Phenomenological explanation of spontaneous polarisation and onset ferroelectric Phase transition in $\text{RbH}_2\text{AsO}_4$ ($\text{RDA}$) crystal

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Abstract By applying two-time thermal dependent Zuberav’s statistical, retarded Green function approach and modified earlier simple PLCM model Hamiltonian by adding some extra terms into it, like third-order and fourth-order, phonon anharmonic interactions, direct spin-spin terms, extra spin-lattice terms, and four body interaction terms, for theoretical investigation of thermal dependent spontaneous polarization and ferroelectric phase transition in the first-order phase, of $\text{RbH}_2\text{AsO}_4$ crystal. It undergoes a ferroelectric phase transition at 109.9K. With the help of Dyson’s equation in the Mean-Field Approximation (MFA), theoretical formulae are obtained for electrical permittivity, tangent delta, Cochran’s mode frequency, spontaneous polarization, and response function. Model values are fitted for the above physical parameters to obtain variations with temperature. A comparison of theoretical finding has been made with the experimental finding reported by Blinc et al [12], and Zolototrubov et al [8].

Keywords: - Coupling constant• Cochran’s mode frequency• Anharmonicity• Tangent delta• Green’s function• Phase transition• and Response function.

1. Introduction

Rubidium dihydrogen arsenate crystal is an inorganic and prototype of an order-disorder class of ferroelectric crystals. Another type is displacive one like $\text{BaTiO}_3$, $\text{SrTiO}_3$, $\text{LiTiO}_3$, etc. $\text{RbH}_2\text{AsO}_4$ crystal is an H-bonded isomorphic crystal of dihydrogen, phosphates, and arsenates of potassium, rubidium, and cesium ($\text{KH}_2\text{PO}_4$, $\text{RbH}_2\text{AsO}_4$, $\text{RbH}_2\text{PO}_4$, $\text{CsH}_2\text{AsO}_4$, and $\text{CsH}_2\text{PO}_4$), etc. and these type of crystals are formed a very interesting and famous group called $\text{KH}_2\text{PO}_4$ family by Schmidt [1]. The investigation of $\text{RbH}_2\text{AsO}_4$ crystal is of obvious interest aroused because of their peculiar properties, which are widely used in computers and electronics as Laser technologies, memory devices, optical devices, pyroelectric detectors, gas sensing material, detectors, and modulators. So, their investigation is useful both from theoretical as well as technological applications. $\text{RbH}_2\text{AsO}_4$ crystal is abbreviated as $\text{RDA}$. Rubidium dihydrogen arsenate crystal is characterized by covalently bonded $\text{AsO}_4$ units by bridging H-bonds and ionic bonding between rubidium cations and $\text{AsO}_4$ anions. It consists of two interpenetrating body-centred lattices of $\text{AsO}_4$ tetrahedral and two Rb lattices, in which the rubidium and arsenate are separated by the c-axis. It undergoes a phase transition at $T_c = 109.9K$. On deuteration, $T_c$ shifts to 163K due to the exchange of proton with hydrogen shows a large isotopic effect. It shows orthorhombic structure when ($T<T_c$) and $H_{2}$ type tetragonal structure above $T_c$. 

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The lattice parameter of RDA crystal are \(a = 7.7865 \AA\), \(b = 7.7865 \AA\), \(c = 70.466 \AA\) and \(\beta = 90^\circ\). The polarization in the RDA crystal is perpendicular to the direction of the Oxygen-Hydrogen-Oxygen bond by. The polarization increases by decreasing the temperature due to protons tunnelling from one minima to another of the potential well-formed near \(T_c\). When the temperature approaches \(T_c\) the spontaneous polarization is continuously decreasing in the ferroelectric phase. Cochran [2] has studied ferroelectric and anti-ferroelectric properties in terms of the normal mode of vibrations in KH\(_2\)PO\(_4\) type crystals.

