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Dielectric Properties of Deuterated Cesium Dihydrogen Phosphate Crystal

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Abstract: Modified two sublattice pseudospin lattice coupled-mode model Hamiltonian has been applied to study the dielectric properties of deuterated cesium dihydrogen phosphate crystal. With the help of model Hamiltonian and Green's function theory, the theoretical expressions for normal mode frequency, dielectric constant and loss tangent are derived. By fitting the model values of different physical parameters, the thermal dependence of the above quantities has been calculated. Our theoretical obtained results are well compared with experimental data.

Keywords: Soft mode frequency, dielectric loss, deuterated cesium dihydrogen phosphate.

Introduction

Cesium dihydrogen phosphate crystal (CsH_2PO_4, abbreviated as CDP) crystal belongs to the potassium dihydrogen phosphate (KDP)-family. The crystal is one of the most promising and highly conductive compounds in the family. The ferroelectricity in the CDP crystal below the Curie temperature $(T_c = 154K)$ was first reported by Seidl in 1950 (Seidl 1950). Below the phase transition, CsH_2PO_4 crystal shows monoclinic crystal structure with space group $P2_1$ and above the curie temperature in paraelectric phase also shows monoclinic crystal structure with space group symmetry $P2_1/m$. On replacing H_2-atoms into D_2-atoms are disordered above the ferroelectric phase transition temperature $(T_c = 154K)$ in CsH_2PO_4 crystal into $T_c = 267K$ in deuterated cesium dihydrogen phosphate crystal (CsD_2PO_4 abbreviated as DCDP) and becomes ordered in one of the possible off-centre sites below the phase transition into ferroelectric phase with space group $P2_1(Z = 2)$. The amount of deuteration was checked by infrared spectroscopy and was found to be larger than 90 per cent (Levstik et al. 1975). The large isotope effect on replacing hydrogen with deuterium demonstrates the importance of the O-H—O hydrogen bonds in the ferroelectric transition of cesium dihydrogen phosphate crystal. The reaction $Cs_2CO_3+2D_3PO_4 = 2CsD_2PO_4+D_2O+CO_2$ synthesized the deuterated analogue CsD_2PO_4 crystal. The Curie point of deuterated cesium dihydrogen phosphate compound $(T_{cD} = 267K)$ (Gesi and Ozawa 1978). Frazer et al. have studied the one-dimensional ordering in order-disorder ferroelectric CsD_2PO_4 and CsH_2PO_4 crystals with the

neutron scattering method (Frazer et al. 1979). Ganguli et al. have studied Green's function theory of phase transition in H-bonded ferroelectric crystals with pseudospin lattice coupled-mode model (Ganguli et al. 1980). Deguchi et al. have studied the static and dynamic properties of dielectric constant in ferroelectric CsH_2PO_4 and CsD_2PO_4 crystals in the frequency range between MHz and 1GHz (Deguchi et al. 1982). Deguhi et al. have studied the effects of deuteration on the dielectric properties of ferroelectric CsH_2PO_4 crystal (Deguchi et al. 1982). Imai studied the anomalous behaviour in the phase transitions of CsH_2PO_4 and CsD_2PO_4 crystals by using the pseudospin, one-dimensional Ising model (Imai 1983). Itoh et al. have studied phase transitions in ferroelectric CsD_2PO_4 crystal by X-ray structure analysis (Itoh et al. 1983). Deguchi et al. have studied the isotope effect on the activation energy of dielectric relaxation in ferroelectric deuterated cesium dihydrogen phosphate crystal (Deguchi et al. 1984). Watari and Matsubara have studied the phase transitions in CsH_2PO_4 and CsD_2PO_4 crystals by using a quasi-one-dimensional transverse Ising model (Watari and Matsubara 1984). Kojyo and Onodera have studied the theory of the ferroelectric phase transition in cesium dihydrogen phosphate and its deuterated form crystals (Kojyo and Onodera 1989). Mamgain and Upadhyay have studied the dielectric properties of cesium dihydrogen phosphate and its deuterated form crystals (Mamgain and Upadhyay 2016).

