

Anharmonicity in isochoric heat capacity for Mg_2SiO_4

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An expression has been formulated to find the values of volume dependence of isochoric heat capacity (C_V). It is employed on Mg_2SiO_4 . It has been found that isochoric heat capacity decreases strongly with increase in compression or pressure. Anharmonicity on C_V for solid under present investigation has been seen above 1500 K under low compression. However, at low temperature, for both low and high compression, and at high temperature under high compression, quasi-harmonic effects are visible. Under high compression, beyond 1200 K the C_V increases slowly monotonically with the temperature. It attains peak value at/around Debye temperature. With increasing compression, the curves become steeper. At high temperatures, C_V under high compressions depart from that estimated by the Dulong-Petit theory.

Keyword: Isochoric heat capacity, Types of materials, Anharmonicity, Quasi-harmonic

1 Introduction

The Gruneisen parameter (γ), first introduced by Gruneisen¹, relates thermal and mechanical properties of a solid and determines the pressure response of a solid to thermal energy. It has been found to be useful tool in describing the equation of state and other substances in condensed phase and molecular vibrations in solids^{2,3}. A new interest has been revived in the study of the Gruneisen parameter since the work of Anderson⁴ who demonstrated its importance in the theory of temperature dependence of bulk modulus. The Gruneisen parameter (γ) as a measure of anharmonicity of molecular vibrations is of present interest as it is a very useful parameter in describing wide variety of properties in geophysics and condensed matter physics. The anharmonicity of various parameters can be qualitatively and quantitatively described in terms of thermal energy and thermal pressure, treated as useful fundamental thermodynamic parameters⁵. Then, the Gruneisen parameter (γ) may be (C_V) treated as a simple ratio of these two basic thermodynamic parameters, involving the isochoric heat capacity (C_V). Isochoric heat capacity (C_V) is an important thermodynamic parameter to interpret the anharmonicity in any solid. The quasi-harmonic and anharmonic effects play an important role in condensed matter physics and geophysics both at the theoretical and experimental levels. Isochoric heat capacity (C_V) of solids is well explained in terms of the harmonic

vibrations of the atomic oscillators⁶⁻⁹. Anharmonicity in the isochoric heat capacity (C_V) has been reported^{2,3,10}. The anharmonicity also causes the existence of soft modes which provide the mechanism for displacive phase transitions¹¹. In quantum crystals, the role of anharmonicity is even more important for a reasonable description of the crystals^{12,13}. Recently, the isochoric heat capacity (C_V) of several one-dimensional classical and quantum potentials was analyzed by Pizarro *et al.*¹⁴. The isochoric heat capacity (C_V) of simple harmonic oscillators of two-level, n -level and infinite number of levels were investigated in more detail by Styer¹⁵. Depending on mineral, the high temperature anharmonic corrections to isochoric heat capacity (C_V) become significant either near the melting point or even at the room temperature¹⁶⁻²⁰.

In this paper we examine to discuss the quasi-harmonic effects and its application. Its application, limited to a certain temperature ranges before anharmonic effects become non-negligible. The quasi-harmonicity is a simple yet effective approximation to thermodynamics properties of minerals. Its effectiveness has become more apparent with the advent of first-principles phonons²¹. This approximation treats phonons as if they did not interact, as a phonon "gas". The system becomes equivalent to a collection of independent harmonic oscillators. As is, the statically constrained quasiharmonicity is a very effective property to study the isochoric heat capacity of solids at low temperatures but not at high temperatures where phonon-phonon interactions, or anharmonic effects, are important. At

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high T , such as near-melting temperatures, the dynamics of ions is more appropriately treated by classical Molecular Dynamics²². The Debye temperature (θ_D) is the conventional upper limit of applicability of the quasi-harmonicity. When C_V at some high temperature exceeds Dulong and Petit limit, $3 pR$ the solid is said to be anharmonic in behaviour. When C_V approaches $3 pR$ as a limit, the solid is said to be quasi-harmonic²³. In the present paper, we formulate the relationship to compute the pressure or volume dependence of isochoric heat capacity. Mg_2SiO_4 is used to testify the present model. Mg_2SiO_4 has been found to be an important material as well as geophysical mineral²⁴. It is one of the few materials for which sufficient data of its properties are available. The wide range of stability in temperature- pressure space and the fact that it is regarded as a major component of the Earth lower mantle makes Mg_2SiO_4 as a special versatile material for the present investigation. We analyse the quasi-harmonic and anharmonic effects in isochoric heat capacity of Mg_2SiO_4 .

