

Study of ferroelectric phase transition and dielectric properties of one dimensional hydrogen bonded crystals

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The third- and fourth-order phonon anharmonic interaction terms and spin-lattice interactions have been considered in the two-sublattice pseudospin-lattice coupled mode model for explaining ferroelectric transition and dielectric properties of lead hydrogen arsenate (a one-dimensional hydrogen bonded ferroelectric). Using double time thermal Green's function technique, expressions for shift and width in frequency, soft mode frequency, dielectric constant and loss tangent have been derived for this crystal. By fitting numeric values of various physical parameters in these expressions, thermal dependences of soft mode frequency, dielectric constant and loss tangent have been calculated. Theoretically obtained thermal variations for dielectric constant has been compared with experimental data of other researchers and with experimentally correlated results for soft mode frequency, which show a good agreement.

Keywords: Ferroelectrics, Lead hydrogen arsenate, Green's function, Dielectric constant, Phase transition.

1 Introduction

Ferroelectric materials show spontaneous electric polarization even in the absence of external electric field. After discovery of ferroelectricity in Rochelle salt crystal this phenomenon has been observed in more than two thousand compounds till date. Ferroelectric materials have been found of great use for example as capacitor materials, memory device materials, electro-optic, optoelectronic, pyroelectric detectors, modulators, display device materials etc. Lead hydrogen arsenate (LHA, PbHAsO_4) crystal is a model crystal to study one dimensional hydrogen bonded order-disorder type ferroelectrics, due to its simple crystal structure. It belongs to lead hydrogen phosphate group of ferroelectrics i.e. PbHPO_4 , BaHPO_4 , CaHPO_4 , CaHAsO_4 , BaHAsO_4 etc.

LHA undergoes ferroelectric to paraelectric ($P2/c \rightarrow Pc$) phase transition at 303K (30°C).¹ The crystal has monoclinic structure in both the phases. The lattice parameters are $a=4.85\text{\AA}$, $b=6.76\text{\AA}$, $c=5.83\text{\AA}$ and $\beta=95.28^\circ$.² The number of molecules in the unit cell is two. The AsO_4 groups are connected by hydrogen bonds $\text{O-H}\cdots\text{O}$ and form linear chains along the c-axis. Spontaneous polarization and dielectric anomaly is observed in

the ac plane. In the high temperature paraelectric phase, the hydrogen atom is disordered across the centre of symmetry, in a strong hydrogen bond between two oxygen atoms. The hydrogen atom gradually orders onto one of the two initially equivalent sites below transition temperature. The hydrogen ordering becomes complete some 100K below the transition temperature.³

Experimental studies on this crystal have been largely made. Mlynarka *et al.*⁴ have done structural and Raman spectroscopy studies of LHA and characterized this mineral. Satyanarayana *et al.*⁵ prepared CuO doped lead arsenate glasses and characterized them by XRD, SEM, EDS and DSC methods. They have carried out optical absorption, luminescence and studied FTIR spectra of this crystal. Wilson *et al.*⁶ have done neutron powder diffraction study of PbHAsO_4 crystal. Bajda *et al.*⁷ studied effects of phosphate on the solubility of LHA. Brezina *et al.*⁸ have done crystal growth and have studied some physical properties of this crystal and its deuterated form.

Mackowiak *et al.*⁹ studied nuclear quadrupole resonance (NQR) frequency of ^{75}As nuclei in PbHAsO_4 from 77K to 255K with hydrostatic pressure. Their results express proton dynamics in hydrogen bonds $\text{O-H}\cdots\text{O}$ between the neighboring AsO_4 groups. Liu *et al.*¹⁰ identified the composition and morphology characteristics of lead arsenates.