In the present study, we have considered modified two sublattice pseudospin lattice coupled (PLCM) model (Ganguli et al. 1980) by adding phonon anharmonic interaction terms (Semwal and Sharma 1974; Upadhyay and Semwal 2002) extra spin-lattice interactions, direct spin-spin interaction and electric field terms is considered for CsD_2PO_4 crystal. Earlier authors (Ganguli et al. 1980; Mamgain and Upadhyay 2016) have not considered third-order phonon anharmonic and extra interaction terms, and they have decoupled the correlation function at an early stage. We have considered the modified model Hamiltonian and Green's function method (Zubarev 1960), the theoretical expressions for normal mode frequency, dielectric constant and loss tangent have been derived. By fitting the model values of various physical parameters in these expressions, the thermal dependence of normal mode frequency, dielectric constant and loss tangent are calculated. The theoretically obtained results are well compared with experimental data.

Theory (Numerical Analysis and Results)

For cesium dihydrogen phosphate crystal, we have used modified two sublattice pseudospin lattice coupled-mode model by adding phonon anharmonic interactions terms along with extra spin-lattice interactions, direct spin-spin interaction and electric field terms (Ganguli et al. 1980) expressed as

$$H = -2\Omega \sum_i (S_{1i}^x + S_{2i}^x) - \sum_{ij} [J_{ij}(S_{1i}^z S_{1j}^z + S_{2i}^z S_{2j}^z) + K_{ij} S_{1i}^z S_{2j}^z] - \sum_{ik} V_{ik}(S_{1i}^x A_k + S_{2i}^x A_k^\dagger)$$
$$- \sum_{ik} V_{ik}(S_{1i}^z A_k + S_{2i}^z A_k^\dagger) + \frac{1}{4}\sum_k \omega_k (A_k^\dagger A_k + B_k^\dagger B_k) - 2\mu E \sum_i (S_{1i}^z + S_{2i}^z)$$
$$- \sum_{ik} V_{ik}(S_{1i}^x A_k^2 + S_{2i}^x A_k^{\dagger 2}) + \sum_{k_1 k_2 k_3} V^{(3)}(k_1, k_2, k_3) A_{k_1} A_{k_2} A_{k_3} + \cdots \quad (1)$$

where Ω is the proton tunnelling frequency and S_i^z and S_i^x are the components of pseudospin operators S. J_{ij} is the interaction constant between the same lattice and K_{ij} is the interaction constant between different lattices. V_{ik} is the linear spin-lattice interaction coupling constant, ω_k is the harmonic phonon frequency, A_k and B_k are the position and momentum operators. Following the Zubarev (Zubarev 1960), we consider the evaluation of Green's function theory

$$G_{ij}(t-t') = \ll S_{1i}^z(t); S_{1j}^z(t') \gg = -\theta(t-t')\langle [S_{1i}^z(t), S_{1j}^z(t')] \rangle \quad (2)$$

where $\theta(t)$ is a unit step function that is zero for $t < 0$ and unity for $t > 0$. The angular bracket $\langle \ldots \rangle$ represents the ensemble average over a grand canonical ensemble. Differentiating Green's function equation (2) twice with respect to time t and time t' respectively by using the modified model Hamiltonian (Ganguli et al. 1980). Apply the Fourier transform in Dyson's equation; we get the final expression for Green's function by applying the symmetric decoupling scheme expressed as

$$G_{ij}(\omega) = \frac{\Omega \langle S_{1i}^x \rangle \delta_{ij}}{\pi[\,\omega^2 - \widetilde{\Omega}^2 - 2i\Omega\Gamma(\omega)]} \quad (3)$$

Solving the equation (3) self consistently, we obtained the final expression for soft mode frequency expressed as

$$\widetilde{\Omega}^2 = \widetilde{\widetilde{\Omega}}^2 + \Delta_{s-p}(\omega) \quad (4)$$

where

$$\widetilde{\widetilde{\Omega}}^2 = \widetilde{\Omega}^2 + \Delta_s(\omega) \quad (5)$$

and the pseudospin frequency is given by

$$\widetilde{\Omega}^2 = a^2 + b^2 - bc \quad (6)$$

where

$$\mathrm{a} = 2J_{ij}\langle S_{1i}^z \rangle + K_{ij}\langle S_{1i}^z \rangle - 2B_{ij}\langle S_{1i}^z \rangle + 2\mu E \quad (7)$$

$$b = 2\Omega \tag{8}$$

where Ω is the tunnelling frequency.

