Pressure dependence of melting temperatures for alkali halides

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Melting curves representing the variations of melting temperature $T_m$ with pressure $P$ have been determined for sixteen alkali halides. The calculations have been performed using Lindemann-Gilvarry law for melting along with an expression for the volume dependence of the Grüneisen parameter. The formulation thus developed can be used to predict melting temperatures for materials at high pressures. It is found that the melting temperature increases with pressure in a non-linear manner such that the slope $dT_m/dP$ decreases continuously with the increase in pressure.

Keywords: Melting curves, Alkali halides, Lindemann-Gilvarry law, Grüneisen parameter

1 Introduction

Thermoelastic properties of solids at high temperatures provide useful insight for understanding the physical mechanisms of melting. The Grüneisen parameter $\gamma$ is a physical quantity of central importance related to thermal as well as elastic properties of solids as follows:

$$\gamma = \frac{\alpha K_T V}{C_V} = \frac{\alpha K_s V}{C_P}$$

where $\alpha$ is the thermal expansivity, $V$ the volume, $K_T$ the isothermal bulk modulus, $K_s$ the adiabatic bulk modulus and $C_V$, $C_P$ are the specific heats at constant volume and constant pressure, respectively.

In general, the melting temperature $T_m$ of solids increases with the increase in pressure. The values of $T_m$ for a solid depend on the frequencies of atomic vibrations in a solid. The pressure derivative of $T_m$, therefore, depends on the pressure derivative of vibrational frequencies or the Grüneisen parameter. The pressure derivative of $T_m$ has been derived using the Lindemann – Gilvarry law. This can be written as follows:

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

or

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

where $K_T$ is the isothermal bulk modulus.

In order to determine values of $T_m$ at different pressures or volumes, we need to know $\gamma$ as a function of pressure $P$ or volume $V$ which should be integrable analytically when used in the Lindemann-Gilvarry law. For this purpose, we take the expression obtained by Srivastava et al. for the reciprocal of $\gamma$ as a function of volume. First we calculate values of $T_m$ at different volumes, and then they are transformed to the corresponding values at different pressures with the help of the Stacey reciprocal K-primed equation of state (EOS). It is found that the Lindemann-Gilvarry law gives $dT_m/dP$ which decreases continuously with the increase in pressure. This finding is consistent with the vacancy model for melting developed by Ksiazek and Gorecki.

2 Method of Analysis

Srivastava et al. have presented the following formulation for the volume dependence of the Grüneisen parameter:

$$\frac{1}{\gamma} = \frac{1}{\gamma_0} + \left( \frac{1}{\gamma_0} - \frac{1}{\gamma_-} \right) \left( \frac{V}{V_0} \right)^n$$

where $n$ is a constant for a given material. $\gamma = \gamma_0$ at $P = 0$, or $V = V_0$ and $\gamma_-$ is the value of $\gamma$ at infinite pressure. $\gamma_-$ is a positive and finite physical quantity. On differentiating Eq. (4), we get the following expression:

$$\frac{-q}{\gamma} = n \left[ \frac{1}{\gamma} - \frac{1}{\gamma_-} \right]$$
where \( q = (d \ln \gamma / d \ln V)_T \) is the second-order Gr"uneisen parameter. At \( P = 0 \), Eq. (5) gives:

\[
T_n = \frac{q_0 \gamma_m}{(\gamma_0 - \gamma_m)} \quad \text{(6)}
\]

At \( P \) tends to infinity, \( \gamma \to \gamma_\infty \), and therefore from Eq. (5) we have \( q_m \to 0 \). Now on differentiating Eq. (5), we get:

\[
\frac{q}{\gamma_\infty} \frac{d}{dV} \frac{d\gamma_\infty}{dV} = -\frac{n}{\gamma_\infty} \frac{d\gamma}{dV} \quad \text{(7)}
\]

which yields

\[
\lambda - q = n \quad \text{(8)}
\]

where \( \lambda = (d \ln q / d \ln V)_T \) is the third-order Gr"uneisen parameter. Since, at infinite pressure \( q_\infty \) tends to zero, Eq. (8) gives:

\[
\lambda_\infty = n \quad \text{(9)}
\]

where \( \lambda_\infty \), the value of \( \lambda \) at infinite pressure is positive and finite, since \( n \) is positive and finite from Eq. (6). It should be mentioned that Eqs (4-9) for \( \gamma, q \) and \( \lambda \) satisfy the thermodynamic constraints at infinite pressure\textsuperscript{16-18}. Eq. (3) can be written as:

\[
\frac{dT_m}{T_m} = -2 \frac{dV}{V} + \frac{2}{3} \frac{dV}{V} \quad \text{(10)}
\]

Using Eq. (4) for \( \gamma \) in Eq. (10), we get:

\[
\frac{dT_m}{T_m} = -2 \frac{2}{x (a + bx^n)} dx + \frac{2}{x} dx \quad \text{(11)}
\]

where \( x = V / V_0 \), \( a = 1 / \gamma \), and \( b = (1 / \gamma_0) - (1 / \gamma_\infty) \). Eq. (11) can be rewritten as follows:

\[
\frac{dT_m}{T_m} = -2 \frac{1}{a} \left[ \frac{1}{x} - \frac{bx^{n-1}}{(a + bx^n)} \right] dx + \frac{2}{3} \frac{dx}{x} \quad \text{(12)}
\]

