Statics and Dynamics of Polar Nanoregions in Pb Based Relaxors

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Abstract

Relaxor ferroelectrics have been known for more than 50 years but their properties are still poorly understood. The dielectric permittivity $\varepsilon$ of the relaxors is much broader in temperature than that of classic ferroelectrics and exhibits significant frequency dispersion. In contrast with the classical ferroelectrics, the peak in the dielectric permittivity of relaxors is not necessarily associated with a structural phase transition. For example the average crystal structure of the model relaxors PbMg$_{1/3}$Nb$_{2/3}$O$_3$ and PbMg$_{1/3}$Ta$_{2/3}$O$_3$ is cubic $Pm\overline{3}m$ above and below the maximum in $\varepsilon$. However, the behavior of the refractive index would suggest that below a certain temperature a polar short-range order (polar nanoregions) appears in these crystals.

This thesis is an experimental investigation of the statics and dynamics of the polar nanoregions in the (1-x)PbMg$_{1/3}$Nb$_{2/3}$O$_3$ -xPbTiO$_3$ (x=0, 0.50), (1-x)PbZn$_{1/3}$Nb$_{2/3}$O$_3$ -xPbTiO$_3$ (x=0.07) and PbMg$_{1/3}$Ta$_{2/3}$O$_3$ relaxors by neutron scattering. The behavior of the chemical structure and of the diffuse scattering as a function of temperature and pressure suggests that mainly the correlations between the Pb displacements are responsible for the formation of the polar nanoregions. There is no evidence of a softening of the lowest transverse optic phonon in these crystals. Instead, the susceptibility associated with the dynamic (quasielastic) component of the diffuse scattering is found to have a similar temperature dependence as the dielectric susceptibility. Therefore, quasielastic scattering seems to play the role of the soft mode in relaxors. Furthermore, the properties of the diffuse scattering suggest that relaxors undergo a random-field transition similar to that observed in some magnetic materials. Possible source of random fields in relaxors is a distribution of two ions with different valencies (e.g. in PbMg$_{1/3}$Nb$_{2/3}$O$_3$ Mg is +2 whereas Nb is +5) on the B site of the ABO$_3$ perovskite structure.
Résumé

Bien que les relaxeurs ferroélectriques soient connus depuis plus de 50 ans, leurs propriétés sont encore mal comprises. La permittivité diélectrique, ε, d’un relaxeur présente une gamme plus large en température que celle d’un ferroélectrique classique et montre également une dispersion importante en fréquence. Contrairement aux ferroélectriques classiques, le pic de permittivité diélectrique ε du relaxeur n’est pas nécessairement associé à une transition de phase structurale. Par exemple, la structure cristalline moyenne de relaxeurs modèles tels que PbMg$_{1/3}$Nb$_{2/3}$O$_3$ et PbMg$_{1/3}$Ta$_{2/3}$O$_3$ est cubique $Pm\bar{3}m$ au-dessus et au-dessous du maximum de la permittivité diélectrique ε. Cependant, le comportement de l’indice de réfraction suggérerait qu’au-dessous d’une certaine température un ordre polaire a courte distance (nano-regions polaires) apparaîtrait dans ce type de cristaux.

Cette thèse présente une investigation expérimentale par diffusion des neutrons des nano-regions des relaxeurs (1-x)PbMg$_{1/3}$Nb$_{2/3}$O$_3$-xPbTiO$_3$ (x=0, 0.50), (1-x)PbZn$_{1/3}$Nb$_{2/3}$O$_3$-xPbTiO$_3$ (x=0.07) et PbMg$_{1/3}$Ta$_{2/3}$O$_3$. L’évolution de la constitution chimique et de la diffusion diffuse en fonction de la température et de la pression suggère que ce sont surtout les corrélations entre les déplacements du plomb qui sont responsables de la formation de nano-regions polaires. Il n’y a pas d’évidence que le mode optique transverse des phonons sont mous dans ces cristaux. Par contre, la susceptibilité associée avec la composante dynamique (quasielastic) de la diffusion diffuse a montré une dépendance en température similaire à la susceptibilité diélectrique. Par conséquent, la diffusion quasiélastique semble jouer un rôle dans les modes mous des relaxeurs. De plus, les propriétés de diffusion diffuse suggèrent que les relaxeurs subissent une transition de champ aléatoire similaire à celle observée dans certains matériaux magnétiques. Ce champ aléatoire dans les
relaxeurs pourrait provenir de la distribution de deux ions ayant différentes valences (par exemple dans PbMg_{1/3}Nb_{2/3}O_3 le Mg a une valence de +2 alors que le Nb a lui une valence de +5) sur le site B de la structure pérovskite ABO_3.
Chapter 1

Introduction

Relaxor ferroelectrics, also known as relaxors, have long been a subject of intense research. They are complex perovskites with the general formula $A'_{x}A^{''}_{1-x}B'_{y}B^{''}_{1-y}O_3$. The crystallographic equivalent positions can be shared by different atoms, $x$ and $y$ being determined by the condition of charge neutrality. A marked feature of relaxors is the frequency-dependent peak of the dielectric permittivity that extends over a wide temperature range and is not necessarily associated with a structural phase transition as it is in the classical ferroelectrics (see Fig. 1.1).

