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Temperature dependence of ferroelectric mode frequency, dielectric constant and loss tangent in $PbHAsO_4$ crystal

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The ferroelectric transition of $PbHAsO_4$ crystal has been studied using two sublattice pseudospin-lattice coupled mode model with addition of third-order and fourth-order phonon anharmonic interactions terms. With the help of double-time thermal Green's function method, expressions for ferroelectric mode frequency, dielectric constant and dielectric loss tangent have been derived. By fitting model values of physical quantities, temperature dependence of ferroelectric mode frequency, dielectric constant and loss tangent have been numerically calculated for $PbHAsO_4$ crystal. Theoretical results have been compared with correlated experimental results of Arend *et al.*[19]. The results obtained in present study are in good agreement with experimental results.

Keywords: Ferroelectric, Dielectric constant, Anharmonic interaction, Loss tangent, Green's function

1 Introduction

Ferroelectric substances have attracted physicists worldwide due to their potential applications in manufacture of small size capacitors of high capacitance, memory devices for electronic computers, as piezoelectric acoustic transducers and pyroelectric infrared detectors[1,2]. Lead mono hydrogen arsenate crystal ($PbHAsO_4$) belongs to lead hydrogen phosphate ($PbHPO_4$) type ferroelectric crystals which are also called monetites as well as schultenites. The direction of spontaneous polarization in these crystal is almost parallel to the direction of O-H….O bond projecting on the (010) plane and the PO_4 groups are bound to one another by the O-H…O bonds in the form of one dimensional chain along the *c*-axis but the PO_4 chains in this salt are not bound to one another by the H bonds. Thus the intra chain coupling (within a chain) is stronger than the inter-chain coupling between the chains. If one compares this crystal with largely studied KH_2PO_4 crystal, one finds that there are three major differences[3] (i) one dimension ordering of protons, (ii) unusual large isotopes effect and (iii) spontaneous polarization direction is not along *c*-axis. So we can say that simple pseudospin lattice coupled mode model cannot be sufficient to explain the nature of ferroelectric transition of $PbHAsO_4$ crystal.

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Lee and Nriagu[4] have made experimental studies to determine stability constants of $PbHAsO_4$ crystal. Deguchi[5] has done dielectric properties studies of $PbHAsO_4$ crystal. Kida *et al.*[6] have carried out ultraviolet optical spectroscopic studies on $PbHAsO_4$ crystal. Deguchi and Nakamura[7] have carried out crystal growth studies on $PbHAsO_4$ crystal. Wilson[8] has carried out neutron diffraction studies on $PbHAsO_4$ crystal. Ohno *et al.*[9] have carried out Raman spectroscopy studies on $PbHAsO_4$ crystal. Kroupa *et al.*[10] have carried out experimental far infrared and dielectric measurements on $PbHAsO_4$ crystal. Earlier theoretical studies on $PbHAsO_4$ crystal were made by many authors to explain dielectric properties and phase transition of $PbHPO_4$ type crystals (including $PbHAsO_4$). Blinc *et al.*[11] have carried out calculations using pseudospin model with additional-spin term ($B_{ij} S_i^x S_j^x$). De Carvalho and Salinas[12] have studied this crystal using pseudospin model without tunneling term. Chunlei *et al.*[13] have studied $PbHPO_4$ type crystals using pseudospin model. They have not considered two sublattice model and phonon anharmonic interactions terms. Zachek *et al.*[14] have studied thermodynamic properties of $PbHPO_4$ and $PbHAsO_4$ crystals. Wesselinowa[15] has studied $PbHPO_4$ type crystals using pseudospin model but she did not studied phase transition and dielectric properties. Chaudhuri *et al.*[16] have studied these crystals using a two sublattice pseudospin lattice coupled mode model. In their pioneering and important work they have studied dielectric constant, spontaneous polarization, specific heat and dissipation factor theoretically and fitted experimental values in their theoretical expressions. However their model and approach are different to our approach. For these crystals they have obtained very interesting results. In the present calculation by modifying two-sublattice-pseudospin-lattice coupled mode model[17] by adding third-and fourth-order phonon anharmonic interactions term expressions for ferroelectric mode frequency, transition temperature, dielectric constant and dielectric tangent loss have been derived for $PbHAsO_4$ crystal. For calculating response functions, the double-time temperature dependent 'Green's function' method[18] has been used.

