Indian Journal of Pure & Applied Physics
Vol. 54, December 2016, pp. 771-776

Temperature dependence of ferroelectric mode frequency, dielectric constant and loss tangent in CsH_2PO_4 and deuterated CsH_2PO_4 crystals

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Received 8 February 2016; revised 22 August 2016; accepted 18 September 2016

The pseudo-spin lattice coupled mode model by adding third- and fourth-order phonon anharmonic interactions and extra spin-lattice interaction term has been considered for CsH_2PO_4 (abbreviated CDP) and deuterated CsH_2PO_4 (abbreviated DCDP) crystals. Expressions for shift and width of response function, vibrational normal mode frequency, dielectric constant and loss tangent have been evaluated. Double time temperature dependent Green's function method has been used for derivation. Fitting the values of model parameters in expressions, the temperature dependence of soft mode frequency, dielectric constant and loss tangent have been calculated. Theoretical results are in agreement with experimental results reported by Blinc *et al*[16].

Keywords: Ferroelectrics, Green function, Dielectric constant, Loss tangent

1 Introduction

There has been considerable interest in the investigation of ferroelectric materials. Ferroelectric materials show peculiar behaviour. They are used in memory devices- as transducers, gas sensing materials, electro-optic materials and pyroelectric detectors in laser devices etc. Potassium dihydrogen phosphate, barium titanate, lithium niobate are examples of ferroelectrics. Cesium dihydrogen phosphate (CsH_2PO_4) crystal is a KDP-type ferroelectric. It undergoes phase transition at 154 K. The lattice parameters of CsH_2PO_4 are a=7.918Å, b=6.387 Å, c=4.885 Å and β=107.6^0. It is an order-disorder type ferroelectric crystal. In this crystal the O-H...O bond forms a double well potential. In the paraelectric phase each proton or hydrogen ion can occupy either of two equilibrium positions along the O-H...O bond, but it is ordered in one of them in the ferroelectric phase. Proton motion between two potential minima along a given O-H...O bond is taken to be via tunnelling. This crystal belongs to space group $P2_1/m$ in monoclinic system. The transition temperature becomes nearly double when H is replaced by deuterium. This is called isotope effect. It shows that protons play important role in transition mechanism in CsH_2PO_4 crystal. On deuteration (CsD_2PO_4) transition temperature shifts to 267 K showing large isotope effect. Experimental studies on CDP and DCDP crystals have been made by many workers. In all phosphate group ferroelectric crystals the transition temperature have two fold increase when they are deuterated (in KDP it becomes 213 K from 123 K,in RbH_2PO_4 it becomes 218 K from 147 K while in case of RbH_2AsO_4 the T_c of its deuterated form shifts 178 K from 110 K etc.). Blinc[1] first suggested that isotope effect is due to tunnelling of hydrogen ions in double well potential in asymmetric O-H...O bonds in these crystals below transition temperature. In deuterated crystals since mass of dipole increases and so tunnelling diminishes. Due to this transition temperature largely increases. Theoretical studies on CDP and DCDP crystals were initiated by Ganguli *et al.*[2] who have considered pseudo spin model. They have used Green's function method and obtained ferroelectric mode frequency, dielectric constant and T_c etc. for these crystals and for similar crystal KDP. Extensive experimental studies on CDP and its deuterated form (DCDP) have been carried out by many experimentalists. Zhang *et al.*[3] have established relationship between dielectric response and potential structure in CDP and DCDP crystals. Brilingas *et al.*[4] have measured dielectric constant of these crystals at different frequencies and discussed relaxational dynamics of these crystals. Schuele and Schmidt[5] have made NMR study on CDP and DCDP crystals. Raman spectra study on these crystals has been made by Wada *et al.*[6], X-ray structure analysis study has been made by Hagiwara and Nakamura[7].