Blinc [3] first explained the isotope effect and all possess electrical properties of first-order in the H-bonded order-disorder type of RDA crystal. Thermodynamic properties of various arsenate like KDA and RDA types of KDP have been measured by Fairall and Reese [4, 5]. In general, the substitution of phosphate to arsenate intensified the first-order characteristics of the phase transitions, and the properties are well explained by the tunnelling clusters theory of Levitskii [6]. Samara [7] has studied the effects of deuteration on the electrical properties of KDP type crystals. Zolototrubov et al [8] have studied phase transition spontaneous polarization in RDA crystal. Jaouadi et al [9] have done characterization, of structure and thermal behaviour of RDA crystal. Tokunaga and Matsubara [10] have studied the theory of Curie’s temperature in KH\(_2\)PO\(_4\) type of crystals. The piezoelectric, and elastic as well as another physical property of normal and deuterated RbH\(_2\)AsO\(_4\) crystal studied by Adhav [11]. Blinic et al [12] have done experimental work, to study ferroelectric phase transition in RbH\(_2\)AsO\(_4\) crystal. A study of RDA crystal at high temperature was carried out by Torijano et al [13] using various techniques like (DSC), (TGA), and (XRD). Stoger [14] has made a refined crystal structure study of RDA crystal. Neves et al [15] have studied electron paramagnetic resonance and proton repulsion in RDA crystal. Uda et al [16] have carried out thermodynamic, thermomechanical, and electromechanical evolution of arsenate type of KDP crystals. Saliger [17] has studied the arsenate type of H-bonded crystals. Etoumi, and Mhiri [18] have studied the kinetic energy of dehydration at Curie’s temperature in KDP type crystals. Ganguli et al [19] have also studied the phase transitions in RDA type H-bonded crystals by using the (PLCM) model and Green’s function technique. They have not considered the four spin coupling terms in their model to explain the physical properties in KH\(_2\)PO\(_4\) type crystals. These authors [19] have decoupled higher-order Green functions by using Tayblivov’s scheme of decoupling. In contrast to their treatment, we shall use a better decoupling scheme. This will enhance the terms in the results. Due to said above treatment all possible interactions will be accounted for in the RbH\(_2\)AsO\(_4\) crystal.

In the theoretical approach presented here, we have considered in this work the direct spin-spin interaction term, extra spin-phonon interaction term, (third-order and fourth-order lattice anharmonic interactions terms), and four body interaction term in the (PLCM) model for explaining the physical properties of RbH\(_2\)AsO\(_4\) crystal. The phonon anharmonic interaction terms and four body interaction term in the PLCM model are the important terms for explaining the physical quantities like permittivity, tangent delta, Cochran’s mode frequency, and polarization for KH\(_2\)PO\(_4\) type crystals. Determination of expressions by modified model, using thermal statistical two times Green function technique. The above quantities have been calculated by using Zuberav’s statistical approach and the Green function technique for different temperatures in RbH\(_2\)AsO\(_4\) crystal. We have compared our theoretical calculated findings with the experimental finding of Blinc et al. [12] and Zolototrubov et al [8].

2. Theoretical Description

2.1 Modified Hamiltonian

For explaining the ferroelectric phase transition, and spontaneous polarisation in RDA crystal, [19] model Hamiltonian is modified by adding extra interaction terms into it as

\[
H = -2\Omega \sum_i S_i x - \frac{1}{2} \sum_{ij} J_{ij} S_i z S_j z + \frac{1}{4} \sum_k \omega_k (A_k^\dagger A_k + B_k^\dagger B_k) - \sum_{ik} V_{ik} S_i^z A_k^z, \tag{1.a}
\]

and
\( H_2 = \sum_{k_1k_2k_3} V^3(k_1, k_2, k_3) A_{k_1} A_{k_2} A_{k_3} - \frac{1}{2} \sum_j B_{ij} S_i^x S_j^x + \frac{1}{4} \sum_{ijkl} J'_{ijkl} S_i^z S_j^z S_k^z S_l^z \) \\
\( + \sum_{k_1k_2k_3k_4} V^4(k_1, k_2, k_3, k_4) A_{k_1} A_{k_2} A_{k_3} A_{k_4} - \sum_{ik} V_{ik} S_i A_k - \sum_{ik} V_{ik} S_i^2 A_k^2, \) 

