Polarizability investigation by first order phase transition in the self-consistent phonon approximation for PSN system

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Considering a quadratic Anharmonic model Hamiltonian and using double time temperature dependent Green's function method and Dyson's equation treatment, expression for polarizability in the frequency response for mixed perovskite type ferroelectrics has been obtained. Using the experimentally observed temperature dependent dielectric constant, loss tangent, soft mode frequency and width for Na$_{1-x}$K$_x$NbO$_3$ (where $x = 0, 0.4$ and $0.5$), the polarizablity has been calculated for these samples at 10 and 100 kHz.

Keywords: Phase transition, Model Hamiltonian, Ferroelectrics

1 Introduction

A model Hamiltonian has been proposed by Pytte for understanding the structural phase transition in perovskite ferroelectrics, the phonon frequency, shift and width have not been explicitly calculated by them, because of early decoupling of correlation functions. The soft mode frequencies are determined for arbitrary temperature by calculating the equations of motion using the Model Hamiltonian and determining the required correlation functions by means of self-consistency conditions. The occurrence of ferroelectricity in perovskite type ceramics such as Na$_{1-x}$K$_x$NbO$_3$ has been established both theoretically and experimentally with the existence of an optic mode of lattice vibration soft mode having wave number zero and a frequency, which is anomalously low and temperature dependent. Microscopic theories of displacive phase transitions have been based on a perturbation expansion of harmonic basis. Since the harmonic soft-mode frequencies are imaginary, the contribution of these modes in the anharmonic terms was neglected. A self-consistent model of the soft mode frequencies was first given by Boccara and Samara by employing the renormalized phonon basis. Their formal treatment represented (the lowest order of) what is now called the self-consistent phonon approximation (SPA). This approximation has been very successful in describing the anharmonic rare-gas solids, including the quantum crystals of solid helium.

Numerical calculations have shown that the SPA gives a first - order transition for a model ferroelectric containing only fourth order anharmonic interactions. This result is surprising because the phenomenological Landau (Devonshire) theory predicts the transition to be second order, when only terms up to fourth order in the polarization are included. Polarizability factor for Na$_{1-x}$K$_x$TaO$_3$ ceramics have already been study by the author. Present result has been obtained by using our previous experimental results with theoretically derived expression for polarizability.

2 Theory

To illustrate the essential features of the SPA and to understand a first-order transition, it is instructive to consider a simple model Hamiltonian with a single degree of freedom:

$$H = \frac{1}{2} \sum P^2 (l) + \sum_{\alpha} \frac{\Omega_{\alpha}^2}{2} Q_{\alpha}^2 (l) - \frac{1}{2} \sum_{\alpha, \beta} V (Q_{\alpha}^2 (l) Q_{\beta}^2 (l')) + \sum_{\alpha} \frac{\Gamma_{\alpha}}{2} Q_{\alpha}^4 (l)$$

where $Q_{\alpha}$ is a localized normal mode coordinates describing the ion displacements in cell 1 and P(l) is the canonical conjugate momentum:

$$[Q_{\alpha}, P_l] = i \delta_{l\alpha}$$

We set $Q_{\alpha} = Q_{\alpha}^0 + U_{\alpha}$, where the thermal average $Q_{\alpha} = \langle Q_{\alpha} \rangle$ measures the distortion from the high
temperature structure, while \( U_1 \) describes the average values. In SPA the free energy \( F = \langle H \rangle - TS \) is obtained by using a harmonic trial density matrix \( \rho_0 \).

The distortion \( Q_0 \) and the effective harmonic force constants are determined by minimizing the free energy. For the Hamiltonian given by Eq. (1) the extremum condition \( \partial F / \partial Q_0 = 0 \) takes the form:

\[
Q_0[\Omega_0^2 - V(0) + \Gamma_0 Q_0^2 + 3 \Gamma \Delta] = 0
\]

where \( V(0) = \sum_{n} V(n') \) and \( \Delta \) is defined below. The effective force constants determine the self-consistent normal mode frequency. For this mode, it is given by:

\[
\omega_q^2 = (\Omega_0^2 + v(0) - \Omega^2 + a^2 q^2)
\]

where

\[
\Omega_0^2 = [\Omega_0^2 - v(0) + 3 \eta Q_0^2 + 3 \eta \Delta]
\]

