Explanation of Onset Ferroelectric Transition and Anomalous Tangent Delta in H-Bonded Rubidium Dihydrogen Phosphate Crystal

Kuldeep Kumar1* Trilok Chandra Upadhyay1

1Department of Physics, HNBGU (A Central University) Srinagar UK, India-246174

*Corresponding Author: kuldeep26811@gmail.com

Received: 28.8.2021; Revised: 19.9.2021; Accepted: 29.9.2021
©Society for Himalayan Action Research and Development

Abstract
The H-bonded ferroelectric and ordered-disordered, type of Rubidium Dihydrogen Phosphate crystal is theoretically investigated. It undergoes a ferroelectric phase transition at 146K. Modified earlier author’s (Ganguli et al, 1980) simple Pseudo Spin Lattice Coupled mode (PLCM) model Hamiltonian by adding some extra interactions term into it, like third-order and fourth-order, phonon anharmonic interactions, direct spin-spin terms, extra spin-lattice terms and four spin coupling terms are added. By using Zaberav’s statistical approach, two times temperature dependent Green function method, and Dyson’s equation in the mean-field approximation (MFA), to obtain the formulae of various quantities like (e), (Ω) and tan(δ). Curie’s temperature, and response function (shift and width) as a function of temperature. Thermal variations of above quantities are obtained for Rubidium Dihydrogen Phosphate (RbH2PO4) crystal. A comparison with theoretical findings has been made with the experimental findings reported by (Peercy et al, 1974) which shows good agreement.

Keywords: Electrical permittivity, Ferroelectricity, Curie’s temperature, Green function, and Response function.

Introduction

The rubidium dihydrogen phosphate crystal is abbreviated as RDP. In the investigations of ferroelectric RbH2PO4 crystal of great interest aroused in the past few years as they have got promising applications in a wide range of areas, due to their interesting properties which are widely used in laser technologies, memory devices, etc. The alkali phosphate H-bonded ferroelectric crystals are very famous called KH2PO4 type crystals because of their isomorphic structure, and their deuterated structure is also fully or partially analogous. The RbH2PO4 crystal is characterised by covalently bonded PO4 units connected by bridging H-bonds and ionic bonding between rubidium cations and PO4 anions, which is responsible for the formation of the minima of double-well potential. The RbH2PO4 crystal is undergone phase transition at Tc = 146K. In the paraelectric phase when (T > Tc) then Oxygen atoms of the Hydrogen bond are located by an axis C2 which implies that the Hydrogen atoms are disordered between two symmetrical positions along with Oxygen-Hydrogen-Oxygen bonds with equal probability. In the ferroelectric phase when (T < Tc) all of the protons are ordered into one of the double-well potentials. The lattice parameters of RbH2PO4 crystal are as β = 90°, (a = 7.608Å), (b = 7.608Å), and (c = 7.296 Å). In deuteration Tc shifts from 146K to 249.8K which shows a large isotopic effect. It is an orthorhombic structure with the PO4 groups are connected by O-H---O bonds below Tc, and a tetragonal structure with the four Rb-PO4 groups in the
unit cell above $T_c$. The (spontaneous polarization) in the RbH$_2$PO$_4$ crystal is perpendicular to the direction of the Oxygen-Hydrogen-Oxygen bond and PO$_4$ group in RbH$_2$PO$_4$ crystal, bonding in three dimensional. (Cochran, 1960) has given the theory of transition in terms of instability against one of the normal modes of vibrations. The experimental and theoretical studies on RbH$_2$PO$_4$ type crystals have been made by many workers. (Blinc, 1960) first explained the isotope effect in RbH$_2$PO$_4$ crystal. (Averbuch and Durif, 1985) have studied the new structure form of RbH$_2$PO$_4$ crystals. (Peercy, 1974) has studied coupled proton-optic mode model for RbH$_2$PO$_4$ and KH$_2$PO$_4$ crystals and calculated the spontaneous polarization, Curie’s temperature, and electrical permittivity. In RbH$_2$PO$_4$ crystal, a Raman study has been done by (Courtens and Vogt, 1985). (Adhav, 1969) has studied the phase transition, piezoelectric and elastic properties in KH$_2$PO$_4$ type H-bonded crystal. (Semwal and Sharma, 1974) have studied the infrared absorption in H- bonded anharmonic crystal and susceptibility by using (PLCM) model and Green function technique as a function of two-time temperature. (Agui et al, 1993) have studied the hydrogen bonds and phosphate (PO$_4$) mode in KH$_2$PO$_4$ and RbH$_2$PO$_4$ crystals which have been investigated by using the inelastic neutron scattering and Raman scattering experiments. (Dulterio and Oweni, 1988) have studied phase transition at high temperature in RbH$_2$PO$_4$ crystals. (Upadhyay and Semwal, 2002) have studied dielectric properties in H-bonded crystals. (Mattauch et al, 2011) have studied x-ray diffraction and high-resolution neutron as a function of temperature in KH$_2$PO$_4$ type H-bonded crystals. (Boysen et al, 2004) have studied conductivity at high temperature and pressure. Dielectric properties in H- bonded crystal of KH$_2$PO$_4$ family studied by (Singh et al, 2021 and Kahan and Upadhayay, 2020). (Ganguli et al, 1980) have studied the phase transitions in KH$_2$PO$_4$ type H-bonded crystals by using the (PLCM) model and Green’s function technique. They modified the earlier author’s model (Zuberav’s, 1960) by adding extra terms and explained the permittivity of KH$_2$PO$_4$ type crystals. (Singh et al, 2021) have not considered the four spin coupling term in their model to explain the dielectric properties of RbH$_2$PO$_4$ crystals. Earlier authors (Singh et al, 2021 and Kahan and Upadhayay, 2020) have not considered the four spin coupling term in their model to explain the ferroelectric properties of the RbH$_2$PO$_4$. In contrast to their treatment (decoupling), we shall use a better decoupling scheme, which will enhance the terms in the results.

