Abstract—The model Hamiltonian proposed by the \cite{Blinck, Fehér} has been modified by considering the lattice anharmonicity up to fourth order for the stochastic motion of groups. The correlations appearing in the dynamic equation have been evaluated using double time thermal retarded Green’s functions and Dyson’s equation. The proton Green’s function and phonon Green’s function have been evaluated for the collective motion of the system, using model Hamiltonian. The higher order correlations in the proton Green’s function have been evaluated using the symmetrical decoupling scheme, after applying the Dyson’s treatment. The expressions for the proton renormalized frequency of the coupled system and collective proton wave half widths have been calculated. The higher order correlations in the phonon response function have been calculated without any decoupling and using renormalized Hamiltonian. The expressions for the renormalized phonon frequency and acoustic phonon widths and shifts have been calculated. Using expectation value of the proton collective mode components at site q \cite{Blinck, Fehér} the temperature dependence of $< S_q^z >$ and $< S_q^x >$ for different values of, have been calculated. This shows the order of phase transition. In paraelectric phase the value of decreases when temperature increases from transition temperature (TC). Our theoretical results fairly agree with experimentally reported results.

Keywords—Green’s function, collective proton frequency width, and proton collective mode components.

I. INTRODUCTION

The anharmonic interactions in solids are profoundly responsible for their physical properties. The study of various thermal and dynamic properties of solid is essentially a many body problem. Usual perturbation theories of the Born-type are not appropriate for solving these problems.\cite{Blinck, Fehér}. The methods of quantum field theory have been widely employed in solving many-body problems in solid state physics. One of them, the thermodynamics Green’s function method has become an invaluable tool in the study of complicated system of the interacting particles in statistical physics. This method is non-perturbative and provides a systematic approach for calculating thermally averaged correlation functions and hence physically observable quantities. Most of the physical properties of a system can be expressed in terms of these Green’s functions which lead to thermally averaged observables. This provides an effective means of calculating the observable macroscopic as well as the microscopic properties of a solid.

In order-disorder dielectrics, as KH$_2$PO$_4$, the transitions is associated with the tunneling of proton through a barrier between two positions of minimum potential energy in the double well potential in the hydrogen bond at the transition temperature. In displacive phase transition is caused due to the displacement of a whole sub lattice of ions of one type relative to other sublattice, e.g., in Ba TiO$_3$ and most of the double oxide ferroelectrics. The atomic displacements at the transition point are small compared to the unit cell dimensions. The dynamical behaviour of two types of distortive structural phase transition (SPT) is also quite different. The order-disorder systems behave like the magnetic ones. In the order-disorder (KDP-type) systems the proton can tunnel through the barrier which separates the two minima of the potential energy in the hydrogen bond and the ground state of the system splits into two levels separated by energy $2\Omega$. The magnitude of $2\Omega$ depends on the overlap of the wave functions appropriate to a proton localized in each of the two minima. However, the protons interact with one another and with other atoms. The result is to give a spectrum consisting of one branch, if there is one proton per unit cell, and the frequency $\Omega(q)$ is temperature dependent 6-8. The system of two energy levels is most conveniently discussed in terms of spin-1/2 system. An account of this approach has been given by Tokunaga and Matsubara and Tokunaga with reference to earlier work by Slater, Blinc, de Gennes and others. The spin can be through of as precessing around the direction along which the field is directed. Above Tc the excitation spectrum shows relaxation character and is centered around $\omega = 0$. Only below Tc, a mode of finite frequency $\omega \neq 0$ is found (as per spin waves in ferromagnets).

Potassium dihydrogen phosphate (KDP), KH$_2$PO$_4$, is the prototype of order-disorder type ferroelectrics. The most important contribution to an understanding of the atomistic mechanism occurring at the ferroelectrics transition of KH$_2$PO$_4$ comes from structural...
investigations by means of X-ray and neutron diffraction\textsuperscript{11-13}. The X-ray data give strong indications as to the location of hydrogen atoms in the lattice from the interatomic distances between oxygen atoms and the neutron diffraction techniques accurately locate the structure\textsuperscript{14-18}. The overall picture of transition occurring in KH\textsubscript{2}PO\textsubscript{4} at 123\textdegree K, as obtained both from X-ray and neutron studies, reveals the role played by the hydrogen atoms in the co-operative phenomenon which leads to ferroelectricity. Simpler mean field theories have been used to gain qualitative physical insights in KDP-systems. In order to go beyond the mean field approximation and to include later –Takagi short range order effects into pseudospin model, Tokunaga and Matsubara\textsuperscript{9}, Matsubara and Yoshimitsu\textsuperscript{19} and Blinc and Svetina\textsuperscript{20} developed a four proton clusters model which takes into account the correlations governing motions of four protons surrounding by a PO\textsubscript{4} group. Vaks et al\textsuperscript{21} used the model of Blinc and Svetina\textsuperscript{20} but could not explain most of the features of KDP-system expect the difference between the Curie and Curie-Weiss temperature. Vaks and Zinenko\textsuperscript{22} performed extensive calculations for the static thermodynamics behaviour in the four-particle cluster approximation and found satisfactory agreement with the experimental data. Similar four particle cluster approximations were made by Yoshimitsu and Matsubara\textsuperscript{23} and Havlin and Sompolinsky\textsuperscript{24}. Their results, however, are in good agreement with experimental results, but they could not explain the observed relaxational behavior of dielectric properties and ultrasonic attenuation explicitly, in KDP-type ferroelectrics.

