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Sound attenuation in doped displacive ferroelectrics

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Abstract. An expression is obtained for the sound attenuation constant in a doped displacive ferroelectrics in the presence of an external electric field, using double-time temperature-dependent Green's function technique. The mass and force constant changes due to impurity atoms, are taken into account along with higher order anharmonic and electric dipole moment terms, in the Silverman-Joseph Hamiltonian. The attenuation constant increases with an external electric field. The soft mode is responsible for the anomalously increasing behaviour of the attenuation constant in the vicinity of the Curie temperature. The results agree with those attained by Tani and Tsuda and Heuter and Neuhaus.

Keywords. Displacive ferroelectrics; anharmonicity and electric dipolemoment; attenuation constant; Curie temperature.

1. Introduction

Ultrasonic measurements have proved to be a sensitive tool for the study of phase changes in solids. This is particularly true when minor lattice distortions (Jones and Holm 1968) are involved, such as those occurring in insulating $SrTiO_3$ at low temperatures, which is cubic at room temperature but transforms to a tetragonal phase below 110°K. Although these structural modifications are minor in nature, it has been demonstrated that their influence on the propagation of ultrasound is dramatic (Jones and Holm 1968). Many experimental (Cowley 1962; Shirane *et al* 1967; Barker and Tinkham 1962; Spitzer 1962; Motegi and Mitsui 1964; Fattuzo and Merz 1967) and theoretical (Cochran 1959; Kurosawa 1961; Anderson 1966; Ginzburg 1960; Tani 1967) work have appeared showing that the soft or ferroelectric mode plays an essential role in displacive ferroelectrics, when the temperature approaches the Curie temperature T_c the soft mode's frequency becomes vanishingly small, resulting in an increase of its amplitude which should influence the acoustic mode (Tani 1969) via phonon-phonon interaction, and is expected to give rise to an anomalous behaviour of sound near T_c. The degeneracy (Tani 1969) of the soft mode with the longitudinal acoustic mode for large wave number gives the characteristic behaviour of the soft mode in displacive ferroelectrics like $SrTiO_3$. Tani and Naoyuki (1969) have also extended the phenomenological theory of sound near the transition point to displacive ferroelectrics and they have shown the anomalously increasing behaviour of the attenuation constant in the vicinity of the Curie temperature.

We have earlier studied the electric field dependence of inelastic neutron scattering cross section (Gairola 1977), thermal conductivity (Naithani *et al* 1977) and micro-

wave absorption (Naithani and Semwal 1978) in displacive ferroelectrics using thermal Green's function technique (Zubarev 1960), with the help of the modified Silverman-Joseph (1963) Hamiltonian. The present study is designed to derive an expression for the attenuation constant of sound in the displacive ferroelectrics. The mass and force constant changes are taken into account in the Silverman-Joseph (1963) Hamiltonian augmented with higher order anharmonic and electric dipole moment terms. The expression obtained for the attenuation constant of sound is qualitatively discussed for various situations.

In § 2, we write the formula of the attenuation constant of sound and the Hamiltonian. Section 3, describes the necessary Green's functions, their evaluations and the expression of the attenuation constant of the sound. In § 4, we have qualitatively discussed the expression of attenuation constant of the sound for various situations.

2. Attenuation constant and the Hamiltonian

The expression for the attenuation constant is given by Tani (1969) as,

$$a_k = \Gamma_k/c, \tag{1}$$

Where c is the sound velocity and Γ_k is the damping constant; Γ_k is also defined as the half width of the frequency response of acoustic phonon mode k, and is given by the imaginary part of the response function $P(\omega)$ (defined in § 3, equation (15)).

For deriving an expression for the response function and hence for the attenuation constant we use the modified Silverman-Joseph Hamiltonian for the doped displacive ferroelectrics in the presence of external electric field. Here we have explicitly taken into account the mass changes and the force constant changes between impurity atom and the host lattice atoms, neglecting the impurity-impurity interactions in the Hamiltonian, which is given by

$$\begin{aligned}\mathcal{H} = {} & \sum_k \hbar\,\omega_k{}^a\,(a_k{}^{a+}\,a_k{}^a + \tfrac{1}{2}) + \sum_k{}' \hbar\,\omega_k{}^0\,(a_k{}^{0+}\,a_k{}^0 + \tfrac{1}{2}) \\ & - (\hbar\,\omega_0{}^0/4)\,(A_0{}^0\,A_0{}^0 + B_0{}^0\,B_0{}^0) + \hbar\,V\,A_0{}^{04} + \hbar\,D_1'\,E\,A_0{}^{03} \\ & - \hbar\,C\,(0,0)\,B_0{}^0\,B_0{}^0 + \hbar\,D\,(0,0)\,A_0{}^0\,A_0{}^0 - \hbar\,B_0{}^0\,X + \hbar\,A_0{}^0\,Y \\ & + \hbar\,Z + \hbar\,A_0{}^0\,P + \hbar\,A_0{}^0\,A_0{}^0\,Q + \hbar\,A_0{}^0\,R + \hbar\,A_0{}^0\,S \\ & + \hbar\,E\,(-\alpha\,A_0{}^0 + A + A_0{}^0\,B^\lambda + C + D_1),\end{aligned} \tag{2}$$

