Temperature Dependence of Dielectric Loss Tangent in KDP (KH₂PO₄) Type Crystals

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Keywords: KDP (KH₂PO₄), soft mode frequency, transverse dielectric loss tangent ($\tan\delta_a$), longitudinal dielectric loss tangent ($\tan\delta_c$).

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Temperature Dependence of Dielectric Loss Tangent in KDP (KH$_2$PO$_4$) Type Crystals

V. S. Bist $^{a}$ & N. S. Panwar $^{a}$

Abstract - Considering third- and fourth-order phonon anharmonic interactions terms in the four particle cluster model Hamiltonian proposed by Blinc et al [1982 J Phys, C15 4661] for the stochastic motion of $^{4}$PO$_2$H$_4$ groups for KDP (KH$_2$PO$_4$) type ferroelectrics, expressions for soft mode frequency and loss tangent are evaluated. For the calculations, method of double time temperature dependent Green’s function has been used. By fitting model values of physical quantities, the dielectric loss in paraelectric phase of KDP (KH$_2$PO$_4$) crystal at 9.2 GHz for field along the a-axis $(\tan \delta_{\alpha})$, and c-axis $(\tan \delta_{\gamma})$ have been calculated which compare well with experimental results of Kaminow et al [1963 Phy Rev,129 1562]. A good agreement has been found. In the microwave frequency rage, an increase in frequency is followed by an increase in transverse and longitudinal dielectric loss tangent. The loss decreases with increase in temperature for KDP (KH$_2$PO$_4$) crystal, in their paraelectric phase. This shows Curie-Weiss type behavior of the dielectric loss tangent.

Keywords: KDP (KH$_2$PO$_4$), soft mode frequency, transverse dielectric loss tangent $(\tan \delta_{\alpha})$, longitudinal dielectric loss tangent $(\tan \delta_{\gamma})$.

1. Introduction

The dynamical properties of ferroelectrics KDP (KH$_2$PO$_4$) type crystals have attracted much interest in recent years, due to their promising applications in electro-optical, thermal detectors, optical communication, memory display, and electronic ceramics industry. Cowley has given the soft mode frequency which largely determines the dielectric, thermal and scattering properties in the ferroelectrics crystals. At transition temperature the frequency of polar soft mode tends to zero and lattice displacement associated with this mode become unstable which explains the anomalous behavior of many of the physical properties of ferroelectric crystals such as dielectric constant and loss. In KDP (KH$_2$PO$_4$) crystal ($T_c=123$ K) the soft mode is connected with the pseudo spin-type motion of the proton between two equilibrium positions in the double minimum type O-H-O bond potential.

Many workers$^{5-10}$ have investigated theoretically the dielectric and other properties of KDP (KH$_2$PO$_4$) type crystals using pseudo spin model and its extension, i.e., pseudo spin lattice coupled mode model. Wang et al$^{11}$ and Jiang et al$^{12}$ have applied undetermined constant method to pseudo spin model with spin coupling term. They have not considered phonon parts in their calculations which however has a very important contribution in crystal. Ganguli et al$^{13}$ have used PLCM model with fourth order phonon anharmonic interaction term. They however decoupled the correlations at an early stage. In doing so some important interactions were disappeared. In this way they could not obtain better and convincing results to explain dielectric and phase transition properties of KDP (KH$_2$PO$_4$) type crystals. Yoshimitsu and Matsubara$^{14}$ and Havlin and Sompolinsky$^{15}$ performed extensive calculations for the static thermodynamics behavior in the four-particle cluster approximation and found satisfactory agreement with the experimental data, but they could not explain the dielectric properties. Ganguli et al$^{16}$ modified Ramakrishnan and Tanaka$^{17}$ theory by considering anharmonic interaction interaction terms. Their treatment explains many features of order-disorder ferroelectrics. However, due to insufficient treatment of anharmonic interactions, they could not obtain quantitatively good results and could not describe some interesting properties, like dielectric, ultrasonic attenuation, etc.

