Ferroelectric Effect Investigation in Some Lead Hydrogen Phosphate Type Crystal

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Abstract: The formulae to describe ferroelectric effect in $PbHPO_4$ (Lead Hydrogen Phosphate) type crystal are derived. For its simple modified model is used. Simple Green Function formalism is used for derivation numerically thermal variations of normal mode frequency (which brings ferroelectric effect) is obtained anomalous dielectric constant and spontaneous polarization are numerically calculated for $PbHSO_4$ of example for different temperatures. Experimental data are matched with our values. Agreement is found good.

Keyword: Green function • Spontaneous Polarization •Tangent Loss • Ferroelectricity

Introduction

The dielectric, ferroelectric and similar other substances have got special chapter in solid state physics. Ferroelectric crystals show polarization in the absence of an electric field. Due to their large uses in electronics technology, these substances are being investigated copiously throughout world. Crystal has a group of ferroelectrics of similar kind. These are $PbHASO_4$, $BaHPO_4$, $CaHPO_4$, $CaHAsO_4$, $BaHAsO_4$, $PbHPO_4$ shows ferroelectric effect below 310K.It is monoclinic in both states. Previously Negran et al (1973) studied phase transition phenomenon at room temperature(310K)for $PbHPO_4$ and $PbHPO_4$. Three-dimensional transverse model used by Chunlei et al (1988) for studying thermodynamic properties of this crystal but not discussed the dynamical properties of the crystal. The dynamical structure factor of $PbHPO_4$ near transition studied by Wesselinowa (1994). Chaudhuri *et al.*(1981) studied $PbHPO_4$ crystal by using fourth order phonon anharmonic term and two sublatticepseudospin-model but could not find out convincing results for permittivity and phase transition phenomenon in $PbHPO_4$ crystal by using the earlier decupling scheme. Litov and Garland (1987) and Smutny and Fousek (1978) has studied ultrasonic attenuation and elastic constant (C_{66}) at different temperatures by application of electric field in $PbHPO_4$ crystal. Mizaras *et al.* (1994) have used gel method to grow LHP crystal, and they have done experimentalultrasonic investigations in the transition temperature zone, and find out the permittivity of LHP crystal and thermal dependent polarization in $PbHPO_4$ crystal. Madhavan *et al.*(2006) have developed $PbHPO_4$ crystal and calculatedelectrical permittivity and tangent delta as a function of temperature. Ratajezak *et al.*(2000)

have studied second harmonic and crystal structural studies of lead hydrogen arsenate crystal. Raman spectrum of ferroelectric properties in soft mode of PbHPO crystal, which was experimentally investigated by Ohno and Lockwood (1987) .Chaudhuri *et al.* (1981) have also studied $PbHPO_4$crystal by using a fourth order phonon anharmonic term two-sublattice pseudospin-lattice coupled mode model but they have not considered any electric field term.Similar work using two-sublattice pseudospin lattice coupled mode mode (Upadhyay and Semwal 2002, Born and Huang 1954, Zubarev 1960) l is extended by adding third and fourth order phonon anharmonic interactions and external electric field terms for $PbHPO_4$crystal (Upadhyaya 2007, 2009a, 2009b). Zachek et al (2014) studied $PbHPO_4$ and $PbHAsO_4$crystals by using the Pseudo-Spin model to find out the thermodynamic properties and electrical permittivity in these crystals. Carvalho and Salinas (1978) obtained spontaneous polarization using in Slater-Takagi model by varying two parameters.

In this paper we shall use modified model Green Function method. We shall derive normal mode frequency, dielectric constant and spontaneous polarization.

