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Soft mode dynamics of perovskite type crystals

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Abstract. The soft mode dynamics and related properties of perovskite, ABO_3-type crystals have been studied using the operator form of the model Hamiltonian proposed by Pytte. The correlations have been evaluated using the double time thermal Green's function technique and Dyson's equation. Without any decoupling, the higher order correlations, appearing in the dynamical equation, have been evaluated using the renormalized Hamiltonian. The dielectric properties are directly related to the optical soft mode. The phonon width and shift have been calculated for different structural phases. The analysis of the temperature dependence of microwave loss tangent and dielectric constant explains the experimental results.

Keywords. Perovskite crystals; tangent loss; dielectric constant; soft mode; Green's function; Dyson's equation; phonon width and shift.

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1. Introduction

The phase transition in perovskite crystals is generally assumed to be due to the instability of temperature-dependent low frequency optical phonon at the transition temperature (Anderson 1958; Cochran 1960). The perovskite type ABO_3 crystals have structural phase transition from the cubic high temperature phase to the tetragonal or trigonal low temperature phase. Phase transition in these crystals occurs due to the displacement of oxygen ions. This displacement is considered the rotation of BO_6 octahedra which are responsible for dielectric properties of ABO_3 crystals. Depending on the relative magnitude of anharmonic interaction coefficients different structural phases occur. The strength of the coupling of anharmonic interaction with the strain determines whether the transition is of first- or of second-order. By displacement of ions from special positions of the lattice for crystals having distorted perovskite structure several modes are involved in various transitions. In the ferroelectric transition, for example in $BaTiO_3$, only one optical mode contributes significantly to the free energy and acoustic modes of small wave vector do not contribute much but appear in the ferroelectric crystals as homogeneous strains of the cubic crystal. Calculations for $SrTiO_3$ show that frequency of the same mode is very sensitive to the details of the interatomic forces (Cowley 1965). The wave vector of this mode which is generally known as the soft mode, is at the R corner $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ of the Brillouin zone in antiferroelectric phase transition and at the centre (0, 0, 0) of the Brillouin zone in ferroelectric phase transition.

A model Hamiltonian has been proposed by Pytte (1972) to describe the ferroelectric transitions in terms of the localized normal mode coordinates. The interactions of the soft mode coordinates with the elastic strain and long wavelength acoustic phonon have been expressed in terms of the localized strain tensor components. The free energy and the normal mode frequencies have been obtained to describe the phase transition but due to the decoupling of the correlation functions at the very beginning, the dielectric properties could not be explained by Pytte.

In the present study the Hamiltonian proposed by Pytte has been designed in terms of creation and annihilation operators. To evaluate the higher order correlation functions the renormalized Hamiltonian has been used. The correlation functions have been evaluated using the Green's function technique and Dyson's equation. Expressions for phonon shift and width and hence the dielectric constant and tangent loss have been obtained. At the microwave frequency the theoretical results are found in good agreement with the experimental results.

2. Model Hamiltonian

The dynamical part of the Hamiltonian has been expressed in terms of creation and annihilation operators. In constructing the model a high temperature cubic phase structure is used as the reference configuration. The harmonic part of the Hamiltonian consists of positive contribution due to the short range forces and negative contribution due to the long range dipolar forces. The anharmonic interactions up to fourth order have been taken into account. The Hamiltonian describes first- or second-order transition depending on the strength of the anharmonic coupling with the strain and is expressed is

$$\begin{aligned} H = \Big[& \tfrac{1}{4} \sum_{\lambda_1 q_1} \varepsilon_{\lambda_1}(q_1) B^{\dagger}_{\lambda_1}(q_1) B_{\lambda_1}(q_1) + \tfrac{1}{4} \sum_{\mu q_1} \omega_\mu(q_1) B^{\dagger}_\mu(q_1) B_\mu(q_1) \\ & + \sum \alpha S^{\dagger}_\mu(q_1) S_\mu(q_1) + \sum \beta S^{\dagger}_{\lambda_1}(q_1) S_{\lambda_1}(q_1) + \sum \gamma S^{\dagger}_\mu(q_1) S_{\lambda_1}(q_1) \\ & + \sum \delta S_{\lambda_2}(q_2) S^{\dagger}_{\lambda_1}(q_1) S_{\lambda_1}(q_1) + \sum \phi S_\mu(q_2) S^{\dagger}_{\lambda_1}(q_1) S_{\lambda_1}(q_1) \\ & + \sum \theta S^{\dagger}_\mu(q_2) S_\mu(q_2) S_{\lambda_1}(q_1) + \sum \psi S^{\dagger}_{\lambda_1}(q_1) S_{\lambda_1}(q_1) S^{\dagger}_{\lambda_2}(q_2) S_{\lambda_2}(q_2) \\ & + \sum \eta S^{\dagger}_\mu(q_2) S_\mu(q_2) S^{\dagger}_{\lambda_1}(q_1) S_{\lambda_1}(q_1) \Big] \end{aligned} \tag{1}$$

where

$$\sum \alpha = \left[\tfrac{1}{4} \sum_{\mu q_1} \frac{\omega_0^2(\mu q_1)}{\omega_\mu(q_1)} + \tfrac{1}{4} \sum_{ij\mu\lambda q_1} g_{ij\lambda} A_\lambda^2 \frac{\alpha_i(\mu q_1)\alpha_j(\mu q_1)}{\omega_\mu(q_1)} \right] \tag{2a}$$

$$\begin{aligned} \sum \beta = \Bigg[& \sum_{\lambda_1 q_1} \Bigg(\tfrac{1}{4}\Omega_0^2 + \tfrac{3}{4}\Gamma_1 \sum_\lambda A_\lambda^2 + \frac{\Gamma_2}{2} \sum_{\lambda \neq \lambda'} A_{\lambda'}^2 \\ & + \tfrac{1}{4} \sum_{ij\lambda} g_{ij\lambda} e_i e_j \Bigg) b^{\dagger}_{\lambda\lambda_1}(q_1) b_{\lambda\lambda_1}(q_1) / \varepsilon_{\lambda_1}(q_1) \\ & + \sum_{i\lambda\lambda'\lambda_1 q_1} G_{i\lambda\lambda'} e_i \frac{b^{\dagger}_{\lambda\lambda_1}(q_1) b_{\lambda\lambda_1}(q_1)}{2\varepsilon_{\lambda_1}(q_1)} \\ & - \tfrac{1}{4} \sum_{\lambda\lambda'\lambda_1 q_1} v_{\lambda\lambda'}(q_1) \frac{b_{\lambda\lambda_1}(q_1) b_{\lambda'\lambda_1}(q_1)}{\varepsilon_{\lambda_1}(q_1)} \Bigg] \end{aligned} \tag{2b}$$