In this work, we considered the extra terms like direct spin-spin interaction term, extra spin-phonon interaction term and (third-order and fourth-order lattice anharmonic interactions terms), in the (PLCM) model for RbH$_2$PO$_4$ crystals to find out theoretical expressions. These extra terms play an important role in explaining the thermal dependent quantities of Cochran’s mode frequency, electrical permittivity, tangent delta, shift-width and tangent delta. We have compared our theoretical calculated findings with the experimental finding of (Peercy et al, 1974).
Modified Hamiltonian and Calculation

For the investigation of ferroelectric properties in RbH₂PO₄ crystals, we consider the modified model as:

\[ H_1 = -2\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z + \frac{1}{4} \sum_k \omega_k (A_k^\dagger A_k + B_k^\dagger B_k) - \sum_{ik} V_{ik} S_i^x A_k, \]

where \( \Omega \) represents the proton tunnelling frequency, \( J_{ij} \) is the interaction constant, \( V_a \) 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. \( V^3 \) \( k_1 k_2 k_3 \) and \( V^4 \) \( k_1 k_2 k_3 k_4 \) represents the (third-order and fourth-order) lattice’s phonon anharmonic interaction terms, \( J_{ijkl} \) represent the four body interaction constant, \( S_i^x A_k \) and \( S_i^x A_k^2 \) terms represent indirect coupling, and \( B_{ij} \) term represents the coupling constant.

