Properties of solids under the effect of high temperature and pressure – NaCl as an example

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A simple theoretical method is used to investigate the properties of solids under varying conditions of temperature and pressure. The case of NaCl is discussed as an example for the entire range of temperature and pressure, viz. from room temperature up to the melting temperature (1000 K) at the pressures varying from atmospheric pressure (referred as $P = 0$) up to the structural transition pressure ($P = 30 \text{ GPa}$). The results obtained for the temperature dependence of thermal expansivity are compared with those based on the widely used Suzuki equation. The results of the pressure dependence of thermal expansivity are compared with Anderson-Masuda relation. The results of Wang and Reber [Phys Chem Miner, 23 (1996) 354] are also included for the sake of comparison. The good agreement with the available theoretical as well as experimental data, supports the simple method used in the present paper.

1 Introduction

Kuswaha & Shanker\(^1\) have compiled the methods reported by earlier workers for the determination of thermal expansivity. Such efforts may be used to study the isobaric ($P = 0$) thermal expansion. Suzuki et al.\(^2\) found what became known as the Suzuki equation, which yield the change in volume $V/V_0$ as a function of temperature $T$ along the $P = 0$ isobar. The detailed analysis of Suzuki equation is available elsewhere\(^2-4\) and the mathematical form reads as follows:

$$V/V_0 = \frac{[1 + 2K - (1 - 4KE_{Th}/Q)]^{1/2}}{2K\alpha}$$  \(\ldots (1)\)

where $K = (B'_{0 r}-1)/2$ and $Q = B_0V_0/Y_0$. $B_0$ $B'_{0 r}$ are the isothermal bulk modulus and its first order pressure derivative, respectively, $Y_0$ is the Gruneisen ratio. The subscript 0 refers to their value at $P = 0$ and $T = 300 \text{ K}$. $E_{Th}$ is the thermal energy, $\alpha$ equal to one, as discussed in detail by Anderson\(^1\). Using the relation $(Y_0E_{Th}/V_0) = P_{Th}$, where $P_{Th}$ is the thermal pressure, Eq. (1) may be rewritten as follows:

$$V/V_0 - 1 = \frac{1 - \{2(B'_{0 r}-1)/B_0\}P_{Th}}{(B'_{0 r}-1)}^{1/2} \quad \ldots (2)$$

Eq. (2) may be used to determine isobaric ($P = 0$) variation of $V/V_0$ versus $T$ or the coefficient of volume thermal expansion $\alpha(T)$. The analytical expression for $\alpha(T)$ found by the differentiation of Eq. (1) is quite complicated. Therefore, the method of numerical differentiation has been suggested\(^1\). Anderson\(^3\) has discussed the limit of Suzuki equation for its applicability at high temperatures. It has been discussed\(^1\) that it yields imaginary results for NaCl at $T > 736 \text{ K}$, and therefore not capable of explaining the thermal expansivity of NaCl at $P = 0$ isobar.

Anderson & Masuda\(^5\) have developed another method for the determination of $\alpha$ under the effect of pressure $P$. The formula reads as follows:

$$\frac{\alpha}{\alpha_0} = \exp \left[ \frac{-\delta(T)(1-n^K)}{k} \right]$$  \(\ldots (3)\)

where $n = V/V_0$ and $\alpha_0$ is the value of $\alpha$ at $n = 1$ for each isotherm. $\delta(T)$ is the value of $\delta(T)$ at high $T$ and $P = 0$, $K = 1.5$. The application of Eq. (3) needs the input parameters measured along the temperature axis at $P = 0$. Thus the problem becomes much difficult when one tries to investigate the properties of solids under the varying conditions of $P$ and $T$. Thus, it is legitimate and may be useful to propose some simple method. In the present paper, an effort is made in this direction by developing a simple method. The method needs the values of input parameters at zero pressure and room temperature to
investigate the behaviour of solids under the varying conditions of pressure and temperature. NaCl is a widely studied inorganic compound, because of its simple structure, high melting temperature and structural transition pressure. For this solid a large amount of theoretical as well as experimental data are available. The author has therefore selected NaCl for the present study, so that the results may be discussed in the light of earlier studies.

2 Method of Analysis

To investigate the properties of solids under varying conditions of pressure and temperature, the theory of equation of state recently developed by Kumar & Bedi is extended. The detailed analysis is available elsewhere and the mathematical form reads as follows:

\[ \frac{V}{V_0} = 1 - \frac{1}{A} \ln \left[ 1 + \frac{A}{B_0} (P - A_0 B_0 (T - T_0)) \right] \]  
\[ \frac{B}{B_0} = \left[ \frac{1}{A} \ln \left[ 1 + \frac{A}{B_0} - A_0 (T - T_0) \right] \right] \]  
\[ \delta_T = \delta_T^0 - \ln \left[ 1 + \frac{AP}{B_0} - A a_0 (T - T_0) \right] \]  

where \( P \) is the pressure, \( T \) the temperature and \( A = (\delta_T^0 + 1) \), 0 refers to the value at room temperature and atmospheric pressure. The coefficient of thermal expansion \( \alpha \) is defined as \( \alpha = (1/V)(dV/dT)_P \). Therefore, from Eq. (4) one can get:

\[ \alpha = \frac{1}{A_0} \ln \left[ 1 + \frac{A}{B_0} - A a_0 (T - T_0) \right] \]  
\[ \{1 + \frac{A}{B_0} - A a_0 (T - T_0) \} \]  

\[ \frac{B}{B_0} = \left[ \frac{1}{A} \ln \left[ 1 + \frac{A}{B_0} - A_0 (T - T_0) \right] \right] \]  
\[ \{1 + \frac{A}{B_0} - A a_0 (T - T_0) \} \]  