$$\sum\gamma=\left[\sum_{\mu\lambda_1 q_1}\left(\sum_{i\lambda\lambda'}G_{i\lambda\lambda'}A_{\lambda'}+\sum_{ij\lambda}g_{ij\lambda}A_\lambda e_j\right)\frac{\alpha_i^\dagger(\mu q_1)b_{\lambda\lambda_1}(q_1)}{(\omega_\mu(q_1)\varepsilon_{\lambda_1}(q_1))^{1/2}}\right] \tag{2c}$$

$$\sum\phi=\left[\sum_{\mu\lambda_1 q_1 q_2}\left(\sum_{i\lambda\lambda'}G_{i\lambda\lambda'}\alpha_i(\mu q_2)b^\dagger_{\lambda\lambda_1}(q_1)b_{\lambda'\lambda_1}(q_1)\right.\right.$$
$$\left.\left.+\sum_{ij\lambda}g_{ij\lambda}e_j\alpha_i(\mu q_2)b^\dagger_{\lambda\lambda_1}(q_1)b_{\lambda\lambda_1}(q_1)\right)\Big/\{2\varepsilon_{\lambda_1}(q_1)(2\omega_\mu(q_2))^{1/2}\}\right] \tag{2d}$$

$$\sum\delta=\left[\sum_{\lambda_1\lambda_2 q_1 q_2}\left(\Gamma_2\sum_{\lambda\neq\lambda'}A_\lambda\frac{b_{\lambda'\lambda_2}(q_2)b^\dagger_{\lambda\lambda_1}(q_1)b_{\lambda\lambda_1}(q_1)}{\varepsilon_{\lambda_1}(q_1)(2\varepsilon_{\lambda_2}(q_2))^{1/2}}\right.\right.$$
$$\left.\left.+\frac{\Gamma_1}{2}\sum_{\lambda}A_\lambda\frac{b_{\lambda\lambda_2}(q_2)b^\dagger_{\lambda\lambda_1}(q_1)b_{\lambda\lambda_1}(q_1)}{\varepsilon_{\lambda_1}(q_1)(2\varepsilon_{\lambda_2}(q_2))^{1/2}}\right)\right] \tag{2e}$$

$$\sum\theta=\left[\sum_{ij\lambda}g_{ij\lambda}A_\lambda\frac{\alpha_i^\dagger(\mu q_2)\alpha_j(\mu q_2)b_{\lambda\lambda_1}(q_1)}{2\omega_\mu(q_2)(2\varepsilon_{\lambda_1}(q_1))^{1/2}}\right] \tag{2f}$$

$$\sum\psi=\sum_{\lambda_1\lambda_2 q_1 q_2}\left(\frac{\Gamma_1}{4}\sum_{\lambda}b^\dagger_{\lambda\lambda_2}(q_2)b_{\lambda\lambda_2}(q_2)b^\dagger_{\lambda\lambda_1}(q_1)b_{\lambda\lambda_1}(q_1)\right.$$
$$\left.+\frac{\Gamma_2}{2}\sum_{\lambda\neq\lambda'}b^\dagger_{\lambda\lambda_2}(q_2)b_{\lambda\lambda_2}(q_2)b^\dagger_{\lambda'\lambda_1}(q_1)b_{\lambda'\lambda_1}(q_1\right)\Big/(4\varepsilon_{\lambda_1}(q_1)\varepsilon_{\lambda_2}(q_2))\Bigg] \tag{2g}$$

$$\sum\eta=\left[\sum_{ij\lambda}g_{ij\lambda}\alpha_i^\dagger(\mu q_2)\alpha_j(\mu q_2)b^\dagger_{\lambda\lambda_1}(q_1)b_{\lambda\lambda_1}(q_1)/(8\omega_\mu(q_2)\varepsilon_{\lambda_1}(q_1))\right] \tag{2h}$$

Γ_1 and Γ_2 are the fourth order anharmonic coupling constants for interaction of same and different optical modes respectively. $G_{i\lambda\lambda'}$ and $g_{ij\lambda}$ are the third and fourth order anharmonic constants respectively, for interaction of soft mode coordinates with the elastic strain and long wavelength acoustic phonons. $v_{\lambda\lambda'}(q)$ describes the Fourier transform of the total long range interactions including the effect of rearranged electronic polarizability as well as direct dipole-dipole interaction of displacements in different cells. Ω_0^2 and $\omega_0^2(\mu q)$ represent squares of the unperturbed optical and acoustical phonon frequencies respectively. A_λ and e_i are thermal averages of the soft mode coordinates and strain respectively. The fluctuations about the average values of the soft mode coordinates and strain are expressed in the usual way,

$$r_\lambda(l)=N^{-1/2}\sum_{\lambda_1 q_1}\exp\{\iota_i\mathbf{q}_1\cdot\mathbf{X}(l)\}(2\varepsilon_{\lambda_1}(q_1))^{-1/2}b_{\lambda\lambda_1}(q_1)S_{\lambda_1}(q_1) \tag{3a}$$

and

$$u_i(l)=\iota(N)^{-1/2}\sum_{\mu q_1}\exp\{\iota\mathbf{q}_1\cdot\mathbf{X}(l)\}(2\omega_\mu(q_1))^{-1/2}\alpha_i(\mu q_1)S_\mu(q_1) \tag{3b}$$

where $\alpha_i(\mu q_1)$ are the polarization tensor components; $\iota=(-1)^{1/2}$, and $\varepsilon_{\lambda_1}(q_1)$ is the frequency of the normal optical mode with wave vector $\mathbf{q}_1$ and polarization index λ_1. $S_{\lambda_1}(q_1)$ and $B_{\lambda_1}(q_1)$ are expressed in terms of annihilation and creation operators with equal amplitudes for forward and backward propagating waves as

$$S_{\lambda_1}(q_1)=[a_{\lambda_1}(q_1)+a^\dagger_{\lambda_1}(-q_1)] \tag{4a}$$

$$B_{\lambda_1}(q_1)=[a_{\lambda_1}(q_1)-a^\dagger_{\lambda_1}(-q_1)] \tag{4b}$$

3. Green's function and the equation of motion

The correlations appearing in the phonon response function can be evaluated using the double time thermal retarded Green's function (Zubarev 1960)

$$G_{\lambda_3\lambda_4}^{q_3q_4}(t-t') = \langle\langle S_{\lambda_3}(q_3)_t; S_{\lambda_4}^{\dagger}(q_4)_{t'}\rangle\rangle$$
$$= -i\theta(t-t')\langle[S_{\lambda_3}(q_3)_t;\ S_{\lambda_4}^{\dagger}(q_4)_{t'}]\rangle \tag{5}$$

where the angular brackets denote the average over the large canonical ensemble and $\theta(t)$ is the usual Heaviside step function, having the properties

$$\theta(t) = 1 \quad \text{for } t > 0$$
$$= 0 \quad \text{for } t < 0. \tag{6}$$