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Nakamota *et al.*[8] have done dielectric measurements on CDP crystal at high pressures. Hosseini *et al.*[9] have made study of effect of surfactants in synthesis of these crystals as proton conductive membrane. Ahn *et al.*[10] have grown CDP and DCDP crystals and made characterization study on these crystals. Schur *et al.*[11] have made lattice dynamics simulation study on these crystals. Iwata *et al.*[12] have made neutron diffraction study on these crystals. Luspin *et al.*[13] have made elastic properties study on CDP and DCDP crystals. Boysen *et al.*[14] have done study of high- temperature behaviour of CDP and DCDP crystals under both ambient and high pressure conditions and found the result that CDP undergoes a polymorphic phase transition at 228±2 °C under atmospheric pressures. Kim *et al.*[15] worked on characterization of the dynamics in the protonic conductor CsH_2PO_4 by ^{17}O solid-state NMR spectroscopy and first principles calculations: correlating phosphate and protonic motion. Earlier researchers[2] have not considered third-order phonon anharmonic interaction term and extra spin-lattice term. They have decoupled the correlations at an early stage. So that they could not produce better and convincing results. In this paper we have considered third-and fourth-order phonon anharmonic interactions terms as well as pseudospin (S_i^x) and phonon (A_k) interaction term. In the present study we shall fit model values of physical quantities in the expressions obtained for CDP and DCDP crystals. Temperature dependences of soft mode frequency, dielectric constant and loss tangent will be calculated for CDP and DCDP crystals. Theoretical variation of normal mode frequency has been compared with variation obtained by correlating with experimental dielectric measurements on CDP and DCDP crystal by Blinc *et al.*[16] Theoretical variations of dielectric constant and loss tangent have been compared with experimental data of Blinc *et al.*[16] for CDP and DCDP crystals.

2 Model Hamiltonian

For ferroelectric CDP and DCDP crystals, the pseudo-spin lattice coupled mode model (earlier used by Ganguli *et al.*[2]) by adding third-and fourth order phonon anharmonic interactions and other terms. The pseudo-spin lattice coupled mode model is expressed as:

$$H_1 = -2\Omega\sum_i S_i^x - \frac{1}{2}\sum_{ij} J_{ij} S_i^z S_j^z + \frac{1}{4}\sum_{ik}\omega_k\left(A_k^+ A_k + B_k^+ B_k\right) - \sum_{ik} V_{ik} S_i^z A_k \quad \text{... (1)}$$

we shall add:

$$H_2 = \sum_{ijk} V^{(3)}(k_1, k_2, k_3) A_{k_1} A_{k_2} A_{k_3} + \sum_{k_1k_2k_3k_4} V^{(4)}(k_1k_2k_3k_4) A_{k_1} A_{k_2} A_{k_3} A_{k_4} - \sum_{ik} V_{ik} S_i^x A_k \quad \text{... (2)}$$

where Ω is proton tunnelling frequency between double well potential O-H...O bonds, S_i^x is *x*-component of the spin variables, J_{ij} is exchange interaction constant, S_i^z is *z*-component of pseudospin variable *S*, V_{ik} is spin- lattice interaction constant A_k and B_k are position and momenta co-ordinates. $V^3(k_1, k_2, k_3)$ and $V^4(k_1, k_2, k_3, k_4)$ are the third and fourth order phonon anharmonic interactions term. The third term in Eq. (2) describes an indirect coupling between the tunnelling motion of one proton and other proton. This term describes the modulation of distance between the two equilibrium sites in the O-H...O bonds. This modulates Ω by non polar optic phonons. We shall consider the total Hamiltonian for our study of CDP and DCDP crystals:

$$H = H_1 + H_2 \quad \text{... (3)}$$

3 Green's Function, Shift and Width

The method of statistical double time temperature dependent Green's function was proposed by Zubarev[19]. Accordingly, for any pair of operators, this is:

$$G_{ij}(t-t') = << S_i^z ; S_j^z >> = -i\theta(t-t') < \left[S_i^z ; S_j^z\right] > \quad \text{... (4)}$$

where θ is unit step function, θ=1 for *t*>*t'* or zero otherwise.

