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Investigation of some temperature dependent ferroelectric properties of RDP crystal using double-time temperature dependent Green's function technique and PLCM model

Pawan Singh,* Muzaffar Iqbal Khan & Trilok Chandra Upadhyay

Department of Physics, H N B Garhwal University, Srinagar (Garhwal) - 246 174, India

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Rubidium dihydrogen crystal's (RDP, RbH_2PO_4) ferroelectric and dielectric properties have been analyzed in the present paper. This crystal belongs to the family of KDP-type ferroelectric and has been extensively studied because of peculiar properties in the area of ferroelectrics. In the present study, we have added some higher-order anharmonic terms in the pseudospin lattice coupled mode model (PLCM) for RDP crystal and have used Green's function technique to solve our different expressions here discussed. We have computed expressions for soft mode frequency, dielectric constant, and loss tangent. We have shown variation of these three properties with temperature and discussed their crystal structure before and after their ferroelectric transition point. We have used model constants from Ganguli. For a suitable temperature range variation of temperature and dielectric constant according to Curie-Weiss behavior can be seen in our result. We have also verified our obtained results to the experimental analysis.

Keywords: RDP, Dielectric properties, Green's function, Loss tangent, Soft mode frequency

Introduction

The dielectric and ferroelectric properties of RDP crystal is studied in present paper. RDP crystal which belongs to KDP family has various applications in day-to-day life. From electronics to mechanical equipment, they advance the life we live. Rubidium dihydrogen Phosphate crystal shows a phase transition at 146K which also shows the isotope effect. Like other members of the KDP family, this crystal remains tetragonal in paraelectric and after T_C it changes to orthorhombic crystal system in ferroelectric phase. This crystal has lattice parameters $a = 7.608\,\text{Å}, b = 7.608\,\text{Å}, c = 7.296\,\text{Å}$ and $\beta = 90°$. It has space group symmetry group $I\bar{4}2d$ in paraelectric and $Fdd2$ in ferroelectric crystal system.[1]

Gaydamaka *et al.*[2] have studied phase composition and phase transitions, spectral characteristics, thermal and transport properties of the system based on the mono-and dihydrogen phosphates of rubidium. Deshpande *et al.*[3] have studied the thermal expansion of RbH_2PO_4 crystal by preparing crystals from slow evaporation of an aqueous solution of hypophosphoric acid.Boysen *et al.*[4] investigated conductivity of phosphates of Potassium and Rubidium dihydrogen crystal at high temperature and pressure. Adhav[5] have studied Elastic, Dielectric and Piezoelectric Properties of RDP crystal and concluded that Rubidium dihydrogen phosphate crystal is not useful in the application of filter networks since the resonator cuts, available only in the z-plane, possess large temperature coefficients of frequency. Agui *et al.*[6] have studied Hydrogen and PO_4 modes of RbH_2PO_4 crystal by inelastic neutron scattering and Raman scattering experiments. authors have revealed that peak in neutron scattering spectra which confirms hydrogen modes changes widths around the T_C which is considered to be due to the order or disorder of PO_4 tetrahedrons which affecting the motion of hydrogen atoms.

Theoretical work on RbH_2PO_4 crystal using Green's function theory of phase transition with PLCM model was studied by Ganguli *et al.*[7] Authors have extended the theory of Ramakrishnan and Tanaka[8] for studying this type of hydrogen bonded crystals by including the phonon anharmonicity and comparing calculated results with experimental data. But they have decoupled correlations at an early stage and were not able to obtain good convincing results. In present work, we have considered higher third and fourth order anharmonic terms and some other terms in our Hamiltonian for getting better results. We have

*Coressponding Author: (E-mail- pawansingh4853@gmail.com)

obtained temperature dependence of soft mode frequency, dielectric constant, and loss tangent for RbH_2PO_4 crystal. For validation of our obtained results, we have shown that it has good agreement with the experimental results of Peercy.[9]