Differentiating (5) twice with respect to time t using the model Hamiltonian (1); taking Fourier transformation and using Dyson's equation (Gairola and Semwal 1977), one obtains

$$G(\omega) = \frac{\varepsilon_{\lambda_4}(q_4)\delta_{\lambda_3\lambda_4}\delta_{q_3q_4}}{\pi\left[\omega^2 - \tilde{\Omega}_{\lambda_4}^2(q_4) - \dfrac{\varepsilon_{\lambda_4}(q_4)}{\pi}F\right]} \tag{7}$$

where

$$F = \langle\langle f_{\lambda_3}(q_3); f_{\lambda_4}^{\dagger}(q_4)\rangle\rangle \tag{8}$$

and

$$f_{\lambda_3}(q_3) = \pi[\gamma_1 S_\mu(q_3) + \delta_1 S_{\lambda_1}(q_1)S_{\lambda_1}(q_1) + \delta_2 S_{\lambda_3}^{\dagger}(q_3)S_{\lambda_1}(q_1) + \phi_1 S_\mu(q_1)S_{\lambda_3}^{\dagger}(q_3)$$
$$+ \theta_1 S_\mu(q_1)S_\mu(q_1) + \psi_1 S_{\lambda_3}(q_3)S_{\lambda_1}^{\dagger}(q_1)S_{\lambda_1}(q_1) + \eta_1 S_\mu^{\dagger}(q_1)S_\mu(q_1)S_{\lambda_3}(q_3)] \tag{9}$$

where γ_1, δ_1, θ_1, etc. are the corresponding values of γ, δ, θ, etc. from (2), obtained by evaluating the respective commutation relations appearing in the Green's function (5). To evaluate F, (8) the cross combinations of correlation functions have not been considered and to evaluate various correlations appearing in $\langle\langle f_{\lambda_3}(q_3) f_{\lambda_4}(q_4)\rangle\rangle$; such as $\langle\langle ab, cd\rangle\rangle$, $\langle\langle abc, def\rangle\rangle$, have been calculated using the renormalized Hamiltonian

$$H_{\text{renormalized}} = \left[\frac{1}{4}\sum_{\lambda q}\frac{\tilde{\Omega}_\lambda^2(q)}{\varepsilon_\lambda(q)} S_\lambda^{\dagger}(q)S_\lambda(q) + \varepsilon_\lambda(q)B_\lambda^{\dagger}(q)B_\lambda(q)\right.$$
$$\left. + \frac{1}{4}\sum_{\mu q}\frac{\tilde{\omega}_\mu^2(q)}{\omega_\mu(q)} S_\mu^{\dagger}(q)S_\mu(q) + \omega_\mu(q)B_\mu^{\dagger}(q)B_\mu(q)\right] \tag{10}$$

one obtains (Naithani and Semwal 1978)

$$\lim_{\varepsilon\to 0} G(\omega + i\varepsilon) = \frac{\varepsilon_{\lambda_4}(q_4)}{\pi[\omega^2 - (\tilde{\tilde{\Omega}}_{\lambda_4}^2(q_4) + \Delta_{\lambda_4}(q,\omega)) + i\Gamma_{\lambda_4}(q,\omega)]} \tag{11}$$

$\Delta_{\lambda_4}(q,\omega)$ and $\Gamma_{\lambda_4}(q,\omega)$ represent phonon shift and width respectively. The soft mode frequency is given by

$$\Omega_{\lambda_4}^2(q_4) = \tilde{\tilde{\Omega}}_{\lambda_4}^2(q_4) + \Delta_{\lambda_4}(q,\omega) \tag{12}$$

where

$$\tilde{\Omega}^2_{\lambda_4}(q_4) = \left\{\left(\Omega_0^2 + 3\Gamma_1 \sum_{\lambda} A_\lambda^2 + 2\Gamma_2 \sum_{\lambda \neq \lambda'} A_{\lambda'}^2 + \sum_{ij\lambda} g_{ij\lambda} e_i e_j\right) b^\dagger_{\lambda\lambda_4}(q_4) b_{\lambda\lambda_4}(q_4) + \sum_{i\lambda\lambda'} (2G_{i\lambda\lambda'} e_i - v_{\lambda\lambda'}(q_4)) b^\dagger_{\lambda\lambda_4}(q_4) b_{\lambda'\lambda_4}(q_4)\right\}$$
$$+ \left\{\Gamma_1 \sum_{\lambda} |b^\dagger_{\lambda\lambda_4}(q_4) b_{\lambda\lambda_4}(q_4)|^2 + 2\Gamma_2 \sum_{\lambda \neq \lambda'} |b^\dagger_{\lambda\lambda_4}(q_4) b_{\lambda'\lambda_4}(q_4)|^2\right\} \times \frac{\coth(\beta\tilde{\Omega}_{\lambda_4}(q_4)/2)}{\tilde{\Omega}_{\lambda_4}(q_4)} + \left\{\frac{\Gamma_1}{2} \sum_{\lambda} |b^\dagger_{\lambda\lambda_4}(q_4) b_{\lambda\lambda_1}(q_1)|^2 + \Gamma_2 \sum_{\lambda \neq \lambda'} |b^\dagger_{\lambda\lambda_4}(q_4) b_{\lambda'\lambda_1}(q_1)|^2\right\} \times \frac{\coth(\beta\tilde{\Omega}_{\lambda_1}(q_1)}{\tilde{\Omega}_{\lambda_1}(q_1)}$$
$$+ \left\{\frac{1}{2}\sum_{ij\lambda} g_{ij\lambda} b^\dagger_{\lambda\lambda_4}(q_4) b_{\lambda\lambda_4}(q_4) \alpha_i^\dagger(\mu q_1) \alpha_j(\mu q_1)\right\} \frac{\coth(\beta\tilde{\omega}_\mu(q_1)}{\tilde{\omega}_\mu(q_1)} \tag{13a}$$

and acoustic mode frequency is

$$\tilde{\omega}^2_\mu(q_4) = \left\{\omega_0^2 + \sum_{ij\lambda} g_{ij\lambda} A_\lambda^2 \alpha_i^\dagger(\mu q_4) \alpha_j(\mu q_4)\right\} + \left\{\frac{1}{2} \sum_{ij\lambda\lambda_1 q_1} g_{ij\lambda} \alpha_i^\dagger(\mu q_4) \alpha_j(\mu q_4) b^\dagger_{\lambda\lambda_1}(q_1) b_{\lambda\lambda_1}(q_1) \frac{\coth(\beta\tilde{\Omega}_{\lambda_1}(q_1)/2)}{\tilde{\Omega}_{\lambda_1}(q_1)}\right. \tag{13b}$$

where $\tilde{\Omega}_{\lambda_1}(q_1)$ and $\tilde{\omega}_\mu(q_1)$ are the values within the first curly $\{\ldots.\}$ brackets in (13a) and (13b) respectively. And $\beta = (k_B T)^{-1}$, k_B is the Boltzmann's constant and T the absolute temperature.

