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Relaxation processes and ultrasonic attenuation in KDP-type ferroelectrics

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Abstract - The anharmonic four - particle cluster model Hamiltonian for stochastic motion of $H_2PO_4^-$ groups has been used to study the physical properties of KDP type ferroelectrics. Using Green's function method and Dyson's equation the renormalized frequency of the coupled system and collective wave half width have been evaluated with the help of model Hamiltonian by considering the anharmonicity upto fourth order. The higher order correlations have been decoupled using symmetric decoupling scheme at the later stage after applying the Dyson's treatment and have been evaluated using the renormalized Hamiltonian. The relaxational behaviour and ultrasonic attenuation have been related to the width of collective mode. The temperature dependence of ultrasonic attenuation coefficient, dielectric constant and loss tangent has been discussed in terms of a relaxational soft mode.

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Keywords : collective proton wave half width, collective phonon mode frequency shift, and relaxation time.

I. Introduction

The study of KH_2PO_4 type ferroelectrics has great significance because the varying properties of these materials are directly related to the industrial applications. The static and dynamical properties of KDP family have been tried on the basis of order-disorder model of dipoles[1] by Tokunaga. These results, however, are in good agreement with experimental results but could not explain the observed relaxational behaviour of dielectric properties and ultrasonic attenuation in KDP type ferroelectrics explicity. Many workers [2-7] have experimentally studied the dielectric properties of KDP type ferroelectrics. Formulae were developed to explain ferroelectric transitions in order-disorder [8-10] type crystals.

In the present study the four particle cluster model , propsed by Blinc and Žekš [11] has been extended to explain the observed relaxational behaviour of dielectric properties and ultrasonic attenuation in KDP-type ferroelectrics.

The model Hamiltonian includes; the proton Hamiltonian, the lattice Hamiltonian, the proton-lattice interaction terms and the anharmonicity upto fourth order . Using the double time thermal retarded Green's function method and Dyson's equation[12-13] the collective mode frequencies and widths have been calculated. The double time thermal Green's function method offers a convenient approach to evaluate the static and dynamical properties in the same formalism.

II. Theory

a) Model Hamiltonian and Equation of Motion

The four particle cluster Hamiltonian by Blinc and Žekš [11] has been modified by considering the lattice anharmonicity upto fourth order for the stochastic motion of $H_2PO_4^-$ groups in a KDP - system. The model Hamiltonian, considered in the present study, includes the proton Hamiltonian, the lattice Hamiltonian, the latticeproton interaction and the anharmonic terms. With these all interaction terms the total Hamiltonian is given by[12] :

$$\begin{aligned} H = & -2\Omega\sum_i S_i^x - \frac{1}{2}\sum_{ij} J_{ij}\, S_i^z S_j^z - \frac{1}{4}\sum_{ijkl} J'_{ijkl}\, S_i^z S_j^z S_k^z S_l^z \\ & + \frac{1}{4}\omega_k \left({}^{+}A_k A_k + {}^{+}B_k B_k \right) + \sum_i \overline{V_{ik}}\, S_i^z A_k \\ & + \sum_{\vec{k}_1,\vec{k}_2,\vec{k}_3} V_3\left(\vec{k}_1,\vec{k}_2,\vec{k}_3\right) A_{\vec{k}_1} A_{\vec{k}_2} A_{\vec{k}_3} \\ & + \sum_{\vec{k}_1,\vec{k}_2,\vec{k}_3,\vec{k}_4} V_4\left(\vec{k}_1,\vec{k}_2,\vec{k}_3,\vec{k}_4\right) A_{\vec{k}_1} A_{\vec{k}_2} A_{\vec{k}_3} A_{\vec{k}_4}. \end{aligned} \qquad (1)$$

Where S_i^x is the tunneling operator, Ω is the proton tunneling frequency, S^z and the half of difference of the occupation probability of the proton in the equilibrium position of a hydrogen bond. J_{ij} is the two body - coupling coefficient and J'_{ijkl} refers to the four body coupling coefficient. ω_k is bare phonon frequency; A_k and B_k are displacement and momentum operators. $\overline{V_{ik}}$ is proton-lattice interaction term; $V_3(\vec{k}_1,\vec{k}_2,\vec{k}_3)$ and $V_4(\vec{k}_1,\vec{k}_2,\vec{k}_3,\vec{k}_4)$ are third - and fourth - order anharmonic coefficients.