$\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) is a model relaxor ferroelectric. It has a cubic $Pm\bar{3}m$ structure at all temperatures in the absence of an external electric field (Smolensky et al. (1984)). When cooled down in an electric field, $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ exhibits a phase transition at about $T_c=210$ K (Schmidt et al. (1982)). The solid solutions of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ with $\text{PtTiO}_3$ (PT) $((1-x)\text{PMN}-x\text{PT})$ are materials with ultrahigh piezoelectric responses of an order of magnitude larger than conventional piezoelectric ceramics. The dielectric permittivity increases with increasing PT concentration, reaching a maximum at the compositions near the morphotropic phase boundary, after which it shows a decreasing trend. Doping also reduces the width in the temperature of the dielectric permittivity and consequently decreases the frequency dispersion of the temperature at which the dielectric permittivity is maximum $T_m$.

Another similar family, with technological application is the solid solution of

1
Chapter 1. Introduction

Figure 1.1: Temperature dependence of the dielectric response measured at different frequencies (20-106 Hz) for (1-x)PMN-xPT compositions (taken from Colla et al. (1998)).

PbZn$_{1/3}$Nb$_{2/3}$O$_3$ with PbTiO$_3$ ((1-x)PZN-xPT ). The phase diagrams of ((1-x)PMN-xPT ) and ((1-x)PZN-xPT ) are complex (see Fig. 1.2), hence these crystals are challenging for fundamental studies. In both families the compositions around the so-called morphotropic phase boundaries are those at which the giant piezoelectric effect occurs. These are (0.68PMN-0.32PT) and (0.92PZN-0.08PT).

The (1-x)PMN-xPT and (1-x)PZN-xPT systems have been investigated by various techniques. Despite this, the microscopic origin of their dielectric properties is under debate.

The dielectric properties of relaxors generally depend on the following external parameters: temperature, pressure and electric field. The general trend of the bulk dielectric properties as a function of the parameters listed above is generally known. The temperature dependence of the dielectric permittivity
Figure 1.2: The phase diagrams of (1-x)PMN-xPT Shuvaeva et al. (2005) and (1-x)PZN-xPT Lima-Silva et al. (2004) showing the symmetries of the different phases. Cubic, tetragonal, rhombohedral and orthorhombic phases are denoted by C, T, R and O. With Cm and Pm are denoted the monoclinic phases, while the symmetry of the phase I’ in (1-x)PMN-xPT is still uncertain.

has been discussed above. The hydrostatic pressure mainly has two effects on the dielectric permittivity. Firstly the pressure suppresses the peak in the dielectric permittivity. Secondly, it shifts its maximum towards lower temperatures. Figure 1.3 exemplifies these effects for PMN.

The origin of the dielectric properties is not completely understood, but it is accepted that the correlated static and/or dynamic ionic displacements that destroy locally the center of symmetry are responsible. X-ray and neutron scattering are well suited to probe the dynamics and the local structure in crystals under different external parameters.

The main focus of this thesis is to ascertain microscopic information related to the crystal structure and lattice dynamics as a function of temperature and hydrostatic pressure in Pb based relaxors. It is hoped that this work contributes to the better understanding of the mechanisms governing the physics of relaxors, that will make it possible to proceed from observation and discovery to the prediction and design of new materials.
Figure 1.3: Dielectric permittivity of PMN as a function of hydrostatic pressure (Nawrocik et al. (2003)).
Chapter 2

Neutron scattering

Neutron scattering is an important experimental technique that allows the measurement of static and dynamic properties of matter. The neutron has a mass $m = 1.675 \times 10^{-27}$ kg and does not carry a charge. Because of this the neutrons can penetrate deeply into matter. The de Broglie wavelength of cold and thermal neutrons is comparable to the interatomic distances in crystals, and so neutrons will be diffracted by a crystalline sample. Since the neutron carries a magnetic moment, it is also sensitive to the magnetic field distribution in the sample. The energy of thermal neutrons is of the same order of magnitude as many excitations in solids. Therefore neutron scattering will probe both the nuclear and magnetic structure and also the dynamical properties in solids.

The neutron scattering experiments consist of analyzing the neutrons state before and after it passes through matter. In non-magnetic materials the neutron only interacts with the nuclei whereas in magnetic materials there is an interaction with the magnetic moment as well as with the nuclei.

Reactors and spallation sources are used to produce neutrons. There are continuous and pulsed sources. The neutron experiments described in this thesis have been performed at the SINQ spallation source and at the FRM-II reactor.

The properties and neutron-scattering cross-section for both nuclear and magnetic scattering will be briefly summarized in the following. Here the important results are simply stated without their associated proofs. The neutron
scattering techniques and instruments used in the experiments will also be discussed.

2.1 Neutron scattering theory

Neutron scattering is a well established technique and the theory of neutron scattering is covered in detail in books, lectures and reviews. In the following I will briefly present the main concepts and results that will be used within this thesis.

In a neutron scattering experiment a collimated beam of neutrons is incident on a target sample, scatters through some interaction with the sample and the momentum and energy transfers of the scattered neutrons are measured using detectors in one or a range of directions.

Let’s first consider a neutron with an initial wavevector $k_i$ incident on a sample which is then scattered into a state with a final wavevector $k_f$. The transfer of momentum to the sample is $Q$, where $Q$ is known as the scattering vector. These three vectors $(k_i, k_f, Q)$ form the so called scattering triangle. In a diffraction experiment the process occurs without energy transfer whereas in an inelastic scattering experiment the neutron loses or gains energy. In both cases the momentum and the energy are conserved:

\[
Q = k_f - k_i, \\
|Q|^2 = k_i^2 + k_f^2 - 2k_i k_f \cos(2\theta), \tag{2.1} \\
\hbar \omega = E_i - E_f,
\]

where $E_i$ and $E_f$ are the initial and final energies of the neutron, and $2\theta$ is the angle between $k_i$ and $k_f$. In an experiment a neutron is detected if it hits the detector, which subtends a solid angle $\Delta \Omega$, and has an energy within the range $\Delta \omega$ around the nominal value $E_f$. If the incoming neutron flux $\Phi_i$ is detected with an efficiency $\eta$, then the detected count rate is:

\[
\eta \Phi_i \frac{d^2 \sigma}{d\Omega d\omega} \Delta \Omega \Delta \omega. \tag{2.2}
\]
2.1. Neutron scattering theory

$d^2\sigma/d\Omega d\omega$ is the double differential cross-section and is the basic quantity measured in a neutron scattering experiment. The scattering cross-section depends on the details of the interaction between the neutron and the sample.