4. Phonon shift and width

By setting the appropriate parameters given by Pytte (1972), for different phases, phonon frequencies from (13) can be calculated. Frequencies thus obtained are similar to the ones obtained by Pytte. In the present paper we have an additional term F containing the higher order correlation functions in the denominator of (7). This term is resulted from the contribution of all possible interactions among the vibrational modes as the higher order correlations have not been decoupled. This leads to the width and shift in the phonon frequency. Pytte has decoupled the correlations in the very beginning and calculated phonon frequencies which one can get from (13). The phonon shift and width for different phases are obtained as follows.

4.1 *Cubic phase*

In the cubic phase for the arbitrary direction of **q** there is a doubly degenerate transverse mode $\tilde{\Omega}_{1T}$ and a singlet longitudinal mode $\tilde{\Omega}_{1L}$. Corresponding to these modes, phonon shift is obtained as

$$\Delta_{1T,L}(q,\omega)=\frac{C_1}{[\omega^2-\tilde{\tilde{\omega}}^2_{\mu 1}]}+\frac{C_2}{[\omega^2-\tilde{\tilde{\omega}}^2_{\mu}(q)]}+\frac{C_3}{[\omega^2-\tilde{\tilde{\Omega}}^2_{1T,L}]}+\frac{C_4}{[\omega^2-9\tilde{\tilde{\Omega}}^2_{1T,L}]} \quad (14)$$

with

$$C_1=\left\{2\left(\sum_i G_{i11}+\sum_{ij} g_{ij1}e_j\right)^2\alpha_i^\dagger(\mu q)\alpha_i(\mu q)\frac{\coth(\beta\tilde{\tilde{\Omega}}_{1T,L}/2)}{\tilde{\tilde{\Omega}}_{1T,L}}\right\} \quad (15a)$$

$$C_2=\left\{\left(\sum_{ij} g_{ij1}\alpha_i(\mu q)\alpha_j(\mu q)\right)^2\frac{n_\mu(q)\coth(\beta\tilde{\tilde{\Omega}}_{1T,L}/2)}{\tilde{\tilde{\omega}}_\mu(q)\tilde{\tilde{\Omega}}_{1T,L}}\right\} \quad (15b)$$

$$C_3=\left\{2\left(\sum_i G_{i1}\alpha_i(\mu q)+\sum_{ij} g_{ij1}e_j\alpha_i(\mu q)\right)^2\frac{\coth(\beta\tilde{\tilde{\omega}}_\mu(q)/2)}{\tilde{\tilde{\omega}}_\mu(q)}+\frac{3}{4}\left(\sum_{ij} g_{ij1}\alpha_i^\dagger(\mu q)\alpha_j(\mu q)\right)^2\frac{\coth^2(\beta\tilde{\tilde{\omega}}_\mu(q)/2)}{\tilde{\tilde{\omega}}^2_\mu(q)}+\frac{2\Gamma_2^2(1+7n_1^2)}{\tilde{\tilde{\Omega}}^2_{1T,L}}+\frac{5\Gamma_1^2(1+7n_1^2)}{16\tilde{\tilde{\Omega}}^2_{1T,L}}\right\}; \quad (15c)$$

$$C_4=\left\{\frac{3(1+3n_1^2)}{16\tilde{\tilde{\Omega}}^2_{1T,L}}(5\Gamma_1^2+32\Gamma_2^2)\right\}; \quad (15d)$$

$$n_1=\coth(\beta\tilde{\tilde{\Omega}}_{1T,L}/2);$$

and phonon width is given by

$$\Gamma_{1T,L}(q,\omega)=\frac{\pi}{2}\left[\frac{C_1}{\tilde{\tilde{\omega}}_{\mu 1}}\{\delta(\omega-\tilde{\tilde{\omega}}_{\mu 1})-\delta(\omega+\tilde{\tilde{\omega}}_{\mu 1})\}+\frac{C_2}{\tilde{\tilde{\omega}}_\mu(q)}\{\delta(\omega-\tilde{\tilde{\omega}}_\mu(q))-\delta(\omega+\tilde{\tilde{\omega}}_\mu(q))\}+\frac{C_3}{\tilde{\tilde{\Omega}}_{1T,L}}\{\delta(\omega-\tilde{\tilde{\Omega}}_{1T,L})-\delta(\omega+\tilde{\tilde{\Omega}}_{1T,L})\}+\frac{C_4}{3\tilde{\tilde{\Omega}}_{1T,L}}\{\delta(\omega-3\tilde{\tilde{\Omega}}_{1T,L})-\delta(\omega+3\tilde{\tilde{\Omega}}_{1T,L})\}\right]; \quad (16)$$

4.2 *Tetragonal phase*

The phonon shift corresponding to $\tilde{\tilde{\Omega}}_{3T}[A_1(TO)]$ mode and $\tilde{\tilde{\Omega}}_{3L}[A_1(LO)]$ mode is obtained as

$$\Delta_3(q,\omega)=\left[\frac{\mathscr{C}_1}{[\omega^2-\tilde{\tilde{\omega}}^2_{\mu 3}]}+\frac{\mathscr{C}_2}{[\omega^2-\tilde{\tilde{\omega}}^2_\mu(q)]}+\frac{\mathscr{C}_3}{[\omega^2-4\tilde{\tilde{\omega}}^2_\mu(q)]}+\frac{\mathscr{C}_4}{[\omega^2-\tilde{\tilde{\Omega}}^2_3]}+\frac{\mathscr{C}_5}{[\omega^2-4\tilde{\tilde{\Omega}}^2_3]}+\frac{\mathscr{C}_6}{[\omega^2-4\tilde{\tilde{\Omega}}^2_1]}+\frac{\mathscr{C}_7}{[\omega^2-g\tilde{\tilde{\Omega}}^2_3]}\right.$$

