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Ultrasonic and Thermophysical Properties of Potassium Halides Crystals

Umesh Chandra Srivastava[1*] and Shyamendra Pratap Singh[2]

[1]Department of Physics, Amity Institute of Applied Sciences, Amity University, Noida-201301, India
[2]Department of Physics, Swami Vivekanand Govt.P.G. College, Lohaghat, Champawat, Uttra khand, India

[*]Correspondence e-mail: ucsrivastava@amty.edu

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ABSTRACT: *In this communication, author is presenting ultrasonic and thermophysical properties of potassium fluoride (KF) and potassium chloride (KCl) by van der Waals three body force shell model with the help of second and third order elastic constants at 100 K–300 K. The elastic constants have been calculated by using Coulomb and Born–Mayer potential with the help of two parameters-distance of nearest neighbour and hardness parameter. We evaluated ultrasonic properties such as elastic constants, wave velocities, Debye temperature- average velocity, conductivity, and ultrasonic attenuation due to phonon–phonon interaction along in different direction [100],[110], and [111] orientations. The achieved results are hold good and are given very important information of these crystal for further investigation.*

Keywords: thermophysical properties, ultrasonic properties, elastic constants, Debye temperature, phonon interaction, VTFSM model

1. INTRODUCTION

The study of propagation of ultrasonic waves in pure liquids and in its mixtures are well established for determining the properties and the structure of matter through intermolecular interactions. Its prime importance in deciding the structure and properties of crystal, phase transitions, etc. In the last decade, we

have observed fascinating progress in the field of ultrasonic. Many experimental investigations of semiconductors, metals, magnetic crystals, quantum liquids, glasses, superconductors, insulators phase transition and particular data have been discussed by ultrasonic. In the study and accurately determination is measured of highly sensitive molecular interactions by use of ultrasonic velocity and their useful acoustical parameters. Velocity of ultrasonic with density, viscosity and dielectric methods by.[1,2] Short range interactions are due to dipole-dipole, dipole-induced dipole, charge transfer, complex formation and bonding interactions. In the present model having long-range screened Coulomb, van der Waals interactions (VWI), three body interaction (TBI) and the short-range overlap interaction repulsion operative up to the second-neighbour ions in potassium fluoride (KF) and potassium chloride (KCl) crystal. The lattice vibrational properties of these crystals by using the three-body force rigid-ion model (TRIM).[3] Thermophysical properties are computed with the application of Coulomb and Born–Mayer potential using distance and hardness parameter.

2. THEORY

The concept of ionic interaction, van der Waals bonding and covalence bonding can be understood easily on the atomistic approach model. The electrostatic or Coulombic energy term is the most important component in ionic or semi–ionic solids. The present model is based on the framework of ion polarisable (RSM) proposed by Dick and Over Hauser and Woods et al. and it successfully applied to study of lattice property, effective up to the second neighbour in short-range interactions.[4,5] The lattice vibrations are quantised in the solid phase and described by quasi-particles. Therefore, for the study of the complete dynamical behaviour of KF and KCl has reported by introducing VWI effect and expression for the contribution of TBI that prove the relevance of use model Van der Waals three body force shell Model (VTBFSM), which has rigorously derived and exactly evaluated in the framework of RSM.[6] The relevant expression and general formalism of VTBFSM model given as:

$$\Phi = \Phi^{C} + \Phi^{R} + \Phi^{TBI} + \Phi^{VWI} \tag{1}$$

where Φ^{C} is a long-range Coulomb interaction potential. Thus, the total Coulomb energy of the crystal is:

$$\Phi^{C}(r) = \sum_{j}{}' \Phi^{c} \alpha_{M} \frac{Z^{2} e^{2}}{r_{O}} (r_{ij})$$

where α_m is the Madelung constant and r_0 is the equilibrium nearest neighbour distance. Second term Φ^{or} is a short-range overlap repulsion potential.

$$\Phi^R(r_{ij}) = ar_{ij}^n \text{ (Born Potential) and}$$

$$\Phi^R(r_{ij}) = b\exp.(-r_{ij}/\rho) \text{ (B-M) Potential}$$

where, a (or b) and η (or ρ) are the Born strength and hardness parameters, respectively. This interaction potential is expressed as:

$$\Phi^{TBI} = \alpha_m \frac{Z^2e^2}{r_0}\left[\frac{2n}{Z} f(r)_0\right] \tag{2}$$

By using the potential energy expression (2), the equations of motion of two cores and two shells can be given as:

$$\omega^2 MU = (R + Z_m C' Z_m)U + (T + Z_m C' Y_m)W \tag{3}$$

$$0 = (T^T + Y_m C' Z_m)U + (S + K + Y_m + C' Y_m)W \tag{4}$$

The introduction of VWI and TBI in the framework of RSM with the elimination of *W* from equation (3) and equation (4) leads to the secular determinant:

$$\left|\underline{D}(\vec{q}) - \omega^2 \underline{M}\,\underline{I}\right| = 0 \tag{5}$$

If we consider only the second neighbour dipole-dipole VWI energy, then it is expressed as:

$$\Phi_{dd}^{VWI}(r) = -S_V\left|\frac{C_{++} + C_{--}}{6r^6}\right| = \Phi^V(r) \tag{6}$$

where, S_v is lattice sum and the constants C_{++} and C_{--} are the van der Waals coefficients corresponding to the positive-positive and negative-negative ion pairs, respectively.