Model Hamiltonian and Method of Calculation

We have considered below modified Hamiltonian for calculations.This Hamiltonian is also presented in earliear paper.[7,11]

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

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

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

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

Where Ω represents proton tunnelling frequency between double-well potential O-H---O bonds, $S^M(M=x,y,z)$ is the M^{th} component of the pseudo-spin variable. J_{ij} and V_{ik} represents exchange interaction constant and spin-lattice interaction constant respectively. A_k and B_k both represent a position and momenta coordinates. 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 total Hamiltonian by using Eqs.(1) and Eqs.(2)

$$H = H_1 + H_2 \quad \ldots (3)$$

We are using method of double time temperature dependent Green's function which was proposed by Zubarev[10]. Accordingly, for any two operators*A* and *B*, this is defined as:

$$G(t-t') = \left\langle\left\langle A(t);B(t')\right\rangle\right\rangle = -i\theta(t-t')\left\langle\left[A(t);B(t')\right]\right\rangle \quad \ldots (4)$$

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

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

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

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

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

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

Different relations of pseudo-spin frequency, modified pseudo-spin frequencyand soft mode frequency are given as:

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

$$\tilde{\Omega}^2 = a^2 + b^2 - bc \quad \ldots (9)$$

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

$$b = 2\Omega \quad \ldots (10)$$

$$c = J_{ij}\left\langle S_j^x\right\rangle - B_{ij}\left\langle S_i^x\right\rangle \quad \ldots (11)$$

From equations (8) and (7), $\Delta(\omega)$ and $\Gamma(\omega)$ are shift and width respectively which are given in our earlier paper.[11]

$\tilde{\Omega}^2$ is modified soft mode frequency which is given as:

$$\hat{\Omega}_{\pm}^{2}=\frac{1}{2}\left[\begin{array}{l}\left(\tilde{\tilde{\omega}}_{k}^{2}-\tilde{\Omega}^{2}\right)^{2}\pm\left(\tilde{\tilde{\omega}}_{k}^{2}-\tilde{\Omega}^{2}\right)\\ \left\{\dfrac{4V_{ik}^{2}\left\langle S_{i}^{x}\right\rangle\Omega\left\langle\omega_{k}\right\rangle}{b}+\dfrac{4\Omega V_{ik}^{2}a\left\langle\omega_{k}\right\rangle\left\langle S_{j}^{z}\right\rangle}{b}+\right\}^{\frac{1}{2}}\\ 4\Omega V_{ik}^{2}\left\langle\omega_{k}\right\rangle\left\langle S_{j}^{z}\right\rangle.....\end{array}\right]\ldots \quad (12)$$

The expression for dielectric constant is obtained as:

$$\in(\omega)-1=(-8\pi N\mu)\left\langle S_{i}^{x}\right\rangle(\omega^{2}-\hat{\Omega}^{2})\left[\left(\omega^{2}-\hat{\Omega}^{2}\right)^{2}+4\Omega^{2}\Gamma^{2}\right]^{-1} \quad \ldots (13)$$

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

$$\tan\delta=\frac{2\Omega\Gamma(\omega)}{\hat{\Omega}^{2}} \quad \ldots (14)$$

We have used various model parameter values appearing in Table 1. to obtain different physical quantities appearing in expressions (12), (13), (14) for temperature dependencies of soft mode frequency, Dielectric constant and loss tangent in RDP crystal.

Results and Discussion

We have used various model values of different physical quantities for RDP crystal here shown in Table 1 from literature[7].

We have calculated temperature dependence of normal mode frequency, dielectric constant and loss tangent. We have shown our results in Figs. 1-3. For validation, we have compared our calculated results are compared with experimental values of Peercy[9].

Earlier authors have decoupled the correlations function at an early stage and hence some important interactions result disappeared from their calculations and results.[11] We have added higher order interaction term i.e. third and fourth order anharmonic interaction term and an extra spin-lattice interaction term for better results. In Fig.1, soft mode frequency goes to a minimum value at the transition point of RDP crystal and then increases confirming Cochran's suggested theory.