2.1 Theoretical Derivation

We consider the simple modified model for $PbHPO_4$ type crystal as–

$$H = -2\Omega \sum_i (S_{1i}^x + S_{2i}^x) - \sum_{ij} J_{ij} [(S_{1i}^z S_{2i}^z) + (S_{2i}^z S_{2i}^z)]$$

$$- \sum_{ij} K_{ij} (S_{1i}^z S_{2i}^z) - 2\mu E \sum_i (S_{1i}^z + S_{2i}^z)$$

$$- \int \sum_{ik} V_{ik} S_{ik}^z A_k - \sum_{ik} V_{ik} S_{2i}^z A_K^+ + \int \frac{1}{4} \sum_k \omega_k (A_k A_k^+$$

$$+ B_k B_k^+ + \sum_{k_1 k_2 k_3} V^{(3)} (k_1, k_2, k_3) A_{k_1} A_{k_2} A_{k_3}$$

$$+ \sum_{k_1 k_2 k_3 k_4} V^{(3)} (k_1, k_2, k_3, k_4) A_{k_1} A_{k_2} A_{k_3} A_{k_4} \ldots\ldots\ldots\ldots\ldots\ldots 1)$$

where Ω is proton tunnelling frequency, S_i^z and $S_i^x$are components of pseudospin variable of S, V_{ik} is spin-lattice interaction, A_k and B_k are positions and momentum operators, ω_k is harmonic phonon frequency $V^{(3)}$ and $V^{(4)}$ are third-and fourth-order atomic force constants, defined by Born and Huang[14]. J_{ij} describes interactions of the diploes fitting to the same and K_{ij} to the different sublattices. μ dipole moment, E is external electric field.

Shift Width and Dyson's Equation

By Zubarev[15] statistical Green function as,

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

Differentiating Eq. (2) twice with respect to time t and t' using the model Hamiltonian (Eq. 1), taking Fourier transformation and applying Dyson's equation, one gets:

$$G_{ij}(\omega) = G^{0}(\omega) + G^{0}(\omega)\tilde{p}(\omega)G^{0}(\omega),$$

……… (3)

Where

$$G^{0}(\omega) = \frac{\Omega < S_{1i}^{x} > \delta_{ij}}{\pi(\omega^{2}-4\Omega^{2})} \qquad \ldots\ldots\ldots\ldots$$

(4)

$$G_{ij}(\omega) = \frac{G^{0}(\omega)}{[1-G^{0}(\omega)\tilde{p}(\omega)]}, \qquad \ldots\ldots\ldots\ldots \quad (5)$$

and

$$\tilde{P}(\omega) = \frac{\pi i\langle[F(t)S_{1j}^{y}]\rangle}{\Omega\langle S_{1i}^{x}\rangle^{2}} + \frac{\pi^{2}}{\Omega^{2}\langle S_{1i}^{x}\rangle^{2}}\langle\langle F_{i}(t); F_{j}'(t')\rangle\rangle, \qquad \ldots\ldots\ldots\ldots \quad (6)$$

and

$$F(t') = 2\Omega J_{ij}(S_{1j}^{x}S_{1i}^{z} + S_{1j}^{z}S_{1i}^{x}) - 2\Omega K_{ij}(S_{1i}^{x}S_{2i}^{z})$$
$$+2\Omega V_{ik}S_{1i}^{x}A_{k} + 2\Omega\Delta(S_{1i}^{x} + S_{2i}^{z}) + 2\Omega V_{ik}A_{k}^{+}S_{2i}^{x} \qquad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

The Green's Function (GF), Eq. (5) can be written as:

$$G(\omega) = \frac{\Omega\langle S_{1i}^{x}\rangle\delta_{ij}}{\pi\left[\omega^{2}-\hat{\Omega}^{2}-\tilde{\tilde{P}}(\omega)\right]}, \qquad \ldots\ldots\ldots\ldots \quad (8)$$

where renormalized frequency $\hat{\Omega}$, in lowest approximation is given as:

$$\hat{\Omega}^{2} = 4\Omega^{2} + \frac{i}{\langle S_{1i}^{x}\rangle}\langle[F, S_{1i}^{y}]\rangle \qquad \ldots\ldots\ldots\ldots \quad (9)$$

and $\tilde{\tilde{P}}(\omega)$ is given as:

$$\tilde{\tilde{P}}(\omega) = \frac{\pi}{\Omega\langle S^{x}\rangle}\langle\langle[F_{i}(t);]F_{j}'(t')\rangle\rangle \qquad \ldots\ldots\ldots\ldots \quad (10)$$

where $\ll F; F' \gg$ is decoupled, and small Green's functions are solved. $\widetilde{P}(\omega)$has two parts: real $(\Delta)$and imaginary $\Gamma(\omega)$.