$$c = 2J_{ij}\langle S_{1i}^{x}\rangle + K_{ij}\langle S_{1i}^{x}\rangle - 2B_{ij}\langle S_{1i}^{x}\rangle \tag{9}$$

where, $\tilde{\Omega}$and$\tilde{\tilde{\Omega}}$ is the first and second pseudospin frequency and $\hat{\Omega}$ is the third and final normal mode frequency. Also $\langle S_1^z\rangle = -S_2^z \neq 0,\ T < T_c$ for the ferroelectric phase. In equations (3) and (4), $\Gamma(\omega)$ and $\Delta(\omega)$ are the width and shift of the response function. After solving the calculations of equation (4), we obtained the final expression for normal mode frequency ($\dot{\Omega}$) expressed as

$$\hat{\Omega}^2 = \frac{\left(\omega_k^2 + \tilde{\tilde{\Omega}}^2\right)}{2} \pm \frac{1}{2}\left\{\left(\omega_k^2 + \tilde{\tilde{\Omega}}^2\right)^2 + 4\{8aV_{ik}^2\langle S_{1i}^z\rangle\omega_k + 2bV_{ik}^2\langle S_{1i}^x\rangle\omega_k + 4bV_{ik}^2\langle S_{1j}^z\rangle\omega_k + \ldots\ldots\}\right\}^{\frac{1}{2}} \tag{10}$$

In equation (10), $\hat{\Omega}$ is the soft mode frequency which becomes zero at transition temperature causing phase transition in cesium dihydrogen phosphate crystal. Following the Zubarev (Zubarev 1960) and Kubo (Kubo 1957), we obtained the dielectric permittivity (ε) for triglycine sulphate crystal as obtained by

$$\varepsilon(\omega) = -\frac{8\pi N\mu^2\langle S_{1i}^{x}\rangle\left(\omega^2 - \hat{\Omega}^2\right)}{\left[\left(\omega^2 - \hat{\Omega}^2\right)^2 + 4\Omega^2\Gamma^2(\omega)\right]} \tag{11}$$

The loss of power in dielectric materials when it is exposed to an applied ac electric field called loss tangent. It is obtained as the ratio of the imaginary part (ε'') and the real part (ε') of the dielectric permittivity, we get

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = -\frac{2\Omega\Gamma(\omega)}{\left(\omega^2 - \hat{\Omega}^2\right)} \tag{12}$$

where ε' is the real part and ε'' is the imaginary part of the dielectric constant. By fitting the model values of various physical parameters from literature given in table (1), the thermal dependence of normal mode frequency, dielectric constant and loss tangent for cesium dihydrogen phosphate crystal have been calculated and shown in figures (1), (2) and (3).

Table 1 Model values of various physical parameters for cesium dihydrogen phosphate (Levstik et al. 1975; Ganguli et al. 1980).

T_c (K)	C (K)	ω_k (cm^{-1})	J_{ij} (cm^{-1})	K_{ij} (cm^{-1})	Ω (cm^{-1})	B_{ij} (cm^{-1})	V_{ik} $(cm^{3/2})$	N_k $(at\ T_c)$	A_k erg/K
267	4.3×10^4	134	399.15	395.96	1.71	0.5	14.16	0.5	8.455

Our theoretical results are well comparing with experimental data of Levstik et al. for cesium dihydrogen phosphate crystal shown in figures (1), (2) and (3), which show good agreement (Levstik et al. 1975).These data are fitted in the calculations with electric field parameters E=1kV/cm and 2μE=0.653 kJ/cm^3. We used the values of $\mu = 2.3 \times 10^{-18}$esu and $N = 0.5 \times 10^{21} cm^{-3}$ throughout numerical analysis for cesium dihydrogen phosphate crystal.