with

$$X = \sum_k\,[C\,(k_a, 0)\,B_k{}^a + C\,(k_0, 0)\,B_k{}^0], \tag{2a}$$

$$Y = \sum_k\,[D\,(k_a, 0)\,A_k{}^a + D\,(k_0, 0)\,A_k{}^0], \tag{2b}$$

$$\begin{aligned}Z = {} & \sum_{k_1, k_2, \lambda}\,[D\,(k_1{}^\lambda, k_2{}^\lambda)\,A_{k_1}{}^\lambda\,A_{k_2}{}^\lambda - C\,(k_1{}^\lambda, k_2{}^\lambda)\,B_{k_1}{}^\lambda\,B_{k_2}{}^\lambda] \\ & + \sum_{k_1, k_2}\,[D\,(k_1{}^a, k_2{}^0)\,A_{k_1}{}^0\,A_{k_2}{}^0 - C\,(k_1{}^a, k_2{}^0)\,B_{k_1}{}^a\,B_{k_2}{}^0],\end{aligned} \tag{2c}$$

$$P = \sum_k F(k)\, A_k^{a+}\, A_k^0, \tag{2d}$$

$$Q = \sum_{k,\lambda} \beta^\lambda(k)\, A_k^{\lambda+}\, A_k^\lambda, \tag{2e}$$

$$R = \sum_{k_1, k_2, k_3} \Phi(k_1, k_2, k_3)\, A_{k_1}^0\, A^a{}_{k_2}\, A^a{}_{k_3}, \tag{2f}$$

$$S = \sum_{k_1, k_2, k_3} \psi(k_1, k_2, k_3)\, A_{k_1}^0\, A_{k_2}^0\, A_{k_3}^0, \tag{2g}$$

$$A = \sum_k A(k)\, A_k^{a+}\, A_k^0, \tag{2h}$$

$$B^\lambda = \sum_k B^\lambda(k)\, A_k^\lambda\, A_k^\lambda, \tag{2i}$$

$$C = \sum_{k_1, k_2, k_3} C'(k_1, k_2, k_3)\, A_{k_1}^0\, A_{k_2}^a\, A_{k_3}^0, \tag{2j}$$

$$D_1 = \sum_{k_1, k_2, k_3} D_1(k_1, k_2, k_3)\, A_{k_1}^0\, A_{k_2}^0\, A_{k_3}^0, \tag{2k}$$

$$V = \psi(0, 0, 0), \tag{2l}$$

$$D'_1 = D_1(0, 0, 0), \tag{2m}$$

With $\lambda = a, 0$; $A_k = a_k + a^+_{-k}$ and $B_k = a_k - a^+_{-k}$, a_k and a_k^+ being the annihilation and creation operators for the mode of wave vector k. Here the parameters $C(k, k')$ and $D(k, k')$ depend upon the changes in the mass and force constant due to substitutional impurities respectively and are given by

$$C(k, k') = (\omega_k\, \omega'_k)^{1/2} \frac{M_\rho^0}{4N\mu_\rho} \sum_\alpha \sigma_\alpha(\rho/k)\, \sigma_\alpha(\rho/k') \left(f \sum_s \exp\left[i(\mathbf{k}+\mathbf{k}') \cdot \vec{\chi}(s)\right] \right.$$

$$\left. - \sum_i \exp\left[i(\mathbf{k}+\mathbf{k}') \cdot \chi(i)\right] \right), \tag{3a}$$

$$D(k, k') = (\omega_k\, \omega'_k)^{-1/2} \frac{1}{4N} \sum_{SK\alpha} \sum_{S'K'\beta} (M^K M^{K'})^{-1/2} \cdot \sigma_\alpha(K/k) \sigma_\beta(K'/k') \times$$

$$\triangle \phi_{\alpha\beta}(SK, S'K') \exp\left\{ i[\mathbf{k} \cdot \vec{\chi}(s) + \mathbf{k}' \cdot \vec{\chi}(s')] \right\} (\delta_{si}\, \delta_{K\rho} + \delta_{s'i}\, \delta_{K'\rho}), \tag{3b}$$

where ω_k is the circular frequency of the normal mode described by $k = (\mathbf{k}_j)$, $\mathbf{k}$ being the phonon wave vector and j the branch index of the phonon dispersion spectrum, and $\sigma(K/k)$ is the associated unit polarization vector (eigenvector) of the lattice mode belonging to the sublattice $K \cdot N$ is the number of unit cells in the lattice, $\vec{\chi}(s)$ gives the position vector of the sth unit cell, the symbol $(i\rho)$ identifies the position of an impurity atom in the ith unit cell. M_ρ^0 is the weighted harmonic mean of the masses of atoms of the type ρ defined by