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Nagarjuna *et al.*¹¹ studied various physical properties of lead arsenate glass system. Zachek *et al.*¹² have studied dielectric, piezoelectric, elastic and thermal characteristics of PbHAsO₄ type crystals using pseudospin model within two particle approximation but they neglected the proton tunneling and proposed that suppression of proton tunneling by short range interactions is valid for PbHAsO₄ type crystals. Wikfeldt *et al.*¹³ have done ab-initio simulations of H-bonded ferroelectrics and they have found that collective transfer of protons along the H-bonding chains facilitated by quantum mechanical tunneling is critical to the order-disorder transition (e.g. PbHPO₄, PbHAsO₄, KDP etc.) and geometrical isotope effect. Shchur¹⁴ has given a unified atomistic lattice dynamics model for hydrogen-bonded crystals. Using this model they studied PbHPO₄, PbDPO₄, CsH₂PO₄ and RbH₂PO₄ crystals and described dielectric properties of these crystals well. This model may also be applied to PbHAsO₄ crystal and its deuterated form which is an isomorph of PbHPO₄ crystal. Magalhaes *et al.*¹⁵ have reviewed thermodynamic stability of lead arsenates.

Chaudhuri *et al.*¹⁶ have studied phase transition in lead hydrogen phosphate type crystals. They have used a two sublattice model with fourth-order phonon anharmonic interaction term. They have however decoupled correlations at early stage and have not considered third-order anharmonic term in their calculations. We have considered two sublattice pseudospin coupled mode model along with these terms in the present paper and have decoupled the correlations at the proper stage. Rawat *et al.*¹⁷ have studied LHA crystal using two sublattice pseudospin-lattice coupled mode model with phonon anharmonic terms but they have not considered extra spin-lattice term in their model. We have also considered extra spin-lattice interaction term. This term represents an indirect coupling between tunneling motion of one proton and the other proton. This modulates distance between two equilibrium sites in O-H---O bonds. This is modulation of tunneling frequency by non-polar phonons.

2 Theory

The two sub-lattice pseudospin-phonon coupled mode model Hamiltonian for one dimensional hydrogen bonded order-disorder ferroelectrics is given by:

$$\begin{aligned}
 H = & -2\Omega \sum_i (S_{1i}^x + S_{2i}^x) - \sum_{ij} J_{ij} (S_{1i}^z S_{1j}^z + S_{2i}^z S_{2j}^z) \\
 & - \sum_{ij} K_{ij} S_{1i}^z S_{2j}^z - \sum_{ik} V_{ik} (S_{1i}^z A_k + S_{2i}^z A_k^+) \\
 & + \frac{1}{4} \sum_k \omega_k (A_k^+ A_k + B_k^+ B_k) - \sum_{ik} V_{ik} (S_{1i}^x A_k + S_{2i}^x A_k^+) \\
 & + \sum_{k_1 k_2 k_3} V^{(3)}(k_1, k_2, k_3) A_{k_1} A_{k_2} A_{k_3} \\
 & + \sum_{k_1 k_2 k_3 k_4} V^{(4)}(k_1, k_2, k_3, k_4) A_{k_1} A_{k_2} A_{k_3} A_{k_4} \\
 & \dots (1)
 \end{aligned}$$

Where, $S_{1\alpha}^m$ and $S_{2\alpha}^m$ (where $m=x$ or z and $\alpha=i$ or j) are α^{th} component of S^m for first and second lattices respectively, J_{ij} and K_{ij} are intra chain and inter chain coupling constants between protons, V_{ik} is spin-phonon interaction constant, Ω is frequency of tunneling of proton between the double well of hydrogen, ω_k is phonon frequency, $V^{(3)}(k_1, k_2, k_3)$ and $V^{(4)}(k_1, k_2, k_3, k_4)$ are third-order and fourth-order phonon anharmonic interaction constants and A_k and B_k are position and momentum operators.