In the present study, the authors consider the four-particle cluster model Hamiltonian with the anharmonic contributions up to fourth order of KDP (KH$_2$PO$_4$) crystal. This model successfully describes the static as well as dynamic properties of KDP (KH$_2$PO$_4$) system along z-directions. The phonon anharmonic interactions have been found very important in explaining dielectric, thermal and scattering properties of solids by many authors$^{4,16-20}$ in the past. We use the double-time thermal dependent retarded Green’s functions techniques$^{18-21}$ and Dyson’s equation for the development and evaluate expressions for proton renormalized frequency of the coupled system, collective proton wave half widths, and loss. Using the model parameters given by Ganguli et al$^{10}$ in the theoretical expression for width, shift, and loss tangent have been calculated for KDP (KH$_2$PO$_4$).
The frequency and temperature dependence of the transverse dielectric loss tangent \( \tan \delta_a \) and longitudinal dielectric loss tangent \( \tan \delta_c \) of KDP (KH\(_2\)PO\(_4\)) at 9.2 GHz and in the temperature ranges (120-150K) for field along the a-axis \( \tan \delta_a \) and c-axis \( \tan \delta_c \) of KDP (KH\(_2\)PO\(_4\)) have been calculated and compared with experimental results of Kaminow et al\(^{22}\).

At higher temperature the loss deviates from the Curie-Weiss type behavior and increases linearly with temperature. This behavior suggests that at higher temperatures the phonon anharmonicity contributes significantly in the observed loss.

**II. Model Hamiltonian**

We use the four-particle cluster model Hamiltonian\(^7\) by including third and fourth order phonon anharmonic interaction terms, which is expressed in our previous paper as\(^{23}\):

\[
H = -2\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z - \frac{1}{4} \sum_{ijkl} J'_{ijkl} S_i^x S_j^x S_k^x S_l^x + \frac{1}{4} \omega_k (A_k^+ A_k + B_k^+ B_k) - \sum_{ik} \frac{x}{i} S_i^x A_k^+, \tag{1}
\]

\[
H = \sum_{k} V_3 (\tilde{k}_1^x \tilde{k}_2^x \tilde{k}_3^x) A_{k_1} \cdot A_{k_2} \cdot A_{k_3}^+ + \sum_{k} V_4 (\tilde{k}_1^x \tilde{k}_2^x \tilde{k}_3^x \tilde{k}_4^x) A_{k_1} \cdot A_{k_2} \cdot A_{k_3}^+ \cdot A_{k_4}^+.
\]

**III. Green’s Function: Shift, Width and Soft Mode Frequency**

Following Zubarev\(^{24}\) we consider the evaluation of Green’s function as

\[
G^{zz}(t-t') = <S_q^z(t); S_q^z(t')> = -j \theta(t-t') <[S_q^x(t), S_q^z(t')]>, \tag{2}
\]

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\(^{23}\) which finally takes the forms

\[
G^{zz}(\omega + j\varepsilon) = \pi^{-1} <S_q^x > \delta_{qq'} [\omega^2 - \tilde{\Omega}^2 + j \Gamma_s(q, \omega)]^{-1}, \tag{3}
\]

\( \tilde{\Omega} \) is the proton renormalized frequency of the coupled system, which on solving self consistently takes the form:

\[
\tilde{\Omega}^2 = \Omega^2 + 2\Omega \Delta_s(q, \omega), \tag{4}
\]

where \( \Delta_s(q, \omega) \) the proton mode frequency shift, \( \Omega \) is the proton tunneling frequency, and \( \tilde{\Omega} \) the renormalized frequency. The collective proton wave half width \( \Gamma_s(q, \omega) \), and collective phonon mode frequency, and collective phonon half widths is given in our previous paper as\(^{25}\):

\[a) \text{ collective proton wave half width} \]

\[
\Gamma_s(q, \omega) = -\frac{4\pi \Gamma_q^2 \omega_q^2 <S_q^x> \delta_{qq'} \Gamma_p^2}{\Omega(\omega^2 - \tilde{\omega}^2)^2 + 4 \omega^2 \Gamma_p^2} + \frac{\pi a^2 b^2}{2\Omega} \left\{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \right\} + \frac{\pi a^2 \tilde{\Omega}^2}{2b} \left\{ \delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \right\}. \tag{5a}
\]

\[b) \text{ collective phonon mode frequency} \]

\[
\tilde{\omega}^2_{q\pm} = \frac{1}{2} \left( \tilde{\omega}^2_q + \tilde{\Omega}^2 \right) \pm \frac{1}{2} \left[ (\tilde{\omega}^2_q + \tilde{\Omega}^2)^2 + 16(\omega_q^2 \Omega <S^x>) \right]^{1/2}, \tag{5b}
\]