In analogy with the spin wave in magnetic system, the pseudo-spin formalism suggests the presence of some proton collective motion. Tokunaga\textsuperscript{10}, Nankovic\textsuperscript{25} and Brout \textit{et al}\textsuperscript{26} independently derived the proton collective modes within the random phase approximation and showed that the softening of this collective mode takes place and its frequency with the longest wavelength vanishes at a critical temperature T\textsubscript{C}. Expressions for longitudinal and transverse susceptibilities were obtained by introducing a phenomenological damping constant for the longitudinal relaxation time between the splitted levels.

Kobayashi\textsuperscript{5} extended the pseudospin model by including the interaction of proton mode with the lowest frequency transverse optic mode of the same symmetry K-PO\textsubscript{4} system. Other workers\textsuperscript{27,29} also suggested the inclusion of spin-lattice interaction term. This extended model explains very well the Raman spectroscopic data. Samara\textsuperscript{30} used this model to explain the results of pressure effect on dielectric properties of KDP-crystals. However, the large shifts of transition temperature corresponding to the small shifts of Curie-Weiss constant on deuteration of KDP could not be explained simultaneously by Kobayashi’s extended model. Houston and Bolten\textsuperscript{31} used Kobayashi’s extended model in their calculations and showed that the Curie-Weiss constant should contain the tunneling term. A number of workers\textsuperscript{6,32-35} used the pseudospin-lattice coupled mode model to elucidate the dielectric and ferroelectric behaviour of order-disorder (KDP-type) ferroelectrics. Jhang \textit{et al}\textsuperscript{36} have applied undetermined constant method to pseudospin model with four spin coupling term. They have not considered phonon part in their calculations which however has a very important contribution in crystals. Some workers\textsuperscript{37-39} have used pseudospin lattice coupled mode (PLCM) model along with phonon anharmonicity up to fourth order for KDP-type crystal. Upahuay and Semwal\textsuperscript{40} have used cubic and quartic phonon anharmonic interactions in the PLCM model for KDP-type crystal to study microwave dielectric tangent losses in KDP and DKDP crystals, their theoretical expressions for frequency, shift and width and soft mode frequency are compared to present study. A good agreement has been found.

In this paper, we consider short range and long range forces, the finite overlap of the protonic wave function between the two sites in a given hydrogen bond, a part of the proton-lattice coupling, and lattice anharmonicity up to fourth order. The approximation, is based on the cluster expansion of the partition function of an order-disorder type hydrogen bonded ferroelectric crystal. The interactions between the four protons surrounding a given PO\textsubscript{4} group are taken into account exactly and the rest is replaced by a molecular field, which is determined self-consistently\textsuperscript{6}. An attempt is made to account for the effect of one proton on the tunneling integral of another. The present approximation reduces in the classical limit to the Senko-Uehling modification of Slater theory. For KH\textsubscript{2}PO\textsubscript{4} the smallest cluster which is compatible with the crystal structure is a four particle one, which takes into account the correlation in the motion of the four protons surrounding a given PO\textsubscript{4} group. The four-body forces, considering the four particle cluster, which is the smallest cluster appropriate for the short-range effect, has been considered for KDP-system. This model is based on the four-particle approximation which was used successfully to describe the static properties of KDP-system along z-direction\textsuperscript{9,20,22}. The advantage of this approximation over mean field
approximation is that, in addition to the long range molecular-field two-body forces, the ST short range four-body interactions are also taken into account.

In the present study, the model Hamiltonian proposed by Blinc and Zĕks has been modified by considering the lattice anharmonicities for the stochastic motion of \( \text{H}_2\text{PO}_4 \) groups in a KH$_2$PO$_4$ system. The model Hamiltonian for this system is a combination of the proton Hamiltonian, the lattice Hamiltonian, the lattice-proton interaction terms and the anharmonic terms up to fourth order. The correlation functions were evaluated using the Green’s function technique and Dyson’s equation. The higher order Green’s functions were evaluated using symmetric decoupling scheme, the cross combinations were not considered because they do not contribute significantly. The expressions for collective proton frequency width, collective phonon mode frequency were obtained. Using parameters values given in tables, the theoretical expression for \( < S^z_i > \) and \( < S^x_i > \), the collective proton wave half width \( \Gamma_s(q, \omega) \) will be calculated. The temperature dependence of \( < S^z > \) and \( < S^x > \) will be calculated and temperature dependence of the collective proton wave half width, collective phonon mode frequency in PE phase for KH$_2$PO$_4$ will be evaluated.