$$+\frac{\mathscr{C}_8}{[\omega^2-(\tilde{\tilde{\Omega}}_3+2\tilde{\tilde{\Omega}}_1)^2]}+\frac{\mathscr{C}_9}{[\omega^2-(\tilde{\tilde{\Omega}}_3-2\tilde{\tilde{\Omega}}_1)^2]}\Bigg] \tag{17}$$

with

$$\mathscr{C}_1=\left\{4A^2\left(\sum_i G_{i33}+\sum_{ij} g_{ij3}e_j\right)^2\alpha_i^\dagger(\mu q)\alpha_i(\mu q)\right\} \tag{18a}$$

$$\mathscr{C}_2=\left\{2\left(\sum_i G_{i33}+\sum_{ij} g_{ij3}e_j\right)^2\alpha_i^\dagger(\mu q)\alpha_i(\mu q)\coth(\beta\tilde{\tilde{\Omega}}_3/2)/\tilde{\tilde{\Omega}}_3\right\} \tag{18b}$$

$$\mathscr{C}_3=\left\{2A^2\left(\sum_{ij} g_{ij3}\alpha_i^\dagger(\mu q)\alpha_j(\mu q)\right)^2\frac{n_\mu(q)}{\tilde{\tilde{\omega}}_\mu(q)}+\left(\sum_{ij} g_{ij3}\alpha_i^\dagger(\mu q)\alpha_j(\mu q)\right)^2 n_\mu(q)\right.$$
$$\left.\times\coth(\beta\tilde{\tilde{\Omega}}_3/2)/\tilde{\tilde{\omega}}_\mu(q)\tilde{\tilde{\Omega}}_3\right\} \tag{18c}$$

$$\mathscr{C}_4=\left\{2\left(\sum_i G_{i33}+\sum_{ij} g_{ij3}e_j\right)^2\alpha_i^\dagger(\mu q)\alpha_i(\mu q)\frac{\coth(\beta\tilde{\tilde{\omega}}_\mu(q)/2)}{\tilde{\tilde{\omega}}_\mu(q)}\right.$$
$$+\frac{3}{4}\left(\sum_{ij} g_{ij3}\alpha_i^\dagger(\mu q)\alpha_j(\mu q)\right)^2\coth^2(\beta\tilde{\tilde{\omega}}_\mu(q)/2)/\tilde{\tilde{\omega}}_\mu^2(q)+\frac{5\Gamma_1^2}{16\tilde{\tilde{\Omega}}_3^2}(1+7n_3^2)$$
$$\left.+\frac{4\Gamma_2^2}{\tilde{\tilde{\Omega}}_1^2}(1+2n_1n_3+n_1^2)+\frac{2\Gamma_2^2}{\tilde{\tilde{\Omega}}_3^2}(n_3^2-1)\right\} \tag{18d}$$

$$\mathscr{C}_5=\{10\Gamma_1^2A^2n_3/\tilde{\tilde{\Omega}}_3\} \tag{18e}$$

$$\mathscr{C}_6=\{16\Gamma_2^2A^2n_1/\tilde{\tilde{\Omega}}_1\} \tag{18f}$$

$$\mathscr{C}_7=\{15\Gamma_1^2(1+3n_3^2)/16\tilde{\tilde{\Omega}}_3^2\} \tag{18g}$$

$$\mathscr{C}_8=\{2\Gamma_2^2(1+2n_1n_3+n_1^2)/\tilde{\tilde{\Omega}}_3\tilde{\tilde{\Omega}}_1^2\} \tag{18h}$$

$$\mathscr{C}_9=\{2\Gamma_2^2(1-2n_1n_3+n_1^2)/\tilde{\tilde{\Omega}}_3\tilde{\tilde{\Omega}}_1^2\}. \tag{18i}$$

And corresponding width is obtained as (16) with respect to (14). The phonon shift corresponding to $\tilde{\tilde{\Omega}}_{1T,L}$ mode in tetragonal phase is

$$\Delta_1(q,\omega)=\left[\frac{\mathscr{C}'_1}{[\omega^2-\tilde{\tilde{\omega}}_{\mu 1}^2]}+\frac{\mathscr{C}'_2}{[\omega^2-\tilde{\tilde{\omega}}_\mu^2(q)]}+\frac{\mathscr{C}'_3}{[\omega^2-4\tilde{\tilde{\omega}}_\mu^2(q)]}+\frac{\mathscr{C}'_4}{[\omega^2-\tilde{\tilde{\Omega}}_1^2]}\right.$$
$$+\frac{\mathscr{C}'_5}{[\omega^2-9\tilde{\tilde{\Omega}}_1^2]}+\frac{\mathscr{C}'_6}{[\omega^2-(\tilde{\tilde{\Omega}}_3+\tilde{\tilde{\Omega}}_1)^2]}+\frac{\mathscr{C}'_7}{[\omega^2-(\tilde{\tilde{\Omega}}_3-\tilde{\tilde{\Omega}}_1)^2]}$$
$$\left.+\frac{\mathscr{C}'_8}{[\omega^2-(\tilde{\tilde{\Omega}}_3+2\tilde{\tilde{\Omega}}_1)^2]}+\frac{\mathscr{C}'_9}{[\omega^2-(\tilde{\tilde{\Omega}}_3-2\tilde{\tilde{\Omega}}_1)^2]}\right] \tag{19}$$

with

$$\mathscr{C}'_1=\left\{4A^2\left(\sum_i G_{i13}\right)^2\alpha_i^\dagger(\mu q)\alpha_i(\mu q)\right\} \tag{20a}$$

$$\mathscr{C}'_2=\left\{2\left(\sum_i G_{i11}+\sum_{ij} g_{ij1}e_j\right)^2\alpha_i^\dagger(\mu q)\alpha_i(\mu q)\coth(\beta\tilde{\tilde{\Omega}}_1/2)/\tilde{\tilde{\Omega}}_1\right\} \tag{20b}$$

$$\mathscr{C}'_3=\left\{\left(\sum_{ij} g_{ij1}\,\alpha_i^\dagger(\mu q)\alpha_j(\mu q)\right)^2 n_\mu(q)\coth(\beta\tilde{\tilde{\Omega}}_1/2)/\tilde{\tilde{\Omega}}_1\tilde{\tilde{\omega}}_\mu(q)\right\}; \tag{20c}$$

