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RESEARCH ARTICLE

Soft Mode Dynamics of Order-Disorder Type Crystals

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Abstract: The soft mode dynamics and related properties of order-disorder type crystals have been studied. The phonon width and shift have been calculated, which lead to the renormalization of the relaxation soft-mode. The dielectric properties are directly related to the relaxational soft mode behavior of stochastic motion of $H_2PO_4^-$ groups in order-disorder (KDP-system) crystals. The analysis of the temperature dependence of microwave loss tangent and dielectric constant explain the experimental results.

Keywords: Relaxational soft- mode, Stochastic motion, Microwave loss tangent

Introduction

The study of order-disorder, KDP-type ferroelectrics has great significance because the varying properties of these materials are directly related to the industrial applications. They represent the most typical hydrogen-bonded ferroelectric with the order-disorder phase transition. This model crystals was studied more in detail than other ferroelectrics and is the most convenient object for the construction of macro- and microscopic theories of such transitions[1,2]. The symmetry of the room temperature phase of KH_2PO_4 is tetragonal $(I\bar{4}2d)$. Below the transition temperature, T_c=123 K, it forms an orthorhombic (Fdd2) structure in the ferroelectric phase. In the ferroelectric phase the positions of all hydrogens are fixed to PO_4 radicals and a spontaneous polarization appears along the c-axis, and is not attributed directly to hydrogen, but to the displacement of K^+ ions and deformation of the tetrahedral of PO_4 radicals which are induced by the ordered arrangement of hydrogen. In the paraelectric phase the hydrogen atoms moves between two equivalent equilibrium positions in the O-H- -O hydrogen bonds, linking the PO_4 tetrahedra and the configuration of hydrogen is random and the spontaneous polarization disappears.

Below transition temperature (T_c) this motion freezes out and the structure orders. This ordering is gradual and accompanied by displacement of the heavy atoms[3]. The real nature of the ferroelectric phase transition and the isotope effect on Tc for $H \rightarrow D$ exchange in KH_2PO_4

or KDP-type ferroelectrics has not been fully explained[3-5]. The proton tunneling mode[6], the earliest model used to explain the isotope effect, predicted the displacive type of phase transition. More recent crystal lattice dynamics measurements, on the other hand, have suggested the order-disorder mechanism of phase transition, an extensively discussed elsewhere[4,5]. Raman spectroscopic studies confirm that the ferroelectric phase transition in KH_2PO_4, KD_2PO_4 and their mixed crystals is due to the "order-disorder dynamics" of PO_4 dipoles[7]. Kaminow and Damen[8] first observed the soft mode associated with the ferroelectric phase transition of the KDP-type crystal at 122.3 K by measuring the low frequency Raman scattering in x (yx)y configuration.

Above T_c the excitation spectrum shows relaxation character and is centered around $\omega = 0$. Only below T_c, a mode of finite frequency $\omega = 0$ is found (as for spin waves in ferromagnets). In the displacive systems a mode of finite frequency exits even above T_c, and tend to freeze out on approaching T_c from above[9]. This soft mode was found extremely fruitful both for experimental and theoretical researches in structural phase transitions of displacive ferroelectrics[10]. 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 over damped. Its temperature dependence cannot be distinguished from a relaxational response[11].

Peercy[12] has measured the pressure and temperature dependence of the soft-mode Raman spectra of KDP in both paraelectric and ferroelectric phases. At low pressure where the soft-mode is overdamped, the relaxation rate was found more reliable parameter than the individual parameters, *i.e*., the acoustic mode frequency and width.

At first, Pak[13] employed Green's function methods in the order-disorder type ferroelectrics, who however, did not consider the anharmonic interactions. The phonon anharmonic interactions have been found very important in explaining dielectric, thermal and scattering properties of solids by many authors[9,14,15] in the past. Pak's theory was further developed by Ramakrishanan and Tanaka[16], 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[17] *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 earlier study[18] we have designed the Blinc and Zeks[3] four-particle cluster model Hamiltonian in terms of phonon anharmonicity upto fourth order[15]. Applying Green's function techniques and Dyson's equation the higher order correlations have been evaluated using the renormalized Hamiltonian. The collective proton wave width and shift, collective phonon half width and mode frequency shift have been evaluated for KDP-type ferroelectrics in this study.