We shall add in \( H_1 \), the \( H_2 \) given by

\[ H = H_1 + H_2. \]

Now by using two-times temperature-dependent statistical method of Green’s function technique by (Zubraver’s, 1960) and double differentiation of w.r.t (t) and (t) of Hamiltonian to obtain Dyson’s equation as;

\[ G_{ij} \omega = G_{ij}^0 \omega + G_{ij}^0 \omega P \omega G_{ij}^0 \omega, \]

we obtain

\[ G_{ij}^0 \omega = \Omega <S_i^x> \delta_{ij} \pi^{-1} (\omega^2 + \Omega^2) \]

\[ P \omega = \pi\Omega^{-1} <S_i^x>^{-1} << F_i(t) ; F_j(t') >>. \]

where \( F_i(t) \) and \( F_i(t') \) are given as

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

\[ F_i' = 2\Omega \sum_i V_{ik} A_k \sum_j S_i^z + \Omega \sum_i V_{ik} A_k^2 \sum_j S_i^z S_j^x - \Omega \sum_i B_{ijk} \sum_j S_i^z S_j^x + \delta ij S_i^z S_j^x - \ldots \]  

(8)

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

\[ G_{ij}^0(\omega) = \Omega \left( \frac{S_i^x}{\omega^2 - \Omega^2} \right) \delta ij \left[ \frac{1}{\pi \left( \omega^2 - \Omega^2 \right)} \right]^{-1}. \]  

(9)

In Eq. (6) \( P(\omega) \) are the response function and \( \Omega \) is the normalized pseudo-spin and different product of operators like \( \Omega J_i S_i^x, \Omega J_j S_j^x \) and \( A, A^\dagger \) etc. contained in Eqn. (7) and (8) which are evaluated after applied decoupling scheme as;

\[ \langle \langle EF;GH \rangle \rangle = \langle \langle EF \rangle \rangle \langle \langle G;H \rangle \rangle + \langle \langle EG \rangle \rangle \langle \langle F;H \rangle \rangle + \langle \langle EH \rangle \rangle \langle \langle F;G \rangle \rangle. \]  

(10)

Now, we resolve \( P(\omega) \) into its real \( \Delta(\omega) \) and imaginary \( \Gamma(\omega) \) parts in which the real part is called (shift) and the imaginary part is called (width). We, therefore, obtain the quantities of \( \Delta(\omega) \) and \( \Gamma(\omega) \) is expressed as \( P(\omega) = \Delta(\omega) + i\Gamma(\omega) \), and the quantities of delta and gamma are as follows

\[ \Delta(\omega) = \frac{4\alpha^2 V_{ik}^2 N_k}{\omega^2 - \omega^2_k} + \frac{4\Omega \alpha V_{ik}^2 \left( S_i^x \right)}{\omega^2 - \omega^2_k} \left( \frac{2}{\omega^2 - \omega^2_k} \right) \frac{\omega^2 - \omega^2_k}{\omega^2} \) \left[ \frac{1}{\pi \left( \omega^2 - \Omega^2 \right)} \right]^{-1}, \]  

(11.a)

Therefore total \( \Delta(\omega) = \Delta_1(\omega) + \Delta_2(\omega) + \ldots. \) 

Now we calculate the value of \( \Gamma(\omega) \)

\[ \Gamma(\omega) = \frac{4\alpha^2 V_{ik}^2 N_k}{2\Omega} \left( \frac{\omega - \omega}{\omega + \omega} \right) \left( \frac{\omega + \omega}{\omega - \omega} \right) + \frac{8\alpha V_{ik}^2 \left( S_i^x \right)}{\omega^2 - \omega^2_k} \frac{\omega^2 - \omega^2_k}{\omega^2} \left( \frac{1}{\pi \left( \omega^2 - \Omega^2 \right)} \right) \left[ \frac{1}{\pi \left( \omega^2 - \Omega^2 \right)} \right]^{-1}, \]  

(11.b)

Therefore total \( \Gamma(\omega) = \Gamma_1(\omega) + \Gamma_2(\omega) + \Gamma_3(\omega) + \ldots. \) 

(12.a)

The final Green function is obtained by replacing the \( P(\omega) \) value from equation (6) for the final Green function expressed as;

\[ G(\omega) = \Omega < S_i^x > \delta ij \left[ \frac{1}{\pi \left( \omega^2 - \Omega^2 \right) - P(\omega)} \right]^{-1}. \]  