(1.b)

wherein equation (1.a) \( \Omega \) represents the proton tunnelling frequency between Oxygen-Hydrogen-Oxygen bonds in alkali phosphate H-bonded \( \text{RbH}_2\text{AsO}_4 \) crystal, \( J_{ij} \) is the interaction between the exchange of pseudo-spins of the Ising type, \( S_i^\alpha (\alpha=x,y,z) \) are the spin half operator’s components along \( x, y, \) and \( z \)-directions, \( V_{ik} \) represent spin-lattice interaction constant, \( A_k \) and \( B_k \) are the displacement operator and the momentum operator. \( A_k^\dagger \) and \( B_k^\dagger \) are conjugate of momentum and displacement operators, and \( \omega_k \) is the phonon harmonic frequency. Where \( H_2 \) in equation (1.b) contains the various terms like \( V^3(k_1, k_2, k_3) \) and \( V^4(k_1, k_2, k_3, k_4) \) represents third-order and fourth-order lattice’s phonon anharmonic interaction terms, \( J_{ij} \) is the four body interaction constant and this interaction plays an important role in the Oxygen Hydrogen-Oxygen bonds. The \( S_i^x A_k \) and \( S_i^x A_k^2 \) terms represent an indirect coupling between proton-proton tunnelling motion, and also represent the variation of space between two sites at an equilibrium distance of Oxygen Hydrogen Oxygen bonds in H bonded \( \text{RbH}_2\text{AsO}_4 \) crystal and \( B_{ij} \) term represent the coupling constant. 

Therefore resultant \( H \) for \( \text{RDA} \) crystal as;

\( H=H_1+H_2. \)

(2)

2.2 Response Function (Shift and Width), and Dyson’s equation

The two-time temperature-dependent statistical method of retarded Green’s function technique by Zubrav [38] is expressed as;

\[ G_{ij}(t-t') = \left\langle \left\langle S_i^x(t) S_j^x(t') \right\rangle \right\rangle = -i\theta(t-t') \left\langle \left\langle S_i^x S_j^x \right\rangle \right\rangle, \]

(3)

where angular bracket in equation (3) \( \left\langle \left\langle \ldots \right\rangle \right\rangle \) represents the Green function notation, \( \langle \ldots \rangle \) represents the average grand canonical ensemble, and \( -i\theta(t-t') \) represent unit step function, and its value is 1 for \( t>t' \) or zero otherwise. Now we write the equation of the Green function given by Equation (3) by using \( H \) in Eq. (2); double time differentiation in terms of \( t \) and \( t', \) and writing in the following form.

\[ G_{ij}(\omega) = G_{ij}^0(\omega) + G_{ij}^0(\omega) P(\omega) G_{ij}^0(\omega). \]

(5)

We, obtain

\[ G_{ij}^0(\omega) = \Omega S_i^x \delta_{ij} \gamma^{-1}(\omega^2-\Omega^2), \]

(6)

and

\[ P(\omega) = \pi \Omega^{-1} S_i^x \gamma^{-1} \left\langle F_i(t); F_j(t') \right\rangle, \]

(7)

where, \( F_i(t) \) and \( F_i(t') \) are given as;
\[ F_i(t) = 2\Omega \sum_i V_{ik} A_k \sum_{ik} S_i^z + 2\Omega \sum_i V_{ik} A_k^2 \sum_{ik} S_i^x - \Omega \sum_i B_{ij} \sum_{ij} \left( S_i^x S_j^x + \delta_{ij} S_i^z S_j^z \right) - \]

\[
\frac{1}{2} \sum_{ij} J_{ij} \left[ 2\Omega \sum_i \left( S_i^x S_i^z + S_i^z S_i^x \delta_{ij} \right) + \frac{1}{2} \sum_i B_{ij} \left( S_i^y S_i^y - S_i^y S_i^y + \delta_{ij} S_i^x S_i^x - \delta_{ij} S_i^z S_i^z \right) \right] + \ldots
\]

\[
= \frac{1}{2} \sum_{ij} J_{ij} \left[ 2\Omega \sum_i \left( S_i^x S_i^z + S_i^z S_i^x \delta_{ij} \right) + \frac{1}{2} \sum_i B_{ij} \left( S_i^y S_i^y - S_i^y S_i^y + \delta_{ij} S_i^x S_i^x - \delta_{ij} S_i^z S_i^z \right) \right] + \ldots
\]