$$1/M_\rho^0 = f/M'_\rho + (1-f)/M_\rho;\ f = n/N, \tag{4}$$

n being the number of impurities, $\mu_\rho = M_\rho\, M'_\rho/(M'_\rho - M_\rho)$ and

$$M^K = M_K + (M_\rho^0 - M_K)\,\delta_{K\rho} \tag{5}$$

M_ρ and M'_ρ are the masses of host and impurity atoms of the ρth kind. Also P, Q, R and S terms are the higher order anharmonic terms and α, A, B^λ; and C and D_1 are the linear, second order and third order electric moment terms and are used in the same sense as in an earlier study (Gairola and Semwal 1977). The primed summation in $\mathcal{H}$ exclude $\mathbf{k}=0$.

In order to get the effect of electric field on the sound attenuation constant, we notice that the most significant electric field-dependent term $(-\hbar\,\alpha E A_0^0)$ in H is linear in A_0^0; which will give no contribution if the Hamiltonian is treated without transformation. So we transform H with the help of transformation operator $S = -igEB_0^0$, which generates unitary transformation according to a general scheme,

$$H_T = \exp(-iS)\,H\exp(iS) = H + i\,[H, S] - \tfrac{1}{2}\,[[H, S], S] + \ldots. \tag{6}$$

The above choice of S eliminates the term $(-h\alpha E\, A_0^0)$ from the Hamiltonian. With the help of above transformation, the transformed Hamiltonian becomes

$$\begin{aligned} H_T = {} & \textstyle\sum_k \hbar\,\omega_k{}^a\,(a_k{}^{a+}\,a_k{}^a + \tfrac{1}{2}) + \sum_k{}' \hbar\,\omega_k{}^0\,(a_k{}^{0+}\,a_k{}^0 + \tfrac{1}{2}) \\ & - \frac{\hbar\,\omega_0{}^0}{4}\,(A_0^0\,A_0^0 + B_0^0\,B_0^0) - \hbar\,B_0^0\,X + \hbar\,A_0^0\,Y + \hbar\,Z + \hbar\,A_0^0\,P \\ & + \hbar\,A_0^0\,A_0^0\,Q + \hbar\,A_0^0\,R + \hbar\,A_0^0\,S + \hbar\,V\,A_0^{04} + \hbar\,E\,(A + A_0^0\,B^\lambda \\ & + C + D_1) + \hbar\,D'_1\,E\,A_0^{03} - \hbar\,C\,(0,0)\,B_0^0\,B_0^0 + \hbar\,D\,(0,0)\,A_0^0 A_0^0 \\ & + \hbar\alpha g E^2 - 2\hbar\,YgE - 2\hbar PgE - 4\hbar\,QgEA_0^0 - 2\hbar RgE \\ & - 2\hbar\,SgE - 8\hbar\,gEVA_0^{03} - 2\hbar\,B^\lambda gE^2 - 6\hbar\,D'_1 gE^2 A_0^{02} \\ & - 4\hbar\,g\,E\,D(0,0)\,A_0^0 + 4\hbar\,g^2\,E^2\,D(0,0) + 4\hbar\,Q\,g^2\,E^2 \\ & + 24\hbar\,g^2\,E^2\,V\,A_0^{02} + 12\hbar\,D'_1\,g^2\,E^3\,A_0^0. \end{aligned} \tag{7}$$

3. Green's functions and the expression of attenuation constant of the sound

To define the response function we now introduce retarded doubletime thermal Green's function (Zubarev 1960) for the acoustical phonon as,

$$\begin{aligned} G^a{}_{k,k'}\,(t-t') &= \langle\!\langle a_k{}^a(t);\, a_{k'}{}^{a+}(t')\rangle\!\rangle \\ &= -i\,\theta(t-t')\,\langle [a_k{}^a(t);\, a_{k'}{}^{a+}(t')]\rangle, \end{aligned} \tag{8}$$

here $\theta(t)$ is the Heaviside step function and $a_k{}^a$, $a_{k'}{}^{a+}$ are the annihilation and creation operators of the acoustic phonon of wave vector k. Now differentiating (8) with

respect to time argument t and fourier transforming the result, the equation of motion of $G^a(\omega)$ with the help of H_T is obtained as,

$$(\omega-\tilde{\omega}_k{}^a)\, G^a(\omega) = \delta_{kk'}/2\pi + \langle\langle F_1{}^a(t);\, a_{k'}{}^{a+}(t')\rangle\rangle, \tag{9}$$

