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# Temperature Dependence of Inverse Dielectric Susceptibility in KDP-Type Crystals

By V. S. Bist & N. S. Panwar

*HNB Garhwal University, India*

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# Temperature Dependence of Inverse Dielectric Susceptibility in KDP-Type Crystals

V. S. Bist<sup>α</sup> & N. S. Panwar<sup>σ</sup>

**Abstract** - By using four particle cluster model Hamiltonian along with third and fourth order phonon anharmonic interaction terms for KDP-type crystals, expressions for renormalized soft mode frequency, and inverse dielectric susceptibility have been obtained. The method of double time temperature dependent Green's function has been used for calculation. Fitting the values of model parameters, the temperature dependence of soft mode frequency and inverse dielectric susceptibility has been evaluated. The inverse dielectric susceptibility was observed increases linearly with temperature, for KDP crystal, in its paraelectric phase. Theoretical results are compared with experimental results of Kim et al [Physics Review B73, 134114 (2006), and Current Applied Physics 9(2009) 1307]. A good agreement has been found between the reported and present results.

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## 1. INTRODUCTION

Potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), potassium dihydrogen arsenate ( $\text{KH}_2\text{AsO}_4$ ) and their deuterated forms, generally called KDP-type ferroelectrics, have been extensively studied due to their promising applications in optical communication, memory display and electro-optic devices. Much theoretical work has been done on KDP-type ferroelectrics as compared to ADP-type antiferroelectrics. KDP crystal undergoes a first order transition at 123 K, accompanied by tetragonal  $I\bar{4}2d(D_{2d}^{12})$ , at room temperature; and orthorhombic  $Fdd2(CD_{2v}^{19})$ , below transition temperature ( $T_c$ ). The  $(\text{H}_2\text{PO}_4^-)$  network, in which each phosphate group is linked by O-H-O bonds to a tetrahedron arrangement of phosphate group neighbors. All KDP-type ferroelectrics and selenites show a nearly two-fold increase (isotope effect) in transition temperature ( $T_c$ ) on deuteration.

The  $\text{KH}_2\text{PO}_4$  (KDP)-type crystals are interesting hydrogen-bonded materials undergoing structural phase transition accompanied by ferroelectricity or antiferroelectricity. In these crystals, it is known that

proton in the double well potentials on the hydrogen bonds are involved in a phase transition accompanied by displacements in the heavy atom (K, P, O) structure. KDP undergoes the ferroelectric phase transition at 123K<sup>1</sup>. An outstanding peculiarity with KDP is the proton-deuteron "isotope effect", that raises the transition temperature by about 100 K mainly due to the change in the O-O separation rather than to a change in the tunneling frequency by the mass change<sup>2</sup>. The protons are self-trapped in one or the other of its equivalent positions according to recent neutron Compton scattering experiments<sup>3</sup>. While the tunneling model does not consider the hydrogen-bond geometry, the  $\text{PO}_4$  tetrahedral distortion has theoretically been shown to give rise to a change in the ground state energy<sup>4, 5</sup>.

Earlier Havlin, Litov, and Uehling<sup>6</sup>, using a mean field approximation, a Curie-type transverse susceptibility was theoretically obtained for  $T > T_c$ , and Semwal and Sharma<sup>7</sup> using Green's function method have studied ferroelectric transition and dielectric properties of KDP-type crystals. Many workers<sup>8-12</sup> have experimentally studied the dielectric properties of these crystals. Expressions for different physical parameters were developed to explain ferroelectric transitions in displacive<sup>13-16</sup> and order-disorder<sup>17-21</sup> type crystals.

In our previous works<sup>20-21</sup> we used the Blinc's Hamiltonian including the lattice anharmonicity upto fourth order, for the stochastic motion of  $\text{H}_2\text{PO}_4^-$  groups. Applying Green's functions techniques and Dyson's equation the higher order correlations were evaluated using the renormalized Hamiltonian. The proton renormalized frequency of the coupled system and collective proton wave half widths have been evaluated. Temperature dependence of relaxation time in KDP-type ferroelectrics, and dielectric properties of order-disorder type crystals, were studied above  $T_c$ . In the present study the same Hamiltonian, same techniques have been used to obtain expressions for renormalized soft mode frequency and inverse dielectric susceptibility. Fitting the values of model parameters in the obtained expressions, the temperature dependence of soft mode frequency and inverse dielectric susceptibility has been evaluated. The inverse dielectric susceptibility increased linearly with temperature for KDP crystal in its paraelectric phase. Theoretical results are compared with experimental result of Kim *et al*<sup>8-9</sup>.