Model values of various physical quantities have been fitted in expressions of ferroelectric soft mode frequency, dielectric constant and dielectric loss tangent and their temperature dependence have been calculated. The theoretical results are compared with experimental results for $PbHAsO_4$ crystal reported by Arend and Blinc[19].

2 Crystal Structure and Model Hamiltonian

The crystal $PbHAsO_4$ contains monoclinic crystal structure in both paraelectric and ferroelectric P_c phases. The lattice parameters of $PbHAsO_4$ are, a=7.11 Å, b=6.94 Å and β =101°35'. There is equal distribution of hydrogen atoms between two off-centre site on O-H…O bonds in paraelectric phases. Ferroelectric phase contains hydrogen atoms order in one of the two possible site on O-H…O bonds.

The two-sublattice pseudospin-lattice coupled mode model Hamiltonian for the quasi-one dimensional $PbHAsO_4$ crystal is modified by third-and fourth-order phonon anharmonic terms as:

$$H = -2\Omega\sum_i\left(S_{1i}^x + S_{2i}^x\right) - \sum_{ij}[J_{ij}\left(S_{1i}^z S_{1j}^z + S_{2i}^z S_{2j}^z\right) + K_{ij}S_{1i}^z S_{2j}^z] - \sum_k V_{ik}\left(S_{1i}^z A_k + S_{2j}^z A_k^+\right) + \frac{1}{4}\sum_k \omega_k\left(A_k^+ A_k + B_k^+ B_k\right) + \sum_{k_1k_2k_3} V^3(k_1,k_2,k_3)A_{k_1}A_{k_2}A_{k_3} + \sum_{k_1k_2k_3k_4} V^4(k_1,k_2,k_3,k_4)A_{k_1}A_{k_2}A_{k_3}A_{k_4} \quad \ldots (1)$$

where $V^3(k_1,k_2,k_3)$ and $V^4(k_1,k_2,k_3,k_4)$ are third-and fourth-order atomic force constants.

3 Green's Functions

We consider the Green's function:

$$G_{ij}(t-t') = \left\langle\left\langle S_{1i}^z(t); S_{1j}^z(t')\right\rangle\right\rangle. = -i\theta(t-t')\left\langle S_i^z(t); S_j^z(t')\right\rangle \quad \ldots (2)$$

where S_{1i}^z and S_{1j}^z are spin operators. On sites i and j, θ is unit step function and $\theta(t)=1$ for $t>0$ and $\theta(t)=0$ for $t<0$. The angular bracket $\langle......\rangle$ denotes ensemble average over a grand canonical ensemble. Differentiating Green's function (2) with respect to time t using model Hamiltonian (Eq. 1) and multiplying both sides by i we obtain:

$$i\frac{dG(t-t')}{dt} = \delta(t-t')\left\langle\left[S_{1i}^z, S_{1j}^z\right]\right\rangle + \left\langle\left\langle\left[S_{1i}^z, H\right]; S_{1j}^z(t')\right\rangle\right\rangle. \quad \ldots (3)$$

We have:

$$\left[S_{1i}^z, H\right] = -2\Omega i\sum S_{1i}^y \quad \ldots (4)$$

We again differentiate Eq. (3) with respect to time t and obtain:

$$i^2\frac{d^2G(t-t')}{dt^2} = \delta(t-t')\left\langle\left[-2\Omega i S_{1i}^y, S_{1j}^z\right]\right\rangle + \left\langle\left\langle\left[-2\Omega i S_{1i}^y, H\right]; S_{1j}^z\right\rangle\right\rangle, \quad \ldots (5)$$

We obtain:

$$\left[-2\Omega i S_{1i}^y, H\right] = 4\Omega^2 S_{1i}^z + 2\Omega iJ\left(S_{1i}^x S_{1j}^z + S_{1i}^z S_{1i}^x\right) \quad \ldots (6)$$

If we Fourier transform Eq. (5), we obtain:

$$\omega^2 G(\omega) = \frac{2\Omega\left\langle S_{1i}^x\right\rangle\delta_{ij}}{2\pi} + \left\langle\left\langle F_{1i}(t); S_{1j}^z(t')\right\rangle\right\rangle + 4\Omega^2 G(\omega) + 2\Omega K_{ij}S_{1i}^x S_{2j}^x + 2\Omega V_{ik}A_k S_{1i}^x + 2\Omega V_{ik}A_k^+ S_{2j}^x \quad \ldots (7)$$