where
$$\begin{aligned} F_1{}^a(t) = {} & D(-k_a, 0)\, A_0{}^0 + C(-k_a, 0)\, B_0{}^0 + [D(-k, k_1{}^0)]\, A_{k_1}{}^0 \\ & + [-2g\, E\, F(-k) + E\, A(-k)]\, A_k{}^0 + C(-k, k_1{}^0)\, B_{k_1}{}^0 \\ & + F(-k)\, A_0{}^0\, A_k{}^0 + 2\beta^a(-k)\, A_0{}^0\, A_0{}^0\, A_k{}^a + [-8g\, E\, \beta^a(-k) \\ & + 2\, E\, B^a(-k)]\, A_0{}^0\, A_k{}^a + \Big[4g\, E \sum\nolimits_{k_1, k_2} \Phi(-k, k_1, k_2) \\ & + 2\, E \sum\nolimits_{k_1, k_2} C'(-k, k_1, k_2)\Big] A_{k_1}{}^0\, A_{k_2}{}^a \\ & + 2 \sum\nolimits_{k_1, k_2} \Phi(-k, k_1, k_2)\, A_0{}^0\, A_{k_1}{}^0\, A^a{}_{k_2}, \end{aligned} \tag{10}$$

and
$$\tilde{\omega}_k{}^a = \omega_k{}^a + 2\, D(-k, k_1{}^a) + 2\, C(-k, k_1{}^a) + 8\, g^2\, E^2\, \beta^a(-k) - 4\, g\, E^2\, B^a(-k). \tag{11}$$

The equation of motion of $\langle\langle F_1{}^a(t);\, a_{k'}{}^{a+}(t')\rangle\rangle$ with respect to time argument t' gives

$$\begin{aligned} (\omega-\tilde{\omega}_k{}^a)\, \langle\langle F_1{}^a(t);\, a_{k'}{}^{a+}(t')\rangle\rangle_\omega = {} & (1/2\pi)\, \langle [F_1{}^a(t);\, a_{k'}{}^{a+}(t')]\rangle \\ & + \langle\langle F_1{}^a(t);\, F_2{}^a(t')\rangle\rangle_\omega, \end{aligned} \tag{12}$$

where
$$\begin{aligned} F_2{}^a(t') = {} & D(-k'_a, 0)\, A_0{}^0\, C(-k'_a, 0)\, B_0{}^0 + [D(-k', k_2{}^0)]\, A_{k_2}{}^0 \\ & + [-2\, g\, E\, F(-k') + E\, A(-k')]\, A_{k'}{}^0 + C(-k', k_2{}^0)\, B_{k_2}{}^0 \\ & + F(-k')\, A_0{}^0\, A_{k'}{}^0 + 2\beta^a(-k')\, A_0{}^0\, A_0{}^0\, A^a{}_{k'} + [-8\, g\, E\, \beta^a(-k') \\ & + 2E\, B^a(-k')]\, A_0{}^0\, A_{k'}{}^a + \Big[4\, g\, E \sum\nolimits_{k'_1, k'_2} \Phi(-k', k'_1, k'_2) \\ & + 2\, E \sum\nolimits_{k'_1, k'_2} C'(-k', k'_1, k'_2)\Big] A_{k'_1}{}^0\, A^a{}_{k'_2} \\ & + 2 \sum\nolimits_{k'_1, k'_2} \Phi(-k', k'_1, k'_2)\, A_0{}^0\, A_{k'_1}{}^0\, A^a{}_{k'_2}. \end{aligned} \tag{13}$$

Substituting (12) in (9), the equation of motion for $G^a(\omega)$ in the lowest approximation, in the form of Dyson equation can be written as,

$$G^a(\omega) = \{\delta_{k,k'}\}/2\pi\, [\omega-\tilde{\omega}_k{}^a - \langle [F_1{}^a(t);\, a_{k'}{}^{a+}(t')]\rangle - P(\omega)]\}, \tag{14}$$

with
$$P(\omega) = 2\pi \langle\langle F_1{}^a(t);\, F_2{}^a(t')\rangle\rangle_\omega. \tag{15}$$

Equation (14) can be rewritten as,

$$G^a(\omega+i\epsilon) = \delta_{k,k'}/2\pi\, \{\omega-\tilde{\tilde{\omega}}_k{}^a) + i\, \Gamma_k(\omega)\}, \tag{16}$$

where the renormalized frequency
$$\tilde{\tilde{\omega}}_k{}^a = \tilde{\omega}_k{}^a + 2\beta^a(-k)\, \langle A_0{}^0;\, A_0{}^0\rangle + \triangle_k(\omega), \tag{17}$$

$$\triangle_k(\omega) = \mathrm{Re}\; 2\pi\, \langle\langle F_1{}^a(t);\, F_2{}^a(t')\rangle\rangle_{\omega+i\epsilon} \tag{18}$$

and
$$\Gamma_k(\omega) = -\,\mathrm{Im}\; 2\pi\, \langle\langle F_1{}^a(t);\, F_2{}^a(t')\rangle\rangle_{\omega+i\epsilon} \tag{19}$$