We consider Green's function:

$$G_{ij}(t-t') = \langle \langle S_{1i}^z(t); S_{1i}^z(t') \rangle \rangle = -i\theta(t-t') \langle [S_{1i}^z(t); S_{1i}^z(t')] \rangle \dots (2)$$

Differentiating Eq. (2) with respect to time t and multiplying by i on both sides we obtain:

$$\begin{aligned}
 & = \delta(t-t') \langle [S_{1i}^z, S_{1j}^z] \rangle - i\theta(t-t') \langle [[S_{1i}^z, H], S_{1j}^z(t')] \rangle \\
 i \frac{dG(t-t')}{dt} & = \delta(t-t') \langle [S_{1i}^z, S_{1j}^z] \rangle - i\theta(t-t') \left\langle i \frac{dS_{1i}^z(t)}{dt}, S_{1j}^z(t') \right\rangle \\
 & = \delta(t-t') \langle [S_{1i}^z, S_{1j}^z] \rangle - i\theta(t-t') \langle [B, S_{1j}^z(t')] \rangle \\
 & \dots (3)
 \end{aligned}$$

Where, $B = [S_{1i}^z(t), H]$. Again differentiating Eq. (3) w.r.t. time t and multiplying by i on both sides we obtain:

$$i^2 \frac{d^2 G(t-t')}{dt^2} = \delta(t-t') \langle [B, S_{1j}^z(t)] \rangle - i\theta(t-t') \langle [[B, H], S_{1j}^z(t')] \rangle$$

$$= \delta(t-t') \langle [B, S_{1j}^z] \rangle - i\theta(t-t') \langle [C, S_{1j}^z(t')] \rangle \quad \dots (4)$$

Where $C = [B, H]$

Fourier transforming Eq. (4) using relations:

$$\delta(t-t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega(t-t')} d\omega \quad \dots (5)$$

$$\frac{dG(t-t')}{dt} = -i\omega \int_{-\infty}^{\infty} G(\omega) e^{-i\omega(t-t')} d\omega \quad \dots (6)$$

$$\frac{d^2G(t-t')}{dt^2} = \omega^2 \int_{-\infty}^{\infty} G(\omega) e^{-i\omega(t-t')} d\omega \quad \dots (7)$$

We obtain:

$$G(\omega) = \frac{1}{2\pi} \frac{\langle 2\Omega S_{li}^x \delta_{ij} + V_{ik} A_k S_{li}^x \delta_{ij} \rangle}{\omega^2 - 4\Omega^2} - \frac{\langle \langle F; S_{1j}^z \rangle \rangle}{\omega^2 - 4\Omega^2} \quad \dots (8)$$

On considering the second term of Eq. (8) as:

$$\Gamma_{ij}(t-t') = \langle \langle F_i(t); S_{ij}^z(t') \rangle \rangle = -\theta(t-t') \langle [F(t), S_{ij}^z(t')] \rangle \quad \dots (9)$$

Differentiating Eq. (9) w.r.t. time t' and multiplying by i on both sides we obtain:

$$\begin{aligned} i \frac{d\Gamma(t-t')}{dt} &= \delta(t-t') \langle [F(t), S_{1j}^z(t')] \rangle - i\theta(t-t') \langle [F(t), [S_{1j}^z(t'), H]] \rangle \\ &= \delta(t-t') \langle [F(t), S_{1j}^z(t')] \rangle - i\theta(t-t') \langle [F(t), B'] \rangle \end{aligned} \quad \dots (10)$$

Where $B' = [S_{1j}^z(t'), H]$. Again differentiating Eq. (10) w.r.t. t' we obtain:

$$\begin{aligned} i^2 \frac{d^2\Gamma(t-t')}{dt^2} &= \delta(t-t') \langle [F(t), B'] \rangle - i\theta(t-t') \langle [F(t), [B', H]] \rangle \\ &= \delta(t-t') \langle [F(t), B'] \rangle - i\theta(t-t') \langle [F(t), C'] \rangle \end{aligned} \quad \dots (11)$$