Now if we consider Green's function:

$$\Gamma(t-t') = \left\langle\left\langle F_{1i}(t); S_{1j}^z(t')\right\rangle\right\rangle, \quad \ldots (8)$$

and differentiate it with respect to time t' we obtain (similarly as before):

$$i\frac{d\Gamma(t-t')}{dt'} = -\delta(t-t')\left\langle\left[F_{1i}(t), S_{1j}^z(t')\right]\right\rangle + \left\langle\left\langle F_{1i}(t); \left[H, S_{1j}^z(t)\right]\right\rangle\right\rangle. \quad \ldots (9)$$

Again differentiating Eq. (9) with respect to time t' we obtain:

$$i\frac{d^2\Gamma(t-t')}{dt'^2} = \delta(t-t')\left\langle -2\Omega i S_{1j}^y\right\rangle\delta_{ij} + \left\langle\left\langle F_{1i}(t); \left[-2\Omega i S_{1j}^y, H\right]\right\rangle\right\rangle. \quad \ldots (10)$$

If we Fourier transform Eq. (10) similarly as before, we obtain:

$$\omega^2\Gamma(\omega) = +4\Omega^2\Gamma(\omega) + \langle\langle F_{1i}(t); F_{1j}(t')\rangle\rangle \qquad \dots (11)$$

Putting value of $\Gamma(\omega)$ from Eq. (11) in to Eq. (8), and writing the resulting equation in the form of Dyson's equation:

$$G(\omega) = \tilde{G}^{o}(\omega) + \tilde{G}^{o}(\omega)\tilde{P}(\omega)G(\omega) \qquad \dots (12)$$

where

$$G^{o}(\omega) = \frac{\Omega\langle S^{x}_{1i}\rangle\delta_{ij}}{(\omega^2 - \tilde{\Omega}^2)}, \qquad \dots (13)$$

$$\tilde{P}(\omega) = \frac{\pi}{\Omega\langle S^{x}_{1i}\rangle\delta_{ij}}\langle\langle F_{1i}(t); F_{1J}(t')\rangle\rangle, \qquad \dots (14)$$

and

$$\tilde{\Omega}^2 = 4\Omega^2 + \frac{i}{\langle S^{x}_{1i}\rangle}\langle[F_{1i}(t); S^{y}_{1j}]\rangle. \qquad \dots (15)$$

Eq. (12) gives value of Green's function $G(\omega)$ as:

$$G(\omega) = \frac{\Omega\langle S^{x}_{1i}\rangle\delta_{ij}}{\pi\left[\omega^2 - \tilde{\Omega}^2 - \tilde{P}(\omega)\right]} \qquad \dots (16)$$

From Eq. (14) it is clear that $\tilde{P}(\omega)$ contains higher order Green's functions. These are decoupled into simpler Green's functions which are evaluated and substituted. Then one obtains value of $\tilde{P}(\omega)$. We separate $P(\omega)$ into its real part called shift (Δ) and imaginary part called width (Γ). We obtain these as:

$$\Delta(\omega) = \frac{a^4}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{b^2c^2}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{V^2_{ik}N_K a^2}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{2V^2_{ik}\langle S^{x}_{1i}\rangle\omega_k\delta_{k-k'}\left(\omega^2 - \tilde{\tilde{\omega}}^2_k\right)}{\left(\omega^2 - \tilde{\tilde{\omega}}^2_k\right) + 4\omega_k^2\Gamma_k^2(\omega)} \qquad \dots (17)$$

and

$$\Gamma(\omega) = \frac{\pi a^4}{4\Omega\tilde{\Omega}}\left[\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\right] + \frac{b^2c^2}{4\Omega\tilde{\Omega}}\left[\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\right] + \frac{2V^2_{ik}\langle S^{x}_{1i}\rangle\omega_k\delta_{k-k'}\left(\omega^2 - \tilde{\tilde{\omega}}^2_k\right)}{\left(\omega^2 - \tilde{\tilde{\omega}}^2_k\right) + 4\omega_k^2\Gamma_k^2(\omega)} + \frac{2V^2_{ik}\langle S^{x}_{1i}\rangle\omega_k\delta_{k-k'}\Gamma_k(\omega)}{\left(\omega^2 - \tilde{\tilde{\omega}}^2_k\right) + 4\omega_k^2\Gamma_k^2(\omega)}. \qquad \dots (18)$$