2.1 Thermodynamically properties of KF and KCl.

Density of state, temperature dependence of free energy, specific heat capacity at constant volume were calculated. Specific heat capacity at constant volume (Cv) was calculated using the following equation.[7,8]

$$U = \int_0^{\upsilon_m} \frac{h\upsilon^3}{e^{h\upsilon/kT} - 1} d\upsilon \tag{7}$$

and $$C_\upsilon = 3NK_B \frac{\sum_\upsilon \{E(x)\} G(\upsilon) d\upsilon}{\sum_\upsilon G(\upsilon) d\upsilon} \quad (8)$$

Debye temperatures have been evaluated by using the magnitude of elastic constants such as evaluating specific heat calculations at low temperatures. It is represented as.

$$\Theta_D = \frac{h}{K_B}\left[\frac{3n}{4\pi}\left(\frac{N_A \rho}{M}\right)\right]^{1/3} V_m \quad (9)$$

2.2 Ultrasonic and Debye Velocities

Ultrasonic velocity plays a vital role in the characterisation of materials. The propagation of ultrasonic waves through anisotropic solids depends on the strains along the <100>, <110> and <111> directions. When ultrasonic waves propagate through a medium, their velocity has three modes of propagation, one longitudinal acoustical (V_L) and two shear acoustical (V_{S1}, V_{S2}). The expressions for V_L, V_{S1}, and V_{S2} are presented elsewhere.[9,10] Along the <100> crystallographic direction:

$$V_L = \sqrt{C_{11}/d} \quad (10)$$
$$V_{s1} = V_{s2} = \sqrt{C_{44}/d}$$

Along the <110> crystallographic direction:

$$V_L = \sqrt{(C_{11} + C_{12} + C_{44})/2d} \quad (11)$$
$$V_{s1} = \sqrt{C_{44}/d}$$
$$V_{s2} = \sqrt{(C_{11} - C_{12})/d}$$

Along the <111> crystallographic direction:

$$V_L = \sqrt{(C_{11} + 2C_{12} + 4C_{44})/3d} \quad (12)$$
$$V_{S1} = V_{S2} = \sqrt{(C_{11} - C_{12} + C_{44})/3d}$$

where d is the density of chosen material. The Debye average velocity V_D can be determined using Debye theory.[10] V_D is average of V_L, V_{S1} and V_{S2} and expressed as:

Along the <100> and <111> direction

$$V_D = \left[\frac{1}{3}\left\{\frac{1}{V_L^3} + \frac{2}{V_s^3}\right\}\right]^{\frac{-1}{3}} \quad (13)$$

Along the <110> direction

$$V_D = \left[\frac{1}{3}\left\{\frac{1}{V_L^3} + \frac{1}{V_{s1}^3} + \frac{1}{V_{s2}^3}\right\}\right]^{\frac{-1}{3}} \quad (14)$$

3. RESULT AND DISCUSSION

In this communication I have investigated about the Ultrasonic and thermophysical properties of KF and KCl by used of [VTBFS] model. The effect of pressure on the crystal structure and electronic-vibrational properties are reported in calculation. The model parameters and input data of KF and KCl are reported in Table 1 and 2, and third order elastic constant (TOEC) and Orientation dependent ultrasonic velocities, Debye velocity in Table 3 and 4 taking the values of input constants from and calculated the model parameter.[11,12] Ultrasonic velocity plays a vital role in the characterisation of KF and KCl. The propagation of ultrasonic waves through anisotropic solids depends on the strains along the <100>, <110>, and <111> directions. The Debye temperature curve Vs temperature has shown in Figure 1 and 2 with the available theoretical and experimental result which has shown parallel to the present calculated results.

Table 1: Input data for KF and KCl in terms of C_{11}, C_{12}, C_{44} in (10^{11} dyn cm^{-2}), r_0 (10^{-8} cm), ϵ_0, ϵ_∞, ν_L (THz) and ν_T (THz).

Input Data	C_{11}	C_{12}	C_{44}	r_0	ϵ_0	ϵ_∞	ν_{LA}	ν_{TA}
KF	7.570[13]	1.350[13]	1.336[13]	2.648[15]	5.50	1.50	5.670[16]	3.730[16]
KCl	4.832[14]	0.542[14]	0.663[14]	2.106[15]	4.85	2.10	3.500[17]	3.180[17]

Table 2: Calculated model parameters of KF and KCl.

Parameter Values	Z_m^2	$r_o f_o'$	A	B	d_1	d_2	Y_1	Y_2
KF	0.8261	–0.0128	–0.5888	–0.3640	0.0831	0.0379	–4.0840	–5.6541
KCl	0.8444	–0.0212	–3.8638	1.2219	0.0362	0.1035	–4.6946	–6.6206

Table 3: Calculated TOEC (in units 10^{12}dyn/cm^2) for KF and KCl.

