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Phase Transition Splitting due to the Soft-mode Interaction with Local Mode

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We consider the effect of the TO soft mode interaction with local, LM, mode at the ferroelectric phase transition, PT, in $KTa_{1-x}Nb_x O_3$ (x=0.15, 0.17) in the mean-field approximation. TO-LM interaction leads to the splitting PT, formation coupled TO-LM modes and additional static Qs, Qφs TO and LM displacements, respectively, at the temperature interval TL<Tc<TR. The resonance damping of the TAW was observed in KTN15 **[3].** We explained the presence of resonance by the dynamics of the off-center Nb^{+5} ions but found simultaneously that the corresponding oscillator force has a peak around Tc. The appearance of Qφs static displacements allows qualitative understanding of the reason for this peak existence. Soft-mode TO-LM interaction leads to the mode repulsing. The observed value of coupled TO-LM mode frequency is decreasing near Tc, but the gap ~1.4 THz is survived. The dielectric susceptibility is often described by the empirical Cole-Cole relaxation expression χCC (α), 0<α<1. Expression χCC does not contain any resonance. We extended **[3]** Cole-Cole expression for the case α>1 and found that in this case susceptibility contains resonance in the complex ω – plane. The measuring **[3]** value of $\alpha_{exp}\approx 1.6$, but any physical explanation was absent. Here we applied for the analysis susceptibility general requirement causality, single - value, and energy dissipation **[10]** and found that α_{exp} is placed inside window of possibilities, 1<α< 2, and corresponding to the high contrast resonance non-overlapping with other resonances. This dynamical complex resonance could not be excited by the low-frequency thermal noise and creates a sharp, strong hole at the correlation functions spectrum at the frequency ω=0.

Introduction

During the last several decades, outstanding progress has been achieved in the experimental and theoretical studies of static critical phenomenon (see for example **[1, 2]**). However, the progress, especially in theory, in the research of the dynamical features of the phase transitions was not so exciting despite their excellent importance for fundamental and applied science. Several years ago, Toulouse et al **[3, 4, 5]** fulfilled detailed high-resolution neutron scattering studies of the TA and TO dynamics in the single crystals $KTa_{1-x}Nb_x O_3$ (x=0.15, 0.17) which could be consider as a "weak" relaxor in comparison with widely research PMN ($PbMg_{1/3}Nb_{2/3}O_3$) and PZN ($PbZn_{1/3}Nb_{2/3}O_3$) ones.

In KTN, the Ta^{+5} ion is replaced by the isovalent Nb^{+5} ion with almost the same ionic radius, while Nb^{+5} replaces the divalent Mg^{+2} ion in PMN and the divalent Zn^{2+} ion in PZN. Hence, chemical disordering leads to the existence of strong static electric random fields in PMN and PZN but not in KTN. Therefore, KTN can probably be considered as a useful model system for the study of relaxor ferroelectrics with homovalent cations $(K_{1-x}Li_x) TaO_3$ (KLT), $Ba(Zr_{1x}Ti_x)O_3$ (BZT), and $Ba(Sn_{1-x}Ti_x)O_3$ (BST). Stock et al [6] shown complicated "fluctuation defects" dynamics in KLT crystal.

The essential feature of all three systems is the presence of off-center ions and the two simultaneous types of dynamics they display, one the local motion within the unit cell and the other the correlated/collective motion of off-center ions in different unit cells. In KTN, the Nb^{+5} ions are displaced from their high symmetry site by 0.145 Å in eight equivalent <111> directions **[7, 8].**

These off-center ions create randomly distributed electric dipoles that can reorient under the action of an external electric field, giving rise to the characteristic relaxor behavior of the dielectric susceptibility. It was shown **[3, 4]** that the observed TA damping can be qualitatively explained by a resonant interaction between the TA phonon and a dispersion less (probably localized) mode, LM, with frequency $\boldsymbol{\omega_R}$ and damping $\boldsymbol{\Gamma_R}$, $\boldsymbol{\Gamma_R} < \boldsymbol{\omega_R}$, $\boldsymbol{\omega_R} \sim 0.7$ THz.

Here we continue our calculations **[3]** in the part concerning the effect of TO-LM interaction at the phase transition. We describe model harmonic resonance (2.), its solution (3.), and Cole-Cole relaxation model **[9]** extended over to the resonance processes (4.). Experimental results are discussed "in parallel" with experimental data.