where

\[
\tilde{\omega}^2_q = \omega^2_q + 8\omega_q (2V_3 + V_4) \coth \left( \frac{\beta \omega_q}{2} \right). \tag{5c}
\]
c) collective phonon half width

$$\Gamma_p = \frac{-4V^2}{q^2} \Omega^2 < S_q^2 > \Gamma_s (q, \omega) + 6\pi \sum q \frac{v_2^2(q, q')}{q} \frac{\omega q n_q}{\omega q} \{\delta(\omega - 2\tilde{\omega}_q) - \delta(\omega + 2\tilde{\omega}_q)\}
$$

$$+ 12\pi \sum q \frac{v_2^2(q, q')}{q} \frac{\omega q^2 q'}{\omega q^2 q'} \{1 + n_q n_q \} \{\delta(\omega - 2\tilde{\omega}_q - \tilde{\omega}_q) - \delta(\omega + 2\tilde{\omega}_q - \tilde{\omega}_q)\}
$$

$$+ (n_q^2 - 1) \{\delta(\omega - 2\tilde{\omega}_q + \tilde{\omega}_q) - \delta(\omega + 2\tilde{\omega}_q - \tilde{\omega}_q)\} + 2(n_q^2 - 1) \{\delta(\omega - \tilde{\omega}_q - \tilde{\omega}_q) - \delta(\omega + \tilde{\omega}_q)\}
$$

$$+ 36\pi \sum q \frac{v_2^2(q, q')}{q} \frac{\omega q^2 q'}{\omega q^2 q'} \{1 + 3n_q^2 \} \{\delta(\omega - 3\tilde{\omega}_q) - \delta(\omega + \tilde{\omega}_q)\} + (n_q^2 - 1) \{\delta(\omega - \tilde{\omega}_q) - \delta(\omega + \tilde{\omega}_q)\}\] (5d)

In the vicinity of transition temperature or in the paraelectric phase one may expand $\tilde{\omega}$ in the power of $(T - T_c)$ around its value at $T_c$ getting immediately

$$\tilde{\omega}_{q} = \left(\frac{\tilde{\omega}_{q}}{q} - \frac{\partial T}{T}ight) (T - T_c) \quad (T = T_c) \quad (6a)
$$

$$\tilde{\omega}_{q} = K(T - T_c) \quad (6b)
$$

IV. LOSS TANGENT

Following Kubo$^{26}$ and Zubarev$^{24}$. The dielectric susceptibility is obtained as

$$\chi_{mn}(\omega) = \lim_{\varepsilon \to 0} - 2\pi N \mu^2 G_{mn}(\omega + j\varepsilon), \quad (7)
$$

where $N$ is the number of unit cell in the sample, and $\mu$ is the effective dipole moment per unit cell. The dielectric constant can be calculated by using the relation $\varepsilon = 1 + 4\pi \chi$, and the real part of which is given by

$$\varepsilon'(\omega) = 1 + 8\pi N \mu^2 \tilde{\omega} (\omega^2 - \tilde{\omega}^2) \left[\omega^2 - (\omega^2 - \tilde{\omega}^2)^2 + 4\omega^2 \Gamma_\delta(\omega)\right]^{-1} \quad (8)
$$

and the tangent loss

$$\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = -\omega \Gamma_p \left[(\omega^2 - \tilde{\omega}^2)\right]^{-1}, \quad (9)
$$

The frequencies $\tilde{\omega}_{\pm}$ are the normal modes of the system. The $\tilde{\omega}_{+}$ mode gives the contribution for weakly temperature transverse relaxation behavior of the observed transverse loss tangent (tan $\delta_{\omega}$) and $\tilde{\omega}_{-}$ mode contribution to the longitudinal relaxation behavior of the observed longitudinal loss tangent (tan $\delta_{\omega}$). The $\tilde{\omega}_{+}$ mode corresponds to transverse $E(x, y)$ mode, which is responsible for the observed transverse dielectric properties of KDP. In the simplest approximation $\tilde{\omega}_{+}$ can be written as $\tilde{\omega}_{+} = K_1 + K_2 T$, ($K_1$, $K_2$ are temperature independent parameter). At microwave frequencies, $\omega, (\omega / \tilde{\omega} = 10^{-3})$, one may approximate $\tilde{\omega} >> \omega$ and $\tilde{\omega} >> \Gamma(\omega)$ so that eq.(9) reduces to

