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Research Article

**Temperature dependent structural Phase transition in Lead Mono
Hydrogen Aresenate crystal**

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Abstract

With the use of the modified pseudospin lattice coupled-mode (PLCM) model by adding third-order and fourth-order phonon anharmonic interactions terms and the statistical Green's function technique a phenomenological explanation of phase transition of the lead monohydrogen arsenate (PbHAsO_4) crystal has been given. Expressions for shift, width, dielectric constant, loss tangent and modified ferroelectric soft mode frequency have been derived theoretically. By fitting model values of various quantities obtained from literature in these derived expressions, their temperature dependence has been evaluated numerically. Present theoretically results agree well with the experimental results of others.

Keywords: Ferroelectric, Dielectric, Soft mode, Pseudo spin, Phase transition

1. INTRODUCTION

Due to promising applications in the field of electronics and technology ferroelectric crystals are continuously being attracted to both scientists and physicists. These crystals are used for preparation of memory devices like capacitors of small size, piezoelectric acoustic

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transducers and pyroelectric infrared detectors^{1,2}. Lead mono hydrogen arsenate (PbHAsO_4) belongs to lead hydrogen phosphate (PbHPO_4) type ferroelectric crystals which are called monetites. In these crystals the direction of the spontaneous polarization is almost parallel to the direction of H- bond O-H...O projecting on the (010) bonds in the form of one dimensional chain along c-axis. The PO_4 chains in this salt are bound to one another by the O-H...O bonds. Thus the intra chain coupling (within a chain) is stronger than the interchain coupling between the chains. If one compares PbHAsO_4 crystal with largely studied KH_2PO_4 crystal, one finds that there are three major differences³ (i) one dimensional ordering of protons (ii) unusual large isotopes effect (iii) spontaneous polarization direction is not along c-axis. Therefore it can be said that on the basis of the simple pseudospin lattice coupled mode model, the nature of ferroelectric transition of PbHAsO_4 crystal cannot be adequately explained. So here in order to explain phase transition in lead monohydrogen arsenate crystal, we should use two-sublattice coupled mode model. Experimental investigations in lead mono hydrogen arsenate crystal have been made by a large number of workers. Deguchi and Nakamura⁴ have made crystal growth studies on lead monohydrogen arsenate crystal. Kroupa *et al.*⁵ have made experimental dielectric and far infrared studied in lead mono hydrogen arsenate crystal. Charykova *et al.*⁶ have studied dielectric properties of lead mono hydrogen arsenate crystal. Lee *et al.*⁷ have carried out experimental determination of stability constants of lead mono hydrogen crystal. Zachak *et al.*⁸ have studied thermodynamic properties of lead mono hydrogen arsenate crystal. In order to explain dielectric properties and ferroelectric structural phase transition, in past, theoretical work have been done by many workers. Using pseudospin model without tunneling term De Carvalho and Salinas⁹ have studied this crystal. By adding two-sublattice term in pseudospin model calculation were made by Blinc *et al.*¹⁰. Two sublattice PLCM model with fourth-order phonon anharmonic term was used by Chaudhuri *et al.*¹¹ in their calculation. However these authors have made decoupling of correlations in early stage, as a result of which some important interactions disappeared in their theoretical derived results. In this paper, with modified PLCM model, by adding third-and fourth-order phonon anharmonic interactions terms and double time temperature dependent Green's function method¹², expressions for shift, width, loss tangent, dielectric constant and modified soft mode frequency have been derived for PbHAsO_4 crystal. Model values of various physical quantities are fitted in the expressions derived theoretically above, and their temperature dependence have been obtained

numerically. Theoretically obtained results have been compared with experimental result of others¹³. A good agreement is observed.