$$\mathscr{C}'_4 = \left\{ 2\left(\sum_i G_{i11} + \sum_{ij} g_{ij1} e_j\right)^2 \alpha_i^\dagger(\mu q)\alpha_j(\mu q) \coth(\beta\tilde{\omega}_\mu(q)/2)/\tilde{\omega}_\mu(q) \right.$$
$$+ \frac{3}{4}\left(\sum_{ij} g_{ij1}\alpha_i^\dagger(\mu q)\alpha_j(\mu q)\right)^2 \coth^2(\beta\tilde{\tilde{\omega}}_\mu(q)/2)/\tilde{\tilde{\omega}}_\mu^2(q)$$
$$+ \frac{5}{16\tilde{\tilde{\Omega}}_1^2}\Gamma_1^2(1+3n_1^2) + \frac{2\Gamma_2^2}{\tilde{\tilde{\Omega}}_1^2}(1+3n_1^2)$$
$$\left. + \frac{2\Gamma_2^2}{\tilde{\tilde{\Omega}}_3^2}(1+2n_1n_3+n_3^2) \right\} \tag{20d}$$

$$\mathscr{C}'_5 = \left\{ \frac{15\Gamma_1^2(1+3n_1^2)}{16\tilde{\tilde{\Omega}}_1^2} + \frac{3\Gamma_2^2(1+3n_1^2)}{\tilde{\tilde{\Omega}}_1^2} \right\} \tag{20e}$$

$$\mathscr{C}'_6 = \{4\Gamma_2^2A^2(n_1+n_3)(\tilde{\tilde{\Omega}}_1+\tilde{\tilde{\Omega}}_3)/\tilde{\tilde{\Omega}}_1\tilde{\tilde{\Omega}}_3\} \tag{20f}$$

$$\mathscr{C}'_7 = \{4\Gamma_2^2A^2(n_1-n_3)(\tilde{\tilde{\Omega}}_3-\tilde{\tilde{\Omega}}_1)/\tilde{\tilde{\Omega}}_1\tilde{\tilde{\Omega}}_3\} \tag{20g}$$

$$\mathscr{C}'_8 = \{\Gamma_2^2(1+2n_1n_3+n_3^2)(\tilde{\tilde{\Omega}}_1+2\tilde{\tilde{\Omega}}_3)/\tilde{\tilde{\Omega}}_1\tilde{\tilde{\Omega}}_3^2\} \tag{20h}$$

$$\mathscr{C}'_9 = \{\Gamma_2^2(1-2n_1n_3+n_3^2)(\tilde{\tilde{\Omega}}_1-2\tilde{\tilde{\Omega}}_3)/\tilde{\tilde{\Omega}}_1\tilde{\tilde{\Omega}}_3^2\} \tag{20i}$$

and the corresponding phonon width is obtained as usual.

4.3 *Trigonal phase*

The shift and phonon width corresponding to $\tilde{\tilde{\Omega}}_{3T,L}$ mode is obtained as

$$\Delta_3(q,\omega) = \left[\frac{\mathscr{C}_1}{[\omega^2-\tilde{\tilde{\omega}}_{\mu 3}^2]} + \frac{\mathscr{C}_2}{[\omega^2-\tilde{\tilde{\omega}}_\mu^2(q)]} + \frac{\mathscr{C}_3}{[\omega^2-4\tilde{\tilde{\omega}}_\mu^2(q)]} + \frac{\mathscr{C}_4}{[\omega^2-\tilde{\tilde{\Omega}}_3^2]} \right.$$
$$+ \frac{\mathscr{C}_5}{[\omega^2-4\tilde{\tilde{\Omega}}_3^2]} + \frac{\mathscr{C}_6}{[\omega^2-4\tilde{\tilde{\Omega}}_1^2]} + \frac{\mathscr{C}_7}{[\omega^2-9\tilde{\tilde{\Omega}}_3^2]}$$
$$\left. + \frac{\mathscr{C}_8}{[\omega^2-(\tilde{\tilde{\Omega}}_3+2\tilde{\tilde{\Omega}}_1)^2]} + \frac{\mathscr{C}_9}{[\omega^2-(\tilde{\tilde{\Omega}}_3-2\tilde{\tilde{\Omega}}_1)^2]} \right] \tag{21}$$

where

$$\mathscr{C}_1 = \left\{ \frac{4}{9}A^2\left(3G_{11}+6G_{44}+6G_{12}+\sum_{ij\lambda} g_{ij\lambda}e_j\right)^2 \alpha_i^\dagger(\mu g)\alpha_i(\mu q) \right\}; \tag{22a}$$

$$\mathscr{C}_2 = \left\{ \frac{2}{9}\left(3G_{11}+6G_{44}+6G_{12}+\sum_{ij\lambda} g_{ij\lambda}e_j\right)^2 \right.$$
$$\left. \times\, \alpha_i^\dagger(\mu q)\alpha_i(\mu q)\coth(\beta\tilde{\tilde{\Omega}}_3/2)/\tilde{\tilde{\Omega}}_3 \right\} \tag{22b}$$

$$\mathscr{C}_3 = \left\{ \left(\sum_{ij\lambda} g_{ij\lambda}\alpha_i^\dagger(\mu q)\alpha_j(\mu q)\right)^2 \frac{n_\mu(q)}{\tilde{\tilde{\omega}}_\mu(q)}\left(\frac{2}{9}A^2 + \frac{\coth(\beta\tilde{\tilde{\Omega}}_3/2)}{9\tilde{\tilde{\Omega}}_3}\right) \right\} \tag{22c}$$

$$\mathscr{C}_4 = \left\{ \frac{2}{9}\left(3G_{11}+6G_{44}+6G_{12}+\sum_{ij\lambda} g_{ij\lambda}e_j\right)^2 \frac{\alpha_i^\dagger(\mu q)\alpha_i(\mu q)}{\tilde{\tilde{\omega}}_\mu(q)} \coth(\beta\tilde{\omega}_\mu(q)/2) \right.$$

$$+\frac{1}{12}\left(\sum_{ij\lambda} g_{ij\lambda}\alpha_i^\dagger(\mu q)\alpha_j(\mu q)\right)^2 \coth^2(\beta\tilde{\omega}_\mu(q)/2)/\tilde{\tilde{\omega}}_\mu^2(q)$$

$$+\frac{5}{4}\left(\frac{\Gamma_1}{4}+\frac{2\Gamma_2}{3}\right)^2\frac{(1+7n_3^2)}{\tilde{\tilde{\Omega}}_3^2}$$

$$+\frac{4(1+2n_1n_3+n_1^2)}{\tilde{\tilde{\Omega}}_1^2}\left(\frac{\Gamma_1}{6}+\frac{2\Gamma_2}{3}\right)^2\Bigg\} \tag{22d}$$

