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Ultrasonic investigation in $KTaO_3$

S C DEORANI, U C NAITHANI* and B S SEMWAL*

Department of Physics, Government College, Sawaimadhopur 322001, India
*Department of Physics, University of Garhwal, Srinagar 246174, India

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Abstract. The anomalous ultrasonic attenuation α_c of longitudinal waves propagating along (100) direction in $KTaO_3$ has been analyzed above the phase transition temperature in the frequency range 150–300 MHz in the paraelectric phase. The attenuation of longitudinal ultrasonic waves in $KTaO_3$ is primarily due to a strong interaction with thermally-excited phonons in the soft mode. Frequency and temperature variations of attenuation are discussed.

Keywords. Displacive ferroelectrics; anharmonicity; phase transition; Curie temperature; Green's function.

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1. Introduction

In recent years, ultrasonic studies have played an increasingly important role in characterizing the behaviour of the systems near the co-operative phase transitions (co-operative ordering of the dipoles which gives rise to the spontaneous polarization is destroyed by thermal agitation above the Curie-temperature) and critical points. One advantage of ultrasonic measurements is that static and dynamic properties can be simultaneously measured. Low frequency acoustic velocities provide precise information about the equilibrium adiabatic properties and the effect of temperature, pressure and external fields can be easily studied. Ultrasonic attenuation data provide informatin about the dynamic behaviour, and from the frequency as well as temperature dependences, the mechanisms involved can be understood. Theoretically new ways of describing critical phenomenon in terms of fluctuation correlations have been of great importance. Emphasis on the dynamic aspects of the theory has increased markedly and this has naturally focussed more attention on ultrasonic work.

It is well known that the soft mode frequency Ω(where $\Omega^2 \sim T - T_c$) is held responsible for the anomalous behaviour of the ferroelectrics at the stage when T approaches the structural phase transition temperature T_c. As the temperature approaches T_c, the frequency of the soft mode becomes small, resulting in an increase of its amplitude (Jones and Holm 1968) and sound mode couples strongly with the soft mode. This anomalously large amplitude of soft modes should influence the acoustic mode via phonon–phonon interactions and is expected to give rise to an anomalous behaviour of sound waves near T_c. These sound modes are longitudinal acoustic modes as in the vicinity of T_c (when $\Omega \to 0$), only the interactions of longitudinal sound remains. In the case of transverse acoustic modes, the interaction between the transverse acoustic and the transverse optic modes is very small, so

expressions for the attenuation and velocity change of sound would not show any abrupt changes (Barrett 1968).

Barrett (1969) reported theoretical and experimental justification for ultrasonic attenuation in $KTaO_3$ with the variation of temperature and frequency. Fleury (1971) also explained theoretically the ultrasonic attenuation in $KTaO_3$. Balagurov *et al* (1970) and Pytte (1970) discussed anharmonic attenuation above phase transition. Naithani and Semwal (1981, 1982) and Naithani and Baluni (1986a) have also derived theoretical expression for attenuation in a doped and undoped displacive ferroelectric with and without external electric field.

The aim of the present work is to study attenuation constant in $K\,T$ above the $P\,T$ with the variation of frequency and temperature and to correlate the results with the results of other workers.

2. Calculations

2.1 *Variation of attenuation with temperature*

Here we derive an expression for attenuation constant. We consider the following Green's function (Zuberov 1960) for the acoustic phonons,

$$G_{kk'}(t-t') = \ll a_k^a(t);\quad a_{k'}^{a+}(t') \gg. \tag{1}$$

The modified Silverman Hamiltonian used in the present study is similar to (8) of Naithani *et al* (1977). Writing the equation of motion for the Green's function (1) with the help of this modified model Hamiltonian, Fourier transforming and writing it in the Dyson's equation form, one obtains

$$G(\omega + i\varepsilon) = \delta_{kk'}/2\pi[\omega - \omega_k^a + i\Gamma_A(\omega)], \tag{2}$$

where $\Gamma_A(\omega)$ is the damping constant in presence of anharmonicity. Expression for $\Gamma_A(\omega)$ becomes (Naithani *et al* 1977a, b)