Where $C' = [B', H]$

Fourier transforming Eq. (11) using relations (5), (6) and (7) for $\delta(t-t')$, $\frac{d^2\Gamma}{dt^2}$ and $\frac{d\Gamma(t-t')}{dt'}$ we obtain:

$$\Gamma(\omega) = \frac{1}{2\pi} \frac{\langle [F, B'] \rangle}{\omega^2 - 4\Omega^2} + \frac{\langle \langle F; F' \rangle \rangle}{\omega^2 - 4\Omega^2} \quad \dots (12)$$

Putting value of $\Gamma(\omega)$ in Eq. (11) above we obtain:

$$G(\omega) = \frac{1}{2\pi} \frac{\langle 2\Omega S_{li}^x \delta_{ij} + V_{ik} A_k S_{li}^x \delta_{ij} \rangle}{\omega^2 - 4\Omega^2} + \frac{1}{2\pi} \frac{\langle [F, B'] \rangle}{(\omega^2 - 4\Omega^2)^2} + \frac{\langle \langle F, F' \rangle \rangle}{(\omega^2 - 4\Omega^2)^2} \quad \dots (13)$$

Simplifying Eq. (13) and writing it in the form of Dyson's Eq.:

$$G_{ij}(\omega) = G_{ij}^o(\omega) + G_{ij}^o(\omega) \tilde{P}(\omega) G_{ij}^o(\omega) \quad \dots (14)$$

We get :

$$G_{ij}^o(\omega) = \frac{\Omega \langle S_{li}^x \rangle \delta_{ij}}{\pi(\omega^2 - 4\omega^2)} \quad \dots (15)$$

$$\tilde{P}(\omega) = \frac{\pi \langle [F, B'] \rangle}{2\Omega^2 \langle S_{li}^x \rangle^2} + \frac{\pi^2 \langle \langle F; F' \rangle \rangle}{\Omega^2 \langle S_{li}^x \rangle^2} \quad \dots (16)$$

We obtain value of Green's function by solving $\langle [F, B'] \rangle$ and $\langle \langle F_i(t); F_j(t') \rangle \rangle$ terms. We decouple higher order Green's functions (in $\tilde{P}(\omega)$) into simpler Green's functions. These are then solved and substituted. We hence obtain:

$$G_{ij}(\omega) = \frac{\Omega \langle S_{li}^x \rangle \delta_{ij}}{\pi[\omega^2 - \hat{\Omega}^2 - 2\Omega i\Gamma(\omega)]} \quad \dots (17)$$

Where

$$\hat{\Omega} = \tilde{\tilde{\Omega}} + \Delta(\omega) \quad \dots (18)$$

$$\tilde{\tilde{\Omega}}^2 = \tilde{\tilde{\Omega}}^2 + 2\Omega\Delta(\omega) \quad \dots (19)$$

$$\tilde{\Omega}^2 = a^2 + b^2 - bc \quad \dots (20)$$

With

$$a = 2J_{ij} \langle S_{1i}^z \rangle + K_{ij} \langle S_{2j}^z \rangle, \quad \dots (21)$$

$$b = 2\Omega, \text{ where } \Omega \text{ is tunneling frequency and} \\ c = 2J_{ij} \langle S_{1i}^x \rangle + K_{ij} \langle S_{2j}^x \rangle \quad \dots (22)$$

The shift $\Delta(\omega)$ in Eq. (18) is given by:

