

Temperature Dependence of Ferroelectric Mode Frequency, Dielectric Constant and Loss Tangent in Deuterated Rubidium Dihydrogen Phosphate Crystal

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Abstract: By fitting model values of physical quantities for deuterated RDP crystal in theoretically derived expressions for FE mode frequency, dielectric constant and loss tangent in our earlier paper temperature dependence of these quantities have been calculated and compared with experimental data of literature value which show a good agreement.

Keywords: Ferroelectrics, Anharmonic, Dielectric constant, Loss tangent, Phase transition

Introduction

Rubidium dihydrogen phosphate (RbH_2PO_4) crystal (RDP) undergoes ferroelectric transition at 146 K. On deuteration (DRDP) T_C shifts to 249 K showing a large isotope effect. This fact suggests that the hydrogen bonds play an important role in the phase transition mechanism.

It is orthorhombic below T_C and tetragonal above T_C . In the $(\text{H}_2\text{PO}_4)^{-1}$ network each phosphate group is linked by $\text{O}-\text{H}\cdots\text{O}$ bonds to tetrahedral arrangement of PO_4 neighbours. Below transition temperature, protons are arranged in ordered pattern. The crystal is orthorhombic in FE phase and tetragonal in paraelectric phase with space group 142d. The lattice parameters are $a=7.607\text{\AA}$, $b=7.607\text{\AA}$, $c=7.299\text{\AA}$ and $\beta=90^\circ$.

Extensive experimental studies on RbH_2PO_4 (RDP) and its deuterated form (DRDP) have been carried out by many experimentalists. Lim and Lee¹ have carried out NMR study on RbD_2PO_4 crystals and discussed the phase transitions. Matsui *et al.*² have done thermal analysis study on these crystals. Botez *et al.*³ have done crystal structure and chemical modification study on RbD_2PO_4 crystals. Magome *et al.*⁴ have done crystal structure study on RbD_2PO_4 crystals. Mattauch *et al.*⁵ have done neutron X-rays diffraction studies on RbH_2PO_4 crystals. Vdovych *et al.*⁶ have done electro caloric effect study on RbD_2PO_4 crystals.

Theoretical studies on DRDP were initiated by Ganguli *et al.*⁷. They have considered pseudo spin model. They⁷ have used Green's function method and obtained soft mode

frequency *etc.* Earlier researchers⁷ have not considered third order phonon anharmonic interaction. They have decoupled the correlations at an early stage. So that they could not produce better and convincing results. In our earlier paper⁸, we have considered phonon anharmonic interaction terms⁹.

In the present study, we shall fit model values of physical quantities in the expressions obtained in our earlier paper⁸ for deuterated RDP crystal. Temperature dependence of ferroelectric mode frequency, dielectric constant and loss tangent will be calculated for DRDP crystal. Theoretical results will be compared with experimental results of Peercy¹⁰.

Calculations and Results

In our earlier paper⁸ a pseudo spin lattice coupled mode model⁷ along with third and fourth order phonon anharmonic interaction terms⁹ have been considered for KDP crystals⁷. The Green's function¹¹ is differentiated twice with respect to time t and t' . With the help of modified Hamiltonian which is then set into Dyson's equation form. As a result Green's function was obtained as:

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

Where

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

$$\tilde{\Omega}^2 = a^2 + b^2 - bc, \quad (3)$$

$$a = J \langle S^z \rangle \quad (4)$$

$$b = 2\Omega \text{ and} \quad (5)$$

$$c = J \langle S^x \rangle \quad (6)$$

$\Delta(\omega)$ and $\Gamma(\omega)$ are shift and width of response function. The values of $\Delta(\omega)$ and $\Gamma(\omega)$ are given in our earlier paper. By solving Eq. (2), the FE mode frequency was obtained as:

$$\hat{\Omega}_{\pm}^2 = \frac{1}{2} \left\{ (\tilde{\omega}_k^2 + \tilde{\Omega}^2) \pm \left[(\tilde{\omega}_k^2 - \tilde{\Omega}^2)^2 + 16V_{ik} \langle S_i^x \rangle \Omega \right]^{\frac{1}{2}} \right\} \quad (7)$$

The dielectric constant \mathcal{E} is related to susceptibility χ as $\mathcal{E} = 4\pi\chi$ which in turn is related to retarded Green's function given in Eq.(2) as $\chi = -\lim_{X \rightarrow 0} 2\pi N\mu^2 G_{ij}(\omega + iX)$.

Therefore, putting the value of Green's function in Eq.(1), the value of dielectric constant \mathcal{E} is obtained as:

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

The dissipation of power when crystal is exposed to electromagnetic field is expressed as loss tangent. The loss tangent is the ratio of imaginary to real parts of dielectric constant;

$$\tan \delta = \frac{2\Omega\Gamma(\omega)}{\hat{\Omega}^2} \quad (9)$$

By using model values⁸ of physical quantities for deuterated RDP crystal presented in Table 1, temperature dependence of ferroelectric mode frequency, dielectric constant and loss tangent have been calculated and shown in Figures 1-3. Calculated temperature dependences have been compared with experimental values of Peercy¹⁰.