The proton Green's function $\langle\langle S_q(t); S_{q'}(t')\rangle\rangle$ and the phonon Green's function $\langle\langle A_q(t); A_{q'}(t')\rangle\rangle$ have been evaluated for the collective motion of the system, using the model Hamiltonian, Eq.1. The higher order correlations in the proton Green's function have been evaluated using the symmetrical decoupling scheme, after applying the Dyson's treatment. With this approach, one gets[12] :

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$$\lim_{\varepsilon\to 0} G^{zz}_{qq'}(\omega + j\varepsilon) = \frac{\Omega < S^x_q > \delta_{qq'}}{\pi\left[\omega^2 - \tilde{\tilde{\Omega}}^2 + j\Gamma_s(q,\omega)\right]}, \quad (2)$$

where $\tilde{\tilde{\Omega}}$ is the proton renormalized frequency of the coupled system, $\Gamma_s(q,\omega)$ and is the collective proton wave half width, given by

$$\Gamma_s(q,\omega) = \pi \sum_{i=1}^{3} G''_{si}(q,\omega) \quad (3)$$

$$\Gamma_s(q,\omega) = \frac{-4\pi \bar{V}_q^2 \omega_q^2 < S^x_q > \delta'_{qq} \Gamma_p}{\Omega\left[(\omega^2 - \tilde{\tilde{\omega}}_q^2)^2 + 4\omega_q^2 \Gamma_p^2\right]} + \frac{\pi bc^2}{2\tilde{\Omega}} \delta\{(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\} + \frac{\pi a^2 \hat{\Omega}}{2b} \delta\{(\omega - \hat{\Omega}) - \delta(\omega + \hat{\Omega})\} \quad (4)$$

where

$$a = J_0 < S^z_q > + J'_0 < S^z_q >^3,\ b = 2\Omega,$$
$$c = J'_0 < S^z_q > + 3J'_0 < S^x_q >< S^z_q >^2,$$
$$\tilde{\Omega} = (a^2 + b^2 - bc)^{1/2}, \hat{\Omega} = (a^2 + n_q \bar{V}_q^2)^{1/2},$$

$\tilde{\tilde{\omega}}_q^2$ is the renormalized phonon frequency, Γ_p is the coupled phonon width, $n_q = \frac{\omega_q}{\tilde{\omega}_q} \coth\left(\frac{\beta\tilde{\omega}_q}{2}\right)$ is the phonon occupation number and $\beta = (k_B T)^{-1}$, k_B is Boltzman constant and T the absolute temperature. Similarly, on solving the phonon Green's function, one obtains

$$G_{qq'}(\omega) = << A_q; A_q^+ >>= \frac{\omega_q \delta_{qq'}}{\pi(\omega^2 - \tilde{\tilde{\omega}}_q^2 + 2j\omega_q \Gamma_p(q,\omega)} \quad (5)$$

Where $\tilde{\tilde{\omega}}_q$ is the renormalized coupled phonon frequency which is obtained, by calculating self consistently, as

$$\tilde{\tilde{\omega}}^2_{q\pm} = \frac{1}{2}(\tilde{\omega}_q^2 + \tilde{\tilde{\Omega}}^2) \pm \frac{1}{2}\left\{(\tilde{\omega}_q^2 + \tilde{\tilde{\Omega}}^2)^2 + 16\bar{V}_q^2 \omega_q \Omega < S^x >\right\}^{1/2} \quad (6)$$

Where

$$\tilde{\omega}_q^2 = \omega_q^2 + 8\omega_q(2V_3 + V_4)\coth\left(\frac{\beta\omega_q}{2}\right) \quad (7)$$