**Author α** : STO (Electronics), Department of (USIC) Instrumentation Engineering, School of Engineering and Technology, HNB Garhwal University Srinagar (Garhwal) Uttarakhand - 24 6174, India.

E-mails : vsbist\_usic68@yahoo.com, vsbistusic1968@gmail.com

**Author σ** : Professor and Dean, School of Engineering and Technology, Head USIC, HNB Garhwal University Srinagar (Garhwal) Uttarakhand - 24 6174, India. E-mail : nspusic@gmail.com

## II. DIELECTRIC SUSCEPTIBILITY

The response of a dielectric field is conveniently described by the dielectric susceptibility. Following Kubo<sup>22</sup> and Zubarev<sup>23</sup>, the general expression for complex dielectric susceptibility tensor  $\chi_{mn}(\omega)$  can be expressed as

$$\chi_{mn}(\omega) = \lim_{\varepsilon \rightarrow 0} -2\pi G_{mn}(\omega + j\varepsilon). \quad (1)$$

Where  $G_{mn}(\omega)$  is the Fourier transform of the retarded double-time thermal Green's function between the  $m^{\text{th}}$  and  $n^{\text{th}}$  components of the crystal dipole moment operators  $\vec{M}(t)$  in the Heisenberg representation, and is defined as

$$\begin{aligned} G_{mn}(t-t') &= \langle\langle M_m(t); M_n(t') \rangle\rangle \\ &= -j\theta(t-t') \langle [M_m(t); M_n(t')] \rangle. \end{aligned} \quad (2)$$

Where  $\theta(t-t')$  is the Heaviside step function and the angular brackets  $\langle \dots \rangle$  denote the thermal ensemble average. The crystal dipole moment  $\vec{M}(t)$  depends on the ionic co-ordinates, like potential energy, and can be expanded in a Taylor's series in terms of ionic displacements. Because of the periodic boundary conditions, i.e., symmetry considerations, imposed on the ionic motions, only the low lying relaxational modes have non-zero polarization associated with them. Thus only the expansion coefficients which correspond to lowest frequency mode, i.e.,  $\vec{M}(q, j)$  (where  $q = 0$  for ferroelectrics, and  $j$  relates the modes of spectrum) contribute to the dielectric susceptibility, significantly. Thus we can write the dielectric susceptibility as

$$\chi_{mn}(\omega) = \lim_{\varepsilon \rightarrow 0} -2\pi N\mu^2 G_{mn}(\omega + j\varepsilon), \quad (3)$$

where  $N$  is the number of unit cells in the sample and  $\mu$  is the effective dipole moment per unit cell, and

$$G_{mn}(\omega + j\varepsilon) = \langle\langle A_q(t); A_q(t') \rangle\rangle = G'(\omega) - jG''(\omega). \quad (4)$$

Where  $G'(\omega)$  and  $G''(\omega)$  are real and imaginary parts of the Green's function defined by<sup>20</sup>. The dielectric constant can be evaluated using the relation

$$\varepsilon(\omega) = 1 + 4\pi\chi = \varepsilon'(\omega) - j\varepsilon''(\omega), \quad (5)$$

where  $\varepsilon'(\omega)$  and  $\varepsilon''(\omega)$  are real and imaginary parts of the dielectric constant. The real part of the dielectric constant can be expressed as

$$\varepsilon'(\omega) - 1 = -8\pi N\mu^2 G'(\omega), \quad (6)$$

and the imaginary part

$$\varepsilon''(\omega) = -8\pi N\mu^2 G''(\omega). \quad (7)$$

Using equation (3) and acoustic phonon Green's function by<sup>20</sup>. The dielectric susceptibility for KDP-system can be obtained as

$$\chi(\omega) = \frac{-2N\mu^2 \tilde{\omega}}{[\omega^2 - \tilde{\omega}^2 + 2j\omega \Gamma_P(\omega)]}. \quad (8)$$

