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Temperature Dependence of Relaxation Rate in KH_2PO_4 above T_c

V. S. Bist [α] & N. S. Panwar [σ]

Abstract - With the help of the modified four-particle cluster model Hamiltonian [GJSFR, 10, 18(2010)], the theoretical expressions for the relaxation rate of polarization fluctuation have been evaluated and discussed for the KH_2PO_4 (KDP)-type crystals by using the double-time thermal dependent retarded Green's functions techniques and Dyson's equation treatment. The correlations appearing in the dynamic equation have been evaluated using double-time thermal dependent retarded Green's functions techniques and Dyson's equation treatment. Without any decoupling the higher order correlations have been evaluated using the renormalized Hamiltonian. By fitting model values in the theoretical expressions, temperature dependence of relaxation rate is calculated for the KH_2PO_4 (KDP)-type crystals. Theoretical results are compared with experimental result of Garland and Novotny [1969 *Phys Rev.* 177 971]. A good agreement has been found.

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I. Introduction

The KH_2PO_4(KDP)-type crystals are interesting hydrogen-bonded materials undergoing structural phase transitions accomplished by ferroelectricity or antiferroelectricity. In these crystals, it is known that protons in the double well potentials on the hydrogen bonds are involved in a phase transition accompanied by displacements in the heavy atoms (K, P, and O) structure. KDP undergoes the ferroelectric phase transition at T_C =123. Above T_C the excitation spectrum shows relaxation character and is centered around $\omega = 0$. Only below T_C, a mode of finite frequency $\omega \neq 0$ is found (as for spin waves in ferromagnets). On the other hand, in displacive systems a mode of finite frequency exits even above T_C, and tends to freeze out on approaching T_C from above[1]. This soft mode was found extremely fruitful both for experimental and theoretical researches in structural phase transitions of displacive ferroelectrics[2]. The soft mode concept has been extended to order-disorder relaxational system[3], wherein a mean field $2\pi/\tau = \omega_{relax} \propto (T - T_C)$; whereas $\omega_{soft} \propto (T - T_C)^{1/2}$ However, if soft mode is overdamped its temperature dependence cannot be distinguished from a relaxational response[4].

Peercy[5] has measured the pressure and temperature dependence of the soft-mode Raman spectra of KDP in both paraelectric (hereafter referred to as PE) and ferroelectric phases. At low pressure where the soft-mode is over damped, the relaxation rate (τ^{-1}) was found more reliable parameter than the individual parameters, i.e., the acoustic mode frequency $(\tilde{\tilde{\omega}}_{\pm}^2)$ and width (Γ_P). Experiments using the Brillouin scattering[6,7] resonance vibration[8,9] and pulse-echo techniques[10] for attenuation studies in these materials reflect the substantial asymmetry in the temperature dependence of the polarization relaxation rate in the PE phases analogous to that of susceptibility[11,12]. Also the attenuation is found strongly frequency dependent and becomes so large to measure close to T_C [11,12]. Many workers[13,14] have experimentally studied the dielectric properties of KDP type ferroelectrics. Formulae were developed to explain ferroelectric transitions in order-disorder[15,16] type crystals.

At first, Pak[17] employed Green's function methods in the order-disorder type ferroelectrics, who however, did not consider the anharmonic interactions. Pak's theory was further developed by Ramakrishanan and Tanaka[18], who calculated the excitation spectrum of the system, but did not consider the anharmonic interactions. Their attempt, however, established the superiority of Green's function method over the other methods. Ganguli[19] et al modified Ramakrishanan and Tanaka theory by considering anharmonic interaction. Their treatment explains many features of order-disorder ferroelectrics. However, due to insufficient treatment of anharmonic interactions, they could not explain quantitatively good results and could not describe some very interesting properties, like dielectric properties, acoustic attenuation, relaxation rate etc.

In our previous studies[20] {hereafter referred to as I (2010), II (2011), and III (2012)} we have designed the Blinc's Hamiltonian in terms of lattice anharmonicity upto fourth order for the stochastic motion of $H_2PO_4^-$ groups. Applying Green's functions techniques and Dyson's equation the higher order correlations have been evaluated using the renormalized Hamiltonian. The

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proton renormalized frequency of the coupled system and collective proton wave half widths have been evaluated in I, Relaxation processes and ultrasonic attenuation in KDP-type ferroelectrics in II, and Dielectric Properties of Order-Disorder Type Crystals in III.