Model Harmonic Resonance

We analyze the effect of the TOW interaction with LM at the phase transition. This interaction is much stronger than TAW-LM one. Calculations are done in the mean-field approximation, MF, that is we consider the effects of frequency dispersion but neglect, for the simplicity, the effects of space dispersion. For the case of cubic crystal lattice free energy (effective potential energy) is written in the well-known form **[1]**

$$FL = \frac{1}{2} a\tau \sum_{k=1}^{k=3} Q_k^2 + u(\sum_{k=1}^{k=3} Q_k^2)^2 + v \sum_{k=1}^{k=3} Q_k^4\,,\ \tau = T/Tc - 1, a > 0 \ (1)$$

Here Q_k is TO displacement in the k-direction, a, u, and v are numerical parameters, T and Tc – ordinary and critical temperatures. We limit here by the case of u>0, v<0, corresponding ground state type (100), (010), or (001). For simplicity we also limit ourselves by the case v=-2/3*u when cubic system is symmetric for the respect of TOW and LOW. For an example TO and LO waves have the same frequency in such case in the crystal stretched along (001) direction. Local modes are described in the harmonic approximation. Corresponding Hamiltonian and part, corresponding TO-LM interaction, are written in the simplest form.

$$HLM = \rho/2\omega 0R^2 \sum_{k=1}^{k=3} Q\varphi_k^2, \quad V_{TO-LM} = \sqrt{\rho} g_0 \omega 0R^2 \sum_{k=1}^{k=3} Q_k Q\varphi_k \ \ (2)$$

ω0R - LM frequency, g0 – dimensionless constant of TO-LM interaction, ρ –renormalization constant. Therefore, we describe LM in the harmonic representation. It seems strange at the first sight, because $\omega 0R \sim 35\ K\ and\ Tc \sim 137\ K$. However, we consider dynamics of the phase transition in the MF, very long waves approximation. During the phase transition average LM levels population is changed very small and we could (at least at the first approximation), apply harmonic LM description, maybe with renormalization,

$\rho = th(\frac{\omega 0R}{2T})$. Probably this renormalization could be absorbed in the redefined new variables and constants, and we will omit factor ρ in the following. Such an approach is not applicable for the case of, say, NMR experiments, when long wave sample excitation is, as a rule, very strong. Therefore, we analyze anharmonic lattice interacting with harmonic LM.

Lattice free energy component contains instability at τ<0.The essential part of model is following. We "solve" model with free energy FL (1) (we title this hypothetical ferroelectric crystal as ***pro-crystal***) and ***ONLY*** excitations in this solved pro-crystal model are interacting with LM (corresponding free energy contribution FLm).

$$FLm = a\tau\big(\theta(\tau) - 2\theta(-\tau)\big) \sum_{k=1}^{k=3} Q_k^2 + u\left(\sum_{k=1}^{k=3} Q_k^2\right)^2 - 2/3u(\sum_{k=1}^{k=3} Q_k^4) + HLM + V_{TO-LM},\ Q_k = Qs_k + Qd_k,\ Q\varphi_k = Q\varphi s_k + Q\varphi d_k\,, \theta(x>0) = 1, \theta(x<0) = 0 \ \ (3)$$

$Qs_k, Q\varphi s_k$ *and* $Qd_k, Q\varphi d_k$ *- static and dynamic* displacements components.

Values of the static displacements $Qs_n, Q\varphi s_n$, corresponding extremum *FLm,* are found from the eq-ns (4)

$$Qs_n \left(2a\tau\big(\theta(\ \tau) - 2\theta(-\tau)\big) + 4u \sum_{k=1}^{3} Qs_k^2 - \frac{8u}{3} Qs_n^2 - g0^2 \omega 0R^2 \right) = 0,\ \ Q\varphi s_n = -g0 * Qs_n, n = 1,2,3 \ \ (4)$$

Frequency of the small vibrations near equilibrium values are defined from the eq-ns (5)

$eqQd_1 = (-\omega^2 + 2a\tau(\theta(\tau) - 2\theta(-\tau))Qd_1 + Qd_1 4u\sum_{k=1}^{3} Qs_k^2 + 8uQs_1(Qs_2Qd_2 + Qs_3Qd_3) + \frac{g0^2\omega0R^4}{\omega^2-\omega0R^2} * Qd_1 = 0, Q\varphi d_1 = g0\frac{\omega0R^2}{\omega^2-\omega0R^2}Qd_1, ..;$ (5)

Selection solution eq-ns (4) is done applying requirement stability, that is positive value of the ***ALL*** eigenvalues eq-ns (5), $\omega^2 > 0$.

It is convenient to introduce left and right critical points selected different solution (4, 5) in each from four temperature interval.