2. THEORITICAL CALCULATIONS

2.1 Model Hamiltonian and Green's function

Lead monohydrogen arsenate crystal consists of the monoclinic crystal structure in both paraelectric and ferroelectric P_c phases. The lattice parameters of $PbHAsO_4$ crystal are $a=4.85 \text{ \AA}$, $b=6.76 \text{ \AA}$, $c=5.83 \text{ \AA}$ and $\beta=95.5^\circ$. There is equal distribution of hydrogen atoms between two off-center site on O-H...O bonds above T_c . In ferroelectric phase hydrogen atoms order in one of the two possible site on O-H...O bonds. For the quasi-one dimensional lead monohydrogen arsenate crystal, the two-sublattice pseudospin-lattice coupled mode model Hamiltonian is expressed as

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

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. The last two terms in above equation are called third-and fourth order anharmonic interactions terms.

2.2.1 Green's functions method

We consider the Green's function

$$\begin{aligned}
 G_{ij}(t-t') &= \langle \langle S_{1i}^z(t); S_{1j}^z(t') \rangle \rangle \\
 &= -i\theta(t-t') \langle S_{1i}^z(t); S_{1j}^z(t') \rangle, \quad (2)
 \end{aligned}$$

where S_{li}^z and S_{lj}^z are spin operators, on sites i and j , θ is unit step function: $\theta(t) = 1$ for $t > 0$, and $\theta(t) = 0$ for $t < 0$. The angular bracket $\langle \dots \rangle$ denotes ensemble average over a grand canonical ensemble.

Differentiating Green's function (2) two times with respect to time t and t' using model Hamiltonian (Eq.1) and multiplying both sides by i and after Fourier transforming we obtain (putting in the form of Dyson equation)

$$G(\omega) = \tilde{G}^\circ(\omega) + \tilde{G}^\circ(\omega)\tilde{P}(\omega)G(\omega), \quad (3)$$

$$\text{where } G^\circ(\omega) = \frac{\Omega \langle S_{li}^x \rangle \delta_{ij}}{(\omega^2 - \tilde{\Omega}^2)}, \quad (4)$$

and

$$\tilde{\Omega}^2 = 4\Omega^2 + \frac{i}{\langle S_{li}^x \rangle} \langle [F_{li}(t); S_{lj}^y] \rangle, \quad (5)$$

and

$$\tilde{P}(\omega) = \frac{\pi}{\Omega \langle S_{li}^x \rangle \delta_{ij}} \langle \langle F_{li}(t); F_{lj}(t') \rangle \rangle. \quad (6)$$

Eq. (3) gives value of Green's function (2) as

$$G(\omega) = \frac{\Omega \langle S_{li}^x \rangle \delta_{ij}}{\pi [\omega^2 - \tilde{\Omega}^2 - \tilde{P}(\omega)]}. \quad (7)$$

It is clear from Eq. (6) that $\tilde{P}(\omega)$ contains higher order Green's functions. These are decoupled into simpler Green's functions which are evaluated and substituted. Then we obtain value of $\tilde{P}(\omega)$. Now we separates $\tilde{P}(\omega)$ in to its real part called shift (Δ) and imaginary part called width (Γ). We obtain these functions as

$$\Delta(\omega) = \frac{a^4}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{b^2 c^2}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{V_{ik}^2 N_K a^2}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{2V_{ik}^2 \langle S_{li}^x \rangle \omega_k \delta_{k-k'} (\omega^2 - \tilde{\omega}_k^2)}{(\omega^2 - \tilde{\omega}_k^2) + 4\omega_k^2 \Gamma_k^2(\omega)}, \quad (8)$$

and

$$\Gamma(\omega) = \frac{\pi a^4}{4\Omega \tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] + \frac{b^2 c^2}{4\Omega \tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] + \frac{2V_{ik}^2 \langle S_{li}^x \rangle \omega_k \delta_{k-k'} (\omega^2 - \tilde{\omega}_k^2)}{(\omega^2 - \tilde{\omega}_k^2) + 4\omega_k^2 \Gamma_k^2(\omega)} + \frac{2V_{ik}^2 \langle S_{li}^x \rangle \omega_k \delta_{k-k'} \Gamma_k(\omega)}{(\omega^2 - \tilde{\omega}_k^2) + 4\omega_k^2 \Gamma_k^2(\omega)}. \quad (9)$$