And

\[ F_i(t) = 2\Omega \sum_i V_{ik} A_k \sum_{ik} S_i^z + 2\Omega \sum_i V_{ik} A_k^2 \sum_{ik} S_i^x - \Omega \sum_i B_{ij} \sum_{ij} \left( S_i^x S_j^x + \delta_{ij} S_i^z S_j^z \right) - \]

\[
\frac{1}{2} \sum_{ij} J_{ij} \left[ 2\Omega \sum_i \left( S_i^x S_i^z + S_i^z S_i^x \delta_{ij} \right) + \frac{1}{2} \sum_i B_{ij} \left( S_i^y S_i^y - S_i^y S_i^y + \delta_{ij} S_i^x S_i^x - \delta_{ij} S_i^z S_i^z \right) \right] + \ldots
\]

Where \( G^0(\omega) \) in Eq. (5) is the zeroth-order Green’s function, and are obtained as

\[
G_{ij}^0(\omega) = \frac{\Omega \left( S_i^x \right) \delta_{ij}}{\pi \left( \omega^2 - \Omega^2 \right)}. \tag{10}
\]

In Eq. (7) \( P(\omega) \) is the response function and \( \Omega \) is the normalized pseudo-spin frequency in the lowest order approximation. Different product of operator’s likes \( x x z \), \( x z z \), \( y y x \), etc. contained in \( F_i(t) \). The product of two operator’s average values can be calculated from the formula

\[
\langle S_i^x S_j^z \rangle = \lim_{\epsilon \to +0} \left[ \frac{1}{e^{\beta \omega - \eta} - e^{-\beta \omega - \eta}} \right]_{\omega = \omega^+ - \infty}^{\omega = \omega^+ + \infty} \langle \langle S_i^x | S_j^z \rangle \rangle_{\omega + i\epsilon} - \langle \langle S_i^x | S_j^z \rangle \rangle_{\omega - i\epsilon} d\omega. \tag{11}
\]

The parameter \( \eta \) was arbitrarily chosen as +1 or -1. If both \( S_i^x \) and \( S_j^z \) are (Bose) operators, \( \eta \) remained as +1, and if they are (Fermi) operators, \( \eta \) is to be -1. Equation (7) contains higher-order Green functions and we have to choose the various appropriate Green functions so that a closed system of the equation is obtained which are evaluated after applied decoupling scheme as

\[
\langle \langle ef; gh \rangle \rangle = \langle \langle ef \rangle \rangle \langle \langle gh \rangle \rangle + \langle \langle eg \rangle \rangle \langle \langle fh \rangle \rangle + \langle \langle eh \rangle \rangle \langle \langle fg \rangle \rangle. \tag{12}
\]
Now, obtained values of the simpler Green function are substituted \( < F_i(t); F_j(t') > \). Therefore we resolve \( P(\omega) \) into its real \( \Delta(\omega) \) and imaginary \( \Gamma(\omega) \) parts called to shift and width. We, therefore, obtain the quantities of \( \Delta(\omega) \) and \( \Gamma(\omega) \) is expressed as

\[
P(\omega) = \Delta(\omega) + i\Gamma(\omega),
\]

where \( \Delta(\omega) \) is expressed as

\[
\Delta_1(\omega) = \frac{4\Omega^2 V_k^2 N_k}{\omega - \Omega} + \Delta_2(\omega) = \frac{4\Omega aV^2_{ik} \left( S_i^z \right)}{(\omega - \omega_k^2)} + \Delta_3(\omega) = \frac{b^2 \Omega a J \left( S_i^z \right)^2}{\omega - \Omega^2} (14.a)
\]

\[
\Delta_4(\omega) = \frac{J_{ij}^2 \Omega \left( S_i^z \right)^2}{2b} + \Delta_5(\omega) = \frac{J_{ij}^2 \Omega \left( S_i^z \right)^2}{\omega - \Omega^2} + \Delta_6(\omega) = \frac{8b \Omega^2 \left( S_i^z \right)^2}{\omega - \Omega^2} (14.b)
\]

Total \( \Delta(\omega) = \Delta_1(\omega) + \Delta_2(\omega) + \Delta_3(\omega) + \Delta_4(\omega) + \Delta_5(\omega) + \Delta_6(\omega) + .... 

And \( \Gamma(\omega) \) is obtained as

\[
\Gamma_1(\omega) = \frac{4\Omega^2 V_k^2 N_k}{\omega - \Omega} \left[ \delta (\omega - \Omega) - \delta (\omega + \Omega) \right] + \Gamma_2(\omega) = \frac{8\Omega aV^2_{ik} \left( S_i^z \right)}{(\omega - \omega_k^2)} \Gamma_k(\omega) + \Gamma_3(\omega) = \frac{b^2 \Omega a J \left( S_i^z \right)^2}{4b \Omega} (15.a)
\]

Total \( \Gamma(\omega) = \Gamma_1(\omega) + \Gamma_2(\omega) + \Gamma_3(\omega) + \Gamma_4(\omega) + \Gamma_5(\omega) + \Gamma_6(\omega) + \Gamma_7(\omega) + .... 