2 Formulation For Isochoric Heat Capacity

The Gruneisen parameter (γ) is usually defined by the relation²⁵:

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

where αK_T , V and C_V are respectively the volume thermal expansivity, isothermal bulk modulus, volume and isochoric heat capacity.

Using Eq. (1), Stacey and Davis²⁶ have given the following thermodynamic identity:

$$\left(\frac{\partial \ln C_V}{\partial \ln V} \right)_T = \delta_T - K'_T + 1 - q \quad \dots (2)$$

where δ_T , K'_T and q are respectively the isothermal Anderson-Gruneisen parameter, first order pressure derivative of isothermal bulk modulus and second Gruneisen parameter. All these parameters are defined as:

$$\delta_T = - \frac{1}{\alpha K_T} \left(\frac{\partial K_T}{\partial T} \right)_P \quad \dots (3)$$

$$K'_T = \left(\frac{\partial K_T}{\partial P} \right)_T \quad \dots (4)$$

in which K_T is the isothermal bulk modulus, defined as:

$$K_T = -V \left(\frac{\partial P}{\partial V} \right)_T \quad \dots (5)$$

and

$$q = \left(\frac{\partial \ln \gamma}{\partial \ln V} \right)_T \quad \dots (6)$$

Sharma and Sharma²⁷ have generalised the isothermal Anderson-Gruneisen parameter in the following manner:

$$\delta_T = \delta_{T_\infty} + (\delta_{T_0} - \delta_{T_\infty}) \left(\frac{V}{V_0} \right)^m \quad \dots (7)$$

where δ_{T_0} and δ_{T_∞} are respectively the values of isothermal Anderson-Gruneisen parameter at zero and at infinite pressure. m is a dimensionless adjustable parameter²⁷. Srivastava and Sinha²⁸ have given the following relation for computing compression dependence of first order pressure derivative of isothermal bulk modulus:

$$K'_T = K'_\infty + (K'_0 - K'_\infty) \left(\frac{V}{V_0} \right)^{K'_0} \quad \dots (8)$$

where K'_0 and K'_∞ are the values of first order pressure derivative of isothermal bulk modulus at zero and at infinite pressure.

Using Eqs (2,6-8) we get:

$$\left(\frac{\partial \ln C_V}{\partial \ln V} \right)_T = \delta_{T_\infty} + (\delta_{T_0} - \delta_{T_\infty}) \left(\frac{V}{V_0} \right)^m - \left[K'_\infty + (K'_0 - K'_\infty) \left(\frac{V}{V_0} \right)^{K'_0} \right] + 1 - \left(\frac{\partial \ln \gamma}{\partial \ln V} \right)_T \quad \dots (9)$$

On integration of above equation one can get the following equation:

$$\frac{C_V}{C_{V_0}} = \left(\frac{V}{V_0} \right)^{(\delta_{T_\infty} - K'_\infty + 1)} \times \frac{\gamma_0}{\gamma} \times \exp \left[A \left(\left(\frac{V}{V_0} \right)^m - 1 \right) - B \left(\left(\frac{V}{V_0} \right)^{K'_0} - 1 \right) \right] \quad \dots (10)$$

where C_{V_0} , γ_0 are the values of isochoric heat capacity C_V and Gruneisen parameter at zero pressure, respectively and A and B are temperature dependent parameters given by following relations:

$$A = \left(\frac{\delta_{T_0} - \delta_{T_\infty}}{m} \right) \quad \dots (11)$$

$$B = \left(\frac{K'_0 - K'_\infty}{K'_0} \right) \quad \dots (12)$$

3 Results and Discussion

At infinite pressure, i.e., $P \rightarrow \infty$ or $V \rightarrow 0$, Eq.(2) becomes:

$$\delta_{T_\infty} = K'_\infty + q_\infty - 1 + C'_{T_\infty} \quad \dots (13)$$

Since at infinite pressure, i.e., $P \rightarrow \infty$ or $V \rightarrow 0$, q_∞ tends to zero²⁶ and C'_{T_∞} tends to zero²⁹, now Eq.(13) takes the following form:

$$\delta_{T_\infty} = K'_\infty - 1 \quad \dots (14)$$

Following Thomas-Fermi theory³⁰⁻³⁴, i.e., $K'_\infty = 5/3$, Eq. (14) results $2/3$ for δ_{T_∞} . The values of δ_{T_∞} for both models²⁴⁻²⁸ satisfy the constraint $0 < \delta_{T_\infty} < K'_\infty$ ³⁵.