$$\begin{aligned}\Gamma_A(\omega) = &-\pi/F(k)|^2 \sum_{\pm}(N_k^o \pm N_o)[\delta(\omega - \Omega \mp \omega_k^o) - \delta(\omega + \Omega \pm \omega_k^o)] \\ &+ 4\pi/\beta^a(k)|^2(1 + N_o^2 + 2N_oN_k^a)[\delta(\omega - 2\Omega - \omega_k^a) - \delta(\omega + 2\Omega + \omega_k^a)] \\ &+ (1 + N_o^2 - 2N_oN_k^a)[\delta(\omega - 2\Omega + \omega_k^a) - \delta(\omega + 2\Omega - \omega_k^a)] \\ &+ \pi\delta^3 \sum_{k_1,k_2} \phi(k_1,k_2,-k)\phi(k_1,k_2,k)[(1 + N_oN_{k_1}^o + N_{k_1}^oN_{k_2}^a + N_oN_{k_2}^a) \\ &\times \{\delta(\omega - \Omega - \omega_{k_1}^o - \omega_{k_2}^a) - \delta(\omega + \Omega + \omega_{k_1}^o + \omega_{k_2}^a)\} \\ &+ (1 + N_oN_{k_1}^o - N_{k_1}^oN_{k_2}^a - N_oN_{k_2}^a)\{\delta(\omega - \Omega + \omega_{k_1}^o + \omega_{k_2}^a) \\ &- \delta(\omega + \Omega - \omega_{k_1}^o - \omega_{k_2}^a)\}]\end{aligned} \tag{3}$$

Here

$$\delta^3 = \delta_{123} + \delta_{213} + \delta_{321}, \tag{4}$$

$$\delta_{123} = \delta_{k_1-k_1'}(\delta_{k_2-k_2'}\delta_{k_3-k_3'} + \delta_{k_2-k_3'}\delta_{k_3-k_2'}), \tag{5}$$

$$\begin{aligned}N_k^\lambda &= \langle A_k^{\lambda+} A_k^\lambda \rangle \\ &= \cot h(\tfrac{1}{2}\beta\hbar\omega_k^\lambda),\end{aligned} \tag{6}$$

$$\beta = (k_B T)^{-1}.$$

Here Ω is the effective frequency of the soft mode. The attenuation is given by (Tani and Tsuda 1969)

$$\alpha_A(\omega) = \Gamma_A(\omega)/c, \tag{7}$$

where c is the sound velocity and the damping constant $\Gamma_A(\omega)$ is given by (3). From (3), (6) and (7), the temperature dependence of attenuation constant, in the high temperature limit can be expressed as,

$$\alpha_A(\omega) \sim C_0 + C_1 T + C_2 T^2,$$

besides the temperature dependence through renormalized frequencies. C_1 and C_2 being the coefficient of T and T^2 respectively in (7). C_0 is independent of temperature and depends mainly upon the impurity.

The increase in attenuation constant with higher order anharmonicity is in accord with the findings of Tani and Tsuda (1969). The fourth order anharmonicity plays an important role in stabilizing the soft mode frequency. The soft ferroelectric mode which has an imaginary frequency ($i\omega_0^o$) in the harmonic approximation is renormalized in presence of anharmonic terms. However, if one is interested in the anomalies, one can approximate the strong temperature dependence of soft mode frequency as $\Omega \propto (T - T_c)^{\frac{1}{2}}$; if the temperature is not very high.

Taking the temperature variation of the soft mode frequency as $\Omega \propto (T - T_c)^{\frac{1}{2}}$, the temperature dependence of $\alpha_A(\omega)$ can be expressed as

$$\alpha_A(\omega) = \left[A_1(\omega) + \left\{ A_2(\omega) + \frac{A_3(\omega)}{(T - T_c)^{1/2}} + \frac{A_4(\omega)}{(T - T_c)^{3/2}} \right\} T + \left\{ A_5(\omega) + \frac{A_6(\omega)}{(T - T_c)^{3/2}} + \frac{A_7(\omega)}{(T - T_c)^2} \right\} T^2 \right], \tag{8}$$

where A_1 is the temperature independent term and A_i's ($i = 2$–4) and A_j's ($j = 5$–7) are the coefficients of T and T^2 respectively which (A_i's and A_j's) are dependent upon higher order anharmonic terms. The expression (8) does not give the explicit temperature dependent of $\alpha_A(\omega)$ because of the renormalized effects. Anharmonicity is necessary in the crystal to observe these effects. It is clear from (8) that as $T \to T_c$, attenuation constant increases anomalously in agreement with the results of Tani and Tsuda (1969) and Pytte (1970). In the vicinity of T_c, the attenuation constant increases anomalously. However, in the low temperature range for the reduced temperature $t[= (T - T_c)/T_c]$, one can approximate (8) as

$$\alpha_A(\omega) \approx A_4(\omega)\{ T/(T - T_c)^{3/2} \}, \tag{9}$$

which is same as obtained by Tani and Tsuda (1969). Thus in the low temperature range, the law $\alpha_A(\omega) \propto T/(T - T_c)^{3/2}$ can be valid to a good approximation to study these properties quantitatively.