**II. Theory**

**Model Hamiltonian**—The model Hamiltonian for KDP system in four particle cluster approximation can be written as a combination of following terms:

\[
H = H_p + H_L + H_{L\leftrightarrow P} + H_A
\]

...(1)

Where \( H_p \) the proton self-energy Hamiltonian, \( H_L \) lattice Hamiltonian, \( H_{L\leftrightarrow P} \) proton-lattice interaction term, \( H_A \) anharmonic term.

**Proton Hamiltonian**—The proton self-energy Hamiltonian can be written as:

\[
H_p = \sum_k \left( \epsilon_{\text{PO}} n_k + V_{\text{SR}} \right)
\]

...(2a)

here \( \epsilon_{\text{PO}} \) is a sum of one particle operators, which extends over all \( \text{PO}_4 \) groups in the crystal as well as overall four hydrogen sites near a given \( \text{PO}_4 \) groups:

\[
H_p = -\frac{1}{2} \Omega \sum_i \sum_{i',j} \left( S^x_{ij} + S_{ij} \right) = -2\Omega \sum_i S_{i}^x.
\]

...(2a.1)

where \( \Omega \) is the proton tunneling frequency, \( S_{ij}^+ = b_{ij}^+ b_{ij} \) and \( S_{ij}^- = b_{ij}^\dagger b_{ij}^\dagger \) with \( b_{ij}^+ \) and \( b_{ij} \).

\((k = \uparrow, \downarrow)\) standing for the proton creation and annihilation operators at \( i, j \) matrix site with state \( k \), and obey the usual anticommutation rules. The sign \( \uparrow \) or \( \downarrow \) means that the proton is created or annihilated near the upper or lower oxygen atom respectively, of a given \( \text{PO}_4 \) ion. \( S^z_i \) is called the tunneling operator, which measures the tunneling power of the proton between the hydrogen double well. The short range energy term:

\[
H_{SR} = -\sum_{i=1}^{N} \sum_{i=1}^{N} \sum_{k,k'} \sum_{j,k''} \epsilon_{ij}^2 \sum_{l,k''} \sum_{j,k''} [n_l n_{k''} + n_{k''} n_l] \cdot
\]

\[= \frac{1}{2} \sum_{ij} J_{ij} S_{ij}^z,\]

where \( n_{ij} \) are proton number operators, defined as:

\[
n_{ij} = b_{ij}^\dagger b_{ij} \text{ obeying the } n_{ij}^+ + n_{ij} = 1,\]

\( J_{ij} \) the two-body coupling coefficient, is the same for energy pair of protons in KDP. The short range measures the energies \( E_{ij} \) associated with different proton configuration around a given \( \text{PO}_4 \) ion as introduced by Slater and Takagi. The long range energy term:

\[
H_{LR} = \frac{1}{4} \sum_{i,j} \sum_{i',j'} \left( n_{ij}^+ - n_{ij} \right) \left( n_{i'j'}^+ - n_{i'j'} \right),\]

\[= -\frac{1}{4} \sum_{i,j} J_{ij} s_{ij}^z s_{i'j'}^z s_{ij}^z s_{i'j'}^z,\]

...(2a.3)

describes the interaction between those proton sites which do not belong to the same \( \text{PO}_4 \) ion. Where \( J_{ij} \) the four body coupling coefficient refers to the four hydrogen bonds in the \( \text{PO}_4 \) group in KDP. \( S_i^z \) is the half of the difference of occupation probabilities for the proton to be found in the two equilibrium positions of the hydrogen bond.

**Lattice Hamiltonian**—The Hamiltonian of the lattice vibrations in the absence of proton motion can be written as:

\[
H_L = \frac{1}{4} \sum_k \omega_k \left( A_k^+ A_k + B_k^+ B_k \right)
\]

...(2b)

where \( \omega_k \) is the initial phonon frequency and \( A_k \) and \( B_k \) are displacement and momentum operators and are related with normal coordinates:

\[
Q_k = \hbar^{1/2} \left( 2\omega_k \right)^{1/2} A_k
\]

and momenta:

\[
P_k = -i \left( \frac{1}{2} \hbar \omega_k \right) B_k, \text{ with } A_k = a_k + a_k^\dagger = A_k^+, \]

\[B_k = a_k - a_k^\dagger = -B_k^+, \text{ where } a_k^\dagger \text{ and } a_k \text{ are phonon creation and annihilation operators with wave vector } k.\]

**Proton-Lattice Interaction Hamiltonian**—The proton-lattice term can be written as:

\[
H_{\text{L-P}} = -\sum_i V_{ik} S_i^z A_k,
\]

...(2c)
where $V_{ik} = \frac{V_{ik}}{(2\omega_k)^{1/2}}$ is the proton-lattice coupling constant.