These frequencies $\tilde{\tilde{\omega}}_\pm$ are the normal modes of the system and are the frequencies which may be used for comparison with other measured response of the system. Furthermore, $\tilde{\tilde{\omega}}_\pm$ are approximately the same frequencies that are obtained by fitting each part of the spectrum independently. The $\tilde{\tilde{\omega}}_-$ mode frequency approaches zero at the T_c. The $\tilde{\tilde{\omega}}_+$ mode, on the other hand, has no critical temperature dependence. The mode $\tilde{\tilde{\omega}}_-$ corresponds to the longitudinal soft $B_2(Z)$ mode which softens when temperature approaches to T_c and $\tilde{\tilde{\omega}}_+$ mode corresponds to the transverse $E(x,y)$ mode which is by far less temperature dependent than the $\tilde{\tilde{\omega}}_-$ mode. $\tilde{\tilde{\omega}}_-$ and modes originate from a zone center ($q = 0$) corresponding to a collective proton motion in the a - b plane . The higher order correlations in the phonon response function have been calculated without any decoupling and using the renormalized Hamiltonian:

$$H_{ren.} = -2\Omega\sum_q S^x_q - \frac{1}{2}\sum_{q,q'} J_q S^z_q S^z_{q'} - \frac{1}{4}\sum_{q,q',-q,-q'} J'_q S^z_q S^z_{q'} S^z_{-q} S^z_{-q'} + \frac{1}{4}\sum_q \frac{\tilde{\omega}_q^2}{\omega_q}\left(A_q^+ A_q + B_q^+ B_q\right) \quad (8)$$

b) Relaxation Time and Ultrasonic Attenuation

The Green's function method and Dyson's equation treatment conveniently describe the transition properties of KDP - system. The coupled frequency and width are measurement of relaxational behavior in this system. In the presence of resonant interaction the relaxation time with the width (Γ_P) [Eq. 4] and collective phonon mode frequency ($\tilde{\tilde{\omega}}^2_\pm$) [Eq. 6] is related as[15]:

$$\tau_p = \frac{2\Gamma_p}{\tilde{\tilde{\omega}}^2_\pm}. \quad (9)$$

From equation (9) we obtain two relaxation times corresponding to $\tilde{\tilde{\omega}}_+$ and $\tilde{\tilde{\omega}}_-$. One corresponding to $\tilde{\tilde{\omega}}_-$ tend to infinity as $T \to T_c$ and the other corresponds to $\tilde{\tilde{\omega}}_+$ be weakly temperature dependent. Due to decoupling of the correlation function in the very beginning the expression for width could not be obtained by Ganguli *et al* [16].The collective frequencies and width give an account of the relaxational behaviour of KDP-system. The respective relaxation times (corresponding to $\tilde{\tilde{\omega}}_+$ and $\tilde{\tilde{\omega}}_-$) lead to the expressions for dielectric constant, tangent loss and acoustic attenuation in the order-disorder system. As from equation (9) the polarization time (τ_p) significantly appears in Eq. (4), its contribution due to the resonant interaction to the attenuation may be written as :

$$\alpha(q,\omega) = \frac{\Gamma(q,\omega)}{C_\mu} \qquad (C_\mu \text{ is ultrasound velocity})$$
$$= \frac{2\pi\bar{V}_q^2 < S^x > \omega^2 \tau_p}{C_\mu \tilde{\tilde{\omega}}_q^2 \Omega(1 + \omega^2\tau_p^2)} + \frac{\pi bc^2}{2\tilde{\Omega}C_\mu}\delta\{(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\} \frac{\pi a^2 \hat{\Omega}}{2bC_\mu}\delta\{(\omega - \hat{\Omega}) - \delta(\omega + \hat{\Omega})\} \quad (10)$$