Figure 1 shows the raw attenuation constant (Bornstein 1975) for longitudinal sound waves propagating in KT along (100) direction at 180 MHz. In the present study, only the net critical relaxation attenuation (α_c) associated with the critical fluctuations above the phase transition temperature T_c is concerned, so the remaining attenuation by extrapolating from the attenuation at much higher temperature should be subtracted as a background. The background attenuation is small, frequency

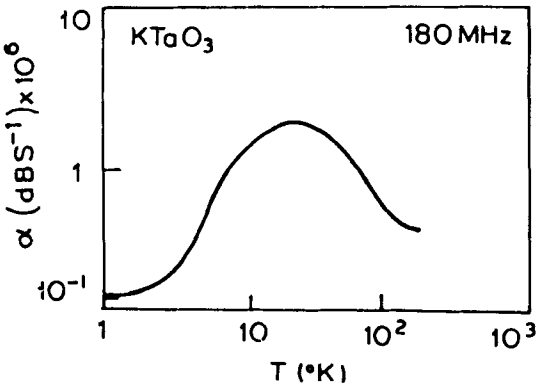

Figure 1. Ultrasonic attenuation of longitudinal wave propagating along (100) direction vs temperature.

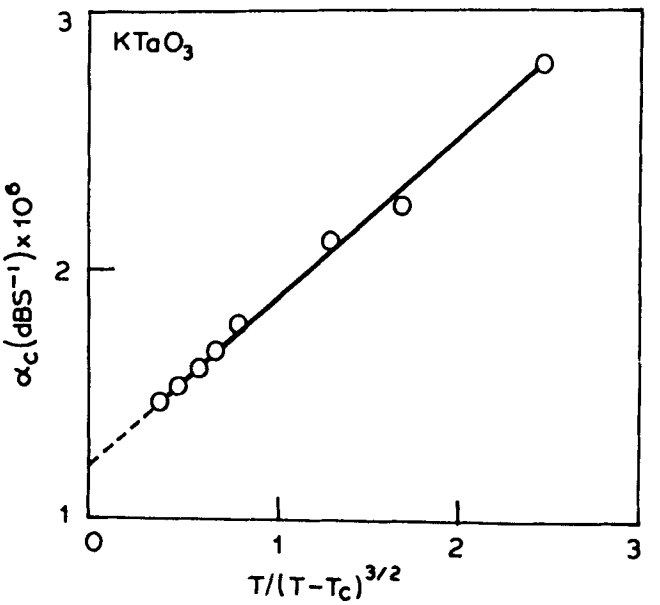

Figure 2. Critical attenuation vs $T/(T-T_c)^{3/2}$.

independent and temperature insensitive. In figure 2, α_c vs $T/(T-T_c)^{3/2}$ is plotted which is a straightline confirming our theoretical results in (9). The law $\alpha_A(\omega) \propto T/(T-T_c)^{3/2}$ is found for the reduced temperature t between 0·2 and 1. α_0 in question, is equal to 0·4 dBS^{-1}.

2.2 *Variation of attenuation with frequency*

In a previous study (Naithani and Semwal 1981), frequency-dependent attenuation constant is given as

$$\alpha_A(\omega) = a_1 + a_2(T)\omega^2 + a_3(T)\omega, \tag{10}$$

where ω^2 dependence arises due to quartic anharmonic interactions while the ω dependence arises due to the cubic anharmonic interaction terms. If we consider only the third order anharmonic interactions, then we have

$$\alpha_A(\omega) \simeq a_1 + a_3(T)\omega, \tag{11}$$

But Garland *et al* (1969, 1984) have given the net attenuation as

$$\alpha_A(\omega) = \alpha_o + \alpha_c, \tag{12}$$

from 11 and (12), we have

$$\alpha_o = a_1, \tag{13}$$

and

$$\alpha_c = a_3\omega, \tag{14}$$

Equation (14) shows that if we take only third order anharmonic interactions then critical attenuation α_c varies linearly with ω, the angular frequency of sound wave, which is in perfect agreement with our previous experimental results for barium titanate (Baluni and Naithani 1986b) and with theoretical and experimental results of others (Pytte 1970; Mavroyami and Pathak 1969; Tani and Tsuda 1969).

Again if we consider quartic anharmonic interactions, then (10) gives

$$\alpha_A(\omega) \simeq a_1 + a_2(T)\omega^2, \tag{15}$$

so

$$\alpha_c(\omega) = a_2\omega^2. \tag{16}$$

The parameter a_2 is calculated by best fitting of data obtained from figure 1 to (16) at $T = 40\,\mathrm{K}$ at frequency 180 MHz.

