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Sound velocity change in doped displacive ferroelectrics

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Abstract. An expression is obtained for the sound velocity change in doped displacive ferroelectrics, in the presence of an electric field by considering higher order anharmonic terms in the modified Silverman-Joseph Hamiltonian. The mass and force constant changes due to impurity may give cancellation effects. The presence of higher order anharmonicity decreases the sound velocity which in turn varies with the applied electric field. The sound velocity decreases anomalously near the Curie temperature.

Keywords. Displacive ferroelectrics; soft mode; sound velocity; Curie temperature.

1. Introduction

In a previous paper (Naithani and Semwal 1978, hereafter referred to as I), we obtained an expression of the sound attenuation constant in doped displacive ferroelectrics, in the presence of an electric field and higher order anharmonicities, by making use of a Hamiltonian proposed by Silverman and Joseph (1963) and the thermal Green's function technique (Zubarev 1960). Studies on ultrasonic propagation velocity in displacive ferroelectrics are available in literature (Barrett 1968; Jones and Holm 1968; Kashida *et al* 1973; Luthi and Meron 1970 and Tani and Naoyuki 1969). The purpose of the present study is to obtain an expression of the sound velocity change in displacive ferroelectrics. The mass and force constant changes due to defect are taken into account in the Silverman-Joseph Hamiltonian augmented with higher order anharmonic and electric-dipolemoment terms. The expression obtained for the sound velocity change is then discussed for various situations.

2. Sound velocity change and the Hamiltonian

The transverse acoustic mode frequency is given by $\omega_k = c\,|k|$, where c is the velocity of the transverse acoustic mode. The velocity change $\triangle c$ is given by Tani and Naoyuki (1969) as,

$$\triangle c = \triangle \omega_k / k, \tag{1}$$

$\triangle \omega_k$ being the change in the transverse acoustic mode frequency of the wave and k the wave number. In order to derive an expression for the velocity change we use

the modified Silverman-Joseph Hamiltonian for the doped displacive ferroelectrics in the presence of an external electric field. We take into account the mass and force constant changes between an impure atom and host lattice atoms, neglecting the impurity-impurity interactions in the Hamiltonian.

3. Green's functions and the expression of the velocity change

The retarded double-time thermal Green's function (Zubarev 1960) is used for the acoustic phonon. The equation of motion of $G(\omega)$ using H_T as also the response function Green's function, etc. are taken from our earlier calculations (Naithani and Semwal 1978). The response function $P(\omega)$ is evaluated in successive approximation. The higher order Green's functions are evaluated with the help of zeroth order renormalised Hamiltonian. Substituting the values of the Green's functions, the expression for the real part of the response function is given by,

$$\triangle_k(\omega) = [\triangle_1(\omega)+\triangle_2(\omega)+\triangle_3(\omega)+\ldots.+\triangle_{10}(\omega)], \tag{2}$$

Here $\triangle_i$, $s(\omega)(i=1, 2\ldots10)$ are the real parts of the Green's functions and with the help of H^0_{ren} the values of $\triangle_i$, $s(\omega)$ are given by

$$\triangle_1(\omega) = |D(-k_a, 0)|^2\, 2\Omega/(\omega^2-\Omega^2), \tag{3a}$$

$$\triangle_2(\omega) = -|C(-k_a, 0)|^2\, 2\Omega/(\omega^2-\Omega^2), \tag{3b}$$

$$\triangle_3(\omega) = |D(-k, k_1^o)|^2\, 2\omega^o_{k_1}/(\omega^2-\omega^{o2}_{k_1}), \tag{3c}$$

$$\triangle_4(\omega) = |C(-k, k_1^o)|^2\, 2\omega^o_{k_1}/(\omega^2-\omega^{o2}_{k_1}), \tag{3d}$$

$$\triangle_5(\omega) = E^2\,[4g^2|F(k)|^2+|A(k)|^2]\, 2\omega^o_k/(\omega^2-\omega^{o2}_k), \tag{3e}$$

$$\triangle_6(\omega) = |F(k)|^2\,\delta'(\omega^o_k/\tilde{\omega}^o_k)\sum_{\pm}(N^o_0\pm\tilde{N}^o_k)\frac{(\Omega\pm\tilde{\omega}^o_k)}{\omega^2-(\Omega\pm\tilde{\omega}^o_k)^2}, \tag{3f}$$