$\tau L = -\frac{g0^2\omega0R^2}{4a} < 0, \tau R = \frac{g0^2\omega0R^2}{2a} > 0, TL = Tc(1+\tau L), TR = Tc(1+\tau R), TL < Tc < TR$ (6)

a) T<TL<Tc. Pro-crystal is ferroelectric (100), additional static displacements are absent, $Qs_n = Q\varphi s_n = 0$, dispersion eq-n $eqa \equiv -\omega^2 - 4a\tau + \frac{g0^2\omega0R^4}{\omega^2-\omega0R^2} = 0$ (7a)

b) TL<T<Tc. Pro-crystal is ferroelectric (100), additional static displacements have symmetry (001). $Qs_1 = Q\varphi s_1 = Qs_2 = Q\varphi s_2 = 0, Qs_3^2 = \frac{3(g0^2\omega0R^2+4a\tau)}{4u}, eqb = -\omega^2 - 8a\tau + 3g0^2\omega0R^2 + \frac{g0^2\omega0R^4}{\omega^2-\omega0R^2} = 0$ (7b)

c) TR>T>Tc. Pro-crystal is paraelectric, additional static displacements have symmetry (001), or similar. $Qs_1 = Q\varphi s_1 = Qs_2 = Q\varphi s_2 = 0, Qs_3^2 = 3(g0^2\omega0R^2 - 2a\tau)/4u, eqc = -\omega^2 - 4a\tau + 3g0^2\omega0R^2 + \frac{g0^2\omega0R^4}{\omega^2-\omega0R^2} = 0$ (7c)

d) T>TR. Pro-crystal is paraelectric, additional static displacements are absent, $Qs_n = Q\varphi s_n = 0$, dispersion eq-n $eqd = -\omega^2 + 2a\tau + \frac{g0^2\omega0R^4}{\omega^2-\omega0R^2} = 0$ (7d)

Retarded <<Qd|Qd>> and <<Qφd|Qφd>> Green functions are calculated by means of eq-ns (8) with added ordinary TO, ΓQ, and LM, $\Gamma\varphi$, damping parameters. For an example, at the region T<TL<Tc

$\ll Qd|Qd \gg_a = 1/2\pi\frac{\theta(\tau L-\tau)}{(-\omega^2 - I\omega\Gamma Q - 4a\tau + \frac{g0^2\omega0R^4}{\omega^2+I\omega\Gamma\varphi-\omega0R^2})}, \ll Q\varphi d|Q\varphi d \gg_a = -1/2\pi\frac{\theta(\tau L-\tau)}{(\omega^2 + I\omega\Gamma\varphi - \omega0R^2 + \frac{g0^2\omega0R^4}{-\omega^2-I\omega\Gamma Q-4a\tau})}$ (8) ...

Correlation functions are calculated by means of the standard method.

$SQdQd = \frac{1}{(1-\exp(-\frac{\omega}{T}))}Im(\ll Qd|Qd \gg), SQ\varphi dQ\varphi d = \frac{1}{(1-\exp(-\frac{\omega}{T}))}Im(\ll Q\varphi d|Q\varphi d \gg)$ (9)

Calculation Results and Experimental Data Discussion

Our model is very simple and schematic. Therefore, we used more-or- less suitable numerical parameters without serious fitting.