We have proposed a simple method to investigate the volume dependence of the isochoric heat capacity C_V at high temperatures of Mg₂SiO₄ up to volume ratio 0.50. We have used the Al'tshuler *et al.* model³⁶ for computing values of volume dependence of the Gruneisen parameter which is given by following relationship:

$$\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty) \left(\frac{V}{V_0} \right)^\beta \quad \dots (15)$$

where β is a parameter suggested by Al'tshuler *et al.*³⁶ as $\beta = \gamma_0 / (\gamma_0 - \gamma_\infty)$ and γ_0 and γ_∞ are the values of Gruneisen parameter at zero pressure and infinite pressure, respectively. Many researchers³⁷⁻³⁹ used the Al'tshuler *et al.*³⁶ formula for the $\gamma(V)$ due to its simplicity and satisfies the thermodynamic constraints, i.e., $\gamma \rightarrow \text{finite}$ as $V \rightarrow 0$. Several researchers^{40,41} found $\gamma_\infty = 1/2$. Additional theoretical studies that give $\gamma_\infty = 1/2$ include, but are not limited to references⁴²⁻⁴⁷.

Nevertheless, some researchers assume $\gamma_\infty = 2/3$ as $V \rightarrow 0$ ⁴⁰. Recently many researchers^{33, 35, 49-51} also preferred $\gamma_\infty = 1/2$ over $\gamma_\infty = 2/3$. Thus in the present study we have used the value of $\gamma_\infty = 1/2$. All input parameters used in calculations are given in

Table 1 — Input parameters used in calculations

T (K)	δ_{T_0} [24]	K'_0 [24]	γ_0 [24]	c_{V_0} (J/gK) [23]	m	β
300	5.94	5.37	1.29	0.83236	2.38	1.63
400	5.58	5.40	1.21	0.97601	2.24	1.70
500	5.49	5.44	1.18	1.04818	2.21	1.74
600	5.48	5.47	1.17	1.09290	2.19	1.75
700	5.49	5.50	1.16	1.12435	2.14	1.76
800	5.47	5.54	1.15	1.14795	2.10	1.77
900	5.46	5.57	1.15	1.16694	1.98	1.77
1000	5.47	5.60	1.14	1.18315	1.80	1.78
1100	5.46	5.63	1.14	1.19724	1.66	1.78
1200	5.49	5.67	1.15	1.20951	1.27	1.77
1300	5.44	5.70	1.15	1.22051	1.24	1.77
1400	5.37	5.73	1.15	1.23083	1.24	1.77
1500	5.38	5.77	1.15	1.24010	1.24	1.77
1600	5.40	5.80	1.14	1.24895	1.24	1.77

Table 1. The presently calculated value of m are found temperature dependent, showing an improvement of previous work²⁷. The calculated values of m and β are given in Table 1. However, the calculated values are limited by the accuracies of available input data as cited in Table 1. It may be noted that the parameter m is found to decrease sharply beyond reference temperature $T = 300$ K and beyond Debye temperature about (≈ 763 K) till 1200 K. However beyond temperature 1200 K it attains a constant value. This trend of constancy of m may possibly be observed up to the melting temperature. However, due to non availability of input data on the parameters involved up to the melting temperature, this trend may be tested, which requires further investigation. Also the calculated values of β in Table 1 are found to be temperature dependent, increasing with increase temperature. It may be interesting to note that the values of β , beyond Debye temperature, are found to be almost constant. The predicted values of the volume dependence of isochoric heat capacity C_V through Equation (9) along with those values calculated by Cynn *et al.*²³ for the sake of comparison for a wide range of temperature up to 1600 K and volume ratio up to 0.50 are also shown in Fig. 1. A close examination of Fig. 1 shows that isochoric heat capacity decreases strongly as volume ratio decreases. This trend is in qualitative agreement with the experimental results of Takayanagi *et al.*⁵² and theoretically agrees with other workers^{5,23}. Figure 2 shows the plots for isochoric heat capacity versus temperature along selected volume ratios. This trend is consistent with those available data on isochoric

