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Dielectric properties of KDP-type ferroelectric crystals in the presence of external electric field

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Abstract. Considering external electric field as well as third- and fourth-order phonon anharmonic interaction terms in the pseudospin-lattice coupled mode (PLCM) model Hamiltonian for KDP-type ferroelectrics, expressions for field-dependent shift, width, renormalized soft mode frequency, Curie temperature, dielectric constant and dielectric loss are evaluated. For the calculation, method of statistical double-time temperature-dependent Green's function has been used. By fitting model values of physical quantities, temperature and electric field dependences of soft mode frequency, dielectric constant and loss have been calculated which compare well with experimental results of Baumgartner [8] and Choi and Lockwood [9]. Both dielectric constant and loss decrease with electric field.

Keywords. Ferroelectrics; pseudospin; soft mode; Green's function; dielectric constant; tangent loss.

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1. Introduction

Potassium dihydrogen phosphate (KH_2PO_4) (KDP) which is the most typical ferroelectric with hydrogen bonds, finds it promising use in electro-optic, piezoelectric and display devices [1]. It is currently being used for laser fusion activity due to its ability to generate second- and third-harmonics of higher power Nd:YAG and Nd:glass lasers [2]. In the paraelectric phase the hydrogen atom moves between two equivalent equilibrium positions in the O–H...O hydrogen bonds, linking the PO_4 tatrahedra. Below T_C this motion freezes out and the structure orders. This ordering is gradual and accompanied by displacements of the heavy atoms [3]. Ferroelectric phase transition and dielectric behaviour of KDP and its isomorphs is often described in terms of pseudospin [4] and its extension, i.e. pseudospin-lattice coupled mode model [5]. According to Cochran [6], frequency of some of the normal mode of vibration of crystal, called soft mode becomes zero at the transition temperature. It is this soft mode, that largely determines the dielectric and scattering properties of ferroelectrics. When an external electric field is applied to ferroelectrics, some very interesting results are observed.

The acoustic experiments of Litov and Garland [7] clearly showed that external electric field has profound effects on temperature dependences of ultrasonic attenuation, and elastic constant in KDP crystal. Baumgartner [8] and Choi and Lockwood [9] have carried out experiments on the effect of external electric field on dielectric measurements in KDP crystals. Tremendous theoretical [10–15] and experimental [16–20] studies have been made to study phase transition and dielectric properties of KDP-type ferroelectrics. However, no theoretical study has been made to study the effect of external electric field on transition and dielectric properties of these crystals.

Therefore, in the present study a pseudospin-lattice coupled mode (PLCM) model is extended by adding third- and fourth-order phonon anharmonic interactions [21] as well as an external electric field term. With the help of extended model for KDP and double-time thermal Green's function technique [22], expressions for electric field-dependent shift, width, soft mode frequency and Curie temperature have been evaluated. Fitting model parameter values for KDP crystal temperature and electric field dependences of the above quantities have been calculated and compared with experimental results of Baumgartner [8] and Choi and Lockwood [9].

2. Model

The PLCM model [10] along with phonon anharmonic interaction terms [23] as well as external electric field term is expressed as

$$H = H_{\mathrm{s}} + H_{\mathrm{sp}} + H_{\mathrm{anh}} + H_{\mathrm{E}},$$

where $H_{\mathrm{s}}, H_{\mathrm{sp}}$ and H_{anh} are the same as given in our previous paper [21] and

$$H_{\mathrm{E}} = +2\mu E \sum_i S_i^z, \tag{1}$$

where S^z is the component of the pseudospin variable, S, E is the external electric field and μ is the dipole moment associated with O–H. . .O bond.

3. Green's function, shift, width and soft mode frequency

Following Zubarev [22] we consider the evaluation of Green's function as

$$G_{ij}(t-t') = \langle\langle S_i^z(t); S_j^z(t')\rangle\rangle = -i\theta(t-t')\langle[S_i^z(t); S_j^z(t')]\rangle, \tag{2}$$

where $\theta(t-t')$ is Heaviside's unit step function, $\theta(t-t') = 1$ for $t > t'$; and $\theta(t-t') = 0$ for $t < t'$.