Spin shift is obtained as:

$$\Delta_s(\omega) = \frac{a^4}{2\Omega(\omega^2 - \widetilde{\Omega}^2)} + \frac{b^2c^2}{2\Omega(\omega^2 - \widetilde{\Omega}^2)}$$

$$+ \frac{V_{ik}^2 N_k a^2}{2\Omega(\omega^2 - \widetilde{\Omega}^2)} + \frac{4\mu^2 E^2 a^2}{2\Omega(\omega^2 - \widetilde{\Omega}^2)} \text{..... ....} (11)$$

Spin Lattice Shift is obtained as:

$$\Delta_{s-p}(\omega) = \frac{2V_{ik}^2 \langle S_{1i}^x \rangle \omega_k \delta_{kk'} (\omega^2 - \tilde{\tilde{\omega}}_k^2)}{\left[(\omega^2 - \tilde{\tilde{\omega}}_k^2)^2 + 4\,\omega_k^2 \Gamma_k^2(\omega)\right]} \text{..... ....} (12)$$

Spin width is obtained as:

$$\Gamma_s(\omega) = \frac{\pi a^4}{4\Omega\widetilde{\Omega}} [\delta(\omega - \widetilde{\Omega}) - \delta(\omega + \widetilde{\Omega})]$$
$$+ \frac{b^2c^2}{4\Omega\widetilde{\Omega}} [\delta(\omega - \widetilde{\Omega}) - \delta(\omega + \widetilde{\Omega})]$$
$$+ \frac{V_{ik}^2 N_k a^2}{4\Omega\widetilde{\Omega}} [\delta(\omega - \widetilde{\Omega}) - \delta(\omega + \widetilde{\Omega})]$$
$$+ \frac{2\mu^2 E^2 a^2}{4\Omega\widetilde{\Omega}} [\delta(\omega - \widetilde{\Omega}) - \delta(\omega + \widetilde{\Omega})] \text{..... ....} (13)$$

Spin-lattice width isobtainedas:

$$\Gamma_s(\omega) = \frac{4V_{ik}^2 \langle S_{1i}^x \rangle \omega_k \delta_{k-k'} (\omega^2 - \tilde{\tilde{\omega}}_k^2)}{\left[(\omega^2 - \tilde{\tilde{\omega}}_k^2)^2 - 4\omega_k^2 \Gamma_k^2(\omega)\right]} \text{..... ....} (14)$$

In the aboveEqs(13) and(14), $\tilde{\tilde{\omega}}_k$isrenormalized phonon frequency phonon and $\Gamma_k(\omega)$is phonon width in the Green's function $G_{kk'}(\omega) = \langle\langle A_k, A_k^+ \rangle\rangle$which are obtained as:

$$G_{kk'}(\omega) = \frac{\omega_k \delta_{k-k'}}{\pi[\omega^2 - \tilde{\tilde{\omega}}_k^2 - 2i\omega_k \Gamma_k(\omega)]} \text{..... ....} (15)$$

Where

$$\tilde{\tilde{\omega}}_k^2 = \tilde{\omega}_k^2 + 2\,\omega_k \Delta_k(\omega) \text{..... ....} (16)$$

$$\tilde{\omega}_k{}^2 = \omega_k^2 + A_k' \text{..... ....} (17)$$

Therefore the phonon Shift $(\Delta_k)$and Width $(\Gamma_k)$are,

$$\Delta_k(\omega) = Re\, P^0\,(k,\omega)$$
$$= 18P \sum k_1 k_2 \left|V^{(3)}(k_1, k_2, -k)\right|^2$$

$$\times \frac{\omega_{k1}\omega_{k2}}{\tilde{\omega}_{k1}\tilde{\omega}_{k2}}\{(n_{k_1}+n_{k_2})\frac{\tilde{\omega}_{k1}+\tilde{\omega}_{k2}}{\omega^2-(\omega_{k1}+\omega_{k2})^2}$$