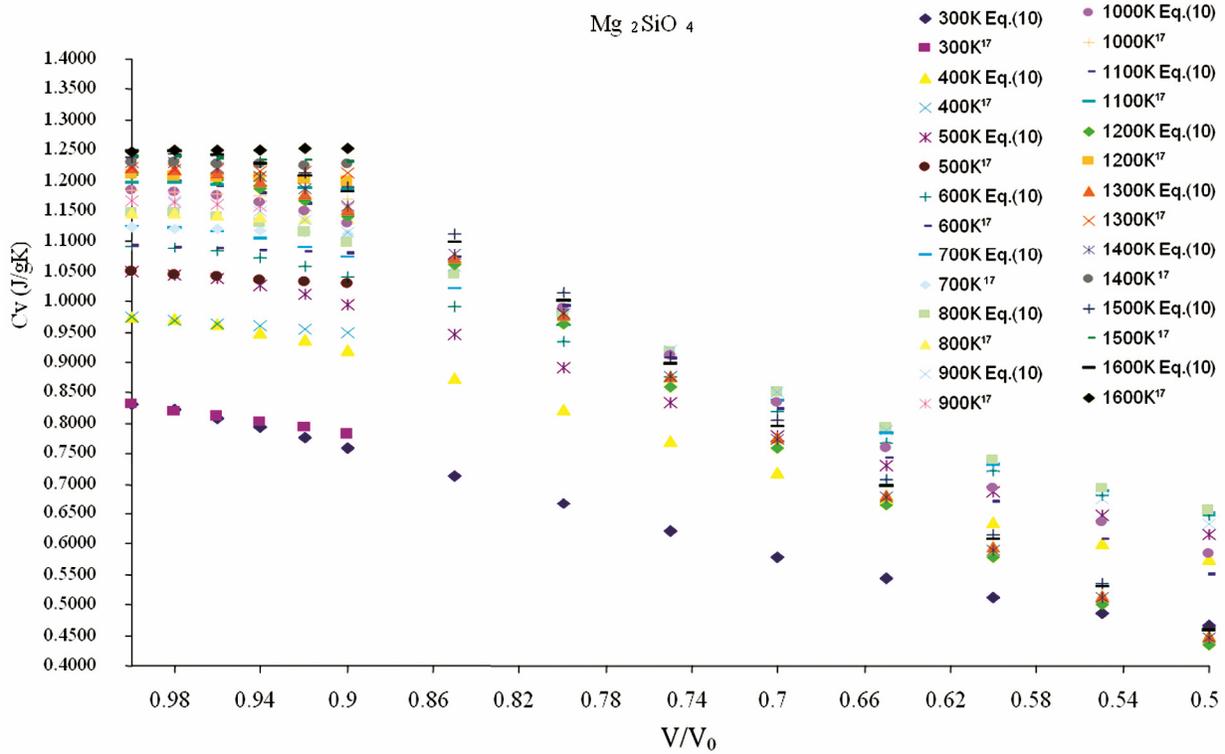


Fig. 1 — Isochoric heat capacity (C_V) vs V/V_0 at different isotherms

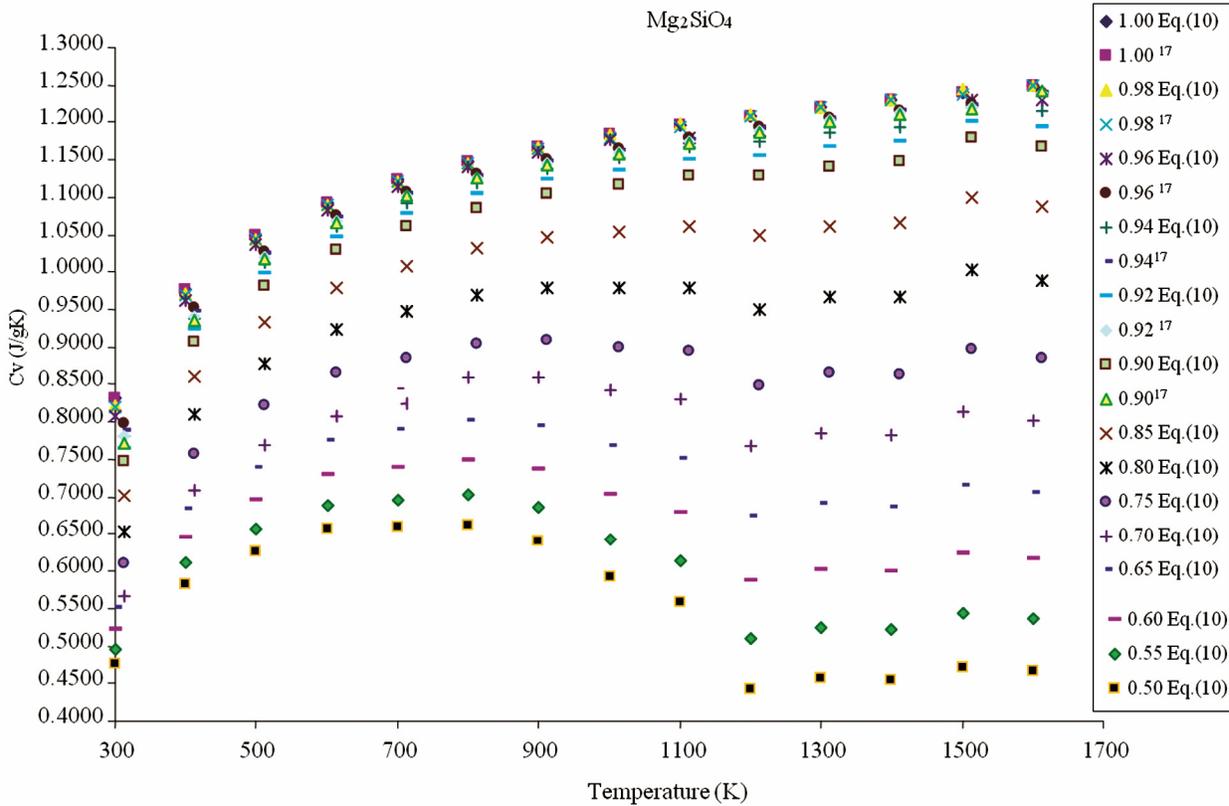


Fig. 2 — Isochoric heat capacity (C_V) vs $T(K)$ at different volume ratio

heat capacity calculated by Cynn *et al.*²³. At low temperature under high compression it attains maximum value at nearly 800 K and decreases to a minimum value at nearly 1200 K, however beyond 1200 K, it grows slowly monotonically with temperature.

It is interesting to note that C_V crosses the Dulong and Petit limit at 1500 K indicating anharmonicity above 1500 K. The present results are consistent with those data calculated by Cynn *et al.*²³. The anharmonic effects are appreciable at higher temperatures since the mean position of the oscillator moves away from its equilibrium position. Due to this reason, the isochoric heat capacity, volume thermal expansivity reflect the anharmonic effects at high temperatures. Because intrinsic temperature effects are more evident at high temperatures, the quasi-harmonic effect becomes insignificant above Debye temperature θ_D ⁵³⁻⁵⁶. Anharmonic effect is more visible at high temperatures under lower compression. However, since quasi-harmonic effects are visible below Debye temperature for both low and high values of compression, as can be seen in Fig. 2. This is in close agreement with earlier studies^{5, 54,57,58} that anharmonic effects decrease with pressure or compression and quasi-harmonic effects increase with pressure or compression.

4 Conclusions