In Eqs (8) and (9), $\Delta_k(\omega)$ is phonon shift and $\Gamma_k(\omega)$ is phonon shift due to third-and fourth-order phonon anharmonic interactions terms. Width, $\Gamma_k(\omega)$ and corresponding shift, $\Delta_k(\omega)$ are obtained in phonon Green's function

$$\langle\langle A_k; A_{k'} \rangle\rangle = \frac{\omega_k \delta_{kk'}}{\pi [\omega^2 - \tilde{\omega}_k^2 - 2i\omega_k \Gamma_k(\omega)]} \quad (10)$$

where

$$\tilde{\omega}_k^2 = \tilde{\omega}_k^2 + 2\omega_k \Delta_k(\omega) \quad (11)$$

$$\tilde{\omega}_k^2 = \omega_k + A_k \quad (12)$$

In Eq. (11), $\Delta_k(\omega)$ is

$$\begin{aligned} \Delta_k(\omega) = & 18P \sum_{k_1 k_2} |V^3(k_1, k_2, -k)|^2 \frac{\omega_{k_1} \omega_{k_2}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}} \left\{ (n_{k_1} + n_{k_2}) \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2})^2} + (n_{k_2} + n_{k_1}) \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2})^2} \right\} \\ & + 48P \sum_{k_1 k_2} |V^4(k_1, k_2, k_3, -k)|^2 \frac{\omega_{k_1} \omega_{k_2} \omega_{k_3}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2} \tilde{\omega}_{k_3}} \left\{ (1 + n_{k_1} n_{k_2} + n_{k_2} n_{k_3} + n_{k_3} n_{k_1}) \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3})^2} \right. \\ & \left. + 3(1 - n_{k_2} n_{k_1} + n_{k_2} n_{k_3} - n_{k_3} n_{k_1}) \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3})^2} + \text{higher terms.} \right\} \quad (13) \end{aligned}$$

$$\begin{aligned} \Gamma_k(\omega) = & 9\pi \sum_{k_1 k_2} |V^3(k_1, k_2, -k)|^2 \frac{\omega_{k_1} \omega_{k_2}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}} \left\{ (n_{k_2} + n_{k_1}) [\delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta(\omega + \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2})] \right. \\ & \left. + (n_{k_2} - n_{k_1}) [\delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_1}) - \delta(\omega + \tilde{\omega}_{k_1} - \tilde{\omega}_{k_1})] (\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_1}) \right\} \\ & + 48\pi \sum_{k_1 k_2} |V(k_1, k_2, k_3, -k_4)|^2 \left\{ 1 + n_{k_1} n_{k_2} + n_{k_2} n_{k_3} + n_{k_3} n_{k_4} \right\} \\ & \times \left[\delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}) - \left\{ \delta(\omega - \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}) \right\} \right] \quad (14) \end{aligned}$$

Now we obtain Green's function (7) finally as

$$G(\omega + iX) = \frac{\Omega \langle S_{li}^x \rangle \delta_{ij}}{\pi [\omega^2 - \hat{\Omega}^2 + 2i\Omega\Gamma(\omega)]} \quad (15)$$

where

$$\hat{\Omega}^2 = \tilde{\tilde{\Omega}}^2 + \Delta(\omega), \quad (16)$$

$$\tilde{\tilde{\Omega}}^2 = \tilde{\Omega}^2 + \Delta(\omega), \quad (17)$$

$$\tilde{\Omega}^2 = a^2 + b^2 - bc, \quad (18)$$

where

$$a = 2J_{ij} \langle S_1^z \rangle + K_{ij} \langle S_2^z \rangle, \quad (19)$$

$$b = 2\Omega, \quad (20)$$

$$c = 2J_{ij} \langle S_1^x \rangle + K_{ij} \langle S_2^x \rangle, \quad (21)$$

If we simplify Eq. (17), we obtain

$$\hat{\Omega}_{\pm}^2 = \frac{1}{2} \left[(\tilde{\Omega}^2 + \tilde{\omega}_k^2) \pm \left\{ (\tilde{\omega}_k^2 - \tilde{\Omega}^2)^2 + 8V_{ik}^2 \langle S_{li}^x \rangle \Omega \right\}^{\frac{1}{2}} \right]. \quad (22)$$

