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Study of Ferroelectric Properties of Hydrogen Bonded Rubidium Dihydrogen Arsenate (RdA) Crystal

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Abstract: A simple pseudospin lattice coupled mode model with addition of third and fourth-order phonon anharmonic interactions terms, direct spin-spin interactions terms and external electric field term has been considered for investigation of transition phenomena and dielectric properties of hydrogen bonded ferroelectric crystal Rubidium dihydrogen arsenate (RDA). A double-time thermal dependent Green's function method has been used for derivation of response function. From response function shift, width and soft mode frequency have been derived for RDA crystal. Response function is also related to dielectric constant which has been obtained in present paper. By fitting model values of different parameters in obtained expressions, the temperature variations of normal mode frequency, dielectric constant, and loss tangent have been calculated numerically for RDA crystal. Our theoretical results are compared with experimental results. It is observed that our theoretical results agree with experimental results. Therefore, it can be concluded that the modified pseudo-spin lattice coupled mode model with the simplest approximation is quite suitable to explain the transition and dielectric properties of RDA crystal.

Keywords: Normal Mode Frequency, Dielectric Constant, Dielectric, Ferroelectrics, Loss Tangent

Introduction

Rubidium dihydrogen phosphate (RDA) is a ferroelectric crystal that undergoes a ferroelectric phase transition at 110.25K. This crystal remains orthorhombic below T_c and tetragonal above T_c. The lattice parameters of tetragonal RbH_2AsO_4 are $a = 7.7933\ \text{Å}, b = 7.7933\ \text{Å}, c = 7.466\ \text{Å}, \beta = 90°$ with space group $I\bar{4}2d$ and in orthorhombic crystal system the space group is $Fdd2$ (Mitsui et. al., 2005). Since the discovery of ferroelectricity, KDP and its isomorphous (e.g. RDP, KDA, RDA) have attracted the interest of many theoretical and experimental researchers, possibly because of their relatively simple structure and very interesting properties related to hydrogen bond system. A most apparent feature in the progress of physics on this KDP-type crystal is the close interplay between theory and experiment which makes major progress in the microscopic understanding of their properties. Many theoretical and experimental works have been done in field of dielectric and ferroelectric properties of RDA crystal. Starting from experimental work, RbH_2AsO_4 (RDA) crystal's phase behavior of above room temperature by different experimental techniques (Torijano et. al., 2000). (Kahol and Dalal, 1994) have studied the Electron spin resonance spectra of AsO_4^{4-} center in RDA and deuterated RDA crystals. (Truesdale et al., 1980) have studied the hysteresis effects in X-ray irradiated KDP, deuterated-KDP, and RDP ferroelectric

single crystals through electron spin resonance. (Adhav, 1969) has studied the physical properties of single crystals of deuterated and undeuterated RbH_2AsO_4. (Kamysheva et al., 1974) have investigated the dielectric and pyroelectric properties of RbH_2AsO_4 single crystal in the ferroelectric phase. (Leung et al., 1973) have studied the behavior of soft mode in RbH_2AsO_4 single crystal. (Tornberg and Lowndes, 1973) have done Raman Spectra of RbH_2AsO_4 and presented it as a function of temperature for the paraelectric phase. (Pimenta et al., 1998) have studied optical-coupled soft mode in ferroelectric rubidium dihydrogen arsenate (RbH_2AsO_4) crystal by experimental techniques of Raman-scattering. Much theoretical work has been done to study the dielectric and ferroelectric transition of RDA crystal. (Slater, 1941) proposed a statistical treatment of phase transition in KDP crystal. Cochran has proposed a fundamental novel idea of soft mode in the theory of ferroelectric phase transition. Cochran has studied the phenomenon of ferroelectric in pseudo-cubic crystals in terms of normal modes of vibration. The study of dielectric and ferroelectric properties of RDA crystal by PLCM model was initiated by (Ganguli et al., 1980) by employing Green's function theory of (Zubarev, 1960), they have decoupled correlation at an early stage. So they were not able to obtain convincing and precise results.

In the present work, we have considered the effect of third and fourth-order anharmonic interactions with some additional terms in our Hamiltonian. We have derived different expressions for soft mode frequency, dielectric constant, and loss tangent. We have numerically calculated values of soft mode frequency, dielectric constant, and loss tangent by fitting our model values in our derived expressions. We have also compared our numerically calculated data to the experimental data of (Blinc et. al., 1973).