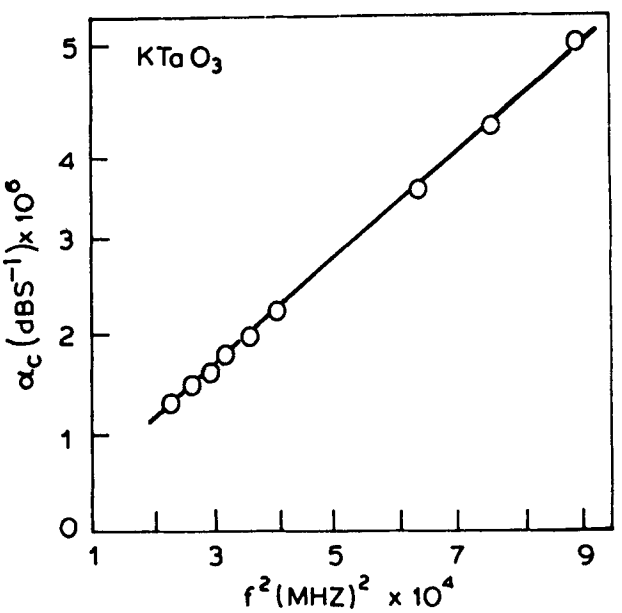

Figure 3. Critical attenuation as a function of f^2 at $\Delta T = 10\,\mathrm{K}$ above T_c.

This gives

$$a_2 = 1{\cdot}74 \times 10^{-13}\,\mathrm{dBS},$$

Thus

$$\alpha_c = 6{\cdot}86 f^2\,\mathrm{dBS}^{-1}, \tag{17}$$

where f is in MHz in the range 150–300 MHz. α_c vs f^2 plot (figure 3) is a straightline. Thus ω^2 dependence of attenuation is in agreement with the experimental and theoretical results of others (Barrett 1968, 1969; Nava *et al* 1968, 1969; Berre *et al* 1969; Todo and Tatsuzaki 1971; Kawashima and Tatsuzaki 1977).

3. Conclusions

From the above discussions, we conclude that at higher temperature above PT, attenuation varies as $T/(T - T_c)^{3/2}$. Attenuation varies linearly with ω if we consider third order anharmonic phonon–phonon interactions only and it varies as ω^2 if fourth order anharmonic interactions are considered. Anharmonicity is necessary in the crystal to observe these dependences.

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References

Balagurov B Ya, Vaks V G and Shktoveskii V I 1970 *Sov. Phys.* **12** 71
Baluni G N and Naithani U C 1986b *Solid State Ionics* **22** 155
Barrett H H 1968 *Phys. Lett.* **A26** 217
Battett H H 1969 *Phys. Rev.* **178** 743
Berre B, Fossheim K and Muller K A 1969 *Phys. Rev. Lett.* **23** 1456
Bornstein L 1975 *Numerical data and functional relationship in science and technology* (New York: Springer Verlag) **9III** S216
Fleury P A 1971 *J. Acoust. Soc. Am.* **49** 1041
Garland C W and Parks G 1969 *Phys. Rev.* **B29** 221
Garland C W and Parks G 1984 *Phys. Rev.* **177** 971
Jones C K and Holm J K 1968 *Phys. Lett.* **A26** 182
Kawashima R and Tatsuzaki I 1977 *J. Phys. Soc. Jpn.* **42** 564
Mavroyami C and Pathak K N 1969 *Phys. Rev.* **182** 872
Naithani U C and Semwal B S 1981 *J. Phys. (Paris)* **42** C-5-659
Naithani U C and Semwal B S 1982 *Proc. Nat. Acad. Sci. India* **52** 381
Naithani U C and Baluni G N 1986a *Indian J. Pure Appl. Phys.* **24** 440
Naithani U C, Gairola R P and Semwal B S 1977a *J. Phys. Soc. Jpn.* **42** 975
Naithani U C, Gairola R P and Semwal B S 1977b *J. Phys. Soc. Jpn.* **43** 954
Nava R, Callapathi R, Ceva H and Martinet A 1968 *Phys. Lett.* **A28** 456
Nava R, Callapathi R, Ceva H and Martinet A 1969 *Phys. Rev.* **188** 1456
Pytte E 1970 *Phys. Rev.* **B1** 926
Tani K and Tsuda N 1969 *J. Phys. Soc. Jpn.* **26** 113
Todo I and Tatsuzaki I 1971 *J. Phys. Soc. Jpn.* **31** 1479
Zuberov D N 1960 *Sov. Phys. Usp.* **3** 320