$$\Delta(\omega) = \frac{a^4}{\omega^2 - \tilde{\Omega}^2} + \frac{b^2 c^2}{\omega^2 - \tilde{\Omega}^2} + \frac{16\Omega V_{ik}^2 a \langle S_{1i}^z \rangle (\omega^2 - \tilde{\omega}_k^2)}{\left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right] b} \\ + \frac{16\Omega^2 V_{ik}^2 N_k}{\omega^2 - \tilde{\Omega}^2} + \frac{4\Omega V_{ik}^2 \langle S_{1i}^x \rangle \omega_k (\omega^2 - \tilde{\omega}_k^2)}{\left(\omega^2 - \tilde{\omega}_k^2 \right)^2 + 4\omega_k^2 \Gamma_k^2(\omega)} \\ + \frac{2\Omega V_{ik}^2 N_k a^2}{\left(\omega^2 - \tilde{\Omega}^2 \right) b} + \frac{4V_{ik}^4 N_k \omega_k a \langle S_{1i}^z \rangle (\omega^2 - \tilde{\omega}_k^2)}{\left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right] b \Omega} \\ + \frac{V_{ik}^4 N_k}{\omega^2 - \tilde{\Omega}^2} + \frac{V_{ik}^4 N_k a^2}{\left(\omega^2 - \tilde{\Omega}^2 \right) b^2} + \frac{\pi V_{ik}^4 N_k}{\left(\omega^2 - \tilde{\Omega}^2 \right) b \Omega} \\ + \frac{2V_{ik}^2 J_{ij}^2 \langle S_{1i}^z \rangle^2 \langle S_{1j}^x \rangle \omega_k (\omega^2 - \tilde{\omega}_k^2)}{\left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right] \Omega} + \frac{V_{ik}^2 J_{ij}^2 N_k a^2 \langle S_{1i}^z \rangle^2}{\left(\omega^2 - \tilde{\Omega}^2 \right) \Omega b} \\ + \frac{2V_{ik}^2 J_{ij}^2 N_k \langle S_{1i}^x \rangle^2}{\omega^2 - \tilde{\Omega}^2} + \frac{V_{ik}^2 K_{ij}^2 N_k \langle S_{1i}^x \rangle^2}{\omega^2 - \tilde{\Omega}^2} \\ + \frac{V_{ik}^2 K_{ij}^2 \omega_k \langle S_{1i}^z \rangle^2 \langle S_{1j}^x \rangle (\omega^2 - \tilde{\omega}_k^2)}{\left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right] \Omega} + \frac{V_{ik}^2 K_{ij}^2 N_k a^2 \langle S_{1i}^z \rangle^2}{\left(\omega^2 - \tilde{\Omega}^2 \right) b^2} \\ + \frac{4V_{ik}^2 N_k \omega_k \langle S_{1i}^x \rangle (\omega^2 - \tilde{\omega}_k^2)}{\left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right] \Omega} \\ \dots (23)$$

Corresponding width $\Gamma(\omega)$ is given by:

$$\Gamma(\omega) = \frac{a^4}{2\tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] + \frac{b^2 c^2}{2\tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] + \\ \frac{32\Omega V_{ik}^2 \langle S_{1i}^z \rangle \omega_k \Gamma_k(\omega)}{b \left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right]}$$

$$\Gamma(\omega) = \frac{a^4}{2\tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] + \frac{b^2 c^2}{2\tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] \\ + \frac{32\Omega V_{ik}^2 \langle S_{1i}^z \rangle \omega_k \Gamma_k(\omega)}{b \left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right]} \\ + \frac{2\Omega V_{ik}^2 N_k a^2}{2\tilde{\Omega} b} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] + \frac{4V_{ik}^2 K_{ij}^2 \langle S_{1i}^z \rangle^2 \langle S_{1j}^x \rangle \omega_k^2 \Gamma_k(\omega)}{b \left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right]} \\ + \frac{16\Omega^2 V_{ik}^2 N_k}{2\tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] + \frac{8\Omega V_{ik}^2 \langle S_{1i}^x \rangle \omega_k^2 \Gamma_k(\omega)}{\left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right]} \\ + \frac{8V_{ik}^2 J_{ij}^2 \langle S_{1i}^z \rangle^2 \langle S_{1j}^x \rangle \omega_k^2 \Gamma_k(\omega)}{b \left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right]} \\ + \frac{V_{ik}^2 K_{ij}^2 N_k \langle S_{1i}^x \rangle^2}{2\tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] + \\ \frac{V_{ik}^2 K_{ij}^2 N_k a^2 \langle S_{1i}^z \rangle^2}{2b^2 \tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] \\ + \frac{16V_{ik}^2 N_k \omega_k^2 \langle S_{1i}^x \rangle \Gamma_k(\omega)}{b \left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right]} + \frac{16V_{ik}^4 N_k \omega_k^2 a \langle S_{1i}^z \rangle \Gamma_k(\omega)}{b^2 \left[(\omega^2 - \tilde{\omega}_k^2)^2 + 4\omega_k^2 \Gamma_k^2(\omega) \right]} \\ + \frac{V_{ik}^4 N_k}{2\tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] + \frac{V_{ik}^4 N_k a^2}{2\tilde{\Omega} b^2} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] \\ + \frac{\pi V_{ik}^4 N_k}{\tilde{\Omega} b^2} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] \\ \dots (24)$$