On integrating Eq. (12), we get:

\[
\ln \frac{T_m}{T_{m0}} = \ln \left[ \frac{(a + b)^x}{(a + bx^n)} \right] \quad \text{(13)}
\]

which gives:

\[
\frac{T_m}{T_{m0}} = x^{2/3} \left[ \frac{(a + b)^x}{(a + bx^n)^{2/3n}} \right] \quad \text{(14)}
\]

where \( T_{m0} \) is the value of melting temperature at \( P = 0 \). Substituting the values of \( a, b, n \) and \( x \) in Eq. (14), we get:

\[
\frac{T_m}{T_{m0}} = \left( \frac{V}{V_0} \right)^{2/3 (\gamma_\infty - 1)^{-1}} \left[ \frac{\gamma_\infty}{\gamma_\infty^{2/3}} \right] \quad \text{(15)}
\]

where \( \gamma_\infty \) and \( \lambda_\infty \) are related to pressure derivatives of bulk modulus as follows\textsuperscript{16}

\[
\gamma_\infty = \frac{K_\infty}{2} - \frac{1}{6} \quad \text{(16)}
\]

and

\[
\lambda_\infty = \frac{K_\infty^{2/3}}{K_0^{2/3}} \quad \text{(17)}
\]

### 3 Results and Discussion

Eq. (14) is used to calculate values of \( T_m \) at different values of \( x = V / V_0 \) using the input data given in Table 1 for sixteen alkali halides\textsuperscript{19-21}. Values of pressures corresponding to given volumes at a fixed value of temperature viz. \( T_{m0} \) for each alkali halide are calculated with the help of the Stacey EOS which is given below:

<table>
<thead>
<tr>
<th>Crystals</th>
<th>( T_{m0} ) (K)</th>
<th>( \gamma_{m0} )</th>
<th>( \gamma_\infty )</th>
<th>( K_{m0} ) (GPa)</th>
<th>( K_0 )</th>
<th>( K_\infty )</th>
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<tr>
<td>LiF</td>
<td>1115</td>
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<td>1.45</td>
<td>43.4</td>
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</tr>
<tr>
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<tr>
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<td>1.51</td>
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</tr>
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</table>
\[
\ln \frac{V}{V_0} = \frac{K'_0}{K_\infty} \ln \left(1 - K'_0 \frac{P}{K}\right) + \left(\frac{K'_0}{K_\infty} - 1\right) \frac{P}{K} \quad \cdots (18)
\]

where \( K'_0 \), \( K'_0 \) and \( K_\infty \) are the values of bulk modulus at zero pressure, pressure derivative of bulk modulus at zero pressure, and pressure derivative of bulk modulus at infinite pressure, respectively. The results for melting temperatures \( T_m \) as a function of pressure \( P \) are given in Table 2 along with the volumes versus pressure for sixteen alkali halides. It

\[
K = K_0 \left(1 - K'_0 \frac{P}{K}\right)^{-K'/K_\infty} \quad \cdots (19)
\]
should be mentioned that the materials become softer at high temperatures close to the melting points. This would imply that a less amount of pressure is required at \( T = T_m \) as compared to that at room temperature in order to compress the solid by the same amount. The compressibility increases and the bulk modulus decreases with the increase in temperature. Values of \( K'_0 \) increase by about ten per cent at melting temperature as compared to the values at room temperature.

The Lindemann–Gilvarry law has been a powerful tool for determining melting temperatures of different solids at high pressures. It is evident from Eqs. (2) and (3) that \( T_m \) increases with the increase in compression or decrease in volume. This is mainly because \( \gamma \) decreases with the increase in pressure. Eq. (2) reveals that the rate of increase of \( T_m \) with \( P \) decreases at high pressures because \( \gamma \) decreases continuously with the increase in pressure. We have used the formula due to Srivastava et al. for the volume dependence of \( \gamma \). Eq. (4), in the Lindemann–Gilvarry equation, to obtain Eq. (15) for determining \( T_m \) at different values of compressions or volume ratios \( V/V_0 \). The results for \( T_m \) (Table 2) are similar to those derived from the vacancy ion model.

It should be pointed out that the melting temperature \( T_m \) becomes infinite at extreme compression (\( V \to 0, P \to \infty \)). This can be verified from Eq. (15) in the limit \( V \) tends to zero. \( \gamma \) tends to \( \gamma_m \) and \( \lambda \) tends to \( \lambda_m \), both \( \gamma_m \) and \( \lambda_m \) remain positive and finite in the limit of extreme compression. Eq. (4) for the volume dependence of \( \gamma \) satisfies the thermodynamic constraints for solids at infinite pressure. These constraints reveal that \( \gamma_0 > \gamma'_m > 0, q_m = 0, \) and \( \lambda_0 > \lambda'_m > 0 \). Eq. (15) has been derived in the present study by taking account of these constraints.

### 4 Conclusions

The present analysis of the pressure dependence of melting temperature \( T_m \) is based on the Lindemann-Gilvarry law which is derived from the Lindemann law of melting by assuming that the ratio of root mean square of vibrational amplitudes to the equilibrium value of interatomic distance remains constant, i.e. does not depend on pressure or density for a given material. The relationship for \( T_m \) as a function of volume has been determined using the reciprocal formula for the volume dependence of the Grüneisen parameter. The present formulation describes adequately some important features of melting, such as (i) \( T_m \) increases with the increase in \( P \), (ii) the slope \( dT_m/dP \) decreases with the increase in \( P \), (iii) \( T_m \) depends on the Grüneisen parameters in the limit of infinite pressures.

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### References