Differentiating Green's function Eq. (4) with respect to times *t* and *t'*, respectively, twice with the help of model Hamiltonian Eq. (3), Fourier transforming and putting in the Dyson's Equation form, one obtain:

$$G_{ij}(\omega) = G_{ij}^0(\omega) + G_{ij}^0(\omega)\tilde{P}(\omega)G_{ij}^0(\omega) \quad \text{... (5)}$$

where,

$$G^0(\omega) = \frac{\Omega < S_i^x >}{\pi\left(\omega^2 - 4\Omega^2\right)} \quad \text{... (6)}$$

and,

$$\tilde{P}(\omega) = \frac{\pi < \left[F_i, B'\right] >}{2\Omega^2 < S_i^x >^2} + \frac{\pi^2 << F_i, F_j >>}{\Omega^2 < S_i^x >^2} \quad \text{... (7)}$$

where,

$$F_i = -\Omega\sum_i\sum_{ij} J_{ij}S_i^xS_j^z - \Omega\sum_i\sum_{ij} J_{ij}S_i^zS_i^x - 2\Omega\sum_i\sum_{ik} V_{ik}A_kS_i^x + 4\Omega\sum_i\sum_{ik} V_{ik}A_kS_i^z$$
$$-\frac{1}{2}\sum_{ik}\sum_{ij} V_{ik}A_kJ_{ij}S_i^xS_j^z - \frac{1}{2}\sum_{ik}\sum_{ij} V_{ik}A_kJ_{ij}S_i^zS_i^x - \sum_{ik} V_{ik}^2A_k^2S_i^x + \sum_{ik} V_{ik}^2A_k^2S_i^z \qquad \text{... (8)}$$

The Green function (GF) can be now be written as:

$$G(\omega) = \frac{\Omega < S_i^x >}{\pi\left[\omega^2 - \tilde{\Omega}^2 - P(\omega)\right]} \qquad \text{... (9)}$$

where,

$$\tilde{\Omega}^2 = 4\Omega^2 + \frac{i}{< S_i^x >} < [F_i(t), S_i^y(t')] > \qquad \text{... (10)}$$

and,

$$P(\omega) = \frac{\pi}{\Omega < S_i^x >} << F_i(t); F_j^{\cdot}(t^{\cdot}) >> \qquad \text{... (11)}$$

Solving Eq. (10) we obtain:

$$\tilde{\Omega}^2 = a^2 + b^2 - bc \qquad \text{... (12)}$$

Where

$$a = J < S_i^z >$$
$$b = 2\Omega$$
$$c = J < S_i^x > .$$

The second term of Eq. (7) is solved by decoupling of higher order Green′s functions $<< F_i, F_j' >>$. The decoupling is done as follow:

$$<< AB;CD >> = < AC ><< B;D >> + < AD ><< B;C >> + < BC ><< A;D >> + < BD ><< A;C >>$$

We obtain value of $P(\omega)$ of Eq. (11). We resolve $P(\omega)$ into real and imaginary parts using formula:

$$\lim_{m\to o} \frac{1}{x + im} = \left(\frac{1}{x}\right) \pm i\pi\delta(x)$$

The real part is called shift $\Delta(\omega)$ and imaginary part is called width $\Gamma(\omega)$. These are obtained, respectively, as:

$$\Delta(\omega) = \frac{a^4}{\left(\omega^2 - \tilde{\Omega}^2\right)} + \frac{b^2c^2}{\left(\omega^2 - \tilde{\Omega}^2\right)} + \frac{V_{ik}{}^2N_ka^2}{\left(\omega^2 - \tilde{\Omega}^2\right)} + \frac{2bV_{ik} < S_i^x > \omega_k\delta_{kk'}}{\left(\omega^2 - \omega_k^2\right)}$$
$$+ \frac{4b^2V_{ik}^2N_k}{\left(\omega^2 - \tilde{\Omega}^2\right)} + \frac{8aV_{ik}^2 < S_i^z > \omega_k\delta_{kk'}}{\left(\omega^2 - \tilde{\omega}_k^2\right)} + \frac{c^2V_{ik}^2N_k}{\left(\omega^2 - \tilde{\Omega}^2\right)} + \frac{V_{ik}^2N_ka^4}{b^2\left(\omega^2 - \tilde{\Omega}^2\right)} +$$
$$\frac{2V_{ik}^4N_k < S_i^x > \omega_k\delta_{kk'}}{\Omega\left(\omega^2 - \tilde{\omega}_k^2\right)} + \frac{6V_{ik}^4N_k < S_i^z > \omega_k\delta_{kk'}a}{b\Omega\left(\omega^2 - \tilde{\omega}_k^2\right)} \qquad \text{...(13)}$$

and,

$$\Gamma(\omega) = \frac{a^4}{2\Omega}\left\{\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right\} + \frac{b^2c^2}{2\tilde{\Omega}}\left\{\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right\} + \frac{V_{ik}^2N_ka^2}{2\tilde{\Omega}}\left\{\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right\}$$
$$+ \frac{2bV_{ik} < S_i^x > \omega_k\delta_{kk'}}{2\tilde{\omega}_k}\left\{\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right\} + \frac{4b^2V_{ik}^2N_k}{2\tilde{\Omega}}\left\{\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right\} + \frac{8aV_{ik}^2 < S_i^z > \omega_k\delta_{kk'}}{2\tilde{\omega}_k}$$
$$\left\{\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right\} + \frac{c^2V_{ik}^2N_k}{2\tilde{\Omega}}\left\{\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right\} + \frac{V_{ik}^2N_ka^4}{2\tilde{\Omega}b^2}\left\{\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right\}$$
$$+ \frac{2V_{ik}^4N_k < S_i^x > \omega_k\delta_{kk'}}{2\Omega\tilde{\omega}_k}\{\delta(\omega - \tilde{\omega}_k) - \delta(\omega + \tilde{\omega}_k)\} + \frac{6V_{ik}^4N_k < S_i^z > \omega_k\delta_{kk'}a}{2b\Omega\tilde{\omega}_k}\{\delta(\omega - \tilde{\omega}_k) - \delta(\omega + \tilde{\omega}_k)\} \qquad \text{... (14)}$$

where $\Gamma_k(\omega)$ is the phonon width due to third and fourth-order phonon anharmonicities. $\tilde{\omega}_k$ and Γ_k are phonon-frequency and phonon width respectively. $\Delta_k(\omega)$ is phonon shift, these are given as:

$$\Delta_k(\omega) = \operatorname{Re} P_k(\omega) = 18P\sum_{k_1k_2} |V^{(3)}(k_1,k_2,-k)|^2 \times \frac{\omega_{k_1}\omega_{k_2}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}}\left\{\begin{matrix}\left(n_{k_1} + n_{k_2}\right)\dfrac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}}{\omega^2 - \left(\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}\right)^2} \\ \left(n_{k_2} - n_{k_1}\right)\dfrac{\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}}{\omega^2 - \left(\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}\right)^2}\end{matrix}\right\}$$
$$+ 48P\sum_{k_1k_2k_3} |V^{(4)}(k_1,k_2,k_3,-k)|^2 \frac{\omega_{k_1}\omega_{k_2}\omega_{k_3}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}\tilde{\omega}_{k_3}} \times \left\{\begin{matrix}\left(1 + n_{k_1}n_{k_2} + n_{k_2}n_{k_3} + n_{k_3}n_{k_1}\right)\dfrac{\omega_{k_1} + \omega_{k_2} + \omega_{k_3}}{\omega^2 - \left(\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}\right)^2} \\ + 3\left(1 - n_{k_1}n_{k_2} + n_{k_2}n_{k_3} - n_{k_3}n_{k_1}\right) * \dfrac{\omega_{k_1} - \omega_{k_2} - \omega_{k_3}}{\omega^2 - \left(\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}\right)^2}\end{matrix}\right\}$$