In the present study, we use the same Hamiltonian as our earlier study. The expressions for phonon width and shift have been evaluated for order-disorder type crystals. As the soft mode influences the acoustic modes via phonon-phonon interaction, the optical soft phonon width and acoustic phonon width are directly related to the acoustic attenuation. By setting the different parameters occurring in the dynamical equation accordingly, the phonon width and shift and hence dielectric constant and acoustic attenuation have been calculated for order-disorder crystals. The theoretical results thus obtained for acoustics attenuation and dielectric constant are in good agreement with the experimental results, reported for order-disorder crystals.

Proton width and Shift

Using double-time thermal Green's function technique and Dyson's equation, the general expression for optical and acoustical modes are obtained as our earlier work[18]. The soft mode frequency is given by

$$\tilde{\tilde{\Omega}}^2 = \tilde{\Omega}^2 + 2\Omega\Delta_S(q,\omega) \tag{1}$$

Where $\tilde{\Omega}^2 = a^2 + b^2 - bc$ with $a = \sum_q J_q < S_q^z > + \sum_q J'_q < S_q^z >^3)$, $b = 2\Omega$ and

$$c = \sum_q J_q < S_q^x > + \sum_q J'_q < S_q^x > < S_q^z >^2.$$

The expectation value of the proton collective mode component at site q have been obtained[3] and given by equation 5 in our earlier study[18]. This represents a system of 3N equations for the average values of the collective mode components. The solution of this system will, however, be stable only if they minimum the free energy, *i.e.*, if $< S_q^z > = < S_q^y > = 0,$ and $< S_q^x >$ is given by equation 5a in earlier study[18], represent paraelectric phase, which exists at all temperature (T > Tc). In ferroelectric phase (T < Tc)[19], the value of $< S_q^x >$ and $< S_q^z >$ are given by equation 5b in earlier study[18]. The acoustic mode frequency is represented as

$$\tilde{\tilde{\omega}}_q^2 = \tilde{\omega}_q^2 + 2\,\omega_q \Delta_P(q,\omega) \tag{2}$$

with $\tilde{\omega}_q^2 = \omega_q^2 + 8\omega_q(2V_3 + V_4)\coth\left(\frac{\beta\omega_q}{2}\right)$. The collective phonon mode frequency is obtained by calculating Equation 2 self consistently and approximating, and represented as

$$\tilde{\tilde{\omega}}_{q\pm}^2 = \frac{1}{2}(\tilde{\omega}_q^2 + \tilde{\tilde{\Omega}}^2) \pm \frac{1}{2}\left[(\tilde{\omega}_q^2 + \tilde{\tilde{\Omega}}^2)^2 + 16\bar{V}_q^2\omega_q\Omega < S^x >\right]^{1/2} \tag{3}$$

Phonon width and Shift

The consideration of four-cluster Hamiltonian along with the third and fourth order anharmonicities for the KDP ferroelectrics leads to the renormalization and stabilization of the relaxational soft mode and the renormalization of the pseudo-spin exchange interaction constant. Thus considering all interactions, expressions for the shift in response frequency and width have been calculated. This lead to the expression for soft mode frequency and dielectric properties. As in our earlier work[18], the collective phonon mode frequency shift and width are obtained as:

$$\Delta_P(q,\omega) = \frac{2\bar{V}_q^2\Omega < S_q^x > (\omega^2 - \tilde{\tilde{\Omega}}^2)\delta_{qq'}}{\omega_q[(\omega^2 - \tilde{\tilde{\Omega}}^2)^2 + 4\Omega^2\Gamma_S^2(q,\omega]} + \frac{24\sum_q V_3^2(qq')\omega_q\,\delta_{qq'}}{\tilde{\omega}[(\omega^2 - 4\tilde{\omega}_q^2)}$$

$$+ \frac{24\sum_q V_4^2(qq')\omega_q\omega_{q'}}{\tilde{\omega}_q^2\tilde{\omega}_{q'}}\left[\frac{(1+2n_q n_{q'} + n_q^2)(2\tilde{\omega}_q + \tilde{\omega}_{q'})}{\omega^2 - (2\tilde{\omega}_q + \tilde{\omega}_{q'})^2} + \frac{(n_q^2 - 1)(2\tilde{\omega}_q + \tilde{\omega}_{q'})}{\omega^2 - (2\tilde{\omega}_q + \tilde{\omega}_{q'})^2} + \frac{2\tilde{\omega}_{q'}(n_q^2 - 1)}{(\omega^2 - \omega_{q'}^2)}\right] \tag{4}$$

$$+ \frac{72\sum_q V_4^2(qq')\omega_q^2}{\tilde{\omega}_q^2}\left[\frac{(1+3n_q^2)}{(\omega^2 - 9\tilde{\omega}_q^2)} + \frac{(n_q^2 - 1)}{(\omega^2 - \omega_{q'}^2)}\right] \quad \text{with}$$

