



Volume Dependence Of The Grüneisen Parameter And The Lindemann Law Of Melting Of Some Ionic And Partially Covalent Solids

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Abstract

Grüneisen parameter is an important physical quantity for investigating thermal and elastic properties of solids at high pressures and high temperatures. The volume dependence of Grüneisen parameter is needed to predict melting temperatures of solids at high pressures with the help of the Lindemann law. A simple linear relationship between Grüneisen parameter and pressures derivative of bulk modulus has been formulated for the entire range of compressions. Values of Grüneisen parameter have been determined for a wide range of compressions in case of NaCl, NaF, LiF, MgO, CaF₂ and SiC. The results for pressure derivative of bulk modulus based on the Holzappel equation of state have been used as input data. A comparison of the values of Grüneisen parameter at different volume compressions determined in the present study in made with the corresponding values obtained from the slopes of melting curves for the solids under study.

Keywords : Grüneisen parameter, pressure derivative of bulk modulus, Lindemann law of melting, ionic and partially covalent binary solids, slopes of melting curves

1. Introduction

The Grüneisen parameter γ is related to thermal and elastic properties of materials (Anderson, 1995; Stacey and David, 2004) as follows

$$\gamma = \frac{\alpha K_T V}{C_V} \quad (1)$$

$$= \frac{\alpha K_S V}{C_P} \quad (2)$$

where α is thermal expansivity,

$$\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)_P \quad (3)$$

also known as volume thermal expansion coefficient. K_T and K_S are isothermal and adiabatic bulk moduli given below

$$K_T = -V \left(\frac{dP}{dV} \right)_T \quad (4)$$

and

$$K_S = -V \left(\frac{dP}{dV} \right)_S \quad (5)$$

where P, V, T and S are thermodynamic variables viz. pressure, volume, temperature and entropy, respectively.

In the present study we determine values of Grüneisen parameter γ at different volume compressions (V/V_0) for NaCl, NaF, LiF, MgO, CaF₂, SiC. We develop a new linear relationship between γ and K' , the pressure derivative (dK/dP) of bulk modulus. The results for P, K and K' have been obtained using the Holzapfel adapted polynomial of second order (AP2) equation of state (EOS) (Holzapfel, 1998). We use the generalized free volume theory for determining γ (Stacey, 2005).

2. Method of Analysis

The Grüneisen parameter γ can be determined for materials at different values of volume compression using the generalized free volume formula (Anderson, 1995)

$$\gamma = \frac{\frac{K'}{2} - \frac{1}{6} - \frac{f}{3} \left(1 - \frac{P}{3K} \right)}{1 - 2f \frac{P}{3K}} \quad (6)$$

Values of pressure P, bulk modulus K and pressure derivative of bulk modulus are determined using an equation of state (EOS). f is known as free volume parameter. Different formulations (Barton and Stacey, 1985; Dugdale and MacDonald, 1953; Slater, 1939; Vashchenko and Zubarev, 1963) were developed for γ by taking different values of f equal to 0, 1, 2 and 2.35.

The volume of a solid decreases under the effect of pressure. The volume ratio V/V_0 decreases i.e. the volume compression is increased. Pressure P and bulk modulus K both increase at high compressions. In the limit of extreme compression ($V \rightarrow 0$), P and K both become infinitely large, but their ratio remains finite (Knopoff, 1963)

$$\left(\frac{P}{K} \right)_\infty = \frac{1}{K'_\infty} \quad (7)$$

where K'_∞ is the value of pressure derivative of bulk modulus in the limit of infinite pressure or extreme compression. It has been found (Stacey and Hodgkinson, 2019) that K' decreases continuously with the increase in pressure, and attains a minimum positive value, $K'_\infty = 5/3$, in the limit of infinite pressure. The Holzapfel EOS is based on the Thomas-Fermi electron gas model for which $K'_\infty = 5/3$. We note from Eq.

(6) and γ depends on P/K and K' . There exists a simple linear relationship between reciprocal k -prime and the ratio P/K (Stacey and David, 2004)

$$\frac{1}{K'} = A + B \frac{P}{K} \quad (8)$$

Applying the boundary conditions at $P = 0$ and $P \rightarrow \infty$, we get

$$A = \frac{1}{K'_0} \quad (9)$$

and

$$B = K'_\infty \left(\frac{1}{K'_\infty} - \frac{1}{K'_0} \right) \quad (10)$$

In view of equations (6) and (8), we can conclude that γ and K' both are related linearly with each other.