Where  $\tilde{\omega}$ ,  $\Gamma_P(\omega)$  are the collective mode frequency, and damping constant, respectively is given by<sup>20</sup>. The range of frequencies used in ultrasound<sup>24</sup>, Brillouin<sup>25</sup> and susceptibility<sup>24</sup> measurement experiments are such that  $\omega \ll \tilde{\omega}$ . Thus equation (8) reduces to

$$\chi(\omega) = \frac{2N\mu^2 \tilde{\omega}}{\tilde{\omega}^2 [1 - j\omega\tau_P]}. \quad (9)$$

Where the polarization relaxation time ( $\tau_P$ ) is given by<sup>26</sup>. This approximation of equation (9) is equivalent to Debye relaxation susceptibility. Furthermore, if  $\omega\tau_P \ll 1$ , which is true for KDP-system<sup>22</sup>, equation (9) can be further reduced to

$$\chi(\omega) = \frac{2N\mu^2 \tilde{\omega}}{\tilde{\omega}^2} (1 + j\omega\tau_P), \quad (10)$$

Using equation (5) in equation (8) expression for dielectric constant, can be obtained as

$$\varepsilon(\omega) - 1 = \frac{-8\pi N\mu^2 \tilde{\omega} \left[ (\omega^2 - \tilde{\omega}^2) - 2j\omega\Gamma_P(\omega) \right]}{\left[ (\omega^2 - \tilde{\omega}^2)^2 + 4\omega^2 \Gamma_P^2(\omega) \right]}. \quad (11)$$

The imaginary part of which can be written as

$$\varepsilon''(\omega) = -\frac{8\pi N\mu^2 \tilde{\omega} 2\omega\Gamma_P(\omega)}{(\omega^2 - \tilde{\omega}^2)^2 + 4\omega^2 \Gamma_P^2(\omega)}. \quad (12)$$

and the real part as

$$\varepsilon'(\omega) - 1 = -\frac{8\pi N\mu^2 \tilde{\omega} (\omega^2 - \tilde{\omega}^2)}{(\omega^2 - \tilde{\omega}^2)^2 + 4\omega^2 \Gamma_P^2(\omega)}, \quad (13)$$

for the experimental range of frequencies,  $\omega \ll \tilde{\omega}$  and ( $\omega\tau_P \ll 1$  for KDP), equation (13) can be reduced to ( $\varepsilon' \gg 1$ )

$$\varepsilon'(\omega) = \frac{8\pi N\mu^2 \tilde{\omega}}{\tilde{\omega}^2 + \omega^2 \tau_p^2} = \frac{8\pi N\mu^2 \tilde{\omega}}{\tilde{\omega}^2}, \quad (14)$$

where  $\tilde{\omega}^2_{\pm}$ ,  $\tilde{\omega}_+$ ,  $\tilde{\omega}_-$ , and  $\tilde{\omega}$  are represented by<sup>20-21</sup>. The inverse susceptibilities, obtained from  $\varepsilon(\omega) = 1 + 4\pi\chi$ .

$$\chi_a^{-1}(\omega) = \frac{\tilde{\omega}^2}{2N\mu^2 \tilde{\omega} - \tilde{\omega}^2}. \quad (15)$$

The dielectric loss ( $\tan \delta$ ), for the dissipation of power in the dielectric crystal is defined as the ratio of imaginary and real parts of the dielectric constant, i.e.,

$$\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = \frac{G''(\omega)}{G'(\omega)}. \quad (16)$$

The dielectric loss tangent ( $\tan \delta$ ) in a dielectric sample given by equation (16), can be further written as

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

The  $\tilde{\omega}_+$  mode gives the contribution for a weakly temperature dependent transverse relaxation behavior of the observed transverse tangent loss ( $\tan \delta_a$ ), can be written as

$$\tan \delta_a = \frac{-\omega\Gamma_p}{(\omega^2 - \tilde{\omega}_+^2)}, \quad (18)$$

$\tilde{\omega}_-$  mode contributes to the longitudinal relaxational behavior of the longitudinal tangent loss ( $\tan \delta_c$ ), which can be written as

$$\tan \delta_c = \frac{-\omega\Gamma_p}{(\omega^2 - \tilde{\omega}_-^2)}. \quad (19)$$

### III. NUMERICAL CALCULATIONS

By using Blinc-de Gennes model parameters for KDP as given by Ganguli et al<sup>28</sup>. We have calculated width, shift, collective phonon mode frequency, transverse dielectric constant  $\varepsilon_a(0)$ , observed dielectric constant  $\varepsilon_c(0)$ , loss tangent and the inverse susceptibilities are calculated using respective equations are tabulated in table 1.