$\Delta(\omega)$ and $\Gamma(\omega)$ are real and imaginary parts of function $\tilde{P}(\omega)$ given by Eq. (16). $\tilde{\omega}_k$ and $\Gamma_k(\omega)$ appearing in Eq. (22) and (23) are modified phonon frequency and phonon width. These are obtained when we solve Green's function for phonons $\langle \langle A_k; A_k^+ \rangle \rangle$.

This Green's function is solved using last three terms of Hamiltonian. We obtain phonon Green's function as:

$$G_{kk'}(\omega) = \frac{\omega_k \delta_{k,k'}}{\pi \left[(\omega^2 - \tilde{\omega}_k^2) - 2i\omega_k \Gamma_k(\omega) \right]} \quad \dots (25)$$

Where

$$\tilde{\omega}_k = \tilde{\omega}_k + 2\omega_k \Delta_k(\omega) \quad \dots (26)$$

$$\Delta_k(\omega) = 18P \sum_{k_1 k_2} |V^{(3)}(k_1, k_2, -k)|^2 \frac{\omega_{k_1} \omega_{k_2}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}} \quad \dots (27)$$

$$\begin{aligned} \Gamma_k(\omega) = & 9\pi \sum_{k_1 k_2} |V^{(3)}(k_1, k_2, -k_3)|^2 \frac{\omega_{k_1} \omega_{k_2}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}} \\ & \left\{ \begin{aligned} & (n_{k_1} + n_{k_2}) \left[\delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta(\omega - \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}) \right] \\ & + (n_{k_2} - n_{k_1}) \left[\delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) \right] \end{aligned} \right\} \\ & (n_{k_1} + n_{k_2}) \left[\delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta(\omega - \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}) \right] + (n_{k_2} - n_{k_1}) \\ & \left[\delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) \right] \\ & + 48\pi \sum_{k_1 k_2 k_3 k_4} |V^{(4)}(k_1, k_2, k_3, -k_4)|^2 \left\{ \begin{aligned} & \frac{(1 + n_{k_1} n_{k_2} + n_{k_2} n_{k_3} + n_{k_3} n_{k_4})}{\left[\delta(\tilde{\omega} + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}) - \delta(\tilde{\omega} - \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}) \right]} \\ & + 3(n_{k_1} n_{k_2} + n_{k_2} n_{k_3} - n_{k_3} n_{k_4}) \left[-\delta(\tilde{\omega} - \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}) \right] \end{aligned} \right\} \\ & + \text{higher order terms.} \quad \dots (28) \end{aligned}$$