**Anharmonic Hamiltonian**—The Hamiltonian of the anharmonic crystal containing $N$ unit cells with $n$ atoms per unit cell in the second quantized form, inclusive of third and fourth order anharmonicities, is given by $^{45}$:

$$H_A = \sum_{k_i,k_2,k_3} V_3 \phi(k_1, k_2, k_3) + \sum_{k_i,k_2,k_3} V_4 \phi(k_1, k_2, k_3) \Delta \phi(k_1, k_2, k_3, k_4),$$

...(2d)

where $V_3$ and $V_4$ are Fourier transform of the third- and fourth-order anharmonic coefficient and are given by Maradudin et al. $^{45}$:

$$V_3 = \frac{1}{(6N)^{1/2}} \phi(k_1, k_2, k_3) \frac{\hbar^3}{8\omega_{k_1}\omega_{k_2}\omega_{k_3}},$$

and

$$V_4 = \frac{1}{(24N)} \Delta \phi(k_1, k_2, k_3, k_4) \frac{\hbar^3}{8\omega_{k_1}\omega_{k_2}\omega_{k_3}},$$

The $\phi$'s are coulomb coefficient defined by Born and Huang $^{48}$ and Semwal and Sharma $^{39}$. Combining equations 2. The resultant Hamiltonian, used in this paper, can be written as:

$$H = -2\Omega \sum_i S_i^z \sum_i^{1/2} J_{i,j} S_j^z - \frac{1}{4} \sum_{i,j,k,l} J_{i,j,k,l} S_i^z S_j^z S_k^z S_l^z + 1/4 \omega_k \sum A_k^z + m_{kg}$$

$$- \sum_i V_{ik} S_i^z A_k + \sum_{k_1,k_2,k_3} V_3 \phi(k_1, k_2, k_3) + \sum_{k_1,k_2,k_3,k_4} V_4 \phi(k_1, k_2, k_3, k_4) \Delta \phi(k_1, k_2, k_3, k_4),$$

...(3)

Using this modified Hamiltonian for the KDP-system and using the green's function method the dielectric properties of KDP-type ferroelectrics will be discussed.

**III. GREEN'S FUNCTION**

Following Zubarev $^{40}$, the proton Green's function is as follows:

$$G_{qq}(\omega) = \langle S_q^z(t); S_q^z(t') \rangle \rangle \quad -j\theta(t-t') \langle [S_q^z(t); S_q^z(t')] \rangle$$

...(4)

where the angular brackets denote the average over the large canonical ensemble and $\theta(t)$ is the usual Heaviside step function, having properties:

$$\theta(t) = 1 \quad \text{for} \quad t > 0 \quad \text{and} \quad \theta(t) = 0 \quad \text{for} \quad t < 0,$$

$$j = (-1)^{1/2}.$$

Differentiating (4) twice with respect to time $t'$ with the help of model Hamiltonian (3) and taking Fourier transformation, one obtains:

$$(\omega^2 - \Omega^2) G_{qq}(\omega) = \frac{\Omega < S_q^z > \delta_{q,q} + \Omega < F_q(t); S_q^z(t') >>}{\pi} + \frac{\Omega < F_q(t); S_q^z(t') >}{\pi},$$

...(5)

and the higher order Green's functions:

$$P_{qq}(t,t') = \langle < F_q(t); S_q^z(t') >> \rangle$$

...(6)

with

$$F_q(t) = \pi \left[ -2V_q S_q^z A_q - \frac{1}{2} J_q(S_q^z S_q^z + S_q^z S_q^z - S_q^z S_q^z - S_q^z S_q^z) + \frac{1}{2} S_q^z S_q^z S_q^z S_q^z - S_q^z S_q^z S_q^z - S_q^z S_q^z S_q^z S_q^z - S_q^z S_q^z S_q^z - S_q^z S_q^z S_q^z S_q^z \right]$$

...(7)

To calculate $P_{qq}(t,t')$, Eq. (6) is differentiating twice with respect to $t'$ from right hand side using the model Hamiltonian Eq. (3), taking Fourier transformation, one obtains:

$$(\omega^2 - \Omega^2) G_{qq}(\omega) = \frac{\Omega < F_q(t); S_q^z > + \Omega < F_q(t); F_q(t') >}{\pi}$$

...(8)

where

$$F_q(t') = \pi \left[ -2V_q S_q^z A_q - \frac{1}{2} J_q(S_q^z S_q^z + S_q^z S_q^z - S_q^z S_q^z - S_q^z S_q^z) + \frac{1}{2} S_q^z S_q^z S_q^z S_q^z - S_q^z S_q^z S_q^z - S_q^z S_q^z S_q^z S_q^z - S_q^z S_q^z S_q^z - S_q^z S_q^z S_q^z S_q^z \right]$$

...(9)

$$\rightarrow \quad P_{qq}(t-t') = \langle < F_q(t); F_q(t') >> \rangle$$

...(10)

Substituting the value of $\rightarrow \quad P_{qq}(t-t')$ from equation (8) to equation (5) and rearranging, and applying the Dyson's equation $^{31}$, writing $G_{qq}(\omega)$ in the first approximation.