In Eqs. (17) and (18) $\Delta_k(\omega)$ is phonon shift and $\Gamma_k(\omega)$ is phonon width due to third-and fourth-order phonon anharmonic interactions terms. $\Gamma_k(\omega)$ and corresponding shift $\Delta_k(\omega)$ are obtained in phonon Green's function:

$$\langle\langle A_k; A_k^{+}\rangle\rangle = \frac{\omega_k\delta_{kk'}}{\pi\left[\omega^2 - \tilde{\tilde{\omega}}^2_k - 2i\omega_k\Gamma_k(\omega)\right]}, \qquad \dots (19)$$

where

$$\tilde{\tilde{\omega}}^2_k = \tilde{\omega}^2_k + 2\omega_k\Delta_k(\omega), \qquad \dots (20)$$

$$\tilde{\omega}^2_k = \omega_k + A_k, \qquad \dots (21)$$

In Eq. (20), $\Delta_k(\omega)$ is:

$$\Delta_k(\omega) = 18P\sum_{k_1k_2}\left|V^3(k_1k_{2-k})\right|^2\frac{\omega_{k_1}\omega_{k_2}}{\tilde{\omega}_{k1}\tilde{\omega}_{k2}}\left\{(n_{k1}+n_{k2})\frac{\tilde{\omega}_{k1}+\tilde{\omega}_{k2}}{\omega^2-(\tilde{\omega}_{k1}+\tilde{\omega}_{k2})^2} + (n_{k_2}+n_{k_1})\frac{\tilde{\omega}_{k1}+\tilde{\omega}_{k2}}{\omega^2-(\tilde{\omega}_{k1}+\tilde{\omega}_{k2})^2}\right\}$$
$$+ 48P\sum_{k_1k}\left|V^{(4)}(k_1k_2k_{3,-k})\right|^2\frac{\omega_{k1}\omega_{k2}\omega_{k3}}{\tilde{\omega}_1\tilde{\omega}_2\tilde{\omega}_{k3}}\left\{(1+n_{k_1}n_{k_2}+n_{k_2}n_{k_3}+n_{k_3}n_{k_1})\frac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3}}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2}\right.$$
$$\left. + 3(1-n_{k_2}n_{k_1}+n_{k_2}n_{k_3}-n_{k_3}n_{k_1})\frac{\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3}}{\omega^2-(\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3})^2}\right\} +$$

higher terms. $\dots (22)$

and in Eq. (19):

$$\Gamma_k(\omega) = 9\pi\sum_{k_1k_2}\left|V^{(3)}(k_1,k_2,-k)\right|^2\frac{\omega_{k_1}\omega_{k_2}}{\tilde{\omega}_{k_1}\tilde{\omega}_{k_2}}\left\{(n_{k_2}+n_{k_1})\left[\delta(\omega+\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}) - \delta(\omega+\tilde{\omega}_{k_1}-\tilde{\omega}_{k_1})\right.\right.$$
$$\left.\left. + (n_{k_2}-n_{k_1})\delta(\omega+\tilde{\omega}_{k_1}+\tilde{\omega}_{k_1}) - \delta(\omega+\tilde{\omega}_{k_1}+\tilde{\omega}_{k_1})\right\}(\omega+\tilde{\omega}_{k_1}+\tilde{\omega}_{k_1})\right\}\Big]$$
$$+ 48\pi\sum\left|V(k_1,k_2,k_3,-k_4)\right|^2\left\{1+n_{k_1}n_{k_2}+n_{k_2}n_{k_3}+n_{k_3}n_{k_4}\right\}$$
$$\times\left[\delta(\omega+\tilde{\omega}_{k_1}+\tilde{\omega}_{k_2}+\tilde{\omega}_{k_3}) - \left\{\delta(\omega-\tilde{\omega}_{k_1}-\tilde{\omega}_{k_2}-\tilde{\omega}_{k_3})\right\}\right]. \qquad \dots (23)$$

