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Pressure-induced phase transition in some alkali halides at high temperature and pressure

VASUDEV THAKRE[a], SADHNA SINGH[b*]
[a]*Sagar Institute of Science & Technology, Gandhi Nagar, Bhopal, India*
[b]*High Pressure Research Lab, Department of Physics, Barkatullah University, Hoshangabad Road, Bhopal-462026, India*

In this paper we have developed a realistic interaction potential model to study the high pressure phase transition of ionic alkali-metal compounds KCl and NaCl, having B_1 structure at room temperature. We have theoretically investigated phase transition pressure and volume collapse of KCl and NaCl at high temperature. In addition, elastic constants at different pressures were discussed, and found results well suited with available experimental data. The thermo dynamical properties of B_1 phase of KCl and NaCl were also predicted. This shows that the inclusion of temperature effect in potential model makes the present model suitable for theoretical high-pressure studies.

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1. Introduction

The $B_1 \rightarrow B_2$ structural transition in alkali chlorides has been attracting much attention for several decades [1-3]. In most of the theoretical work [3-5], since the first-principle calculations demand much CPU time and memories, the phenomenological model are playing an important role in simulations for $B_1 \rightarrow B_2$ phase transition and these models also explain interatomic forces fully. The alkali halides are the simplest ionic solids on which a lot of experimental and theoretical work has been done [6] to validate new theories. They generally crystallize in either the NaCl (B_1) or the CsCl (B_2) structure. Their elastic, dynamic and thermodynamic properties have been extensively investigated by various experimental and theoretical workers [7,8]. These solids undergo structural phase transition $B_1 \rightarrow B_2$ at elevated pressures [9]. A survey of the literature reveals that, although a large amount of experimental work has been done on the phase transition in alkali halides [10], less attention has been paid to their theoretical understanding. The structural phase transitions of KCl and NaCl were found at about 2.3 GPa and 28.8 GPa respectively. Moreover, there are no studies reported on the phase transition pressure at high temperatures. Therefore, we have devoted efforts to the structural, elastic and thermo physical properties of these compounds by taking the role of temperature.

In the present paper, we have used three body potential model including the temperature effect. This model is able to explain the Cauchy violation ($C_{12} \neq C_{44}$) in second order elastic constants. We have studied the phase transition pressure and volume change of KCl and NaCl compounds at high temperature and the second order elastic constants are also calculated. The purpose of this work is to study the structural, elastic and thermo physical properties at high temperature of KCl and NaCl compounds theoretically. The importance of three-body interactions in potential model to improve results is well established and has also been emphasized by others like Sims et al. [11], Froyen and Cohen[12], Zhang and Cohen [13] and Chelikowsky [14]. We have employed our TBIP approach [15,16] to study high-pressure behavior. The present potential model includes the long-range Columbic, three-body interaction, short-range overlap repulsive interaction operative up to second neighbor ions within Hafemeister and Flygare approach [17,18].

2. Potential model and method of calculation

It is well known that pressure causes a compression in the crystal, and consequently it alters the charge distribution of the electron shells. As a result of this, a deformation of the overlapping electron shells of the adjacent ions takes place which leads to an increased charge-transfer (or three-body interaction (TBI)) [15]. This interaction becomes more important to consider due to the decrease in inter-ionic spacing of the lattice crystal when pressure gets increased and when anions experience sufficient overlap. Besides, enhance in overlap energy the transferred charge due to the overlap in electron shells, modifies the ionic charge which modifies the coulomb energy by {1+(2n/z)}, where n and z are the number of electrons in outermost shell and ionic charge of the compound. The *f(r)* is the TBI parameter and is dependent on the nearest neighbor distance (r) as [15];

$$f(r) = f_0 \exp\left(\frac{-r}{\rho}\right) \qquad (2.1)$$

The effect of TBI is introduced in the expression of Gibbs free energy, (G = U + PV -TS), in order to obtain the stability condition for a crystal structure. Here U is the internal energy, which at T=0K is equivalent to the lattice energy, S is the vibrational entropy at absolute temperature T. Since the theoretical calculations are done at T=0 K, hence the Gibbs free energy is equivalent to enthalpy (H). This is not a realistic approach because experiments are carried out at room temperature and not at T=0K. This fact causes discrepancy in comparability of theoretical results with experimental data. To obtain better comparability with experimental results and to develop a realistic approach we have taken account of the room temperature in pressure induced theoretical calculations. The Gibbs free energies for rock salt (B_1, real) and CsCl (B_2, hypothetical) structures at room temperature T=300K is given by:

$$G_{B1}(r) = U_{B1}(r) + PV_{B1} - TS_1 \tag{2.2}$$

$$G_{B2}(r) = U_{B2}(r) + PV_{B2} - TS_2 \tag{2.3}$$

With V_{B1} (=2.00r^3) and V_{B2} (=1.54r'^3) as the unit cell volumes, S_1 and S_2 are the entropies for B_1 and B_2 phases, respectively. In fact, the condition for a transition is that the difference in free energy between two phases approaches to zero.

