Hypersonic and dielectric studies of disordered single crystals, Rb1-x(ND4)xD2AsO4, Na1/2Bi1/2TiO3 and PbMg1/3Nb2/3O3, by brillouin scattering and dielectric measurements by Chi-Shun Tu

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Montana State University
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Abstract:
Temperature and frequency dependent measurements of dielectric permittivity, acoustic sound velocity and damping have been carried out by using Brillouin light scattering and a capacitance and conductance component analyzer on two different types of ferroelectrics, i.e. (i) FE-AFE mixed deuteron glasses Rbl-x(ND4)xD2AsO4 (x=0, 0.10, 0.28), (ii) relaxor ferroelectrics Na1/2Bi1/2TiO3 (NBT) and PbMg1/3Nb2/3O3 (PMN).

In this study, three important results have been observed: (1) A broad and high-value maximum in dielectric permittivity has been observed in relaxors NBT and PMN, which indicates that these materials could be used for electrostrictive displacement transducers. (2) In FE-AFE mixed glasses DRADA-x, a _η2μ_-type quadratic coupling, squared in order parameter and linear in strain, becomes the main coupling contribution as ammonium ND4 concentration x increases from 0 to an intermediate value. The results also confirm the presence of PE/FE phase coexistence in DRADA-0.10. (3) For both FE-AFE mixed glasses and relaxor ferroelectrics, the order parameter(s) fluctuations, which are generated by the local random fields originating from short-range randomly-placed cations, are the main dynamic mechanisms for hypersonic and dielectric anomalies. In DRADA-0.10 and 0.28, these local randomly-placed ions are ND4+ and Rb+ ions. In PMN, those randomly-placed cations are Mg+2 and Nb+5 which are randomly placed at B-site positions. In NBT, those randomly-placed cations are Na+1 and Bi+3 which are placed randomly at A-site positions.

Two models, i.e. superparaelectric cluster and extrinsic bulk conductivity, also have been proposed to explain the high-temperature and low-frequency dielectric anomaly in NBT. The elastic stiffness and compliance constants are also calculated for PMN.
HYPERSONIC AND DIELECTRIC STUDIES OF DISORDERED SINGLE CRYSTALS, \( \text{Rb}_{1-x}(\text{ND})_x\text{D}_2\text{AsO}_4 \), \( \text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3 \) AND \( \text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 \), BY BRILLOUIN SCATTERING AND DIELECTRIC MEASUREMENTS

by

Chi-Shun Tu

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

MONTANA STATE UNIVERSITY
Bozeman, Montana

September, 1994
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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the college of Graduate Studies.

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Signature

Date Oct. 3, 1994
to my wife Rong-Mei (Ruth), because of whom all things are possible,

and to my son Stachus, in whom I find the reasons
VITA

The author was born Chi-Shun Tu on January 21, 1962 in Kaohsiung, Taiwan. He is the fourth child of Rou-Nu Tu (deceased) and Hsiu-Hsia Tsai Tu and has three older sisters and one younger brother. He was married to Rong-Mei (Ruth) Chien in 1988 and has one son, Stachus Igu Tu.

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In this study, three important results have been observed: (1) A broad and high-value maximum in dielectric permittivity has been observed in relaxors NBT and PMN, which indicates that these materials could be used for electrostrictive displacement transducers. (2) In FE-AFE mixed glasses DRADA-x, a $\eta^2\mu$-type quadratic coupling, squared in order parameter and linear in strain, becomes the main coupling contribution as ammonium ND$_4$ concentration x increases from 0 to an intermediate value. The results also confirm the presence of PE/FE phase coexistence in DRADA-0.10. (3) For both FE-AFE mixed glasses and relaxor ferroelectrics, the order parameter(s) fluctuations, which are generated by the local random fields originating from short-range randomly-placed cations, are the main dynamic mechanisms for hypersonic and dielectric anomalies. In DRADA-0.10 and 0.28, these local randomly-placed ions are ND$_4^+$ and Rb$^+$ ions. In PMN, those randomly-placed cations are Mg$^{+2}$ and Nb$^{+5}$ which are randomly placed at B-site positions. In NBT, those randomly-placed cations are Na$^{+1}$ and Bi$^{+3}$ which are placed randomly at A-site positions.

Two models, i.e. superparaelectric cluster and extrinsic bulk conductivity, also have been proposed to explain the high-temperature and low-frequency dielectric anomaly in NBT. The elastic stiffness and compliance constants are also calculated for PMN.
CHAPTER 1

INTRODUCTION

Introduction to Disordered Crystals

If the composition in a crystal is not completely uniform (compositional heterogeneity) down to the unit cell scale or has cation fluctuations statistically or dynamically, then the crystal is usually called "disordered". In terms of symmetry, "disordered" means that there is no long-range translational symmetry inside the crystal. Among disordered materials, many experiments have concentrated on two different systems, i.e. ferroelectric (FE)-antiferroelectric (AFE) mixed crystals with the general formula \( A_{1-x}(NH_4)_xH_2BO_4 \) \( [A=Rb, K, Cs \text{ and } Tl, B=P \text{ and } As] \)\(^{2-11} \) and complex relaxor ferroelectrics with formula \( (A'_xA''_{1-x})^{+2}B'^{4+}O_3^{-2} \) or \( A^{+2}(B'_xB''_{1-x})^{4+}O_3^{-2} \).\(^{1,12,13} \) In these systems, local random fields originating from randomly-placed cations (or ions) play an important role for physical properties such as acoustic (sound velocity and damping) and dielectric anomalies. Since local random fields can suppress the long-range electric ordering and produce the order parameter fluctuations, a normal sharp phase transition usually is not observed in these materials. "Diffuse" (non-sharp peak) phase transition is the typical anomalous characteristic of these disordered materials. The two-dimensional distributions of ions (or cations) for both ordered and disordered states are given schematically in Fig. 1.
For relaxor ferroelectrics, one can use thermal treatments such as annealing, quenching and ratio of cations to control ordering. In FE-AFE mixed proton glasses, the crystal ordering depends on ammonium concentration. From experimental results, some general differences have been found between ordered and disordered ferroelectrics:

(1) Ordered (normal):

a) Sharp dielectric phase transition at $T_c$

b) Stable remanent polarization
c) No strong dielectric frequency dependence at phase transition
d) Stable birefringence
e) No local random fields
f) Usually no intermediate phase between high- and low-symmetries

(2) Disordered:

a) Diffuse dielectric transition which doesn't correspond to any specific change of symmetry (or phase)
b) No stable remanent polarization
c) Strong frequency dependence at diffuse transition
d) No stable birefringence
e) Strong local random fields
f) Usually associated with a sequence of phase transitions, i.e. one (or more) intermediate phase occurred between high- and low-symmetries

In this study, five different single crystals have been measured, i.e. FE-AFE mixed deuteron glasses, Rb_x(ND_4)_1-xD_2AsO_4 with x=0, 0.10 and 0.28 and complex relaxor ferroelectrics, Pb(Mg_{1/3}Nb_{2/3})O_3 (PMN) and Na_{1/2}Bi_{1/2}TiO_3 (NBT). The introductions to these two different systems are given below.

Relaxor Ferroelectrics (RF)

Perovskite is the name of the mineral calcium titanate (CaTiO_3). Most of the useful piezoelectric (ferroelectric) crystals, such as barium titanate (BaTiO_3), lead titanate (PbTiO_3), lead zirconate titanate (PbZr_{1-x}Ti_xO_3), lead lanthanum zirconate titanate (PLZT), sodium bismuth titanate Na_{1/2}Bi_{1/2}TiO_3 and lead magnesium niobate Pb(Mg_{1/3}Nb_{2/3})O_3 etc., have perovskite-type structure, i.e. ABO_3-type unit cell. Here "O" is oxygen, "A" represents a cation with a larger ionic radius, and "B" a cation with a
smaller ionic radius. Fig. 2 shows a typical cubic $\text{ABO}_3$ perovskite-type structure in the paraelectric phase and possible directions of distortion in the ferroelectric phase.$^{14}$

![Figure 2. A perovskite cubic unit cell. The point group usually is m3m for a paraelectric cubic $\text{ABO}_3$ perovskite-type structure. Solid lines indicate the $\text{BO}_6$ octahedron. $A_4$ indicates one of three 4-fold rotation axes and 4mm is the usual corresponding point group in the tetragonal ferroelectric phase. $A_3$ indicates one of four 3-fold rotation axes and 3m is the usual corresponding point group in the trigonal ferroelectric phase.](image)

Many of the complex relaxor ferroelectrics with perovskite-type structure are compounds with either $\text{A}^{+2}\text{B}^{+4}\text{O}_3^{-2}$ or $\text{A}^{+1}\text{B}^{+5}\text{O}_3^{-2}$-type formula. In the perovskite family, there are many compounds with the formula $\text{A}^{+3}\text{B}^{+3}\text{O}_3^{-2}$, but among them no ferroelectrics have been discovered.$^{13}$

The perovskite structure is essentially a three-dimensional network of $\text{BO}_6$ octahedra (see Fig. 2). It may also be regarded as a cubic close-packed arrangement of $\text{A}$ and $\text{B}$ ions with $\text{B}$ ions filling the octahedral interstitial positions.$^{13}$ The packing situation of this structure may be characterized by a tolerance factor $t$, which is defined by the following equations:$^{13}$
\[ R_A + R_o = t\sqrt{2}(R_B + R_o) \]  

(1)

or

\[ t = \frac{R_A + R_o}{\sqrt{2}(R_B + R_o)} \]  

(2)

where \( R_A, R_B \) and \( R_o \) are the ionic radii of A, B and O ions, respectively. When \( t \) is equal to 1, the packing is said to be ideal. When \( t \) is larger than 1, there is too large a space available for the B ion, and therefore this ion can "move" inside its octahedron. In general, to form a stable perovskite structure, one requires that \( 0.9 < t < 1.1 \). Besides the ionic radii, other factors, such as polarizability and character of bonds, must also be taken into account.\(^\text{13}\)

The term "complex relaxor ferroelectrics" generally refers to the complex perovskites in which the charge classifications of \( (A',A''_x1-x)+2B^{4+}O_3^2 \) or \( A'^2(B',B''_{1-x})_{x}^{4+}O_3^2 \) etc. are satisfied and unlike-valence cations belonging to a given site (A or B) are present in the correct ratio for charge balance, but are situated randomly on these cation sites. For example, sodium bismuth titanate \( Na_{1/2}Bi_{1/2}TiO_3 \) has two unlike valence cations \( Na^+ \) and \( Bi^{+3} \) distributed in the A site and lead magnesium niobate \( Pb(Mg_{1/3}Nb_{2/3})O_3 \) has two unlike valence cations \( Mg^{+2} \) and \( Nb^{+5} \) distributed in the B site.\(^\text{1,15,16}\) These randomly different cation charges give rise to random electric fields and cause random elastic distortion fields in microregions. These random fields tend to make the phase transitions "diffuse" instead of sharp as in normal ferroelectrics, and complicate the task of determining structure and state of electric order. The electric properties of relaxor ferroelectrics also depends on the cation ordering degree. The degree of ordering inside a crystal depend on several things such as method of crystal growth, cation valence, and thermal treatment (e.g. quenching and annealing). In certain compounds,
such as PbSc$_{1/2}$Ta$_{1/2}$O$_3$ (PST) and PbIn$_{1/2}$Nb$_{1/2}$O$_3$ (PIN), the driving force for cation ordering is such that long-range coherence and corresponding normal FE (or AFE) behavior can be achieved through thermal annealing.\textsuperscript{15} An additional complication is the aging effect which can span a wide time scale in a nonlinear manner. Relaxor ferroelectrics usually exhibit a sequence of anomalies in the dielectric response as temperature changes.\textsuperscript{1,16} However, the dielectric maximum does not clearly mark a phase transition into a low-symmetry region.

It is important to note that B-site order in A$^{+2}$B'(B''$_x$B''''$_{1-x}$)$^{+4}$O$_3^{-2}$ compounds could be either stoichiometric (ordered) or nonstoichiometric (disordered) as shown in Fig. 3.\textsuperscript{1,15}

![Figure 3. Mixed-ion arrangements of (a) ordered and (b) disordered cubic perovskite ABO$_3$ structure.](image)

For example, B-site order in x=1/2 compounds, e.g. Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ and Pb(Mg$_{1/2}$W$_{1/2}$)O$_3$, results in an average valence of +4 and thus is referred to as stoichiometric ordering.\textsuperscript{15} In contrast, nonstoichiometric ordering is found in x=1/3 compounds, e.g. Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ and Pb(Cd$_{1/3}$Nb$_{2/3}$)O$_3$ where a tendency toward 1:1
B'B' order is observed and as such the average charge value is lower than the expected valence of +4. The overall defect chemistry and average compensation mechanism of the nonstoichiometric ordering are not well understood at this time.

A sequence of phase transitions with one or two intermediate phase is a characteristic of complex relaxor ferroelectrics. A general schematic phase diagram is given in Fig. 4.

\[
\begin{array}{c|c|c}
\text{Low-symmetry} & ? & \text{High-symmetry} \\
\hline
\text{L.T.} & \text{Temperature} & \text{H.T.}
\end{array}
\]

Figure 4. A general schematic phase diagram vs. temperature for complex relaxor ferroelectrics. "?" indicates one or two intermediate regions.

**Proton (or Deuteron) Glasses (PG)**

At room temperature, the hydrogen-bonded phosphates (MH\(_2\)PO\(_4\)) and arsenates (MH\(_2\)AsO\(_4\)) (M=Na, K, Rb, Cs, Ag, Tl and NH\(_4\)) form a class of KDP-type isostructural crystals of tetragonal symmetry. The structure of KH\(_2\)PO\(_4\) (KDP) at room temperature is given in Fig. 5.

![Structure of KDP](image)

Figure 5. The structure of KDP at room temperature. Here just a few hydrogen bonds are shown.
When M is an alkali ion, the low-temperature state is ferroelectric. However, it should be noted that RDP can be grown in either a tetragonal or a monoclinic structure. Fig. 6 is the c-axis projection of KDP structure in the ferroelectric phase ($T<T_c$).

![Figure 6. Projection of KDP along c-axis in the ferroelectric phase ($T<T_c$). The solid line inside the square connects oxygen atoms at the same height.](image)

The KDP-type structure consists of two interpenetrating sublattices. One is a body-centered sublattice of PO$_4$ tetrahedra and the other is a body-centered sublattice of K$^+$ ions. The hydrogen atoms are dynamically fluctuating between off-center positions but are statistically distributed at the centers of the O⋯H⋯O bonds in the paraelectric (PE) phase. They are in ordered off-center positions in the ferroelectric (FE) phase. In the FE phase the protons are either close to the "upper oxygens" or "lower oxygens" and the non-zero net polarization depending on domain type arises from the displacement of K$^+$ and P$^{5+}$ ions along the c-axis direction.

The ammonium compounds which exhibit a paraelectric (PE)-antiferroelectric (AFE) phase transition have NH$_4^+$ substituted for K$^+$ position in the KDP-type unit cell. Two of the four "ammonium" protons form short bonds with the surrounding PO$_4$ tetrahedra as seen in Fig. 7.
Figure 7. The structure of ADP projected along the c-axis. A NH$_4^+$ at height 0 is shown attached to nearby oxygens of PO$_4$ tetrahedra. The heights in unit of c of the phosphorus centers of the PO$_4$ tetrahedral are indicated. The PO$_4$ tetrahedron located above the ammonium, at height 1/2, and a number of protons, are not shown. The off-center motion of the ammonium ion is indicated by the arrow. This is one of the four possible directions of this arrow in the (001) plane.

In the antiferroelectric phase the positions of the "acid" protons are such that each PO$_4$ tetrahedron has one close proton each at the upper and the lower sides, unlike in KDP where in the FE phase all the "acid" protons are attached either to the top or bottom of the PO$_4$ tetrahedron. Such an arrangement of the "acid" protons results in local dipoles alternately pointing "up" and "down" along the a-axis (or b-axis) direction as shown in Fig. 8, and yielding zero net polarization.

Figure 8. Schematic representation of the antiferroelectric phase of ADP (or ADA)
It is important to note that the deuterated isomorphs show enhanced electric-ordering temperatures (isotope effect).\(^{17}\) For instance, \(T_c\) is 146 K for Rb\(\text{H}_2\text{PO}_4\) and \(T_c\) is 218 K for Rb\(\text{D}_2\text{PO}_4\). Such isotope effects occur not only for pure ferroelectrics but also for FE-AFE mixed crystals.\(^2\)

The FE-AFE mixed crystals \(\text{A}_{1-x} (\text{NH}_4)_x \text{H}_2\text{BO}_4\) and \(\text{A}_{1-x} (\text{ND}_4)_x \text{D}_2\text{BO}_4\) usually exhibit a frequency dependent dielectric anomaly instead of a phase transition for certain intermediate values of \(x\). In these systems, competition between the FE and the AFE orderings which are characterized by specific configurations of the acid protons, plays an important role for dynamic anomalies. The random distribution of the Rb (or K, Cs, Tl) and NH\(_4\) (or ND\(_4\)) cations is the origin of the local random fields. At lower temperature the system eventually becomes nonergodic in which case the system is frozen completely on a practical time scale.\(^8\) This behavior is reminiscent of that of magnetic spin glasses, except that the random bias field caused by random Rb and NH\(_4\) neighbor placement biasing the O-H…O bonds smears out the spin glass "transition". However, whether there is a real ergodic-nonergodic transition is still an open question. From the experimental results, it was found that small amounts of ammonium admixtures are sufficient to stabilize the tetragonal structure even at low temperature. A typical schematic phase diagram of proton (or deuteron) glass is shown in Fig. 9.\(^7,18\)

Figure 9. Schematic phase diagram of FE-AFE mixed glasses such as RADP. PG: proton glass, PE/FE: PE and FE phase coexistence region.
Previous Knowledge for Crystals Discussed in This Thesis

$\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ (NBT)

$\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ undergoes a cubic-tetragonal-trigonal succession of structural phase transitions, ending in a ferroelectric state at room temperature. Different studies on NBT have been published in many papers, but its behavior is still far from clear. Most of the contradictions concern the number and location of different phases as well as the electrical state in each phase. According to x-ray and neutron measurements there are two structural phase transitions in NBT from the high-temperature cubic phase to a tetragonal and then a trigonal phase. The tetragonal phase seems to be ferroelastic as shown by domain pattern visualization. However, the question of whether this phase is polar is still open. Some dielectric measurements indicate that an antiferroelectric phase exists between the tetragonal ferroelastic and trigonal ferroelectric phases. However, x-ray and neutron scattering studies have not provided any evidence to support this view. Neutron scattering indicates that the transition between tetragonal and trigonal phases is characterized by a region of phase coexistence. However, the nature of the high-frequency dielectric maximum near 640 K is still an open question.

$\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN)

Dielectric results of PMN shows a frequency dependent “diffuse” phase transition associated with a broad maximum around 270 K. This anomaly is attributed to quenched random electric fields originating from charged compositional fluctuations. Under a strong bias electric field ($\geq 4$ kV/cm), an additional dielectric peak occurs at $T_C \approx 210$ K below which the random fields are overcome by the external electric field.

In the supposedly disordered PMN single crystal, a microstructure on a nanometric length scale with 1:1 cation ordering in B site was reported. Such 1:1 ordering, when charge neutrality requires 1:2 stoichiometry, implies locally charged
regions causing fields which induce random polarization. Recent results show only a 5% tendency toward 1:1 ordering in these microregions.\textsuperscript{34}

Three recent models for the relaxor ferroelectric crystal PMN have been proposed, namely the random field model (RF),\textsuperscript{31} the dipolar glass model\textsuperscript{35} and the structural model.\textsuperscript{36} The first two models are based on the temperature and electric field responses of these microdomains. The last model, based on x-ray and neutron powder diffraction at 5 K, indicates an average cubic structure even at 5 K, but with some 20% of the material in non-cubic FE microdomains near 100 Å size.

The RF model postulates random electric fields originating in a peculiarity of PMN's structure, i.e. local nonstoichiometric order causing local net charge, resulting in microdomains polarized along the 8 \langle 111 \rangle directions, and assumes that the cubic anisotropy corresponding to these 8 directions is low enough so that the random fields can suppress the FE transition.

In the dipolar glass model for PMN, the "pseudospins" are nanometer-sized superparaelectric clusters which correspond to the microdomains in the random fields model. This model assumes that these superparaelectric clusters can flip at higher temperature, but freeze into a random configuration at lower temperature. However, the random field model seems to imply that microdomains have fixed orientations determined by local fields.

Recent results of the linear birefringence \( \Delta n \approx \langle P_{||}^2 \rangle - \langle P_{\perp}^2 \rangle \) in PMN under an external electric field suggest an equilibrium phase transition temperature \( T_c \) in the absence of the random fields, 200 K < \( T_c \) < 234 K.\textsuperscript{31} In addition, by fitting the time dependence of the linear birefringence with two different exponents \( \beta \) below and above 212 K, Westphal \textit{et al.} propose that the Curie temperature of PMN is \( T_c \approx 212 \) K. Viehland \textit{et al.} also claim that the freezing temperature is \( T_f \approx 217 \) K in PMN below which a dramatic change of the relaxation time distribution is observed and is interpreted as a
result of a long-range correlation of polar microdomains. Recent quasielastic-neutron scattering (QES) on PMN supports the above interpretations and shows that the correlation length is nearly temperature independent with a maximum value of 200 Å below −217 K.

\[ \text{Rb}_{1-x}(\text{ND}_4)_x \text{D}_2\text{AsO}_4 (\text{DRADA} - x = 0, 0.10, \text{and} 0.28) \]

Pure DRDA (x=0) single crystal exhibits a first-order PE↔FE phase transition at T_c=165 K as observed from spontaneous polarization measurement. The ND_4^+ deuteron NMR spectra of DRADA-0.10 showed a gradual disappearance of the doublet near 131 K where the single broad linewidth grows to its full size, from which it is concluded that below 131 K the FE phase portion is greater than PE in the crystal and becomes the dominant ordering. This result is consistent with the presence of PE/FE phase coexistence as evidenced by dielectric results which show that a gradual ferroelectric transition begins at T_m=146 K and is mostly completed at ~120 K. The remaining PE material begins exhibiting dielectric dispersion characteristic of deuteron glass below a frequency-dependent temperature T_g, which is 60 K at 50 kHz. DRADA−0.28 has only a frequency dependent dielectric anomaly separating PE from deuteron glass behavior at T_g~65 K (f=0.1 MHz). Field-heated, field-cooled and zero-field-heated static permittivity revealed that below T_c~38 K (nonergodic temperature) the system enters a nonergodic state in which for practical purposes the acid deuteron of the O-D…O bond is frozen completely.