After arranging the terms, the final form of $G_{qq}(\omega)$ becomes:

$$G_{qq}(\omega) = \frac{\Omega < S_q^z > \delta_{q,q} + \Omega < F_q(t); S_q^z(t') >>}{\pi} + \frac{\Omega < F_q(t); S_q^z(t') >}{\pi} \mathcal{O}(\omega)$$

...(11)

where the renormalized frequency is

$$\mathcal{O}^2 = a^2 + b^2 - bc$$

...(12)

and

$$a = J_0 < S_q^z > + J_0' < S_q^z >^2,$$

...(12a)

$$b = 2\Omega,$$

...(12b)

$$c = J_0' < S_q^z > + 3J_0' < S_q^z >^2 < S_q^z >,$$

...(12c)
and 
\[ J_0 = \sum_q J_q \text{, and } J'_0 = \sum_q J'_q \]  

\[ \text{(12d)} \]

The expectation values of the proton collective mode components at site \( q \) have been obtained by Blink and Žeks as:
\[ < S_q > = \frac{Tr S_q e^{-\beta[3]_{MFA}}}{Tr e^{-\beta[3]_{MFA}}} = \frac{d. \log \Omega}{d. \beta |\tilde{\Omega}|} = 1 \frac{1}{2} \tilde{\Omega} \tanh \left( \frac{\beta \tilde{\Omega}}{2} \right) \]  

\[ \text{(13)} \]

so
\[ < S_q^x > = \frac{\Omega}{\tilde{\Omega}} \tanh \left( \frac{\beta \tilde{\Omega}}{2} \right) \],

\[ \text{(13a)} \]

\[ < S_q^y > = 0, \]

\[ < S_q^z > = \frac{(J_0 < S_q^z > + J'_0 < S_q'^z >)}{2\tilde{\Omega}} \tanh \left( \frac{\beta \tilde{\Omega}}{2} \right). \]

\[ \text{(13b)} \]

Equations (13) represent a system of 3\( N \) equations for the average values of the collective mode components. The solution of this system will, however, be stable only if they minimize the free energy, i.e., if 
\[ < S_q^z >= < S_q^y > = 0. \]

and so
\[ < S_q^z > = \frac{\Omega}{4\Omega^2 - 2\Omega_0 < S_q^z >} \tanh \left( \frac{4\Omega^2 - 2\Omega_0 < S_q^z >}{2k_B T} \right) \]  

\[ \text{(14)} \]

The higher order Green’s functions are evaluated using symmetrical decoupling scheme, the cross combinations are not considered because they do not contribute significantly. Putting the evaluated value of higher order Green’s functions \(< F_q (t); F_q (t') >; \) in Equation (11), one gets:
\[ \lim_{\epsilon \to 0} G_{qq} (\omega + j\epsilon) = \frac{\Omega < S_q^z > \delta_{qq}}{\pi \left( \omega^2 - \Omega^2 + 4\alpha_0^2 \Gamma_p \right)}, \]  

\[ \text{(16)} \]

where \( \tilde{\Omega} \) is the proton renormalized frequency of the coupled system, which on solving self consistently takes the form:
\[ \tilde{\Omega}^2 = \Omega^2 + 2\Omega \Delta_s (q, \omega), \]

\[ \text{(17)} \]

and
\[ \Delta_s (q, \omega) = \frac{1}{2\Omega} \sum_{i=1}^{3} G_{ii} (q, \omega) \]

\[ \text{(18)} \]

where
\[ G_{s1} (q, \omega) = \frac{2\tilde{\Omega}^2}{\Omega} \frac{\omega_q < S_q^1 > (\omega^2 - \tilde{\omega}_q^2)}{(\omega^2 - \tilde{\omega}_q^2)^2 + 4\omega_0^2 \Gamma_p^2}, \]

\[ \text{(18a)} \]

and
\[ G_{s2} (q, \omega) = \frac{b_0^2}{(\omega^2 - \tilde{\Omega}^2)} \]

\[ \text{(18b)} \]

and
\[ G_{s3} (q, \omega) = \frac{a_0^2 \tilde{\Omega}^2}{2\Omega (\omega^2 - \tilde{\Omega}^2)} \]

\[ \text{(18c)} \]

with
\[ \tilde{\Omega}^2 = (a_0^2 + n_q \tilde{\omega}_q^2) \]

\[ \text{(19)} \]

and \( \Gamma_s (q, \omega) \) is the collective proton wave half width, given by:
\[ \Gamma_s (q, \omega) = \pi \sum_{i=1}^{3} G_{ii} (q, \omega) \]

\[ \text{(20)} \]

where
\[ \Gamma_{s1} (q, \omega) = \frac{-4\tilde{\Omega}^2 \omega_q^2 < S_q^1 > \delta_{qq} \Gamma_p}{\Omega (\omega^2 - \tilde{\omega}_q^2)^2 + 4\omega_0^2 \Gamma_p^2} \]

\[ \text{(20a)} \]
\[ \Gamma_{s_2}(q, \omega) = \pi G_{s_2} = \frac{\pi b c^2}{2 \Omega} \left\{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \right\}, \]

and

\[ \Gamma_{s_3}(q, \omega) = \pi G_{s_3} = \frac{\pi n^2}{2b} \left\{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \right\} \]