$$\tan \delta = -\omega \Gamma(\omega) \tilde{\omega}^{-2} \quad (10)
$$

Now writing $\Gamma(\omega)$ in the form of

$$\Gamma(\omega) = \alpha + \beta T + \gamma T^2
$$

and by making use of Eq.(6) for $\tilde{\omega}$ we obtain eq. (10) in the form of

$$(T - T_C) \tan \delta = -\omega(A + BT + CT^2), \quad (11)
$$

Where $A = \alpha K^{-1}$, $B = \beta K^{-1}$, and $C = \gamma K^{-1}$, $K$ being given by eq (6) and $\alpha, \beta$ and $\gamma$ are obtained with the help of Eqs. (5a to 5d) which comes out as
\[ \alpha = \frac{2\pi \bar{q}^2 \omega_q^2 \Omega}{\Omega (\omega^2 - \bar{\omega}^2)^2} \left[ \left\{ \delta(\omega - \bar{\Omega}) - \delta(\omega + \bar{\Omega}) \right\} \right] \]

\[ \beta = \frac{24\pi \bar{q}^2 \omega_q^2 \Omega k}{(\omega^2 - \bar{\omega}^2)^2} \sum |V(3(qq'))^2 \left( \frac{\omega_q \omega q'}{(\omega_q \omega q')^2} \right) \left[ \delta(\omega - 2\bar{\omega}q - \bar{\omega}q') - \delta(\omega + 2\bar{\omega}q + \bar{\omega}q') \right] \]

\[ + \left( \frac{\omega_q^2}{\omega q} - 1 \right) \left\{ \delta(\omega - 2\bar{\omega}q + \bar{\omega}q') - \delta(\omega + 2\bar{\omega}q - \bar{\omega}q') \right\} + 2\left( \frac{\omega_q^2}{\omega q} - 1 \right) \left\{ \delta(\omega - \bar{\omega}q) - \delta(\omega + \bar{\omega}q) \right\} \]

\[ \gamma = \frac{144\pi \bar{q}^2 \omega_q^2 \Omega K}{(\omega^2 - \bar{\omega}^2)^2} \sum |V(4(qq'))^2 \left( \frac{\omega_q^2}{(\omega_q)^4} \right) \left[ 1 + 3 \frac{\omega_q^2}{\omega q} \right] \left\{ \delta(\omega - 3\bar{\omega}q) - \delta(\omega + 3\bar{\omega}q) \right\} \]

\[ + \left( \frac{\omega_q^2}{\omega q} - 1 \right) \left\{ \delta(\omega - \bar{\omega}q) - \delta(\omega + \bar{\omega}q) \right\} \]

V. Numerical Calculations

By using Blinc-de Gennes model parameter values for KDP (KH₂PO₄) crystal as given by Ganguli et al. have been given in Table-1, we have calculated loss tangent of KDP (KH₂PO₄) at 9.2 GHz for fields along the a-axis (tan δₐ), and c-axis (tan δₖ), collective phonon mode frequency (\( \omega_{\tilde{b}} \)), and Collective phonon half width (\( \Gamma(\omega) \)) in paraelectric phase, given in Table-2.

<table>
<thead>
<tr>
<th>( \Omega ) (cm⁻¹)</th>
<th>( J ) (cm⁻¹)</th>
<th>( J' ) (cm⁻¹)</th>
<th>( T_C ) (K)</th>
<th>( V/kT_C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>82</td>
<td>334</td>
<td>440</td>
<td>123</td>
<td>0.299</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>125</th>
<th>130</th>
<th>135</th>
<th>140</th>
<th>145</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>tan δₐ</td>
<td>0.004</td>
<td>0.00398</td>
<td>0.00397</td>
<td>0.00396</td>
<td>0.00395</td>
<td>0.00394</td>
</tr>
<tr>
<td>tan δₖ</td>
<td>0.068</td>
<td>0.033</td>
<td>0.0279</td>
<td>0.0253</td>
<td>0.0247</td>
<td>0.0241</td>
</tr>
<tr>
<td>( \Gamma(cm^{-1}) \times 10^{-3} )</td>
<td>2.87</td>
<td>2.31</td>
<td>1.76</td>
<td>1.88</td>
<td>1.90</td>
<td>1.92</td>
</tr>
<tr>
<td>( \bar{\omega}(cm^{-1}) )</td>
<td>45.65</td>
<td>57.04</td>
<td>58.69</td>
<td>63.04</td>
<td>64.91</td>
<td>66.78</td>
</tr>
</tbody>
</table>