$$\Delta G = \Delta H - T\Delta S \tag{2.4}$$

The first term in energies (2.2) and (2.3) are lattice energies for B_1 and B_2 structures and they are expressed as

$$\begin{aligned} U_{B1} &= \frac{-(\alpha_M z^2 e^2)}{r} - \frac{12\alpha_M z e^2}{r} f(r) \\ &+ 6b\beta_{ij}.\exp\left(\frac{r_i + r_j - r}{\rho}\right) + 6b\beta_{ii}.\exp\left(\frac{2r_i - 1.41r}{\rho}\right) \\ &+ 6b\beta_{jj}.\exp\left(\frac{2r_j - 1.41r}{\rho}\right) \end{aligned} \tag{2.5}$$

$$\begin{aligned} U_{B2} &= -\frac{\alpha_M' z^2 e^2}{r'} - \frac{16\alpha_M' z e^2}{r'} f(r') \\ &+ 8b\beta_{ij}.\exp\left(\frac{r_i + r_j - r}{\rho}\right) + 3b\beta_{ii}\exp\left(\frac{2r_i - 1.154r'}{\rho}\right) \\ &+ 3b\beta_{jj}\exp\left(\frac{2r_j - 1.154r'}{\rho}\right) \end{aligned} \tag{2.6}$$

Here β_{ij} is the Pauling coefficient, r_i (r_j) is the ionic radii of i(j) ions, S_1 and S_2 are the entropies, ρ (b) are the range (hardness) parameters.

The first terms in Eqs. (2.5) and (2.6) consist of long-range Coulomb energy, second terms are three-body interactions corresponding to the nearest neighbor separation r (r') for B_1 (B_2) phases, third terms are the energies due to the overlap repulsion represented by Born-Mayer potential for (i,j) ions, and extended up to the second neighboring ions in fourth and fifth terms by using Hafemeister and Flygare (HF) type potential. Now the entropy difference in the last term of Eqs. (2.2) and (2.3) can be calculated from the relation used by Shanker et al. [20,21]

$$S_1 - S_2 = \int_1^2 \left(\frac{C_1 - C_2}{T}\right) \tag{2.7}$$

here, 1 and 2 stand for the B_1 and B_2 phases, C_1 and C_2 are the specific heats of two phases at constant pressure and their values can be calculated by the knowledge of Gruneisen parameter (γ) and linear isothermal temperature coefficient (β) as:

$$C_i = \frac{\{\beta V_i(B_T)\}_i}{\gamma_i} \tag{2.8}$$

Here, Gruneisen parameter (γ) can be calculated by well known formula as follows [19]

$$\gamma = \frac{r_0}{6}\left[\frac{U'''(r_0)}{U''(r_0)}\right] = \frac{-r_0}{6\rho} \tag{2.9}$$

In order to access the relative merit of the present potential, we have calculated the compressibility (*β*), molecular force constant (*f*), infrared absorption frequency (υ_o), Debye temperature (θ_D), which is directly derived from the cohesive energy *U(r)*. Their expressions [32] are given below:

The compressibility is well known to be given by

$$\beta = \frac{3Kr_0}{f} \tag{2.10}$$

In terms of molecular force constant

$$f = \frac{1}{3}\left[U_{SR}''(r) + \frac{2}{r}U_{SR}'(r)\right]_{r=r_0} \tag{2.11}$$

With $U_{SR}(r)$ as the short range nearest neighbor (k≠k') part of *U(r)*. This force constant *f* leads to the infrared absorption frequency with the knowledge of the reduced mass (*μ*) of the halide crystals.

$$\nu_0 = \frac{1}{2\pi}\left(\frac{f}{\mu}\right)^{1/2} \tag{2.12}$$

This frequency gives us the Debye temperature

$$\theta_D = \frac{\hbar\nu_0}{k} \tag{2.13}$$

Where ħ=h/2π, with h and k as the Planck and Boltzmann constants, respectively.