The above obtained shift \( \Delta(\omega) \) and width \( \Gamma(\omega) \) are obtained due to extra interaction terms which are due to the decoupling of higher-order Green function at the proper stage, unlike the previous authors [37, 16 and 17]. Width \( \Gamma(\omega) \) is added to unmodified frequency \( \Omega \). Although the half-width \( \Gamma(\omega) \) of certain absorption experiments is at half the maximum of the curve. It is seen that \( \Gamma(\omega) \) and \( \Delta(\omega) \) obtained in the present work contain more terms as obtained earlier authors [37, 16 and 17]. This is because we have considered direct spin-spin interaction terms, extra spin-lattice terms, four body interaction terms, and four spin coupling terms in model Hamiltonian. We aim to take into account all
possible interactions which can take place in the \( \text{RbH}_2\text{AsO}_4 \) crystal. The equations (14) and (15) \( \Gamma_k(\omega) \)

\[ \approx \approx \]

and \( \omega_k \) are obtained in which \( \omega_k \) represent changed phonon frequency and \( \Gamma_k(\omega) \) represent phonon frequency width respectively, which are modified during the evaluation of Green function \( \langle \langle A_k; A_k^\dagger \rangle \rangle \) for phonon

\[ \approx \approx \]

where \( \omega_k = \omega_k + 2 \omega_k \Delta_k(\omega) \).

Now, from equations (14) and (15) the value of \( \Delta_k(\omega) \) and \( \Gamma_k(\omega) \) are obtained as follows

\[ \Delta_k(\omega) = R e P_k = 18 P \sum_{k_1 k_2} \left| \nu^2(k_1, k_2) \right|^2 \times \omega_{k_1} \omega_{k_2} \left[ \begin{array}{cc} \omega_{k_1} \omega_{k_2} \\ \omega_{k_1} \omega_{k_2} \end{array} \right]^{-1} \]

and

\[ \Gamma_k(\omega) = I m z P_k(\omega) = 9 \pi \sum_{k_1 k_2} \left| \nu^2(k_1, k_2) \right|^2 \times \omega_{k_1} \omega_{k_2} \left[ \begin{array}{cc} \omega_{k_1} \omega_{k_2} \\ \omega_{k_1} \omega_{k_2} \end{array} \right]^{-1} \]

Here \( n_i = \frac{\omega_k}{\omega_k \coth \left( \frac{\hbar \omega_k}{2 k T} \right)} \), and \( P \) represents the principal part of the above equation.

### 2.3 Permittivity (\( \varepsilon \)) and Tangent delta (\( \delta \))

Following by Zubérav’s [20], the susceptibility (\( \chi \)) is expressed as

\[ \chi = \lim_{\varepsilon \to 0} 2 \pi N \mu^2 \left( \omega + i \chi \right), \]

The electrical permittivity \( (\varepsilon) \) associated with the susceptibility of permittivity \( (\chi) \) as

\[ \varepsilon(\omega) = (1 + 4 \pi \chi). \]

When it comes to ferroelectrics, then \( \varepsilon \approx 1 \), so \( \varepsilon = 4 \pi \chi \). We obtained the expression for electrical permittivity as

\[ \varepsilon(\omega) = \frac{-8 \pi N \mu^2 \Omega \langle \langle S_i^\dagger \rangle \rangle}{\left[ \omega^2 - \Omega^2 + 4 \Omega^2 \Gamma^2 \right]}. \]
In the RbH₂AsO₄ ferroelectric crystal, some of the energy is lost in the shape of heat called tangent delta, denoted by \( \tan \delta \) expressed as
\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = -\frac{2 \Omega \Gamma(\omega)}{\omega^2 - \Omega^2}.
\]

2.4 Cochran’s soft mode frequency and Curie’s temperature \( (T_c) \)

The final Green function is obtained as
\[
G(\omega) = \frac{\Omega \langle S_i^X S_j^Y \delta_{ij} \rangle}{\pi \omega^2 - P(\omega)}.
\]