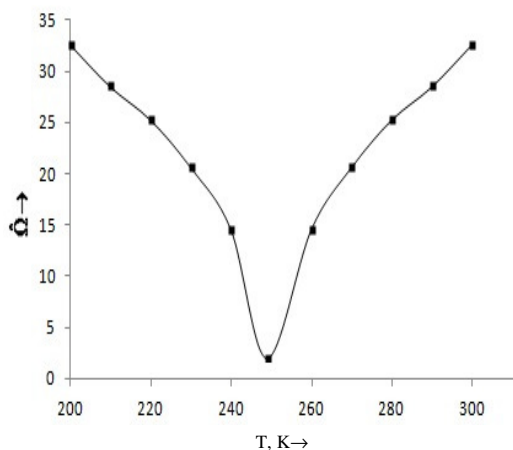


Figure 1. Calculated temperature dependence of ferroelectric mode frequency ($\hat{\Omega}$) in deuterated RbH_2PO_4 crystal — correlated with Exp¹⁰ ■

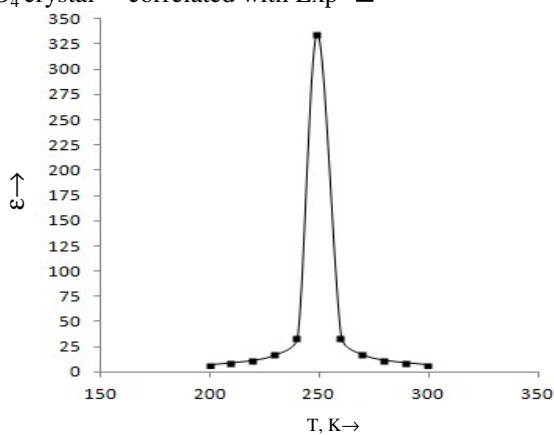


Figure 2. Calculated temperature dependence of dielectric constant (ϵ) in deuterated RbH_2PO_4 crystal —, Exp¹⁰ ■

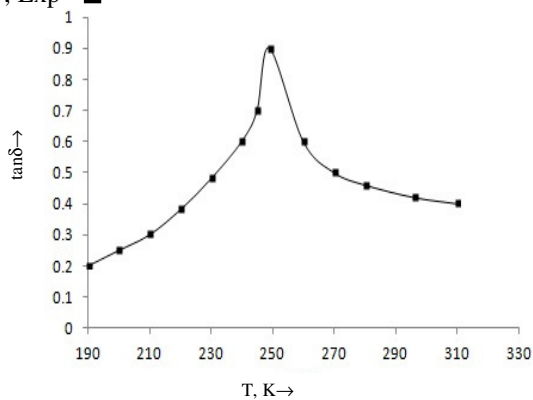


Figure 3. Calculated temperature dependence of tangent loss ($\tan \delta$) in deuterated RbH_2PO_4 crystal —, Exp¹⁰ ■

Table 1. Model values of physical quantities for deuterated RDP crystal

T_C, K	Ω, cm^{-1}	J	J^*	V_{ik}	$N \times 10^{19}$	$\mu \times 10^{-18}$	C, K	ω_k, cm^{-1}	$A_k \times 10^{17},$ erg K^{-1}
249	0.652	486.68	644.60	51.74	947.05	1.5	335.11	153	10.133

Discussion

In the present work, by fitting model values for deuterated RDP in the expressions obtained for RDP in our earlier paper⁸, the temperature dependence of ferroelectric mode frequency, dielectric constant and loss tangent has been calculated. Theoretically calculated results compare well with experimentally reported results for deuterated RDP crystal by Peercy¹⁰.

The main aim of the present work is to explain isotope effect in DRDP. On deuteration, the transition temperature shifts from 146 to 249 K and both dielectric constant and loss tangent versus temperature curves shift to quite new values. Our expressions for transition temperature T_C with values for DRDP explain fairly isotope effect on T_C . Our expressions Eq.(7)-(9) explain temperature dependence of ferroelectric frequency, dielectric constant and loss tangent for DRDP. The change in tunneling frequency is mainly responsible for isotope effect in DRDP crystal. Hence, with the expressions obtained for RDP crystals and different values of physical quantities for DRDP crystal, one can explain ferroelectric, dielectric and isotope effects in deuterated RDP crystal.

Conclusion

Present study reveals that the modified model *i.e.* pseudo spin lattice coupled mode model with addition of third and fourth order phonon anharmonic interactions terms explain quantitatively well the ferroelectric and dielectric behaviours of pure as well as deuterated RDP crystal. Theoretical results agree with experimental results of Peercy¹⁰ which show the applicability of the present modified model for both RDP and DRDP crystals.

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