The soft mode frequency for PbHAsO₄ crystal can be obtained by solving Eq. (17) with the help of Eqs. (18)-(28). We thus get:

$$\hat{\Omega}^2 = \frac{1}{2} \left[\left(\tilde{\omega}_k^2 + \hat{\Omega}^2 \right) \pm \left(\tilde{\omega}_k^2 - \hat{\Omega}^2 \right)^2 + 8 \left(\frac{4V_{ik}^2 a \langle S_{ii}^z \rangle + 2\Omega V_{ik}^2 \langle S_{ii}^z \rangle \omega_k + \frac{2V_{ik}^2 J_{ij}^2 \langle S_{ii}^z \rangle^2 \langle S_{ii}^z \rangle \omega_k}{b}}{+ V_{ik}^2 K_{ij}^2 \langle S_{ii}^z \rangle \langle S_{ii}^z \rangle^2 \omega_k + 4V_{ik}^2 N_k \langle S_{ii}^z \rangle \omega_k + \frac{4V_{ik}^2 N_k a \langle S_{ii}^z \rangle \omega_k}{b^2}} \right)^{\frac{1}{2}} \right]^{\frac{1}{2}} \quad \dots (29)$$

Applying the condition of stability $\hat{\Omega} \rightarrow 0$ as $T \rightarrow T_c$ expression for transition temperature T_c is obtained easily:

$$T_c = \eta \left[2k_B \tanh^{-1} \left(\frac{4\Omega^2}{J'} \right) \right]^{-1}, \quad \dots (30)$$

$$\text{With } J' = J + \frac{2V_{ik}^2 \omega_k^2}{\tilde{\omega}_k^2}, \quad \dots (31)$$

$$\eta^2 = (2J - K)^2 \sigma^2 + 4\Omega^2 \text{ and } \langle S_1^z \rangle = -\langle S_2^z \rangle = \sigma \quad \dots (32)$$

We see from Eq. (23) that ferroelectric mode frequency is a function of $\tilde{\omega}_k$ which depends upon phonon anharmonic interaction.

Electrical susceptibility χ is related to Green's function as¹⁸:

$$\chi = -\lim_{x \rightarrow 0} 2\pi\chi N\mu^2 G_{ij}(\omega + ix) \quad \dots (33)$$

The dielectric constant ε is related to susceptibility as:

$$\varepsilon = 1 + 4\pi\chi \quad \dots (34)$$

For ferroelectrics, $\varepsilon \gg 1$ therefore

$$\varepsilon = 4\pi\chi \quad \dots (35)$$

Replacing value of χ from Eq. (36) in Eq. (34):

$$\varepsilon = - \frac{8\pi N\mu^2 \Omega \langle S_{ii}^x \rangle \delta_{ij}}{\left[(\omega^2 - \hat{\Omega}^2) - 2\Omega i \Gamma(\omega) \right]} \quad \dots (36)$$

Tangent loss is the ratio of imaginary part and real part of dielectric constant:

$$\tan \delta = - \frac{2\Omega \Gamma(\omega)}{\omega^2 - \hat{\Omega}^2} \quad \dots (37)$$

Equation (36) shows that the tangent loss depends on the tunneling frequency Ω , width function $\Gamma(\omega)$ and soft mode frequency $\hat{\Omega}$.

3 Results and Discussion

Using model values of different physical quantities; $\Omega=0.21\text{cm}^{-1}$, $V_{ik}=0.02\text{cm}^{-1}$, $J_{ij}=186\text{cm}^{-1}$, $K_{ij}=93\text{cm}^{-1}$, $\mu=1.8 \times 10^{-18}\text{esu}$, $N=5.2 \times 10^{22}\text{cm}^{-3}$, $\omega_k=14\text{cm}^{-1}$, temperature dependence of soft mode frequency, dielectric constant and loss tangent have been calculated. Our results for dielectric constant have been compared with the experimental data of Arend *et al.*¹ The graphs are shown in Figs. 1-3.