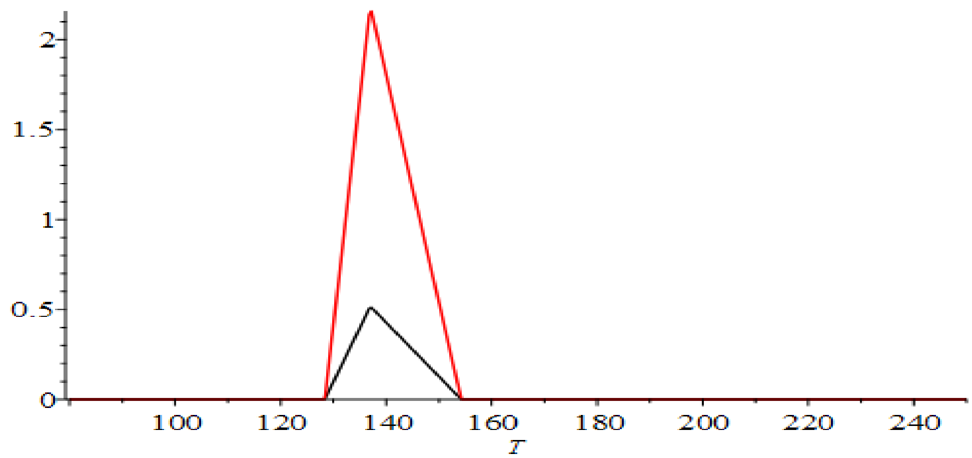

Figure 01: Values of static additional TO, Qs^2/u, and LM, $Q\varphi s^2/u$, displacements vs temperature. Tc= 137, ω0R=0.7, a=8.22, g0=2.05, ΓQ=0.2, Γφ=0.4 (K, THz). These displacements lead to the contribution to the elastic diffuse scattering intensity proportional Qs^2, $Q\varphi s^2$ and peaked around T=140 K .The observed [3] integral intensity of the elastic neutron diffuse scattering

at KTN15 goes through a clear maximum around 130 K and was considered as evidence of PNR appearance. However, the origin of these PNRs was unknown.

TA dynamics was studied in KTN15, and resonance TA damping was certainly observed [3]. However, value of the matrix element of the resonance transition (oscillator force) has maximum at T~140 K. We supposed [3] mechanism leading to this peak existence. Off-center tunneling Nb^{+5} ion creates energy level structure. Direct TA-LM transition (~0.7 THz) is forbidden. PNR polarization leads to the level mixing and "opening" this transition. Static LM displacement Qφs leads to the level mixing, opening resonance transition, and could create discussed peak without any additional prepositions about PNR.

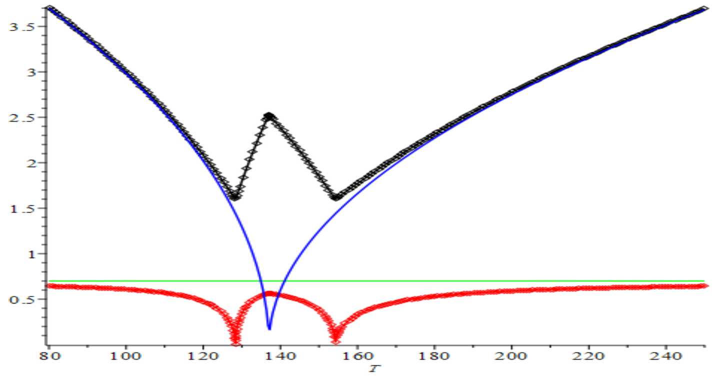

Figure 02: Coupled TO-LM mode (eq-ns (7), black, red); no-interacting modes (g_0=0, blue, green). Phase transition splitting and mode repulsing evidence.

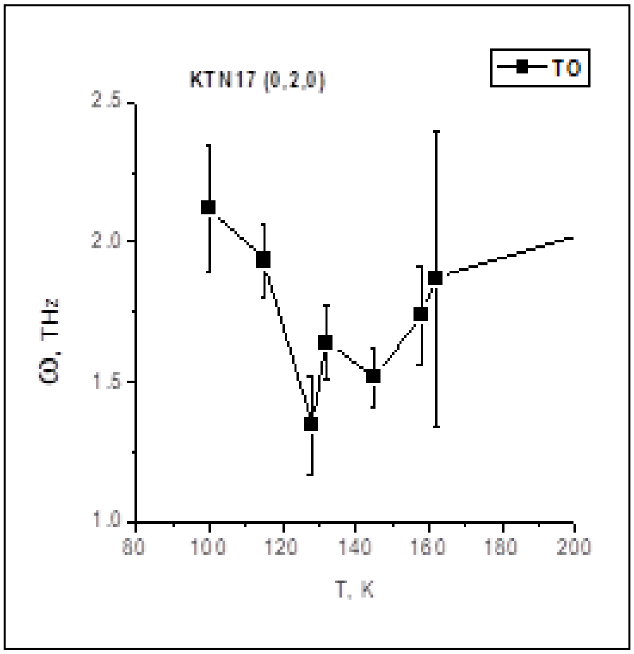

Figure 03: KTN 17. Soft-mode (0,2,0) spectrum temperature dependence [3],[4],[5]. TO (020) excitations with frequency ~0.5 THz was also observed (not shown here).

Model Complex Dynamical Resonance

Relaxation models (Debye, Cole-Cole, Havriliak – Negami [9]) are widely applied for the analysis of electric susceptibility complex objects. For example, Cole-Cole susceptibility is written as

$$\chi_{CC}{}^{1} = (1 + (\exp(-\tfrac{I\pi}{2})\omega\,_{\tau CC)}{}^{\alpha CC})^{-1} \quad , 0 < \alpha CC < 1$$

Frequency scale is defined by the value of the relaxation time τ_{cc}. It is supposed for convenience $\tau_{cc}=1$ in the following.