This frequency with negative sign is called the modified ferroelectric soft mode frequency which becomes zero at transition temperature and gives rise to ferroelectric transition.

Applying condition of stability i.e. $\hat{\Omega} \rightarrow 0$ at $T \rightarrow T_c$, we obtain formula for transition temperature

$$T_c = \frac{\eta}{2k_B \tanh^{-1} \left(\frac{\eta^3}{4\Omega^2 J^*} \right)}, \quad (23)$$

where

$$\eta^2 = (2J - K)^2 \sigma^2 + 4\Omega^2, \quad (24)$$

and

$$J^* = (2J + K) + \frac{2V_{ik}^2 \tilde{\omega}_k^2}{[\tilde{\omega}_k^4 + 4\omega_k \Gamma_k^2]}. \quad (25)$$

The electrical susceptibility χ expresses the effect of applying electric field on dielectric crystal. It is related to Green's function $G(\omega + ix)$ as

$$\chi = -\lim_{x \rightarrow 0} 2\pi N \mu^2 G_{ij}(\omega + ix), \quad (26)$$

where N is the number of dipoles having dipole moment μ in unit volume. Dielectric constant ϵ is related to χ as

$$\epsilon = 1 + 4\pi\chi \quad (27)$$

For ferroelectric crystals $\epsilon \gg 1$. Hence we obtain using Eqs. (26) and (15)

$$\epsilon = -\frac{8\pi N \mu^2 \Omega \langle s_{li}^x \rangle \delta_{ij}}{\pi[(\omega^2 - \tilde{\Omega}^2)^2 + 4\Omega^2 \Gamma^2(\omega)]} \quad (28)$$

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

$$\tan \delta = \frac{\epsilon''}{\epsilon'}. \quad (29)$$

We obtain from Eq. (28) $\tan \delta$ as

$$= -\frac{2\Omega\Gamma(\omega)}{(\omega^2 - 4\hat{\Omega}^2)}. \quad (30)$$

3. NUMERICAL CALCULATION AND DISCUSSION

We consider values $\Omega=0.3\text{cm}^{-1}$, $J=186\text{cm}^{-1}$, $K=93\text{cm}^{-1}$, $N_k=0.1$, $V_{ik}=25\text{cm}^{-1}$, $\omega_k=16\text{cm}^{-1}$ for PbHAsO_4 crystal from literature¹¹. We have obtained temperature dependence of frequency $\tilde{\Omega}$, $\tilde{\tilde{\Omega}}$ and $\hat{\Omega}$ and dielectric constant ϵ and loss tangent ($\tan\delta$) using our expressions (18), (17), (16), (28) and (30). The results have been shown in figures 1, 2 and 3. The theoretical results have been compared with the experimental results of others¹³ for PbHAsO_4 crystal for dielectric constant, loss tangent and soft mode frequency. Our results agree with the results of others¹³.

