''_S(V_0)} - \frac{p'''_H(V_0)}{p''_H(V_0)} \right). \tag{3}$$

In expression (3) the shock adiabat $p_H(V)$ is represented by the formula

$$p_H(V) = \frac{C^2 (V_0 - V)}{[V_0 - \lambda (V_0 - V)]^2}, \tag{4}$$

which corresponds to a linear dependence of the shock wave speed D on the particle velocity U

$$D = C + \lambda U. \tag{5}$$

For the isentrope $p_S(V)$ we employ the expressions

$$p_S(V) = \frac{2E_0\alpha}{3V_0} \left(\frac{V_0}{V}\right)^{2/3} \left[\exp 2\alpha \left(1 - \left(\frac{V}{V_0}\right)^{1/3}\right) - \exp \left(1 - \left(\frac{V}{V_0}\right)^{1/3}\right) \alpha\right]; \tag{6}$$

$$p_S(V) = \frac{E_0 n (n-1)}{V_0} \left[\left(\frac{V_0}{V}\right)^{n+1} - \left(\frac{V_0}{V}\right)^{n}\right], \tag{7}$$

corresponding to the Morse formula [Eq. (6)] and the Lennard-Jones formula [Eq. (7)]; E_0 and V_0 are the internal energy and the volume of the material under normal conditions; α and n are parameters characterizing the bonding forces in the material. If now we invoke the relation

$$\lambda = (\alpha + 2)/4 = (n + 1)/2,$$

obtained with the aid of the Eqs. (1), (6), and (7), we obtain, in the case of Eq. (6),

$$\gamma_0 = (25\alpha^2 + 36\alpha - 92)/(36\alpha + 72) \tag{8a}$$

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TABLE 1

Material	α	n	γ_0 from (8a)	γ_0 from (9a)	γ_{0T}
Li	2,34	1,67	0,83	1,01	0,89
Na	2.91	1,89	1,27	1,33	1.31
Al	3,48	2,20	1,70	1,81	2,14
K	2,84	1,96	1,47	1,44	1,34
Ti	3,49	2,21	1,71	1,82	1.28
V	3,53	2,24	1,74	1,87	1,38
Fe	3,91	2,40	2,02	2,10	1,70
Co	3,74	2.33	1,90	1,99	1,95
Ni	3,89	2,41	2,01	2,12	1,83
Cu	4,02	2,45	2,10	2,18	1,96
Zn	5,07	2,92	2,88	2.88	2,03
Rb	3,32	2,02	1,58	1,52	1,85
Y	3,10	2,03	1,41	1,54	1,00
Mo	4,28	2,57	2,30	2.36	1,61
Ag	4,56	2,70	2,50	2,35	2,43
Sn	3,82	2,36	1,96	2,04	2,22
La	2,53	1,77	0,98	1,15	0,66
Au	4,55	2,74	2,50	2,61	3,06
Pb	4,62	2,71	2,55	2,56	2,74
Th	3,01	1,99	1,34	1,48	1,34

TABLE 2

Material	λ	γ_0 from (8b)	γ_0 from (9b)	γ_{0T}
LiF	1,6	2,39	1.80	1,63
LiCl	1,5	2,09	1.50	1,81
LiBr	1,4	1,79	1.20	1,94
NaF	1,42	1,85	1.26	1,51
NaCl	1,37	1,70	1.11	1,62
NaBr	1,30	1,49	0.90	1,65
KCl	1,53	2,18	1,59	1,49
KBr	1,53	2,18	1.59	1,50
PbCl	1,50	2,09	1.50	1,39
PbBr	1,56	2.27	1.68	1,42

or

$$\gamma_0 = (25\lambda^2 - 16\lambda + 4)/9\lambda; \tag{8b}$$

in the case of Eq. (7)

$$\gamma_0 = (3/2)(n - 1) \tag{9a}$$

or

$$\gamma_0 = 3(\lambda - 1). \tag{9b}$$

This approach makes it possible to consider the first and subsequent derivatives with respect to the volume of the equilibrium Grüneisen coefficient, viz., γ_0', γ_0'', etc., expressions for which are obtained from formulas connecting the higher-order derivatives of $p_H(V)$ and $p_S(V)$ at the point V_0 (see [4]). From the quantities γ_0', γ_0'', etc. we can determine, with the required accuracy, the dependence of the Grüneisen coefficient on the volume with the aid of the expansion

$$\gamma(V) = \gamma_0 + \gamma_0'(V - V_0) + \frac{1}{2}\gamma_0''(V - V_0)^2 + \ldots.$$

We calculated the Grüneisen coefficients for 20 metals using static compression data and the formulas (8a) and (9a). In our calculations we determined the parameters α and n from experimental isotherms of static compression, which were measured in [5-7] with pressures up to 45 kbar. In treating the experimental points by means of Eqs. (6) and (7) we replaced the quantity E_0 by the free energy corresponding to isothermal compression of the undeformed material from [8] while the values of α and n were taken to be the same on the isentrope and the isotherm. As to the accuracy of these approximations we note, in particular, the agreement to within several percent of the bulk modulus K_0, calculated from Eqs. (6) and (7), with the experimental values given in [9]. The fact that we can use the isothermal values of α and n in the Eqs. (6) and (7) is corroborated by the proximity of the adiabatic and isothermal derivatives of the bulk modulus with respect to the pressure, viz., K_0' (see [10]), the latter being connected with the parameters α and n through the relations $K_0' = 2n + 1$, $K_0' = \alpha + 1$.

The calculated values of the parameters α and n, along with the Grüneisen coefficients γ_0 determined from them, are displayed in Table 1. Presented also in this table are the values of γ_{0T}, obtained from the thermodynamic definition of the Grüneisen coefficient (see [11]). It is evident from Table 1 that for the majority of the metals the quantities γ_0 and γ_{0T} agree well with one another. One of the reasons for the noticeable deviation in the cases of Ti, Zn, Y, and Mo is, apparently, the insufficient accuracy of the linear relation (5); one can expect that by taking into account the quadratic term in the D versus U relation the agreement with experiment will be improved (see [12]).

We remark that the use in [5, 7] of polynomial expressions for calculating the Grüneisen coefficient instead of expressions (6) and (7) leads to negative values for γ_0. This is due to the fact that a three-term polynomial does not afford sufficient accuracy for calculating the third derivative of the pressure.

We used shock compression data and formulas (8b) and (9b) to calculate the Grüneisen coefficient for ten ionic crystals. For the parameter λ, in the case of lithium and sodium compounds, we took the experimental values from [1] (from [13] for NaF); in the case of potassium and rubidium compounds, for which the phase transition from a B1 lattice to a B2 lattice was investigated, we employed the theoretical values for the B1 phase calculated in [2, 13]. The parameters λ from [1, 2, 13, 14], as well as the values of γ_0 calculated from them, are shown in Table 2 along with the γ_{0T} values from [2, 14]. As can be seen from Table 2, there is a good correlation between the values of γ_0 and the thermodynamic values of γ_{0T}.

Comparison shown here of our calculated results with experimental data confirms the accuracy of our approach and also its potential usefulness for materials with a complex structure.

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