### 2.1.1 Neutron scattering cross-section

The derivation of the following results can be found in more detail in, for example, the books by Squires (1996) and by Furrer et al. (2009). Here the important results are simply stated without their associated proofs.

The total scattering cross-section, $\sigma_{\text{tot}}$, counting neutrons scattered in any direction, is defined as the total number of neutrons scattered per time unit and normalized by the incident neutron flux. In a real experiment only some of the scattered neutrons are detected. To describe this the differential cross-section and the double differential cross-section are introduced. The differential cross-section, $d\sigma/d\Omega$, is the number of neutrons that are scattered into a certain direction per time unit, regardless of their energy. The double differential cross-section is the number of neutrons that are scattered per second into a certain direction with a certain range of energy values.

The neutron scattering is shown experimentally to be a very weak process. To obtain the expression of the scattering cross-section the interacting potential between the neutron and the sample can be considered as a small perturbation of the system. As I already mentioned, in a neutron scattering experiment one needs to detect the change in the state of the neutrons due to the interaction with the sample. Fermi’s golden rule is used to calculate the probability of a transition from an initial state $\langle \lambda |$ to a final state $\langle \lambda' |$. The double cross-section is expressed as follows:

$$
\left( \frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{coh}} = \left( \frac{m}{2\pi\hbar^2} \right)^2 \frac{k_f}{k_i} \sum_{\lambda',\sigma'} \sum_{\lambda,\sigma} p_{\lambda}\sigma \left| \langle k_f, \sigma', \lambda' | \hat{U} | k_i, \sigma, \lambda \rangle \right|^2 
$$

$$
\times \delta (\hbar\omega + E_i - E_f),
$$

(2.3)

$\sigma$ and $\sigma'$ are the spin states before and after the scattering process. $p_\lambda$ is the thermal population factor and $p_\sigma$ is the polarization probability. The $\delta$
function ensures energy conservation. $\hat{U}$ is the interaction operator of the neutron with the sample. The scattering cross-section is therefore dependent on the type of interaction.

To describe the interaction of the neutron with nuclei at fixed positions $R_j$ the Fermi pseudopotential is used:

$$\hat{U}(r) = \frac{2\pi\hbar^2}{m} \sum_j b_j \delta(r - R_j). \quad (2.4)$$

The scattering length, $b_j$, for nuclear neutron scattering varies randomly from one element to another and can take positive, negative and even imaginary values.

In the case of magnetic scattering the interaction is with the electromagnetic field, $H(r)$, due to the intrinsic spin and orbital momentum of unpaired electrons in magnetic ions in the sample. The interaction potential for this case is:

$$\hat{U}(r) = \hat{\mu} \cdot H(r) = -\gamma \mu_N \hat{\sigma} \cdot H(r), \quad (2.5)$$

where $\mu$ is the magnetic moment operator of the neutron, $\gamma$ the gyromagnetic ratio, $\mu_N$ the nuclear magneton and $\hat{\sigma}$ is the Pauli spin operator. Since the materials described in this thesis are nonmagnetic, I will only describe the cross-sections for the nuclear elastic and inelastic scattering.

### 2.1.2 The response function $S(Q, \omega)$

Van Hove (1954) showed that the scattering cross-section can also be expressed in terms of the response function $S(Q, \omega)$:

$$\left( \frac{d^2\sigma}{d\Omega d\omega} \right) = N b \frac{k_f}{k_i} b^2 S(Q, \omega), \quad (2.6)$$

where
2.1. Neutron scattering theory

\[ S(Q, \omega) = \frac{1}{2\pi \hbar N} \sum_{j,j'} \int_{-\infty}^{\infty} e^{-i\omega t} \langle e^{-iQ \cdot r_{j'}(0)} e^{-iQ \cdot r_j(t)} \rangle dt, \]

(2.7)

N is the number of nuclei, \( b \) the scattering length, \( t \) is the time and the angle brackets denote the average. By using this formalism it is possible to separate the contribution arising from the experimental setup \( (k_i/k_f) \) and the scattering function \( S(Q, \omega) \) which depends only on the momentum and the energy transferred from the neutron to the sample. Hence it provides information about the positions and the motions of the nucleus in the sample.

For unpolarized neutrons it is possible to express the double differential cross-section as a sum of a coherent and incoherent scattering.

For the elastic scattering case the incoherent scattering is:

\[ \left( \frac{d\sigma}{d\Omega} \right)_{incoh} = \frac{\sigma_{incoh}}{\pi} \frac{k_f}{k_i} S(Q, \omega), \]

(2.8)

with \( \sigma_{incoh} = 4\pi \langle b \rangle^2 - \langle b^2 \rangle \). \( \sigma_{incoh} \) is usually measured at an arbitrary point in the \((Q, \omega)\) space away from the Bragg and phonon scattering and then subtracted from the data.

The coherent scattering:

\[ \left( \frac{d^2\sigma}{d\Omega d\omega} \right)_{coh} = \frac{\sigma_{coh}}{4\pi} \frac{k_f}{k_i} S(Q, \omega), \]

(2.9)

with \( \sigma_{coh} = 4\pi \langle b \rangle^2 \), results from interference effects between the nuclei and is observed as elastic Bragg scattering and inelastic phonon scattering.