In the present paper, an expression was formulated to study the compression dependence of isochoric heat capacity C_V for Mg₂SiO₄. C_V is found to decrease with compression strongly along isotherms. Anharmonicity on C_V for solid under present investigation has been seen above 1500 K under low compression. However, at low temperature, for both low as well as high compression and at high temperature, under high compression quasi-harmonic effects are evident thereby showing consistency with other studies⁵⁹. Above 1200 K under high compression, the heat capacity is found to increase slowly monotonically with temperature⁶⁰. At high temperatures it may be observed that the isochoric heat capacity under high compressions departs from that estimated by the Dulong-Petit theory. It attains peak value at/around Debye temperature (≈ 763 K). At low compression, the curves are flat. With increasing compression, the curves become steeper. For high compression, the curve around the peak value is steeper than that for low compression. This indicates that the smaller is the value of compression

greater is the departure of C_V from the peak value and vice-versa. It is worth mentioning here that above Debye temperature, the anharmonicity of molecular vibration may be determined primarily from the anharmonicity of isochoric heat capacity. This suggestion for intermolecular contribution to isochoric heat capacity, based on anharmonic effects, is in close agreement with the results obtained earlier^{2,3} in case of polymers, using thermo-acoustic data. However, this requires further investigations. Such a study is expected to play a significant role in developing further understanding of the influence of molecular order, structure and intermolecular interactions upon the macroscopic thermodynamic and anharmonic properties of substances in the condensed phase.

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