To understand elastic properties of these alkali halides we have calculated second-order elastic constants (SOEC), (C_{11},C_{12} and C_{44}) and their pressure derivatives at room temperature 300K, since these elastic constants are functions of first and second order derivatives of short-range potentials, so their calculations provide knowledge about the effect of short-range forces on these material [21,22]. The expressions for SOE constants are as follows:

$$C_{11} = \frac{e^2}{4r_0^4}\left[-5.112z\{z+12f(r)\}+A_1+\left(\frac{A_2+B_2}{2}\right)+9.3204r_0f'(r)\right] \tag{2.14}$$

$$C_{12} = \frac{e^2}{4r_0^4}\left[0.226z\{z+12f(r)\}-B_1+\left(\frac{A_2-5B_2}{2}\right)+9.3204r_0f'(r)\right] \tag{2.15}$$

$$C_{44} = \frac{e^2}{4r_0^4}\left[2.556\ z\{z+12\ f(r)\}+B_1+\left(\frac{A_2+3B_2}{4}\right)\right] \tag{2.16}$$

In Eqs. (2.14)-(2.16), first term represents the long-range coulomb interaction, second term represents the contribution due to TBI and remaining contribute overlap repulsion expressed in term of the short-range parameters (A_1, B_1) and (A_2, B_2) for the nearest neighboring (nn) and next nearest neighboring (nnn) ions, and these expression are taken from [16,21,23].

The TBIP model cited above contains three model parameters (ρ,b, f (r)) namely range, hardness and three-body force parameters. Their values have been determined from the knowledge of lattice parameter and by solving the equilibrium conditions.

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0 \tag{2.17}$$

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 9kr_0B_T \tag{2.18}$$

3. Result and discussion

The stable phase is associated with minima of energy. The structural phase-transition pressures were calculated by minimizing the lattice energies given in Eqs. (2.5) and (2.6) at different pressures in order to obtain the inter-ionic separations r and r' corresponding to B_1 and B_2 phases. Now we have evaluated the corresponding Gibbs free energies GB_1 (r) and GB_2 (r') and their respective differences ΔG = (GB_2 (r) − GB_1 (r')). As the pressure increases this value of ΔG decreases and approaches zero at the transition pressure (P_t). Beyond this pressure, ΔG becomes negative as the phase B_2 becomes stable. These differences have been plotted against pressure (P) as shown in fig.1 and fig.5, and are indicated by arrows for KCl and NaCl. It is clear from fig.1 and 5 and table 1 that phase transition $B_1 \rightarrow B_2$ occurs at about 2.3 GPa and 28.8 GPa for KCl and NaCl which are close to experimental results 2 GPa and 29 GPa.. Besides, the values of relative volume change (V(P, T)/V(0, T)) associated with various compressions have been obtained and plotted against pressure in fig.2 and fig.6 the values corresponding to phase transition are well listed in Table 2. It is clear from Table 2 and fig.2 and fig.3 that our calculated volume collapses from TBIP model are 11.34% and 3.59% for KCl and NaCl respectively, which are close to experimental values and reported by other works.

Table 1. Input crystal data and model parameters

Compound	r_i (Å)	r_j (Å)	r (Å)	B_T (GPa)	β(10^{-6}K)	b (10^{-19}J)	ρ(Å)	f(r)
KCl	1.33 [a]	1.81 [a]	3.14	17.3 [b]	37.0 [c]	0.11	0.3081	-0.0087
NaCl	0.95[a]	1.81[a]	2.838	24[b]	39.6[c]	0.21	0.3010	-0.0338

a- Ref. [24] ,b-Ref. [25],c- Ref. [31]