For theoretical calculation the model values of various physical quantities appearing in the expressions for soft mode frequency, dielectric constant and loss tangent are fitted in the theoretical expressions for lead hydrogen arsenate crystal. Temperature dependences of soft mode frequency, dielectric constant and loss tangent are calculated, as shown in Figs. 1-3, respectively. The theoretical values of ferroelectric mode frequency for lead hydrogen arsenate are compared with the values obtained by correlating experimental data of Arend *et al.*¹ for dielectric constant. Theoretically obtained

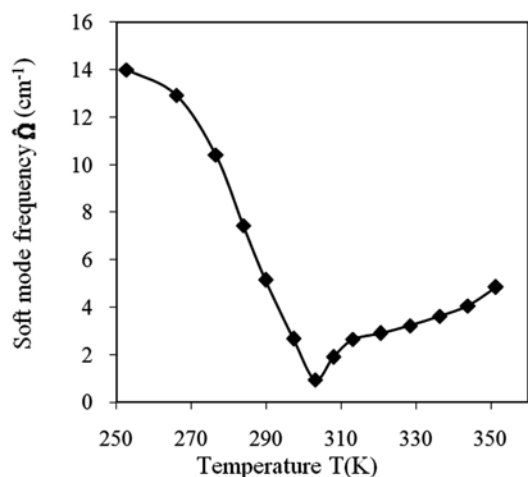


Fig. 1 — Temperature dependence of soft mode frequency in lead hydrogen arsenate crystal (— our calculation, \blacklozenge correlated values of soft mode frequency with experimental values of Arend *et al.*¹ for dielectric constant).

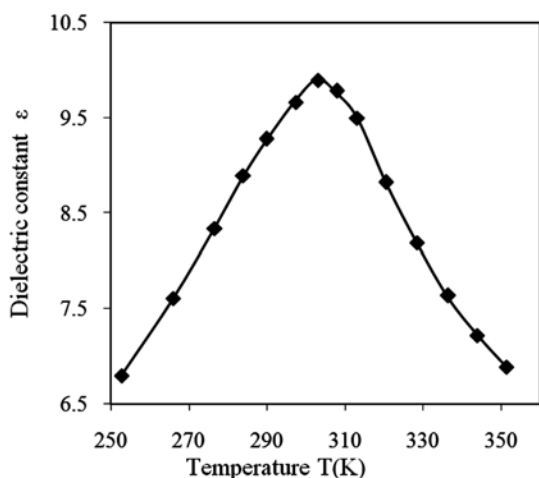


Fig. 2 — Temperature dependence of dielectric constant in lead hydrogen arsenate crystal (— our calculation, \blacklozenge experimental values of Arend *et al.*¹).

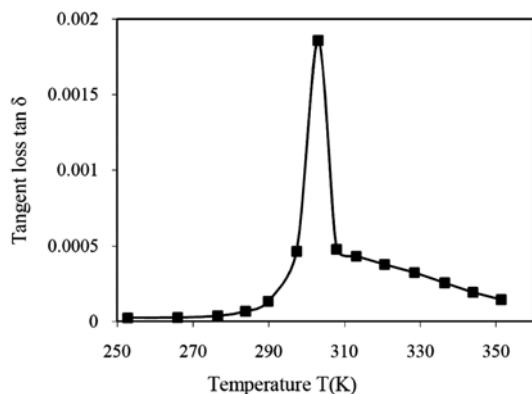


Fig. 3 — Temperature dependence of loss tangent in lead hydrogen phosphate crystal \blacklozenge (— our calculation).

results for dielectric constant are compared with the experimental data¹ for LHA crystal. Present results agree with the experimental results of these researchers.

4 Conclusions

From present study it is clear that a definite shift appears into soft mode frequency, which is due to spin-phonon interaction, anharmonic interaction and extra spin-lattice interaction. The inclusion of third and fourth-order phonon anharmonic terms and extra spin-lattice interaction term in the Hamiltonian gives shift in ferroelectric mode frequency. These terms stabilize the frequency via pseudospin-phonon interaction. This frequency varies with temperature in accordance with Cochran's assumption and explains the phase transition in one dimensional hydrogen bonded order-disorder type ferroelectric crystals accurately.

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