Now we obtain Green's function (Eq. (16)) finally as:

$$G(\omega + iX) = \frac{\Omega\langle S^{x}_{1i}\rangle\delta_{ij}}{\pi\left[\omega^2 - \hat{\Omega}^2 + 2i\Omega\Gamma(\omega)\right]}, \qquad \dots (24)$$

where

$$\hat{\Omega}^2 = \tilde{\tilde{\Omega}}^2 + \Delta(\omega), \quad \ldots (25)$$

$$\tilde{\tilde{\Omega}}^2 = \tilde{\Omega}^2 + \Delta(\omega), \quad \ldots (26)$$

$$\tilde{\Omega}^2 = a^2 + b^2 - bc \quad \ldots (27)$$

where

$$a = 2J_{ij} < s_1^z > + K_{ij} < s_2^z >, \quad \ldots (28)$$

$$b = 2\Omega, \quad \ldots (29)$$

$$c = 2J_{ij} < s_1^x > + K_{ij} < s_2^z >, \quad \ldots (30)$$

If we simplify Eq. (25), we obtain:

$$\hat{\Omega}_{\pm}^2 = \frac{1}{2}\left[\left(\tilde{\Omega}^2 + \tilde{\omega}_k^2\right) \pm \left\{\left(\tilde{\tilde{\omega}}_k^2 - \tilde{\tilde{\Omega}}^2\right)^2 + 8V_{ik}^2\left\langle S_{1i}^x\right\rangle\Omega\right\}^{\frac{1}{2}}\right]. \quad \ldots (31)$$

This frequency containing negative sign is the ferroelectric mode frequency which becomes zero at transition temperature and gives rise to ferroelectric transition.

By applying condition of stability, i.e., $\hat{\Omega} \to 0$ at $T \to T_c$, one obtains formula for transition temperature:

$$T_c = \frac{\eta}{2k_B \tanh^{-1}\left(\frac{\eta^3}{4\Omega^2 J^*}\right)}, \quad \ldots (32)$$

where

$$\eta^2 = (2J - K)^2\sigma^2 + 4\Omega^2, \quad \ldots (33)$$

and

$$J^* = (2J + K) + \frac{2V_{ik}^2\tilde{\tilde{\omega}}_k^2}{[\tilde{\tilde{\omega}}_k^4 + 4\omega_k\Gamma_k^2]}. \quad \ldots (34)$$

4 Dielectric Constant and Loss Tangent

The effect of external electric field on crystals is expressed by electrical susceptibility (χ). χ has related to Green's function $G(\omega + ix)$ as:

$$\chi = -\lim_{x \to 0} 2\pi N\mu^2 G_{ij}(\omega + ix). \quad \ldots (35)$$

where N is number of dipoles having dipole moment μ in unit volume. The dielectric constant $\in$ is related to χ as:

$$\in = 1 + 4\pi\chi. \quad \ldots (36)$$

In ferroelectric crystals $\in >> 1$. Hence we obtain using Eqs. (35) and (36) $\in$ as:

$$\in = -\frac{8\pi N\mu^2\Omega < s_{1i}^x > \delta_{ij}}{\pi\left[(\omega^2 - \hat{\Omega}^2)^2 + 4\Omega^2\Gamma^2(\omega)\right]}. \quad \ldots (37)$$

The loss of power in ferroelectrics (dielectrics) due to orientation of dipoles is expressed as loss tangent $(\tan\delta)$ which is defined as:

$$\tan\delta = \frac{\in''}{\in'}. \quad \ldots (38)$$

We can easily obtain from Eq. (37) and (38) loss tangent as:

$$\tan\delta = -\frac{2\Omega\Gamma(\omega)}{\left(\omega^2 - 4\hat{\Omega}^2\right)}. \quad \ldots (39)$$

5 Numerical Calculation and Results

With the help of model values[16] for $PbHAsO_4$ crystal, T_c=303.14 K, Ω=0.3 cm^{-1}, J=186 cm^{-1}, K=93 cm^{-1}, N_k=0.1, V_{ik}=25 cm^{-1}, ω_k=16 cm^{-1}, $\mu_k = 0.6 \times 10^{-18}$cgs, and $N = 2.5 \times 10^{21}$, we have calculated temperature dependency of $\left\langle S_1^x\right\rangle$, $\left\langle S_2^x\right\rangle$, $\left\langle S_1^z\right\rangle$, and $\left\langle S_2^z\right\rangle$ as shown in Table 1. With the