+ higher terms . ... (15)

$$\Gamma_k(\omega) = \operatorname{Im} P_k(\omega) = 9\pi\sum_{k_1k_2} V^{(3)}(k_1,k_2,-k)|^2 \times \frac{\omega_{k_1}\omega_{k_2}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}}\left\{\begin{matrix}\left(n_{k_1} + n_{k_2}\right)\begin{bmatrix}\delta\left(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}\right) \\ - \delta\left(\omega - \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}\right)\end{bmatrix} \\ \left(n_{k_2} - n_{k_1}\right)\begin{bmatrix}\delta\left(\omega + \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}\right) \\ - \delta\left(\omega - \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}\right)\end{bmatrix}\end{matrix}\right\}$$

$$+ 48\pi\sum_{k_1k_2k_3} |V^{(4)}\left(k_1,k_2,k_3,k_4\right)|^2 \times \begin{bmatrix}\delta\left(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}\right) \\ - \delta\left(\omega - \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}\right)\end{bmatrix}$$
$$\times \left[\left(1 + n_{k_1}n_{k_2} + n_{k_2}n_{k_3} + n_{k_3}n_{k_1}\right)\frac{\omega_{k_1}\omega_{k_2}\omega_{k_3}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}\tilde{\omega}_{k_3}}\right]$$

+higher terms ...(16)

4 Normal Mode Frequency

By putting value of $P(\omega)$ in Eq.(9), the value of Green′s function (GF) is finally obtained as:

$$G(\omega+i\varepsilon)=\pi^{-1}<S_i^x>\delta_{ij}\left[\left(\omega^2-\hat{\Omega}^2\right)+2i\Omega\Gamma(\omega)\right]^{-1},$$

where,

$$\hat{\Omega}^2=\tilde{\Omega}^2+\Delta(\omega). \qquad \text{... (17)}$$

Solving Eq.(17) self consistently, we obtain renormalized frequency as:

$$\hat{\Omega}^2=\frac{1}{2}\left(\tilde{\omega}_k^2+\tilde{\tilde{\Omega}}^2\right)\pm\frac{1}{2}\left[\left(\tilde{\omega}_k^2-\tilde{\tilde{\Omega}}^2\right)^2+4\begin{pmatrix}2bV_{ik}<S_i^x>\omega_k\delta_{kk'}+8aV_{ik}^2<S_i^z>\omega_k\delta_{kk'}\\+\dfrac{2V_{ik}^4N_k<S_i^x>\omega_k\delta_{kk'}}{\Omega}+\dfrac{6V_{ik}^4N_k<S_i^z>\omega_k\delta_{kk'}a}{b\Omega}\end{pmatrix}\right]^{\frac{1}{2}} \qquad \text{... (18)}$$

The frequency $\hat{\Omega}$ is the normal mode frequency which decreases with temperature from below T_c, and so is responsible for ferroelectric phase transition.

5 Dielectric Constant and Tangent Loss

The response of crystal to electric field is expressed by electrical susceptibility which using Zubarev′s[17] formalism is expressed as:

$$\chi=-\lim_{\in\to o}2\pi N\mu^2G_{ij}(\omega+i\varepsilon)\ . \qquad \text{.. (19)}$$

where, N is no of dipoles having dipole moment μ in the sample using relation $\varepsilon=1+4\pi\chi$. The expression for dielectric constant with the help of Eq. (17) and Eq. (19) can be expressed as:

$$\varepsilon(\omega)-1=4\pi\left(-2\pi N\mu^2\right)<S^x>\left(\omega^2-\hat{\Omega}^2\right)\left[\left(\omega^2-\hat{\Omega}^2\right)^2+4\Omega^2\Gamma^2\right]^{-1} \qquad \text{... (20)}$$