For coherent elastic nuclear scattering cross-section the response function is:

\[ S(Q, \omega) = \delta(\hbar \omega) \frac{1}{N} \left( \sum_{j,j'} e^{iQ \cdot (r_j - r_{j'})} \right). \]

(2.10)

Using Eq. 2.10 it is possible to derive the coherent elastic cross-section:
Chapter 2. Neutron scattering

\[
\frac{d\sigma}{d\Omega}{}_{coh} = N_0 \frac{(2\pi)^3}{v_0} \sum_{\tau} |F(Q)|^2 \delta(Q - \tau).
\] (2.11)

\(N_0\) is the number of cells and \(v_0\) is the volume of a cell. \(F(Q)\) is the structure factor and is expressed as:

\[
F(Q) = \sum_d e^{-W_d(Q)} b_d e^{iQ \cdot d},
\] (2.12)

where \(b_d\) is the coherent scattering length of the atom located at position \(d\) in the unit cell. \(e^{-W_d(Q)}\) is the Debye-Waller factor and \(Q\) the scattering vector given in Eq. 2.2. The Debye-Waller factor takes into account that the atoms are not frozen to their lattice sites, but rather undergo a certain amount of thermal motion about an equilibrium position. As a function of temperature this thermal motion also changes, and the result is that the intensity of the Bragg peaks is affected. More details about the Debye-Waller factor will be discussed in Chapter 3.1.1.

As I have mentioned \(S(Q, \omega)\) contains information about both, positions and the movement of the atoms in a sample. If the elastic contribution is subtracted we are left with the part of \(S(Q, \omega)\) that describe the dynamic properties of a sample. In some cases the exact form of \(S(Q, \omega)\) is unknown. However, in practice it is useful to use an approximate function with which to fit the data. This function must obey general properties of the response function, which can be derived from linear response theory. \(S(Q, \omega)\) must satisfy the principle of detailed balance:

\[
S(-Q, -\omega) = e^{-\hbar \omega/k_B T} S(Q, \omega),
\] (2.13)

where \(k_B\) is the Boltzmann’s constant, \(T\) is the temperature, and \(\omega\) is assumed to be positive at low \(T\). The probability of the neutron exiting the system is greater than the system losing energy to the incident neutron. \(S(Q, \omega)\) must also obey the fluctuation dissipation theorem which states that the dynamic part of the response function can be related to the imaginary part of the susceptibility by
\[ S(Q, \omega) = \frac{\chi''(Q, \omega)}{1 - e^{-\hbar \omega/k_B T}}, \]  

(2.14)

where \( \chi'' \) is the imaginary part of the dynamical susceptibility.

This formalism, has been used in this thesis to describe the phonon spectra and the quasielastic scattering. More details about the form of \( S(Q, \omega) \) used in the present studies will be described in the Chapter 5 and Chapter 6.

### 2.2 Instrumentation

Most of the results presented in this thesis are obtained using the TASP triple-axis spectrometer, located at SINQ spallation source. For the investigations of the quasielastic scattering in 50\%PMN-50\%PT we used the PANDA triple-axis spectrometer, located at FRM-II reactor. A schematic representation of a triple-axis spectrometer is shown in the Fig. 2.1.

The incident neutron energy is chosen by use of a monochromator composed of

![Figure 2.1: Schematic representation of a triple-axis spectrometer.](image-url)
an array of single crystals. The initial energy and corresponding wave vector are selected by a Bragg reflection. The final energy of the neutrons is selected in the same way by the analyzer. The intensity of the scattered neutrons at the resulting energy and wave vector transfer can then be determined. In general, the final energy of the neutrons is fixed by the analyzer and scans are made by varying either the wave vector transfer (constant-energy scans) or the energy (constant-Q scans). The resolution of the measurement is dependent on the angular divergence of the neutron beam and the mosaic spread of the monochromator and analyzer crystals. Collimators can be used to reduce the angular divergence of the beam and the monochromator and the analyzer curvature can be set to optimize the intensity for the desired resolution. To avoid the contamination by the $\lambda/2$ scattering from monochromator and/or the analyser, two types of filters are commonly used: beryllium-filters and pyrolytic graphite filters (PG). The monitors are used to estimate the number of neutrons at different locations. They are especially necessary when the incident neutron flux is not constant in time as is the case of the spallation sources.

The powder and single crystal diffractometers have also been used. The investigation of the chemical structure of PMN has been performed with the High-Resolution Powder Diffractometer for Thermal Neutrons (HRPT) at SINQ. The schematic representation of a powder diffractometer is shown in the Fig.2.2.

In order to check the quality as well as the orientation of the crystals, the two-axis diffractometer Morpheus has been used. The two-axis diffractometer has a similar design as the triple-axis spectrometer shown in Fig. 2.1, but without the analyzer. Because of this it can be used only in diffraction mode.

More details about the neutron scattering instruments used in this work can be found at:

http://sinq.web.psi.ch/sinq/instr/tasp/tasp_n.html,
http://www.frm2.tum.de/en/science/spectrometer/panda,
http://sinq.web.psi.ch/sinq/instr/hrpt,
Figure 2.2: Schematic representation of a powder diffractometer.
Chapter 3

Chemical structure of PMN
3.1 Introduction

PMN has a disordered perovskite structure (see Fig. 3.1). Pb atoms are located at the (0,0,0) Wyckoff position. At (0.5,0.5,0) positions on the center of the cubic faces are located the O atoms distributed octahedrally around the Mg$^{+2}$/Nb$^{+5}$ ions located at (0.5,0.5,0.5). The Mg and Nb ions are arranged randomly accordingly, so as to make the system charge neutral (1/3 for Nb and 2/3 for Mg).