Ferroelectric Cochran’s mode of frequency expressed as;
\[
\Omega^2 = \Omega^2 + 2\Omega \{ \Delta_4(\omega) + \Delta_5(\omega) + \ldots \}. \tag{25}
\]

In equation (15) we have obtained as
\[
\approx \Omega^2 = \Omega + 2\Omega \{ \Delta_1(\omega) + \Delta_2(\omega) + \Delta_3(\omega) \}, \tag{26}
\]

And
\[
\approx \Omega^2 = a^2 + b^2 - bc, \tag{27}
\]

where
\[
\Omega = \Omega_1 \pm \Omega_2 \Omega \langle S_i^X S_i^Y \rangle V N_1 + b \langle \Omega_a J \rangle S_i^Z \tag{28.b}
\]

The above expressions contain effects of direct spin-spin interaction, four body interaction and extra
spin-lattice interaction. The frequency critically depends upon temperature. If we apply transition condition i.e. \( \Omega \rightarrow 0 \) as \( T \rightarrow T_c \), and in paraelectric phase \( \langle S_i^z \rangle = 0 \). The condition gives

\[
T_c = \frac{\Omega}{2K_B \tanh^{-1} \left( \frac{4\Omega}{J^2} \right)},
\]

(30)

2.5 Spontaneous Polarization (\( P_s \))

The temperature dependence of the spontaneous polarization due to tunnelling of a proton from one of the minima to another is proportional to \( \langle S_i^z \rangle \). The expression for spontaneous polarization by using the PLCM model is (2) as;

\[
P_s = 2N \mu \frac{\Omega \langle J_{ij} \rangle}{\Omega} \tanh \frac{\Omega}{K_B T},
\]

(31)

where \( \langle S_i^z \rangle \) represent the pseudospins which is along the direction of the z-axis and \( \mu \) represents the dipoles moment and \( N (0.8 \times 10^{21} \text{ cm}^{-3}) \) represents the number of dipoles in a unit cell. It has occurred only when \( (T<T_c) \) but in the case of \( (T>T_c) \) then is equal to zero. At very low-temperature \( T<<T_c \) the expression for spontaneous polarization are obtained as;

\[
P_s = N \mu \frac{\Omega \langle J_{ij} \rangle}{\Omega} \tanh \frac{\Omega}{K_B T},
\]

(32)

where \( J \) is the interaction constant, and \( \Omega \) represent the protons tunnelling motion.

3. Results and Discussions.

To summarize, we fitted the model values of different quantities occurring in expressions from the literature [37], for RbH\(_2\)AsO\(_4\) crystal as shown in Table (1). We have calculated values of \( \langle S_i^x \rangle \) and \( \langle S_i^z \rangle \) for RbH\(_2\)AsO\(_4\) crystal using formulae

\[
\langle S_i^x \rangle = \frac{2\Omega}{\Omega} \tan h \frac{\Omega}{K_B T}, \quad \text{(33.a)}
\]

and

\[
\langle S_i^z \rangle = \frac{\Omega \langle J_{ij} \rangle}{\Omega} \tanh \frac{\Omega}{K_B T}.
\]

(33.b)

Then we have calculated values of \( \Delta(\omega) \) and \( \Gamma(\omega) \) by fitting values of coefficients from table-I given below and values of \( \langle S_i^x \rangle \) and \( \langle S_i^z \rangle \) for different temperature for RbH\(_2\)AsO\(_4\) crystal. The \( \Gamma(\omega) \) functions are calculated using the following relation

\[
\delta(X) = \frac{1}{\pi} \frac{\epsilon}{X^2 + \epsilon^2}, \quad \text{for very small } \epsilon \rightarrow 0.
\]

However, we are not giving here numerically calculated values of all \( \Delta(\omega) \) and \( \Gamma(\omega) \) functions, for avoiding an unnecessary increase in the length of the paper.

