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RESEARCH ARTICLE

Temperature Dependence of Soft Mode Frequency, Dielectric Constant and Loss Tangent of Deuterated Lead Hydrogen Phosphate Crystal

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Abstract: By fitting model values for physical quantities for $PbDPO_4$ crystal in theoretical expressions for soft mode frequency, dielectric constant and loss tangent derived in our earlier paper for $PbHPO_4$ crystal temperature variations of these quantities have been calculated near transition temperature. Present results agree with experimental data reported in the literature. Isotope effects on both transition temperature and Curie-Weiss constant have been explained for $PbDPO_4$ crystal beautifully.

Keywords: Ferroelectrics, Green's function, Deuterated, Anharmonic

Introduction

Ferroelectric lead hydrogen phosphate ($PbHPO_4$) crystal causes transition around 310 K. Large isotope effect, *i.e*., shift of transition temperature to 452 K on deuteration suggests that hydrogen bonds play an important role in transition mechanism. Lead deuterium phosphate (LDP) is monoclinic in both polar and non-polar phases. Crystal can be grown by slow evaporation method. Extensive experimental studies have been carried out on $PbDPO_4$ crystal. Lockwood *et al*[1]., Ohno *et al.,*[2] and Lawrencic and Petzelt[3] have done Raman Spectroscopic studies. Deguchi and Nakamura[4] have done dielectric measurements on $PbDPO_4$ crystal. Sasaki and Ohno[5] have made luminescence studies of $PbDPO_4$ crystal. Madhavan *et al.*[6] have done crystallization of doped $PbHPO_4$ crystal. Zacheke*t al*.[7] have studied thermodynamic and dielectric properties of $PbHPO_4$ (LHP) crystal. Nakamoto *et al.*[8] have done x-ray powder studies of $PbHPO_4$ crystal under pressure. Theoretical studies on $PbHPO_4$ were initiated by De Carvalho and Salinas[9] who used Ising model to obtained formula for susceptibility of $PbHPO_4$ crystal. Blinc *et al.*[10] have used modified Ising model (two-sublattice pseudo-spin model) to explain susceptibility of $PbHPO_4$ crystal. Chaudhuri *et al.*[11] have used two-sublattice pseudo-spin model to explain transition and susceptibility of $PbHPO_4$ crystal. Qin *et al.*[12] have used grossly pseudo-spin model to explain order parameter of transition in $PbHPO_4$.Similar model has been used by

Wesselinowa[13] to explain central peak in $PbHPO_4$ and terms for $PbHPO_4$ type crystals. With the help of this Hamiltonian and method of double time thermal Green's functions of Zubarev[15], the Green's function method, we had derived expressions for soft mode frequency, dielectric constant and loss tangent for $PbHPO_4$ crystal. By fittingmodel values of physical quantities for lead deuterium phosphate crystal in the expressions obtained in our earlier paper, for lead hydrogen phosphate crystal, temperature dependence of soft mode frequency, dielectric constant and loss tangent will be calculated for LDP crystal. Theoretical results will be compared with experimental results of Ohno and Lockwood[2].

Calculation and Results

The evaluated Green's function

$$G_{ij}(t-t') = \left\langle\left\langle S_i^z(t); S_j^z(t')\right\rangle\right\rangle \tag{1}$$

Was evaluated rigorously which was then obtained[14] as

$$G_{ij}(\omega) = \pi^{-1}\Omega\left\langle S_{i1}^x\right\rangle\delta_{ij}[(\omega^2 - \hat{\Omega}^2) + 2\Omega i\Gamma(\omega)]^{-1} \tag{2}$$

where

$$\hat{\Omega}^2 = \tilde{\Omega}^2 + \Delta(\omega), \tag{3}$$

$$\tilde{\Omega}^2 = a^2 + b^2 - bc, \tag{4}$$

$$a = 2J_{ij} < S_1^z > + K_{ij} < S_2^z >, \tag{5}$$

$$b = 2\Omega \text{ and} \tag{6}$$

$$c = 2J_{ij} < S_1^x > + K_{ij} < S_2^x > \tag{7}$$

In Eqs. (2) and (3), $\Gamma(\omega)$ and $\Delta(\omega)$ are width and its corresponding shift respectively. Values of these have been given in our earlier paper[14]. Solving Eq.(3) $\hat{\Omega}$ was obtained as

$$\hat{\Omega}_{\pm}^{\ 2} = \frac{1}{2}\left[\left(\tilde{\Omega}^2 + \tilde{\omega}_k^2\right) \pm \left\{\left(\tilde{\tilde{\omega}}_k^{\ 2} - \tilde{\tilde{\Omega}}^2\right)^2 + 16V_{ik}^2\left\langle S_{1i}^x\right\rangle\Omega\right\}^{\frac{1}{2}}\right] \tag{8}$$

The dielectric constant $\in$ was obtained as

$$\in = -8\pi N\mu^2\langle S_1^x\rangle(\omega^2 - \tilde{\Omega})[(\omega^2 - \tilde{\Omega})^2 + 4\Omega^2\Gamma(\omega)^2]^{-1} \tag{9}$$

The dielectric loss tangentwas obtained as

$$\tan\delta = 2\Omega\Gamma(\omega)\hat{\Omega}^{-2} \tag{10}$$

The various terms appearing in Eq.(2) to Eq.(10) have been clearly defined in our Table 1, temperature dependences of soft mode frequency,dielectric constant and loss tangent have been calculated and shown in Figures 1-3 calculated values have compared with experimental values of Ohno and Lockwood[2].