We extended the Cole-Cole model for the case α>1 and applied this approach to the analysis resonance TAW damping in KTN15 **[3].** Here we continue studies of the extended Cole-Cole model in the complex $\omega-$ plane.

$\chi_{eCC}{}^{1} \equiv (1+(\exp(-\frac{I\pi}{2})\omega_{)}{}^{\alpha})^{-1}$, $\alpha>1$, $\omega=|\omega|\exp(I\Psi)$ (10)

Susceptibility χ_{eCC} has poles at

$\omega_p=\exp(I\Psi_p)$, $\Psi_p=\frac{\pi(2k+1)}{\alpha}+\frac{\pi}{2}$, k=0,∓1,∓2,∓.. (11)

Function χ_{eCC} should be analytical in the upper semi plane, Im(ω) ≥ 0 due to the causality requirements (Landau, Lifschitz, **[10]**) and single-valued. Therefore, we make cut in ω-plane from 0 to -I∞ and receive,

$0>\Psi_p\geq-\frac{\pi}{2}$ or $\frac{3\pi}{2}>\Psi_p>\pi$ (12)

Expressions (11) and (12) lead to the limits at the value of α compatible with pole existence,

$\alpha_p=\alpha*\theta(\alpha-2n-1)\theta(4n+2-\alpha)$, $n=0,+1,+2,+\cdots$,

$\theta(x>0)=1,\ \theta(x<0)=0$ (13)

We title these poles as complex dynamical resonances, CDR. Poles are symmetrically placed,

$$\Psi_{pL(R)}(\alpha,n)=\frac{\pi}{2}\pm\frac{\pi(2n+1)\theta(\alpha-2n-1)\theta(4n+2-\alpha)}{\alpha} \quad (14)$$

Damping ΓeCC and resonance frequency ω_{eCC} are defined by the expressions:

$\Gamma_{eCC}=-\theta(\alpha-2n-1)\theta(4n+2-\alpha)*\sin\left(\Psi_{pR}(\alpha,n)\right)$,

$|\omega_{eCC}|=\theta(\alpha-2n-1)\theta(4n+2-\alpha)*|\cos\left(\Psi_{pR}(\alpha,n)\right)|$ (15)

It is known that the imaginary part of the susceptibility defines energy dissipation. Therefore, exists (Landau, Lifschitz, **[10]**) additional requirement that Im(χ)>0 at ω>0 and Im(χ)<0 at ω<0. This requirement could be fulfilled by application expression χ_{eCCf} instead of χ_{eCC},

$\chi_{eCCf}=fmod*\chi_{eCC}$,

fmod $=(-1)^f$, $f=1+\theta(\alpha-1)\theta(2-\alpha)+\sum_{m=1}^{m=\infty}\theta(\alpha-4m)\theta(4m+2-\alpha)$, fmod (α=1.6) =1 (16)

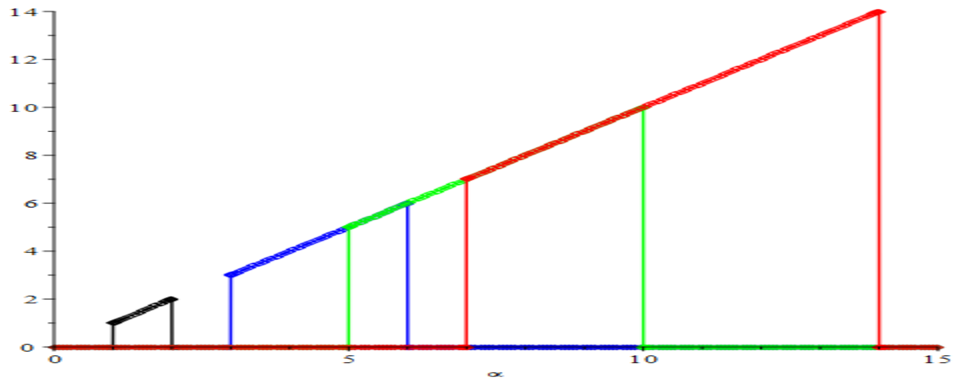

Figure 04: Available poles position α_p αs function of α: black, n=0; blue, n=1; green, n=2; red, n=3.