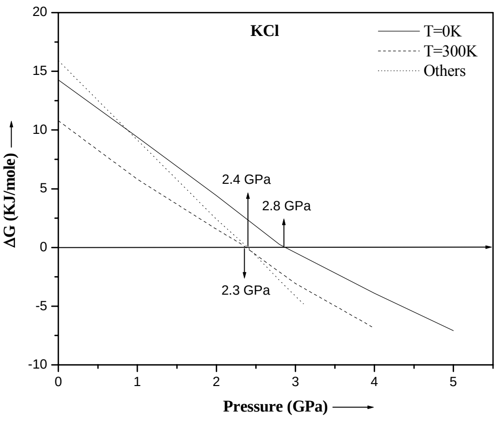

Fig.1: Variation of Gibbs free energy differences ΔG (KJ/Mole) with pressure

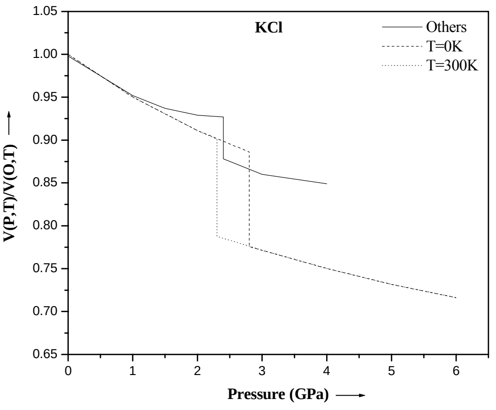

Fig.2: Variation of relative volume with pressure.

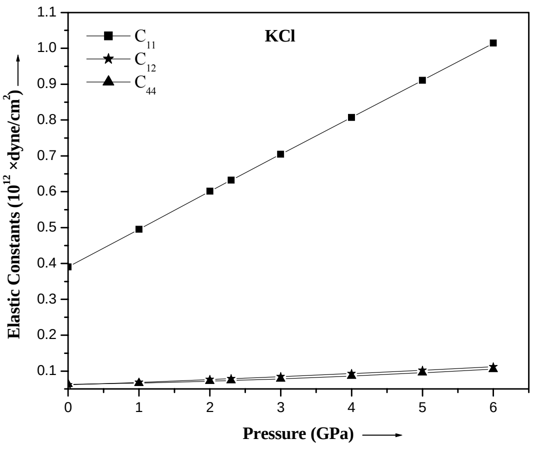

Fig.3. Variation of elastic constants with pressure at T=300K.

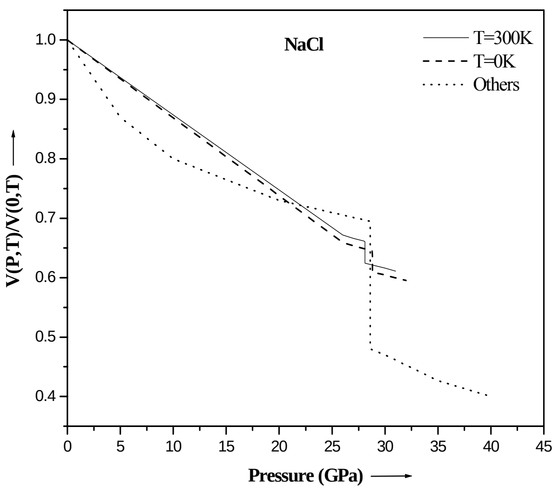

Fig.6: Variation of relative volume with pressure.