Or in the distorted phase, using Eq. (3):

\[
\Omega_0^2 = 2 \eta Q_0^2
\]

The correlation function \( \Delta = \langle U_1 U_2 \rangle \) is determined with the help of the fluctuation dissipation theorem:

\[
\Delta = N^{-1} \sum_q 1/2 \omega_q^{-1} \coth 1/2 \beta \omega_q
\]

for simplicity, we consider the limit \( \omega_q / kT \ll 1, \Delta \) may be approximated by the Ornstein-Zemike form:

\[
\Delta = kTN^{-1} \sum_q (\Omega_0^2 + a^2 q^2)^{-1}
\]

Evaluating the summation in the Debye-approximation, we obtain:

\[
\Delta = \Delta_0 - \Delta_r
\]

where

\[
\Delta_0 = 3kT / \omega_d^2 \quad \text{and} \quad \Delta_r = \Delta_0 (\Omega_0 / \omega_d) \tan^{-1} (\omega_d / \Omega)
\]

On substituting in Eq. (9), we get:

\[
\Delta = 3kT / \omega_d^2 - \Delta_0 (\Omega / \omega_d) \tan^{-1} (\omega_d / \Omega)
\]

\[
= 3kT / \omega_d^2 - 3kT / \omega_d^2 [\Omega / \omega_d^2 (\Omega / \omega_d)] \tan^{-1} (\omega_d / \Omega)]
\]

\[
3kT / \omega_d^2 [1 - (\Omega / \omega_d) \tan^{-1} (\omega_d / \Omega)]
\]

where \( \omega_d = a_q D, q D \) being the Debye wave vector.

\( \Delta_r \) denotes the contribution to \( \Delta \) due to long wavelength fluctuation. For \( Q_0 \neq 0 \) Eq. (9) may be written as:

\[
a(T - T_c) + \eta Q_0^2 - 3 \eta \Delta_r = 0
\]

where

\[
a = 9 \eta K_B / \omega_d^2
\]

\[
T_c = a^{-1}[v(0) - \Omega_0^2]
\]

and \( v(0) = T_c a_r^2 \Omega_0^2 \)

Because \( \Delta_r \) is linear in \( \Omega \) as \( \Omega \to 0 \), it follows from Eqs (6) and (11) that transition is first order. However, it is important that the linear term giving rise to the first order transition is entirely due to the long wavelength fluctuations.

On substituting Eqs (6,7,13) in Eq. (5), we get the expression as:

\[
Q_0^2 = 9 K_B / \omega_d^2 [T_c - (1 - \Omega / \omega_d) \tan^{-1} (\omega_d / \Omega) T]
\]

On substituting the experimental results of soft frequency (\( \Omega \)), natural frequency of the system (\( \omega_d \)) for Na\(_{1-x}\)K\(_x\)NbO\(_3\) (x=0,0.4 and 0.6)\(^2\) we get the variation of \( Q_0^2 \) with temperature in Tables 1 and 2 and have been plotted in Figs 1 and 2, respectively.

Fig. 1 — Variation of polarizability factor \( (Q_0^2) \times 10^{-50} \) with temperature for Na\(_{1-x}\)K\(_x\)NbO\(_3\) system at 10 kHz
3 Results and Discussion

Using our experimental results for temperature and frequency dependence dielectric constant, tangent loss and width for NaNbO$_3$, Na$_{0.6}$K$_{0.4}$NbO$_3$ and Na$_{0.5}$K$_{0.5}$NbO$_3$, polarizability factors obtained by first order phase transition in the self-consistent phonon approximation by using the formula obtained by Pytte$^9$, have been calculated for these mixed systems in continuation with our previous paper$^7,8$. The polarizability factor at 10 and 100 kHz frequency has been shown in Tables 1 and 2 and Figs 1 and 2, respectively. It is observed that polarizability tends to decrease up to the first transition temperature (orthorhombic-tetragonal) thereafter, it increases and then tends to zero up to second transition temperature (tetragonal cubic). In the temperature range 465±20°C and 665±20°C anomalous behaviour has been observed due to phase transition. It can be understood that the polarization mode is temperature dependent.

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