**Purpose and Outline of The Present Work**

Both piezoelectric (strain linearly proportional to applied electric field) and electrostrictive (strain proportional to square of applied electric field) effects are important phenomena in ferroelectrics. These two intrinsic electric responses have
been used for applications in many ways such as nanometer-scale actuators and sensors. The main advantages of electrostrictive actuators include insignificant hysteresis and less creep and susceptibility aging (gradual change in response with time) which are the problems of piezoelectric actuators (or sensors). Brillouin light scattering and dielectric methods are powerful tools to understand both piezoelectric and electrostrictive couplings. The elastic stiffness and piezoelectric stress constant can also be obtained from these measurements. The overall purpose of this study is to provide a basis for improving properties useful in applications and extending the useful temperature range upward and downward in disordered ferroelectrics.

In this study, FE-AFE mixed glasses Rb$_{1-x}$(ND$_4$)$_x$D$_2$AsO$_4$ (x=0, 0.10, and 0.28) and complex perovskites Na$_{1/2}$Bi$_{1/2}$TiO$_3$ and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ have been measured by two different methods, i.e. Brillouin light scattering ($\theta_s=180^0$, 32.6$^0$ and 12.6$^0$) and dielectric permittivity ($\varepsilon^*=$$\varepsilon'$–$\varepsilon''$) between 0.02 and 300 kHz. The experimental procedure will be discussed in chapter 2.
CHAPTER 2

EXPERIMENTAL PROCEDURES

Crystal Growth and Sample Preparation

Single crystals of Rb$_{1-x}$(ND$_4$)$_x$D$_2$AsO$_4$, (x=0, 0.10, 0.28) for Brillouin scattering and dielectric permittivity measurements were grown here from aqueous solutions with certain ratios of RbD$_2$AsO$_4$ (DRDA) and (ND$_4$)D$_2$AsO$_4$ (DADA) at room temperature. These starting materials were grown by following chemical reactions:

\[
\begin{align*}
\text{Rb}_2\text{CO}_3 + \text{As}_2\text{O}_5 + \text{D}_2\text{O} & \quad \Rightarrow \quad 2\text{RbD}_2\text{AsO}_4 + \text{CO}_2 \\
(\text{ND}_4)_2\text{CO}_3 + \text{As}_2\text{O}_5 + 2\text{D}_2\text{O} & \quad \Rightarrow \quad 2(\text{ND}_4)\text{D}_2\text{AsO}_4 + \text{CO}_2
\end{align*}
\]

These DRADA crystals were carefully polished to be rectangular with average size of 1.2 x0.4 x 0.2 cm$^3$. A general growth formula for this type of mixed crystals is given below.

\[
\begin{align*}
\text{KDP-type FE crystals} + \text{ADP-type AFE crystals} & \quad \Rightarrow \quad \text{FE-AFE glasses} \\
\downarrow & \quad \downarrow & \quad \downarrow \\
(1-x)\text{AH}_2\text{BO}_4 + x\cdot\text{NH}_4\text{H}_2\text{BO}_4 & \quad \Rightarrow \quad \text{A}_{1-x}(\text{NH}_4)_x\text{H}_2\text{BO}_4 \\
(1-x)\text{AD}_2\text{BO}_4 + x\cdot\text{ND}_4\text{D}_2\text{BO}_4 & \quad \Rightarrow \quad \text{A}_{1-x}(\text{ND}_4)_x\text{D}_2\text{BO}_4
\end{align*}
\]

(Here A=Rb, K, Cs and Tl, B=P and As)
The solvent for deuterated crystals is heavy water. Such a "solution growth" is a two component system, i.e. solute and solvent, and so requires simultaneous control of two parameters (temperature and concentration $x$) during the crystallization process. The difficulty of crystal growth also depends on whether the cation sizes match each other. For instance, the rubidium and ammonium ions are a nearly perfect match in size, so high-quality and strain-free mixed single crystals of $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ can be grow at all concentrations $x$.\textsuperscript{18}

Relaxor ferroelectric single crystals NBT and PMN were grown by the Czochralski method in A. F. Ioffe Physical Technical Institute, with dimensions 5.57×6.03×5.74 (mm)$^3$ and 5.37×4.77×2.82 (mm)$^3$, respectively. The Czochralski growing method can be found in Ref. 38. For dielectric measurements, a silver paste (Ted Pella #16032) was used for the electrodes.

**Dielectric Permittivity**

For the audio frequency range (0.02−300 kHz), a Wayne-Kerr Model 6425 Precision Component Analyzer with 4-lead connections was used for capacitance and conductance measurements. A Leybold RGD-210 closed cycle helium refrigerator was used for low temperatures (10-300 K) with a silicon diode temperature sensor put immediately below the sample holder. For high temperatures (300-900 K), an oven was used with a calibrated LakeShore PT-103 platinum resistance thermometer which was put just above the sample. The temperature accuracy is about ±0.1 K. All data were collected automatically with frequency swept in steps from 0.02 to 300 kHz. The measuring voltage was 0.5 V. The error of the dielectric relative permittivities ($\varepsilon'$ and $\varepsilon''$) is about 0.05%.
Brillouin Light Scattering

The light scattering caused by acoustic phonons is called Brillouin scattering, for which the frequency shift $\Delta \nu$ is between 0.01 and 5 cm$^{-1}$. In Raman scattering, the frequency shift $\Delta \nu$ is usually caused by molecular vibrations or optical phonons and is generally larger than 5 cm$^{-1}$. The elastic or quasielastic ($\Delta \nu = 0$) scattering processes which are caused by inhomogeneous distribution of the refractive index in a crystal are called Rayleigh scattering.

For visible light (usually from a high intensity laser beam), the photon wave vectors (of order $10^5$ cm$^{-1}$), i.e. $\lambda \sim 5000$ Å, are small compared with the Brillouin zone dimension (of order $10^8$ cm$^{-1}$), thus information is provided by Brillouin scattering only about phonons in the immediate neighborhood of $\bar{k} = 0$. In order to estimate the order of magnitude of the acoustic phonon cutoff frequency $\omega_c$, a simple dispersion curve $\omega(k)$ of the longitudinal mode from a monatomic linear chain with only nearest-neighbor interaction is considered in Fig. 10.39

![Dispersion curve of $\omega(k)$ of the longitudinal mode from a monatomic linear chain. At any frequency below the cutoff frequency $\omega_c = 2\sqrt{K/M}$, two waves can propagate in both directions with opposite wave numbers.](image)

For a monatomic linear chain lattice, the acoustic phonon frequency is $\omega = 2\sqrt{K/M}|\sin ka / 2|$.39 $K$ is the force constant whose value depends on temperature
and different vibration modes. \( M \) is the mass of the atom. For small wave number, i.e. \( ka \ll 1 \), we then have \( \omega = \sqrt{\frac{K}{M}} \), i.e. \( \sqrt{\frac{K}{M}} = \omega / k = V_0 \). \( V_0 \) is the acoustic phonon velocity near the Brillouin zone center, i.e. \( \tilde{k} \sim 0 \). When the wavelength is of the order of magnitude of the interatomic distance \( a \) (\( ka \) comparable to \( \pi \)), the frequency of acoustic phonons is bounded by the cutoff frequency, i.e. \( f_c = \sqrt{\frac{K}{M}} / \pi = V_0 / \pi \). The \( V_0 \) in dielectric solids lies between \( 10^3 \) and \( 10^4 \) m/s. The interatomic distance is a few Å. Taking \( V_0 = 5 \times 10^3 \) m/s and \( a = 5 \) Å, the cutoff frequency is \( f_c = 3.2 \times 10^{12} \) GHz.

Brillouin light scattering can provide three types of basic information; (i) acoustic phonon frequency shift (sound velocity) from which the elastic and piezoelectric constants can be obtained, (ii) half-width at half height (damping or life time of phonon) and (iii) intensity of background which usually is related to the central component.

General Description of Experiment

The Brillouin spectra were obtained from several different scattering angles which include backscattering (\( \theta_s = 180^\circ \)) and small angles (\( \theta_s = 12.6^\circ, 32.6^\circ \)). Scattering angle means the angle between incident and scattered wave vectors inside the crystal. An actual determination of scattering angle is given in Fig. 11.

![Diagram of Brillouin scattering angle](image)

**Figure 11.** The determination of the Brillouin scattering angle \( \theta \).

\( \theta \) : scattering angle

\( n \) : refractive index
The scattering geometry is usually expressed by a notation such as Z(X,Y)X for light scattering by a crystal. The notation stands for $\mathbf{K}_i(\mathbf{E}_i, \mathbf{E}_s)\mathbf{K}_s$ where $\mathbf{E}_i$ and $\mathbf{E}_s$ are polarization vectors of the incident (I) and scattered (S) beams, respectively. The first and last letters of Z(X,Y)X indicate that the propagation directions of the incident and scattered beams are parallel to the Z and X axes, respectively. The two letters in parentheses indicate that the polarization directions of the incident and scattered beams are parallel to the X and Y axes, respectively. Therefore, Z(X,Y)X corresponds to the experimental set-up illustrated in Fig. 12a. In case of isotropic materials (or in case the detailed specification of the scattering geometry is unnecessary or difficult), the geometry is expressed by two letters such as HV. "HV" means that $\mathbf{E}_i$ is parallel to the plane and $\mathbf{E}_s$ is perpendicular to the plane, as illustrated in Fig. 12b. The plane is determined by $\mathbf{K}_i$ and $\mathbf{K}_s$.

Figure 12. Symbols of scattering geometries. (a) Z(X,Y)X, (b) HV.
In order to reduce the low-lying frequency mode of the Raman spectra, a narrow-band (1 Å) interference filter was used. All samples were illuminated by a Lexel Model 95-2 argon laser with λ=514.5 nm. Scattered light was analyzed by a Burleigh five-pass Fabry-Perot interferometer. The laser line broadening due to the jittering was claimed by the manufacturer to be about 10 MHz (half-width).

For small angle (θ<180°) Brillouin scattering, the experimental set-up is shown in Fig. 13. The lens L₁ serves to focus the incident beam into the sample which was set in the closed-cycle cryostat. The distance between L₂ and the sample is the focus length of lens L₂. The scattered beam from the sample is collected by L₂ and then becomes parallel. The lens L₃ focuses the parallel scattered light at the center of a 200 μm-radius pinhole, and the transmitted light is collimated by the lens L₃. The collimated beam passes a narrow-band (1 Å) interference filter and then enters a Burleigh five-pass Fabry-Perot interferometer. The light from the Fabry-Perot interferometer is focused at the end of the telemeter with a 200 μm pinhole.

A Model R464 head-on photomultiplier (PMT) was used to collect the transmitted light from the telemeter. A home-made high voltage power supply provides a maximum voltage of 1450 V for the cathode of the PMT. A home-made voltage amplifier was used to amplify the analog output from the PMT. The analog output from the amplifier was fed into a home-made analog→TTL transformer and then connected with a Dell 486 computer through a Computer Boards Inc. Model CIO-AD08 (8-channel) AD/DA converter. The Brillouin spectrum was displayed on the screen and stored as an ASCII file. A shutter was used to reduce the Rayleigh line intensity. If the intensity of the Rayleigh line exceeds a certain value which was determined beforehand, the shutter is closed during the Rayleigh spectrum range. After a certain closing time which was also programmed preliminarily, it will be opened during the Brillouin spectrum range.
Figure 13  Brillouin scattering set-up for small angles.
Figure 14  Brillouin scattering set-up for backscattering.
Fig. 14 is the experimental set-up for backscattering in which a 5×5 mm² prism was used to reflect the laser beam into L₃.

A LABTECH NOTEBOOK software was modified with an AD/DA converter to interface the shutter, TTL transformer and ramp function generator. A detailed connection scheme between converter and instruments is given in Fig. 15.

![Connection Diagram](image.png)

Figure 15. The actual experimental connection between AD/DA converter and instruments.

Before acquiring a Brillouin spectrum, an adjusting program whose operation was observed on the computer screen was used to optimize the spectrum by optimizing the intensity of the Rayleigh lines. Acquisition of spectra is accomplished under computer control. The frequency interval of each scan is about 1.2 free spectral range.
(FSR), within which two elastic peaks (Rayleigh lines) were included. Usually, each scan took 100 or 200 s depending on the intensity of the signal. A typical Brillouin spectrum is given in Fig. 16. The two maxima on both sides are Rayleigh peaks and the two smaller peaks between them are the Brillouin components.

![Brillouin spectrum diagram](image)

Figure 16. A typical Brillouin spectrum. d is the space between two mirrors of the Fabry-Perot interferometer. FSR means free spectral range.

A Leybold RGD-210 closed-cycle refrigerator which can operate from 10 to 475 K under vacuum (<10^{-3} torr) was used for temperature control with a LakeShore DRC-91C temperature controller. Fig. 17 shows the relative positions of sample, sensor and light beam in the closed-cycle helium refrigerator.
Figure 17. Actual positions of crystal, thermal sensor and laser beam in the closed-cycle helium refrigerator.

The temperature reading error was controlled to better than ±0.1 K and temperature was measured to ±0.01 K by using a calibrated silicon diode thermal sensor placed on the optical sample holder. For higher temperature (300-900 K), a closed oven with four windows was used with a calibrated LakeShore PT-103 platinum resistance thermometer and a manual controlled power supply. The temperature accuracy is about ±0.1 K.

Characteristics of the Fabry-Perot Interferometer

The Fabry-Perot interferometer plays a key role in Brillouin light scattering. For better understanding of how the frequency shift and half-width were measured and determined, we briefly review its characteristics here.

The condition for constructive interference for a transmitted wave front is

\[ 2nd \cos \theta = m\lambda \]  

(3)
where \( n \) is the refractive index of the medium between the two reflecting mirror surfaces, \( d \) is the mirror spacing, and \( \theta \) is the inclination of the normal of the mirror surface to the wave front direction. \( m \) is the order of interference and \( \lambda \) is the wavelength of the laser beam. In our case, the incident laser beam is perpendicular to the mirror surface (\( \theta = 0 \)). Since the medium between the two mirrors is air, the refractive index is \( n = 1 \). Therefore, Eq. (3) becomes

\[
d = \frac{m\lambda}{2}
\]

(4)

If \( d \) decreases by \( \lambda/2 \), a wave with the same wavelength is still able to pass the interferometer but the order of the interference lowers by one. Also, there will be another wave with different wavelength that may pass but with the same \( m \)th order interference. Hence we have

\[
d = (m-1)\frac{\lambda_1}{2} = m\frac{\lambda_2}{2}
\]

(5)

\[
\delta\lambda = \lambda_1 - \lambda_2 = \frac{\lambda_1^2}{2d}
\]

(6)

\( \delta\lambda \) is called the free spectral range (FSR). In term of frequency \( v \),

\[
2d = \frac{mc}{\nu_1}
\]

(7)

\[
2d = \frac{(m-1)c}{\nu_2}
\]

(8)
where c is the speed of light. From Eqs. (7) and (8), one can obtain

\[ \Delta \nu = \frac{c}{2d} \] (Hz) \hspace{1cm} (9)

or

\[ \Delta \nu = \frac{1}{2d} \text{ (cm}^{-1}) \] \hspace{1cm} (Note: 1 cm\(^{-1}\) = 30 GHz) \hspace{1cm} (10)

Here \( \Delta \nu \) is the frequency interval between two nearest bright interference fringes (or Rayleigh peaks) and also called the free spectral range (FSR).

Assume the optical length \( d \) changes by \( \lambda_i/2\alpha \), where \( \alpha \) is not an integer. The wave front of wavelength \( \lambda_3 \) is allowed to pass this interferometer if the following formula is satisfied:

\[ 2(d - \frac{\lambda_i}{2\alpha}) = (m - i)\lambda_3 \] \hspace{1cm} (11)

where \( m \) and \( i \) are integers. Then

\[ \lambda_3 = \frac{2(d - \frac{\lambda_i}{2\alpha})}{2d \left( \frac{1}{\lambda_i} - \frac{1}{\lambda_i} \right)} \] \hspace{1cm} (12)

Here we have used the relation, \( 2d = m\lambda_i \). Then

\[ \Delta \lambda = \lambda_3 - \lambda_i = \frac{\lambda_i^2 (i - \frac{1}{i\lambda_i})}{2d (1 - \frac{i\lambda_i}{2d})} \] \hspace{1cm} (13)
Normally \( m \gg i \) and \( 2d \gg i\lambda (\lambda \approx 5 \times 10^{-5} \text{ cm}) \), so

\[
\Delta \lambda = \frac{\lambda^2 (i - \frac{1}{\alpha})}{2d} = (i - \frac{1}{\alpha}) \cdot \text{FSR}
\]  

(14)

or

\[
\Delta \nu = (i - \frac{1}{\alpha}) \cdot \text{FSR}
\]  

(15)

Here \( \Delta \nu \) is the frequency shift from the original wave (Rayleigh line) and \( i \) is the shift order which is with respect to the Rayleigh line and is different from the order of interference. Experimental determination of shift order of Brillouin components will be discussed later in this chapter.

The Fabry-Perot interferometer which we used for experiments is a Burleigh Instr. Model RC-140. It uses matched sets of piezoelectric PZT transducers constructed from interferometrically matched PZT discs. This PZT material offers linearity and hysteresis characteristics better than 1% and 0.5%, respectively. The RC-42 Ramp Function Generator drives the FP interferometer. The ramp generator controls the PZT to provide two functions, i.e. scanning and alignment.

The finesse is the measurement of the interferometer's ability to resolve closely spaced lines (close frequencies). The finesse \( (F_1) \) for our system was about 40 (for single pass). For multi-pass system, the finesse is

\[
F_p = \frac{F_1}{(2^p - 1)^{\frac{1}{2}}}
\]  

(16)

where \( p \) is the number of passes. In our five-pass system, the finesse is about 104. The contrast of multi-pass system is also improved significantly.
Pre-Alignment of Fabry-Perot Interferometer

This is a rough parallel alignment procedure for Fabry-Perot mirrors and is critical for obtaining Brillouin spectrum. It should be completed before measurement. Before doing this pre-alignment, the ramp generator needs to be set at the following position: power "on", three biases "one and half turn" , ramp bias "one quarter turn" and others "off". The cover of the Fabry-Perot interferometer must be removed and a piece of paper is placed in front of the front mirror as shown in Fig. 18a. A reflective mirror was used to reflect the interference pattern into the observer's eyes. How do you know that the two mirrors are on "rough" parallel position? The trick is to move the reflective mirror along the triangle indicated by dashed lines in Fig. 18b and adjust the two bigger knobs (labeled "L" and "R" in Fig. 18b) until the radius of the interference rings (shown in Fig. 19)40 is almost constant everywhere.

Figure 18. (a) A set-up for pre-alignment of the Fabry-Perot interferometer mirrors. (b) The dashed line indicates the path along which the reflective mirror is moved to check the radius of interference rings.
Brillouin Spectrum Analysis

Typical traces of the Brillouin spectrum have been shown in Fig. 16. The determination of phonon frequency shift and half-width can be done by selecting a suitable FSR, i.e. suitable Fabry-Perot spacing $d$ (FSR$=1/2d \text{ cm}^{-1}$). One should avoid having the two Brillouin peaks close to each other so that they overlap, or separated too much so that they move into the "skirts" of the Rayleigh peaks. Since different materials have different values of frequency shift, a larger FSR ($-2\text{cm}^{-1}=60 \text{ GHz}$) usually is chosen first in order to have the Brillouin peaks appearing in first order with respect to the Rayleigh peak (see Fig. 20a). With such a large FSR, one can easily determine the actual phonon frequency shift range. However, a large FSR will reduce the resolution of phonon half-width. Thus, a smaller FSR is preferred in actual measurement, so that the
Brillouin peaks appear in the higher (second or third) order with respect to the Rayleigh peak (see Fig. 20b).

Figure 20. (a) An illustration of the Brillouin spectrum with larger FSR=α. R and B represent the Rayleigh and Brillouin components, respectively. (b) An illustration of the Brillouin spectrum with smaller FSR=α/2.

The frequency shift can be determined by the following equation

$$\Delta \nu = \frac{L}{M} \text{FSR}$$  \hspace{1cm} (17)

where L is the total channel number between the Brillouin peak and Rayleigh line and M is the total channel number between the two nearest Rayleigh peaks. Here the Brillouin component has a half-width $\delta \nu$ (at half height) that arises from the finite lifetime of the phonons responsible for the scattering. A typical Lorentz profile equation which is a result of the assumption that phonons decay in time as $e^{-\delta \nu t}$, can be used to fit the spectrum, i.e.
\[ I(x) = \frac{A}{B^2 + (x - C)^2} + D \]  

(18)

where \( I(x) \) is the spectrum intensity and \( x \) is the channel number. \( D \) is the background intensity and \( A \) is an arbitrary number. From fitting, the frequency shift \( \Delta \nu \) and observed half-width \( \delta \nu_{\text{obs}} \) can be determined as

\[ \Delta \nu = (N - 1 + \frac{C}{M}) \cdot \text{FSR} \]  

(19)

\[ \delta \nu_{\text{obs}} = \frac{2B}{M} \cdot \text{FSR} \]  

(20)

where \( N \) is an integer (1, 2, 3 etc.). \( N=1 \) means that the Brillouin peak appears in first order with respect to the Rayleigh peak, and so on.