The Green's function (2) is evaluated using Hamiltonian (1) following the procedure of our earlier paper [21] which finally takes the form

$$G(\omega + i\varepsilon) = \pi^{-1}\langle S_i^x\rangle\delta_{ij}[\omega^2 - \hat{\Omega}^2 + 2i\Omega\Gamma(\omega)]^{-1}, \tag{3}$$

where

$$\hat{\Omega}^2 = \tilde{\tilde{\Omega}}^2 + 2\Omega\Delta_4(\omega), \tag{4}$$

with

$$\tilde{\Omega}^2 = a^2 + b^2 - bc, \tag{5}$$

$$\tilde{\tilde{\Omega}}^2 = \tilde{\Omega}^2 + 2\Omega[\Delta_1(\omega) + \Delta_2(\omega) + \Delta_3(\omega)], \tag{6}$$

$$a = (J\langle S^z\rangle + 2\mu E), \quad b = 2\Omega, \quad C = J\langle S^x\rangle, \tag{7}$$

$$\Delta(\omega) = \Delta_1(\omega) + \Delta_2(\omega) + \Delta_3(\omega) + \Delta_4(\omega), \tag{8}$$

with

$$\Delta_1(\omega) = a^4 L, \tag{9}$$

$$\Delta_2(\omega) = 4\mu^2 E^2 a^2, \tag{10}$$

$$\Delta_3(\omega) = V_{ik} a^2 N_k L, \tag{11}$$

$\Delta_4(\omega)$ is the same as given in our earlier paper [21], where

$$L = [2\Omega(\omega^2 - \tilde{\Omega}^2)]^{-1}, \tag{12}$$

$$\Gamma(\omega) = \Gamma_1(\omega) + \Gamma_2(\omega) + \Gamma_3(\omega) + \Gamma_4(\omega), \tag{13}$$

where

$$\Gamma_1(\omega) = \pi a^4 (2\Omega\tilde{\Omega})^{-1} M, \tag{14}$$

$$\Gamma_2(\omega) = 2\pi\mu^2 E^2 a^2 (2\Omega\tilde{\Omega})^{-1} M, \tag{15}$$

$$\Gamma_3(\omega) = \pi V_{ih}^2 a^2 N_k (2\Omega\tilde{\Omega})^{-1} M, \tag{16}$$

Γ_4 is the same as given in our earlier paper [21], with

$$M = [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})]. \tag{17}$$

Solving eq. (25) self-consistently (following our [21] procedure) one obtains renormalized frequency

$$\hat{\Omega}^2 \pm = \frac{1}{2}(\tilde{\tilde{\omega}}_k^2 + \tilde{\tilde{\Omega}}^2) \pm [(\tilde{\tilde{\omega}}_k^2 - \tilde{\tilde{\Omega}}^2) + 8V_{ik}\langle S^x\rangle\Omega]^{1/2}. \tag{18}$$

The frequency $\hat{\Omega}_-$ is the electric field-dependent soft mode frequency which critically depends on temperature and electric field. This frequency is responsible for phase transition.

4. Field-dependent Curie temperature

The Curie temperature, $T_{\rm C}$, can easily be obtained by applying the stability condition of paraelectric phase, i.e. $\hat{\Omega}_{-} \to 0$ as $T \to T_{\rm C}$, which gives at once

$$T_{\rm C} = \frac{D}{2k_{\rm B}\tanh\left(\frac{2D}{J'}\right)}, \quad \text{with} \tag{19}$$

$$J' = J + \frac{V^2\tilde{\tilde{\omega}}_k^2}{[\tilde{\tilde{\omega}}_k^4 + 4\omega_k\Gamma_k^2]}, \quad \text{and} \tag{20}$$

$$D^2 = (4\Omega^2 + 4\mu^2 E^2). \tag{21}$$

5. Dielectric properties in the presence of electric field

The response of a crystal to external electric field is expressed by electrical susceptibility, which using Kubo's [24] and Zubarev's [22] formalisms, is expressed as

$$\chi = -\lim_{\varepsilon\to 0} 2\pi N\mu^2 G_{ij}(\omega + i\varepsilon), \tag{22}$$

where N is the number of dipoles having dipole moment μ in the sample. By using the usual relation $\varepsilon = 1 + 4\pi\chi$, and eqs (3) and (22) the expression for real part of dielectric constant can be expressed as

$$\varepsilon'(\omega) - 1 = 4\pi(-2\pi N\mu^2)\langle S^x\rangle(\omega^2 - \tilde{\tilde{\Omega}}^2)[(\omega^2 - \tilde{\tilde{\Omega}}^2)^2 + 4\Omega^2\Gamma^2]^{-1}. \tag{23}$$

The dissipation of power in dielectric material can conveniently be expressed as tangent loss. Using eq. (23) one obtains

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = -\frac{2\Omega\Gamma(\omega)}{(\omega^2 - \tilde{\tilde{\Omega}}^2)}. \tag{24}$$

6. Numerical calculation and discussion

By using model values of various quantities in expressions from literature[10] (given in table 1) temperature and electric field dependences of width, shift, soft mode frequency, dielectric constant and loss for KH_2PO_4 crystal have been calculated and compared with experimental results of others [8,9] (figures 1–4).