3. Results and Discussion

The linear relationship between γ and K' can be written as follows (Shanker et al., 2017)

$$\gamma = mK' + C \quad (11)$$

where m and C are constants for a given material. Eq. (11) at $P = 0$ becomes

$$\gamma_0 = mK'_0 + C \quad (12)$$

At infinite pressure

$$\gamma_\infty = mK'_\infty + C \quad (13)$$

Equations (12) and (13) give

$$m = \frac{\gamma_0 - \gamma_\infty}{K'_0 - K'_\infty} \quad (14)$$

and

$$C = \gamma_0 - K'_0 \left(\frac{\gamma_0 - \gamma_\infty}{K'_0 - K'_\infty} \right) \quad (15)$$

Values of m and C for each material can be determined using the input parameters given in Table 1. Values of K' as a function of V/V_0 have been determined recently by Solanki et al. (2024). We can thus determine γ versus V/V_0 with the help of Eq. (11) taking K' at different values of V/V_0 . The results for γ versus V/V_0 for different solids are given in Figure 1. The results thus obtained are compared with the values based on experimental melting data. According to the Lindemann law of melting we can write

$$\frac{d \ln T_m}{d \ln V} = -2 \left[\gamma - \frac{1}{3} \right] \quad (16)$$

which can also be written as

$$\frac{1}{T_m} \frac{dT_m}{dP} = \frac{2\left(\gamma - \frac{1}{3}\right)}{K} \quad (17)$$

Equation (17) can be used to determine γ from the slopes of melting curves based on the experimental data. These are shown by data points in Figure 1 for six binary solids. The good agreement between the calculated and experimental values reinforces the validity of γ and K' linear relationship.

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Table 1: Values of input parameters for six binary solids (Sunil et al, 2024). $K'_\infty = 5/3$, $\gamma_\infty = 1/2$ for all the solids.

Parameters	NaCl	NaF	LiF	MgO	CaF2	SiC
K_0 (GPa)	24.0	46.5	66.5	162	81.7	241
K'_0	5.35	5.28	5.30	4.15	5.22	2.84
γ_0	1.59	1.72	1.63	1.54	1.90	1.06

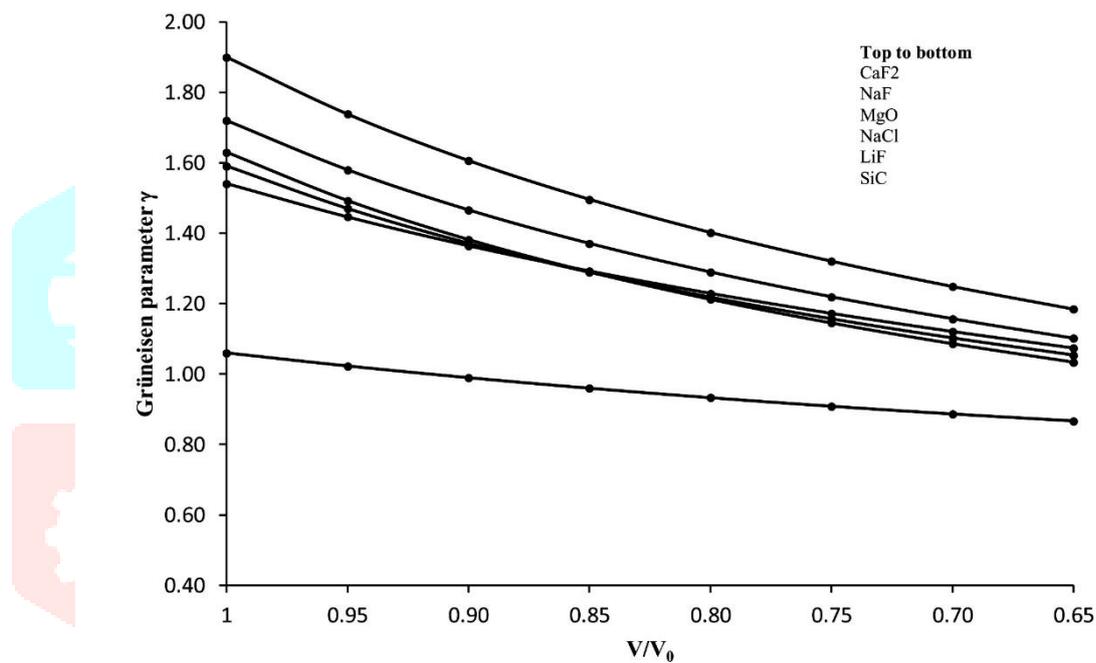


Figure 1: Plots of Grüneisen parameter γ vs. volume compression V/V_0 for six binary solids. The experimental values determined from the slopes of melting curves (Sunil et al, 2024) are shown by the symbol (\bullet).