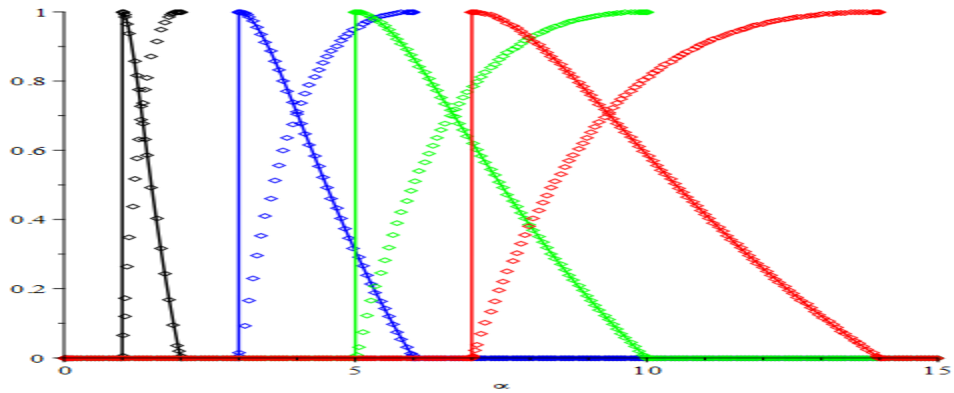

Figure 05: Values of the resonance damping Γ_{eCC}, (point line) and frequency ω_{eCC} (point) as function of α for n=0,1,2,3. Damping is strong at the beginning of corresponding region, α≈1,3,5,7 and small at α≈2,6,10,14.

We define resonance contrast, RC, as value of

$$RC \equiv \frac{|resid(\chi_{eCC})|}{\Gamma_{eCC}} = \frac{1}{\alpha_p \Gamma_{eCC}} \qquad (17)$$

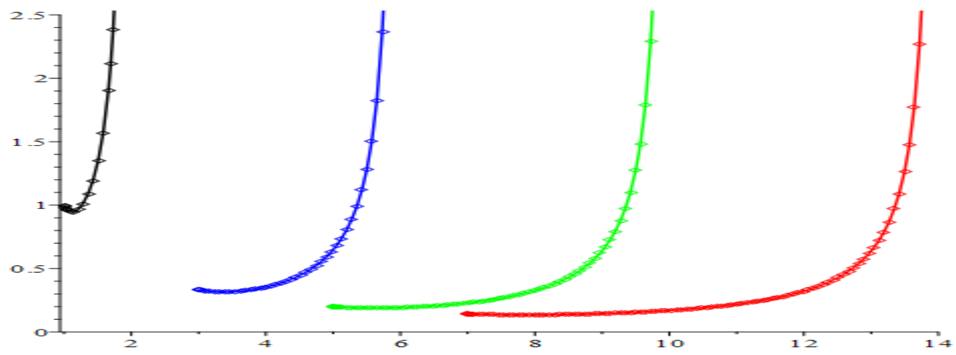

Figure 06: Resonance contrast as function of α for n=0,1,2,3.

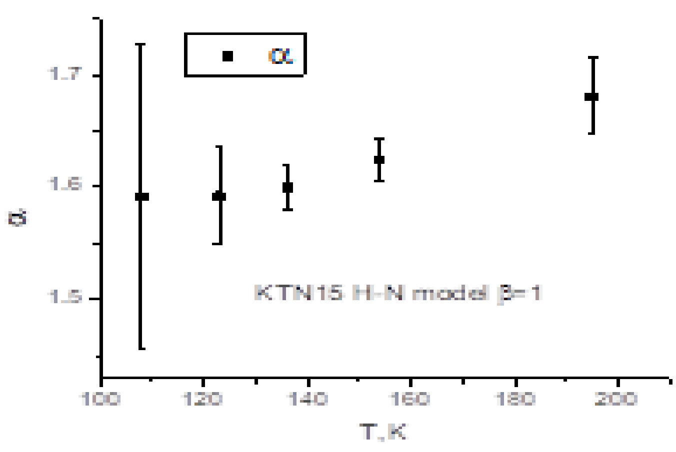

Figure 07: KTN15. The observed **[3]** value of the parameter α≈1.6±0.05 appears in the "allowed" interval 1< α <2 and corresponds to the high contrast resonance non-overlapping with other resonances.

Correlation functions corresponding CDR are calculated like the case of the harmonic resonance model but with replacement,

$+\frac{g0^2\omega 0R^4}{\omega^2+I\omega\Gamma\varphi-\omega 0R^2}$ by $(-1) * g0^2\omega 0R^2\chi_{eCCf}$.