$$+\{(n_{k_2}+n_{k_1})\frac{\tilde{\omega}_{k1}+\tilde{\omega}_{k2}}{\omega^2-(\omega_{k1}+\omega_{k2})^2}$$

$$+48P\sum \left|V^{(4)}(k_1,k_2,k_3,-k\right|^2 \frac{\omega_{k1}\omega_{k2}\omega_{k3}}{\tilde{\omega}_{k1}\tilde{\omega}_{k2}\tilde{\omega}_{k3}}$$

$$\times\{(1+n_{k1}n_{k2}+n_{k2}n_{k3}+n_{k3}n_{k1})$$

$$\times\frac{\tilde{\omega}_{k1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3}}{\omega^2-(\tilde{\omega}_{k1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3})^2}$$

$$+3(1-n_{k2}n_{k1}+n_{k2}n_{k3}-n_{k3}n_{k1})$$

$$\times\frac{\tilde{\omega}_{k1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3}}{\omega^2-(\tilde{\omega}_{k1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3})^2}+$$ higher terms

} .... (17)

Phonon width

$$\Gamma_k(\omega) = Im\,P\,(k,\omega)$$
$$= 9\pi\sum\left|V^{(3)}(k_1,k_2,-k)\right|^2\frac{\omega_{k1}\omega_{k2}}{\tilde{\omega}_{k1}\tilde{\omega}_{k2}}$$
$$\{(n_{k2}+n_{k1})[\{\delta(\omega+\tilde{\omega}_{k1}+\tilde{\omega}_{k1})-\delta(\omega-\tilde{\omega}_{k1}-\tilde{\omega}_{k1})+(n_{k2}-n_{k1})\delta(\omega+\tilde{\omega}_{k1}+\tilde{\omega}_{k1}) - \delta(\omega+\tilde{\omega}_{k1}+\tilde{\omega}_{k1})\}]$$
$$+48\pi\sum\left|V^{(3)}(k_1,k_2,k_3,-k_4)\right|^2$$
$$\times\{1+n_{k1}n_{k2}+n_{k2}n_{k3}+n_{k3}n_{k4}\}$$
$$\times\left[\delta(\omega+\tilde{\omega}_{k1}+\tilde{\omega}_{k2}+\tilde{\omega}_{k3})-[\delta(\omega-\tilde{\omega}_{k1}-\tilde{\omega}_{k2}-\tilde{\omega}_{k3})]\right] \text{................} (18)$$

In Eqs (17) and (18) $n_{ki} = Coth\left(\frac{\tilde{\omega}_{ki}}{k_B T}\right)$

Putting values of $\tilde{\tilde{P}}(\omega)$ in Eq. (8), Green's function finally becomes:

$$G(\omega) = \frac{\Omega\langle S_{1i}^{x}\rangle\delta_{ij}}{\pi\left[\omega^2 - \hat{\Omega}^2 - 2i\Omega\Gamma(\omega)\right]} \quad \text{.................... (19)}$$

The quantities $n_{ks} = \coth\frac{\tilde{\omega}_{ks}}{k_B T}$ where k_B Boltzmann's constant temperature and s is numerical index s=1, 2, 3, 4the frequency $\hat{\Omega}$ is given by:

$$\hat{\Omega}^2 = \tilde{\Omega}^2 + 2\Omega\Delta_{s-p}(\omega) \quad \text{....... .... (20)}$$

and

$$\tilde{\tilde{\Omega}}^2 = \tilde{\Omega}^2 + 2\Omega\Delta_s(\omega) \quad \text{.................... (21)}$$

$$\breve{\Omega}^2 = 4\Omega^2 + \frac{1}{\Omega\langle S_{1i}^{x}\rangle}\langle[F, S_{1i}^{y}]\rangle \quad \text{............(22)}$$

and Eq. (22) second term is evaluated using mean field approximation, i.e. correlations are finite, i.e.:

$$\frac{S_{1i}^{z}}{a} = \frac{S_{1i}^{x}}{b} = \frac{1}{2\tilde{\Omega}}\tanh\beta\frac{\tilde{\Omega}}{2} \quad \text{............(23)}$$

which gives

$$\tilde{\Omega}^2 = a^2 + b^2 - bc \text{............(24)}$$

Where $a = 2J_0\langle S_1^{z}\rangle + K_0\langle S_2^{z}\rangle$,............(25)

$$b = 2\Omega \text{............(26)}$$

and $$c = 2J_0\langle S_1^{x}\rangle + K\langle S_2^{x}\rangle \quad \text{............(27)}$$

where J_0 and K_0 are equilibrium values of J_{ij} and K_{ij}.

Soft mode frequency and transition temperature

If we solve Eq. (20) self consistently we obtain:

$$\hat{\Omega}_{\pm}^2 = \frac{1}{2}\left(\tilde{\tilde{\omega}}_k^2 + \tilde{\tilde{\Omega}}^2\right) \pm \frac{1}{2}\left[\left(\tilde{\tilde{\omega}}_k^2 - \tilde{\tilde{\Omega}}^2\right)^2 + 8V_{ik}^2\langle S_{1i}^{x}\rangle\Omega\right]^{1/2} \quad \text{........(28)}$$

The Curie temperature is given by

$$T_c = \frac{\eta}{2k_B\tanh^{-1}\left(\frac{\eta^3}{4\Omega^2\Gamma'}\right)} \text{............(29)}$$

Where $\eta^2 = (2J-K)^2\sigma^2 + 4\Omega^2$…………(30a)

$\langle S_1^z \rangle = -\langle S_1^z \rangle = 0$…………(29a) …………(30b)

$J^* = (2J+K) + \frac{2V_{ik}^2 \tilde{\omega}_k^2}{[\tilde{\omega}_k^4 + 4\omega_k \Gamma_k^2]}$…………(31)

Dielectric Constant and LossTangent

Capacitivity $\chi$is given as,

$\chi = -\lim_{X\to 0} 2\pi N\mu^2 G_{ij}(\omega + iX)$…………(32)

Permittivity($\in$)is given by,

$\in = 1 + 4\pi\chi$…………(33)

By substitution of $\chi$is given as,

$\in(\omega) \gg 1\ in\ Ferroelectric\ Crystals$

$\in(\omega) = (-8\pi N\mu^2)\langle S_1^x\rangle(\omega^2 - \hat{\Omega}^2)\left[(\omega^2 - \hat{\Omega}^2)^2 + 4\Omega^2\Gamma^2\right]^{-1}$…………(34)

Power lost as heat is called tangent loss, given as ratio of ϵ'' to ϵ'.

$tan\,\delta = \frac{\epsilon''}{\epsilon'}$…………(35)

Where $\in''$ and $\in'$are imaginary and real parts of dielectric constant

$tan\,\delta = -\frac{2\Omega\Gamma(\omega)}{(\omega^2 - \hat{\Omega}^2)}$…………(36)

Where $\Gamma(\omega)$ and $\hat{\Omega}$are given previously.

Spontaneous Polarization

The Spontaneous Polarization (Ps) is given by Halblutzel[18]

$Ps = 2N\mu(\langle S_1^z\rangle + \langle S_2^z\rangle)$ ……………

(37)

Putting the values of $N\mu$ and $\langle S_1^z\rangle$ and $\langle S_2^z\rangle$ we obtain the value of Ps for Rochelle salt. We compare our results. A good agreement is obtained.