Table 1: Calculated values for KDP crystal in PE phase

| Temperature (K)                                           | 125    | 130     | 135     | 140     | 145     | 150     | Reference            |
|-----------------------------------------------------------|--------|---------|---------|---------|---------|---------|----------------------|
| $\Gamma_p(\omega) \times 10^{-4}$<br>( $\text{cm}^{-1}$ ) | 2.87   | 2.31    | 1.76    | 1.88    | 1.90    | 1.92    | 20                   |
| $\tilde{\omega}$ ( $\text{cm}^{-1}$ )                     | 45.65  | 57.04   | 58.69   | 63.04   | 64.91   | 65.85   | 20                   |
| $\varepsilon_a(0)$                                        | 63     | 62      | 61      | 60      | 59      | 58      | 21                   |
| $\varepsilon_c(0)$                                        | 35714  | 6144    | 2286    | 874     | 486     | 359     | 21                   |
| $\tan \delta_a$                                           | 0.004  | 0.00398 | 0.00397 | 0.00396 | 0.00395 | 0.00394 | 21                   |
| $\tan \delta_c$                                           | 0.067  | 0.035   | 0.0261  | 0.0255  | 0.0250  | 0.02    | 21                   |
| $\tilde{\omega} \times 10^3$ (MHz)                        | 1.3685 | 1.7104  | 1.7594  | 1.8898  | 1.9459  | 1.9476  | <i>Present study</i> |
| $\chi_a^{-1} \times 10^{-3}$                              | 202.68 | 206     | 209.4   | 212.9   | 216.6   | 220.04  | <i>Present study</i> |
| $\chi_c^{-1} \times 10^{-4}$                              | 3.518  | 20.45   | 54.99   | 143.78  | 259.13  | 408.49  | <i>Present study</i> |

### IV. TEMPERATURE DEPENDENCE OF INVERSE DIELECTRIC SUSCEPTIBILITY

The inverse dielectric susceptibility has been calculated in the paraelectric phase at 10 GHz for KDP crystal obtained from  $\varepsilon(\omega) = 1 + 4\pi\chi$ . The temperature variations of inverse dielectric susceptibility have also

shown in figures 1 and 2. The theoretical results are in fair agreement with experimental result of Kim et al<sup>8</sup>. The solid lines are linear fits above  $T_c$ .

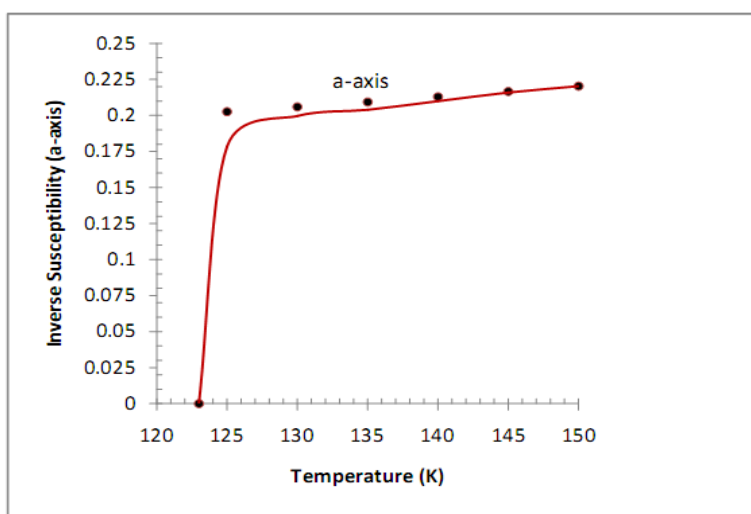


Figure 1 : Temperature dependence of inverse susceptibility in KDP crystal (a-axis)