(here in the expression of $\tilde{\omega}_k{}^a$, we have neglected the average displacement $\langle A_0{}^0 \rangle$ such terms give no contribution to physical quantities, because the contribution is of higher order of $1/N$, N being the system size, and hence it vanishes as N tends to infinity). The response functioning $P(\omega)$ defined by (15) can be evaluated in successive approximations. In this approximation one can write, from (10) and (13),

$$\langle\!\langle F_1{}^a(t); F_2{}^a(t') \rangle\!\rangle_\omega = G_1(\omega) + G_2(\omega) + G_3(\omega) + G_4(\omega) + G_5(\omega) + G_6(\omega) + G_7(\omega) + G_8(\omega) + G_9(\omega) + G_{10}(\omega) \qquad (20)$$

$i = 1, \ldots, 10$

where the Green's functions $G_i(t-t')$, $i=1, \ldots, 10$ are defined by

$$G_1(t-t') = |D(-k_a, 0)|^2 \langle\!\langle A_0{}^0; A_0{}^0 \rangle\!\rangle, \qquad (21a)$$

$$G_2(t-t') = -|C(-k_a, 0)|^2 \langle\!\langle B_0{}^0; B_0{}^0 \rangle\!\rangle, \qquad (21b)$$

$$G_3(t-t') = |D(-k, k_1{}^0)|^2 \langle\!\langle A_{k_1}{}^0, A_{k_2}{}^0 \rangle\!\rangle, \qquad (21c)$$

$$G_4(t-t') = |C(-k, k_1{}^0)|^2 \langle\!\langle B_{k_1}{}^0; B_{k_2}{}^0 \rangle\!\rangle, \qquad (21d)$$

$$G_5(t-t') = [4g^2E^2 |F(k)|^2 + E^2 |A(k)|^2] \langle\!\langle A_k{}^0; A_{k'}{}^0 \rangle\!\rangle, \qquad (21e)$$

$$G_6(t-t') = |F(k)|^2 \langle\!\langle A_0{}^0 A_k{}^0; A_0{}^0 A_{k'}{}^0 \rangle\!\rangle, \qquad (21f)$$

$$G_7(t-t') = 4|\beta^a(k)|^2 \langle\!\langle A_0{}^0 A_0{}^0 A_k{}^a; A_0{}^0 A_0{}^0 A_{k'}{}^a \rangle\!\rangle, \qquad (21g)$$

$$G_8(t-t') = \left[16g^2E^2 \sum_{k_1, k_2} |\Phi(-k, k_1, k_2)|^2 + 4E^2 \sum_{k_1, k_2} |C'(-k, k_1, k_2)|^2\right] \langle\!\langle A_{k_1}{}^0 A_{k_2}{}^a; A_{k'_1}{}^0 A_{k'_2}{}^a \rangle\!\rangle. \qquad (21h)$$

$$G_9(t-t') = [64g^2E^2 |\beta^a(k)|^2 + 4E^2 |B^a(k)|^2] \langle\!\langle A_0{}^0 A_k{}^a : A_0{}^0 A_{k'}{}^a \rangle\!\rangle \qquad (21i)$$

and

$$G_{10}(t-t') = 4 \sum_{k_1 k_2} |\Phi(-k, k_1, k_2)|^2 \langle\!\langle A_0{}^0 A_{k_1}{}^0 A_{k_2}{}^a; A_0{}^0 A_{k'_1}{}^0 A_{k'_2}{}^a \rangle\!\rangle. \qquad (21j)$$

In writing these Green's functions, we have for convenience suppressed the time arguments t and t' on the right hand side of (21) and we have used the relations $F(-k)=F(k)$; $\beta^\lambda(-k)=\beta^\lambda(k)$; $A(-k)=A(k)$ and $B^\lambda(-k)=B^\lambda(k)$.

The higher order Green's functions, appearing on the right hand side of (21) are evaluated with the help of the following zeroth-order renormalized Hamiltonian

$$\mathcal{H}^0{}_{\text{ren}} = \frac{\hbar}{4} \sum_{k, \lambda} \{(\tilde{\omega}_k{}^{\lambda 2} / \omega_k{}^\lambda) A_k{}^{\lambda +} A_k{}^\lambda + \omega_k{}^\lambda B_k{}^{\lambda +} B_k{}^\lambda\} + (\hbar\Omega/4)(A_0{}^0 A_0{}^0 + B_0{}^0 B_0{}^0). \qquad (22)$$

Substituting the values of the Green's functions (eqs (21)), the expression for the width of the acoustic phonon is given by,

$$\Gamma_k(\omega) = 2\pi\ [\Gamma_1(\omega) + \Gamma_2(\omega) + \ldots + \Gamma_{10}(\omega)] \tag{23}$$

where $\Gamma_{i,s}(\omega)$ (i=1–10) are the imaginary parts of the Green's functions appearing in (21) and with the help of (22) the values of $\Gamma_{i,s}(\omega)$ are given by,

$$\Gamma_1(\omega) = \tfrac{1}{2} \mid D(-k_a, 0) \mid^2 \{\delta(\omega) - \Omega\ \delta(\omega + \Omega)\}. \tag{24a}$$

$$\Gamma_2(\omega) = -\tfrac{1}{2} \mid C(-k_a, 0) \mid^2 \{\delta(\omega - \Omega) - \delta(\omega + \Omega)\}, \tag{24b}$$