The dissipation of power can conveniently be expressed in dielectrics as tangent loss (tanδ) as:

$$\tan\delta=\frac{\varepsilon''}{\varepsilon'} \qquad \text{... (21)}$$

Using Eq. (21) one obtains:

$$\tan\delta=\frac{-2\Omega\Gamma(\omega)}{\left(\omega^2-\hat{\Omega}^2\right)} \qquad \text{... (22)}$$

At microwave frequencies $\omega<<\hat{\Omega}$, above Eq. (22) reduces to:

$$\tan\delta=\frac{2\Omega\Gamma(\omega)}{\hat{\Omega}^2} \qquad \text{... (23)}$$

6 Results and Discussion

By using model values[2] of various physical quantities in expressions from literature, temperature dependence of normal mode frequency, width, shift and dielectric constant for CDP and DCDP crystals have been calculated and have been shown in Figs 1-6 and corresponding values are listed in Table 1.

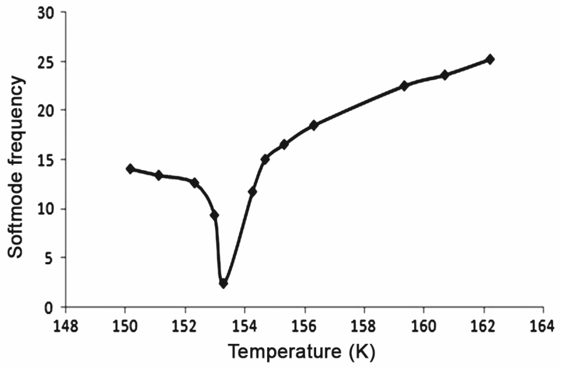

Fig 1 – Temperature dependence of soft mode frequency $\hat{\Omega}$ (cm^{-1}) in CDP crystal (— present calculation, ♦ correlated values with experimental values of Blinc *et al.*[16])

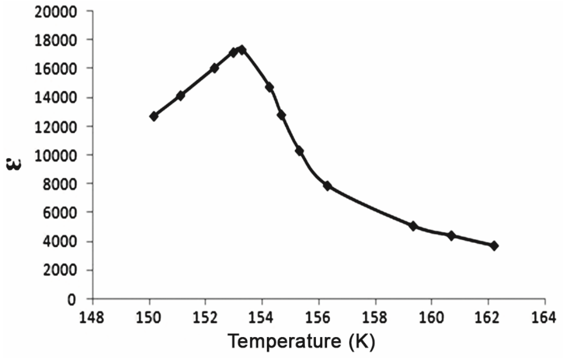

Fig 2 – Temperature dependence of dielectric constant (ε) in CDP crystal (—present calculation, ♦ correlated with experimental values of Blinc *et al.*[16])

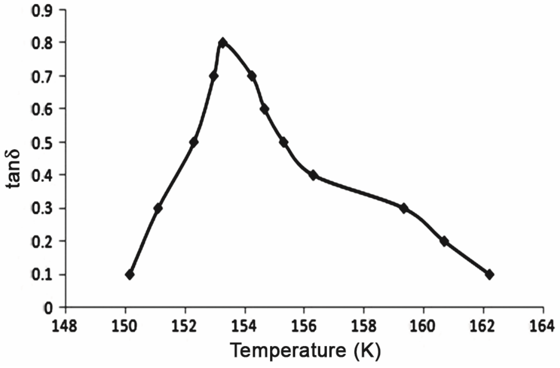

Fig 3 – Temperature dependence of loss tangent (tan δ) in CDP crystal (—present calculation, ♦ correlated with experimental values of Blinc *et al.*[16])

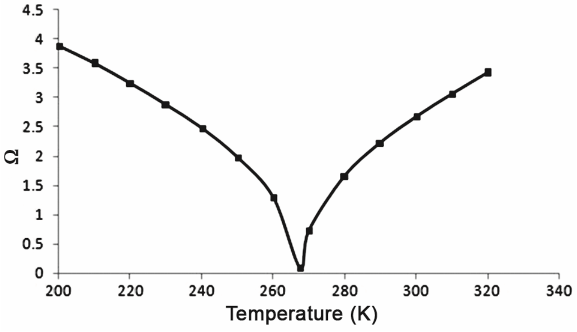

Fig 4 – Temperature dependence of soft mode frequency $\hat{\Omega}$ (cm^{-1}) in DCDP crystal (—present calculation, ♦ correlated values with experimental values of Blinc *et al.*[16] for dielectric constant)