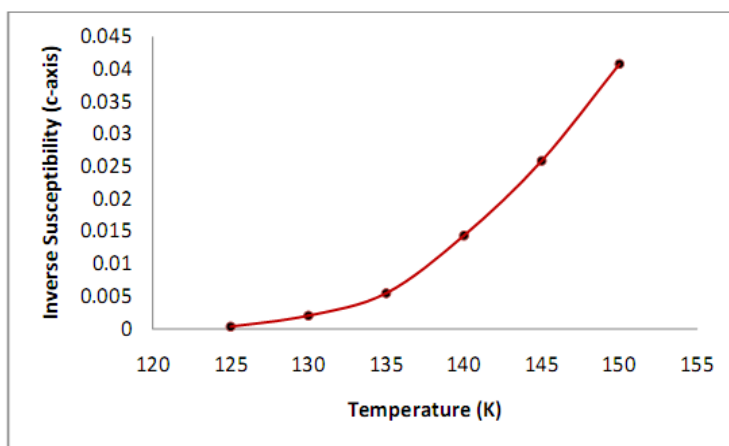


Figure 2 : Temperature dependence of inverse susceptibility in KDP crystal (c-axis)

## V. FREQUENCY DEPENDENCE OF DIELECTRIC LOSS

Putting calculated value of  $\Gamma_p(\omega)$ ,  $\tilde{\omega}$ , in the temperatures region  $T > T_c$ , into equations (18) and

(19), dielectric loss is obtained for KDP crystals at 9.2 GHz at 123K. The variations are shown in figure 3. The increase in loss is followed by an increase in frequency in KDP crystal. The dielectric loss versus  $(T-T_c)^{-1}$  for KDP crystal is shown in figure 4.

