

Temperature Dependence of Soft Mode Frequency, Dielectric Constant and Loss Tangent in Deuterated KDP Crystal

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Abstract: By fitting model values for physical quantities for deuterated KDP crystal in theoretically derived expressions for soft 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 Kaminow which show a good agreement.

Keywords: Ferroelectrics, Green's functions, Dielectric constant, Loss tangent, Phase transition

Introduction

Potassium dihydrogen phosphate KH_2PO_4 crystal undergoes ferroelectric transition at 123 K. The large isotope shift of phase transition temperature (T_c 229 K for KD_2PO_4) suggests that the proton dynamics plays an essential role in phase transition mechanism. KDP (KH_2PO_4) crystal is model order-disorder ferroelectric crystal. Its isomorphs constitute a large group of ferroelectric crystals. It is ferroelectric below 123 K (orthorhombic) and paraelectric above 123K (tetragonal). The lattice parameters are $a=7.899\text{\AA}$, $b= 6.325\text{\AA}$, $c=4.890\text{\AA}$ and $\beta=108.29^\circ$. The PO_4 groups are connected by O-H---O bonds, which forms double-well potential. Below T_c protons are ordered in one of two minima of potential.

Extensive experimental studies on KDP and its deuterated form (DKDP) have been carried out by many experimentalists. Leroudier *et al.*¹ have done crystal growth study of KDP and DKDP crystals. Li *et al.*² have also made crystal growth and optical studies of KDP and DKDP crystals. Strukov *et al.*³ have made hysteresis loop and specific heat studies on KDP and DKDP crystals. Ettomi *et al.*⁴ have made thermal analysis studies on KDP and DKDP crystals. Chai *et al.*⁵ have made Raman scattering studies on KDP and DKDP crystals. Abalmassov *et al.*⁶ have made dielectric susceptibility and Raman scattering studies on DKDP crystals. Pereira *et al.*⁷ have done Raman scattering studies on DKDP crystals.

Theoretical studies on KDP were initiated by Ganguli *et al.*⁸ who have considered pseudo spin model. They have used Green's function method and obtained soft mode frequency, dielectric susceptibility and transition temperature *etc.*

Earlier researchers⁸ 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 paper, we have considered third and fourth order phonon anharmonic terms.

In the present study we shall fit model values of physical quantities in the expressions obtained in our earlier paper⁹ for KDP crystal. Temperature dependences of soft mode frequency, dielectric constant and loss tangent will be calculated for KD₂PO₄ crystal. Theoretical results will be compared with experimentally reported results of Kaminow¹⁰.

Calculation and Results

In our earlier paper a pseudo-spin – lattice coupled mode model⁹ along with third and fourth-order phonon anharmonic interactions terms¹¹ has been considered for KDP type crystals. Using this Hamiltonian, the double-time thermal Green's function¹² was evaluated which 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

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

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

$$a = J_0 \langle S^z \rangle, \quad (4)$$

$$b = 2\Omega; \quad (5)$$

$$c = J_0 \langle S^x \rangle \quad (6)$$

In Eqs. 1 and 2, $\Gamma(\omega)$ and $\Delta(\omega)$ are width and shift respectively which are given in our earlier paper, $\hat{\Omega}$ is modified soft mode frequency given as;

$$\hat{\Omega}^2 = \frac{1}{2} \left\{ \left(\tilde{\omega}_k^2 + \tilde{\Omega}^2 \right) \pm \left[\left(\tilde{\omega}_k^2 - \tilde{\Omega}^2 \right)^2 + 16 V_{ik} \langle S_1^x \rangle \Omega \right]^{1/2} \right\}. \quad (7)$$

The dielectric constant was obtained⁹ as;

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

The dielectric tangent loss was given by;

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

The terms appearing in Eqs(1)-(9) have been defined in our earlier paper⁹. By using model values of physical quantities appearing in expressions (7), (8) and (9) (Table 1) their temperature dependences are calculated for DKDP crystal. The values of $\langle S_1^z \rangle$, $\langle S_1^x \rangle$ are calculated using their expressions in our earlier paper⁹. Then values of $\hat{\Omega}$, ϵ and $\tan \delta$ are

calculated for DKDP crystal and shown in Figures 1-3. The calculated values of $\hat{\Omega}$, ε and $\tan\delta$ for DKDP crystal have been compared with experimental values of Kaminow¹⁰.