![The perovskite crystal structure of PMN.](image)

The dielectric propierties of a material are, as previously pointed out, directly related to the chemical structure. PMN has a centrosymmetric space group Pm$ar{3}$m. Consequently, the polarization should be zero. In reality, a nonzero polarization is observed already at 620 K much above $T_c=210$ K. The question therefore arises as to how to reconcile the coexistence of the nonzero polarization with the centrosymmetric crystal structure. This can be explained by assuming that locally, the structure deviates from the average structure and leads to the formation of polar regions. Therefore, a detailed knowledge of the crystal structure is essential for understanding the dielectric properties of these materials.

I have investigated the crystal structure of PMN under high hydrostatic pres-
3.1 Introduction

sures at room temperature and as a function of temperature at ambient pressure. The aim was to obtain quantitative information about the deviation from the centrosymmetric crystal structure that may influence the dielectric properties.

3.1.1 Neutron powder diffraction

Powder diffraction is a powerful technique that allows quantitative information about the chemical structure of a material to be obtained. In a neutron diffraction experiment, neutrons are scattered by nuclei, and by atomic magnetic moments. Since in PMN there are no magnetic moments the interaction is only with the nuclei. For now I shall only consider nuclear scattering. The analytical expression of the coherent elastic cross section that applies in neutron diffraction is as given in Chapter 2:

\[
\frac{d\sigma}{d\Omega} = N_0 \frac{(2\pi)^3}{v_0} \sum_{\tau} |F(Q)|^2 \delta(Q - \tau). \tag{3.1}
\]

The \(\delta(Q - \tau)\) function tells us that the intensity will be found only at the wave vectors \(Q\) equal to the reciprocal lattice vectors \(\tau\). \(F(Q)\) is the structure factor and has the following form:

\[
F(Q) = \sum_d e^{-W_d(Q)} b_d e^{i\tau \cdot d}, \tag{3.2}
\]

where \(b_d\) is the scattering length of the atom located at position \(d\) in the unit cell.

\[
T_d(Q) = e^{-W(Q)} = e^{-\frac{1}{2} \langle (Q \cdot u)^2 \rangle} \tag{3.3}
\]

is known as the temperature factor. If the temperature factors are the same for all the atoms in the unit cell, one can factor out the term \(e^{-W(Q)}\) from the summation in Eq.3.2.

The quantity that affects the scattering cross section is \(e^{-2W(Q)}\) and is called the Debye-Waller factor. This factor is a direct measure of the change in the
scattered intensity due to the thermal vibrations with the displacement \( u \). In
the case of isotropic vibrations an isotropic mean-squared displacement from
the equilibrium position \( u_{iso} = \langle u^2 \rangle \) can be defined. For this simplified case,
by using Eq. 3.3 and replacing \(|Q| = 4\pi \sin \theta / \lambda \) from the Bragg law in Eq. 3.2,
one gets,

\[
W = 8\pi^2 u_{iso} \sin^2 \theta / \lambda^2 = B \sin^2 \theta / \lambda^2,
\]

(3.4)

where \( B = 8\pi^2 u_{iso} \) is called the “B factor” and is an important parameter
that is used in the refinement of the crystal structure.

In many cases the atomic vibrations are not isotropic. To find out the
anisotropic displacements one needs to calculate the dot product \( \langle (Q \cdot u)^2 \rangle \)
from Eq. 3.3. If \( Q = (Q_1, Q_2, Q_3) \) and \( u = (x, y, z) \) is expressed in a Cartesian
coordinate system, then the dot product is:

\[
Q \cdot u = Q_1 x + Q_2 y + Q_3 z,
\]

(3.5)

so that

\[
\langle (Q \cdot u)^2 \rangle = Q_1^2 \langle x^2 \rangle + Q_2^2 \langle y^2 \rangle + Q_3^2 \langle z^2 \rangle + 2Q_1 Q_2 \langle xy \rangle + 2Q_1 Q_3 \langle xz \rangle + 2Q_2 Q_3 \langle yz \rangle,
\]

(3.6)

or in matrix notation:

\[
\langle (Q \cdot u)^2 \rangle = Q^T \langle uu^T \rangle Q,
\]

(3.7)

where \( Q \) is a column vector while \( \langle uu^T \rangle \) is a symmetric 3 \times 3 matrix:

\[
B = \begin{pmatrix}
\langle x^2 \rangle & \langle xy \rangle & \langle xz \rangle \\
\langle yx \rangle & \langle y^2 \rangle & \langle yz \rangle \\
\langle zx \rangle & \langle yz \rangle & \langle z^2 \rangle
\end{pmatrix}.
\]

(3.8)

The \( B \) matrix is called the mean-squared displacement matrix.
In the structural refinements, the anisotropic thermal vibrations are considered as a fraction of the lattice parameters that are not necessarily expressed in a Cartesian coordinate system. To obtain the displacements, a "$\beta$" matrix is used that is of the form:

$$
\beta = \begin{pmatrix}
\beta_{11} & \beta_{12} & \beta_{13} \\
\beta_{12} & \beta_{22} & \beta_{23} \\
\beta_{13} & \beta_{23} & \beta_{33}
\end{pmatrix},
$$

(3.9)

The matrix elements are dimensionless and are related to the atomic displacements by the following expression:

$$
\beta_{ij} = 2\pi^2 a_i^* a_j^* u_i u_i,
$$

(3.10)

where $a_i^*, a_j^*$ are the reciprocal lattice parameters. In the structural refinements the symmetry operations are used to identify the nonzero elements. For example, in this work I have used the $\beta$ matrix to estimate the anisotropic displacements of the $O$ atoms in PMN. For this case the matrix reduces to:

$$
\beta = \begin{pmatrix}
\beta_{11} & 0 & 0 \\
0 & \beta_{11} & 0 \\
0 & 0 & \beta_{33}
\end{pmatrix}.
$$

(3.11)

From the analysis of Eqs 3.1 - 3.11, one can see that neutron diffraction experiments can provide information on the symmetry and size of the unit cell, chemical composition, atomic positions and atomic vibrations in crystals.