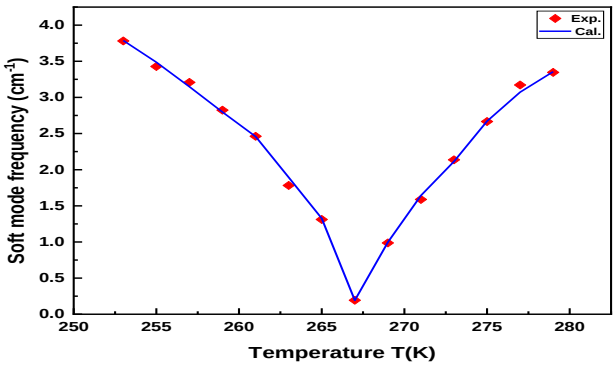

Figure 1 Temperature dependence of normal mode frequency for DCDP crystal [◆correlated values with experimental data of Levstik et al. (Levstik et al. 1975), ─ Present calculation]

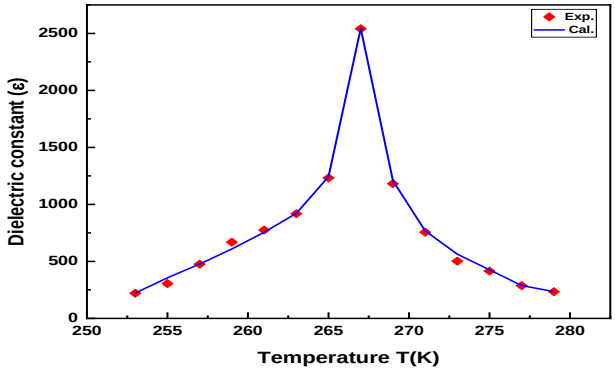

Figure 2 Temperature dependence of dielectric constant for DCDP crystal [◆ experimental data of Levstik et al. (Levstik et al. 1975), ─ present calculation]

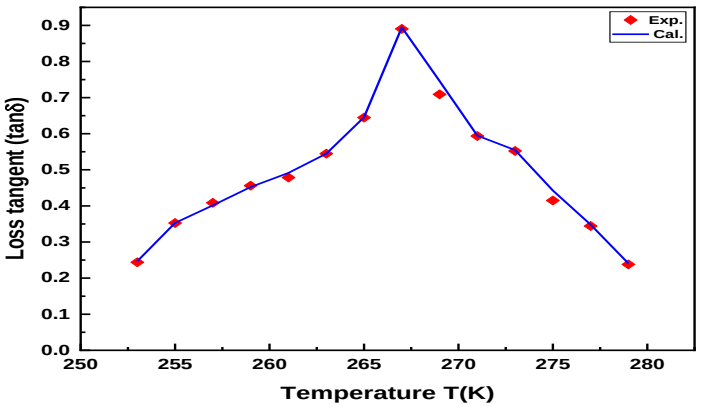

Figure 3 Temperature dependence of loss tangent for DCDP crystal [◆correlated values with experimental data of Levstik et al. (Levstik et al. 1975), Present calculation]

The theoretical variations of soft mode frequency with thermal dependence compared with correlated values obtained from the experimental data of Levstik et al. (Levstik et al. 1975). The calculated dielectric constant (ε) versus thermal dependence and dielectric tangent loss ($\tan\delta$) versus thermal dependence curves agree with experimental data of Levstik et al. (Levstik et al. 1975). Earlier authors (Ganguli et al. 1980; Mamgain and Upadhyay 2016) have decoupled the correlations functions at an early stage. Therefore, some important results are disappeared. Equation (10) shows that ferroelectric soft mode frequency decreases below Curie temperature (T_c), becoming minimum at transition temperature then increases. Thus, confirming Cochran's theory suggested the behaviour. The dielectric constant (ε) first increases from below Curie temperature (T_c) becoming large near T_c then decreases. Similarly, the dielectric tangent loss shows its behaviour.

Conclusions

In the present paper, the modified two sublattice pseudospin lattice coupled-mode model by adding anharmonic phonon interactions, extra spin-lattice interaction, direct spin-spin interactions, as well as external applied electric field terms explains well the thermal dependence of normal mode frequency, dielectric constant and loss tangent for CsD_2PO_4 crystals. Earlier authors (Ganguli et al. 1980; Mamgain and Upadhyay 2016) did not consider various interactions terms that we have considered. Hence our theoretical results are good compared with experimental data of Levstik et al. (Levstik et al. 1975). Our model theory may also apply to other similar order-disorder type crystals such as KH_2AsO_4, CsH_2AsO_4 and RbH_2AsO_4 etc.

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