Table 1 – Calculated values of $\left\langle S_1^x\right\rangle, \left\langle S_2^x\right\rangle, \left\langle S_1^z\right\rangle$ & $\left\langle S_2^z\right\rangle$ for $PbHAsO_4$ crystal

T (K)	$\left\langle S_1^x\right\rangle \times 10^{-4}$	$-\left\langle S_2^x\right\rangle \times 10^{-4}$	$\left\langle S_1^z\right\rangle \times 10^{-5}$	$-\left\langle S_2^z\right\rangle \times 10^{-4}$
264.54	0.1260	0.5000	0.7300	0.2560
277.02	0.1440	0.4800	0.7020	0.2413
283.72	0.1532	0.4400	0.6950	0.2350
286.40	0.1599	0.4280	0.6860	0.2300
289.08	0.1637	0.3990	0.5689	0.1813
294.44	0.1744	0.3710	0.5690	0.1795
298.46	0.1811	0.3610	0.5640	0.1763
303.14	0.1831	0.3242	0.5649	0.1760
309.18	0.1780	0.3450	0.5622	0.1760
311.39	0.1745	0.3480	0.5609	0.1760
313.20	0.1708	0.3510	0.5605	0.1760
319.40	0.1585	0.3520	0.5579	0.1760
327.71	0.1448	0.3521	0.5565	0.1760
335.06	0.1315	0.3522	0.5552	0.1760
340.42	0.1241	0.3533	0.5550	0.1760

Table 2 – Calculated values of Δ_1, Δ_2, Δ_3, Δ_4 and $\Delta(\omega)$ for $PbHAsO_4$ crystal

T (K)	$\Delta_1\times10^{-15}$ (cm^{-1})	$\Delta_2\times10^{-7}$ (cm^{-1})	$\Delta_3\times10^{-8}$ (cm^{-1})	$\Delta_4\times10^{-5}$ (cm^{-1})	$\Delta(\omega)\times10^{-5}$ (cm^{-1})
264.54	58.1721	11.6423	60.8170	98.4375	98.6147
277.02	84.4331	279.7490	73.3220	112.5000	115.3708
283.72	118.7180	503.8520	86.9951	119.6875	124.8130
286.40	135.0320	617.4100	92.8081	124.9219	131.1888
289.08	159.2300	747.2010	100.8160	127.8906	135.4634
294.44	186.3210	954.5690	109.1160	136.2500	145.9048
298.46	205.7430	1065.2000	114.6950	141.6406	152.4073
303.14	217.1320	1193.1200	117.8680	143.0469	155.0959
309.18	198.8290	1072.4100	112.7540	139.0625	149.8994
311.39	190.4520	1022.4500	110.3390	136.3281	146.6630
313.20	187.8920	969.6940	109.5790	133.4375	143.2440
319.40	172.5840	822.4570	104.9800	123.8281	132.1577
327.71	163.8900	661.7920	102.2580	113.1250	119.8452
335.06	156.5670	506.2540	99.9050	102.7344	107.8968
340.42	155.4160	426.1510	99.5160	97.5781	101.9391

Table 3 – Calculated values of the Γ_1, Γ_2, Γ_3, Γ_4 and $\Gamma(\omega)$ for $PbHAsO_4$ crystal

T (K)	$\Gamma_1\times10^{-15}$ (cm^{-1})	$\Gamma_2\times10^{-6}$ (cm^{-1})	$\Gamma_3\times10^{-8}$ (cm^{-1})	$\Gamma_4\times10^{-2}$ (cm^{-1})	$\Gamma(\omega)\times10^{-2}$ (cm^{-1})
264.54	42.9834	1.9431	77.4894	0.1969	0.1971
277.02	62.3877	46.6901	93.4225	0.2250	0.2298
283.72	87.7207	84.0929	110.8440	0.2394	0.2479
286.40	99.7751	103.0460	118.2510	0.2498	0.2603
289.08	117.6550	124.7080	128.4540	0.2558	0.2684
294.44	137.6730	159.3180	139.0290	0.2725	0.2886
298.46	152.0230	177.7810	146.1380	0.2833	0.3012
303.14	160.4390	199.1310	150.1800	0.2861	0.3062
309.18	146.9150	178.9850	143.6650	0. 2781	0.2962
311.39	140.7250	170.6470	140.5870	0.2727	0.2899
313.20	138.8330	161.8420	139.6200	0.2669	0.2832
319.40	127.5220	137.2680	133.7590	0.2477	0.2615
327.71	121.0980	110.4530	130.2910	0.2263	0.2374
335.06	115.6870	84.4938	127.2940	0.2055	0.2140
340.42	114.8370	71.1245	126.7980	0.1952	0.2024