The Anderson-Gruneisen parameter \( \delta_T \) is defined as:

\[ \delta_T = \delta_T^0 - \ln \left[ 1 + \frac{AP}{B_0} - A a_0 (T - T_0) \right] \]  

3 Application Results and Discussion

By making use of Eq. (4), the values of \( V/V_0 \) are investigated as a function of temperature along different isobars and reported in Fig. 1. The input data\(^3\) are: \( B_0 = 24 \text{ GPa, } \delta_T^0 = 5.56 \) and \( B_0 = 5.39 \). Using the values of \( P_0 \) from Anderson, the values of \( V/V_0 \) at different \( T \) values are computed from Suzuki relation [Eq. (2)] at \( P = 0 \) isobar. These results are reported in Fig. 1 along with the results from the data of Wang & Reeber. Most of the results obtained are available up to 700 K. The author, therefore selected 700 K as a comparison point and data for \( V/V_0 \) are reported in Table I. The results obtained in the present work are very close to the results reported by Anderson\(^3\), and Wang & Reeber\(^4\). The results obtained by Suzuki formula are slightly low. At higher temperatures, the available data of Wang & Reeber are used for comparison; a good agreement is obtained (Fig. 1). This demonstrates the effect of pressure on thermal expansion. It is found that thermal expansion is effected by pressure and it decreases as pressure is increased. Moreover, the isobar of \( P = 30 \text{ GPa} \) is almost parallel to the temperature axis. This shows that at high pressure, the effect of temperature is cancelled by the effect of pressure.

<table>
<thead>
<tr>
<th>Reported by</th>
<th>( V/V_0 )</th>
</tr>
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<tbody>
<tr>
<td>Anderson(^3)</td>
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</tr>
<tr>
<td>Wang and Reeber(^4)</td>
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</tr>
<tr>
<td>Suzuki Formula (Eq. 2)</td>
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<tr>
<td>Present work (Eq. 4)</td>
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Table I — Comparison of \( V/V_0 \) at \( T = 700 \text{ K} \) reported by earlier workers

The values of \( \alpha \) calculated using Eq. (5) are reported in Figs 2 and 3 for the entire range of \( P \) and \( T \). The results of \( \alpha \) as a function of \( P \) and \( T \) reported by Wang & Reeber\(^4\) are also given for the sake of comparison. The calculated values of \( \alpha \) at \( P = 0 \), are found to lie between the two sets of the results reported by Wang & Reeber\(^4\) and Anderson\(^3\) up to 600 K. Above 600 K, the calculated values of \( \alpha \) are found to have a more rapid increase with the values of Wang & Reeber\(^4\), but this difference becomes very small as \( P \) is increased. This rapid increase of \( \alpha \) with \( T \) at \( P = 0 \), near melting temperature is
consistently with theories of melting of alkali halides as discussed in detail by Shanker & Kumar\(^a\) showing that \(\alpha \rightarrow \infty\) at \(T \rightarrow T_M\). Anderson and Masuda have reported Eq. (3) for the determination of \(\alpha\) as a function of \(\eta\) along different isotherms. Making the use of \(\eta\) values reported by Birch\(^b\), \(\alpha_0\) (\(T\)) from Suzuki relation, and \(\delta_{\alpha}\) (\(T\)) from Anderson\(^c\), the values of \(\alpha\) are obtained along different isotherms using Eq. (3). The results thus obtained are reported in Fig. 4 along with those obtained using Eq. (5) reported in the present work. A good agreement is found. Here, it is pertinent to mention that the use of Anderson-Masuda relation [Eq. (3)] needs the values of \(\eta\) along the isotherm considered and \(\delta_{\alpha}\) \(\alpha\) measured as a function of temperature at \(P = 0\), as input data. On the other hand, Eq. (5) needs the input data at room temperature \(T = 300\) K and \(P = 0\). Thus, the application of Eq. (5) is simple as compared with Eq. (3).
The calculated values of bulk modulus as a function of $T$ at different $P$ using Eq. (6) are reported in Fig. 5. Anderson\(^8\), Wang & Reeber\(^8\) have reported the variation of bulk modulus under the effect of temperature at $P = 0$. These results are also included in Fig. 5 for the sake of comparison. A good agreement is obtained. The bulk modulus is found to decrease by increasing temperature and it
increases with increasing pressure. The decreasing behaviour of bulk modulus with increasing temperature is found to be less as the pressure increases. Along the highest pressure isobar \( (P = 30 \text{ GPa}) \) the percentage decrease the bulk modulus from 300 to 1000 K is found to be 4.58 \%, which is very small as compared with the percentage decrease (48.8 \%), along \( P = 0 \) isobar. Thus it seems that at high temperatures, the effect of temperature is cancelled by the effect of pressure. The relation investigated for \( \delta_r \) as a function of \( P \) and \( T \) [Eq. (7)] is used to predict the values of \( \delta_r \) for the entire range of \( P \) and \( T \). The results obtained are reported in Fig. 6. The temperature dependence of \( \delta_r \) at \( P = 0 \) is compared with the results reported by earlier workers\(^{18}\). At most of the temperatures, the author’s predicted values lie in between the two sets of result\(^{18}\), \( \delta_r \) is found to decrease by increasing pressure, which is consistent with the recent research in high-pressure physics as discussed in detail by Anderson\(^1\).

To summarise, the author has presented a simple method based on the knowledge of equation of state to investigate the properties of solids under varying conditions of pressures and temperatures. A good agreement with the available theoretical as well as experimental data supports the validity of the simple method. The studies have been presented for the entire range of pressure and temperature even in the absence of experimental or theoretical data. Such an analysis may be useful for those engaged in the research at high pressures and high temperatures.

References