The ultrasonic attenuation given by Eq. (10) peaks for $\omega\tau_p \cong 1$. Corresponding to $\tilde{\tilde{\omega}}_-$ mode and for the temperature such that $\omega\tau_p << 1$, Eq.(10) can be written, in the first approximation, as :

$$\alpha(q) = \frac{k\omega^2\tau_p}{|T_c - T|} + \alpha_0. \quad (11)$$

Equation (11) explains the experimental observations, the anomaly near T_c the ω^2 and dependence of attenuation coefficient. In the absence of

tunneling, the polarization relaxation time (τ_p) can be easily related to the microscopic motion of the hydrogen or deuteron in the bond and the net charge in the z-direction polarization is a consequence of proton jumps that create Takagi groups, $H_2PO_4^-$. Eq.(11) predicts that is proportional to the ω^2 , for temperature above T_c . The fact that α is proportional to the $\tilde{\tilde{\omega}}_-^2$ is equivalent to saying that $\omega\tau_p << 1$; which is true for KDP.

c) Dielectric Constant and Loss Tangent

The real and imaginary parts of dielectric constant can be written as :

$$\varepsilon'(\omega) = -8\pi N\mu^2 G'(\omega), \tag{12}$$

and

$$\varepsilon''(\omega) = -8\pi N\mu^2 G''(\omega), \tag{13}$$

Where $G'(\omega)$, and $G''(\omega)$ are the real and imaginary parts of the Eq. (5). N is the number of unit cells in the sample and the effective dipole moment per unit cell. For the experimental range of frequencies, $\omega << \tilde{\tilde{\omega}}$ and $\omega\tau_p << 1$ for KDP, Eq.(12) reduces to :

$$\varepsilon'(\omega) = \frac{8\pi N\mu^2\tilde{\omega}}{\tilde{\tilde{\omega}}^2} \tag{14}$$

Where $\tilde{\omega}$ is given by Eq.(7) and $\tilde{\tilde{\omega}}$ by Eq.(6). The $\tilde{\tilde{\omega}}_+$ mode corresponds to E(x,y) mode and may be attributed to the observed transverse dielectric properties of KDP. In the simplest approximation $\tilde{\tilde{\omega}}_+ = K_1 + K_2 T$, where K_1 and K_2 are temperature independent parameters. This mode along with Eq.(14) explains the observed transverse dielectric constant ε_a' obtained from integrated intensity of Raman spectroscopy[15] and those measured by Kaminow *et al*[17]. This indicates that the low frequency $\tilde{\tilde{\omega}}_-$ mode is closely related to the macroscopic dielectric constant ε_c' .This also suggests that the $\tilde{\tilde{\omega}}_+[E(x,y)]$ mode Raman spectrum originates neither from the second order Raman scattering nor from density of states due to the local disorder above T_c but from one of the collective modes at the center of the Brillouin zone. This low frequency $\tilde{\tilde{\omega}}_+$ mode appears also in a deuterated KDP (DKDP), although the intensity is about one-third of the KDP, which indicates the possibility that the spectrum in due to the hydrogen collective motion.

The observed dielectric constant (ε_c') of KDP along c-axis may be explained in terms of $\{\tilde{\tilde{\omega}}_-(B_{2(z)})\}$ mode. As $\tilde{\tilde{\omega}}_- \propto (T - T_c)$, Eq. (14) can be expressed as:

$$\varepsilon_c' = \frac{C}{(T - T_C)}, \tag{15}$$

which explains the observed Curie-Weiss behaviour of dielectric constant along the c-axis in KDP[17]. As temperature $T \to T_c$, ε_c' tends to maximum value, which is consistent with the theory of Upadhyay[10] for ADP-type crystals. The dielectric loss ($\tan\delta$) for the dissipation of power in a dielectric crystal is defined as

$$\tan\delta = \frac{G''(\omega)}{G'(\omega)}, \tag{16}$$

which can be written as :

$$\tan\delta = \frac{-\omega\Gamma_p}{(\omega^2 - \tilde{\tilde{\omega}}^2)}. \tag{17}$$

For experimental values of the applied field frequency ω ,one has $\omega\tau_p << 1$ for KDP system, then Eq. (17) can be written as:

$$\tan\delta = \frac{\omega\tau_p}{2} \tag{18}$$

Where τ_p is given by Eq . (9). The $\tilde{\tilde{\omega}}_+$ mode gives the contribution for weakly temperature dependent transverse relaxational behaviour of the observed transverse tangent loss ($\tan\delta_a$) and $\tilde{\tilde{\omega}}_-$ mode contributes to the longitudinal relaxational behaviour of the observed longitudinal tangent loss ($\tan\delta_c$) in KDP[14].