help of these pseudo-spin values we have calculated temperature dependence of shift and width using expressions (17) and (18) as shown in tables (see 2 and 3) given below. By using values given in Tables 1–3 we calculated temperature dependency of dielectric constant $(\in)$, frequencies $\tilde{\Omega}$, $\tilde{\tilde{\Omega}}$ and $\hat{\Omega}$ and loss tangent $(\tan\delta)$ using our expressions (31), (37), and (39), respectively (see Tables 2–6). These have been shown in Figs 1–3, respectively. The results for soft mode frequency have been compared with correlated values obtained from experimental data for dielectric constant of Arend and Blinc[19] for $PbHAsO_4$ crystal. A good agreement is observed.

Table 4 – Calculated values of ∈ for $PbHAsO_4$ crystal

T (K)	∈
264.54	7.0703
277.02	8.0856
283.72	8.6068
286.40	8.9855
289.08	9.2024
294.44	9.8104
298.46	10.2026
303.14	10.3088
309.18	10.0182
311.39	9.8190
313.20	9.6091
319.40	8.9114
327.71	8.1357
335.06	7.3828
340.42	7.0097

Table 5 – Calculated values of $\tilde{\Omega}$, $\tilde{\tilde{\Omega}}$ and $\hat{\Omega}$ for $PbHAsO_4$ crystal

T (K)	$\tilde{\Omega}$	$\tilde{\tilde{\Omega}}$	$\hat{\Omega}$
264.54	0.5998	0.6021	0.6021
277.02	0.5995	0.6019	0.6019
283.72	0.5991	0.6018	0.6018
286.40	0.5990	0.6017	0.6017
289.08	0.5988	0.6016	0.6016
294.44	0.5984	0.6014	0.6014
298.46	0.5983	0.6013	0.6013
303.14	0.5980	0.6011	0.6011
309.18	0.5982	0.6012	0.6012
311.39	0.5983	0.6013	0.6013
313.20	0.5984	0.6014	0.6013
319.40	0.5986	0.6015	0.6015
327.71	0.5989	0.6017	0.6017
335.06	0.5991	0.6020	0.6020
340.42	0.5993	0.6021	0.6021

Table 6 – Calculated values of $\tan\delta$ for $PbHAsO_4$ crystal

T (K)	$\tan\delta \times 10^{-2}$
264.54	0.3262
277.02	0.3804
283.72	0.4107
286.40	0.4313
289.08	0.4449
294.44	0.4787
298.46	0.4998
303.14	0.5083
309.18	0.4915
311.39	0.4810
313.20	0.4698
319.40	0.4336
327.71	0.3934
335.06	0.3544
340.42	0.3350

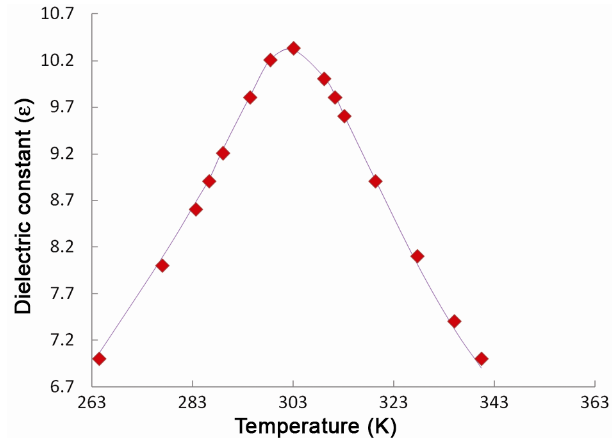

Fig. 1 – Temperature dependence of dielectric constant (∈) of $PbHAsO_4$ crystal (— Present calculation; ♦Experimental results of Arend and Blinc[19])