### 3.1.2 Principles of the crystal structure refinement

In powder samples, ideally there is no preferential orientation. The sample scatters from all (h,k,l) planes at once. Different crystallographic structure models can be tested by comparing observed and calculated spectra. Equation 3.1 describes the physics of powder diffraction but in order to explain
quantitatively the intensities, one needs to take into account some other factors, such as instrumental resolution. The observed Bragg intensities have a Gaussian rather than delta function type line-shape due to the instrumental resolution. The Gaussian full width at half maximum $\Gamma$ depends on the scattering angle $2\theta$ as follows:

$$\Gamma(2\theta) = \sqrt{Utan^2\theta + Vtan\theta + W},$$  \hspace{1cm} (3.12)

where $U$, $V$, $W$ are instrumental parameters that depend on the particular design of the instrument. The measured values of intensities are also affected by other factors such as absorption of the sample, the angle at which the scattering occurs or by the neutrons that arrive from the environment at the detector position etc. The increase in scattering at low angles is taken into account by the Lorentz factor $L(\theta) = 1/sin\theta sin2\theta$ and the unwanted neutrons that are counted, as background correction. The fact that a set of $(h,k,l)$ planes with different orientation in the crystal are equivalent (with the same planar distance and structure factor ) is taken into account by $m_{hkl}$ the multiplicity of the Bragg reflection. The expression of the intensity is of the form:

$$I_{i,obs} \sim m_{hkl} |F_{hkl}|^2 L(\theta_i) exp \left( -4ln2 \left[ \frac{2\theta_i - 2\theta_{hkl}}{\Gamma} \right]^2 \right).$$  \hspace{1cm} (3.13)

To analyze the data I have used the FullProf program (Rodríguez-Carvajal (1993)) that implements the Rietveld refinement method. Rietveld refinement can be linked to a complex curve fitting problem which is largely constitutes of the minimization of the $\chi^2$ function:

$$\chi^2 = \sum_{i=1}^{n} w_i \left( y_i - y_{c,i}(\alpha) \right)^2,$$  \hspace{1cm} (3.14)

where $y_i$ is the number of counts observed at the scattering angle $i$, $y_{c,i}(\alpha)$ is the calculated intensity function of the parameter vector $\alpha = (\alpha_1, \alpha_2, \alpha_3...\alpha_n)$ and $w_i = \frac{1}{\sigma_i}$, where $\sigma_i$ is the variance of $y_i$.

To judge the reliability of a fit, several agreement factors are defined. There
should be an agreement between the observed and the calculated profiles. This is further extracted from the contribution of the following factors: profile factor $R_p$, weighted profile factor $R_{wp}$, Bragg profile factor $R_B$. They are mathematically expressed as the following:

\[
R_p = 100 \frac{\sum_{i=1,n} |y_i - y_{c,i}|}{\sum_{i=1,n} y_i},
\]

\[
R_{wp} = 100 \left[ \frac{\sum_{i=1,n} w_i |y_i - y_{c,i}|^2}{w_i \sum_{i=1,n} y_i^2} \right]^{1/2},
\]

\[
R_{exp} = 100 \left[ \frac{n - p}{w_i \sum_{i=1,n} y_i^2} \right]^{1/2},
\]

\[
R_B = \frac{\sum_{i} |I_{obs,i} - I_i(calc, i)|}{\sum_i I_{obs,i}},
\]

where $I_{obs,i}$ and $I_{calc,i}$ are the observed and the calculated integrated intensities of a reflection $i$; $n$ is the number of steps in the scan and $p$ is the number of refined parameters. From these parameters, the most meaningful is the $R_{wp}$, because the numerator is the $\chi^2$ that is being minimized. The goodness of a fit $S$ is defined as the ratio between $R_{wp}$ and $R_{exp}$ and the reduced $\chi$-square is the square of $S$. 
3.2 Powder diffraction study as a function of temperature in PMN

In this section I will describe the investigation of the chemical structure of PMN (Rotaru et al. (2008a)) by powder diffraction. The measurements were carried out using the multidetector high-resolution powder diffractometer (HRPT) (Fischer et al. (2000)) located at the SINQ neutron spallation source (Fischer (1997)) at the Paul Scherrer Institut, Switzerland. The aim was to obtain quantitative information about the evolution of the atomic displacements as a function of temperature as part of the systematic investigation of static and dynamic properties of PMN.

A typical pattern taken at 300K and ambient pressure is shown in Fig. 3.2. To begin with a simple Pm\(\bar{3}\)m perovskite model was used to fit the data. The chemical composition was fixed by charge neutrality. The atomic coordinates were set as: \(d_{Pb}=a(0,0,0)\) at \(d_{O_1}=a(0.5,0.5,0)\), \(d_{O_2}=a(0,0.5,0.5)\), \(d_{O_3}=a(0.5,0.5,0)\) with Mg and Nb sharing the position \(d_{Mg/Nb}=a(0.5,0.5,0.5)\) in the center of the \(O\) octahedra. The structural parameters used for fitting were: the cubic lattice parameter \(a = b = c\), the isotropic temperature factor of \(Pb\), Mg/Nb and the components of \(O\)’s thermal ellipsoid (anisotropic factors). The result of the fit is shown in Fig. 3.2a. Visual inspection of the fit shows a satisfactory agreement, but, the temperature factor of the \(Pb\) converges to a nonphysical value of 4.452 Å².