The acoustic phonon width and shift are obtained analogously from the acoustic phonon Green’s function \( \langle \langle A_q; A_q^+ \rangle \rangle \). Using the model Hamiltonian, equation (3), one has

\[ G_{qq}(\omega) = \frac{\omega_q \delta_{qq}}{\pi (\omega^2 - \tilde{\omega}_q^2 + 2j \omega_q \Gamma_p(q, \omega))}, \]

where

\[ \tilde{\omega}_q^2 = \tilde{\omega}_q^2 + 2\omega_q \Delta_p(q, \omega) \]

with

\[ \tilde{\omega}_q^2 - \omega_q^2 + \omega_q \left\{ 16 \sum_q V_3(q) \cosh \frac{\beta \omega_q}{2} + 8 \sum_q V_4(q) \cosh \frac{\beta \omega_q}{2} \right\} \]

and the collective phonon mode frequency shift

\[ \Delta_p(q, \omega) = \sum_{i=1}^3 G_{qi}^*(q, \omega); \]

where

\[ G_{1p}(q, \omega) = \frac{2V_q^2 \Omega < S_q^+ > (\omega^2 - \tilde{\omega}_q^2) \delta_{qq}}{\omega_q \left\{ (\omega^2 - \tilde{\omega}_q^2)^2 + 4\Omega^2 \Gamma_p^2(q, \omega) \right\} \}, \]

\[ G_{2p}(q, \omega) = \frac{24 \sum_q V_3^2(q) \omega_q n_q}{\omega_q (\omega^2 - 4\tilde{\omega}_q^2)}, \]

and

\[ G_{3p}(q, \omega) = \frac{24 \sum_q V_4^2(q) \omega_q \omega_q}{\omega_q \tilde{\omega}_q}, \]

\[ \left[ \frac{(1 + 2n_q \omega_q + n_q^2)(2\tilde{\omega}_q + \omega_q)}{\omega_q^2 - (2\tilde{\omega}_q + \omega_q)^2} + \frac{(n_q^2 - 1)(2\tilde{\omega}_q - \omega_q)}{\omega_q^2 - (2\tilde{\omega}_q - \omega_q)^2} + \frac{2\omega_q (n_q^2 - 1)}{(\omega_q^2 - \tilde{\omega}_q^2)} \right] \]

\[ \left\{ \frac{(1 + 3n_q^2)}{(\omega_q^2 - 9\tilde{\omega}_q^2)} + \frac{(n_q^2 - 1)}{(\omega_q^2 - \tilde{\omega}_q^2)} \right\} \]

\[ \cdots (20b) \]

\[ \cdots (20c) \]

\[ \cdots (20d) \]

Calculating equation (22) self consistently and approximating, the collective phonon mode frequency is obtained as:

\[ \tilde{\omega}_q^2 = \frac{1}{2} \left\{ (\tilde{\omega}_q^2 + \tilde{\omega}_q^2) \right\} \pm \frac{1}{2} \left\{ (\tilde{\omega}_q^2 + \tilde{\omega}_q^2) + 16V_q^2 \omega_q \Omega < S^x > \right\} \]

\[ \cdots (25) \]

where

\[ \tilde{\omega}_q^2 = \omega_q^2 + 8\omega_q (2V_3 + V_4) \cosh \left( \frac{\beta \omega_q}{2} \right) \]

\[ \cdots (26) \]

The frequencies \( \tilde{\omega}_q \) are the normal modes of the system and are the frequencies which be used for comparison with other measured responses of the system\(^2\). Furthermore, \( \tilde{\omega}_q \) are approximately the same frequencies that obtained by fitting each part of spectrum independently\(^3\). The \( \tilde{\omega}_q \) mode frequency approaches zero at the \( T_c \). The \( \tilde{\omega}_q \) mode, on the other hand, has no critical temperature dependence. The \( \tilde{\omega}_q \) mode corresponds to the longitudinal soft \( \beta(z) \) mode\(^4\), which softens when temperature approaches \( T_c \) and \( \tilde{\omega}_q \) mode corresponds to the transverse \( \beta(x,y) \) mode\(^4\), which has by far less temperature dependence than the \( \tilde{\omega}_q \) mode.

\( \tilde{\omega}_q \) and \( \tilde{\omega}_q \) modes originate from a zone center phonon \( \omega = 0 \) corresponding to a collective proton motion in the \( a-b \) plane. Equation (15a) is obtained using the model Hamiltonian equation (3) and equation (24b) and (24c). The higher order correlations in the phonon response function are obtained without any decoupling and using the renormalized Hamiltonian:

\[ H_{ren} = -2\Omega \sum_q S_q^+ \sum_{q,q} \left\{ \frac{j_{q,q} \delta_{q,q}}{4} \sum_{q,q} \right\} \]

\[ \cdots (27) \]

