A PHENOMENOLOGICAL THEORY OF ULTRASONIC ATTENUATION IN FERROELECTRICS

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The complex damping constant of an ultrasonic wave in a ferroelectric crystal which is non-piezoelectric above the Curie temperature was calculated in the hydrodynamic approximation. The interaction of the ultrasound with polarization waves is expressed in terms of electrostrictive constants. Ferroelectrics both of the relaxation and displacive type are treated in an unified way. The frequency and temperature dependence of the sound attenuation constant and frequency shift was studied in detail for two typical representatives of ferroelectrics, i.e. barium titanate and tri-glycine sulphate.

1. INTRODUCTION

Ultrasonic measurements are one of useful methods of studying ferroelectric phase transitions. Due to the electromechanical coupling of ultrasonic wave with polarization, the polarization anomalies manifest themselves as anomalies in ultrasonic attenuation. Since the wave length of ultrasound is much longer than the lattice constant it is possible to describe the interaction of ultrasound with polarization $P$ phenomenologically in terms of piezoelectric constants $a_{ip}$ and electrostrictive constants $g_{ip}$.

The piezoelectric type of interaction was studied by many authors [1] and their conclusions are in a good agreement with experiments [2]. This type of interaction plays a role in all ferroelectrics below the Curie point $T_c$ and since it is much stronger than the electrostrictive interaction it determines the ultrasonic properties above $T_c$ in ferroelectrics which are piezoelectric above $T_c$ as for example KH$_2$PO$_4$ and Rochelle salt. On the other hand, the ultrasonic properties above $T_c$ in ferroelectrics non-piezoelectric above $T_c$ are determined by the electrostrictive type of interaction which has been investigated so far much less. This problem was treated phenomenologically in [3, 4] for ferroelectrics with a purely relaxation mechanism of polarization and microscopically for a one-dimensional model of displacive ferroelectrics in [5, 6]. In this paper we will study the behaviour of ultrasound in ferroelectrics non-piezoelectric above $T_c$ both in ferroelectrics of purely relaxation type (TGS) and of displacive type (BaTiO$_3$). The problem will be treated phenomenologically (as in [3]) with the aid of the generalized theory of Brownian motion [7].

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2. DAMPING CONSTANT OF ULTRASONIC WAVE

According to [7] the equation of motion for the creation operator \( a_k^* \) of a sound wave can be written in the form of the generalized Langevin equation

\[
\frac{d a_k^*(t)}{dt} = -i\omega_k a_k^*(t) + (a_k^*, a_k)^{-1} \int_0^t (f_k(t-s), f_k^*) a_k^*(s) \, ds = f_k(t),
\]

where

\[
(X, Y) = \beta^{-1} \int_0^\beta \langle e^{iH_X e^{-iH}} Y \rangle - \langle X \rangle \langle Y \rangle.
\]

In the classical limit \( (X, Y) = \langle XY \rangle - \langle X \rangle \langle Y \rangle ; \beta = (k_B T)^{-1}, H \) is the total Hamiltonian of the crystal and the frequency of the ultrasonic wave is given by \( \omega_k = = (a_k^*, a_k) \cdot (a_k^*, a_k)^{-1} \). The random force \( f_k \) acting on \( a_k^* \) is defined at time \( t = 0 \) by the relation

\[
f_k = a_k^* - i\omega_k a_k^* \approx i\hbar [H_{\text{int}}, a_k^*]
\]

where \( H_{\text{int}} \) is the interaction Hamiltonian of sound wave with the crystal. Time evolution of the random force is determined by the operator \((1 - P)L\) where \( L \) is the Liouville operator and \( P \) is the projection operator onto \( a_k^* \) defined by the relation \( PX = (X, a_k)(a_k^*, a_k)^{-1} a_k^* \). The complex damping constant \( \Gamma_k \) of the sound wave is given by [8]

\[
\Gamma_k \equiv \gamma_k - i\Delta \omega_k = (a_k^*, a_k)^{-1} \int_0^\infty (f_k(t), f_k^*) e^{-i\omega_k t} \, dt.
\]

The attenuation constant \( \alpha_k \) is defined as \( \alpha_k = \gamma_k/\nu_k \) where \( \nu_k \) is the sound speed. It should be pointed out that \( \Gamma_k \) is given by formula (3) under isothermic conditions of sound propagation only. At typical ultrasonic frequencies, however, the sound propagates under adiabatic conditions. The difference between these two regimes depends on the ratio of the thermal expansion coefficient and specific heat at constant pressure [9] which has no anomaly in the vicinity of \( T_c \) (private communication of Dr. V. Janovec). Since we are interested in anomalous properties of the sound in the vicinity of \( T_c \), it is sufficient to study the isothermic sound.

Let us now write the interaction energy \( U_{\text{int}} \) of the strain with polarization in a non-piezoelectric crystal in the usual form

\[
U_{\text{int}}(r) = g_{\alpha\beta\gamma} P_\alpha(r) P_\beta(r) u_\gamma(r).
\]

Introducing the Fourier transform of polarization

\[
P_\alpha(k) = V^{-1} \int_V P_\alpha(r) e^{-i\mathbf{k} \cdot \mathbf{r}} \, dV
\]