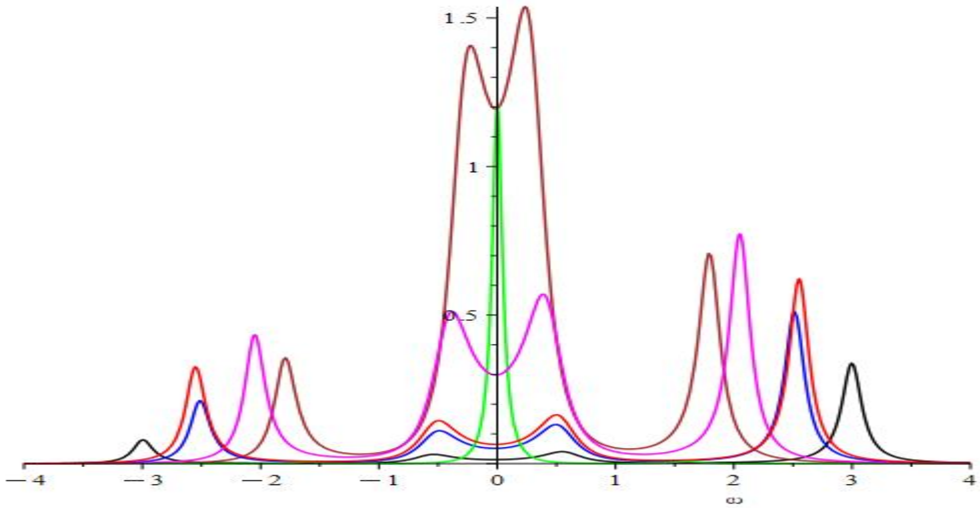

Figure 08: Correlation function SQdQd for the case of the harmonic resonance. T= 100, 125, 137.2 155,170, 190 (black, brown, blue, green, magenta, red). TL=128.37, Tc=137, TR=154.25. Vertical green scale x0.01.

Correlation function SQdQdeCCf for the case of complex dynamical resonance has some peculiarity.

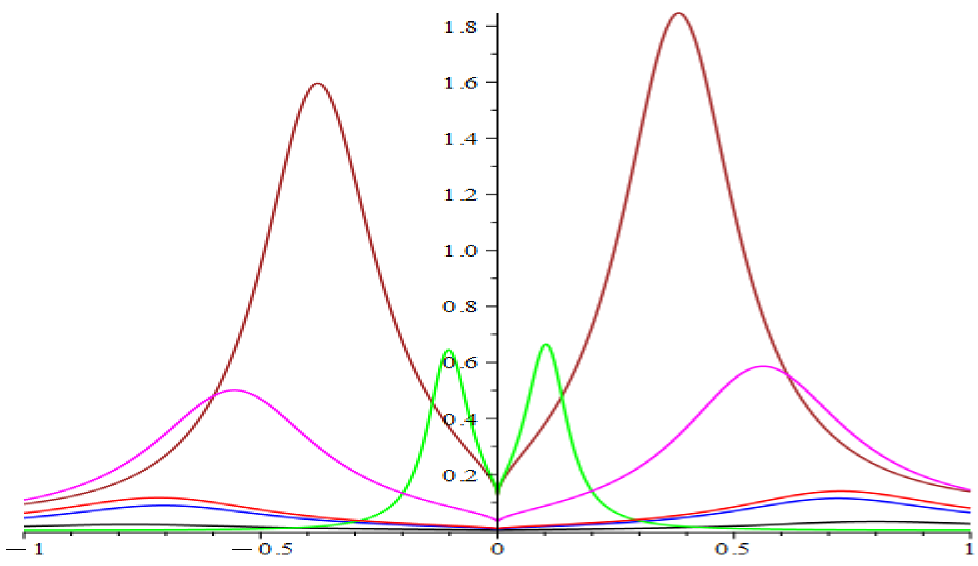

Figure 09: Correlation function (central part) SQdQdeCCf for the case of complex dynamical resonance, α=1.6. T= 100, 125, 137.2, 155, 170, 190. SQdQdeCCf has a sharp, strong central hole at ω=0 in contrast with SQdQd. It appears because Im(χeCC) ~|ω|^α and therefore complex dynamical resonance isn't excited by the low-frequency thermal noise.