VI. Frequency Dependence of Loss Tangent

Loss tangent is frequency dependent. For microwave engineering, lossy materials are given with dielectric constant (\( \varepsilon_r \)) and loss tangent (tan δ)

Putting calculated values of \( \Gamma(\omega) \) and \( \bar{\omega} \) for different temperatures into equation (10) or (11), loss tangent is obtained in paraelectric phase of KDP (KH₂PO₄) in 9.2 GHz at 98 K for field along the a-axis (tan δₐ), and c-axis (tan δₖ). The variations of dielectric loss tangent versus frequency are shown in Fig. 1 and 2. The increases in frequency (1-30GHz) is followed by an increase in loss (1-12) X10². Our theoretical results fairly agree with experimentally reported results within experimental errors.
Figure 1: Frequency dependence of loss tangent of KDP ($\text{KH}_2\text{PO}_4$) at 98 K for fields along the $a$-axis, $\left(\tan \delta_a\right)^{22}$, our calculation.

Figure 2: Frequency dependence of loss tangent of KDP ($\text{KH}_2\text{PO}_4$) at 98 K for fields along the $c$-axis, $\left(\tan \delta_c\right)^{22}$, our calculation.
VII. Temperature Dependence of Loss Tangent

Using equations (10) or (11) and our calculated values from Table-2, we have calculated loss tangent at 9.2 GHz in the temperature range (120 -150 K) for fields along the a-axis ($\tan \delta_a$), and c-axis ($\tan \delta_c$) for KDP ($\text{KH}_2\text{PO}_4$) crystals. We have calculated losses at 9.2 GHz frequency because we have experimental data available only at this frequency range. The transverse dielectric tangent loss ($\tan \delta_a$), and longitudinal dielectric tangent loss ($\tan \delta_c$) versus temperature are shown in Fig. 3 and 4. It is found to have a relatively low $\tan \delta$ value, indicating that it possess lesser number of electrically active defects, which is a vital parameter of electro-optics device fabrications. It is also observed that the higher dielectric loss occurs at high temperatures. Our theoretical results are in good agreement with experimental results of Kaminow and Harding $^{22}$. 

**Figure 3**: Temperature dependence of loss tangent of KDP ($\text{KH}_2\text{PO}_4$) at 9.2 GHz for fields along a-axis ($\tan \delta_a$) $^{22}$, our calculation
Figure 4: Temperature dependence of loss tangent of KDP (KH₂PO₄) at 9.2 GHz for fields along the c-axis, \((\tan \delta_c)^{22}\), our calculation

VIII. Conclusion

In this paper, by modifying the four-particle cluster model for KDP (KH₂PO₄) type ferroelectric crystal by adding anharmonic contributions up to fourth order, we have evaluated theoretically the expressions for the soft mode frequency, and loss tangent. Using Blinc-de Gennes model parameter value given by Ganguli et al \(^{10}\), we have calculated temperature variation of loss tangent of KDP (KH₂PO₄) at 9.2 GHz. From the present study, it is concluded that the consideration four-particle cluster model Hamiltonian along with the third and fourth-order anharmonicity for the KDP (KH₂PO₄) type ferroelectrics leads to renormalization and stabilization of the relaxational soft mode. The decoupling of the correlations appearing in the dynamical equations after applying Dyson’s equation, result in shift in frequency and facilitate the calculation of damping parameter, which is related to loss tangent. The present results reduce to results of others workers \(^{5,6,9,11,12}\) if width and shift are neglected. Only Ganguli et al \(^{10}\) have considered fourth-order anharmonic term but they also could not do it in a convenient way as they truncated the spin correlations at an early stage, and so could not obtain width and shift. In this way they could not explain dielectric loss and also could not obtain better results as...
reported by us. Our equations (10) and (11) along with figures 1 and 2 show that loss tangent \( \delta \) vary linearly with frequency which is in agreement with experiments. The temperature dependence of loss tangent in paraelectric phase of KDP (KH\(_2\)PO\(_4\)) at 9.2 GHz for field along the a-axis (\( \tan \delta_a \)) and c-axis (\( \tan \delta_c \)) have been calculated which compare well with experimental results of Kaminow et al\[22\]. A good agreement has been found. At higher temperature the losses deviates from the Curie-Weiss type behavior and increases linearly with temperature. This behavior suggests that at higher temperatures the phonon anharmonicity contributes significantly in the observed loss.

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