$$\mathscr{C}_5=\{10A^2(\Gamma_1+4\Gamma_2)^2 n_3/9\tilde{\tilde{\Omega}}_3\} \tag{22e}$$

$$\mathscr{C}_6=\{4A^2(\Gamma_1+4\Gamma_2)^2 n_1/9\tilde{\tilde{\Omega}}_1\} \tag{22f}$$

$$\mathscr{C}_7=\{5(\Gamma_1+4\Gamma_2)^2(1+3n_3^2)/48\tilde{\tilde{\Omega}}_3^2\} \tag{22g}$$

$$\mathscr{C}_8=\{(\Gamma_1+4\Gamma_2)^2(1+2n_1n_3+n_1^2)(\tilde{\tilde{\Omega}}_3+2\tilde{\tilde{\Omega}}_1)/18\tilde{\tilde{\Omega}}_3\tilde{\tilde{\Omega}}_1^2\} \tag{22h}$$

$$\mathscr{C}_9=\{(\Gamma_1+4\Gamma_2)^2(1-2n_1n_3+n_1^2)(\tilde{\tilde{\Omega}}_3-2\tilde{\tilde{\Omega}}_1)/18\tilde{\tilde{\Omega}}_3\tilde{\tilde{\Omega}}_1^2\} \tag{22i}$$

with

$$n_1=\coth(\beta\tilde{\tilde{\Omega}}_1/2) \quad \text{and} \quad n_3=\coth(\beta\tilde{\tilde{\Omega}}_3/2);$$

The corresponding phonon width is obtained as usual. The phonon shift corresponding to $\tilde{\tilde{\Omega}}_{1T,L}$ mode is given by

$$\Delta_1(q,\omega)=\Bigg[\frac{\mathscr{C}'_1}{[\omega^2-\tilde{\tilde{\omega}}_{\mu 1}^2]}+\frac{\mathscr{C}'_2}{[\omega^2-\tilde{\tilde{\omega}}_\mu^2(q)]}+\frac{\mathscr{C}'_3}{[\omega^2-4\tilde{\tilde{\omega}}_\mu^2(q)]}+\frac{\mathscr{C}'_4}{[\omega^2-\tilde{\tilde{\Omega}}_1^2]}$$
$$+\frac{\mathscr{C}'_5}{[\omega^2-4\tilde{\tilde{\Omega}}_1^2]}+\frac{\mathscr{C}'_6}{[\omega^2-9\tilde{\tilde{\Omega}}_1^2]}+\frac{\mathscr{C}'_7}{[\omega^2-(\tilde{\tilde{\Omega}}_1+\tilde{\tilde{\Omega}}_3)^2]}$$
$$+\frac{\mathscr{C}'_8}{[\omega^2-(\tilde{\tilde{\Omega}}_1-\tilde{\tilde{\Omega}}_3)^2]}+\frac{\mathscr{C}'_9}{[\omega^2-(\tilde{\tilde{\Omega}}_1+2\tilde{\tilde{\Omega}}_3)^2]}$$
$$+\frac{\mathscr{C}'_{10}}{[\omega^2-(\tilde{\tilde{\Omega}}_1-2\tilde{\tilde{\Omega}}_3)^2]}\Bigg] \tag{23}$$

with

$$\mathscr{C}'_1=\left\{\frac{2}{9}A^2\left(6G_{44}+\sum_{ij\lambda}g_{ij\lambda}e_j\right)^2\alpha_i^\dagger(\mu q)\alpha_i(\mu q)\right\} \tag{24a}$$

$$\mathscr{C}'_2=\Bigg\{\left(G_{11}+2G_{12}-G_{44}+\frac{1}{6}\sum_{ij}e_j[g_{ij1}+g_{ij2}+4g_{ij3}]\right)^2$$
$$\times\frac{2\alpha_i^\dagger(\mu q)\alpha_i(\mu q)}{\tilde{\tilde{\Omega}}_1}\coth(\beta\tilde{\tilde{\Omega}}_1/2)\Bigg\} \tag{24b}$$

$$\mathscr{C}'_3=\Bigg\{\left(\sum_{ij}[g_{ij1}+g_{ij2}-2g_{ij3}]\alpha_i^\dagger(\mu q)\alpha_j(\mu q)\right)^2\frac{A^2 n_\mu(q)}{9\tilde{\tilde{\omega}}_\mu(q)}$$
$$+\left(\sum_{ij}[g_{ij1}+g_{ij2}+4g_{ij3}]\alpha_i^\dagger(\mu q)\alpha_j(\mu q)\right)^2\frac{n_\mu(q)\coth(\beta\tilde{\tilde{\Omega}}_1/2)}{36\tilde{\tilde{\Omega}}_1\tilde{\tilde{\omega}}_\mu(q)}\Bigg\} \tag{24c}$$

$$\mathscr{C}'_4=\Bigg\{2\left(G_{11}+2G_{12}-G_{44}+\tfrac{1}{6}\sum_{ij}e_j[g_{ij1}+g_{ij2}+4g_{ij3}]\right)^2\alpha_i^\dagger(\mu q)\alpha_i(\mu q)$$
$$\times\coth(\beta\tilde{\tilde{\omega}}_\mu(q)/2)/\tilde{\tilde{\omega}}_\mu(q)$$

$$+\frac{1}{48}\left(\sum_{ij}[g_{ij1}+g_{ij2}+4g_{ij3}]\alpha_i^{\dagger}(\mu q)\alpha_j(\mu q)\right)^2 \coth^2(\beta\tilde{\omega}_\mu(q)/2)/\tilde{\omega}_\mu^2(q)$$

$$+\frac{5(\Gamma_1+2\Gamma_2)^2(1+7n_1^2)}{64\tilde{\tilde{\Omega}}_1^2}+\frac{(\Gamma_1+10\Gamma_2)^2(1+7n_1^2)}{144\tilde{\tilde{\Omega}}_1^2}$$

$$\left.+\frac{(\Gamma_1+4\Gamma_2)^2(1+2n_1n_3+n_3^2)}{18\tilde{\tilde{\Omega}}_3^2}\right\} \tag{24d}$$

$$\mathscr{C}'_5=\{2A^2(\Gamma_1-2\Gamma_2)^2 n_1/3\tilde{\tilde{\Omega}}_1\} \tag{24e}$$

$$\mathscr{C}'_6=\left\{\frac{(1+3n_1^2)}{\tilde{\tilde{\Omega}}_1^2}[\tfrac{15}{16}(\Gamma_1+2\Gamma_2)^2+\tfrac{1}{48}(\Gamma_1+10\Gamma_2)^2]\right\} \tag{24f}$$