Relaxation function

$$F_{CDR}(t,\alpha) \equiv \int_{-\infty}^{\infty} \chi_{eCCf}(\omega)\exp(-I\omega t)\,d\omega \ (18)$$

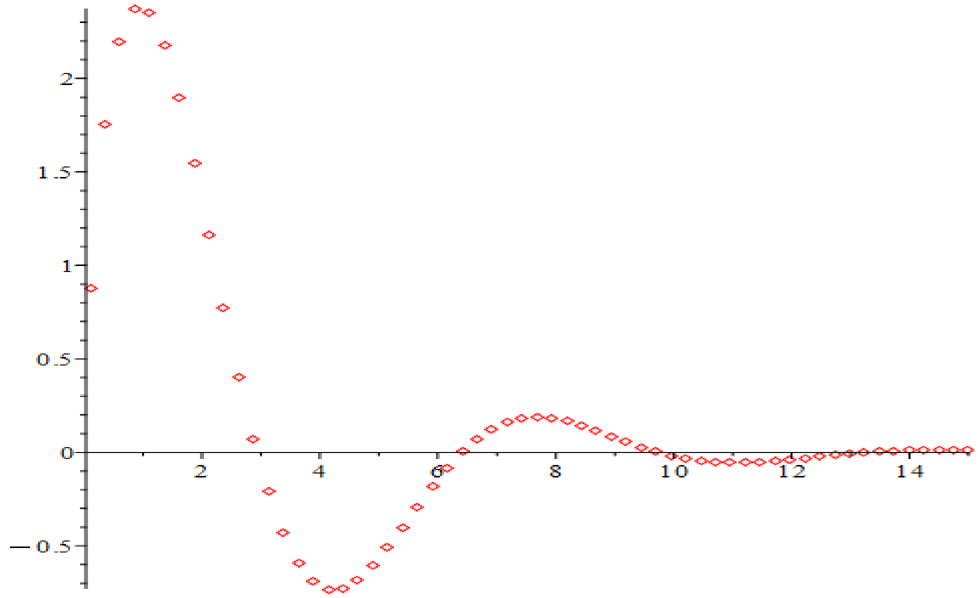

Figure 10: The unusual shape of the relaxation function corresponding CDR, F_{CDR} (t, 1.6). F_{CDR} (t<0, 1.6) =0; F_{CDR} (t, 1.6) ~$t^{0.6}$, t->+0, and decay after several damping oscillations.

Summary

1) We consider phase transition in ferroelectric - weak relaxor - KTN15, KTN17 in the frame of pro-crystal model. Pro-crystal is ordinary ferroelectric, soft-mode excitation in which interacts with local modes, created by off-center Nb^{+5} ions. This TO-LM interaction leads to the creation static TO, Qs, and LM, Qφs, displacements, and coupled dynamic Qd, Qφd. Calculations were done in the simplest mean field approximation.

2) Therefore, two critical points at TL, TR, TL<Tc<TR appears instead of one. We observed early **[3]** resonance damping of the TA wave in KTN15 (frequency ~0.7 THz) and peak at the temperature dependence of the resonance transition oscillator force. Static displacement Qφs presence "allows" to understand (roughly) genesis of this peak.

3) Qd – Qφd modes are repulsing in an agreement with the observed frequency gap in the soft-mode spectrum in KTN17 **[3].**

4) The rich structure of the observed TO spectrum leads to the preposition that the collective interactions between off-center Nb^{+5} are essential. It is known that dielectric parameters are well described in many cases by the empirical Cole-Cole relaxation expression $\chi_{CC} = \frac{1}{1+(\exp(-\frac{I\pi}{2})\omega\tau_{CC})^{\alpha}}$, $0 < \alpha < 1$. We extended **[3]** Cole-Cole expression for the case α>1 and found that in this case susceptibility contains resonance (pole) in the complex ω – plane. Here we applied for the analysis extended Cole-Cole expression general requirements of single-value and causality and found that the first available isolated complex dynamic resonance appears at 1<α<2. The observed **[3]** value is α_{exp} ≈1.6±0.05. An effect of other "resolved" CDRs at α>3 is under discussion.

5) We also calculated correlation functions corresponding Qd-Qd displacements for the case of harmonic resonance (SQdQd) and complex dynamic resonance, SQdQdeCCf, and found that the last spectrum contains a sharp, strong central hole at ω=0 in contrast with SQdQd. It appears because Im (χ_{eCCf})~ $|\omega|^{\alpha}$, $\alpha \approx 1.6$ and dynamical complex resonance isn't excited by the low-frequency thermal noise.

6) It is necessary to note that relaxation function corresponding CDR, F_{CDR} (t, α), has non usually shape: F_{CDR} (t<0, 1.6)=0, but F_{CDR} (t, 1.6)~$t^{0.6}$ at t->+0 and decay after several damping oscillations.

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