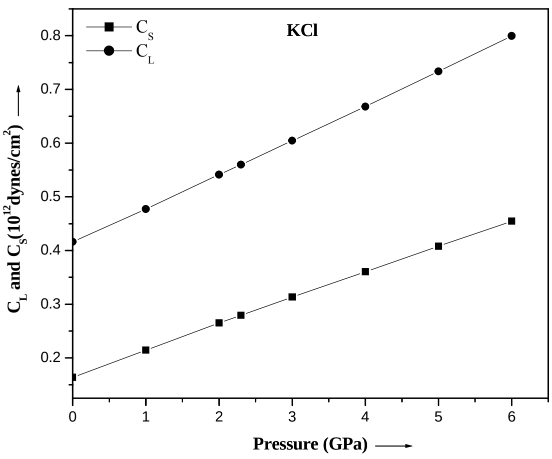

Fig.4: Variation of combination of elastic constants with pressure

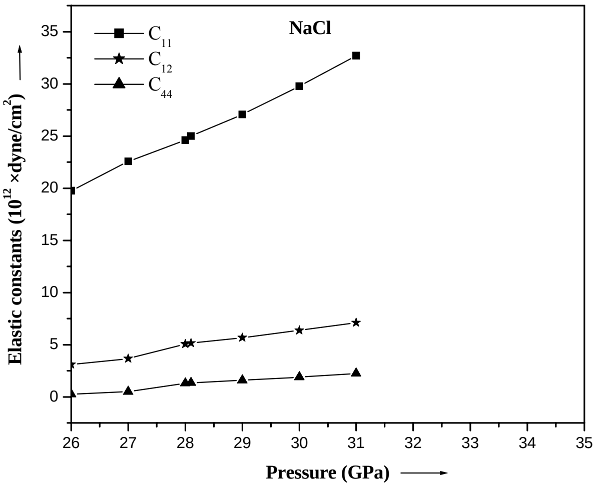

Fig.7. Variation of elastic constants with pressure at T=300K

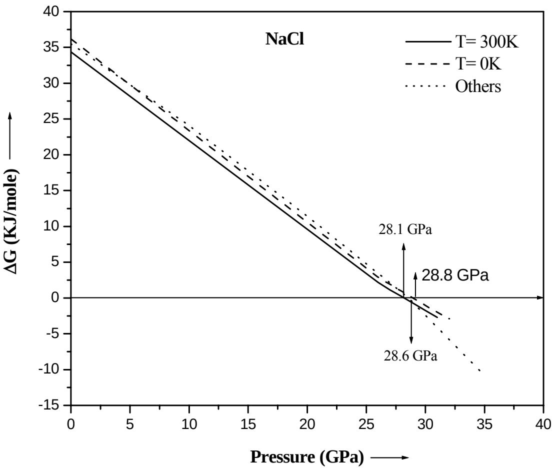

Fig.5. Variation of Gibbs free energy differences ΔG (KJ/Mole) with pressure.

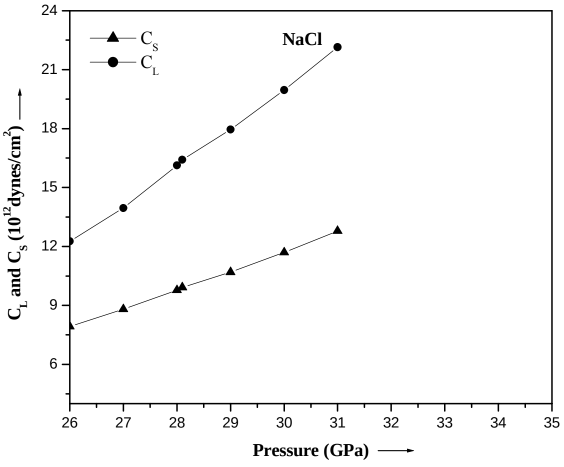

Fig.8: Variation of combination of elastic constants with pressure

Table 2. Calculated transition pressures and volume collapses.

Compound	Transition	Temperature (K)	Transition pressure (GPa)			Volume collapse (%)		
			Present	Exp.	Others	Present	Exp.	Others
KCl	$B_1 \rightarrow B_2$	0	2.8	2.0 [a]	2.4 [b]	11.02	14.3 [d]	12.3 [b]
		300	2.3	-	-	11.34	-	-
NaCl	$B_1 \rightarrow B_2$	0	28.8	29.0 [a]	28.6 [b] 27.4 [c]	3.56	5.8 [d]	4.50 [b]
		300	28.1	-	-	3.59	-	-

a-Ref. [26], b- Ref. [25], c- Ref. [27], d- Ref. [28]

We can understand the elastic properties and interatomic behavior of present compounds by means of elastic constants and their combinations. We have computed the second-order elastic constants and they are shown in Table 3. The quantities C_{44} and C_S are the shear and tetragonal moduli of a cubic crystal. It is necessary for lattice to satisfy Born criterion for mechanically stable state. For this purpose, the elastic energy density must be a positive definite quadratic function of strain. In order to fulfill the above criterion, the principal minor (Eigen values) of the elastic constant matrix should all be positive. TBIP model confirmed that the features of this compound show the same trend as reported earlier for pressure dependence of elastic stiffness for NaCl compound possessing the B_1 structure [29]. Vukcevich [30] also stated the high-pressure stability criterion for ionic crystal, the stable phase of a crystal is one in which the shear elastic constant C_{44} is non-zero (for mechanical stability) and which has the lowest potential energy among the mechanically stable lattices. Thus, the stability of NaCl (B_1)-type structure in terms of elastic constants should satisfy the following conditions:

$$B_T = \frac{1}{3}\left(C_{11} + 2C_{12}\right) > 0$$

$$C_{44} > 0 \quad \text{and} \quad C_S = \frac{\left(C_{11} - C_{12}\right)}{2} > 0 \qquad (3.1)$$

The elastic properties of solids are related to many fundamental solid state properties, such as equation of state (EOS), specific heat, thermal expansion, Debye temperature, Gruneisen parameter, melting point etc. They provide us the valuable information about interatomic interaction, the binding characteristics between adjacent atomic planes, and about the anisotropic character of the bonding and structural stability. To understand the behavior of present halides at high temperatures, we need to have reliable values of elastic constants corresponding to their temperatures. Therefore, we have developed the realistic TBP model, including the role of temperature for predicting the values of elastic constants, phase transition pressure and volume collapse for solids at higher temperatures.