$$\triangle_7(\omega) = |\beta^a(k)|^2\,\delta(\omega^a_k/\tilde{\omega}^a_k)\left[(1+N^{o2}_0+2N^o_0\tilde{N}^a_k)\frac{(2\Omega+\tilde{\omega}^a_k)}{\omega^2-(2\Omega+\tilde{\omega}^a_k)^2}\right.$$
$$\left.-(1-N^{o2}_0)\frac{\tilde{\omega}^a_k}{\omega^2-(\tilde{\omega}^a_k)^2}\right], \tag{3g}$$

$$\triangle_8(\omega) = E^2\left[16g^2\sum_{k_1k_2}|\Phi(-k, k_1, k_2)|^2+4\sum_{k_1k_2}|C'(-k, k_1, k_2)|^2\right]$$
$$\delta'(\omega^o_{k_1}\omega^a_{k_2}/\tilde{\omega}^o_{k_1}\tilde{\omega}^a_{k_2})\sum_{\pm}(\tilde{N}^o_{k_1}\pm\tilde{N}^a_{k_2})\frac{(\tilde{\omega}^o_{k_1}\pm\tilde{\omega}^a_{k_2})}{\omega^2-(\tilde{\omega}^o_{k_1}\pm\tilde{\omega}^a_{k_2})^2}, \tag{3h}$$

$$\triangle_9(\omega) = E^2\ [64g^2\,|\beta^a(k)|^2 + 4\,|B^a(k)|^2]\ \delta'(\omega_k^a/\tilde{\omega}_k^a)$$

$$\sum_{\pm} (\tilde{N}_k^a \pm N_0^a) \frac{(\Omega \pm \tilde{\omega}_k^a)}{\omega^2 - (\Omega \pm \tilde{\omega}_k^a)^2}, \tag{3i}$$

$$\text{and } \triangle_{10}(\omega) = \sum_{k_1,k_2} |\,\Phi\,(-k, k_1, k_2)\,|^2\,(2\delta) \left(\frac{\omega_{k_1}^o\ \omega_{k_2}^o}{\tilde{\omega}_{k_1}^o\ \tilde{\omega}_{k_2}^o}\right)$$

$$\Big\{(1 + N_0^o\,\tilde{N}_{k_1}^o + N_0^o\,N_{k_2}^o + \tilde{N}_{k_1}^o\,N_{k_2}^o) \frac{(\Omega + \tilde{\omega}_{k_1}^o + \tilde{\omega}_{k_2}^o)}{\omega^2 - (\Omega + \tilde{\omega}_{k_1}^o + \tilde{\omega}_{k_2}^o)^2}$$

$$+ (1 - N_0^o\,\tilde{N}_{k_1}^o + N_0^o\,\tilde{N}_{k_2}^o - \tilde{N}_{k_1}^o\,\tilde{N}_{k_2}^o) \frac{(\Omega - \tilde{\omega}_{k_1}^o - \tilde{\omega}_{k_2}^o)}{\omega^2 - (\Omega - \tilde{\omega}_{k_1}^o - \tilde{\omega}_{k_2}^o)^2}\Big\}, \tag{3j}$$

$$\delta' = \delta_{k_1 - k_1'}\,\delta_{k_2 - k_2'} + \delta_{k_1 - k_2'}\,\delta_{k_2 - k_1'}\ , \tag{3k}$$

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

with $$\delta_{123} = \delta_{k_1 - k_1'}\,(\delta_{k_2 - k_2'}\,\delta_{k_3 - k_3'} + \delta_{k_2 - k_3'}\,\delta_{k_3 - k_2'}), \tag{3l}$$

$$\tilde{N}_k^\lambda = (\omega_k^\lambda/\tilde{\omega}_k^\lambda)\ \cot h\ (\hbar\ \omega_k^\lambda/2\ k_B\ T), \tag{3m}$$

and $$N_0^o = \cot h\ (\hbar\ \Omega/2\ k_B\ T). \tag{3n}$$

In equation (3*n*), Ω is the effective frequency of the soft mode. (see equation (26) of I) The ultrasonic frequencies ω will be smaller than the Cochran mode frequency Ω in cubic ferroelectrics. Therefore, in the limit $\omega \ll \Omega$, $\triangle_k(\omega)$ given by (3) will be negative. Since we are interested in the anomalous behaviour of sound velocity change near the Curie temperature, we approximate $\Omega \propto (T - T_c)^{1/2}$. However the presence of defects and electric field will change the Curie temperature. T_c is the temperature at which the optic mode frequency goes to zero, and not the actual transition temperature T_0 of the crystal.