For determination of natural-phonon half-width \( \delta \nu_{\text{ph}} \), the natural-phonon spectrum and the instrumental function were assumed to have a Lorentz distribution, and the broadening due to collection optics was assumed to have rectangular distribution. In this case, the natural-phonon half-width \( \delta \nu_{\text{ph}} \) is given by

\[ \delta \nu_{\text{ph}} = (\delta \nu_{\text{obs}}^2 - \delta \nu_{\text{ang}}^2)^{\frac{1}{2}} - \delta \nu_{\text{inst}} \]  

(21)

where \( \delta \nu_{\text{obs}} \), \( \delta \nu_{\text{inst}} \), and \( \delta \nu_{\text{ang}} \) represent the observed, instrumental, and collection optical half-widths, respectively.

The Brillouin line broadening \( \delta \nu_{\text{ang}} \) due to finite collection angle \( \delta \theta_{\text{ap}} \) is described by a well-known formula which to second order in \( \delta \theta \) is
\[
\frac{\delta v_{\text{ang}}}{\Delta v} = \frac{\cot(\frac{\theta}{2})\delta \theta_{\text{sp}}}{2} \frac{(\delta \theta_{\text{sp}})^2}{8}
\] (22)

where \( \theta \) is the scattering angle and \( \Delta v \) is the phonon frequency shift. In our case, \( \delta \theta_{\text{sp}} \) is \(-0.057\) (radians) obtained from measurements of fused quartz. According to Eq. (22), the broadening problem is severe in near-forward scattering (or small scattering angles) for which \( \cot(\theta/2) \) is large. The half-width of the Rayleigh line in fused quartz was taken as the instrumental broadening \( \delta v_{\text{ins}} \).
CHAPTER 3

THEORY

Dielectric

The generally employed principle behind making measurements on a certain system is to subject it to a "force" and then examine how the system responds. In the dielectric case, the "force" is an electric field. In order to reflect the intrinsic properties of the system, the applied field should be "suitably small". In other words, the applied perturbation must not alter the nature of the system under study. This, in fact, is the essence of the linear response theory (LRT). Within this general framework two kinds of measurements may be performed: (i) response, in which the equilibrium value of some properties of the system under the influence of a time-independent field is measured, (ii) relaxation, in which a time-independent field that has been applied on the system for a long time is removed and the "free decay" of a system property such as polarization is investigated.

In dielectric materials, the intrinsic polarization is usually made up of three different components according to the nature of the charges displaced, i.e., electronic, ionic, and orientational (dipolar) polarizations. Only the dipolar contribution which comes from the reorientation of permanent dipoles, may lag the applied field and thus be responsible for dielectric dispersion at audio or radio frequencies. The other two
contributions (electronic and ionic) will become responsible for dispersion only if frequencies above $10^{12}$ Hz are applied.

Space charge (interfacial layers)\textsuperscript{43} polarization is an extrinsic effect and usually arises from the presence of electrons or ions capable of migrating over distances of macroscopic magnitude. Some of these charge carriers tend to become trapped and accumulate at lattice defects, impurity centers, voids, or at electrode surfaces and so distort the field and produce an apparent increase in the dielectric permittivity.\textsuperscript{43} Interfacial polarization is of particular importance in heterogeneous or multiphase (or multilayer) materials. Due to the differences in the electrical conductivity of the phases present, charges move through the more conducting phases and build up on the surfaces that separate these from the more resistive phases.

For large fields, nonlinear properties of polarization $P$ against the electric field $E$ are the characteristic of ferro- and antiferroelectrics, and other dielectrics to a smaller extent. At constant temperature, the electric field $E$ can be expressed by the Taylor series expansion as\textsuperscript{17}

$$E = \frac{1}{\chi} P + \zeta P^3 + \zeta_5 P^5$$

Here, $\chi$ is the static electric susceptibility. $\zeta$ and $\zeta_5$ are coefficients of the dielectric nonlinearity. If the applied electric field is small enough, however, the higher order nonlinear terms will not be evident. This is the case that we will be dealing with here. So, we will limit ourselves to the treatment of linear dielectric media, i.e. $P = \chi E$.

The dielectric permittivity tensor $\epsilon_\theta$ is defined from the relationship between electric field and electric displacement, i.e.

$$\tilde{D}(t) = \epsilon_\theta \tilde{E}(t) + \tilde{P} = \epsilon_\theta \tilde{E}(t)$$

(24)
i.e.

\[ D_i = \varepsilon_0 \varepsilon_{ij} E_j \]  \hspace{1cm} (25)

where \( \varepsilon_0 \) is the MKS constant.

In the simplest case, i.e. a harmonic electric field \( \vec{E} = E_0 e^{i\omega t} \) propagating in the material, the electric displacement can be given by

\[ \vec{D}(\omega, T) = \vec{D}_0(T) e^{i(\omega t - \delta)} \]  \hspace{1cm} (26)

i.e.

\[ D_{\omega i}(T) e^{i\delta(\omega)} = \varepsilon_0 \varepsilon_{ij}(\omega, T) E_{\omega j} \]  \hspace{1cm} (27)

This expression allows us to define the complex dielectric permittivity as

\[ \varepsilon_{ij}^*(\omega, T) = \varepsilon_{ij}(\omega, T) - i \varepsilon_{ji}(\omega, T) \]  \hspace{1cm} (28)

i.e.

\[ \varepsilon_{ij}(\omega, T) = \frac{D_{\omega i}(T) \cos \delta(\omega)}{\varepsilon_0 E_{\omega j}} \; ; \; \varepsilon_{ij}(\omega, T) = \frac{D_{\omega i}(T) \sin \delta(\omega)}{\varepsilon_0 E_{\omega j}} \]  \hspace{1cm} (29)

The quantity \( \varepsilon_{ij}^*(\omega) \) determines the component of \( D(t) \) with a phase difference of \( \pi/2 \) with respect to \( E(t) \) and can be easily shown to be proportional to the dissipated power density \( (= \omega \varepsilon_0 \varepsilon^* E_0^2 / 2) \) in the dielectric. For this reason, \( \varepsilon^*(\omega) \) is also called the loss factor.
In the actual measurement, the capacitance $C$ and conductance $G$ were detected and then used in the following relationships to obtain complex dielectric permittivity, i.e.

$$C^* = C - i \frac{G}{\omega} = \frac{\partial Q}{\partial V} = \frac{\partial (A \varepsilon_0 \varepsilon E)}{\partial V} = \frac{\varepsilon_0 A \varepsilon^*}{d} = C_0 \varepsilon^*,$$  \hspace{1cm} (30)

$$\varepsilon_{ij}(\omega, T) = \frac{C_{ij}(\omega, T)}{C_0}$$ $$\varepsilon_{ij}^*(\omega) = \frac{G_{ij}(\omega, T)}{\omega C_0}$$  \hspace{1cm} (31)

where $C_0 = \varepsilon_0 A / d$ is the geometrical capacitance, i.e., the capacitance that we would obtain from the parallel plate capacitor when the sample is removed. $A$ is the sample area which is contacted with electrode and $d$ is the sample thickness. $\omega = 2\pi f$ (Hz) is the angular frequency.

The elements of dielectric tensor $\varepsilon_{ij}^*$ usually are anisotropic and depend on crystal symmetry. From thermodynamic arguments, we know that the dielectric permittivity tensor is symmetric, i.e. $\varepsilon_{ij}^* = \varepsilon_{ji}^*$. Following are different dielectric tensors which correspond to different crystal symmetries along some specific symmetry directions.\(^\text{14}\)

**Triclinic:**

$$\varepsilon_{ij}^* = \begin{bmatrix} \varepsilon_{11}^* & \varepsilon_{12}^* & \varepsilon_{13}^* \\ \varepsilon_{12}^* & \varepsilon_{22}^* & \varepsilon_{23}^* \\ \varepsilon_{13}^* & \varepsilon_{23}^* & \varepsilon_{33}^* \end{bmatrix}$$

**Monoclinic:**

$$\varepsilon_{ij}^* = \begin{bmatrix} \varepsilon_{11}^* & \varepsilon_{12}^* & 0 \\ \varepsilon_{12}^* & \varepsilon_{22}^* & 0 \\ 0 & 0 & \varepsilon_{33}^* \end{bmatrix}$$ (\(\hat{z}\) along the 2-fold axis)
Orthorhombic: \( \varepsilon_{ij}^* = \begin{bmatrix} \varepsilon_{11}^* & 0 & 0 \\ 0 & \varepsilon_{22}^* & 0 \\ 0 & 0 & \varepsilon_{33}^* \end{bmatrix} \) (three 2-fold axes are axes)

Trigonal

and

Tetragonal: \( \varepsilon_{ij}^* = \begin{bmatrix} \varepsilon_{11}^* & 0 & 0 \\ 0 & \varepsilon_{11}^* & 0 \\ 0 & 0 & \varepsilon_{33}^* \end{bmatrix} \) (\( \hat{z} \) along the n-fold axis, n\( \geq 2 \))

and

Hexagonal

Cubic: \( \varepsilon_{ij}^* = \begin{bmatrix} \varepsilon_{11}^* & 0 & 0 \\ 0 & \varepsilon_{11}^* & 0 \\ 0 & 0 & \varepsilon_{11}^* \end{bmatrix} \)

A cubic crystal is an isotropic dielectric medium, i.e. the elements of the dielectric tensor are diagonal and equal, and do not depend on any reference axis.\(^{14}\)

**Dipolar Relaxation Equations**

For most practical cases, the dielectric relaxation behavior of reorienting dipoles can be described quantitatively by the following equation:

\[
\varepsilon^*(\omega, T) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + [i\omega\tau(T)]^{1-\alpha}}^\beta
\]  \( (32) \)

The different values of parameters \( \alpha \) and \( \beta \) are corresponding to different models. For practical purposes, three most useful empirical models are given below.
(1) Debye equation: $\alpha=0$, $\beta=1$\textsuperscript{44}

In this equation, there is a single relaxation time $\tau$. The real and imaginary parts of the dielectric permittivity can be separated as

$$
\varepsilon'(\omega, \tau) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + \omega^2 \tau^2} \quad \text{and} \quad \varepsilon''(\omega, \tau) = \frac{\alpha \tau(\varepsilon_s - \varepsilon_{\infty})}{1 + \omega^2 \tau^2} \tag{33}
$$

The Cole-Cole plot of $\varepsilon''$ vs. $\varepsilon'$ for various $\omega$ is a semicircle with its center at $(\varepsilon_{\infty} + \varepsilon_s)/2$ on the $\varepsilon'$ axis.

(2) Cole-Cole equation: $0<\alpha<1$, $\beta=1$\textsuperscript{44}

In this case, the inverse of the relaxation time $\tau$ has a frequency distribution. The real and imaginary parts of dielectric permittivity can be given by

$$
\varepsilon'(\omega, \tau) = \varepsilon_{\infty} + \frac{1}{2}(\varepsilon_s - \varepsilon_{\infty}) \left[ 1 + \frac{\sinh(1-\alpha)x}{\cosh(1-\alpha)x + \sin \frac{1}{2} \alpha \pi} \right] \tag{34}
$$

$$
\varepsilon''(\omega, \tau) = \frac{1}{2}(\varepsilon_s - \varepsilon_{\infty}) \left[ \frac{\cos \frac{1}{2} \alpha \pi}{\cosh(1-\alpha)x + \sin \frac{1}{2} \alpha \pi} \right] \tag{35}
$$

where $x=\ln(\omega_m/\omega)$. In these equations, $\omega_m \tau=1$ is the condition for the peak maximum in $\varepsilon''$. When plotting these equations in a Cole-Cole plot, we obtain a circular arc with its center lying below the real $\varepsilon'$ axis and intersecting the $\varepsilon'$ axis at angles of $\pi(1-\alpha)/2$ from a vertical line through the center.

(3) Cole-Davison equation: $\alpha=0$, $0<\beta<1$\textsuperscript{44}

This description provides an asymmetric broadening (toward high frequencies) of a Debye peak by the introduction of the parameter $\beta$. In a Cole-Cole plot, this equation produces a right skewed arc.\textsuperscript{5,44}
In terms of frequency domain, these three different behaviors can be described as shown in Fig. 21.

Figure 21. The Debye, Cole-Cole and Cole-Davison relaxation distribution functions.

Superparaelectric Model (nano-scale polar cluster)\textsuperscript{16}

The behavior of dielectric permittivity in relaxor ferroelectrics usually is dependent on the size of polar cluster (or polar domain) which is induced by locally nonstoichiometric charged region. In the limit $N \to \infty$ ($N$ is the number of dipole in a cluster), we would have a long-range-order ferroelectric phase transition which usually occurs at lower temperature. At high temperature, i.e. $N \to 1$, the real part of the dielectric permittivity $\varepsilon'$ should obey the Curie law $\varepsilon' = 1 + p^2/(\varepsilon_0 V kT)$. Here $p$ is the dipole moment of a unit cubic cell, $V$ is the cell volume, $\varepsilon_0$ is the MKS constant, $k$ is Boltzmann's constant and $T$ is absolute temperature. At low temperature, if $N$ remains finite (i.e. superparaelectric moment) instead of infinity, then the dc $\varepsilon'$ should obey the $N$-dipole-cluster Curie law $\varepsilon' = Np^2/(\varepsilon_0 V kT)$. In the following we will show a simple superparaelectric model in the DC limit.\textsuperscript{16}

If we assume that each dipole interacts with the other dipoles in the same cluster, i.e. long-range interaction, then the Hamiltonian for one $N$-dipole cluster in an electric field $E$ is
\[ H = -\sum_{i=1}^{N} \left[ p E S_i + J S_i \sum_{j<i} S_j \right] \]
\[ = -p E \sum_{i=1}^{N} S_i - \frac{J}{2} \left[ \sum_{i=1}^{N} S_i \sum_{j=1}^{N} S_j - \sum_{k=1}^{N} S_k^2 \right] \]
\[ = -p E \sum_{i=1}^{N} S_i - \frac{J}{2} \left( \sum_{i=1}^{N} S_i \right)^2 + \frac{NJ}{2} \quad (36) \]

where J represents a positive (ferroelectric) interaction which for mathematical and computational simplicity is assumed to exist among all dipoles in the N-dipole cluster. \( p \) is the dipole moment of an unit cubic cell. We define \( n_+ \) as the number of dipole moment parallel to the field, i.e.

\[ \text{\( N = n_+ + n_- \)} \]

\[ \sum_{i=1}^{N} S_i = m = n_+ - n_- = 2n_+ - N \quad (37) \]

Here we have assumed that each dipole has direction either along +z (\( \uparrow \)) or -z (\( \downarrow \)). "m" is the net dipole. Then, the partition function, \( Z \), can be given by

\[ Z = \sum_{n_+=0}^{N} \left( \frac{N}{n_+} \right) e^{\frac{p E}{kT} n_+ + \frac{J}{2kT} (m^2 - N)} \quad (38) \]

Usually, \( pE/kT \) is much smaller than 1, i.e.

\[ \frac{pE}{e^{kT} m} \approx 1 + \frac{pE}{kT m} \quad (39) \]
Therefore, the mean aligned dipole excess and dc dielectric permittivity are given by

\[
\langle n_+ - n_- \rangle = \langle m \rangle = 1 + \sum_{n_+}^{N} \frac{N!}{n_+! (N-n_+)!} \frac{pE}{m^2} \frac{2^{(m^2-N)/2kT}}{e^{-m^2/2kT}}
\]

from Eq. (24), we have

\[
\varepsilon' (f=0,T) = 1 + \frac{p < m >}{Ne_0 EV}
\]

where \( p < m > / NV \) is the cluster polarization. \( V \) is the unit cell volume \(-(4\AA)^3\).

If \((T-T_0)/T_0 >> 2/N\), where \(T_0 = NJ/k\), we can approximate the sum by an integral with limits extending to infinity, and replace the binomial coefficients by a gaussian, i.e.

\[
\sum_{n_+}^{N} \frac{N!}{n_+! (N-n_+)!} \Rightarrow 2^N \sqrt{\frac{2}{\pi N}} \int_{0}^{\infty} \frac{(2n_+-N)^2}{2N} \ e^{-m^2/2N} \ dm_+ (dm_+ = \frac{1}{2} \ dm)
\]

\[
= 2^N \sqrt{\frac{2}{\pi N}} \int_{0}^{\infty} \frac{m^2}{2N} \ e^{-m^2/2N} \ dm
\]

Here we use the relation

\[
\left( \int_{-\infty}^{\infty} e^{-x^2} = 2 \int_{0}^{\infty} e^{-x^2} \right)
\]

Therefore, Eq. (40) becomes
At higher temperature for which Eq. (43) is valid we obtain the Curie-Weiss law by substituting Eq. (43) into Eq. (41)

\[ \varepsilon' = \frac{p^2}{4 \varepsilon_0 V k(T - T_0)} \]  

(44)

A dimensionless logarithmic derivative or "steepness parameter" \( S \) can be defined as

\[ S \equiv \frac{T \left( \frac{d\varepsilon'}{dT} \right)}{\varepsilon'} = \frac{d(\ln \varepsilon')}{d(\ln T)} \]  

(45)

which is -1 in the Curie-law regions at very low and very high temperatures and which should have greatest magnitude near \( T_0 \).
Equivalent Circuits of Dielectric Function

Strong dispersive dielectric behavior at low frequencies had been noted for a long time in many dielectric materials. As one knows, the interfacial effect also shows a strong dielectric frequency dispersion and could be reproduced by an equivalent circuit of capacitance in series with parallel G-C (see Fig. 22f). This kind of inhomogeneous medium effect is already known under the general name of Maxwell-Wagner effect and it can be developed as a direct counterpart to the distributions of Debye-like relaxation behavior in a dipolar material. This model therefore, has all the superficial attraction, as well as all drawbacks of the distribution theories. Several equivalent circuits which represent several physical situations are given in Fig. 22. Following are some relations which might be helpful to understand Fig. 22.

\[
Z = Y^{-1} = R + \frac{-i}{\omega C} \quad \text{(for a series R-C circuit)}
\]

\[
Y = (\varepsilon'' + i\varepsilon') \omega \frac{\varepsilon_0 A}{d} \quad \text{(for sample, A:area, d:thickness)}
\]

\[
C' = C + i\frac{G}{\omega} \quad \text{and} \quad Y = G + i\omega C
\]

Brillouin Light Scattering

Spectrum and Principle of Brillouin Scattering

In this section we will present a theory of Brillouin light scattering from the viewpoint of classical electromagnetism. For practical interest, we will be limited to the case of the radiation zone (R >> λ >> r), i.e., the wavelength of the emitted radiation λ (~5000 Å) is much greater than the dimension r (~1 Å) of the radiating source. R is the distance between observation point and origin. In this case, the vector potential \( \vec{A} \) can be given by
Figure 22. Schematic representations of the properties of simple circuit combinations of ideal, frequency-independent elements of capacitance $C$, conductance $G$ or resistance $R$, and inductance $L$, as shown in first column. The second column gives the complex impedance plot $Z$, the third the complex admittance plot $Y$ and the fourth the complex capacitance $C^\ast$. The fifth column gives the corresponding plots of log $C'(\omega)$ (solid line) and log $C''(\omega)$ (dotted line), against log $\omega$. Arrows indicate the sense of increasing frequency. Vertical and horizontal axes are imaginary and real parts, respectively.
\[
\vec{A}(\vec{R}, \omega) = \sum_{m=0}^{46} \frac{(-i k)^m}{c R m!} \int \vec{J}(\vec{r}, \omega) (\hat{n} \cdot \vec{r})^m d^3r
\]

where \(\hat{n}\) is the unit vector of \(\vec{R}\). "\(r\)" is the position of the radiating source inside the medium. Since the terms of \(k^m (\hat{n} \cdot \vec{r})^m\) go as \((d/\lambda)^m \ll 1\), the dominant term is for \(m=0\) (dipole radiation). Then the vector potential becomes

\[
\vec{A}(\vec{R}, \omega) = \frac{e^{ikR}}{cR} \int \vec{J}(\vec{r}, \omega) d^3r
\]

\[
= -i k \frac{e^{ikR}}{cR} \vec{P}(r, \omega); \quad [\int \vec{J}(\vec{r}, \omega) d^3r = -i \omega \int \vec{P}(\vec{r}, \omega) d^3r]
\]

with

\[
\vec{P} = \int \vec{P}(\vec{r}, \omega) d^3r
\]

\(\vec{P}\) is the electric dipole moment. In the radiation zone, the fields are \(\vec{B} = \nabla \times \vec{A}\) and \(\vec{E} = \vec{B} \times \hat{n}\), i.e.

\[
\vec{E}(\vec{R}, t) = \frac{1}{R} \hat{n} \times \left[ \frac{\omega^2}{c^2} \int \vec{P}(\vec{r}, \omega) \exp^{-i\omega(t - \frac{R}{c})} d^3r \right] \hat{n}
\]

\[
= \frac{1}{c^2 R} \hat{n} \times \left[ \hat{n} \times \frac{\partial^2 \vec{P}(t')}{\partial t'^2} \right]
\]

Here we use the relation \(\vec{E}(\vec{R}, t) = \vec{E}(\vec{R}, \omega) e^{-i\omega t}\). \(t' = t - \frac{n|\vec{R} - \vec{r}|}{c} = t - \frac{nR}{c}\) is the retarded time inside the medium. If the incident light intensity is weak, then the local polarization would be written approximately by
where $\bar{\alpha}$ is the tensor of polarizability. $E_{in}$ is the electric field of the incident wave within the medium. If it is a plane-wave field, then

$$\bar{E}_{in}(r,t) = \bar{E}_o e^{i(k_o \cdot r - \omega_o t)}$$

(51)

where $k_o = n\omega_o / c$ is the wave vector of the light wave and $n$ is the refractive index of the medium. A light scattering diagram is shown in Fig. 23.

