Analysis of temperature dependence of thermal pressure of solids

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Thermal pressure is an important physical quantity playing the central role in the evaluation of high temperature equations of state for solids. Recently, Kumar and Singh, [Indian J Phys, 78 (2004) 1225] have studied several formulations for the temperature dependence of thermal pressure demonstrating the inadequacies of the models developed by earlier researchers. It is emphasized in the present work that the method adopted by Kumar and Singh is seriously flawed and inconsistent with the recent findings. The Suzuki formulation for volume thermal expansion has been derived correctly in the present study and found to be in close agreement with the experimental data on thermal pressure for various solids considered by Kumar and Singh.

Keywords: Thermal pressure, Thermal expansivity, Equation of state
IPC Code: G01L; G01N25/04; B01J3

1 Introduction

Equation of state for a solid describes pressure-volume-temperature relationship expressed as follows:

\[ P(V,T) = P(V,T_0) + \Delta P_{th} \]  

where \( P(V,T) \) is the pressure at volume \( V \) and temperature \( T \), \( P(V,T_0) \) is the isothermal pressure-volume relationship at room temperature \( T_0 = 300K \), and \( \Delta P_{th} \) is the difference in the values of thermal pressures at temperature \( T \) and that at room temperature. Thus, we can write:

\[ \Delta P_{th} = P_{th}(T) - P_{th}(T_0) \]

Kumar and Singh\(^2\) have used the Maxwell’s thermodynamic relationship:

\[ \frac{\partial P}{\partial T} \frac{\partial \alpha}{\partial V} = -\frac{\partial P_{th}}{\partial \alpha} = \alpha K_T \]

where \( \alpha \) is the thermal expansivity and \( K_T \) is the isothermal bulk modulus. Eq. (3) can be integrated to yield:

\[ \Delta P_{th} = \int_{T_0}^{T} (\alpha K_T) dT \]

Eq. (4) has been approximately written as:

\[ \Delta P_{th} = \alpha K_T (T - T_0) \]

This equation [Eq. (3) of Ref. (2)] has been used by Kumar and Singh to calculate thermal pressures taking the values of \( \alpha \) and \( K_T \) for different solids at room temperature [given in Table 1 of [Ref. (2)]. On the basis of the results, thus, obtained, Kumar and Singh have concluded that the method based on Eq. (5) does not yield agreement with the experimental values of thermal pressure\(^3\). It should be emphasized that Eq. (5) can be derived from Eq. (4) only when the product \( \alpha K_T \) remains constant in the temperature range \( T_0 - T \). Kumar and Singh has completely ignored the variations of \( \alpha K_T \) with the change in temperature which are quite significant particularly in the temperature range from room temperature up to the Debye temperature \( \theta_D \). For the solids under study, the Debye temperature is much higher than the room temperature, the variation of \( \alpha K_T \) with temperature must have been taken into account by Kumar and Singh. For example, in case of MgO the variation of \( \alpha K_T \) with temperature is shown in Fig. 1. Thus, a constant value of \( \alpha K_T \) and that too at

<table>
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room temperature used by Kumar and Singh Eq. (5) is not valid. In the present study, we take into account this effect and then demonstrate that the results are improved and come very close to the experimental values.

The second and equally important point is regarding the Suzuki equation for volume thermal expansion. Kumar and Singh have used an incorrect formulation for the Suzuki equation. We present here the correct derivation and find that the results obtained are in close agreement with the experimental data.

### 2 Evaluation of Thermal Pressure

The variation of the product $\alpha K_T$ for MgO with temperature is shown in Fig. 1. The similar variation is found for other geophysical minerals considered by Kumar and Singh, viz. $\text{Al}_2\text{O}_3$, MgO, olivine, pyrope-rich garnet, grossular garnet. The variation of $\alpha K_T$ with $T$ is not constant for the entire range of temperature (Fig. 1). It is observed that $\alpha K_T$ can be taken as nearly constant at higher temperatures $T>\theta_D$, the Debye temperature. Thus, an appropriate method for evaluating the thermal pressure with the help of Eq. (4) is to split it as follows:

$$\Delta P_{th} = \frac{T}{\theta_D} \alpha K_T \frac{d}{dT} + \frac{T}{\theta_D} \alpha K_T \frac{d}{dT} + \ldots + \frac{T}{\theta_D} \alpha K_T \frac{d}{dT}$$

where the initial temperature $T_0 = 300K$. In Eq. (6), $\Delta P_{th}$ is split in different terms at temperature interval of 100 K. For each interval, the value of $\alpha K_T$ has been taken as an average of the two values corresponding to lower and upper limits of integration. The results for $\Delta P_{th}$ obtained from Eq. (6), are given in Table 2 and found to present extremely good agreement with