In the present problem the change in transverse acoustic mode frequency of the wave can be written as,

$$\triangle\ \omega_k = \tilde{\tilde{\omega}}_k^a - \omega_k^a, \tag{4}$$

where the renormalised frequency $\tilde{\tilde{\omega}}_k^a$ is given by,

$$\tilde{\tilde{\omega}} = \tilde{\omega}_k^a + 2\,\beta^a\,(-k)\,\langle A_0^o;\, A_0^o\rangle + \triangle_k(\omega), \tag{4a}$$

with $$\tilde{\omega}_k^a = \omega_k^a + 2\ D\ (-k, k_1^a) + 2\ C\ (-k, k_1^a)$$

$$+ 8\ g^2\ E^2\ \beta^a\,(-k) - 4\ g\ E^2\ B^a\,(-k), \tag{4b}$$

and $\triangle_k(\omega)$ being the real part of the response function (equation (2)). Thus, using (4) one can obtain the expression of the sound velocity change (equation (1)). Taking the temperature variance of the soft mode frequency as $\Omega \propto (T-T_c)^{1/2}$ for small values of k (in the limit $\omega \ll \Omega$), the temperature dependence of the sound velocity change can be expressed as,

$$\triangle c = \frac{1}{k}\Big[A_1 + A_2 E^2 + (A_3 + A_4 E^2) T + (A_5 + E^2 A_6 T + A_7 T^2) \frac{1}{(T-T_c)^{1/2}} + (A_8 + A_9 T + A_{10} E^2) \frac{T}{(T-T_c)} + A_{11} \frac{T^2}{(T-T_c)^{3/2}}\Big], \tag{5}$$

where A_i's ($i=1, .., 11$) denote the temperature and electric field independent terms in $\triangle\omega_k$ (equation (4) for $\omega \ll \Omega$). A_1 is only defect-dependent, while the rest depend upon impurity concentration, anharmonic force constants and electric moment terms. The expression (5) does not give the explicit temperature dependence of $\triangle c$ because of the renormalisation effects. The renormalised frequencies of each phonon mode appearing in real and imaginary parts of polarisation operator may produce some change in the temperature dependence. The various temperature dependences of $\triangle c$ given in (5) are due to temperature variance of soft mode frequency ($\Omega \alpha (T-T_c)^{\frac{1}{2}}$) and higher order anharmonicities present in the crystal. The T and and T^2 dependences of $\triangle c$ are due to third- and fourth-order anharmonicities respectively in the presence of higher order electric moment terms. One can see from equation (1), (3) and (4) impurity influences change in velocity. The magnitude of the parameters C (mass change) and D (harmonic force constant changes) determines the magnitude of the defects to $\triangle c$. It is also evident from (3a) and (3b) that the mass and force constant changes due to impurity also give cancellation effects. We also see from (3e), (3h), (3i) and (4b) that change in sound velocity depends upon the applied electric field and the signs and relative magnitudes of the higher order anharmonic and electric dipole moment coefficients. The electric field dependence of $\triangle c$ at a constant temperature (well above T_c) can be given as, $K_1 + K_2 E^2$, where K_1 and K_2 are field independent coefficients. The relative magnitudes and signs of the coupling coefficients determine the change in sound velocity due to an applied electric field.

Near the Curie temperature T_c, the frequency of soft mode tends to zero and hence the N_0^o appearing in (3) tends to infinity, decreasing the sound velocity anomalously. This agrees with the findings of Tani and Naoyuki (1969). However, Tani and Naoyuki (1969), using correlation function of Mori (1965) have taken the anharmonicity upto third order only in the Silverman-Joseph Hamiltonian for a pure displacive ferroelectrics; we have taken the anharmonicity upto the fourth order in the presence of both the impurity and electric field. Thus taking the modified Hamiltonian and using the Green's function technique (Zubarev 1960), we have obtained in (5) the temperature dependence of the sound velocity change.

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