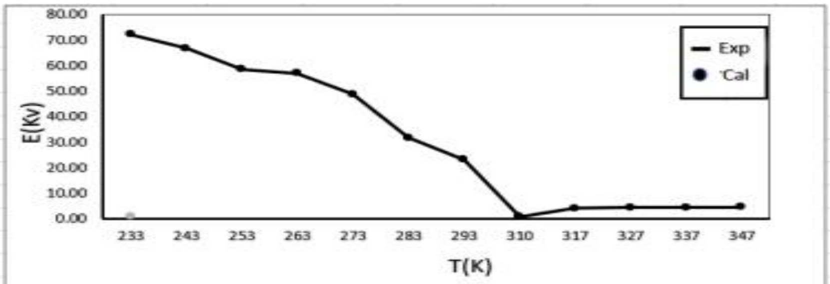

Fig.-1, Calculated electric field and temperature dependence of soft mode frequency in $PbHPO_4$ ▬; exp.[10] ●

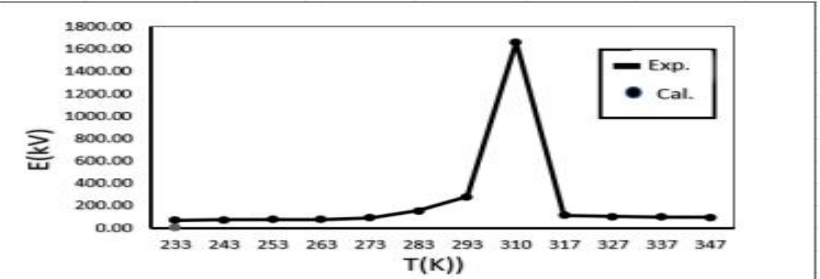

Fig.-2, Calculated electric field and temperature dependences of dielectric constant in $PbHPO_4$ ▬ ; exp.[10]●

Table 1 — Model values of physical parameters for $PbHPO_4$ crystal (Ref. 4)

ω_0^2 (cm^2)	Ω (cm^{-1})	J (cm^{-1})	K (cm^{-1})	V_{ik} ($cm^{-3/2}$)	$T_c(K)$ (cm^{-1})	C (k)	$\mu(10^{18}esu)$	$\Omega^2 J^*$ (cm^{-3})	$\Omega^2(2J+K)$ (cm^{-1})	ΩV_{ik} ($cm^{-5/2}$)
13.32	2.16	172.37	86.18	30.93	310	2773	0.55	2699	2024	76.75

Table 2- Calculated temperature dependence of Spontaneous Polarization in $PbHPO_4$

$T(K)$	$Ps \times 10^7 (c/cm^2)$
233	1.8
243	1.7
253	1.6
263	1.5
273	1.4
283	1.1
293	0.8
303	0.5
306	0.3
310	0.0

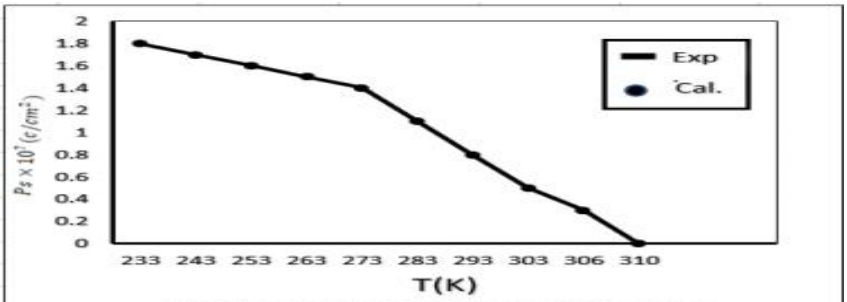

Fig-3, Spontaneous polarization for $PbHPO_4$ ▬ ; exp.[18] ●

Numerical Calculation

With the help of formulae numerical values of $\tilde{\Omega}$, ϵ and tan δ have been calculated for $PbHPO_4$ crystal (Figures 1, 2 and 3).

Discussion

The modified model explains values of $\hat{\Omega}$, ϵ and tanδ which are in good agreement with experimental data for $PbHPO_4$ of other workers.

Conclusion

It can be concluded our modified model is quite successful in explaining ferroelectric effect in $PbHPO_4$ type all crystals. The formulae obtained in this work will give numerical thermal variations of $\hat{\Omega}$, ϵ, and Ps for all other $PbHASO_4$, $BaHPO_4$, $CaHPO_4$, $CaHAsO_4$, $BaHAsO_4$ crystal quite similarly.

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