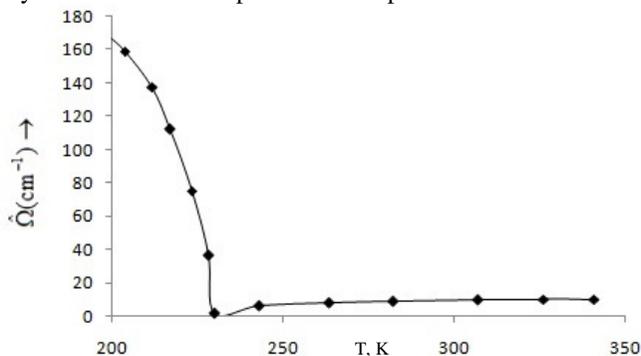


Figure 1. Calculated temperature dependence of soft mode frequency ($\hat{\Omega}$) in deuterated KDP crystal correlated with exp—, Exp¹⁰ ●

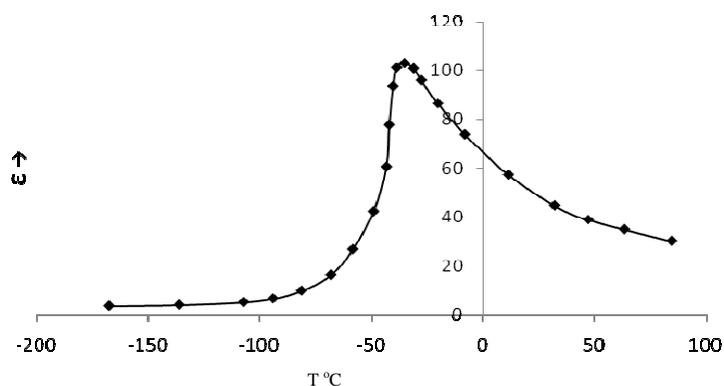


Figure 2. Calculated temperature dependence of dielectric constant (ε) in deuterated KDP crystal—, Exp¹⁰ ●

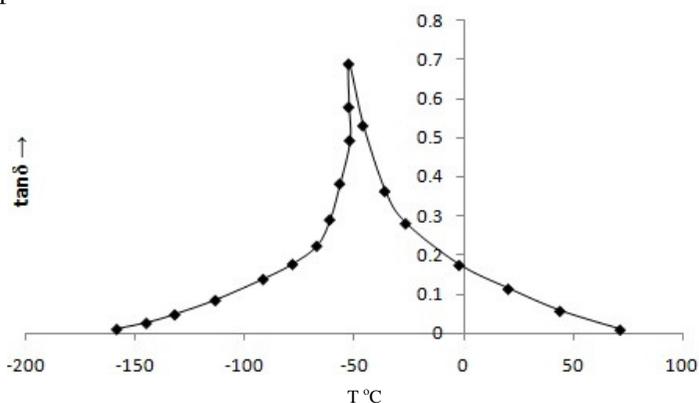


Figure 3. Calculated temperature dependence of loss tangent ($\tan\delta$) in deuterated KDP crystal—, Exp¹⁰ ●

Table 1. Model values of physical quantities for DKDP crystal (ref. 15)

Ω , cm^{-1}	J , cm^{-1}	J^* , cm^{-1}	V_{ik} , cm^{-1}	T_c K	ω_k	C	μ , esu	$A_k(\text{erg/K})$
0.486	472	626	0.299	229	153	373	1.3×10^{-18}	9.7×10^{17}

Discussion

In the present work, by fitting model values of physical quantities in the expressions obtained in our earlier paper for DKDP crystal, thermal variations of soft mode frequency, dielectric constant and loss tangent have been calculated. Theoretical results have been compared with experimentally reported results for deuterated KDP crystal. Our model for KDP type crystals, *i.e.* pseudo spin-lattice coupled mode model along with third- and fourth-order phonon anharmonic terms explains consistently and simply the salient features of phase transition and dielectric properties of KDP and DKDP crystals. The main aim of the present work is to explain isotope effect in DKDP. On deuteration, the transition temperature shifts from 123 to 229 K and both dielectric constant and loss tangent *versus* temperature curves shift to quite new values. Our expression for transition temperature T_c with values for DKDP crystal explains fairly isotope effect on T_c . Our expressions given in Eqs (8-10) explain temperature dependence of ferroelectric frequency, dielectric constant and loss tangent for DKDP. The change in tunneling frequency is mainly responsible for isotope effects in DKDP crystal. Hence, with the expressions obtained for KDP crystal with and different values of physical quantities for DKDP crystal, one can explain ferroelectric, dielectric and isotope effects in deuterated KDP 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 KDP crystal. Theoretical results agree with experimental results, which show the applicability of the present modified model for both KDP and DKDP crystals.

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