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Fig. 1 — Plot of $\alpha K_T$ at $P=0$ versus $T$ from $T=0$ to high temperatures for MgO from Anderson.
Table 2 — Comparison between the values of $P_{th}$ (GPa) for solids calculated from the Suzuki equation (Eq. 15), Eq. (6) and experimental results given by Anderson

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The experimental values. Thus, the conclusion drawn by Kumar and Singh that Eq. (4) does not yield agreement with experimental data is not correct. This demonstrates the importance of the effect arising from the variation of $\alpha K_T$ with $T$. Kumar and Singh have taken the room temperature value of $\alpha K_T$ for the entire range of temperatures which is not justified.

3 Suzuki-formulation

The Mie-Grüneisen expression for thermal pressure is given as:

$$P_{th} = \frac{\gamma}{V} E_{th}$$

where $\gamma$ is the Mie-Grüneisen parameter and $E_{th}$ is the energy arising from temperature excitation, called the thermal energy. Thus, the Mie-Grüneisen EOS is written as:

$$P = P_0(V) + \frac{\gamma E_{th}}{V}$$

Another way of representing Eq. (8) is:

$$\frac{V}{V_0} - 1 = \frac{\frac{\gamma E_{th}}{V} + \frac{\gamma E_{th}}{V}}{(K\varepsilon - 1)}$$

where $G(V)$ is a product of pressure and volume. Assuming an infinitesimal elasticity, Grüneisen eliminated $P_0$ by taking:

$$K_T \Delta V = P_0$$

where $\Delta V = V/V_0$

We then expand $G(V)$ as a Taylor’s series to the second order in $\Delta$. According to the method of Suzuki

$$\Delta E_{th} \left( \frac{\gamma}{V_{th}} \right) = \frac{k}{K_T} \Delta V - \frac{\gamma E_{th}}{V_0}$$

which is Eq. (7) in the paper by Kumar and Singh, here $Q = \frac{K_T V_0}{\gamma}$.

There is no problem up to this point, but Eqs (8) and (9) reported by Kumar and Singh are not correct. The thermal energy $E_{th}$ is changed to thermal pressure $P_{th}$ using Eq. (7).
\[
P_n = K_T \frac{3V}{V_0} - \frac{3V}{2V_0} \frac{\dot{\rho}}{\dot{\rho}_0} K_T (K_T - 1) \frac{3V}{V_0} - \frac{3V}{2V_0} \frac{\dot{\rho}}{\dot{\rho}_0} 
\]

Thus, in place of Eqs (8) and (9), we get Eqs (14) and (15). We calculate the values of thermal pressure using Eq. (15) and taking the input data on \( K_T \), \( K_T^0 \) and \( V/V_0 \) given in Table 1. The values of thermal pressure, thus, calculated for the minerals under study are found to present good agreement with the experimental data.

4 Conclusion

Our results calculated from Eqs (6) and (15) for five minerals under study give close agreement with the experimental values of thermal pressure at different temperatures\(^3\). We have shown that the approximation taken by Kumar and Singh\(^2\) that the value of \( \alpha K_T \) evaluated at \( T = 300 \) K remains the same at higher temperatures is not correct. Due to this invalid approximation, the results obtained by Kumar and Singh\(^2\) [from their Eq. (3)] deviate much from the experimental data\(^3\). We have also removed the mistake in the paper by Kumar and Singh\(^2\) in deriving the formulation for the Suzuki equation. The correct derivation for the Suzuki equation given in the present paper yields reasonably good agreement with the experimental values for all the minerals under study. It should be emphasized that the two modifications considered in the present study in the from of Eqs (6) and (15) are of fundamental importance in the theory of thermal expansively of solids.

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References