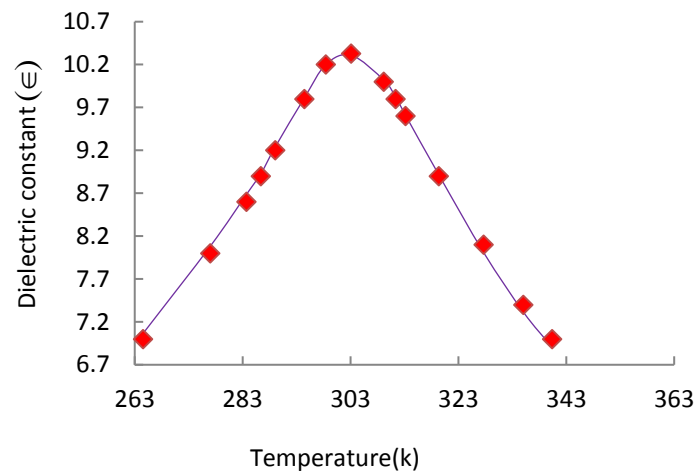


Figure 1: Temperature dependence of dielectric constant ϵ of PbHAsO_4 crystal (— Present calculation; \blacklozenge Experimental results of Arend *et al.*¹³).

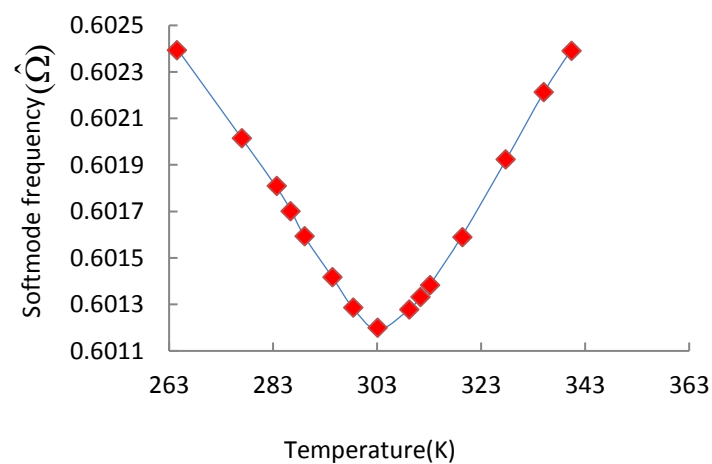


Figure 2: Temperature dependence of soft mode frequency $\hat{\Omega}_{(\text{cm}^{-1})}$ of PbHAsO_4 crystal (— Present calculation; \blacklozenge Experimentally correlated results of Arend *et al.*¹³ for dielectric data).

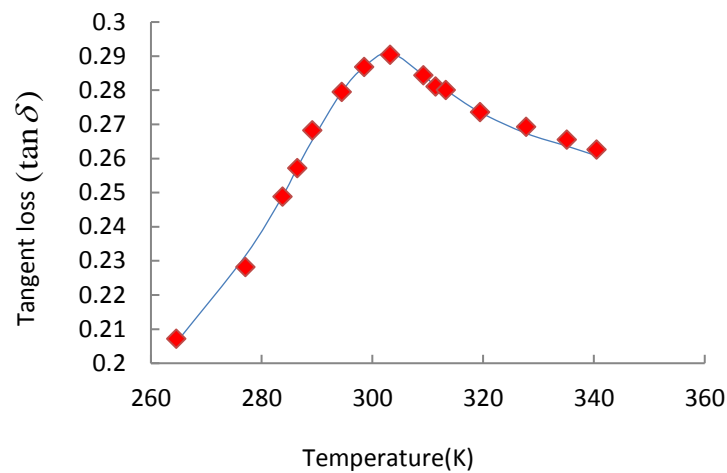


Figure 3: Temperature dependence of tangent loss ($\tan\delta$), (—Our calculation, \blacklozenge Experimental values of Arend et al¹³.)

4. CONCLUSIONS

It is clear from above discussion that the two-sublattice pseudospin-lattice coupled mode model with the third-and fourth-order phonon anharmonic interactions terms explains well, the dielectric and ferroelectric properties of PbHAsO_4 crystal. Our results are much better than results of others ¹¹since we have not decoupled the correlations at an early stage. We have decoupled them at proper stage. Shift, width and modified soft mode frequency are 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. Phase transition of other similar crystals such as BaHPO_4 , CaHPO_4 etc. can be explained on the basis of our theoretical results.

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