(13)
The various expressions for unmodified frequency and Cochran’s mode frequency are given as:

\[
\hat{\Omega}^2 = \tilde{\Omega}^2 + 2\hat{\Omega} \Delta_s \omega + \Delta_3 \omega + ... + \Delta_{26} \omega .
\]  

(14)

In equation (11) we have obtained as

\[
\tilde{\Omega}^2 = \Omega + 2\Omega \Delta_1 \omega + \Delta_3 \omega + \Delta_5 \omega .
\]

(15.a)

and

\[
\tilde{\Omega}^2 = 4\hat{\Omega}^2 + \frac{i}{\Omega} \left( \langle F, S_i^y \rangle \right).
\]

(15.b)

Above equation Eqn. is solved by using the mean field approximation, and the value of \(\Omega^2\) is

\[
\hat{\Omega}^2 = a^2 + b^2 - bc,
\]

(16)

where

\[
a = \left( J + 3J' \langle S_i^z \rangle^2 + 2Bi \right) \langle S_i^z \rangle.
\]

(17)

\[
b = 2\Omega,
\]

is the modified pseudo spin frequency called

\[
c = \left( J + 3J' \langle S_i^z \rangle^2 + 2Bi \right) \langle S_i^x \rangle.
\]

(19.a)

and

\[
\tilde{\Omega}^2 = \frac{1}{2} \left( \Omega^2 \pm 4\hat{\Omega}^2N_k + B_i^2\Omega \langle S_i^y \rangle \right).
\]

Above equation Eqn. is solved by using the mean field approximation, and the value of \(\Omega^2\) is

\[
\hat{\Omega}^2 = \left( \omega_k + \Omega^2 \right) \pm \left( \omega_k + \Omega^2 \right)^2 + 8 \left\{ \frac{4V_i^2 \Omega^2N_k}{b} + \frac{4V_i^2 \Omega \langle S_i^z \rangle^2}{b} \right\} \omega_k
\]

(20)
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. \( \Omega \to 0 \) as \( T \to T_c \), and in paraelectric phase \( \langle S_i^x \rangle = 0 \). The condition gives:

\[
T_c = \frac{\Omega}{2K_B \tanh \left( \frac{4\Omega}{J} \right)} .
\]

(21)

The expressions for electrical permittivity and tangent delta are as follows;

\[
\varepsilon = \frac{\omega}{8\pi N \mu^2 \Omega \left( \langle S_i^x \rangle \right)} \left[ \frac{\omega^2 - \Omega^2}{\omega^2 - \Omega^2 + 4\Omega^2 i^2} \right]^{-1} .
\]

(22)

In the RbH\(_2\)PO\(_4\) ferroelectric crystal, some of the energy is lost in the shape of heat called tangent delta, denoted by \( \tan \delta \) expressed as;

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon} = -2(\Omega \Gamma \omega) \left( \frac{\omega^2 - \Omega^2}{\omega^2 - \Omega^2 + 4\Omega^2 i^2} \right)^{-1} .
\]

(23)

Results and Discussions.

Now, by fitting the model values of different quantities occurring in expressions from the literature (Ganguli et al, 1980), for RbH\(_2\)PO\(_4\) crystal as shown in Table (1). We have calculated values of \( \langle S_i^x \rangle \) and \( \langle S_i^z \rangle \) for RbH\(_2\)PO\(_4\) crystal using formulae

\[
\langle S_i^x \rangle = \frac{2\Omega}{\tilde{\Omega}} \tanh \frac{\tilde{\Omega}}{K_B T},
\]

(24.a)

and

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

(24.b)
Thus we obtain thermal variations of electrical permittivity (ε), Cochran’s mode frequency ($\omega^2$), and tangent delta (tan δ). These quantities are respectively shown in Fig. 1, 2, and 3. We observe from Fig. 1 at transition temperature (146K), the electrical permittivity first increases, from the low-temperature side, being anomalously high at a transition temperature (146K) then decreases above it. From Fig. 2 we infer that Cochran’s mode frequency first decreases from the low-temperature side becoming smallest at the transition point (146K) then remains constant above it. We see in Fig. 3 that the tangent delta increases from the low-temperature side becoming largest at the transition point and then decreases above it.