The large value of the B factor suggests the \(Pb\) is displaced. The next step was to allow the \(Pb\) atoms to be displaced from the \((0,0,0)\) position. The high symmetry cubic directions \(<100>, <111>, <110>\) as well as in a random \(<hkl>\) direction were tested. A comparison of the fits is summarized in Table 3.1. Allowing the \(Pb\) atoms to be displaced, the \(B\) factor decreases to 0.9319 Å² for the \(<110>\) direction. If we opt to displace \(Pb\) in a random \(<hkl>\) direction, then we should note that the values of the parameters are the same within the error bars.

When the \(Pb\) atoms are at \(a(x,0,0)\) there is a six-fold degeneracy, at \(a(x,x,x)\) eight-fold, at \(a(x,x,0)\) twelve-fold and at the general position \(a(x,y,z)\) forty-
Figure 3.2: Neutron powder diffraction patterns of PMN collected at 300K. (a) fitted with Pb fixed at (0,0,0) position and (b) fitted with Pb displaced in the <1,1,0> directions.
Table 3.1: Comparison of the fit parameters for different direction of Pb displacements.

<table>
<thead>
<tr>
<th>direction of the shift</th>
<th>Rp</th>
<th>Rwp</th>
<th>Rexp</th>
<th>$\chi^2$</th>
<th>B(Pb) Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;100&gt;</td>
<td>12.8</td>
<td>10.7</td>
<td>3.43</td>
<td>9.69</td>
<td>1.4324(±0.0509)</td>
</tr>
<tr>
<td>&lt;111&gt;</td>
<td>11.9</td>
<td>9.95</td>
<td>3.43</td>
<td>8.41</td>
<td>1.1418(±0.0391)</td>
</tr>
<tr>
<td>&lt;110&gt;</td>
<td>11.7</td>
<td>9.78</td>
<td>3.43</td>
<td>8.11</td>
<td>0.9319(±0.0379)</td>
</tr>
<tr>
<td>&lt;hkl&gt;</td>
<td>11.7</td>
<td>9.77</td>
<td>3.43</td>
<td>8.11</td>
<td>0.9061(±0.0396)</td>
</tr>
</tbody>
</table>

eight fold degeneracy. Keeping this in mind and comparing the $R$ factors ($R_p$, $R_{wp}$, $R_{exp}$), one can easily notice that the quality of the fit improves as the degeneracy increases. In other words the closer the distribution of the Pb atoms is to a sphere the better the fits get.

For the final refinements of the data we chose a model that assumes the Pb to be displaced along <110> direction. The displacements of the O and of Mg/Nb ions were taken into account by their temperature factors. The temperature factor of Mg/Nb ions is isotropic while the $\beta$ matrix of O has only non-zero elements along the diagonal. Figure 3.3 shows the spectra at 410 K and 30 K fitted with the model described above. The agreement between the observed and the calculated spectra is good at these two temperatures as well as the other temperatures that were investigated. However, a decrease of the fit quality at low temperatures can be seen. By comparing visually the spectra at the two temperatures shown in the Fig. 3.3 one can see that the background becomes modulated in the 30 K spectra. The inset in Fig. 3.3 shows more clearly the shoulders around the reflection. This behavior is a signature of the diffuse scattering arising from the short range correlations that developed as the temperature is lowered. To investigate the elastic scattering around the Bragg reflections other experiments have been performed and will be described in the Chapter 4.

In Figs 3.4 and 3.5 the results of the fits are summarized. Figure 3.4a shows the evolution of the displacements of $X_{Pb}$, as a function of temperature and compare it to the lattice parameters in Fig. 3.4b. One observes an important
Figure 3.3: Neutron powder diffraction patterns of PMN collected at 410 K and 30 K, respectively. The spectra have been fitted as described in the text. Note the modulated background at 30 K.

increase of the Pb’s displacements as a function of temperature, whereas the lattice constant remains almost constant. In Fig. 3.5 the evolution of the root mean-square (RMS) displacements as a function of temperature are shown
Figure 3.4: (a) Temperature dependence of the amplitude of Pb displacements $X_{\text{Pb}}$ in PMN; (b) The Pb displacements versus the cubic lattice parameter.

for the Pb, Mg/Nb and for the O atoms. For all atoms, there is a weak temperature dependence of the RMS displacements.

The chemical structure is also pressure dependent. Hence, this study was extended with an investigation under high hydrostatic pressure (Rotaru et al. (2008a)). The experimental procedure and results are discussed in the next section.
3.2. Powder diffraction study as a function of temperature in PMN

Figure 3.5: Temperature dependence of the root mean squares displacements of Pb, Mg/Nb and O.
3.3 Powder diffraction study as a function of hydrostatic pressure in PMN

Measurements at ambient temperature and applied pressure were carried out using $\lambda = 1.4940$ Å. The pressure was applied using opposed-anvil techniques employing a Paris-Edinburgh VX 5 press (details of the experimental setup are described elsewhere (Klotz et al. (2005))). A 4:1 mixture of methanol:ethanol was used to produce hydrostatic conditions within the pressure range. The powder sample had a volume of $30 \ mm^3$. The applied pressures were estimated from the change in the unit cell volume of PMN by using the third-order Birch-Murnaghan equation of state:

$$p = \frac{3}{2}B \left[ x^{-\frac{2}{3}} - x^{-\frac{5}{3}} \right] \times \left\{ 1 - \frac{3}{4} (4 - B') \left[ x^{-\frac{2}{3}} - 1 \right] \right\},$$

(Murnaghan, 1937; Birch, 1947) with $B = 104$ GPa, $B' = 4.7$ taken from Chaabane et al. (2003). $p$ is the pressure and $x = \frac{a^3}{a_0^3}$, where $a$ and $a_0$ are the cubic lattice parameters at the measured pressure $p$ and at a pressure of reference respectively.