$$\Gamma_3(\omega) = \tfrac{1}{2} \mid D(-k, k_1^0) \mid^2 \{\delta(\omega) - \omega_{k_1}{}^0) - \delta(\omega + \omega_{k_1}{}^0)\}, \tag{24c}$$

$$\Gamma_4(\omega) = \tfrac{1}{2} \mid C(-k, k_1^0) \mid^2 \{\delta(\omega - \omega_{k_1}{}^0) - \delta(\omega + \omega_{k_1}{}^0)\}, \tag{24d}$$

$$\Gamma_5(\omega) = \tfrac{1}{2}\ [4g^2 E^2 \mid F(k) \mid^2 + E^2 \mid A(k) \mid^2] \{\delta(\omega - \omega_k{}^0) - \delta(\omega + \omega_k{}^0)\}, \tag{24e}$$

$$\Gamma_6(\omega) = \mid F(k) \mid^2 (\delta'/4)\ [(\omega_k{}^0/\tilde{\omega}_k{}^0) \sum_{\pm} (\tilde{N}_k{}^0 \pm N_0{}^0) \{\delta(\omega - \Omega \pm \tilde{\omega}_k{}^0) - \delta(\omega + \Omega \mp \tilde{\omega}_k{}^0)\} + 2N_0{}^0 \{\delta(\omega - 2\Omega) - \delta(\omega + 2\Omega)\}], \tag{24f}$$

$$\Gamma_7(\omega) = \mid \beta^a(k) \mid^2 (\delta/2)\ (\omega_k{}^a/\tilde{\omega}_k{}^a)\ [(1 + (N_0{}^0)^2 + 2N_0{}^0 \tilde{N}_k{}^a) \{\delta(\omega - \tilde{\omega}_k{}^a - 2\Omega) - \delta(\omega + \tilde{\omega}_k{}^a + 2\Omega)\} - [1 - (N_0{}^0)^2] \{\delta(\omega - \tilde{\omega}_k{}^a) - \delta(\omega + \tilde{\omega}_k{}^a)\}], \tag{24g}$$

$$\Gamma_8(\omega) = [16g^2 E^2 \textstyle\sum_{k_1, k_2} \mid \phi(-k, k_1, k_2) \mid^2 + 4E^2 \sum_{k_1, k_2} \mid C'(-k, k_1, k_2) \mid^2]\ (\delta'/2)\ (\omega_{k_1}{}^0\ \omega_{k_2}{}^a)/(\tilde{\omega}_{k_1}{}^0\ \tilde{\omega}_{k_2}{}^a) \times \sum_{\pm} (\tilde{N}_{k_1}{}^0 \pm \tilde{N}_{k_2}{}^a) \{\delta(\omega - \tilde{\omega}_{k_1}{}^0 \pm \tilde{\omega}_{k_2}{}^a) \times - \delta(\omega + \tilde{\omega}_{k_1}{}^0 \pm \tilde{\omega}_{k_2}{}^a)\}, \tag{24h}$$

$$\Gamma_9(\omega) = [64g^2 E^2 \mid \beta^a(k) \mid^2 + 4E^2 \mid B^a(k) \mid^2]\ (\delta'/4)\ (\omega_k{}^a/\tilde{\omega}_k{}^a) \sum_{\pm} (\tilde{N}_k{}^a \pm N_0{}^0) \{\delta(\omega - \tilde{\omega}_k{}^a \mp \Omega) - \delta(\omega + \tilde{\omega}_k{}^a \pm \Omega)\}, \tag{24i}$$

and

$$\Gamma_{10}(\omega) = 4 \textstyle\sum_{k_1, k_2} \mid \Phi(-k, k_1, k_2) \mid^2 (\delta/4)\ (\omega_{k_1}{}^0\ \omega_{k_2}{}^a)/\tilde{\omega}_{k_1}{}^0\ \tilde{\omega}_{k}{}^a)$$
$$[(1 + N_0{}^0 (\tilde{N}_{k_1}{}^0 + \tilde{N}_{k_2}{}^a) + \tilde{N}_{k_1}{}^0\ \tilde{N}_{k_2}{}^a) \{\delta(\omega - \Omega - \tilde{\omega}_{k_1}{}^0 - \tilde{\omega}_{k_2}{}^a) - \delta(\omega + \Omega - \tilde{\omega}_{k_1}{}^0 - \tilde{\omega}_{k_2}{}^a)\} + (1 - N_0{}^0 (\tilde{N}_{k_1}{}^0 + \tilde{N}_{k_2}{}^a) + \tilde{N}_{k_1}{}^0 \tilde{N}_{k_2}{}^a) \{\delta(\omega - \Omega + \tilde{\omega}_{k_1}{}^0 + \tilde{\omega}_{k_2}{}^a) - \delta(\omega + \Omega - \tilde{\omega}_{k_1}{}^0 \tilde{\omega}_{k_2}{}^a)\}], \tag{24j}$$