III. Temperature Dependence of Relaxation Time

The relaxation time (τ_p) has been calculated from the attenuation and dielectric data and compared with the observations from other methods [13,15]. These values have been given in Table-1. The temperature dependence of relaxation time calculated form different data for KDP-type crystals is shown in Fig.1.

Table 1 : Temperature dependence of Relaxation time in paraelectric phase for KH_2PO_4

Temperature (K)	Relaxation time calculated from attenuation data(α)[15]	Relaxation time calculated from dielectric data[17]		Relaxation time obtained by spectral line width[18]
	$\tau(\times10^{-12})$sec.	$\tau_a(\times10^{-13})$sec.	$\tau_c(\times10^{-12})$sec.	$\tau(\times10^{-12})$sec.
125	2.24	1.38	2.28	2.50
130	1.26	1.37	1.21	1.31
135	0.90	1.37	0.90	0.91
140	0.84	1.37	0.88	0.85
145	0.80	1.36	0.86	0.80

The soft mode in this system is of classical relaxational charcter. Polarization relaxation time (τ_p), calculated from [Eq. (18)] using the loss data and attenuation coefficient data, are consistent and give the $\omega\tau_p$ values well below unity for KDP-type system. These results suggest that the observed dielectric and attenuation behaviour of the KDP is of relaxational type.