To analyze the origin of the scattering, it is convenient to decompose $\alpha$ into its time average part $\langle \alpha \rangle$ and the time-space fluctuations $\delta\alpha(r,t)$ produced by the thermal fluctuations in the medium. The thermal fluctuations cause off-diagonal components to appear in the polarizability tensor, so we have

$$\bar{p}(r,t') = \left[ \langle \bar{\alpha} \rangle + \delta\bar{\alpha}(r,t') \right] \cdot \bar{E}_o e^{i(k_o \cdot r - \omega_o t')}$$

(52)

$$\frac{d\bar{P}}{dt'} = \left[ -i\omega_o \langle \bar{\alpha} \rangle - i\omega_o \delta\bar{\alpha} + \frac{d(\delta\bar{\alpha})}{dt'} \right] \cdot \bar{E}_o e^{i(k_o \cdot r - \omega_o t')}$$

(53)
Since the characteristic frequencies of thermal fluctuations are small ($\lesssim 10^{13}$ Hz) compared to the light frequency in the optical region ($\sim 10^{15}$ Hz), we can regard $\delta \alpha$ as a very weak function of time, i.e.

$$\frac{d^2 \bar{P}}{dt'^2} = \left[ -\omega_o^2 <\bar{\alpha}> - \omega_o^2 \delta \bar{\alpha} - 2i\omega_o \frac{d(\delta \bar{\alpha})}{dt'} + \frac{d^2(\delta \bar{\alpha})}{dt'^2} \right] \bar{E}_0 e^{i(k_o \bar{r} - \omega_o t')}$$

Substituting Eqs. (54) and (55) into Eq. (49) and carrying out the integration over the illuminated volume $V$ at the retarded time $t'$, we obtain

$$\bar{E}_{Total} = \int_V \bar{E}(R, t) d^3 r = -\left(\frac{\omega_o}{c}\right)^2 \frac{1}{R} \hat{n} \times \left[ \hat{n} \times \int_V \delta \bar{\alpha} \cdot \bar{E}_0 e^{i(k_o \bar{r} - \omega_o t' - \frac{|\bar{R} - \bar{r}|}{c})} d^3 r \right]$$

$$= -\left(\frac{\omega_o}{c}\right)^2 \frac{1}{R} \hat{n} \times \left[ \hat{n} \times \int_V \delta \bar{\alpha} \cdot \bar{E}_0 e^{i(k_o \bar{r} - \omega_o t') + i \bar{K}' \cdot (\bar{R} - \bar{r})} d^3 r \right]$$

Here we have used the relations

$$\bar{K}' = \frac{n\omega_o}{c} \hat{n}; \quad \hat{n} = \frac{\bar{R} - \bar{r}}{|\bar{R} - \bar{r}|}$$

The integral in Eq. (56) gives the superposition of phases of waves scattered from each illuminated point in the crystal. The contribution to the integral from the $<\bar{\alpha}>$ term is zero except in the forward direction. This light oscillates at the same frequency as the
incident field and results only in elastic scattering. Scattering out of the incident direction results entirely from fluctuations \( \delta \vec{\alpha} \) in the polarizability.

We can decompose the fluctuations into their spatial Fourier components

\[
\delta \vec{\alpha}(\vec{r},t') = \left( \frac{1}{2\pi} \right)^{\frac{3}{2}} \sum_{\mu} \int \delta \vec{\alpha}(\vec{q}) e^{i \frac{\vec{q} \cdot (\vec{r} - \vec{r}')}{c} + \frac{n|\vec{R} - \vec{r}'|}{c}} \, d^3q
\]  

(58)

where \( \vec{q} \) is the wave-vector of the fluctuation and \( \omega_{\mu}(\vec{q}) \) is the frequency of the fluctuation corresponding to this wave vector, i.e. \( \omega_{\mu}(\vec{q}) = c|\vec{q}| \). The index \( \mu \) denotes the possibility of a number of branches in the dispersion. In general, \( \omega_{\mu}(\vec{q}) \) can be complex to include a description of the damping of the fluctuation. \( \omega_{\mu}(\vec{q}) \) is double-valued with \( \pm \) for the degeneracy in the dispersion for positive and negative running waves.

\[
\mathcal{E}_{\text{Total Scatt.}} = - \left( \frac{1}{2\pi} \right)^{\frac{3}{2}} \left( \frac{\omega_o}{c} \right)^{\frac{3}{2}} \sum_{\mu} \hat{n} \times \int \delta \vec{\alpha}(\vec{q}) \cdot \vec{E}_0 e^{i(k_o \cdot \vec{r} - \omega_o t + iK' \cdot (\vec{R} - \vec{r}) + \frac{n\omega_{\mu}(\vec{q})|\vec{R} - \vec{r}|}{c}} \, d^3r \, d^3q
\]  

(59)

The exponential part of Eq. (59) can be rearranged as

\[
e^{i(k_o \cdot \vec{r} - \omega_o t) + iK' \cdot (\vec{R} - \vec{r})} e^{i[\vec{q} \cdot \vec{r} + \omega_{\mu}(\vec{q}) t + \frac{n\omega_{\mu}(\vec{q})|\vec{R} - \vec{r}|}{c}}
\]

\[
e^{i(k_o \cdot \vec{r} - \omega_o t + iK' \cdot (\vec{R} - \vec{r}) e^{i\vec{q} \cdot \vec{r} + \omega_{\mu}(\vec{q}) t + k_{\mu} \cdot (\vec{R} - \vec{r})]
\]

\[
e^{i(k_o \cdot \vec{r} - \omega_o t) e^{i[\vec{q} \cdot \vec{r} + \omega_{\mu}(\vec{q}) t] e^{i[(K' + k_{\mu}) \cdot (\vec{R} - \vec{r})]
\]
Here we have used $\bar{k}_\mu = \frac{n\omega_\mu}{c} \hat{n}$ and $\bar{K} = \bar{K}' \pm \bar{k}_\mu$. Thus

$$E_{\text{scatt}}^{\text{Total}} = -\left(\frac{1}{2\pi}\right)^2 \frac{\omega_\mu}{c} \sum_\mu \hat{n} \times \left[ \hat{n} \times \int_V \delta \hat{\alpha}(\bar{q}) \cdot \vec{E}_0 e^{i[K - (\omega_\omega \pm \omega_\mu(\bar{q}))t]} e^{i[\bar{K} - \bar{q}]} \frac{d^3 r}{d^3 q} \right]$$

$$= -\left(\frac{\omega_\mu}{c}\right)^2 \frac{1}{R} \sum_\mu \hat{n} \times \left[ \hat{n} \times \int_{\bar{q}} \delta \hat{\alpha}(\bar{q}) \cdot \vec{E}_0 e^{i[K - (\omega_\omega \pm \omega_\mu(\bar{q}))t]} \right]$$

$$= -\left(\frac{\omega_\mu}{c}\right)^2 \frac{1}{R} \sum_\mu \hat{n} \times \left[ \hat{n} \times \delta \hat{\alpha}(\bar{q}) \cdot \vec{E}_0 e^{i[K - (\omega_\omega \pm \omega_\mu(\bar{q}))t]} \right]$$

$$= -\left(2\pi\right)^2 \frac{\omega_\mu}{c} \frac{1}{R} \sum_\mu \hat{n} \times \left[ \hat{n} \times \delta \hat{\alpha}(\bar{q}) \cdot \vec{E}_0 e^{i[K - (\omega_\omega \pm \omega_\mu(\bar{q}))t]} \right]$$

We have used the delta function relation, i.e.

$$\int_V e^{i[\bar{K}_0 + \bar{q} - \bar{K}] \bar{r}} d^3 r = (2\pi)^3 \delta(\bar{K}_0 + \bar{q} - \bar{K})$$

Thus the wave vector which produces the scattering in the direction $\hat{n}$ is that which satisfies the implicit equation

$$\bar{q} = \bar{K} - \bar{K}_0$$

$$|\bar{K}| = K = \frac{n}{c} (\omega_\omega \pm \omega_\mu) = \frac{n\omega_\mu}{c}$$
where $\mathbf{K}$ is the wave vector of the scattered photon and $\mathbf{k}_0$ is the wave vector of the incident photon. $\mathbf{q}$ is the wave vector of the lattice fluctuation. Eqs. (63) and (64) represent the conservation of momentum among these three wave vectors, and conservation of energy, respectively. The plus and minus signs correspond to the so-called anti-Stokes and Stokes lines in the spectrum, respectively. Momentum conservation among photons and phonon is illustrated in Fig. 24.

\[ \mathbf{q}^2 = \mathbf{K}^2 + k_0^2 - 2\mathbf{Kk}_0 \cos \theta \]

\[ = \left( \frac{n_s \omega_s}{c} \right)^2 + \left( \frac{n_i \omega_i}{c} \right)^2 - \frac{2n_i n_s \omega_s \omega_i}{c^2} \cos \theta, \]  

(65)

where $n_i$ and $n_s$ are refractive indices for incident and scattered light respectively.
Because of $\omega_1 \ll \omega_0$ ($\omega_1/\omega_0 \sim 10^{-5}$), so we have $\omega_s \sim \omega_0$, i.e.

$$q = \frac{\omega_0}{c} \left( n_1^2 + n_2^2 - 2n_1n_s \cos \theta \right)^2.$$

In an optically isotropic medium such as a cubic system, the index ellipsoid is a sphere $[(x_1^2 + x_2^2 + x_3^2)/\varepsilon = 1]$ and $n_1 = n_3 = n$. Then Eq. (66) becomes

$$q = \frac{2n\omega_0}{c} \left( \frac{1}{2} - \frac{1}{2} \cos \theta \right)^2 = \frac{2n\omega_0}{c} \sin \frac{\theta}{2},$$

(67)

$$q = \frac{2\pi\Delta \nu}{V}, \quad (\omega_0 = 2\pi v_0).$$

(68)

where $V$ is the phonon velocity (sound velocity) and $\Delta \nu$ is the phonon frequency (or Brillouin frequency shift). From Eqs. (67) and (68), we have

$$\frac{\Delta \nu}{\nu} = \frac{V}{c} \frac{2n \sin \frac{\theta}{2}}{2}.$$

(69)

In an anisotropic medium, the index ellipsoid shown in Fig. 25 has important properties. The directions (polarizations) of the electric displacement vectors $\vec{D}_1$ and $\vec{D}_2$ of two waves are along the semi-axes of the ellipse obtained from the cross section of the index ellipsoid inside the crystal with the equatorial plane which is perpendicular to the wave vector. The indices are equal to the lengths of the semi-axes of the ellipse.\textsuperscript{14}

For optically biaxial crystals (triclinic, monoclinic and orthorhombic systems), the three principal axes of an ordinary ellipsoid are 2-fold rotation axes. An ordinary ellipsoid $[x_1^2/n_1^2 + x_2^2/n_2^2 + x_3^2/n_3^2 = 1, \ n_1 \neq n_2 \neq n_3]$ has two circular equatorial cross sections which are symmetric with respect to two of the principal axes and which contain
the third axis. The directions orthogonal to these particular cross sections are the optical axes, i.e. only one index remains (the radius of the circle), waves with all polarization directions have the same velocity and there is no double refraction.

Figure 25. Index ellipsoid. Two waves, polarized along $\vec{D}_1$ and $\vec{D}_2$ (mutually orthogonal), can propagate in the $\vec{k}$ direction (applicable to both incident and scattered beams), with different velocities.

For optically uniaxial crystals (trigonal, tetragonal and hexagonal systems), one of the principal axes is a n-fold rotation axis $A_n$ ($n>2$) and is the axis of revolution of the index ellipsoid. If the propagation direction is along $A_n$, the cross section of the index ellipsoid is a circular section, so the index is the same for any polarization direction. Thus the crystal will behave as an isotropic material for a wave propagating along $A_n$ which is the optical axis. In this case, the equation for the index ellipsoid is $\frac{x_1^2}{n_1^2} + \frac{x_2^2}{n_2^2} + \frac{x_3^2}{n_3^2} = 1$.\(^{14}\)

In Brillouin scattering, one might worry about the problem of different indices and velocities inside the crystal caused by optical anisotropy. However, the difference between the principal indices is always small. The index ellipsoid is very close to a sphere. For instance, the indices of quartz are $n_x=1.5442$ and $n_e=1.5533$.\(^{14}\)
Brillouin scattering is a tool for measurement of elastic constants (stiffness) and piezoelectric stress constants. The calculation presented here is a basic theory for a non-piezoelectric material. The dynamic equation of lattice motion for a phonon can be written as

\[ \rho \frac{d^2 u_i}{dt^2} = \frac{dT_{ij}}{dx_j} \]  

(70)

where \( u_i \) is the displacement in the \( i \)th direction, \( \rho \) is the crystal density and \( T_{ij} \) are elements of the stress tensor. One can use the generalized Hooke's law to form the relation between the stresses and the strains, i.e.

\[ T_{ij} = C_{ijkl}^E S_{kl} \quad (i,j,k,l=1,2,3 \text{ or } x,y,z) \]  

(71)

and

\[ S_{kl} = \frac{1}{2} \left( \frac{du_k}{dx_l} + \frac{du_l}{dx_k} \right) \]  

(72)

where the \( C_{ijkl}^E \) are the elastic stiffness constants (Young's Modulus) at constant electric field and \( S_{kl} \) are the strain components. Substituting Eqs. (71) and (72) into Eq. (70) yields the phonon wave equations

\[ \rho \frac{d^2 u_i}{dt^2} = C_{ijkl} \frac{1}{2} \frac{d}{dx_j} \left( \frac{du_k}{dx_l} + \frac{du_l}{dx_k} \right) \]  

(73)

One can exchange "k" and "l" symbols, i.e.
Since elastic stiffness constants is a symmetry tensor,

\[ C_{ijkl}^E = C_{ijlk}^E, \]

and Eq. (73) becomes

\[ \rho \frac{d^2 u_i}{dt^2} = C_{ijkl}^E \frac{d^2 u_k}{dx_j dx_l}, \quad (74) \]

We seek plane-wave solutions of the phonon equation of motion in which the displacement vector can be written as

\[ u_i = u_{io} e^{i(\vec{q} \cdot r - \omega t)}, \quad \omega = 2\pi \Delta v \text{ (Brillouin shift)} \quad (75) \]

where \( u_{io} \) is the displacement and \( i \) is the polarization index of the phonon. From Eqs. (68) and (74), we have

\[ \rho V^2 u_i = C_{ijkl}^E I_j I_k u_k \quad (76) \]

where \( V \) is the sound velocity. \( I_j \) and \( I_l \) are the components (projections) of the unit phonon wave vector \( \vec{q} = \frac{\vec{q}}{|\vec{q}|} \) along the \( j \)- and \( l \)-axes. From now on, we will omit the superscript "E" for elastic stiffness constants, i.e. \( C_{ijkl} \equiv C_{ijkl}^E \).

For \( i=1 \), from Eq. (76) one has
\[
\rho V^2 u_1 = C_{1111} I_1 I_1 u_1 + C_{1112} I_1 I_2 u_1 + C_{1113} I_1 I_3 u_1 \\
+ C_{1121} I_1 I_1 u_2 + C_{1122} I_1 I_2 u_2 + C_{1123} I_1 I_3 u_2 \\
+ C_{1131} I_1 I_1 u_3 + C_{1132} I_1 I_2 u_3 + C_{1133} I_1 I_3 u_3 \\
+ C_{1211} I_2 I_1 u_1 + C_{1212} I_2 I_2 u_1 + C_{1213} I_2 I_3 u_1 \\
+ C_{1221} I_2 I_1 u_2 + C_{1222} I_2 I_2 u_2 + C_{1223} I_2 I_3 u_2 \\
+ C_{1231} I_2 I_1 u_3 + C_{1232} I_2 I_2 u_3 + C_{1233} I_2 I_3 u_3 \\
+ C_{1311} I_3 I_1 u_1 + C_{1312} I_3 I_2 u_1 + C_{1313} I_3 I_3 u_1 \\
+ C_{1321} I_3 I_1 u_2 + C_{1322} I_3 I_2 u_2 + C_{1323} I_3 I_3 u_2 \\
+ C_{1331} I_3 I_1 u_3 + C_{1332} I_3 I_2 u_3 + C_{1333} I_3 I_3 u_3
\] (77)

It is more convenient to use matrix notation than tensor notation, i.e.

Tensor notation: 11 22 33 23,32 13,31 12,21
Matrix notation: 1 2 3 4 5 6

After changing tensor to matrix notation, Eq. (77) becomes

\[
\rho V^2 u_1 = C_{11} I_1 I_1 u_1 + C_{16} I_1 I_2 u_1 + C_{15} I_1 I_3 u_1 \\
+ C_{16} I_1 I_1 u_2 + C_{12} I_1 I_2 u_2 + C_{14} I_1 I_3 u_2 \\
+ C_{15} I_1 I_1 u_3 + C_{14} I_1 I_2 u_3 + C_{13} I_1 I_3 u_3 \\
+ C_{61} I_2 I_1 u_1 + C_{66} I_2 I_2 u_1 + C_{63} I_2 I_3 u_1 \\
+ C_{66} I_2 I_1 u_2 + C_{62} I_2 I_2 u_2 + C_{64} I_2 I_3 u_2 \\
+ C_{63} I_2 I_1 u_3 + C_{64} I_2 I_2 u_3 + C_{62} I_2 I_3 u_3 \\
+ C_{53} I_3 I_1 u_1 + C_{56} I_3 I_2 u_1 + C_{55} I_3 I_3 u_1 \\
+ C_{56} I_3 I_1 u_2 + C_{52} I_3 I_2 u_2 + C_{54} I_3 I_3 u_2 \\
+ C_{53} I_3 I_1 u_3 + C_{54} I_3 I_2 u_3 + C_{55} I_3 I_3 u_3
\] (78)

The elastic stiffness constant tensor depends on the crystal symmetry and the reference frames. For orthorhombic (for all classes if three orthogonal diad axes are chosen as the reference frame), cubic (for all classes) and tetragonal (for classes 4mm,
The 6x6 coefficients \( C_{ij} \) are symmetric with respect to the main diagonal. Thus, Eq. (78) becomes

\[
\rho V^2 u_1 = (C_{11} I_1^2 I_1 + C_{55} I_3^2 I_3 + C_{66} I_2^2 I_2) u_1 + (C_{12} I_1 I_2 + C_{66} I_2 I_1) u_2 + (C_{13} I_1 I_3 + C_{55} I_3 I_1) u_3
\]

(79)

Similarly, for \( i = 2 \) and \( 3 \), we have

\[
\rho V^2 u_2 = (C_{66} I_2 I_1 + C_{12} I_1 I_2) u_1 + (C_{66} I_1 I_3 + C_{22} I_2 I_2 + C_{44} I_3 I_3) u_2 + (C_{23} I_2 I_3 + C_{44} I_3 I_2) u_3
\]

(80)

\[
\rho V^2 u_3 = (C_{55} I_3 I_1 + C_{13} I_3 I_2) u_1 + (C_{44} I_3 I_3 + C_{23} I_3 I_2) u_2 + (C_{44} I_2 I_3 + C_{33} I_3 I_3 + C_{55} I_1 I_1) u_3
\]

(81)

For non-trivial solutions of this set of Eqs. (79), (80) and (81), the following determinant of the coefficient matrix must vanish for an arbitrary phonon wave direction \( \vec{q} \) in the
crystal. This secular equation yields three eigenvalues which are associated with sound velocities of three phonon waves propagating in the same direction, and three mutually orthogonal eigenvectors which are the polarizations (displacement direction) of waves.

\[
\begin{vmatrix}
C_{11}I_1 + C_{33}I_3 + C_{44}I_4 - \rho V^2 & C_{12}I_2 + C_{66}I_6 & C_{13}I_3 + C_{66}I_6 \\
C_{66}I_6 + C_{12}I_2 + C_{44}I_4 - \rho V^2 & C_{22}I_2 + C_{44}I_4 & C_{23}I_3 + C_{44}I_4 \\
C_{33}I_3 + C_{11}I_1 & C_{44}I_4 + C_{23}I_3 & C_{55}I_5 + C_{55}I_5 - \rho V^2
\end{vmatrix} = 0
\]

(82)

Four phonon propagation directions are discussed below:

(i) Phonon wave propagating along [100] direction ($\bar{q} // [100]$), i.e. $I_1 = 1$, $I_2 = I_3 = 0$, then Eq. (82) becomes

\[
\begin{vmatrix}
C_{11} - \rho V^2 & 0 & 0 \\
0 & C_{66} - \rho V^2 & 0 \\
0 & 0 & C_{55} - \rho V^2
\end{vmatrix} = 0
\]

(83)

The roots of this equation, i.e. the corresponding values of $\rho V^2$, are $C_{11}$, $C_{66}$ and $C_{55}$. The unit eigenvector $\mathbf{u} = (u_1, u_2, u_3)$ for the eigenvalue $\rho V^2 = C_{11}$ can be obtained by

\[
\begin{pmatrix}
0 & 0 & 0 \\
0 & C_{66} - \rho V^2 & 0 \\
0 & 0 & C_{55} - \rho V^2
\end{pmatrix}
\begin{pmatrix}
u_1 \\
u_2 \\
u_3
\end{pmatrix} = \begin{pmatrix} 0 \\
0 \\
0 \end{pmatrix} = 0
\]

(84)

Thus

\[
\begin{pmatrix}
u_1 \\
u_2 \\
u_3
\end{pmatrix} = \begin{pmatrix} 1 \\
0 \\
0 \end{pmatrix}
\]

Similarly for $\rho V^2 = C_{66}$ and $\rho V^2 = C_{55}$, the polarization vectors are
Finally, we have

\[
\begin{pmatrix}
u_1 \\ u_2 \\ u_3
\end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \text{for } \rho V^2 = C_{66}
\]

\[
\begin{pmatrix}
u_1 \\ u_2 \\ u_3
\end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad \text{for } \rho V^2 = C_{55}
\]

The orientations of the phonon propagation wave vector and the three wave polarizations are given in Fig. 26.