$$\delta' = (\delta_{k_1 - k'_1}\ \delta_{k_2 - k'_2} + \delta_{k_1 - k'_2}\ \delta_{k_2 - k'_1}) \tag{24k}$$

$$\delta = \delta_{123} + \delta_{213} + \delta_{321}),$$

with $$\delta_{123} = (\delta_{k_1} - k'_1\,\delta_{k_2} - k'_2\,\delta_{k_3} - k'_3 + \delta_{k_1} - k'_1\,\delta_{k_2} - \delta k'_3\,\delta_{k_3} - k'_2), \tag{24l}$$

$$\tilde{N}_k^{\lambda} = (\omega_k^{\lambda}/\tilde{\omega}_k^{\lambda}) \cot \hbar\ (\hbar\,\omega_k^{\lambda}/2k_BT), \tag{24m}$$

and $$N^0_0 = \cot \hbar\ (\hbar\,\Omega/2k_BT), \tag{24n}$$

where Ω is the effective frequency of the soft made. The expression for this frequency can be obtained (Naithani 1978) by starting with the soft mode Green's function

$$G_0^0(\omega) = \langle\!\langle\, A_0^0(t);\ A_0^0(t')\,\rangle\!\rangle. \tag{25}$$

Writing its equation of motion and fourier transforming, the expression for the soft mode frequency Ω can be easily given by

$$\Omega^2 = -\,(\omega_0^0) + 4\omega_0^0\ D(0,0) + \omega_0^0\ E^2\,(96g^2\,V - 24gD'_1)$$

$$+\ \omega_0^0\,(4\bar{Q}) + \triangle_0^0(\omega), \tag{26}$$

where $$\bar{Q} = (1/4\pi)\ [\langle 4Q\rangle + 6V\,\langle A_0^0;\ A_0^0\rangle] \tag{27}$$

and $\triangle_0^0(\omega)$ is the shift of the frequency response of soft phonon mode. Here one can easily see that this frequency (Ω) is stabilized in the presence of electric field, defects and the anharmonicities. If all the above effects are neglected, this frequency Ω is imaginary due to the cancellation of the competing forces. The impurity, anharmonicity and the increasing electric field increase the soft mode frequency as evident from (26). In the high temperature limit the temperature dependence of the soft mode's frequency can be expressed as,

$$\Omega^2 = -\,(\omega_0^0) + 4\omega_0^0\ D(0,0) + \omega_0^0\ E^2\,(96g^2\,V - 24gD'_1)$$

$$+\ \triangle_0^0\,(\nu_D^2) + (\gamma_1 + \gamma_2 T + \gamma_3 T^2 + \gamma_4 E^2 T), \tag{28}$$

where $\triangle_0^0(\nu_D^2)$ is the temperature-independent contribution in $\triangle_0(\omega)$ due to defects and γ_i's ($i = 1-4$) are the anharmonic coefficients. Equation (28) can be rewritten as

$$\Omega^2 = K_1 + K_2 T + K_3 T^2, \tag{29}$$

K_1, K_2 and K_3 being the temperature independent terms in (26). If the temperature is not very high, one can neglect K_3 and thus (29) reduces to the form

$$\Omega^2 = K_1 + K_2 T = K_2(T - T_c); \tag{30}$$

with $$T_c = -\,K_1/K_2. \tag{31}$$

We neglect the T^2 terms because we are interested in the anomalous behaviour of sound attenuation constant in the vicinity of Curie temperature. Hence we approximate $\Omega \propto (T - T_c)^{1/2}$ if the temperature is not very high. It is evident from (31) that in

presence of both the defect and an electric field the Curie temperature T_c will change. Thus knowing the imaginary part (19) of the response function (15) we can write the expression of the attenuation constant (1) of the sound as,

$$\alpha_k = \Gamma_k/c = (2\pi/c)\,\Gamma_i(\omega), \tag{32}$$

where $\Gamma_i(\omega)$ are the imaginary parts of the Green's functions $G_i(\omega)$ (eqs (21)) and are defined in (24). It is clear from (32) that the impurity, electric field and temperature dependence of α_k is directly governed by Γ_k which is defined in (23). Thus, taking the dispersion of the soft mode frequency as $\Omega \propto (T - T_c)^{1/2}$ for small values of k, the temperature dependence of the attenuation constant of sound can be expressed as,

$$\alpha_k = (2\pi/c)\,[A_1 + (A_2 + A_3T + A_4E^2)T + (A_5 + A_6T + A_7E^2)$$

$$[T/(T - T_c)^{1/2}] + A_8[T^2/(T - T_c)^{1/2}] + A_9[T^2/(T - T_c)], \tag{33}$$

where A_i's (i=1–9) denote the temperature and electric field independent terms in $\Gamma_i(\omega)$ (eqs (24)). A_1 is only defect-dependent while the rest depend upon impurity concentration, anharmonic force constants and electric moment terms. The expression (33) does not give the explicit temperature dependence of α_k because of the renormalization effects which are of two-types. The renormalized frequencies of each phonon mode appearing in real and imaginary parts of polarization operator may produce some change in the temperature dependence.