The collective phonon half width is obtained as:

\[ \Gamma_p(q, \omega) = \Gamma_{p_1} + \Gamma_{p_2} + \Gamma_{p_3} \]

\[ \cdots (28) \]
\[ \Gamma_{\text{Ph}}(q, \omega) = \pi G_{\text{Ph}}(q, \omega) = \frac{-4P_{\text{eff}}^2 \Omega^2 < S' > \Gamma_q(q, \omega)}{\omega_q \left[ (\omega^2 - \bar{\Omega}^2)^2 \right] + 4\Omega^2 \Gamma_q^2(q, \omega)}; \]

\[ \Gamma_{\text{PE}}(q, \omega) = \pi G_{\text{PE}}(q, \omega) = 6\pi \sum_q V_q^2(q, q') \frac{\partial^2 G_q}{\partial^2 q} \left[ \delta(\omega - 2\delta_q) - \delta(\omega - 2\delta_q) \right] \]

where \( n_q = \frac{\omega_q}{\omega_q} \coth \left( \frac{\beta \omega_q}{2} \right) \) is the phonon occupation number and \( \beta = (k_B T)^{-1} \), \( k_B \) is Boltzman constant and \( T \) the absolute temperature. In the PE phase \( < S' > = 0 \), and the stability limit of the PE phase is determined by the temperature where \( \tilde{\omega}_q \) approaches zero, i.e., \( \tilde{\omega}_q \to 0 \) as \( T \to T_C \). In the vicinity of transition temperature in the PE phase one may expand \( \tilde{\omega}_q^2 \) in the power of \( (T - T_C) \) around its value at \( T_C \) getting immediately

\[ \tilde{\omega}_q^2 = \left( \frac{\partial \tilde{\omega}_q^2}{\partial T} \right)_{T=T_C} (T - T_C), \quad \text{(23a)} \]

\[ \tilde{\omega}_q^2 = \gamma (T - T_C). \quad \text{(23b)} \]

With

\[ \gamma = \frac{\Omega^2 J}{k_B T_C^2 \cosh^2 \left( \frac{\Omega}{k_B T_C} \right)} \]

When \( T \to T_C, \tilde{\omega}_q \to 0 \), equation (17) gives

\[ T_C = \frac{\Omega}{k_B \tanh^{-1} \left( \frac{4\Omega}{J} \right)} \quad \text{(24)} \]

where

\[ J = J_0 + \left. \frac{2V_q^2 \omega_q}{\tilde{\omega}_q} \right|_{T=T_C} \quad \text{(25)} \]

Now following Kuo\(^{55}\) and Zubarev\(^{56}\) the real part of dielectric constant (\( \varepsilon \)) of KDP crystal can be expressed with the help of Green function (4) as:

\[ \varepsilon - 1 = -\frac{8\pi \eta u^2 \tilde{\omega} \left( \omega^2 - \tilde{\omega}^2 \right)}{\left( \omega^2 - \tilde{\omega}^2 \right)^2 + 4\omega^2 \Gamma_p^2(\omega)}, \]

\[ \ldots (27) \]

Numerical calculations of width, shift and collective phonon mode frequency in PE phase

By using the parameter values from the literature\(^{40,43-46}\), the temperature dependence for \( < S_q^2 > \) and \( < S'_q > \) in KH\(_2\)PO\(_4\) for different values of \( J' \), (a) \( J' = J/3 \), (b) \( J' = 4J/3 \), (c) \( J' = 7J/3 \), the collective proton frequency width \( \Gamma_q(q, \omega) \) in PE phase for KH\(_2\)PO\(_4\), and the collective phonon mode frequency \( \tilde{\omega}_q^2 \) in PE phase for
KH$_2$PO$_4$ are calculated using respective equations and are presented in Table 1 and 2.

Temperature dependence of $<S^z_q>$ and $<S^x_q>$.

Using calculated values of $<S^z_q>$ and $<S^x_q>$ from Table 1, the $<S^z_q>$ and $<S^x_q>$ versus temperature plot for KH$_2$PO$_4$ is shown in Fig. 1. The theoretical results are good agreement with theoretical result of others. In Fig. 1, curve 'a' is the case of $J' = J/3 < 4J/3$, curve 'b' $J' = 4J/3 < 7J/3$, curve 'c' $J' = 7J/3 > 4J/3$. In curve 'a' and 'b', value of $<S^z_q>$ increases to the saturated value 0.5 from zero, when temperature decreases from transition temperature. That is the case of second order phase transition. But in curve 'c', the change of $<S^z_q>$ with temperature starts from a non zero value $<S^z_q>$ at point A that is to say, when temperature decreases $<S^z_q>$ increases to the saturation value from the finite value of $<S^z_q>$. This is the case of first order phase transition. The temperature at point ‘A’ is transition temperature ($T_c$), and the value of $<S^z_q>$ at ‘A’ is discontinuity of $<S^z_q>$.

The temperature at point ‘A’ is transition temperature ($T_c$), and the value of $<S^z_q>$ at ‘A’ is discontinuity of $<S^z_q>$. The value of $<S^x_q>$ decreases when temperature decreases in the ferroelectric phase. On the other hand, in PE phase the value of $<S^x_q>$ decreases when temperature increases from transition temperature ($T_c$). Our theoretical results fairly agree with experimentally reported result within experimental errors.