Figure 26. Orientations of phonon propagation wave vector \( \mathbf{q} \parallel [100] \) and three wave polarizations.

(ii) Phonon propagating along [001] direction (\( \mathbf{q} \parallel [001] \)), i.e. \( I_3 = 1, I_1 = I_2 = 0 \).

Then Eq. (82) becomes
The eigenvalues \( \rho V^2 \) of this equation and the corresponding eigenvectors are

\[
\begin{align*}
\rho V_L^2 &= C_{33} \\
\bar{n}_L &= (0,0,1) \\
& \text{longitudinal (LA) mode} \\
\rho V_{T1}^2 &= C_{44} \\
\bar{n}_{T1} &= (0,1,0) \\
& \text{transverse (TA) mode} \\
\rho V_{T2}^2 &= C_{55} \\
\bar{n}_{T2} &= (1,0,0) \\
& \text{transverse (TA) mode}
\end{align*}
\]

(iii) Phonon propagating along \([110]\) direction \((\bar{q} // [110])\), i.e. \(I_1=I_2=\sqrt{\frac{1}{2}}, I_3=0\). Then Eq. (82) becomes

\[
\begin{vmatrix}
\frac{1}{2}(C_{11} + C_{66}) - \rho V^2 & \frac{1}{2}(C_{12} + C_{66}) & 0 \\
\frac{1}{2}(C_{66} + C_{12}) & \frac{1}{2}(C_{66} + C_{22}) - \rho V^2 & 0 \\
0 & 0 & \frac{1}{2}(C_{55} + C_{44}) - \rho V^2
\end{vmatrix} = 0
\]

\[
[(C_{11} + 2\rho V^2)(C_{66} + C_{22} - 2\rho V^2) - (C_{12} + C_{66})^2](C_{55} + C_{44} - 2\rho V^2) = 0
\]

In case of tetragonal symmetry with classes 4mm, \(\overline{4}2m\), 422, 4/mmm, one can use the following further symmetry relations

\[C_{11} = C_{22}, \quad C_{13} = C_{23}, \quad C_{44} = C_{55}\]

Thus Eq. (87) becomes
The eigenvalues $\rho V^2$ of this equation and the corresponding eigenvectors are

$$\rho V_L^2 = \frac{C_{11} + C_{12} + 2C_{66}}{2} \quad \tilde{n}_L = \frac{1}{\sqrt{2}} (1,1,0) \quad \text{LA}$$

$$\rho V_{T_1}^2 = \frac{C_{11} - C_{12}}{2} \quad \tilde{n}_{T_1} = \frac{1}{\sqrt{2}} (1,-1,0) \quad \text{or} \quad \frac{1}{\sqrt{2}} (-1,1,0) \quad \text{TA}$$

$$\rho V_{T_2}^2 = C_{44} \quad \tilde{n}_{T_2} = (0,0,1) \quad \text{TA}$$

The orientations of the phonon propagation wave vector and the three wave polarizations are given in Fig. 27.

Figure 27. Orientations of phonon propagation wave vector $\bar{q} // \{110\}$ and three wave polarizations.

\(\text{(v) Phonon propagation in the (001) plane ($\bar{q} // \{h,k,0\}$), i.e. } I_1 = \cos \theta, I_2 = \sin \theta, I_3 = 0\ (\theta \text{ is the angle between phonon wave vector and [100] a-axis). Then Eq. (82) becomes}

\[
\begin{vmatrix}
C_{11} \cos^2 \theta + C_{66} \sin^2 \theta - \rho V^2 & (C_{12} + C_{66}) \cos \theta \sin \theta & 0 \\
(C_{12} + C_{66}) \cos \theta \sin \theta & C_{66} \cos^2 \theta + C_{22} \sin^2 \theta - \rho V^2 & 0 \\
0 & 0 & C_{44} \sin^2 \theta + C_{55} \cos^2 \theta - \rho V^2
\end{vmatrix} = 0 \quad (89)
\]
In the case of tetragonal symmetry with classes 4mm, 42m, 422, 4/mmm, i.e. $C_{11} = C_{22}$, $C_{44} = C_{55}$, we have

\[
\begin{vmatrix}
C_{11}\cos^2 \theta + C_{66}\sin^2 \theta - \rho V^2 & (C_{12} + C_{66})\cos \theta \sin \theta & 0 \\
(C_{12} + C_{66})\cos \theta \sin \theta & C_{66}\cos^2 \theta + C_{11}\sin^2 \theta - \rho V^2 & 0 \\
0 & 0 & C_{44} - \rho V^2
\end{vmatrix} = 0 \quad (90)
\]

\[
[(C_{11}\cos^2 \theta + C_{66}\sin^2 \theta - \rho V^2)^2 - (C_{12} + C_{66})^2\cos^2 \theta \sin^2 \theta]\cdot (C_{44} - \rho V^2) = 0 \quad (91)
\]

Thus, the eigenvalues $\rho V^2$ of this equation and the corresponding eigenvectors are

\[
\rho V_L^2 = C_{11}\cos^2 \theta + C_{66}\sin^2 \theta + (C_{12} + C_{66})\cos \theta \sin \theta \quad \bar{n}_L = (\cos \theta, \sin \theta, 0)
\]

\[
\rho V_{T_1}^2 = C_{11}\cos^2 \theta + C_{66}\sin^2 \theta - (C_{12} + C_{66})\cos \theta \sin \theta \quad \bar{n}_{T_1} = (\sin \theta, -\cos \theta, 0)
\]

or $(-\sin \theta, \cos \theta, 0)$

\[
\rho V_{T_2}^2 = C_{44} \quad \bar{n}_{T_2} = (0, 0, 1)
\]

The orientations of the phonon propagation wave vector and the three wave polarizations are given in Fig. 28.

Figure 28. Orientations of phonon propagation wave vector $\bar{q} / /[\cos \theta, \sin \theta, 0]$ and three wave polarizations.
So far, the calculations presented above are only suitable for a non-piezoelectric material. For a phonon propagating in piezoelectric materials, Eq. (71) for the stress becomes\(^{14}\)

\[
T_{ij} = C_{ijkl} S_{kl} - e_{\alpha ij} E_{\alpha} = C_{ijkl} \frac{\partial u_k}{\partial x_l} + e_{\alpha ij} \frac{\partial \phi}{\partial x_{\alpha}} \tag{92}
\]

where \(\phi\) is the electric potential. Then, Eq. (74) becomes

\[
\rho \frac{\partial^2 u_i}{\partial t^2} = C_{ijkl} \frac{\partial^2 u_k}{\partial x_j \partial x_l} + e_{\alpha ij} \frac{\partial^2 \phi}{\partial x_j \partial x_{\alpha}} \tag{93}
\]

However, the electric displacement

\[
D_{\beta} = e_{\beta kl} S_{kl} + \varepsilon_{\beta \alpha} E_{\alpha} = \varepsilon_{\beta kl} \frac{\partial u_k}{\partial x_l} - \varepsilon_{\beta \alpha} \frac{\partial \phi}{\partial x_{\alpha}} \tag{94}
\]

must obey the Poisson equation \(\partial D_{\beta} / \partial x_{\beta} = 0\) for an insulator, i.e.

\[
e_{\beta kl} \frac{\partial^2 u_k}{\partial x_l \partial x_{\beta}} - \varepsilon_{\beta \alpha} \frac{\partial^2 \phi}{\partial x_{\alpha} \partial x_{\beta}} = 0 \tag{95}
\]

Therefore, with \(\beta \rightarrow j\) for Eq. (95), the equation (93) of motion can be written as

\[
\rho \frac{\partial^2 u_i}{\partial t^2} = C_{ijkl} \frac{\partial^2 u_k}{\partial x_j \partial x_l} + e_{\alpha ij} \frac{\partial^2 u_k}{\partial x_j \partial x_{\alpha}} = (C_{ijkl} + \varepsilon_{j\alpha} \frac{\varepsilon^S_{ijkl}}{\varepsilon_{j\alpha}}) \frac{\partial^2 u_k}{\partial x_j \partial x_{\alpha}} \tag{96}
\]
So, the difference in the phonon equation of motion between non-piezoelectric and piezoelectric crystals is

\[ C_{ijkl} \rightarrow \Gamma_{ijkl} = C_{ijkl}^E + \frac{e_{ijkl}}{\varepsilon_{j\alpha}} \]  

(97)

where \( e_{ijkl} \) is the piezoelectric stress constant and \( \varepsilon_{j\alpha} \) is the dielectric permittivity at constant strain (high frequency limit). Following is a simple case for a phonon propagating along the [100] direction (\( \vec{q} \parallel [100] \)) with tetragonal symmetry (class: 4mm) in a piezoelectric crystal, i.e.

\[
\begin{bmatrix}
0 & 0 & 0 & 0 & e_{113} & 0 \\
0 & 0 & 0 & e_{113} & 0 & 0 \\
e_{311} & e_{311} & e_{333} & 0 & 0 & 0 \\
e_{311} & e_{311} & e_{333} & 0 & 0 & 0 \\
e_{311} & e_{311} & e_{333} & 0 & 0 & 0 \\
\end{bmatrix}
\]

then Eq. (83) becomes

\[
\begin{vmatrix}
C_{11} - \rho V^2 & 0 & 0 & 0 \\
0 & C_{66} - \rho V^2 & 0 & 0 \\
0 & 0 & C_{55} + \frac{e_{15}^2}{\varepsilon_{11}^2} - \rho V^2 & 0 \\
\end{vmatrix} = 0
\]

(98)

The eigenvalues \( \rho V^2 \) of this equation and the corresponding eigenvectors are

\[
\begin{align*}
\rho V_{L}^2 &= C_{11} & \vec{n}_L &= (1,0,0) & \text{LA mode} \\
\rho V_{T1}^2 &= C_{66} & \vec{n}_{T1} &= (0,1,0) & \text{TA mode} \\
\rho V_{T2}^2 &= C_{55} + \frac{e_{15}^2}{\varepsilon_{11}^2} & \vec{n}_{T2} &= (0,0,1) & \text{TA mode}
\end{align*}
\]
Selection Rules of Scattered Light

In general, the propagation of light radiation in a crystal can be described completely in term of the dielectric impermeability tensor \( \beta_{ij} \). By definition, we have\(^{14} \):

\[
\beta_{ij} = [\epsilon^{-1}]_{ij} \quad \text{or} \quad \vec{\epsilon} \cdot \vec{\beta} = \vec{I}
\]  

(99)

where \( \vec{\epsilon} \) is the dielectric tensor. According to the quantum theory of solids, the dielectric permittivity tensor depends on the distribution of electric charges in the crystal. The action of an external electric field results in a redistribution of the bond charges and a slight deformation of the ionic lattice. This result is reflected in a change of the dielectric impermeability tensor. This is the electro-optic effect. If we neglect higher-order term, then we have

\[
\delta\beta_{ij} = r_{ijk}E_k + p_{ijrs}T_{rs}
\]  

(100)

where \( r_{ijk} \) and \( p_{ijrs} \) are linear electro-optic and photo-elastic (elasto-optical) coefficients, respectively. In Brillouin scattering, we only consider the second term, namely

\[
\delta\beta_{ij} = p_{ijrs}T_{rs}
\]  

(101)

The photo-elastic coefficient tensor depends on the crystal symmetry. For orthorhombic (all classes), cubic (all classes) and tetragonal (classes: 4mm, \( \overline{4}2m \), 422 and 4/mmm) etc., the photo-elastic coefficients matrix can be expressed as
Following is a sample calculation showing how to obtain selection rules for different phonon modes. In this illustration we consider the case of phonon propagation along the [010] (b-axis) direction ($\vec{q} \parallel [010]$):

For a longitudinal phonon polarized along [010], $u_1 = u_3 = 0$, $u_2 = e^{i\vec{q} \cdot \vec{r}}$, thus

- \( T_{11l} = 0 \)
- \( T_{12l} = 0 \)
- \( T_{13l} = 0 \)
- \( T_{21l} = 0 \)
- \( T_{22l} \neq 0 \)
- \( T_{23l} = 0 \)
- \( T_{31l} = 0 \)
- \( T_{32l} = 0 \)
- \( T_{33l} = 0 \)

From Eq. (101), we have

- $\delta \beta_{11} = p_{12} T_{22l}$
- $\delta \beta_{12} = 0$
- $\delta \beta_{13} = 0$
- $\delta \beta_{21} = 0$
- $\delta \beta_{22} = p_{22} T_{22l}$
- $\delta \beta_{23} = 0$
- $\delta \beta_{31} = 0$
- $\delta \beta_{32} = 0$
- $\delta \beta_{33} = p_{32} T_{22l}$

Thus, in this case the fluctuation of the dielectric impermeability tensor $\beta$ is

\[
\delta \beta = \begin{bmatrix}
\delta \beta_{11} & 0 & 0 \\
0 & \delta \beta_{22} & 0 \\
0 & 0 & \delta \beta_{33}
\end{bmatrix}
\]

The total dielectric impermeability tensor $\beta$ is

\[
P_{mn} = \begin{bmatrix}
P_{11} & P_{12} & P_{13} & 0 & 0 & 0 \\
P_{21} & P_{22} & P_{23} & 0 & 0 & 0 \\
P_{31} & P_{32} & P_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & P_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & P_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & P_{66}
\end{bmatrix}
\]
\[
\begin{align*}
\beta_{ij} &= B_0 + \delta \beta = \\
&= \begin{bmatrix}
\beta_{110} + \delta \beta_{11} & 0 & 0 \\
0 & \beta_{220} + \delta \beta_{22} & 0 \\
0 & 0 & \beta_{330} + \delta \beta_{33}
\end{bmatrix}
\end{align*}
\]

Since \( \vec{\epsilon} \cdot \vec{\beta} = 1 \), the total dielectric tensor \( \vec{\epsilon} \) turn out to be

\[
\varepsilon_{ij} = \begin{bmatrix}
\frac{1}{\beta_{110} + \delta \beta_{11}} & 0 & 0 \\
0 & \frac{1}{\beta_{220} + \delta \beta_{22}} & 0 \\
0 & 0 & \frac{1}{\beta_{330} + \delta \beta_{33}}
\end{bmatrix}
\]

\[
\begin{align*}
\Delta &= \begin{bmatrix}
\frac{1}{\beta_{110}} - \frac{\delta \beta_{11}}{\beta_{110}^2} & 0 & 0 \\
0 & \frac{1}{\beta_{220}} - \frac{\delta \beta_{22}}{\beta_{220}^2} & 0 \\
0 & 0 & \frac{1}{\beta_{330}} - \frac{\delta \beta_{33}}{\beta_{330}^2}
\end{bmatrix}
\end{align*}
\]

\[
\begin{align*}
\Delta &= \begin{bmatrix}
\frac{1}{\beta_{110}} & 0 & 0 \\
0 & \frac{1}{\beta_{220}} & 0 \\
0 & 0 & \frac{1}{\beta_{330}}
\end{bmatrix}
\end{align*}
\]

\[
\begin{align*}
\frac{\delta \beta_{11}}{\beta_{110}} & & \frac{\delta \beta_{22}}{\beta_{220}} & & \frac{\delta \beta_{33}}{\beta_{330}}
\end{align*}
\]

\[
\begin{align*}
= \varepsilon_{ij0} + \delta \varepsilon_{ij}
\end{align*}
\]

For our experimental situation, the polarization of the incident light is along [001]. Thus the fluctuation of the electric displacement is

\[
\delta \vec{D} = \delta \vec{\varepsilon} \cdot \vec{E} = -\frac{\delta \beta_{33}}{\beta_{330}} \begin{bmatrix}
0 \\
0 \\
1
\end{bmatrix}
\]

\[\text{(102)}\]
From Eq. (61), we know

\[ \vec{E}_{\text{scatt}} \propto \hat{n} \times (\hat{n} \times \delta \vec{D}) \propto [001] \]

Thus, the polarization of the scattered light is along the [001] direction. This means that for the longitudinal phonon mode the scattered light has the same polarization as the incident light.

For transverse phonons polarized along [100], \( u_2 = u_3 = 0, u_1 \propto e^{i \vec{k} \cdot \vec{r}} \),

\[
\begin{align*}
T_{11T} &= 0 & T_{12T} &\neq 0 & T_{13T} &= 0 \\
T_{21T} &\neq 0 & T_{22T} &= 0 & T_{23T} &= 0 \\
T_{31T} &= 0 & T_{32T} &= 0 & T_{33T} &= 0
\end{align*}
\]

and

\[
\begin{align*}
\delta \beta_{11} &= 0 & \delta \beta_{12} &= 2 p_{66} T_{12T} & \delta \beta_{13} &= 0 \\
\delta \beta_{21} &= 2 p_{66} T_{12T} & \delta \beta_{22} &= 0 & \delta \beta_{23} &= 0 \\
\delta \beta_{31} &= 0 & \delta \beta_{32} &= 0 & \delta \beta_{33} &= 0
\end{align*}
\]

Here we have used the symmetry relation, \( T_{12T} = T_{21T} \). Thus, in this case the fluctuation of the dielectric impermeability tensor \( \beta \) is

\[
\delta \beta_0 = \begin{bmatrix}
0 & \delta \beta_{12} & 0 \\
\delta \beta_{21} & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]
The total dielectric impermeability tensor $\beta$ is

$$\beta_{ij} = \beta_{ij0} + \delta \beta = \begin{bmatrix} \beta_{110} & \delta \beta_{112} & 0 \\ \delta \beta_{121} & \beta_{220} & 0 \\ 0 & 0 & \beta_{330} \end{bmatrix}$$

Since $\bar{\varepsilon} \cdot \bar{\beta} = \bar{I}$, i.e.

$$\begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{bmatrix} \begin{bmatrix} \beta_{110} & \delta \beta_{112} & 0 \\ \delta \beta_{121} & \beta_{220} & 0 \\ 0 & 0 & \beta_{330} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

(103)

Solving Eq. (101), we obtain

$$\varepsilon_{ij} = \varepsilon_{ij0} + \delta \varepsilon_{ij} = \begin{bmatrix} 1 \\ \frac{1}{\beta_{110}} \delta \beta_{112} \\ \delta \beta_{21} \beta_{110} \beta_{220} \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

$$\delta \varepsilon_{ij} = \begin{bmatrix} 0 \\ \frac{1}{\beta_{110}} \delta \beta_{112} \\ \delta \beta_{21} \beta_{110} \beta_{220} \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

The fluctuation of the electric displacement is

$$\delta \bar{D} = \delta \bar{\varepsilon} \cdot \bar{E} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

(104)
Thus, there is no scattered light for this phonon mode.

For transverse phonons polarized along [001], i.e. $u_2 = u_1 = 0$, $u_3 \approx e^{i\eta \cdot r}$,

\[
\begin{align*}
T_{11M} = 0 & \quad T_{12M} = 0 & \quad T_{13M} = 0 \\
T_{21M} = 0 & \quad T_{22M} = 0 & \quad T_{23M} \neq 0 \\
T_{31M} = 0 & \quad T_{32M} \neq 0 & \quad T_{33M} = 0
\end{align*}
\]

and

\[
\begin{align*}
\delta \beta_{11} = 0 & \quad \delta \beta_{12} = 0 & \quad \delta \beta_{13} = 0 \\
\delta \beta_{21} = 0 & \quad \delta \beta_{22} = 0 & \quad \delta \beta_{23} = 2 \beta_{23} T_{23M} \\
\delta \beta_{31} = 0 & \quad \delta \beta_{32} = 2 \beta_{32} T_{23M} & \quad \delta \beta_{33} = 0
\end{align*}
\]

Here we have used the symmetry relation, $T_{23M} = T_{32M}$. In the same way we find the fluctuation in the dielectric permittivity tensor

\[
\delta \varepsilon_{ij} = \begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & \frac{-\delta \beta_{23}}{\beta_{23} \beta_{330}} \\
0 & \frac{-\delta \beta_{32}}{\beta_{220} \beta_{330}} & 0
\end{bmatrix}
\]

Thus the fluctuation of the electric displacement is

\[
\delta \vec{D} = \delta \vec{\varepsilon} \cdot \vec{E} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \frac{\delta \beta_{23}}{\beta_{220} \beta_{330}} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}
\]

From Eq. (61), we know
\[ \vec{E}_{\text{scatt}} \propto \hat{n} \times (\hat{n} \times \delta \vec{D}) \propto [010] \]

Thus, the polarization of the scattered light is along the [010] direction. This means that for this transverse phonon mode the scattered light polarization is perpendicular to the incident light polarization.

In the same way we can obtain polarizations of scattered light for longitudinal (LA) and transverse (TA) modes for phonons propagating along different directions. In summary, one can find the following selection rules for Brillouin light scattering: (i) The polarization of the scattered light by the LA phonons in a crystal which has one of these symmetries; orthorhombic (all classes), cubic (all classes) and tetragonal (classes: 4mm, \( \bar{4}2m \), 422 and 4/mmm), is the same as for the incident light. (ii) The polarization of the scattered light by one of the two TA modes is perpendicular to the polarization of the incident light. The other TA mode does not produce scattered light.