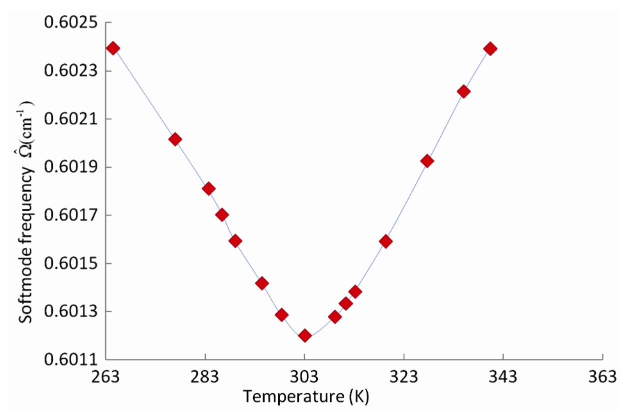

Fig. 2 – Temperature dependence of soft mode frequency $\hat{\Omega}(cm^{-1})$ of $PbHAsO_4$ crystal (— Present calculation; ♦experimentally correlated results of Arend and Blinc[19]) for dielectric data

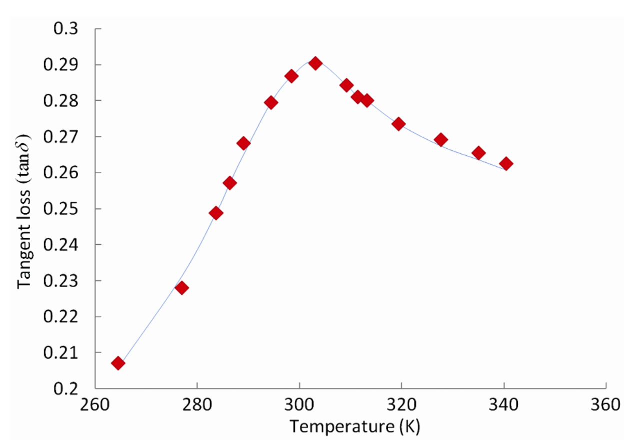

Fig. 3 – Temperature dependence of tangent loss $(\tan\delta)$, (— Present calculation, ♦Experimental values of Arend and Blinc[19])

6 Discussion

By using modified model and Green' function methods we have derived expression for shift, width, soft mode frequency, dielectric constant and loss tangent for $PbHAsO_4$ crystal. Due to decoupling at proper stage unlike Chaudhuri *et al.*[16] we could obtained much better results (quantitative) to explain temperature dependence of soft mode frequency, dielectric constant and loss tangent in $PbHAsO_4$ crystal. Our Equation (31) shows that soft mode frequency explicitly on pseudospin frequency $\tilde{\Omega}$ and $\tilde{\Omega}$ depends upon tunneling frequency Ω, inter-and intrachain interactions J and K. Soft mode frequency also depends upon phonon anharmonic frequency $\tilde{\tilde{\omega}}_k$ and spin-lattice interaction constant V_{ik}. Equation (31) shows that phonon anharmonic interactions terms have important contribution. Equation (31) shows that soft mode frequency $(\hat{\Omega})$ first decreases up to T_c then increases above T_c. Equation (37) shows that dielectric constant depends upon tunneling frequency Ω and soft mode frequency $\hat{\Omega}$. The expression (37) shows that dielectric constant first increases from below up to transition temperature then decreases. Equation (39) shows that loss tangent depends upon tunneling frequency Ω and soft mode frequency $\hat{\Omega}$. Loss tangent first increases from below, up to T_c and then decreases.

7 Conclusions

It is clear from above discussion that the two-sublattice pseudospin-lattice coupled mode model with the third-and fourth-order phonon anharmonic interaction terms explained clearly, the dielectric and ferroelectric properties of $PbHAsO_4$ crystal. Our results are much better than results of others[17] since we have not decoupled the correlations at an early stage, we have decoupled them in proper stage. Shift, width and modified soft mode frequency is the result of present calculation. As a result of which we obtained much better theoretical expressions to explain phase transition, ferroelectric and dielectric properties of $PbHAsO_4$ crystal and similar other crystals. Other similar crystals such as $BaHPO_4$, $CaHPO_4$, $PbHPO_4$ etc. can be explaining on the basis of our theoretical results.

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