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

$$n_q = \frac{\omega_q}{\tilde{\omega}_q}\coth\left(\frac{\beta\tilde{\omega}_q}{2}\right), \text{ and } \hat{\Omega} = (a^2 + n_q \bar{V}_q^2)^{1/2}$$

and collective phonon half width is obtained as

$$\Gamma_P = \frac{-4\bar{V}_q^2\,\Omega^2 < S_q^x > \Gamma_s(q,\omega)}{[(\omega^2 - \tilde{\tilde{\omega}}^2)^2 + 4\Omega^2\Gamma_s^2(q,\omega)]} + 6\pi\sum_q V_3^2(q,q')\frac{\omega_q n_q}{\tilde{\omega}_q}\left[\delta(\omega - 2\tilde{\omega}_q) - \delta(\omega + 2\tilde{\omega}_q\right]$$

$$+ 12\pi\sum_q \frac{V_3^2(q,q')\,\omega_q\,\omega_{q'}}{\tilde{\omega}_q^2\,\tilde{\omega}_{q'}^2}\left[(1 + 2n_q n_{q'} + n_q^2)\{\delta(\omega - 2\tilde{\omega}_q - \tilde{\omega}_{q'}) - \delta(\omega + 2\tilde{\omega}_q + \tilde{\omega}_{q'})\}\right.$$

$$\left. + (n_q^2 - 1)\{\delta(\omega - 2\tilde{\omega}_q + \tilde{\omega}_{q'}) - \delta(\omega + 2\tilde{\omega}_q - \tilde{\omega}_{q'})\} + 2(n_q^2 - 1)\{\delta(\omega - \tilde{\omega}_{q'}) - \delta(\omega + \tilde{\omega}_{q'})\}\right] \quad (5)$$

$$+ 36\pi\sum_q V_4^2(q,q')\frac{\omega_q^2}{\tilde{\omega}_q^2}\left[\frac{(1+3n_q^2)}{3\tilde{\omega}_q}\{\delta(\omega - 3\tilde{\omega}_q) - \delta(\omega + \tilde{\omega}_q\} + (n_q^2 - 1)\{\delta(\omega - \tilde{\omega}_q) - \delta(\omega + \tilde{\omega}_q\}\right]$$

Comparison with Experiments and Discussion

Following Kubo[20] and Zubarev[21]. The dielectric susceptibility is obtained as

$$\chi(q,\omega) = \frac{-2N\mu^2\tilde{\omega}}{[\omega^2 - \tilde{\tilde{\omega}}^2 + 2j\omega\Gamma_P(q,\omega)]} \quad (6)$$

Where N is the number of unit cell in the sample and μ is the effective dipole moment per unit cell. $\tilde{\tilde{\omega}}_q^2 = \tilde{\omega}_q^2 + 2\,\omega_q\Delta_P(q,\omega)$

$\Delta_s(q,\omega)$ is the shift in phonon frequency and $\Gamma_P(q,\omega)$ is the phonon width. The dielectric constant can be calculated by using the relation

$$\varepsilon = 1 + 4\pi\chi, \quad (7)$$

Using equation (7), the expression for dielectric constant from equation 6 can be obtained as $\varepsilon'(\omega) - 1 = \dfrac{-8\pi N\mu^2\tilde{\omega}\left[(\omega^2 - \tilde{\tilde{\omega}}^2) - 2j\omega\Gamma_p(\omega)\right]}{[(\omega^2 - \tilde{\tilde{\omega}}^2)^2 + 4\omega^2\Gamma_p^2(q,\omega)]}$

the imaginary part of which can be written as

$$\varepsilon'(\omega) = \frac{8\pi N\mu^2\tilde{\omega}\,2\,\omega\Gamma_p(\omega)}{[(\omega^2 - \tilde{\tilde{\omega}}^2)^2 + 4\omega^2\Gamma_p^2(q,\omega)]},$$