In the present study, we use same Hamiltonian as in previous studies. Expression for the relaxation rate of polarization fluctuation have been evaluated and discussed for the KH_2PO_4 (KDP)-type crystals by using the double-time thermal dependent retarded Green's functions techniques and Dyson's equation treatment and model Hamiltonian. By fitting model values in the theoretical expressions, temperature dependence of relaxation rate is calculated for KH_2PO_4 crystal. Theoretical results are compared with experimental result of Garland and Novotny[12]. A good agreement has been found.

II. Relaxation Rate

The relaxation rate is obtained as[18]:

$$\tau_p^{-1} = \tilde{\tilde{\omega}}_{\pm}^2 \times (2\Gamma_p)^{-1}. \qquad (1)$$

Where for resonant interaction $(\Omega = \omega_q)$ $\tilde{\tilde{\omega}}_-$ is the collective phonon mode frequency {represented by equation (6) in II} and for small q limit, we obtain the collective proton mode frequency width (Γ_q),for $\omega << \tilde{\tilde{\omega}}.$, from equation (20) in I, by using a four cluster model Hamiltonian {represented by equation (3) in I}, and Green's function technique and Dyson's equation as:

$$\Gamma = (2\bar{V}_q^2 \omega_q^2 < S_q^x > \tau_p) \times \left\{ \tilde{\tilde{\omega}}_q^2 \Omega \left(1 + \omega_q^2 \tau_p^2 \right) \right\}^{-1} + (\pi b c^2) \times (2\tilde{\Omega})^{-1} \left[\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \right] + (\pi a^2 \tilde{\Omega}) \times (2b)^{-1} \left[\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega}) \right] \qquad (2)$$

III. Numerical Calculations and Result

By using model values of physical quantities given by Ganguli[19] *et al* (Table 1 in III), from calculated values of $< S^x >$, Γ_P and $\tilde{\tilde{\omega}}_-$,(Table 1, and 2 respectively in II),and ultrasonic attenuation coefficient $\alpha(q)$ given by Litov and Garland[21] for KDP .The calculated value of temperature dependence of relaxation rate (τ_p^{-1}) in PE phase for KDP crystal have been calculated and summarized in Table (1). The values of relaxation rate in PE phase are plotted against temperature in figure 1. The theoretical results of present study are compared with the experimental result of Garland and Novotny[12], which shows good agreements.

Table 1 : Temperature dependence of the relaxation rate in PE phase for KDP crystal

Temperature (K)	125	130	135	140	145	Reference
$\alpha(cm^{-1})$	0.106	0.0553	0.0468	0.0382	0.034	*21*
$\tau_p^{-1} \times 10^{11} (\sec^{-1})$	4.09	7.93	11.11	11.90	12.50	*Present study*
$\tau_p^{-1} \times 10^{11} (\sec^{-1})$	1.3	3.55	5.5	-	-	*12*

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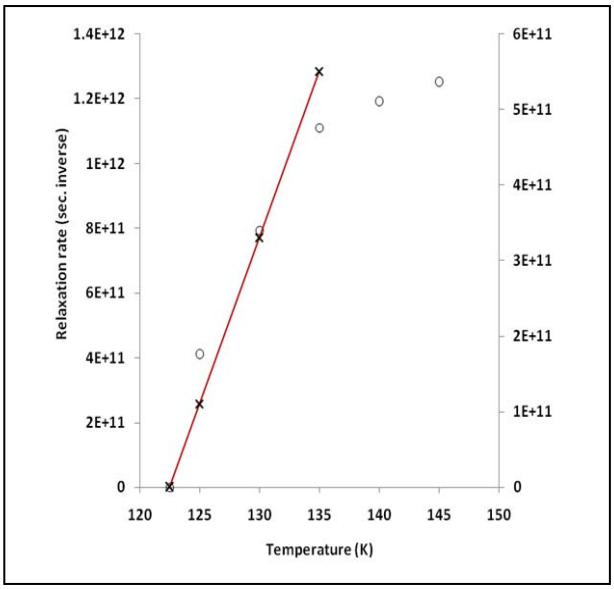

Figure 1 : Temperature dependence of the relaxation rate (τ_p^{-1}) in KH_2PO_4 above Tc. The solid line represents the experimental result of Garland and Novotny[12] (shown by ×××) and theoretical result of present calculation (shown by o o o).