$$\mathscr{C}'_7=\{A^2(\Gamma_1+4\Gamma_2)^2(n_1+n_3)(\tilde{\tilde{\Omega}}_3+\tilde{\tilde{\Omega}}_1)/9\tilde{\tilde{\Omega}}_1\tilde{\tilde{\Omega}}_3\} \tag{24g}$$

$$\mathscr{C}'_8=\{A^2(\Gamma_1+4\Gamma_2)^2(n_1-n_3)(\tilde{\tilde{\Omega}}_3-\tilde{\tilde{\Omega}}_1)/9\tilde{\tilde{\Omega}}_1\tilde{\tilde{\Omega}}_3\} \tag{24h}$$

$$\mathscr{C}'_9=\{(\Gamma_1+4\Gamma_2)^2(1+2n_1n_3+n_3^2)(\tilde{\tilde{\Omega}}_1+2\tilde{\tilde{\Omega}}_3)/36\tilde{\tilde{\Omega}}_1\tilde{\tilde{\Omega}}_3^2\} \tag{24i}$$

$$\mathscr{C}'_{10}=\{(\Gamma_1+4\Gamma_2)^2(1-2n_1n_3+n_3^2)(\tilde{\tilde{\Omega}}_1-2\tilde{\tilde{\Omega}}_3)/36\tilde{\tilde{\Omega}}_1\tilde{\tilde{\Omega}}_3^2\} \tag{24j}$$

and corresponding width is obtained as usual.

5. Comparison with experiments and discussion

Following Kubo (1957) and Zubarev (1960) the dielectric susceptibility is obtained as

$$\chi(q,\omega)=-\frac{2N\mu^2\varepsilon_\lambda(q)}{[\omega^2-\Omega_\lambda^2(q)+i\Gamma_\lambda(q,\omega)]}; \tag{25}$$

where N is the number of the unit cells in the sample and μ is the effective dipole moment per unit cell.

$$\Omega_\lambda^2(q)=\tilde{\tilde{\Omega}}_\lambda^2(q)+\Delta_\lambda(q,\omega);$$

$\Delta_\lambda(q,\omega)$ is the shift in phonon frequency and $\Gamma_\lambda(q,\omega)$ is the phonon width.

The dielectric constant can be calculated by using the usual relation

$$\varepsilon=1+4\pi\chi; \tag{26}$$

the real part of which is given by

$$\varepsilon'-1=-\frac{8\pi N\mu^2(\omega^2-\Omega_\lambda^2(q)\varepsilon_\lambda(q))}{[(\omega^2-\Omega_\lambda^2(q))^2+\Gamma_\lambda^2(q,\omega)]}; \tag{27}$$

and the tangent loss

$$\tan\delta=\varepsilon''/\varepsilon'=\Gamma_\lambda(q,\omega)/[\omega^2-\Omega_\lambda^2(q)]; \tag{28}$$

where ε'' is the imaginary part of equation (25), and $\varepsilon'\gg 1$; $\delta(X)$ in $\Gamma_\lambda(q,\omega)$ is calculated using the formula (Bohlin and Högberg 1969)

$$\delta(X)=\frac{\varepsilon}{\pi(X^2+\varepsilon^2)};\quad \varepsilon \text{ is very small.} \tag{29}$$

A plausible explanation of the origin of temperature dependence of the microwave loss tangent and dielectric constant is possible, if the paraelectricity of the ABO_3-perovskites is regarded as originating from a temperature dependent optical soft mode frequency. A transverse microwave radiation field derives the soft transverse optical mode of the material in a forced vibration. Energy is transferred from the electromagnetic field to this lattice mode and is degraded into other vibrational modes. This is the likely origin of microwave loss. The soft mode frequency is very large as compared to the microwave frequency ω ($\omega/\Omega \simeq 10^{-3}$) 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 the dielectric constant can be written as

$$\varepsilon' = 8\pi N \mu^2 \varepsilon_\lambda(q)/\Omega_\lambda^2(q). \tag{30}$$

The strain components vary with temperature as (Feder and Pytte 1970)

$$e_i(T) \propto \overset{+}{\Delta}(T); \quad \text{where } \overset{+}{\Delta}(T) = \coth(\beta\tilde{\Omega}/2)/\tilde{\Omega}$$

and for $T \sim T_c$, it follows from molecular field approximation that

$$\overset{+}{\Delta}(T) - \overset{+}{\Delta}(T_c) \propto |T - T_c|$$

and to the first approximation

$$\Omega_\lambda^2(q) \simeq \text{constant} \times (T - T_c) \tag{31}$$

and (30) becomes

$$\varepsilon' = \text{constant}/(T - T_c). \tag{32}$$

Similarly, the microwave tangent loss

$$\begin{aligned} \tan\delta &= -\Gamma_\lambda(q,\omega)/(T - T_c) \\ &= \omega(\alpha + \beta T + \gamma T^2)/(T - T_c). \end{aligned} \tag{33}$$

The frequency of different modes in different phases and the free energy for perovskite crystals have been evaluated but dielectric properties could not be explained by Pytte (1972). This may be due to the fact that correlations appearing in the dynamical equation have been decoupled at the early stage and interaction between different branches of the vibrational modes have not been taken into account. In the present study the correlation functions have not been decoupled and are evaluated using the renormalized Hamiltonian. This leads to the width and shift in the phonon frequency. The phonon width and shift are directly related to the dielectric properties.

Equations (32) and (33) describe the behaviour of $SrTiO_3$ (Rupprecht and Bell 1962) quite well. The dielectric constant exhibits no relaxation at the highest microwave frequency (35 GHz). The Curie-Weiss behaviour of tangent loss in $SrTiO_3$ and $SrTiO_3$ with impurities (Rupprecht and Bell 1962), shows that this contribution is due to the temperature independent term α in (33). This suggests that imperfections cause damping. The imperfections couple the soft mode to other modes and provide a mechanism for scattering of energy out of the driven mode. At higher temperatures the loss deviates strongly from the Curie-Weiss type behaviour and increase linearly with temperature. This behaviour assumes that at higher temperatures lattice anharmonicity is responsible for the observed loss. $BaTiO_3$ (Benedict and Durand 1958), $CaTiO_3$ (Linz and Herrington 1958): $KTaO_3$, $KTaO_3$: $NaTaO_3$ (Agrawal and Rao 1970) exhibit the same behaviour.

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 semiconduction 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 anharmonicity may be responsible for the observed behaviour of the microwave tangent loss.

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