**Static Coupling Theory of First-Order Phase Transition**

In principle, the acoustic coupling contributions include both static and dynamic effects. Although the dynamic coupling always produces a negative contribution (softening) to the real part of the complex elastic stiffness change \( \Delta c^* \), the static effect can have either sign contribution, depending on whether the phase transition is of first or second order. According to the Landau free energy expansion with a single order parameter, the second-order transition gives a negative contribution in elastic stiffness change but the first-order transition can give either a positive (hardening) or negative contribution for both linear and quadratic couplings. Several first-order examples that show different elastic coupling behaviors can be found in Refs. 17 and 46.

The details of second-order coupling theory have been discussed elsewhere.\(^{47}\) In the following, the first-order case, i.e. \( a_4 < 0 \) and \( a_6 > 0 \), will be discussed. In the spirit
of the Landau theory of phase transitions, the free energy, with one order parameter, can be expressed by

\[ F(\eta, \mu, T) = F_0(T) + \frac{1}{2} a_2(T) \eta^2 + \frac{1}{4} a_4 \eta^4 + \frac{1}{6} a_6 \eta^6 + \cdots + \frac{1}{2} b_2 \mu^2 + \frac{1}{4} b_4 \mu^4 + \cdots + F_c(\eta, \mu) \]

(106)

\[ F_c(\eta, \mu) = \beta \eta \mu + \gamma \eta^2 \mu + \alpha \eta \mu^2 + \cdots \]

(107)

where \( \eta \) and \( \mu \) designate the order parameter and the strain, respectively. The coupling terms \( F_c \) describes the interaction between strain and order parameter. \( \beta \) is the linear piezoelectric coefficient and \( \gamma \) is the quadratic electrostrictive coefficient. The elasticity \( C=C^\infty-\Delta C \) is given by

\[ C = \rho V^2 = C^\infty - \chi \left( \frac{\partial^2 F_c}{\partial \mu \partial \eta} \right)^2; \quad \chi = \left( \frac{\partial^2 F}{\partial \eta^2} \right)^{-1} \eta = \eta_s \]

(108)

where \( \rho \) is the sample density and \( V \) is the sound velocity. \( C^\infty \) is obtained in the high frequency limit. From Eqs. (106) and (108), we get

\[ C = C^\infty - \beta^2 \chi \quad \text{for linear coupling} \]

(109)

\[ C = C^\infty - \gamma^2 \chi \eta_s^2 \quad \text{for quadratic coupling} \]

(110)

where \( \eta_s \) is determined by \( \left( \partial F / \partial \eta \right)_{\eta = \eta_s} = 0 \). From Eqs. (106)-(1108), we can get the following results for the low temperature ordered phase, i.e. \( \eta_s \neq 0 \)
\[ \chi = \left( 2a_4 \eta_s^2 + 4a_6 \eta_s^4 \right)^{-1} \]  

\[ \eta_s^2 = \frac{-a_4 \pm \sqrt{a_4^2 - 4a_2a_6}}{2a_6} \]

\[ \Rightarrow \quad C = C^\infty - \frac{\beta^2a_6}{a_4^2 - 4a_2a_6 \pm 3a_4 \sqrt{a_4^2 - 4a_2a_6}} \quad \text{linear coupling} \]

\[ C = C^\infty \pm \frac{\gamma^2}{2\sqrt{a_4^2 - 4a_2a_6}} \quad \text{quadratic coupling} \]

Therefore, for a first-order transition, the elasticity \( C = C^\infty - \Delta C \) could be step-like up (positive contribution) or down (negative contribution) across the phase transition region for quadratic coupling. However, for a second-order transition, the elasticity always exhibits a downward step around \( T_c \) as temperature decreases for quadratic coupling.

Figure 29. (a) Elasticity vs. temperature for (i) \( \beta \eta \mu \) linear coupling, (ii) \( \gamma \eta^2 \mu \) quadratic coupling, solid line for either second-order or first-order and dotted line only for first-order and (iii) \( \alpha \eta^2 \mu^2 \) coupling. (b) The dynamic effects for a second-order \( \eta^2 \mu \)-type quadratic coupling in typical pure ferroelectrics. \( v \) is phonon frequency shift and \( \delta \) is phonon damping.
Fig. 29a gives the general behaviors of the elastic moduli for the three dominating lowest order coupling terms for both first- and second-order transitions. Fig. 29b gives the dynamic effects for a second-order $\eta^2\mu$-type quadratic coupling in typical pure ferroelectrics.\textsuperscript{48}

**Debye Anharmonic Approximation**

In order to estimate the coupling effect in proton glass crystals, we will calculate the bare (uncoupled) phonon frequency, $\omega_a$, by fitting the high temperature values (in the uncoupled region) of the measured frequency shift. The bare phonon frequency usually is defined for the phonon frequency in the absence of a phase transition. The temperature dependence of $\omega_a$ can be described by the Debye anharmonic approximation as follows:\textsuperscript{10}

\[
\omega_a(T, x) = \omega_a(0, x) \left[ 1 - A(x) \Theta(x) F\left(\frac{\Theta(x)}{T}\right) \right]
\]  

(113)

where $\Theta(x)$ is the Debye temperature, $x$ is the ammonium concentration, $A(x)$ represents the amount of anharmonicity and $F$ is the Debye function for internal energy,\textsuperscript{49}

\[
F\left(\frac{\Theta}{T}\right) = \frac{3}{\Theta^4} \int_0^\Theta \frac{u^3}{e^u - 1} \, du
\]

(114)

as tabulated, for example, by Abramowitz and Stegun.\textsuperscript{50}
Dynamic Effects

Two different damping mechanisms are usually responsible for acoustic anomalies, namely the Landau-Khalatnikov mechanism (relaxation portion) and order parameter fluctuations. A strong Landau-Khalatnikov mechanism contribution which is associated with a sharp damping maximum usually occurs for linear $\eta\mu$-type coupling (piezoelectric) material such as KDP family crystals. Here $\eta$ is the order parameter and $\mu$ is the strain. On the other hand, the Landau-Khalatnikov mechanism also represents a relaxation characteristic of the order parameter to a strain.

The order parameter fluctuation damping which usually is associated with a broad maximum is a characteristic of a quadratic $\eta^2\mu$-type coupling (electrostriction), squared in order parameter and linear in strain. For theoretical description, an approach which is based on the classical fluctuation-dissipation theorem can be used:

$$\text{Im} c_{mn}(\omega) = \frac{\omega V}{2kT} \int_{-\infty}^{+\infty} e^{i\omega t} \langle \delta \sigma_m(t) \delta \sigma_n^*(0) \rangle dt$$ (115)

It connects the dissipative (imaginary) part of the elastic modulus to the Fourier transform of a time-correlation function of internal stress fluctuation $\delta \sigma_m$ in a volume $V$. After several steps of calculation, the following result can be obtained:

$$\text{Im} c_{mn}(\omega) = \frac{\omega V}{2kT} \sum_{i,j,k,l} \gamma_{ijm} \gamma_{kln} \{4 \langle Q_i \rangle \langle Q_k \rangle \int_{-\infty}^{+\infty} e^{i\omega t} \langle \delta Q_j(t) \delta Q_l^*(0) \rangle dt - \int_{-\infty}^{+\infty} e^{i\omega t} \langle \delta Q_j(t) \delta Q_k^*(0) \delta Q_l^*(0) \rangle dt \}$$ (116)

The sum of a Landau-Khalatnikov contribution in the first term and a fourth-order correlation function describing the fluctuations is obtained.
CHAPTER 4

RESULTS AND DISCUSSION

\[ \text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{AsO}_4 \ (x=0, 0.10, 0.28) \]

Brillouin Back-Scattering Along LA[100] Phonon Direction\(^{51}\)

Actual LA[100] phonon spectra of the anti-Stokes Brillouin component are shown in Figs. 30-32 for \(x=0\), 0.10 and 0.28, respectively. The data shown here are for several temperatures near the maximum value of half-width. The solid lines are fits of the Lorentz profile, from which the half-width \(\delta v_{\text{obs}}\) and frequency shift \(\Delta v\) can be obtained. The frequency shift for each compound indicates a positive coupling contribution with decreasing temperature. Comparing the half-width for different \(x\) values, we notice that the average damping value increases as ammonium concentration increases. This dependence may result from the stronger local structural FE/AFE competition that can induce larger fluctuations, especially for intermediate \(x\) values such as \(0.3 \leq x \leq 0.7\) in RADP.\(^3\)

The temperature dependences of the Brillouin shift and half-width for \(x=0\), 0.10 and 0.28 are shown in Figs. 33-35, respectively. The solid lines in frequency shift are the calculations of Eq. (113) with parameters of Table 1. These parameters \(A\), \(\omega_0(T=0)\) and \(\Theta\) of Table 1 are from the fits of Eq. (113) to the high temperature (\(\geq 270\) K) measured values of the Brillouin shift. Here we assume that temperatures above 270 K are far above the coupled region since all phase transitions occur below 200 K. One finds that \(\Theta\)
and $\omega_a(0,x)$ tend to increase from the DRDA side to the DADA side, as expected in view of the higher frequency of the modes on the DADA-rich side. Also, the anharmonic factor $A$ increases with ND$_4$ content.

<table>
<thead>
<tr>
<th></th>
<th>$\omega_a(T=0)$</th>
<th>$A$ (K$^{-1}$)</th>
<th>$\Theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(GHz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DRDA</td>
<td>26.08</td>
<td>$2.70\times10^{-4}$</td>
<td>400</td>
</tr>
<tr>
<td>DRADA-0.10</td>
<td>26.37</td>
<td>$2.76\times10^{-4}$</td>
<td>480</td>
</tr>
<tr>
<td>DRADA-0.28</td>
<td>27.20</td>
<td>$2.84\times10^{-4}$</td>
<td>520</td>
</tr>
</tbody>
</table>

TABLE 1. Parameters from the fits of Eq. (113) to measured values of frequency shift at high temperature.

Fig. 33 for $x=0$ (pure DRDA) shows a sharp damping peak at 164.8 K associated with an upward step in frequency which is expected, since the KH$_2$PO$_4$ (KDP) family has linear $\eta\mu$-type piezoelectric coupling. Here $\eta$ is the order parameter and $\mu$ is the strain. Such a sharp damping maximum for longitudinal acoustic phonons can be connected with the Landau-Khalatnikov relaxation-type mechanism. The dashed line in half-width of Fig. 33 is a qualitative estimate for this relaxation portion. We also try to estimate the pure lattice-anharmonic contribution by solid circles, which is the typical anharmonic half-width observed in Brillouin scattering for dielectrics. For linear coupling with the assumption of a single relaxation time, the sound velocity and the attenuation $\alpha$ in the FE phase can be given by

$$V^2 = V_o^2 - \frac{V_o^2 - V_0^2}{1 + \frac{\omega^2}{\omega_0^2}}$$

(117)
\[ \alpha = \frac{\omega^2 \tau_0 t^{-1}}{2 V^3} \frac{V_\infty^2 - V_0^2}{1 + \omega^2 \tau_0 t^{-2}} \]  \hfill (118)

where \( t \) is the reduced temperature \( (T_c - T)/T_c \), and \( \tau_o \) is the elementary individual-dipole relaxation time in the expression \( \tau = \tau_o t^{-1} \) for the relaxation time \( \tau \). The velocities \( V_\infty \) and \( V_0 \) designate the high- and low-frequency limit velocities, respectively. From Eqs. (117) and (118) we can obtain the relation

\[ \omega \tau_o = \frac{T_c - T_m}{T_c}. \]  \hfill (119)

By this relation we can calculate the elementary relaxation time \( \tau_o \). Here, \( T_m = 164.8 \text{ K} \) is the temperature at which the half-width is maximum and the FE transition temperature \( T_c \) is defined as the point at which the frequency shift curve is steepest. For the LA[100] phonons of DRDA, we obtain the following result:

\[ T_c - T_m \sim 0.1 \text{ K} \]
\[ \tau_o \sim 2.3 \times 10^{-14} \text{ s} \]
\[ \tau \sim 3.8 \times 10^{-12} / (T_c - T) \text{ s} \]

The elementary dipole relaxation time \( \tau_o \) obtained from the LA[100] phonons of DRDA is short compared to that of other order-disorder ferroelectrics. For instance, \( \tau_o \) is \( 1.2 \times 10^{-13} \text{ sec} \) for potassium dihydrogen phosphate (KDP) and \( 1.3 \times 10^{-12} \text{ sec} \) for deuterated potassium dihydrogen phosphate (DKDP).\(^{41}\)
Instead of a sharp peak, the damping data of Fig. 34 for $x=0.10$ exhibit a smooth growth from $-200$ down to $-130$ K, associated with a slowly rising anomaly in frequency shift above the Debye curve of Eq. (113). Such an increasing of damping which begins far above $T_m=146$ K must be associated with the order parameter fluctuations. A qualitative estimate of this fluctuation contribution is given by the solid curve in Fig. 34 with maximum near 146 K. Beside this broad damping background, one can note that there is an additional peak appearing near 130 K which can be connected with the Landau-Khalatnikov maximum.

What are the origins of these two damping maxima in DRADA-0.10? The ND$_4^+$ deuteron NMR spectra of DRADA-0.10 showed a gradual disappearance of the doublet near 131 K where the single broad linewidth grows to its full size, from which it was concluded that below 131 K the FE phase portion is greater than PE in the crystal and becomes the dominant ordering.$^7$ This result is consistent with the presence of PE/FE phase coexistence as evidenced by dielectric results which show that a gradual ferroelectric transition begins at $T_m=146$ K and is mostly completed at $-120$ K. Furthermore, the real part of dielectric permittivity $\epsilon_{11}(T)$ shows deviation from the Curie-Weiss law below 160 K. This high-temperature dielectric anomaly below 160 K can be associated with the onset of short-range order due to partial freezing-in of the ND$_4$ reorientations and implies a growth of local structural competition (between FE and AFE ordering). On the whole, one can expect that such FE/AFE ordering competition, which can suppress a long-range-order ferroelectric transition and generate the order parameter fluctuations, is responsible for both FE/PE phase coexistence and development of the broad damping peak centered at $-146$ K. Also, the rapid growth of FE ordering near 130 K is the origin of the Landau-Khalatnikov-like maximum in DRADA-0.10.

A even stronger damping temperature dependence which shows a growth from $-300$ down to $-120$ K (see Fig. 35) is observed for $x=0.28$, associated with a smoothly
rising frequency shift. This strong broad damping reveals that fluctuations are the dominant dynamic mechanism. As one knows, the dynamic fluctuation contribution for longitudinal acoustic phonons is a characteristic of a $\eta^2\mu$-type coupling, squared in order parameter and linear in strain.\textsuperscript{47} However, it is difficult to see a Landau-Khalatnikov maximum (associated with the Edwards-Anderson order parameter in this case) above such a strong fluctuation background. Taking into account earlier dielectric permittivity $\varepsilon_{11}(T)$ results which showed a deviation from the Curie-Weiss law below 140 K, we conclude that neither FE nor AFE ordering but rather the local structural competition mechanism (between FE and AFE orderings) is the origin of this strong broad damping anomaly centered near 120 K. Since the fluctuations usually indicate a random force resulting from the substitutional disorder, the difference of damping behavior between DRADA-0.28 and DRADA-0.10 also implies that this random force is stronger in the $x=0.28$ crystal.

A main feature of the acoustic phonon spectra in DRADA ($x=0, 0.10,$ and $0.28$) for LA[100] phonons is that the frequency shift shows a positive (hardening) instead of a negative coupling contribution (softening) at the phase transition. The sign of the coupling contribution may be related to the temperature responses of lattice parameters $a(T)$ and $c(T)$. A smaller lattice constant is usually associated with a stiffer interatomic force constant and implies a contraction $\Delta a$ which leads to the LA[100] phonon hardening. However, the measurements we performed on pure DRDA for LA[001] (c-axis) phonons, not reported here, revealed a negative contribution at the FE transition temperature. This may be related to the expansion $\Delta c$ observed in the related crystal KH$_2$PO$_4$ just below $T_c$.\textsuperscript{17}
Figure 30. Anti-Stokes components of the LA[100] Brillouin frequency shift for temperatures around the maximum value of half-width for DRDA. The open circles are the measured data and solid lines are the Lorentz fits.
Figure 31. Anti-Stokes components of the LA[100] Brillouin frequency shift for temperatures around the maximum value of half-width for DRADA-0.10. The open circles are the measured data and solid lines are the Lorentz fits.
Figure 32. Anti-Stokes components of the LA[100] Brillouin frequency shift for temperatures around the maximum value of half-width for DRADA-0.28. The open circles are the measured data and solid lines are the Lorentz fits.
Figure 33. Frequency shift and half-width vs. temperature of the LA[100] phonons for DRDA. The solid line for frequency shift is the Debye anharmonic calculation with parameters from Table 1. The dashed line and solid circles for half-width are the qualitative estimates for the Landau-Khalatnikov and pure lattice anharmonic contributions, respectively. The error bar indicates the error range for the half-width experimental points.
Figure 34. Frequency shift and half-width vs. T of the LA[100] phonons for DRADA-0.10. The solid line for frequency shift is the Debye anharmonic calculation with parameters from Table 1. The solid line and solid circles for half-width are the estimates of fluctuations and pure lattice anharmonic contributions, respectively. The dashed line is a guide to the eye. The error bar indicates the error range for the half-width experimental points.
Figure 35. Frequency shift and half-width vs. temperature of the LA\[100\] phonons for DRADA-0.28. The solid line for frequency shift is the Debye anharmonic calculation with parameters from Table 1. The dashed line is a guide to the eye. The error bar indicates the error range for the half-width experimental points.
Na$_{1/2}$Bi$_{1/2}$TiO$_3$ (NBT)

Frequency Dependent Dielectric Results$^{16}$

Fig. 36 reveals a new large anomaly at higher temperature region. In comparison with this anomaly, the "old" and well-known anomalies in the temperature regions indicated by arrows A and B in Fig. 36 are very small. The new anomaly in the C region was not seen previously in NBT, but similar anomalies have been observed in other perovskite crystals and ceramics. We will consider separately each of these three regions.

First, the anomaly in region A was found by Smolensky et al.$^{12}$ At frequencies below 200 Hz we could hardly see this anomaly against the large background of dielectric permittivity. It appears as a pronounced shoulder in the region $0.2<f<1$ kHz (Fig. 37 inset). The two curves labeled 2 at 500 kHz were also measured on a NBT single crystal by Pronin et al.$^{20,21,25}$ These two sets of data agree well in the peak value and in the specific difference in behavior on the left side of the $\varepsilon'$ peak in heating and cooling runs. Curve 3 (at 160 kHz) reproduces a recent result for an NBT single crystal,$^{16,28}$ which is quite different from our data. Curve 4 in Fig. 37 represents very different behavior of NBT ($f=200$ kHz). We attribute these differences to sample quality and consider our NBT sample to be of good quality. Measurements in the frequency range 0.1–100 kHz show no evident dispersion for the peak position at $T\sim640$ K and are in agreement with most other results.$^{16}$

Secondly, in region B a dielectric permittivity anomaly was found with frequency dispersion.$^{16,12}$ Remanent polarization disappears completely above 550 K as shown in Fig. 38, so this dispersion can be attributed to domain wall displacement. Our measurements agree perfectly with those previous measurements and indirectly confirm the onset of ferroelectric behavior below 550 K.$^{16}$
In region C, a huge frequency dependent peak for the real part \( \varepsilon' \) of the dielectric permittivity was found in the higher temperature region (Figs. 36, 39 and 40a). A corresponding \( \varepsilon'' \) contribution also shows a round shoulder between 650 and \(-800\) K (Fig. 40b). This hump is only seen clearly at frequencies below 1 kHz. The growth in \( \varepsilon'' \) was drastic enough to arouse suspicion about the correctness of the \( \varepsilon' \) measurements. To check their correctness, we compared the dielectric measurements in NBT and in a sample of the well-known relaxor ferroelectric PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\) (PMN) under similar conditions. As shown in Fig. 40, at high temperatures above \(-800\) K at nearly the same level of \( \varepsilon'' \) we did not find a pronounced peak in \( \varepsilon' \) for PMN (Fig. 40a). We conclude that the huge peak of \( \varepsilon' \) in NBT is not an artifact.

In the following, three possible models will be presented for these large low-frequency permittivity and loss anomalies.

**Superparaelectric Cluster Model.**\(^\text{16}\) In this model, we assume that the electrical response has two parts, i.e. the frequency-independent (probably ionic) conductivity response of free charges and the frequency-dependent polarization response of bound charges. Based on these assumptions, the permittivities can be written as

$$
\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon_p' - i\left(\varepsilon_p'' + \varepsilon_c''\right);
\varepsilon_c'' = \frac{\sigma_c}{2\pi f\varepsilon_0}
$$

(120)

$$
\sigma_c = \sigma_0 e^{-W/T}
$$

(121)

Here the p and c subscripts refer to polarization and conductivity contributions, \( \varepsilon_0 \) is the MKS constant, f is the measurement frequency, and we assume a thermally activated conductivity as in Eq. (121). We obtained \( \sigma_0 = 2.12 \times 10^7 \) S/m and \( W = 18860 \) K by fitting the portion of the lowest-frequency (20 Hz) data in Fig. 41a which coincides with higher-
frequency data and thus represents the frequency-independent contribution from the conductivity. The remainder $\varepsilon_p''$ curves for various frequencies left after subtracting the conductivity contribution appear in Fig. 41b.