4. Discussion

In the present study we have derived an expression for the attenuation constant of sound and discussed its impurity, electric field and temperature dependence, in a doped displacive anharmonic ferroelectric crystal, using double time thermal Green's function technique (Zubarev 1960). Both the mass and force constant changes due to doping, are taken into account, in the crystal Hamiltonian augmented with higher order anharmonic and electric dipole moment terms.

Looking upon (24) and (33) we see that the squares of the magnitudes of the coefficients responsible for the force constant change and mass change D and C respectively occur always with opposite signs. Hence their effect seems to mutually compensate each other's effect, to some extent. The magnitudes of the defect parameters C and D are responsible for the change in attenuation constant. The defect parameters C and D and hence the defect concentration will decide the limit of attenuation. Further it is clear from (33) that the attenuation constant increases with an applied electric field. This is also shown by Heuter and Neuhaus (1955) in their experiments of sound attenuation in displacive ferroelectrics in the vicinity of the Curie temperature T_c. We also see that the presence of the higher order anharmonic and electric dipole moment terms increases the attenuation constant (eqs (24) and (33)).

In the vicinity of the Curie temperature T_c, the soft mode's frequency Ω, which is imaginary in harmonic approximations and becomes temperature dependent due to

anharmonic terms, becomes vanishingly small and N_0^0 (eq. (24)) becomes anomalously large and hence the attenuation constant increases anomalously. These results agree with the results of Tani and Tsuda (1969). One can see in (26) for Ω^2 that the soft mode frequency is stabilized in the presence of the defects, anharmonicity and electric field. In the absence of all the above effects, this frequency Ω is imaginary which is due to the cancellation of the competing forces. The impurity, anharmonicity and the increasing electric field increase the soft mode frequency (eq. (26)). Since we are interested in the anomalous behaviour of sound attenuation constant in the vicinity of the Curie temperature, by neglecting the T^2 term in (29), we approximate $\Omega \propto (T - T_c)^{1/2}$. However, the presence of defects and electric field will change the Curie temperature. The expression (33) does not show the explicit temperature dependence of αs since the factors $(\omega_{k_1}\ \omega_{k_2}\ldots/\tilde{\omega}_{k_1}\ \tilde{\omega}_{k_2}\ldots)$ appearing in imaginary parts of polarization operator may also produce some change in temperature dependence as the renormalized frequencies of each phonon mode are temperature dependent.

The exact magnitude of α_k is not possible without using a specific model for the crystal. However, the qualitative dependence of the attenuation constant discussed in this paper agrees with the previous theoretical and experimental results. The treatment adopted here leads one to see the comparative variation of the attenuation constant of sound with the variation of the defect, and electric field parameters. An expression for the velocity change will be given separately.

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References

Anderson P W 1966 *Sov. Phys. Izv.*
Barker A S Jr and Tinkham M 1962 *Phys. Rev.* **125** 1527
Cowley R S 1962 *Phys. Rev. Lett.* **9** 159
Cochran W 1959 *Phys. Rev. Lett.* 3 413
Fattuzo E and Merz W J 1967 *Ferroelectricity* (North-Holland)
Gairola R P and Semwal B S 1977 *J. Phys. Soc.* Jpn **42** 608
Gairola R P and Semwal B S 1977 *J. Phys. Soc. Jpn* **42** 975
Ginzburg V L 1960 *Sov. Phys. Solid State* **2** 1824
Heuter N P and Neuhaus D P 1955 *J. Acoust. Soc. Am.* **27** 292
Jones C K and Hom J K 1968 *Phys. Lett.* **A26** 182
Kurosawa T 1961 *J. Phys. Soc. Jpn.* **16** 1928
Motegi H and Mitsui T 1964 *J. Phys. Chem. Solids* **25** 253
Naithani U C, Gairola R P and Semwal B S 1977 *J. Phys. Soc. Jpn.* **43** 204
Naithani U C and Semwal B S 1978 *J. Phys. Soc. Jpn.* (Communicated)
Silverman B D and Joseph R I 1963 *Phys. Rev.* **129** 2062
Semwal B S and Sharma P K 1974a *Prog. Theor. Phys.* **51** 639
Semwal B S and Sharma P K 1974b *J. Math. Phys.* **15** 648
Shirane G, Frazer B C, Minkiewicz V J, Leake J A and Liz A 1967 *Phys. Rev. Lett.* **19** 234

Sharma P K and Bahadur Rita 1975 *Phys. Rev.* **12** 448
Tani K 1967 *Phys. Lett.* **A25** 400
Tani K 1969 *J. Phys. Soc. Jpn.* **26** 93
Tani K and Naoyuki T 1969 *J. Phys. Soc. Jpn.* **26** 113
Zubarev D N 1960 *Sov. Phys. Usp.* **3** 320