Our expressions (18), (23), (24) and (17) show that the dielectric constant, Curie temperature, dielectric loss and soft mode frequency respectively are all explicitly electric field dependent. The dielectric constant decreases with increase in electric field. Loss also decreases with increase in electric field. Curie temperature decreases with electric field. The effect of electric field is to shift the peak of dielectric constant to higher temperatures. The effect of electric field is to slightly cool the crystal. Our theoretical results for electric field dependences of dielectric constant

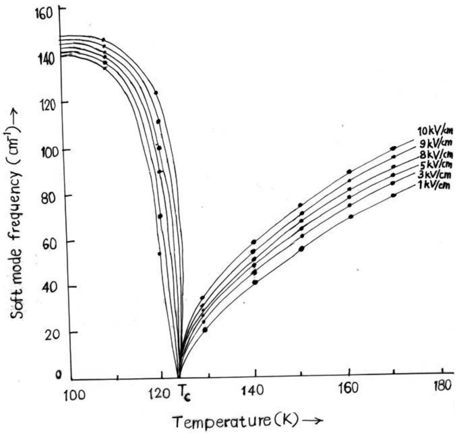

Figure 1. Electric field and temperature dependences of soft mode frequency in KDP crystal. Present calculation (–), experimental results [8,9] (●).

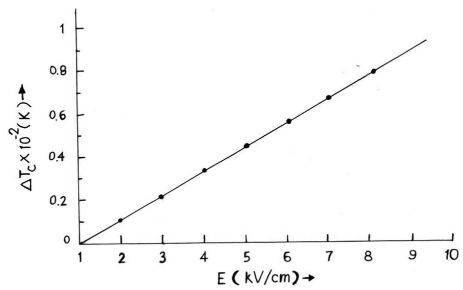

Figure 2. Electric field dependence of T_{C} in KDP crystal. Present calculation (–), experimental results [8,9] (●).

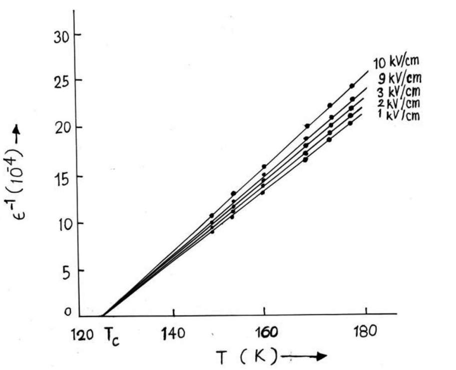

Figure 3. Temperature dependence of dielectric constant for different electric fields in KDP crystal. Present calculation (–), experimental results [8,9] (●).

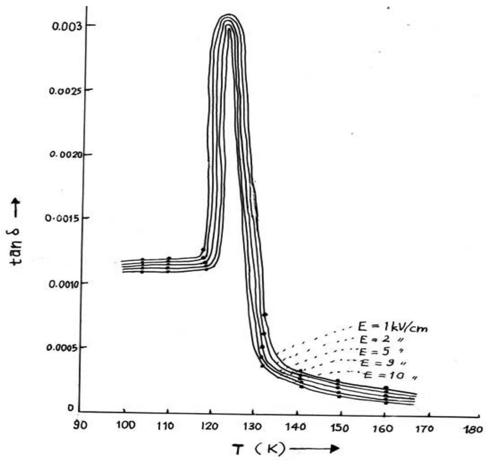

Figure 4. Temperature dependence of dielectric loss for different electric fields in KDP crystal. Present calculation (–), experimental results [8,9] (●).

loss and soft mode for different temperatures and change in Curie temperature with electric field compare well with experimental results of Baumgartner [8] and Choi and Lockwood [8]. Hence the pseudospin-lattice coupled model along with third- and fourth-order phonon anharmonic interaction and external electric field terms explains phase transition and dielectric properties of KDP-type crystals. By using model values and expressions obtained in the present work for other isomorphous crystals of KDP, similar results can be obtained.

Table 1. Model values of physical parameters for KDP crystal.

Ω (cm^{-1})	J (cm^{-1})	J' (cm^{-1})	V_{ik} (cm^{-1})	ω_k (cm^{-1})	$\mu \times 10^{18}$ (cgs)	T_C (K)
82	344	440	25.56	153	1.8	123

E (kV/cm)	1	2	3	4	5	6	7	8	9	10
$2\mu E$	0.067	0.13	0.20	0.26	0.33	0.40	0.47	0.52	0.60	0.67

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