Input Data	C_{111}	C_{112}	C_{123}	C_{144}	C_{166}	C_{456}
KF	–10.813	–0.249	0.265	0.264	–0.475	0.263
KCl	–7.596	–0.254	0.118	0.132	–0.237	0.140

Table 4: Orientation dependent ultrasonic velocities V_L, V_{S1}, V_{S2} and V_D (in 10^3ms^{-1}) of KF and KCl at room temperature.

Material Orientation	VL (Longitudinal Acoustical)		VS1 (Ist Shear acoustic)		VS2 (2nd Shear acoustic)		VD (Debye Temperature)	
	KF	KCl	KF	KCI	KF	KCI	KF	KCI
<100>	10.79173	8.31725	4.53363	3.08087	4.53363	3.08087	5.12952	2.43856
<110>	9.44294	6.92530	4.53363	3.08087	9.78224	7.83692	6.14005	4.24270
<111>	8.77058	6.14312	6.24294	4.86172	6.24294	4.86172	6.17842	5.16966

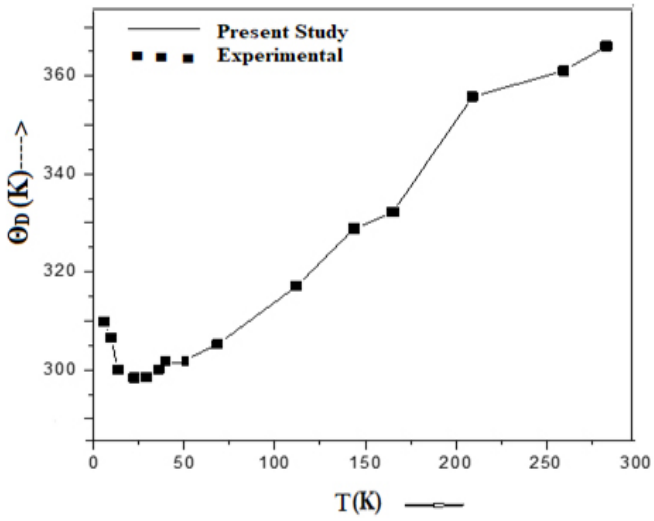

Figure 1: Debye temperature variations of KF.

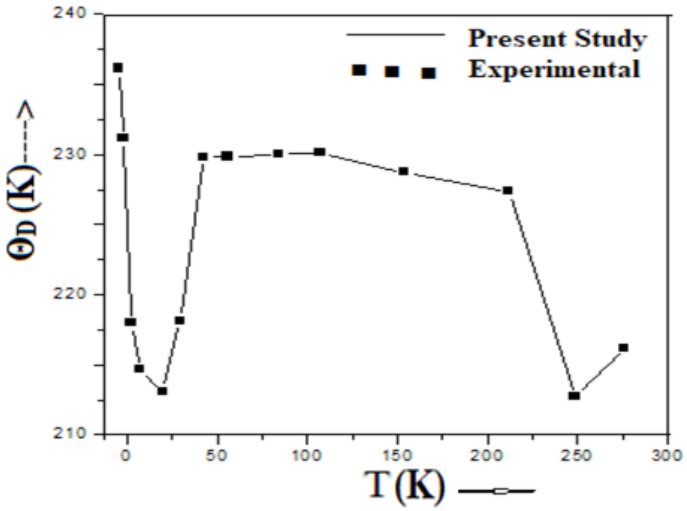

Figure 2: Deby temperature variations of KCl.

The Debye temperature is an empirical parameter in the Debye specific heat formula. Debye treated the thermal behaviour of solids as dominated by homogeneous isotropic massless phonons or quantised lattice vibrations.

4. CONCLUSION

The ultrasonic and thermophysical properties with lattice dynamical calculations for KF and KCl based on different available parameters. While calculating the parameters of the modified –three body shell Model (TSM), we have used the values of elastic data, which are relatively larger than the values used in earlier calculation. Orientation dependent ultrasonic velocities in Table 3 reported theoretically by using the experimental data.[13–17] The physical significance of the model theory (VTBFS) is emphasised on account of the following facts:

(a) it satisfies all the symmetry requirements of a perfect crystal;

(b) it satisfies the stability condition of crystal;

(c) to explain various thermal and vibrational properties of different crystals of this (NaCl-structure) family.

In the present study, despite the lower symmetry of KF and KCl, the uncertainty as to the exact nature of the distortion of the lower–temperature structure. Our theoretical study at lower temperature shows a better agreement, but at higher temperature, slight disagreement may be ascribed to the non-inclusion of the harmonic interactions in using present model, which it may be inferred that the incorporation of van der Waals interactions is essential. The Complete lattice dynamical, thermodynamical property of KF and KCl theoretically reported has agreed with different reported data.[15–22] The authors and more researchers have already used the present model and successfully reported the value of alkali halides and semiconductor materials.[23–32] To sum up, we can say that the contributions of VWI are essential for the description of the lattice dynamics and thermodynamical study of KF and KCl crystal.

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