Table1. Model values of physical quantities for deuterated lead hydrogen phosphate crystal

T_c(K)	Ω (cm^{-1})	J (cm^{-1})	K (cm^{-1})	V_{ik} (cm^{-1})	$\omega^{1/2}$ ($cm^{-1/2}$)	C (K)	μ (esu)
452	0.27	251	125	63	0.30	2939	0.6×10^{-18}

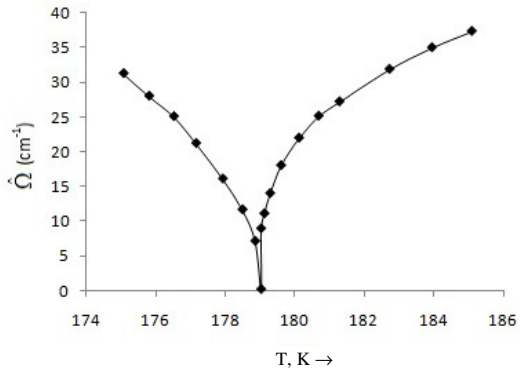

Figure 1. Temperature dependence of soft mode frequency in $PbDPO_4$ crystal (— Our calculation, ●Correlated experimental values of Ohno and Lockwood[2])

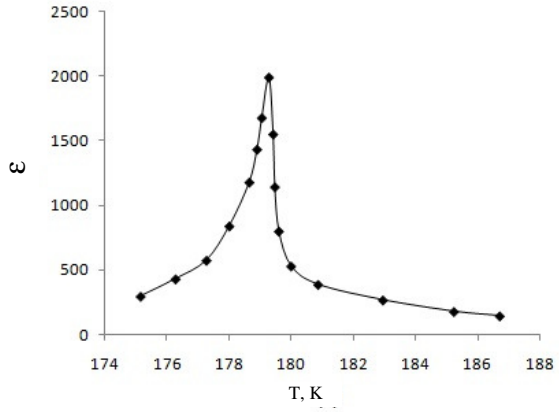

Figure 2. Temperature dependence of dielectric constant ϵ in $PbDPO_4$crystal (— Our calculation,●Experimental values of Ohno and Lockwood[2])

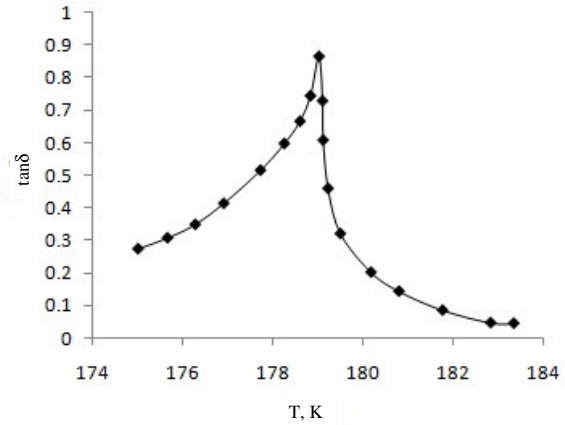

Figure 3. Temperature dependence of loss tangent tanδ in $PbDPO_4$ (—Our calculation, ●Experimental values of Ohno and Lockwood[2])

Discussion

In this work, by fitting model values for deuterated lead phosphate crystal in the expressions obtained for lead hydrogen phosphate crystal in our earlier paper, the temperature dependences of soft mode frequency, dielectric constant and loss tangent have been calculated. Theoretical calculated results of Ohno and Lockwood[2] for lead deuterated phosphate crystal.

The main aim of the present work is to explain isotope effect in $PbDPO_4$ crystal. On deuteration the transition temperature shifts from 310 K to 452 K. Both dielectric constant and tangent loss *versus* temperature curves shift to quite new values. Our formula for transition temperature T_C with different values of physical quantities for $PbDPO_4$ crystal explains fairly isotope effect on T_C. The expressions obtained is our earlier work for $PbHPO_4$ have been found quite adequate to explain temperature dependence of soft mode frequency, dielectric constant and loss tangent of $PbDPO_4$ with a good accuracy.

Conclusion

Present study reveals that the modified model used in our earlier work for $PbHPO_4$ crystal does explain isotope effect on transition temperature in $PbDPO_4$ crystal reported by Ohno and Lockwood earlier. This shows the applicability of modified model used in our earlier work for both $PbHPO_4$ and $PbDPO_4$ crystals.

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