Therefore, we obtain thermal variations of electrical permittivity (\( \epsilon \)), Cochran’s mode frequency \( \Omega \), tangent delta (\( \tan \delta \)), and spontaneous polarization (\( P_s \)). These quantities are respectively shown in Fig.1,
2, 3 and 4. We observe from fig. (1), Cochran’s mode frequency first decreases from the low-temperature side becoming smallest at the transition point (109.9K) then slightly increases and remains constant above it. From fig. (2), we infer that the electrical permittivity first increases, from the low-temperature side, being anomalously high at a transition temperature (109.9K) then decreases above it. From figure (3) we find that the tangent delta increases from the low-temperature side becoming largest at the transition point and then decreases above it. From fig. (4), we infer that the spontaneous polarization increases with decreasing temperature and have a maximum value of 0.05 μC-cm⁻¹ at temperature T=109.9K, and decreases as temperature approaches T_c=109.9K, and almost vanishes afterwards. We have compared our theoretical finding for frequency mode of Cochran, electrical permittivity, and tangent delta with correlated data, and experimental data respectively of other workers for RbH₂AsO₄ crystal.

Table 1. Model values for undeuterated RbH₂AsO₄ crystal given by Ganguli et al. [19].

| RbH₂AsO₄ crystal symbol | Constant values | Unit |
|--------------------------|-----------------|------|
| T_c                      | 109.91          | K    |
| J                        | 241.12          | cm⁻¹ |
| J                        | 321.50          | cm⁻¹ |
| V₁                        | 25              | cm⁻¹ |
| Ω                        | 3.80            | cm⁻¹ |
| ω₀                        | 128.5           | cm⁻¹ |
| C                        | 247.00          | cm⁻¹ |
| μ                        | 1.8×10⁻¹⁸       | cm⁻¹ |
| A₀                        | 7.763           | cm⁻¹ |
| N                        | 0.8×10⁻¹³       | cm⁻¹ |
| B_ij                      | 0.003           | cm⁻¹ |
| N_k at Curie’s temp       | 1.20            | cm⁻³ |

Fig.1- Calculated Cochran’s frequency versus temperature in RbH₂AsO₄ Crystal; our calculated values denoted by solid — line (▲), correlated with experimental data denoted by a dotted line •••• (♦) of Blinc et al [12].
Fig. 2 - Calculated Electrical permittivity ($\varepsilon$) versus temperature in RbH$_2$AsO$_4$ Crystal; our calculated values denoted by solid — line (▲), correlated with experimental data denoted by a dotted line (♦) of Blinc et al [12].

Fig. 3 - Calculated Tangent delta ($\delta$) versus temperature in RbH$_2$AsO$_4$ Crystal; our calculated values denoted by solid — line (▲), correlated with experimental data denoted by a dotted line (♦) of Blinc et al [12].

Fig. 4 - Calculated Spontaneous Polarization ($P_s$) versus temperature in RbH$_2$AsO$_4$ Crystal; our calculated values denoted by solid — line (▲), correlated with experimental data denoted by a dotted line (♦) of Zolototrubov et al [8].
4. Conclusion

This paper extends the simple PLCM model of the previous author’s work [19] with the help of a modified Hamiltonian by adding terms for four body interaction, direct spin-spin interaction term, extra spin-lattice interaction term, third and fourth-order anharmonic terms, and four body spin coupling terms into the PLCM model Hamiltonian for \( \text{RbH}_2\text{AsO}_4 \) crystal. We have obtained modified expression for Cochran’s mode frequency, electrical permittivity, tangent delta, response function (shift and Width), Curie’s temperature (\( T_c \)), and spontaneous polarization (\( P_s \)) which shows that the extra terms considered in the model play an important role by using the theory of Zubarev’s statistical article and temperature-dependent Green’s function to explain successfully the phase transition in \( \text{RbH}_2\text{AsO}_4 \) crystal. In the present calculation, we have obtained more rigorous formulae. Earlier authors have not considered the extra terms which we have considered. They have decoupled the extra terms and higher-order Green functions which we have considered earlier. Now, we have also decoupled them at the proper stage which gives better results than [19]. We conclude that the extra terms added in the PLCM model are quite important. These explain expressions adequately phase transition, Cochran’s mode frequency electrical permittivity, tangent delta \( \delta \), and Curie’s temperature (\( T_c \)) of \( \text{KH}_2\text{AsO}_4 \) crystal, and this type of model will also be applicable for H-bonded alkali phosphate crystals which are isomorphous to \( \text{KH}_2\text{PO}_4 \), \( \text{RbH}_2\text{PO}_4 \), \( \text{RbH}_2\text{AsO}_4 \), and \( \text{CsH}_2\text{AsO}_4 \).

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