Figs. 39 and 41b can be viewed as the respective real and imaginary parts of the polarization contribution to the permittivity. Cole-Cole plots based on these data appear in Fig. 42 for temperatures of 600, 650, 700, and 750 K. All these plots have the typical semicircular shape, with circle center somewhat below the real axis. Extrapolation of these circular arcs clockwise to the real axis provides estimated dc permittivity at 650 and 700 K, at which temperatures the polarization could not develop the full dc response at the lowest frequency of 20 Hz.

Fig. 43 compares permittivity peak location and magnitude for heating and cooling runs. The $\varepsilon'$ peaks occur at the same temperature upon heating and cooling at 100 Hz and 10 kHz. For 1 kHz the heating run peak is at 813 K while the cooling run peak is at 800 K. We attribute this difference to a slight thermal hysteresis in the cubic/tetragonal ferroelastic phase transition found at 820 K. This transition is the probable reason for the drop between 800 and 830 K of the difference $[J_h - J_h'/(J_h + J_c)]$ in peak $\varepsilon'$ magnitudes upon heating ($J_h$) and cooling ($J_c$) shown for several frequencies in the upper right inset of Fig. 43.16

The dielectric behavior must be considered in conjunction with the NBT crystal structure, particularly as there appears to be a first-order ferroelastic cubic to tetragonal transition at $T_{c1} = 820$ K. The order parameter (proportional to the square root of the tetragonal M-superlattice reflection intensity) is nonzero above $T_{c1}$, abruptly more than doubles at $T_{c1}$, and gradually doubles again as temperature drops to 640 K. Below this temperature there is a rapid drop of the M reflection and rapid rise of the R (trigonal) superlattice reflection, both accompanied by about 50 K thermal hysteresis and by coexistence of the M and R reflections.
The large dielectric peak at high temperature can be explained by assuming that these data lie in the crossover region from independent dipole moments to superparaelectric moments of N dipoles. We will show that a superparaelectric model reproduces the general shape of this dc envelope. The higher-temperature part of the crossover region, which we barely reached in our measurements, should obey a Curie-Weiss law \( \varepsilon' = C/(T - T_0) \). Most of our observed \( \varepsilon' \) envelope lies near \( T_0 \) where this \( \varepsilon' \) vs. \( T \) envelope becomes nearly a straight line.

With the help of Eqs. (40) and (41), we can calculate the dielectric permittivity in the crossover region. Fig. 39 shows the calculations for \( N = 54 \) and \( N = 125 \), with dipole moment \( p \) adjusted so that at 800 K these curves cross the "dc" \( \varepsilon' \) curve (the curve along which low-frequency \( \varepsilon' \) curves coincide). The fit is better for \( N = 125 \), but a larger \( N \) would fit still better.

To understand better where our data fit on the overall superparaelectric model permittivity curve, the logarithmic plot of permittivity against temperature in Fig. 44 is helpful. The calculated superparaelectric response for \( N = 125 \) dipoles in a cluster appears in Fig. 44. The -1 slope regions at high temperature corresponding to independent dipoles and at low temperature corresponding to superparaelectric clusters are clearly evident. Our data, superimposed on this curve in the inset, appear only in the crossover region. The central portion of our data rises more steeply than the calculated curve but fits reasonably well, whereas there are large deviations of our data at the two ends. We now discuss how all these deviations are related to the structure, in particular to the tetragonal order parameter measured by Vakhrushev et al. obtained from the neutron M-reflection intensity.\(^{16,26}\)

To model the effects of the transitions from cubic to tetragonal and tetragonal to trigonal phases, we assume that the number of clusters varies as the tetragonal order parameter. The tetragonal order parameter is assumed proportional to the square root of
the M-reflection intensity. Multiplying the superparaelectric cluster model permittivity of Eq. (41) by this temperature-dependent order parameter yields the calculated dc permittivity shown in the inset of Fig. 44.

Quite good agreement is seen in the inset of Fig. 44 between the calculated and "measured" dc permittivity. "Measured" is put in quotes because below 750 K the dc permittivity is found by a three-step process: First the conductivity contribution is subtracted from $\varepsilon''$ to find the polarization contribution $\varepsilon_p''$, then Cole-Cole plots of $\varepsilon_p''$ vs. $\varepsilon'$ are made, and finally the circular arcs of these plots are extrapolated clockwise until they cross the $\varepsilon'$ axis at the assumed value of dc $\varepsilon'$. Confidence in this process is enhanced by the good fit of the data to circular arcs. Near 600 K the arcs become too short for accurate extrapolation. From 750 to 885 K the "measured" dc permittivity is taken as the "envelope" line in Fig. 39 along which low-frequency $\varepsilon'$ curves coincide.

The parameters predicted by the superparaelectric model can be compared with those for BaTiO$_3$-family crystals to see if they are reasonable. Fitting the model with $N=125$ to the dielectric data at 800 K we have, from the T vs. $\varepsilon'$ data, $\varepsilon'=2.55\times10^4$, which corresponds to a dipole moment $p$ of $1.12\times10^{-28}$ (C m) per 0.4x0.4x0.4 (run)$^3$ unit cell, giving a Curie-Weiss constant of $C=1.6\times10^6$ K. The closest comparison can be made with PbTiO$_3$, which like BaTiO$_3$ has a ferroelectric transition from a cubic to a tetragonal phase. For BaTiO$_3$ this transition is only at 393 K, whereas in PbTiO$_3$ it is at 763 K which is much nearer the 820 K value reported by Vakhrushev et al. for NBT. PbTiO$_3$ has $P_s=0.75$ (C m$^2$) giving $p=4.47\times10^{-29}$ (C m) and has $C=4.1\times10^5$ K. These values of $p$ and $C$ are about 3 times lower than for the above fit of the data to the superparaelectric model with $N=125$. Taking another approach, we can fit the superparaelectric model with the $p$ value from PbTiO$_3$ to the dc $\varepsilon'$ value of $1.56\times10^5$ at 640 K, obtained by extrapolating the Cole-Cole curve. At this temperature the permittivity is not increasing so fast with decreasing temperature, so it is reasonable to
assume that the permittivity is close to obey the low-temperature form, \( \varepsilon' = N p^2/(\varepsilon_0 V k T) \).

We then get \( N=391=(7.31)^3 \) which correspond to a 2.92 nm cube for a superparaelectric cluster, whereas \( N=125=5^3 \) correspond to a 2.00 nm cube. We conclude that we can obtain a fairly good fit with reasonable parameters if the superparaelectric moment correlation length is 2 to 3 nm.

The dynamic behavior of the large low-frequency peak is most strikingly illustrated by Fig. 45. Here we plot two experimental parameters against inverse temperature. One is \( \tau_{pk} \), the inverse of the measurement angular frequency for which the dc \( \varepsilon' \) peak occurs at the given temperature. These peaks are quite sharp, so this \( \tau_{pk} \) is a good approximation to the dielectric relaxation time. The other parameter plotted is the "RC" relaxation time for the crystal, which as for any leaky dielectric is defined as

\[
\tau_{RC} = RC = \varepsilon_0 \varepsilon_{dc} \frac{A}{d} \cdot R = \varepsilon_0 \varepsilon_{dc} \frac{A}{d} \cdot \frac{d}{A} \rho = \rho \varepsilon_0 \varepsilon_{dc}
\]

(122)

where \( \rho \) is the inverse of the conductivity \( \sigma \) displayed in Fig. 6a and determined as described in the associated text.

We see there is excellent agreement between these two \( \tau \)'s over four decades of magnitude, and we emphasize that there are no adjustable parameters or model-dependent assumptions entering into these \( \tau \)'s. We interpret this close agreement as showing that the mobile charge redistribution time \( \tau_{RC} \) required for rearrangement of carriers around a given superparaelectric cluster is the relaxation time \( \tau_{pk} \) required for the cluster to reorient in the applied electric field. In other words, the cluster is "frozen" against polarization reversal until this charge redistribution can occur. The charge redistribution in turn is influenced by the cluster, as evidenced by the appearance of \( \varepsilon'_{dc} \) in Eq. (122) for the charge redistribution time \( \tau_{RC} \). However, we have developed no quantitative model for this dynamic process.
The superparaelectric clusters undoubtedly have internal barriers to polarization reversal, as proposed by Cross. He estimated barriers of order 3000 K for larger clusters of volume $(20 \text{ nm})^3$. This is an order of magnitude smaller than the energies corresponding to the slopes in Fig. 45, so the internal barriers do not appear to govern the dynamics in the NBT clusters.

The frequency dependence of $\varepsilon'(f,T)$ is illustrated for five temperatures in Fig. 46. The crystal undergoes a relaxation process in the high temperature region for frequencies below 50 kHz. The solid curves are fits to the Cole-Cole equation. The fits of Eq. (34) to the real part of the permittivity with $\varepsilon_\infty = 1280$ are presented in Fig. 46. The parameters from fits at five temperatures are shown in Table 2 which indicates a millisecond relaxation time region between 700 and 800 K, which agrees with the data $(\tau_{pk}$ and $\tau_{rc})$ as shown in Fig. 45.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>650 K</th>
<th>700 K</th>
<th>750 K</th>
<th>800 K</th>
<th>850 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f^{-1}_{0}(10^{-3} \text{ s})$</td>
<td>384.7</td>
<td>33.99</td>
<td>8.65</td>
<td>1.12</td>
<td>0.30</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.104</td>
<td>0.122</td>
<td>0.158</td>
<td>0.103</td>
<td>0.195</td>
</tr>
<tr>
<td>$\varepsilon_{dc}$</td>
<td>576000</td>
<td>117300</td>
<td>74830</td>
<td>26290</td>
<td>10930</td>
</tr>
</tbody>
</table>

Table 2. The parameters from fits of Eq. (34) to the real part of permittivity ($\varepsilon'$) at five temperatures.

The parameter $\varepsilon_{dc}(T)$ also shows good agreement with the data from extrapolation of Cole-Cole plots (Fig. 42), except at T=650 K. The relaxation time distribution parameter shows a drop (~35%) around 800 K as temperature increases, which may correspond to the paraelectric to ferroelastic phase transition.
Figure 36. The temperature dependence of the real part of the dielectric relative permittivity in NBT at two frequencies upon heating. The A, B, and C arrows indicate three anomalous regions.
Figure 37. Comparison of the dielectric anomaly in region A. The curves 3 and 4 show only heating and cooling runs respectively. The inset shows that this anomaly is hidden by an increasing background at lower frequencies.
Figure 38. The temperature dependences of remanent polarization, $P_r$, and dielectric permittivity ($\varepsilon'$) upon heating in region B where a ferroelectric state exists.
Figure 39. The real part of dielectric permittivity vs. temperature in region C at various frequencies upon heating. The solid line is the calculation of Eq. (41) with N=54 and dashed line is the calculation of Eq. (41) with N=125.
Figure 40. (a) The temperature dependence of the real part ($\varepsilon'$) of the dielectric permittivity in NBT and PMN at 100 Hz upon cooling. (b) The temperature dependence of the imaginary part ($\varepsilon''$) of the dielectric permittivity in NBT and PMN at 100 Hz upon cooling.
Figure 41. (a) $\sigma(=2\pi f\varepsilon_0\varepsilon^\prime)$ vs. temperature at five different frequencies. The solid line is the fit of Eq. (91) for $\sigma_c$ with parameters $\sigma_0=2.12\times10^7$ (Ωm)$^{-1}$ and $\omega=18860$ K. (b) The imaginary part of dielectric permittivity, $\varepsilon_p''=\Delta\sigma/(2\pi f\varepsilon_0)$, vs. temperature at five different frequencies. Here $\Delta\sigma=\sigma-\sigma_c$. 
Figure 42. Complex representation of the NBT dielectric permittivity at four different temperatures. The numbers on the points indicate the frequencies in Hz. The dashed lines are regression lines.
Figure 43. The strong thermal hysteresis behavior in region C at four different frequencies (10 kHz and 100 kHz in the left inset). Right inset: the difference of heating and cooling peak values shows a drop in the region of the ferroelastic phase transition at $T_{c1}-820$ K. The numbers on the points indicate the frequencies in kHz. The dashed line is a regression line.
Figure 44. The temperature behavior of dc permittivity, $\varepsilon'$, calculated from Eq. (41) with $N=125$. Inset: solid hexagons are from Eq. (41) with $N=125$, squares are the "measured" dc permittivity, solid circles are proportional to the tetragonal order parameter from neutron scattering, and triangles are the calculated dc permittivity as defined by the dc permittivity from Eq. (41) multiplied by the tetragonal order parameter. All curves are adjusted to cross at 800 K.
Figure 45. Relaxation times, $\tau_{pk}$ and $\tau_{rc}$, vs. $1000/T$. The solid and dashed lines are fits of equation $\tau=\tau_0 e^{W/T}$ with $\tau_0=5.57\times10^{-18}$ s, $W=25090$ K for $\tau_{pk}$, and $\tau_0=3.54\times10^{-21}$ s, $W=30720$ K for $\tau_{rc}$.
Figure 46. The real part of dielectric relative permittivity $10^{-4} \varepsilon'$ vs. frequency (Hz) at five temperatures. The solid curves are fits of Eq. (34) with parameters of Table 2.
Surface-Modified Bulk Effect. A series of two parallel RC circuits which represent two surfaces and bulk (sample) can be used to describe a high-impedance surface layer problem. Fig. 47 is the circuit for this model.

![Diagram](image)

**Figure 47.** (a) An actual connection of sample and electrodes. (b) A series of two parallel RC circuits. $Z_1 = \frac{1}{R_1} + i\omega C_1$ and $Z_2 = \frac{1}{R_2} + i\omega C_2$

Following are equations which were used for this model.

$$Z = Z_1 + Z_2 = \frac{R_1}{1 + i\omega C_1 R_1} + \frac{R_2}{1 + i\omega C_2 R_2} = \frac{n - id}{D} = Z' - Z''$$ (123)

$$D = 1 + \omega^2 (C_1 R_1^2 + C_2 R_2^2) + \omega^4 C_1^2 C_2^2 R_1^2 R_2^2$$

$$n = R_1 + R_2 + \omega^2 R_1 R_2 (C_1^2 R_1 + C_2^2 R_2)$$

$$d = \omega [C_1 R_1^2 + C_2 R_2^2 + \omega^2 (C_1 + C_2) C_1 C_2 R_1^2 R_2^2]$$

$$R_i = \frac{\rho_i d_i}{A} = \frac{d_i}{A \sigma_i} = \frac{d_i}{A \sigma_i \varepsilon_i} e^{-W_i/T}$$

$$C_i = \frac{\varepsilon_0 \varepsilon_i A}{d_i} \text{ or } \varepsilon_i = \frac{C_i}{C_0} \quad (i=1,2)$$
where $d_1$ and $d_2$ are the thicknesses for sample and surface layer, respectively. We assume that both $R$'s are thermaly activated and that the $C$'s are independent of temperature. $W_i$ is the activation energy. Here we chose $\varepsilon_i = 100$ for both bulk and surface layer. For some parameters, this model reproduces a shoulder in $\varepsilon''$ similar to that seen in Fig. 41a as shown in Fig. 48. However, Fig. 48 shows only a plateau in $\varepsilon'$ and not the experimentally observed peak. The plateau level is independent of frequency whereas experimentally the peak amplitude increases rapidly with falling temperature. The failure to reproduce this characteristic peak behavior seems to rule out the possibility of the blocking surface interpretation.

**Extrinsic Bulk Conductivity Model.** In this model, a spatial power law for the distribution of barriers caused by crystal imperfection was assumed as

$$U(r) = B + B_0 \left( \frac{r}{R + r} \right)^\gamma$$

The large conductivity activation energy is associated with the high barrier for the carrier (ion or electron) to hop from one site to the next. The hopping conductivity obeys the equation $\sigma(T) = n v \exp(-B / kT) e^{2} a_{0}^{2} / kT$. $a_{0} \sim 4\text{Å}$ is one lattice constant and $n$ is the carrier concentration. More detail of this model and analysis can be found in Ref. 52.
Figure 48. Plots of Eq. (124) with parameters: \( d_{\text{bulk}} = 1 \text{ mm}, \) \( d_{\text{sur}} = 10^{-4} \text{ mm}, \) \( W_{\text{bulk}} = 20000 \text{ K}, \) \( W_{\text{sur}} = 30000 \text{ K}, \) \( \varepsilon'_{\text{bulk}} = \varepsilon'_{\text{sur}} = 100, \) and \( \sigma_0 = 10^7 \text{ (ohm-m)}^{-1}. \)
Fig. 49 illustrates qualitatively the changes in the Brillouin spectra obtained at different temperatures. The free spectral ranges of the interferometer are 30.20 GHz for all spectra at T>235 K and 34.60 GHz for the spectrum at the bottom of Fig. 49 at T<78 K so that the Brillouin doublet in NBT appears in the second order with respect to the Rayleigh line. As seen from the spectra, the position and especially the half-width of the Brillouin components are strongly temperature dependent. Fig. 49 also shows that the background in the Brillouin spectra changes drastically and has the largest value at ~650 K which exceeds many times the peak intensity of the Brillouin doublet. Qualitatively, the same behavior was found from the central peak intensity as observed in Raman scattering. Strong background due to existence of a central peak in light scattered from NBT is the main origin of the spread in data point (Brillouin shift and half-width) in the vicinity of the anomalies.

Both the Brillouin shift and Brillouin half-width exhibit some anomalies in the vicinity of the first phase transition from a cubic to tetragonal phase at T_{c1}~830 K. An increase of damping begins far above T_{c1} in the cubic paraphase (see Fig. 50) and can be connected with the contribution of order parameter fluctuations. The dashed curve in Fig. 50 is a qualitative estimate of fluctuation contribution. Beside the broad damping background, there is an additional peak in the tetragonal phase close to T_{c1}. This latter peak can be attributed to the usual Landau-Khalatnikov mechanism but now it is shifted into the tetragonal phase due to frequency dispersion. Such a combination which includes both the Landau-Khalatnikov mechanism and order parameter fluctuations for longitudinal acoustic phonons implies that the $\eta^2 u$-type quadratic coupling, squared in order parameter and linear in strain, is the dominant mechanism in NBT.

Fig. 51 reveals a broad velocity dip, a broad damping peak and a strong background intensity. According to neutron scattering data, a first-order phase transition
occurs at $T_{c1} \sim 820$ K from a cubic paraphase to a tetragonal ferroelastic phase. The tetragonal distortion corresponds to an irreducible representation at the M point of the cubic phase Brillouin zone. The appearance, development and disappearance of the M-point superlattice reflections observed in neutron diffraction is illustrated in Fig. 52.

The next transition at $T_{c2} \sim 593$ K is to a trigonal phase. The trigonal structure is not a subgroup of the tetragonal structure, but its distortion corresponds to an irreducible representation at the R point of the cubic phase Brillouin zone. The tetragonal and trigonal phases coexist over a temperature range, and the point of maximum coexistence in the heating run is taken as $T_{c2}$ in the phase diagram in Fig. 52. However, there is a sharp cusp at 640 K in the M-point neutron reflection intensity which signals the high-temperature onset of this transition. All the Brillouin scattering measurements were carried out upon heating.

The neutron scattering data indicate that the phase transitions at $T_{c1}$ and $T_{c2}$ are initiated by some irreducible representations at the M and R points of the cubic phase Brillouin zone, respectively. It is well-known that in both these cases the anomalies for longitudinal acoustic phonons can be described by the $Q\eta^2u$-type coupling. However, neither the step-like anomaly for sound velocity nor the Landau-Khalatnikov maximum for damping could be observed with certainty in the vicinity of $T_{c2}$. The velocity dip and damping peak look like reflections of each other in a horizontal mirror plane (Fig. 51a and 51b).

Fig. 51b shows considerable anomalous gradual growth in damping over a wide temperature range. Such behavior caused by fluctuations could originate in randomly-placed Na$^+$ and Bi$^{3+}$ cations. The usual Landau theory is a perturbation approximation and is not valid if large fluctuations exist. In NBT the separate relaxation portions of the acoustic anomaly which should be a sharp anomaly near the phase transition were not observed.
A "hybridization" may prevent us from observing relaxation contributions of the usual form as seen in many ferroelectrics and ferroelastics. The "hybridization" may occur in NBT between two transitions, i.e. from the cubic phase to the tetragonal phase at $T_{c1}$ and to the trigonal phase at $T_{c2}$. However, a linear superposition of two anomalies at the $T_{c1}$ and $T_{c2}$ phase transitions cannot fit the data either. Both the velocity minimum and the damping maximum occur near $T \approx 650$ K which is between $T_{c1} \approx 820$ K and $T_{c2} \approx 593$ K. This leads us to suggest a coupling of two different order parameter fluctuations. Each type of fluctuation contributes to acoustic anomalies with the same $\eta^2u$-type coupling between the fluctuating order parameter and strain.

As discussed above, the positions of this dielectric maximum at $T \approx 640$ K and hypersonic damping maximum peak at $T \approx 650$ K are probably initiated by competition of two coupled order parameters between two structural instabilities. The shift of damping maximum (measurements at about $5 \times 10^{10}$ Hz) relative to the dielectric anomaly (measurements at $10^5$ Hz) is clearly seen. The shift may be due to the frequency dependence of fluctuations coupling electrostrictively to strain.

Fluctuations of the coupled order parameters or hybridized fluctuations manifest themselves in the spectra of high-frequency light scattering also. A preliminary indication of increased central peak intensity between $T_{c1}$ and $T_{c2}$ was obtained in the Raman scattering study. Fig. 51c shows a drastic background increase between $T_{c1}$ and $T_{c2}$ compared to the level outside these transitions. This background corresponds to the peak intensity of the central component if there is only one broad central peak as suggested by the Raman spectra. The background increase when approaching $T_{c2}$ from below and $T_{c1}$ from above is comparable to the evolution of both the central peak in Raman scattering and overdamped soft modes detected in neutron scattering.