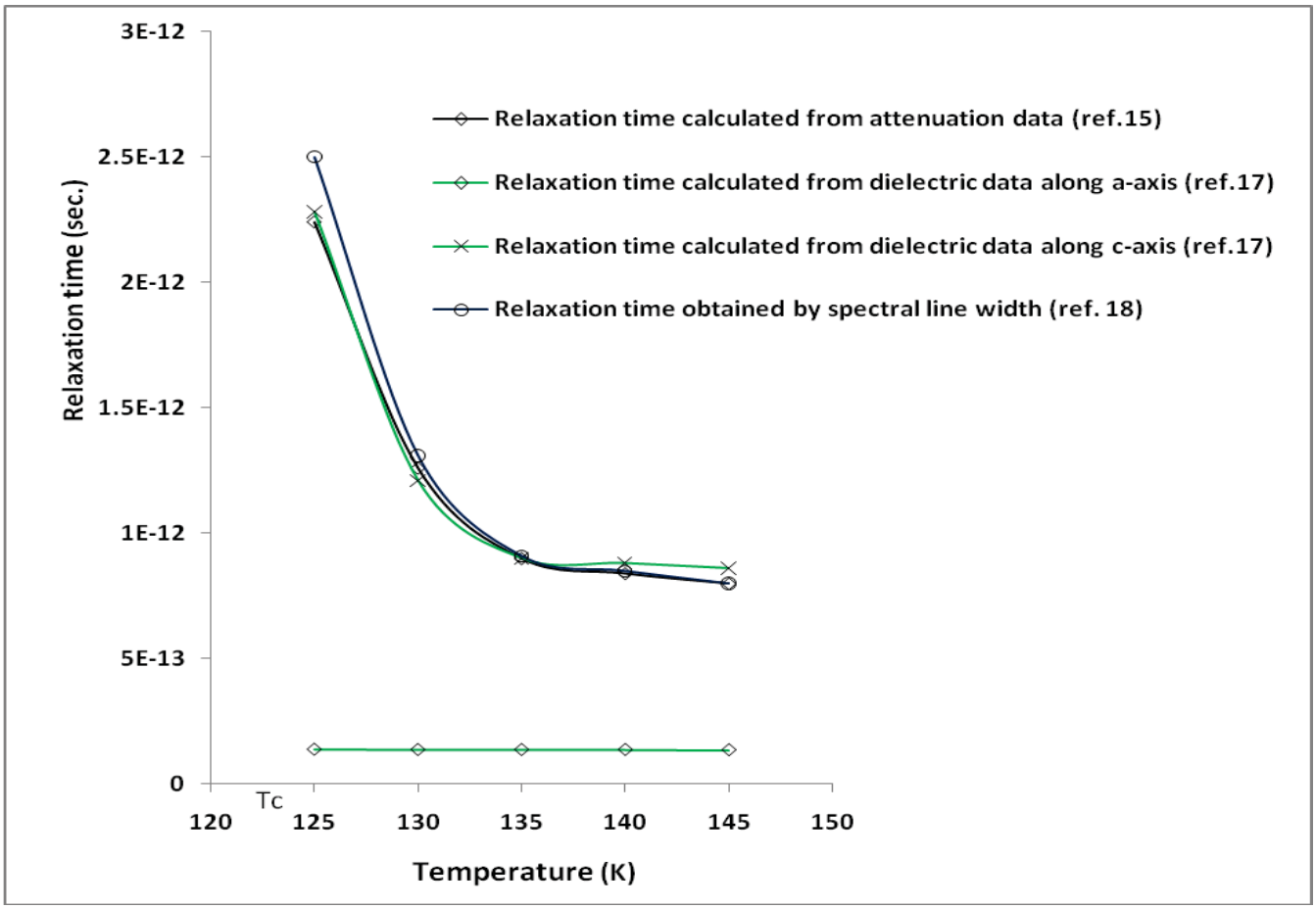

Fig.1: Temperature dependence of relaxation time calculated form different data in paraelecteic phase for KDP-type crystals.

The tangent loss is associated with the damping parameter (Γ_p). Damping can be understood as the creation of a virtual polarization mode excited by the transverse electromagnetic radiation and its subsequent decay into phonons by scattering from crystal defects, anharmonicity, etc. At the higher temperature the loss deviates from the Curie-Weiss behaviour and increases linearly with temperature. This behaviour suggests that at higher temperatures the phonon anharmonicity contributes significantly to the observed loss.

IV. Result and Discussion

From the present study, it can be concluded that the consideration of four cluster Hamiltonian alongwith the third - and fourth - order anharmonicities for the KDP-type ferroelectrics lead to the renormalization and stabilization of the relaxational soft mode and renormalization of the pseudo-spin exchange interaction constant. After applying Dyson's treatment and the decoupling of the correlation, appearing in the dynamical equation, it results, shift in frequency and facilitates the calculation of damping parameter, which is related to the relaxation time.

The present results reduce to the results of others [16, 19] if the width and shift are neglected. The method of double time thermal Green's function and Dyson's equation formalism have been found convenient and systematic to give the static and dynamical properties of a single framework of KDP-type system using four-cluster Hamiltonian alongwith phonon anharmonicities.

The anomalous behaviour of order-disorder KDP type ferroelectrics finds explanation by the consideration of collective proton-phonon interaction and third-and fourth- order phonon anharmonicities in the four-particle cluster Hamiltonian. The dielectric properties and ultrasonic attenuation strongly depend on the relaxational behaviour of the stochastic motion of $H_2PO_4^-$ group in KDP type ferroelectrics.

V. Conclusions

From this study we have calculated collective proton wave half width, collective phonon mode frequency shift in the frerquency response by considering higher order anharmonicity upto fourth order, which was not done by earlier workers, hence they could not calculate width and shift in the frequency response. We have calculated the relaxation time by using both the formalism i.e., proton Green's function methods and phonon Green's function method. We compare the present obtained relaxation time with those calculated by earlier worker and conclude that our result are good agreement with those of earlier worker [15,17,18], which is shown in Table-1 and Fig. 1.

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