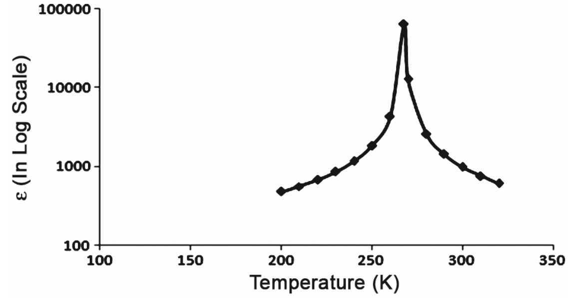

Fig 5 – Temperature dependence of dielectric constant (ε) in DCDP crystal (—present calculation, ♦ correlated with experimental values of Blinc *et al.*[16])

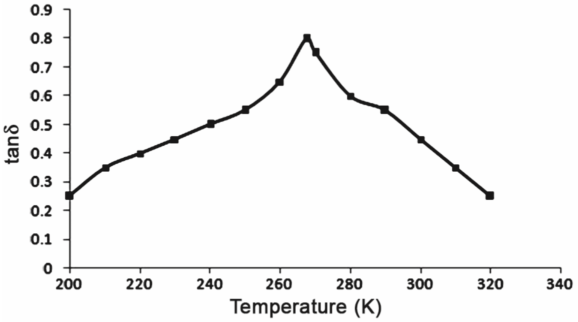

Fig 6 – Temperature dependence of loss tangent (tan δ) in DCDP crystal (—present calculation, ♦ correlated with experimental values of Blinc *et al.*[16])

Table 1 – Model values of physical quantities for CDP and DCDP* crystals

T_c (K)	Ω (cm^{-1})	J (cm^{-1})	J^* (cm^{-1})	V_{ik} (cm^{-1})	ω_k (cm^{-1})	$\mu \times 10^{-18}$ (esu)
154	80	350	450	1.72	130	2.3
267*	1.710*	399.15*	395.96*	14.16*	130*	2.3*

The theoretical variations of normal mode frequency with temperature are compared with values obtained by correlating the experimental results of Blinc *et al*[16]. The calculated dielectric constant versus temperature and loss tangent versus temperature curves agree with experimental data of Blinc *et al*[16]. Earlier workers[2] have decoupled the correlations functions at an early stage. Therefore some important interactions disappeared from their results. Equations (15), (17) and (18) show that if third-order phonon anharmonic interactions terms and extra spin-lattice interactions terms are neglected, our expressions reduce to the expressions of earlier authors[2]. The width and shift are contributions of present work. Equation (18) shows that soft mode frequency $\hat{\Omega}$ decreases from below T_c becoming very small at transition temperature, then increases. Thus confirming Cochran's suggested behaviour. The dielectric constant first increases from below T_c becoming large near T_c then decreases. Similarly loss tangent shows its behaviour.

7 Conclusions

Present study shows that the modified pseudospin-lattice coupled mode model along with third- and fourth-order phonon anharmonic interactions and extra spin-lattice interactions terms explains well the temperature dependence of normal mode frequency, dielectric constant and loss tangent in CDP and DCDP crystals. Earlier authors[1] did not consider terms which we have considered. Hence our results are much better and convincing, which agree with experimental results of Blinc *et al*[16]. Present results may also be useful to other similar crystals RbH_2PO_4, KH_2AsO_4, RbH_2AsO_4 and CsH_2AsO_4.

Acknowledgements

One of the author AM is thankful to UGC, New Delhi for a Research Fellowship to H N B Grahwal University, Srinagar (Garhwal).

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