Model Hamiltonian and Method of Calculation

We have used the modified Pseudo-spin lattice coupled model (Ganguli et al., 1980) by adding terms given in Eq. (2)

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

We have added third and fourth order anharmonic terms and some other terms in H_1

$$H_2 = \sum_{k_1k_2k_3} V^{(3)}\left(k_1,k_2,k_3\right)A_{k_1}A_{k_2}A_{k_3} + \sum_{k_1k_2k_3k_4} V^{(4)}\left(k_1,k_2,k_3,k_4\right)A_{k_1}A_{k_2}A_{k_3}A_{k_4}$$

$$-\sum_{ik} V_{ik}S_i^x A_k - \sum_{ik} V_{ik}S_i^x A_k^\dagger + \frac{1}{2}\sum_{ij} B_{ij}S_i^x S_j^x - \sum_{ik} V_{ik}S_i^x A_k^2 - 2\mu E\sum_i S_i^z \qquad (2)$$

Where Ω represents proton tunnelling frequency between double-well potential O-H---O bonds, $S^L(L=x,y,z)$ is the L^{th} component of the pseudo-spin variable. A_k and B_k both represent a

position and momenta coordinates. J_{ij} and V_{ik} represents exchange interaction constant and spin-lattice interaction constant respectively. $V^{(3)}(k_1,k_2,k_3)$ and $V^{(4)}(k_1,k_2,k_3,k_4)$ terms represent anharmonic interactions of third and fourth order. B_{ij} represents interaction of the transverse field with one proton to another proton. We have considered the total Hamiltonian by adding equations given by Eq. (1) and Eq. (2)-

$$H = H_1 + H_2 \tag{3}$$

We are using the method of double time temperature dependent Green's function which was proposed by (Zubarev, 1960). Accordingly, for any two operators *A* and *B*, this is defined as

$$G(t-t') = \langle\langle A(t); B(t')\rangle\rangle = -i\theta(t-t')\langle[A(t); B(t')]\rangle \tag{4}$$

Differentiating twice equation (3) with respect to time t and t', with help of Hamiltonian used given by equation (2) and after Fourier transformation, setting equation (3) into Dyson's equation framework, Green's function is obtained as

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

Where $G_{ij}^0(\omega)$ is given as

$$G_{ij}^0(\omega) = \frac{\Omega\langle S_i^x\rangle}{\pi(\omega^2 - 4\Omega^2)} \tag{6}$$

Now, getting the final form of $G(\omega)$

$$G(\omega) = \frac{\Omega\langle S_i^x\rangle\delta_{ij}[(\omega^2 - \hat{\Omega}^2) + 2i\Omega\Gamma(\omega)]^{-1}}{\pi} \tag{7}$$

Eqns. (8-11) relates pseudo-spin frequency, modified pseudo-spin frequency and soft mode frequency and are given as-

$$\hat{\Omega} = \tilde{\Omega}^2 + \Delta(\omega) \tag{8}$$

$$\tilde{\Omega}^2 = a^2 + b^2 - bc \tag{9}$$

$$a = J_{ij}\left\langle S_j^z \right\rangle - B_{ij}\left\langle S_i^z \right\rangle + 2E\mu \tag{10}$$

$$b = 2\Omega \tag{11}$$

$$c = J_{ij}\left\langle S_j^x \right\rangle - B_{ij}\left\langle S_i^x \right\rangle \tag{12}$$

$\tilde{\tilde{\Omega}}$ is modified soft mode frequency which is given by Eq. (12) and we compute soft mode frequency using Eq.(8).

$$\tilde{\tilde{\Omega}}^2 = \tilde{\Omega}^2 + \sqrt{\left\{\begin{array}{l} a^4 + b^2c^2 + \frac{1}{4}a^2J_{ij}^2\left\langle S_i^z \right\rangle^2 + 4b^2J_{ij}^2\left\langle S_i^x \right\rangle^2 + J_{ij}^2V_{ik}^2N_k\left\langle S_i^x \right\rangle^2 + a^2V_{ik}^2N_k \\ +b^2V_{ik}^2N_k + \frac{4\Omega V_{ik}^2N_ka^2}{b} + 4\Omega^2B_{ij}^2V_{ik}^2\left\langle S_i^x \right\rangle N_k + 2\mu^2E^2V_{ik}^2N_ka^2 \end{array}\right\}} \tag{13}$$

The expression for dielectric constant is obtained as;

$$\in(\omega) - 1 = (-8\pi N\mu)\left\langle S_i^x \right\rangle(\omega^2 - \hat{\Omega}^2)\left[\left(\omega^2 - \hat{\Omega}^2\right)^2 + 4\Omega^2\Gamma^2\right]^{-1} \tag{14}$$

And, the dissipation of power loss at microwave frequencies ω □ $\hat{\Omega}$, loss tangent can be defined as

$$\tan\delta = \frac{2\Omega\Gamma(\omega)}{\hat{\Omega}^2} \tag{15}$$

Results

We have used various model values (given in Table 1.) of different physical quantities for RDA crystal from literature[12]. We have calculated temperature dependence of soft mode frequency, dielectric constant, and loss tangent. We have shown our theoretically derived results in Figures (1-3). For validation, we have compared our calculated results with experimental values of (Blinc et. al., 1973).