Table 1 Calculated values for KDP crystal.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$&lt;S^z_q&gt;$</th>
<th>$&lt;S^x_q&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J' = J/3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.5</td>
<td>0.499</td>
</tr>
<tr>
<td>40</td>
<td>0.498</td>
<td>0.499</td>
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<tr>
<td>60</td>
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<td>80</td>
<td>0.257</td>
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<tr>
<td>100</td>
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<tr>
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</tr>
<tr>
<td>150</td>
<td>0.00</td>
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</table>

Table 2 Calculated values KDP crystal.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\Gamma (cm^{-1}) \times 10^{-4}$</th>
<th>$\bar{\omega} (cm^{-1})$</th>
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<tr>
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<tr>
<td>145</td>
<td>1.90</td>
<td>64.91</td>
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</table>
Fig. 1 Temperature dependence of $< S^z >$ for different values of $J'$. (Series1) $J' = J/3$, (Series2) $J' = 4J/3$, (Series3) $J' = 7J/3$ (present study), and $< S^z >$ for different values of $J'$. (Series4) $J' = J/3$, (Series5) $J' = 4J/3$, (Series6) $J' = 7J/3$ (present study), in KH$_2$PO$_4$

![Graph showing temperature dependence of $< S^z >$ for different values of $J'$ in KH$_2$PO$_4$.]

Fig 2 Temperature dependence of collective proton frequency width ($\Gamma$) in PE phase for KH$_2$PO$_4$ (present study).

![Graph showing temperature dependence of collective proton frequency width ($\Gamma$) in PE phase for KH$_2$PO$_4$.]
Fig. 3 Temperature dependence of collective phonon mode frequency $\left( \tilde{\omega}_{\text{~}} \right)$ in PE phase for KH$_2$PO$_4$ (present study).

C. Temperature dependence of collective proton frequency width and collective phonon mode frequency in PE phase
Using calculated values of collective proton frequency width ($\Gamma$) and collective phonon mode frequency ($\tilde{\omega}_{\text{~}}$) in PE phase for KH$_2$PO$_4$ from Table 2. The temperature variations are shown in graphs as shown in Fig. 2 and 3.

IV. CONCLUSION
From the present study, it can be concluded that the consideration of four - particle cluster Hamiltonian alongwith the third - and fourth - order anharmonicities for the KDP- type ferroelectrics lead to the renormalization and stabilization of the relaxational soft mode and renormalization of the pseudo-spin exchange interaction constant. The decoupling of the correlation appearing in the dynamical equation results in shift in frequency and facilitates the calculation of damping parameter, which is related to the relaxation time. In the present study the modified four-particle cluster model with phonon anharmonic interaction terms up to fourth order have been used to obtain expressions for the collective proton wave half width, collective phonon mode frequency and shift. The method of double time thermal Green’s function technique and Dyson’s equation has been used for the evaluation. Many worker 9,19-24 used four proton cluster model but could not explain most of the features of KDP-system except the difference between the Curie and Curie-Weiss temperature. Vaks and Zinenko 22 Yoshimitsu and Matsubara 23 and Havlin and Sompolinsky 24 performed extensive calculations for the static thermodynamics behaviour in the four-particle cluster approximation and found satisfactory agreement with the experimental data, but they could not explain the observed relaxational behaviour of dielectric properties and ultrasonic attenuation explicitly.

Ganguli et al 6 modified Ramakrishnan and Tanaka theory by considering anharmonic interaction. Their treatment explains many features of order-disorder ferroelectrics. However, due to insufficient treatment of anharmonic interactions, they could not obtain quantitatively good results and could not describe some interesting properties, like dielectric, ultrasonic attenuation, etc.

Blinc and Zeks 32 obtain, the expectation value of proton collective mode component at site $q$: $< S_{\text{~}}^x >$ and $< S_{\text{~}}^y >$, in present study, we use different values of $J'$. In lower value of $J'$, $< S_{\text{~}}^z >$ shows a second order phase transition. While higher value $J'$, $< S_{\text{~}}^z >$ is the case of first order phase transition. The value of $< S_{\text{~}}^x >$ decreases
when temperature decreases in the ferroelectric phase, in PE (PE) phase the value of \(<S^2>\) decreases when temperature increases from transition temperature (Tc). Silsbee, Uehling and Schmidt (SUS)57 showed that the Slater-Takagi model can predict either first or second order transitions. Later it was found experimentally 58 that the KDP transition is of first order.

The present results reduce to the results of others6,34 if the width and shift are neglected. The method of double time thermal Green’s function and Dyson’s equation formalism have been found convenient and systematic to give the static and dynamical properties of a single framework of KDP-type system using four-cluster Hamiltonian alongwith phonon anharmonicities. Our theoretical calculation fairly agree with experimentally59-61 reported results within experimental errors.

The anomalous behaviour of order-disorder KDP type ferroelectrics finds explanation by the consideration of collective proton-phonon interaction and second-and fourth-order phonon anharmonicities in the four-particle cluster Hamiltonian. The dielectric properties and ultrasonic attenuation strongly depend on the relaxational behaviour of the stochastic motion of \(\text{H}_2\text{PO}_4^-\) group in KDP type ferroelectrics.

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