IV. Discussion and Conclusions

The polarization relaxation rate τ_p^{-1} has been calculated from the elastic constants and attenuation data[18] for KH_2PO_4 and KD_2PO_4. It is seen that[11] the temperature dependence of τ_p^{-1} can be given by $\tau_p^{-1} = b\left|T - T_c\right|$ where b is the polarization relaxation rate parameter. In Table (2), the value of b by fitting $b\left|T - T_c\right| = \tau_p^{-1}$ with experiments, for several KDP-type crystals been summarized:

Table 2 : Polarization relaxation rate parameter (b) in the expression $\tau_p^{-1} = b\left|T - T_c\right|$

Compound	$b\times10^{10}$ $Sec.^{-1}K^{-1}$ $(T > T_C)$	$b\times10^{10}$ $Sec.^{-1}K^{1}$ $(T < T_C)$	References
KD_2PO_4	0.40 0.27 0.36 0.24	3.0 - - -	11 22 23 24
KH_2PO_4	4.2 2.8 1.5 -	- 1.6 - 400	12 25 26 27
CsH_2AsO_4 KH_2AsO_4	1.6 3.6	- -	28 29

It is observed that in KD_2PO_4, b is about 7.5 times larger for $T < T_c$ than for $T > T_c$. When one compares KH_2PO_4 with KD_2PO_4, it is found that the b values are quite similar below T_c, but are almost an order of magnitude larger in KH_2PO_4 than the KD_2PO_4, for $T > T_c$. In CsH_2AsO_4 and KH_2AsO_4, for $T > T_c$, b has values similar to that of KH_2PO_4. The very large b value for the ferroelectric phase of the KDP reported by Harnik and Shimshoni[27] was derived from the study of longitudinal ultrasonic wave propagating along the ferroelectric axis. The reason for the large discrepancy between these values and those obtained from shear measurements by Litov and Garland[18] has not been resolved. It may due to the fact that the relational formulism discussed by them does not apply to this case.

The transition temperature (T_c) and the critical relaxation rate inferred from an analysis of the ultrasonic attenuation is very sensitive to deuteration table 2. It is observed that the ratio $b_H \; to \; b_D \cong 8.3$ for KDP. Furthermore, dielectric relaxation measurements on CsH_2AsO_4 (CDP) and CsD_2PO_4 yield the ratio CsD_2PO_4 of at all values of[30] $(T\text{-}Tc)$ also these crystals have a chain like structure which is quite different from that of KDP. The qualitative explanation of isotope effect was proton tunneling[9].

The data on temperature and pressure measurements[5] show that $T\tau_a^{-1}$ is linear with temperature dependence for measurements at high pressure. This behaviour is similar to the temperature depend previously found [28, to 31] for the relaxation rate τ_a^{-1}. From these studies, it is observed that $T\tau_a^{-1}$ extrapolates to zero~ 4^0 below T_c, which agree within experimental uncertainty with the result for $\tilde{\tilde{\omega}}^2$ by Ramakrishna and Tanaka[18].

From equation (1), one would expect τ_p^{-1} to be linear in T and to vanish at $T=Tc$, the straight line shown in figure (1), is given by:

$$\tau = (2.44\times10^{-12})\times(T - T_C)^{-1} \qquad (3)$$

Such short relaxation time (2.44×10^{-12} sec.) can only be determined from acoustic measurement at $10^7 - 10^8$ Hz, because of the large value of $(\tilde{\tilde{\omega}}_-)^{-1}$ near T_c. In view of the very rapid variation with temperature in both α and $(\tilde{\tilde{\omega}}_-)^{-1}$ for KDP, it is not surprising that the temperature dependence of τ_p is somewhat difficult to measure. The above results for KH_2PO_4 can be compared with those of ultrasonic investigation[12] in KD_2PO_4, in which it was found that

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$\tau = (24.4 \times 10^{-11}) \times (T - T_C)^{-1}$, where $T_C = 205.6\,K$ for the incompletely deuterated samples. This tenfold increase in relaxation time on deuterated seems quite reasonable in view of stochastic motion of $H_2(D_2)PO_4$ over a potential barrier which seems an intrinsic feature of this ferroelectric transition. By fitting model values in the theoretical expressions, temperature dependence of relaxation rate is calculated for KH_2PO_4 crystal. Theoretical results are compared with experimental result of Garland and Novotny[12]. A good agreement has been found

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