Table 1 — Model values of Physical quantities for RDP crystal.[7]

$T_c\,(K)$	J^*, cm^{-}	J', cm^{-}	V_{ik}, cm^{-}	ω_k, cm^{-}	C, K	Ω, cm^{-}
146	20	60	25	128.5	238	1.5

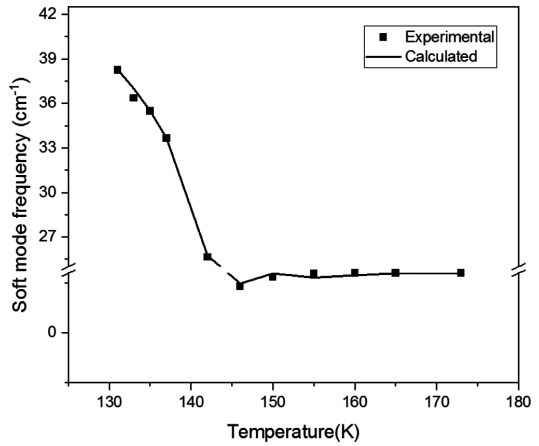

Fig. 1 — Temperature dependence of soft mode frequency (cm^{-1}) in RDP crystal.(—Calculated, ■ Correlated Experimental values). For validation, it is compared with Peercy.[9]

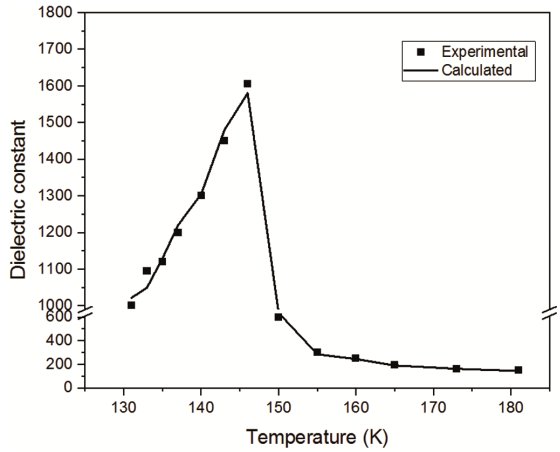

Fig. 2 — Temperature dependence of Dielectric constant in RDP crystal.(—Calculated, ■ Correlated Experimental values). For validation, it is compared with Peercy.[9]

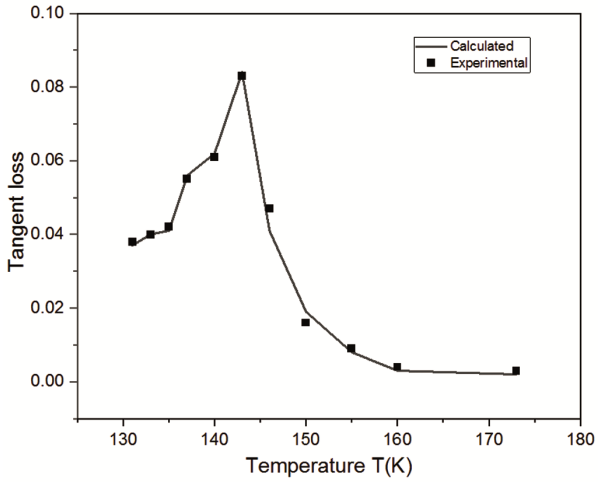

Fig. 3 — Temperature dependence of loss tangentin RDP crystal.(—Calculated, ■ Correlated Experimental values). For validation, it is compared with Peercy.[9]

In Fig. 2 Dielectric constant first increases and becomes large near T_c and then decreases. Similarly, in Fig. 3, loss tangent shows its behavior.

Conclusions

The present paper shows that 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 RDP crystal. We have also shown that our obtained results agree with the experimental results of Peercy[9]. This theoretical investigation may also be useful for other hydrogen bonded ferroelectric likeKH_2PO_4, RbH_2AsPO_4, CsH_2PO_4, and CsH_2AsO_4.

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