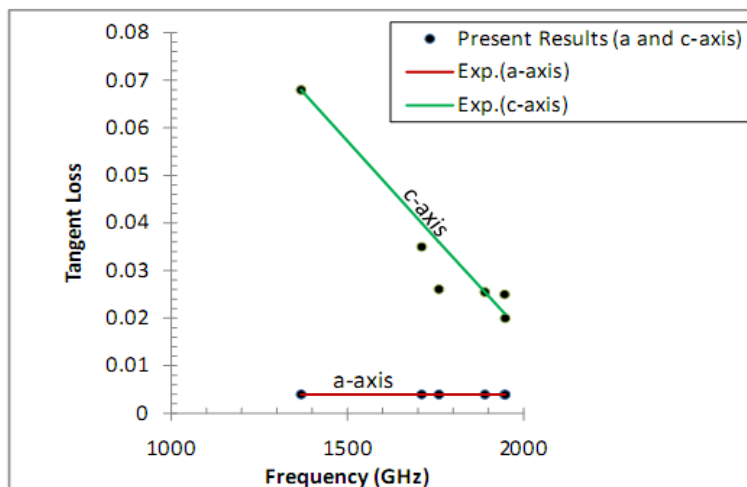


Figure 3 : Frequency dependence of dielectric loss in KDP crystal

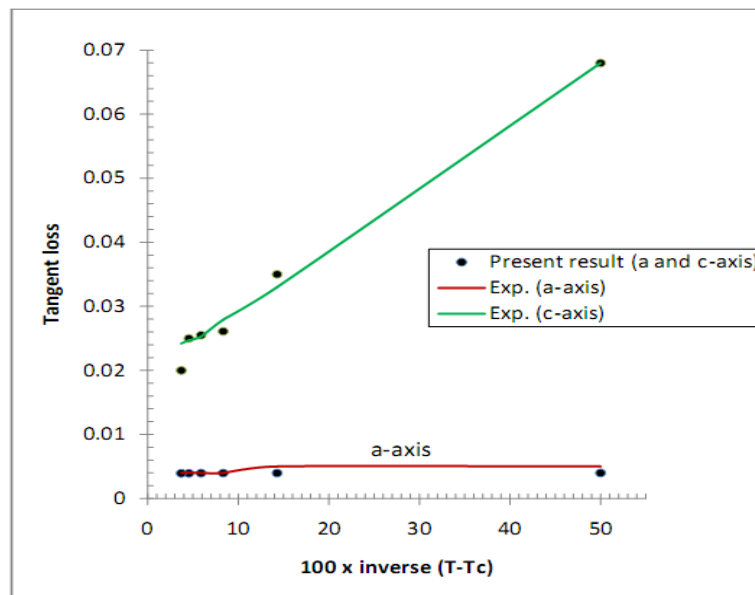


Figure 4 : Temperature dependence of dielectric loss in KDP crystal

## VI. RESULT AND DISCUSSION

In this paper, the four-particle cluster model Hamiltonian for KDP-type ferroelectric crystals has been modified by adding the third and fourth order phonon anharmonic interaction terms. Expressions for the inverse susceptibility and tangent loss are evaluated theoretically. Using model value as given by Ganguli<sup>28</sup>, temperature variations of these quantities for KDP crystal were calculated. Present work differs with the earlier works in the sense of that phonon anharmonic terms are not considered in that work. Ganguli et al<sup>28</sup> have considered the higher order anharmonic phonon-interaction terms and find the exact isotope dependence of Curie-Weiss constant, specific heat and electrical susceptibility, but they could not explain the behavior of loss parameter, width and shift in pseudospin-lattice coupled mode (PLCM) frequency due to early decoupling of correlation functions.

Ramakrishnan and Tanaka<sup>29</sup>, using the fermions Green's function, showed that with Tyablikov-type decoupling<sup>30</sup> the transverse susceptibility of KDP reproduces, the result of Havlin, Litov and Uehling<sup>6</sup>. They concluded that the use of Green's function offers a systematic approach to the study of both static and dynamical aspects of ferroelectric phase transition in KDP and showed the superiority of Green's-function method over the usual mean-field and linearized Bloch equation of motion method.

Due to anharmonic phonon interactions, decay processes takes place. For example, third order interaction leads to the decay of a virtual phonon into two real phonons or the virtual phonon may be destroyed by scattering a thermally excited phonon. Similar processes occur for fourth-and higher order interactions.

In figure 4, the loss shows Curie-Weiss behavior, i.e., losses are proportional to  $(T-T_c)^{-1}$  in the vicinity of  $T_c$  which is in agreement with earlier experiments<sup>32</sup>. The phonon anharmonic interactions significantly contribute to temperature dependence of soft mode, dielectric constant and loss, at and above  $T_c$ .

## VII. CONCLUSIONS

Present study shows that soft mode theory successfully explains the dynamics of ferroelectric transition in KDP in a quite similar way as the antiferroelectric transition in ADP, which shows the possibility of a unified theory of ferroelectric and antiferroelectric transitions. It reveals that four particle cluster mode Hamiltonian, alongwith third and fourth order anharmonic interactions, explains phase transition and the dielectric properties of KDP-type ferroelectric crystals. The result of present calculation can also be extended to explain phase transition and the dielectric properties of other ferroelectric crystals such as Cs H<sub>2</sub>PO<sub>4</sub>, RbH<sub>2</sub>PO<sub>4</sub>, PbH<sub>2</sub>PO<sub>4</sub>, TiH<sub>2</sub>PO<sub>4</sub><sup>8-11</sup>.

The observed dielectric susceptibility may be expressed as a linear combination of the susceptibility originating due to the two relaxation times ( $\tau_1$ , and  $\tau_2$ ):  $\tau_1$  corresponding to  $\tilde{\omega}_-$ , tends to infinity as  $T \rightarrow T_c$  and the other  $\tau_2$ , corresponding to a  $\tilde{\omega}_+$ , is weakly temperature dependent.

$$\chi = \frac{\chi_1}{1 + j\omega\tau_1} + \frac{\chi_2}{1 + j\omega\tau_2}$$

$\chi_1$  and  $\chi_2$  represent the contribution of the static susceptibility ( $\chi_0$ ) from the two relaxation

modes. From these results we conclude the following properties of the susceptibility  $\chi(\omega)$  in the present approximation: (i) the static susceptibility is mainly contributed from  $\chi_1$ . (ii) in the dynamic susceptibility  $\chi(\omega)$ , the first part contributes significantly, i.e., contribution from the first mode which vanishes at  $T = T_c$ , just as in Mason theory<sup>27</sup>, because of the fact that  $\chi_1 \rightarrow \infty$ , as  $\tau_1 \rightarrow \infty$  at  $T \rightarrow T_c$ . (iii) The contribution to  $\text{Re } \chi(\omega)$  from the second mode remains finite at  $T_c$ , although its magnitude is of negligible order.

The inverse dielectric susceptibility increases linearly with temperature for KDP crystal in its paraelectric phase.

## VIII. ACKNOWLEDGEMENT

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