Table (1):- Constant values for RbH$_2$PO$_4$ crystal given by (Ganguli et al, 1980).

<table>
<thead>
<tr>
<th>$T_c$ (K)</th>
<th>$J$ cm$^{-1}$</th>
<th>$J'$ cm$^{-1}$</th>
<th>$V_{ik}$ cm$^{-3}$</th>
<th>$\Omega$ cm$^{-1}$</th>
<th>$\omega k$ cm$^{-1}$</th>
<th>$C$ (K)</th>
<th>$\mu$ e.s.u. cm$^{-1}$</th>
<th>$N$ cm$^{-1}$</th>
<th>$B_{ij}$ cm$^{-1}$</th>
<th>$N_k$ cm$^{3}$</th>
<th>$V_{ik}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>146.9</td>
<td>60</td>
<td>20</td>
<td>0.252</td>
<td>78.40</td>
<td>12.5</td>
<td>238.90</td>
<td>1.8 $10^{-18}$</td>
<td>0.8 $10^{21}$</td>
<td>0.078</td>
<td>1.20</td>
<td>0.126</td>
</tr>
</tbody>
</table>

**Fig.1**-Calculated electrical permittivity (ε) versus temperature in RbH$_2$PO$_4$ Crystal; our calculated values denoted by dotted line ▲ correlated with experimental data denoted by a solid line ♦ of (Peercy et al, 1974).

**Fig.2**-Calculated Cochran’s mode frequency ($\omega^2$) versus temperature (T) in RbH$_2$PO$_4$ Crystal; our calculated values denoted by dotted line ▲ correlated with experimental data denoted by the solid blue line ♦ of (Peercy et al, 1974).
Fig. 3 - Calculated tangent delta (δ) versus temperature (T) in RbH$_2$PO$_4$ crystal; our calculated values denoted by dotted line ▲ correlated with experimental data denoted by the solid blue line ◦ of (Peercy et al, 1974).

Conclusions

The work presented in this paper is the extension of the previous author’s work (Singh et al, 2021 and Ganguli et al, 1980) with the help of modified Hamiltonian by adding terms for four body interaction, direct spin-spin interaction term, extra spin-lattice interaction term and third and fourth-order anharmonic terms into PLCM model for RbH$_2$PO$_4$ crystal. We have obtained modified expression for Cochran’s mode frequency, electrical permittivity, tangent delta and spontaneous polarization shows that due to other terms considered in the model. We have obtained more rigorous formulae. These formulae show that other interaction terms are important in the ferroelectric RbH$_2$PO$_4$ crystal which belongs to the family of KH$_2$PO$_4$ crystals. The present calculation shows that all the interactions considered in the model are important. They contribute to the ferroelectric and dielectric behaviour of RbH$_2$PO$_4$ crystal. These terms explain expressions adequately phase transition, Cochran’s mode frequency electrical permittivity, tangent delta δ, and Curie temperature ($T_c$), and this type of model will also be applicable for crystals that are isomorphs to KH$_2$PO$_4$ type crystals.

Acknowledgement

The authors are grateful to Prof S C Bhatt (EX-HOD), Prof P D Semalty (EX-HOD), Prof O P S Negi (VC-IGOU) Haldwani, Prof Mahavir Singh (EX-VC) Shimla, Prof H C Chandola (HOD-KU Nainital), Dr. Manish Uniyal for their suggestions and encouragement. Kuldeep Kumar is thankful to Mr Pawan Singh, Mr Muzaffar Iqbal Khan, Mr Aditya Joshi, and Mr Mool Chand for encouragement. Kuldeep Kumar is thankful to MOTA, New- Delhi for financial support.

References