The studies are well known to supply useful information about change in the character of the covalent and ionic forces induced in the crystal as it is subjected to the phase transformation. We have calculated the variation of the second order elastic constants of the materials under study. We have reported the second order elastic constants at T=300K for different pressures in Table 3. The variation of second order elastic constant (SOEC's) with pressure of the present compounds have been plotted in fig.3 and fig.7 for KCl and NaCl respectively. It is clear from figures that in case of KCl and NaCl, it is found that C_{11} varies largely under the effect of pressure as compared with the variation in C_{12} and C_{44}. Since the elastic constant C_{11} represents elasticity in length. A longitudinal strain produces a change in C_{11}. The elastic constants C_{12} and C_{44} are related to the elasticity in shape, which is a shear constant. A transverse strain causes a change in shape without change in volume. Therefore, C_{12} and C_{44} are less sensitive of pressure as compared to C_{11}. As pressure increases, C_{11} and C_{12} of the B_1 phase at zero pressure increases monotonically, but C_{44} decreases monotonically. The values of the combinations of elastic constants $C_S = (C_{11}-C_{12})/2$ and $C_L = (C_{11}+C_{12}+2C_{44})/2$ are plotted against pressure and are shown in fig.4 and fig.8 for KCl and NaCl respectively.

Table 3. Calculated elastic constants and their combinations (10^{12} ×dyne/cm^2).

Compound	Pressure	C_{11}	C_{12}	C_{44}	C_S	C_L
KCl	(Exp.)	0.3980 [a]	0.0610 [a]	0.0630 [a]	-	-
	0	0.3903	0.0613	0.0631	0.1636	0.4161
	1	0.4953	0.0685	0.0662	0.2146	0.4774
	2	0.6016	0.0765	0.0716	0.2650	0.5413
	2.3	0.6323	0.0786	0.0734	0.2794	0.5600
	3	0.7048	0.0846	0.0783	0.3132	0.6046
	4	0.8069	0.0932	0.0862	0.3604	0.6681
	5	0.9110	0.1024	0.0952	0.4079	0.7338
	6	1.0145	0.1117	0.1049	0.4548	0.7997
NaCl	(Exp.)	0.4790 [a]	0.1150 [a]	0.1270 [a]	-	-
	0	0.5730	0.1152	0.1450	0.2575	0.0060
	26	19.7552	3.0981	0.2425	7.9285	12.2691
	27	22.5735	3.6664	0.4869	8.8035	13.9568
	28	24.6020	5.0522	1.3036	9.7749	16.1307
	28.1	24.9907	5.1499	1.3468	9.9204	16.4172
	29	27.0684	5.6752	1.5835	10.6966	17.9553
	30	29.7620	6.3616	1.8945	11.7002	19.9563
	31	32.6943	7.1150	2.2379	12.7897	22.1425

a-Ref. [24]

We have also calculated thermo physical properties of NaCl and KCl at T=300K. The thermo physical properties provide us the interesting information about the substance. The Debye temperature θ_D reflect its structure stability, the strength of bonds between its separate elements, structure defects availability and its density. Compressibility is used in the earth science to quantify the ability of a soil to reduce in volume with pressure. The thermo physical properties are listed in table 4. Due to the lack of experimental data, we could not compare them with our results. As to the best of our knowledge the value of the thermal properties for NaCl and KCl have not yet been measured or calculated, hence our results can serve as a prediction for future investigations.

Table 4. Thermal properties of NaCl and KCl at T=300K.

Compound	f	θ_D/K	υ_o (10^{12}Hz)
KCl	2.0262×10^4	304	4.0970
NaCl	3.1887×10^4	319	5.9266

3. Conclusions

Finally, from the present theoretical investigation we have noticed that the crystallographic pressure-induced phase transition from B_1 to B_2 structure analysis should be done at room temperature rather than at $T = 0$K. In order to meet the above defined condition, we obtained good comparative results regarding the phase transition pressure and the volume discontinuity in pressure–volume phase diagram with the experimental data using our realistic model.

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*Corresponding author: drsadhna10@gmail.com