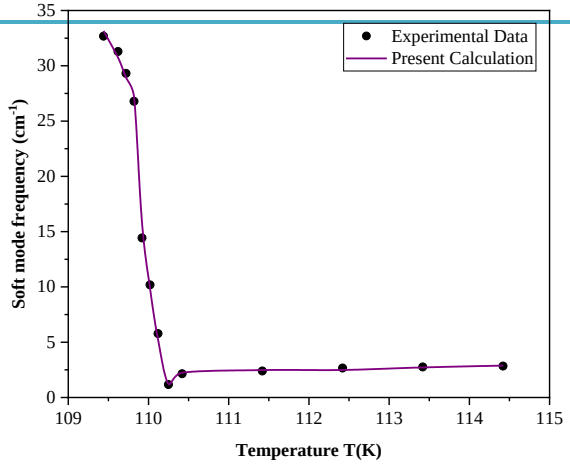

Fig. 1. Temperature dependence of soft mode frequency in RDA crystal. (—Calculated, ● Correlated Experimental values). For validation, it is compared with (Blinc et. al., 1973).

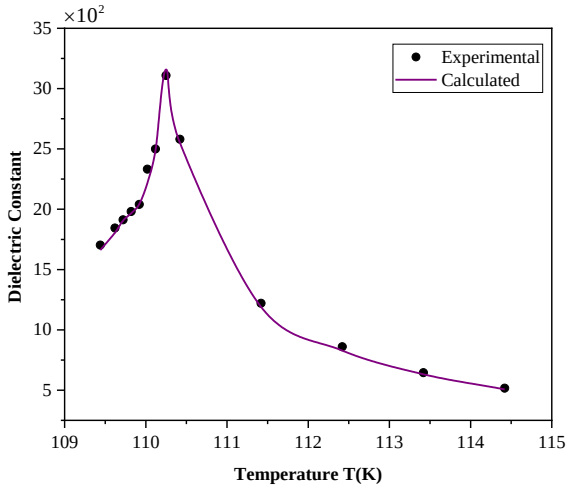

Fig. 2. Temperature dependence of Dielectric constant in RDA crystal. (—Calculated, ● Correlated Experimental values). For validation, it is compared with (Blinc et. al., 1973).

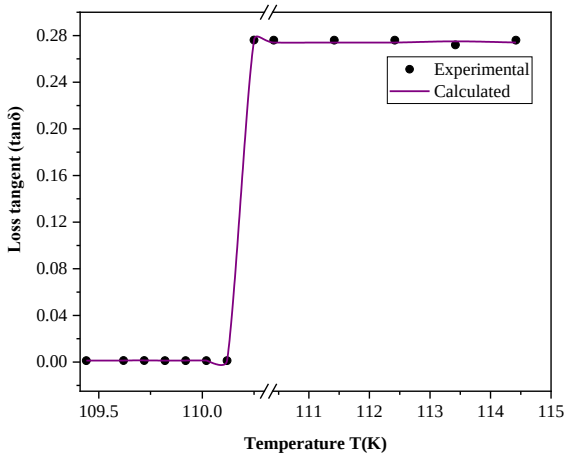

Fig. 3. Temperature dependence of loss tangent in RDA crystal. (—Calculated, ● Correlated Experimental values). For validation, it is compared with (Blinc et. al., 1973).

Table1. Model values of Physical quantities for RDA crystal (Ganguli et al., 1980).

Ω (cm^{-1})	J (cm^{-1})	J' (cm^{-1})	T_c (K)	V_{1k} (cm^{-1})	ω_k (cm^{-1})	$\mu \times 10^{18}$ (esu-cm)	$N \times 10^{-22}$ (cm^{-3})	B_{1j} (cm^{-1})
0.9	238.8	321.50	110.25	14.66	26	1.5	0.76	0.918

Discussion and conclusion

Earlier authors have decoupled the correlations function at an early stage and hence some important interactions result were not included in their calculations and results. We have added higher order interaction terms i.e. third and fourth order anharmonic interaction terms and some other interaction terms to study different kinds of interactions in our results. In fig.1, the soft mode frequency goes to a minimum value at the transition point of RDA crystal and then increases which is following Cochran's suggested theory. In fig.2, the dielectric constant first increases, and then it becomes large at near T_c and then decreases. Similarly, in fig.3, the loss tangent shows its behavior. The present study shows that the pseudospin-lattice coupled mode model along with higher order anharmonic terms i.e. third and fourth-order phonon anharmonic interaction terms and some spin-lattice interaction terms can explain the temperature dependence of ferroelectric mode frequency, dielectric constant, and loss tangent in RDA crystal. We have also shown that our obtained results agree with the experimental results of (Blinc et. al., 1973). This theoretical investigation may also be useful for other hydrogen-bonded ferroelectric like KH_2PO_4, RbH_2AsPO_4, CsH_2PO_4, and CsH_2AsO_4.

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