The shaded region in Fig. 52 shows the coexistence range of the R- and M-point superlattice reflections, which corresponds to the trigonal and tetragonal phases.
The acoustic anomalies have no obvious relation to this coexistence region centered near 600 K because their extrema (at T~650 K) (Fig. 51a and 51b) are significantly shifted to higher temperatures. Although the neutron measurements can separate information from different points in the Brillouin zone so superlattice structures of different types (M and R) were studied independently (Fig. 52), the light scattering spectra show an integral response.

A theoretical interpretation recently appeared for the polarization response of crystals with structural and ferroelectric instabilities. A simple model with two coupled structural and ferroelectric order parameters "shifts" the main dielectric anomaly from the ferroelectric transition to the structural one. One could not apply this model directly because NBT has two structural instabilities rather than one. However, the above "shift" makes it seem likely that those acoustic and dielectric responses of NBT are modified by the coupling between different order parameters.
Figure 49. Brillouin backscattering spectra of NBT at different temperatures near the damping maximum.
Figure 50. Damping of the longitudinal acoustic phonons vs. temperature in the vicinity of the cubic-tetragonal phase transition.
Figure 51. Temperature dependence of different characteristics in NBT: (a) Brillouin shift of the longitudinal acoustic phonons vs. T; (b) Half-width of Brillouin components at half maximum (or damping) vs. T; the instrumental broadening was subtracted; (c) Intensity of the background in the Brillouin spectra vs. T.
Figure 52. Intensity of the superlattice reflections from M and R points of the cubic Brillouin zone obtained in neutron scattering measurements vs. T to show the range of phase coexistence (shaded region). The phase sequence in NBT is shown at the top; I: paraelectric and paraelastic, II: ferroelastic, III: antiferroelectric(?), IV: ferroelectric. The corresponding crystal symmetries are shown in the middle. All data were obtained on heating runs.
Dielectric and Brillouin Scattering Results

Actual LA[001] phonon spectra of the anti-Stokes and Stokes Brillouin components for $\theta_s=180^\circ$ are shown in Fig. 53. The data shown here are for several temperatures near the maximum value of half-width. Both frequency shift and half-width exhibit a strong temperature dependence over a wide temperature range. Fig. 53 also shows that the background in the Brillouin spectra changes drastically and has the larger values at $T>\sim290$ K. Since Brillouin spectra are sensitive to the central peak near the Brillouin zone center, this background anomaly implies an evolution of the central peak as evidenced by Raman scattering which indicates a strong central peak range between $\sim300$ and $\sim500$ K. However, central peak analysis is difficult because the peak is often superimposed by low-frequency Raman modes with complicated temperature dependence. Thus, a correlation between acoustic phonon damping and a central component in PMN is not clear yet.

The accumulated data for backscattering ($\theta_s=180^\circ$) are shown in Fig. 54. The data indicate that a broad phonon softening starts at $T>475$ K and reaches a minimum near 290 K, associated with a broad maximum in damping. The velocity and damping temperature dependences look like reflections of each other. Such a growth of damping over a wide temperature range reveals that order parameter fluctuations are the dominant dynamic mechanism. As one knows, the dynamic fluctuation contribution is a characteristic of a $\eta^2\mu$-type quadratic coupling (electrostriction), squared in order parameter and linear in strain. However, a typical step-like frequency softening for $\eta^2\mu$-type coupling is not observed in this case. Beside this broad damping background, one can note that there is an additional damping peak near 212 K which can be connected with
the typical Landau-Khalatnikov maximum (relaxation-type). For comparison, dielectric measurements were also carried out at several frequencies and are presented in Fig. 54c.

What are the origins of these two damping peaks in PMN? The temperature dependence of the linear birefringence $\Delta n = <P^2/> - <P^2>$ in PMN under an external electric field suggests an equilibrium phase transition temperature $T_c$ in the absence of random field, in the range $200 \text{ K} < T_c < 234 \text{ K}$. In addition, by fitting the time dependence of the linear birefringence with two different exponents $\beta$ below and above $212 \text{ K}$, Westphal et al. propose that the Curie temperature of PMN is $T_c \sim 212 \text{ K}$. Viehland et al. also claim that the freezing temperature is $T_f \sim 217 \text{ K}$ below which a dramatic change of the relaxation time distribution is observed which is interpreted as a result of a long-range correlation of polar microdomains. Recent quasielastic-neutron scattering (QES) on PMN supports the above interpretations and shows that the correlation length is nearly temperature independent with a maximum value of 200 Å below ~217 K. Since the Landau-Khalatnikov contribution is sensitive to the occurrence of long-range FE ordering, one can attribute this Landau-Khalatnikov-like maximum in PMN to the rapid growth of FE ordering at $T_c \sim 212 \text{ K}$.

The diffuse phase transition around 260 K is attributed to quenched random electric fields originating from charged compositional fluctuations at the B site of the $\text{ABO}_3$ structure. These random fields can suppress a long-range-order ferroelectric transition and generate dynamical order parameter fluctuations. Thus, one can expect that such random fields are responsible for the evolution of the broad damping background with a maximum near 290 K (see Fig. 54b) and modification of $\eta^2\mu$-type frequency softening, i.e. a broad dip instead of a typical step-like anomaly. Similar acoustic anomalies, i.e. a broad damping maximum and a broad velocity dip which does not correspond to any specific phase transition or structural instability, are also observed in Na$_{1/2}$Bi$_{1/2}$TiO$_3$ (NBT). The fluctuations in NBT are attributed to random fields
originating from short-range randomly-placed $\text{Na}^+$ and $\text{Bi}^{+3}$ cations at the A site of ABO$_3$ structure instead of $\text{Mg}^{+2}$ and $\text{Nb}^{+5}$ at the B site for PMN. Such acoustic similarity between PMN and NBT seems to imply the importance of short-range randomly-placed cations on complex ferroelectric relaxors.

The longitudinal LA[001] and transverse TA[001] phonon data for scattering angle $\theta_s=32.6^\circ$ are shown in Fig. 55. A phonon frequency softening is also observed at this angle for both LA and TA phonon modes, with a broad minimum at $T\sim280$ K. According to Eq. (22), the relative error in damping for the small-angle scattering is much larger than for the backscattering, thus the natural-phonon half-width $\delta_{\nu_{ph}}$ for small angles is not very meaningful. Our measurements are limited not only by the broadening of the collection angle but also by the broadening of the incident-laser light source and the resolution of the Brillouin spectrometer. Fig. 56 shows also a softening for $\theta_s=13.0^\circ$ and indicates a frequency minimum for both LA and TA modes at $T\sim270$ K. As one can see, due to dispersion the frequency minimum shifts to lower temperature as frequency (or scattering angle) decreases.

A broad phonon softening has been observed for both LA[001] and TA[001] modes starting at $T>475$ K followed by a hardening around 280 K. For $\theta_s=180^\circ$, a strong broad damping background is observed and is connected with order parameter fluctuations. An additional Landau-Khalatnikov maximum is also observed at $T_c\sim212$ K and implies a rapid evolution of long-range correlation of polar microdomains. Similar results are also obtained from our Brillouin scattering on Na$_{1/2}$Bi$_{1/2}$TiO$_3$, i.e. a strong broad damping background and broad frequency softening. We conclude that the random-ion-caused fluctuations must play a important role for the similar acoustic anomalies in these complex ferroelectric relaxors.
Figure 53. Anti-Stokes and Stokes components of the LA[001] Brillouin spectra for temperatures near the maximum damping value for $\theta_s=180^\circ$ in PMN. The frequency interval between the two Rayleigh peaks is 17.035 GHz (FSR).
Figure 54. (a) Frequency shift and (b) Half-width vs. temperature of the LA[001] phonons for \( \theta_s = 180^\circ \). (c) The real part of dielectric permittivity vs. temperature at four different frequencies. The dashed line indicates the ferroelectric phase transition temperature \( T_c \approx 212 \) K.
Figure 55. (a) Frequency shift and (b) Half-width vs. temperature of the LA[001] phonons for $\theta_s=32.6^\circ$. (c) Frequency shift vs. temperature of the TA[001] phonons. The dashed line is a guide to the eye.
Figure 56. (a) Frequency shift and (b) Half-width vs. temperature of the LA[001] phonons for $\theta_s = 12.6^o$. (c) Frequency shift vs. temperature of the TA[001] phonons. The dashed line is a guide to the eye.
Determination of Elastic Stiffness Constants\textsuperscript{14,55}

The high temperature phase in PMN is cubic with point group m3m whereas below 200 K a small trigonal distortion was observed by Shebanov from single crystal studies. Thus, we can consider cubic symmetry for calculation of elastic stiffness constants in PMN, i.e.

\[
\begin{bmatrix}
C_{11}^E & C_{12}^E & C_{13}^E & 0 & 0 & 0 \\
C_{12}^E & C_{22}^E & C_{23}^E & 0 & 0 & 0 \\
C_{13}^E & C_{23}^E & C_{33}^E & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44}^E & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44}^E & 0 \\
0 & 0 & 0 & 0 & 0 & C_{44}^E
\end{bmatrix}
\]

In our experimental situation, the phonon is along the [001] direction. From Eq. (85), one obtains

\[
\rho V_{LA}^2 = C_{11}^E = C_{22}^E = C_{33}^E
\]

\[
\rho V_{TA1}^2 = \rho V_{TA2}^2 = C_{44}^E = C_{55}^E = C_{66}^E
\]

From Eq. (69),

\[
V = \frac{\lambda_o \Delta v}{2 n \sin \left(\frac{\theta}{2}\right)}
\]

where V is the phonon velocity, \Delta v is the phonon frequency (or Brillouin frequency shift) and \lambda_o is the wavelength of the incident light. Thus, one has the following relations
\[ C_{ii}^E = C_{22}^E = C_{33}^E = \rho \left( \frac{\lambda \Delta V_{TA}}{2n \sin(\theta/2)} \right)^2 \]  
\[ (126) \]
\[ C_{44}^E = C_{55}^E = C_{66}^E = \rho \left( \frac{\lambda \Delta V_{TA}}{2n \sin(\theta/2)} \right)^2 \]  
\[ (127) \]

where \( \Delta V_{LA} \) and \( \Delta V_{TA} \) are the longitudinal and transverse phonon frequency shifts, respectively. Since thermal strain \( \Delta L/L_0 \) is almost zero below 400 K, we will use the crystal density at room temperature, i.e. \( \rho = 8.12 \times 10^3 \text{ kg/m}^3 \), for elastic stiffness calculation between 400 and 200 K. The temperature dependent refractive indices \( n(T) \) are obtained from Ref. 56. Furthermore, one can use the relation of the compliance constant tensor \( C_{ij}^E \) to obtain \( S_{ij}^E \), i.e.

\[ s_{\alpha \beta} C_{\beta \gamma}^E = \delta_{\alpha \gamma}. \]  
\[ (128) \]

where \( \delta_{\alpha \gamma} \) is the unit tensor of dimension 6. Thus, we have

\[
\begin{pmatrix}
    C_{11}^E & C_{12}^E & 0 & 0 & 0 & 0 \\
    C_{12}^E & C_{22}^E & 0 & 0 & 0 & 0 \\
    C_{22}^E & C_{12}^E & 0 & 0 &! 0 & 0 \\
    0 & 0 & 0 & C_{44}^E & 0 & 0 \\
    0 & 0 & 0 & 0 & C_{44}^E & 0 \\
    0 & 0 & 0 & 0 & 0 & C_{44}^E
\end{pmatrix}

\times
\begin{pmatrix}
    s_{11}^E & s_{12}^E & s_{12}^E & s_{12}^E & s_{12}^E & s_{12}^E \\
    s_{12}^E & s_{11}^E & s_{12}^E & s_{12}^E & s_{12}^E & s_{12}^E \\
    s_{12}^E & s_{12}^E & s_{11}^E & s_{12}^E & s_{12}^E & s_{12}^E \\
    0 & 0 & 0 & s_{44}^E & 0 & 0 \\
    0 & 0 & 0 & 0 & s_{44}^E & 0 \\
    0 & 0 & 0 & 0 & 0 & s_{44}^E
\end{pmatrix}

= \begin{pmatrix}
    1 & 0 & 0 & 0 & 0 & 0 \\
    0 & 1 & 0 & 0 & 0 & 0 \\
    0 & 0 & 1 & 0 & 0 & 0 \\
    0 & 0 & 0 & 1 & 0 & 0 \\
    0 & 0 & 0 & 0 & 1 & 0 \\
    0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}
\]

Table 3 lists the elastic stiffness constants and compliance constants of PMN (with cubic point group m3m) at several temperatures. As seen in Table 3, both elastic stiffness constants \( C_{11}^E \) and \( C_{44}^E \) show a softening around 280 K as observed in the Brillouin phonon frequency shift. We attribute the slight difference in \( C_{11}^E \) from \( \theta = 180^\circ \) and \( \theta = 32.5 \pm 0.2^\circ \) to the error of determination for smaller angles.
Table 3. Elastic stiffness and compliance constants of PMN at several temperatures from two scattering geometries $\theta_s = 180^\circ$ and $32.5\pm0.2^\circ$.

Table 4 compares the elastic stiffness constants at room temperature for several different ABO$_3$-type ferroelectric crystals.

Table 4. Comparison of elastic stiffness and compliance constants at room temperature.

One can note that the elastic stiffness constants $C_{ij}^E$ of these pure perovskite-type ferroelectric single crystals are larger than those in the complex crystal PMN.
CHAPTER 5

CONCLUSIONS

Comparison of Results

Beside some differences between the pure ferroelectric crystal DRDA and deuteron glasses DRADA-0.10 and 0.28 as indicated in chapter 4, several important similarities and differences have been found through this study between these disordered materials, i.e. deuteron glasses DRADA-0.10 and 0.28, and the relaxor ferroelectrics PMN and NBT.

Similarities Among PMN, NBT and DRADA-0.10 and 0.28\textsuperscript{51-55}

(1) For all these crystals, DRADA-0.10 and 0.28, NBT and PMN, a broad maximum in dielectric permittivity has been observed. For both DRADA-0.28 and PMN, this broad dielectric peak value is frequency dependent.

(2) For DRADA-0.10 and 0.28, PMN and NBT, the temperature dependence of hypersonic damping shows a strong growth over a wide temperature range, which is attributed to order parameter(s) fluctuations. For DRADA-0.28, PMN and NBT, the damping peak occurs at higher temperature than the dielectric permittivity maximum. This shift of the damping maximum (measurements at 10^{10} Hz) relative to the dielectric anomaly (measurements at 10^5 Hz) can be attributed to the frequency dispersion. However, these peaks do not correspond to any specific phase (or structural) transitions.
(3) For DRADA-0.10 and 0.28, PMN and NBT, the local random fields originating from randomly-placed cations (or ions) play an important role for both hypersonic and dielectric anomalies. In DRADA-0.10 and 0.28, these randomly-placed ions are ND$_4^+$ ions which tend to AFE ordering and Rb$^+$ ions which tend to FE ordering. In PMN, those randomly-placed cations are Mg$^{+2}$ and Nb$^{+5}$ randomly located at B-site positions. In NBT, those randomly-placed cations are Na$^{+1}$, Bi$^{+3}$ ions randomly located at A-site positions.

(4) For DRADA-0.10 and 0.28, NBT and PMN, a $\eta^2\mu$-type quadratic (electrostrictive) coupling, squared in order parameter and linear in strain, is the main coupling contribution to acoustic anomalies.

(5) For DRADA-0.1, NBT and PMN, a sequence of phase transitions has been observed.

(6) For both PMN and NBT, the damping peak is associated with a broad phonon softening in sound velocity with a minimum centered at the same temperature. These anomalies could not be explained by either the Landau-Khalatnikov maximum for damping or by a step-like coupling for sound velocity.

(7) Both DRADA-0.10 and PMN show an additional Landau-Khalatnikov peak which indicates the onset of long-range FE ordering.

**Differences Among PMN, NBT and DRADA-0.10 and 0.28**

(1) The dielectric and hypersonic anomalies in NBT can be attributed to the fluctuations of two coupled order parameters which are initiated from two different structural instabilities and induce a intermediate transition between two different structures, i.e. tetragonal and trigonal symmetries. In PMN, the diffuse phase transition around 270 K is attributed to quenched random electric fields originating from charged compositional fluctuations at the B site of the ABO$_3$ structure. For deuteron glasses
DRADA-0.10 and 0.28, the competition between FE ordering and AFE ordering is the origin for both the dielectric and hypersonic anomalies.

(2) In PMN the random electric fields have been attributed to charges in small regions in which according to transmission electron microscopy the Mg\textsuperscript{2+} and Nb\textsuperscript{5+} ions tend to order with a 1:1 ratio rather than the 1:2 ratio required for charge neutrality\textsuperscript{32-34}. In NBT, however, a 1:1 ratio for ordered Na\textsuperscript{+} and Bi\textsuperscript{3+} cations is stoichiometric and will not cause longer-range random electric fields. Instead, it is assumed that local charged regions in NBT originates from the random distribution of Na\textsuperscript{+} and Bi\textsuperscript{3+} cations.

(3) The dielectric permittivities of PMN and NBT are much larger than those in the deuteron glasses DRADA-0.10 and 0.28. The dielectric and hypersonic anomalies of both PMN and NBT occur at much higher temperatures than those in deuteron glasses DRADA-0.10 and 0.28.

(4) Both PMN and NBT exhibit a broad phonon softening along the [001] (or [100], or [010]) direction. However, both deuteron glasses DRADA-0.10 and 0.28 show a phonon hardening along the [100] or [010] (a or b axis) direction.

Applications

Due to increasing interest in displacement transducers needed in different fields, especially optics, precision machinery and the microelectronics industry, recent developments in electromechanical actuators have been remarkable over the last few years. However, as is well documented in the literature, the true response of the piezoelectric materials deviates significantly from the ideal. There are four principal causes of nonideal behavior: hysteresis, aging effects, nonlinearity and creep. Electrostriction is a phenomenon which gives rise to a strain proportional to the square of the applied electric field. It can be observed in all dielectrics: amorphous and
crystalline, regardless of symmetry. For centrosymmetric phases (such as m3m, 3m, 4/mmm, 4/m etc.), the electrostrictive equation is:

\[ S_i = Q_{mi} P_m^2 = Q_{mi} \varepsilon_0^2 \varepsilon_{mm}(E) - 1^2 \varepsilon_m^2 \equiv Q_{mi} \varepsilon_0^2 \varepsilon_{mm}(E) \varepsilon_m^2 \]  \hspace{1cm} (129)

and

\[ Q_{mi} = \begin{pmatrix}
Q_{11} & Q_{12} & Q_{12} & 0 & 0 & 0 \\
Q_{12} & Q_{11} & Q_{12} & 0 & 0 & 0 \\
Q_{12} & Q_{12} & Q_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & Q_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & Q_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & Q_{44}
\end{pmatrix} \]

\( Q_{mi} \) are the elements of the electrostrictive tensor (using Voigt notation). Strains induced in a crystal due to the electrostrictive effect are, in general, very small. According to Eq. (129), in materials with a high dielectric permittivity (such as PMN, NBT etc.), however, it is possible to obtain electromechanical coupling as strong as that in the strongest piezoelectric materials. Several papers have proved from measurements on relaxor ferroelectrics that the electrostrictive properties of relaxor ferroelectrics offer several advantages over normal piezoelectric transducers: (1) large electrostrictive strains comparable to the best piezoelectric ceramics; (2) excellent positional reproducibility (insignificant hysteresis); (3) no poling is required, resulting in no aging effects; (4) very low thermal expansion coefficients (good thermal stability), (5) short response time.\(^{57-59}\) Nomura et al. also found that the electrostrictive coefficients \( Q_{mi} \) increase with the degree of cation disorder.\(^{57}\) By using multilayer technology in an electrostrictive device, one can also increase the strain (displacement) significantly because the total displacement is proportional to the square of the number of layers, an important advantage over piezoelectric materials.\(^{57}\)
An electrostrictive displacement transducer can be used in the following fields: (1) optical devices: deformable mirror (to produce large deformations without hysteresis), Fabry-Perot resonator, etc. (2) surface physics: atomic force microscope (AFM), etc. (3) precision machinery and microelectronics. More actual examples can be found in Refs. 57 and 58.

Since the conductance of mixed FE-AFE crystals shows a strong temperature dependence at low temperature, they could be used to be a temperature sensor for low temperature after calibration. In a still lower temperature range, below the onset of the ferroelectric transition in proton glasses showing coexistence, the capacitance temperature dependence could be used for this purpose too.

**Recommended Additional Work on This Problem**

(1) In this study, only qualitative explanations are given for hypersonic anomalies in the relaxors NBT and PMN and deuteron glasses DRADA-0.10 and 0.28. Further theoretical models for these anomalies are important to understand these similarities and differences between these complicated disordered systems. (2) As mentioned in Ref. 16, the high-temperature (T>640 K) and low-frequency dielectric anomaly in NBT is still not clear. The question whether it is due to intrinsic properties, extrinsic bulk conductivity or an interfacial effect needs more experiments such as low-frequency dielectric measurements and reasonable physical models for its answer. (3) Phonon softening has been seen in the RADP-x system along the [110] phonon direction for both LA and TA modes, so one may expect to observe a similar softening behavior in DRADA-0, 0.10 and 0.28 along the [110] direction if large clean crystals can be grown. (4) Further studies such as neutron scattering on DRADA-0.10 and 0.28 are critical for understanding the mechanism of ordering competition and the reason why those
hypersonic anomalies occur far above any phase transitions. (5) One could measure
dielectric permittivity on NBT under a strong external electric field. One may see a
nonlinear effect or an anomaly similar to that observed on PMN, i.e. an additional
dielectric peak where the random fields are overcome by the external field. (6) More
Brillouin scattering experiments along different phonon directions on NBT and DRADA-x are necessary for calculating elastic constants.
REFERENCES CITED