and the real part as

$$\varepsilon'(\omega) - 1 = -\frac{8\pi N \mu^2 \tilde{\omega}(\omega^2 - \tilde{\tilde{\omega}}^2)}{[(\omega^2 - \tilde{\tilde{\omega}}^2)^2 + 4\omega^2 \Gamma_p^2(q,\omega)]} \tag{8}$$

and the tangent loss

$$\tan\delta = \frac{\varepsilon''}{\varepsilon} = \frac{-\omega\Gamma_p}{[(\omega^2 - \tilde{\tilde{\omega}}^2)]} \tag{9}$$

The soft mode frequency is very large as compared to the microwave frequency $\omega, (\omega / \tilde{\tilde{\omega}} = 10^{-3})$ and no relaxation effects are observed. Due to this appreciable difference between the microwave frequency and the normal optical phonon frequency, the real part of dielectric constant can be written as

$$\varepsilon'(\omega) = \frac{8\pi N\mu^2 \tilde{\omega}}{\tilde{\tilde{\omega}}^2} \tag{10}$$

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

$$\tilde{\tilde{\omega}}_{q-} \to 0 \text{ as } T \to T_c \text{ or } \tilde{\tilde{\omega}}_{q-}^2 \cong \text{constant} \times (T - T_c) \tag{11}$$

And equation (10) becomes

$$\varepsilon_C' = \frac{\text{constant}}{(T - T_C)}, \tag{12}$$

Similarly, microwave tangent loss

$$\tan\delta = \frac{-\omega\Gamma_P}{(T - T_C)} = \frac{-\omega(\alpha + \beta T + \gamma T^2)}{(T - T_C)}, \tag{13}$$

Tokunaga and Matsubara[22] Matsubara and Yoshimitsu[23] and Blinc and Svetina[24] developed a four proton clusters model which takes into account the correlations governing motions of four protons surrounding by a PO_4 group. Vaks *et al*.,[25] used the model of Blinc and Svetina[24] but could not explain most of the features of KDP-system except the difference between the Curie and Curie-Weiss temperatures. Vaks and Zinenko[26] performed extensive calculations for the static thermodynamic behavior in the four-particle cluster approximation and found satisfactory agreement with the experimental data. Similar four-particle cluster calculations were made by Yoshimitsu and Matsubara[27] and Havlin and Sompolinsky[28]. Their results, however, are in good agreement with experiment results, but they could not explain the observed relaxational behavior of dielectric properties and ultrasonic attenuation, explicitly, in KDP type ferroelectrics.

In the present study we have used a cluster of four protons, Hamiltonian is given in our earlier work[18]. The cluster approximation along with anharmonic interactions among heavy ions, take an account of strong short range correlation among protons and heavy ions in

KDP-system and gives satisfactory result for equilibrium properties of KDP. The correlations function have not been decoupled and are evaluated using renormalized Hamiltonian. This leads to the width and shift in the phonon frequency, which are directly related to the dielectric properties.

Equations 12 and 13 describe the behavior of KH_2PO_4 quit well. In the paraelectric phase, the dielectric constant of order-disorder type ferroelectric follows the Curie-Weiss law with $C=10^3$ K, when temperature is measured in K. The dielectric constant exhibits no relaxation at higher microwave frequency (35GHz). The Curie-Weiss behavior of tangent loss in KDP, shows that this contribution is due to the temperature independent term α in Equation 13. This suggests that imperfections cause damping. At higher temperatures the loss deviates strongly from the Curie-Weiss type behavior and increase linearly with temperature. This bevaviour assumes that at higher temperatures lattice anharmonicity is responsible for the observed loss.

The temperature dependence of microwave loss tangent in KDP is empirically represented by Equation 13. This dependence can be explained in terms of slowing down of a relaxational mode. The frequency dependence of microwave loss tangent for these samples is linear and similar is the temperature dependence at higher temperatures. This increase in loss is not due to the bulk electronic semi conduction because this would lead to expect a reciprocal dependence on frequency of tangent loss. The temperature dependence of the loss does not appear to be exponential. So third-and fourth-order anharmonocity may be responsible for the observed behavior of the microwave tangent loss.

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