Figure 3.6 shows representative diffraction patterns obtained close to ambient pressure and at highest pressure $P = 8.37$ GPa in order to emphasize the changes. Sharp superlattice reflections indexed as $(\frac{h}{2}, \frac{k}{2}, \frac{l}{2})$ ($h, k, l$- odd) have been reported previously by Chaabane et al. (2003) above $\sim 4$ GPa in PMN by X-ray diffraction. Within the statistical accuracy of the present measurements, reflections of this type are not observed. Nonetheless, the chemical structure of PMN is well described by the Pm$\bar{3}$m space group at all pressures.

Figure 3.7 shows the evolution of the $Pb$ displacements along the $<110>$ direction ($X_{Pb}$) and the RMS displacements of Mg/Nb and $O$ in PMN as a function of pressure. All these quantities vary approximately linearly with pressure. The main effects observed in the present study is the significant decrease in amplitude of the $Pb$ displacements and an increase of the anisotropy of the $O$ temperature factors at higher pressures. These results are very similar to
3.3. Powder diffraction study as a function of pressure in PMN

Figure 3.6: Neutron powder diffraction patterns of PMN collected at nominal pressures of (a) $P=0.04$ GPa and (b) $P=8.37$ GPa. Observed data points, calculated profiles and difference curves are shown. The row of ticks corresponds to the calculated positions of diffraction peaks. Peaks at $2\theta=86.5^\circ$ and $128.5^\circ$ are from the cubic boron nitride anvils.
Figure 3.7: (a) Pressure dependence of the amplitude of Pb displacements $X_{\text{Pb}}$ in PMN. (b) Root mean square displacements of the O ions versus applied pressure. The values $U_{O<110>$ of O corresponding to 5.75 GPa and 8.37 GPa were fixed at the minimum positive values in such a way that the reliability factors take minimum values; (c) Root mean square displacements of the Mg/Nb ions vs applied pressure.
those of PbMg$_{1/3}$Ta$_{2/3}$O$_3$, apart from the fact that the RMS displacements of Mg/Ta in PMT were found to increase with increasing pressure (Gvasaliya et al. (2006)) while the RMS displacements of Mg/Nb in PMN do not vary significantly up to $\sim$ 8 GPa. As for PbMg$_{1/3}$Ta$_{2/3}$O$_3$, I analyzed the changes in the anisotropy of the $O$ temperature factors as a function of the amplitude of the $Pb$ displacements combining the pressure and temperature-dependent results. The lattice parameters, the nominal pressures and the amplitudes of the $Pb$ displacements are given in Table 3.2.

Table 3.2: Pressure dependence of the lattice parameter and of the Pb’s displacements.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Lattice parameter (Å)</th>
<th>Pb displacement (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>4.04842(6)</td>
<td>0.223(3)</td>
</tr>
<tr>
<td>1.99</td>
<td>4.02368(6)</td>
<td>0.188(3)</td>
</tr>
<tr>
<td>3.74</td>
<td>4.00376(5)</td>
<td>0.157(3)</td>
</tr>
<tr>
<td>5.75</td>
<td>3.98245(5)</td>
<td>0.128(4)</td>
</tr>
<tr>
<td>8.37</td>
<td>3.9569(1)</td>
<td>0.106(9)</td>
</tr>
</tbody>
</table>

Figure 3.8 shows the evolution of the $<110>$ and the $<001>$ components of the $O$ temperature factor as a function of the amplitude of the $Pb$ displacements $X_{Pb}$. It can be clearly seen that these components are evolving in the opposite directions: the component directed from $Pb$ to $O$ increases significantly with decreasing Pb displacement and the Mg/Nb-O bond exhibits a slight decrease.
Figure 3.8: (a) Components of the O thermal ellipsoid vs. the amplitude of Pb displacements measured as a function of pressure. The values of pressure and corresponding amplitudes of the Pb displacements are given in Table 3.2. (b) Components of the O thermal ellipsoid measured at ambient pressure in the temperature range $T=30 \ K$-$410 \ K$. 
Chapter 4

Diffuse scattering in Pb based relaxors
Chapter 4. *Diffuse scattering in Pb based relaxors*

4.1 Introduction

A very important concept in the physics of relaxors is the existence of polar nanoregions. The polar nanoregions are found to exist in many relaxor ferroelectric systems and were first experimentally shown by Burns and Dacol (1983). They observed that the refractive index departs from a linear behavior when the crystal is cooled down. The temperature at which this phenomena occurs is called the Burns temperature and is denoted in the literature as $T_d$. Burns interpreted this observation as evidence of the creation of randomly distributed polar-nanometer size regions. In a scattering experiment these small regions are seen as diffuse scattering. In Chapter 3, I have presented the powder diffraction study of the chemical structure in PMN. It was found that the Pb is displaced from the $(0,0,0)$ position and the displacements increase as the temperature is lowered. The Pb displacements are accompanied by an increase in the anisotropy of the $O$ temperature factors. Another observation of the study was that the background becomes more and more modulated as the temperature is lowered (see Fig.3.3). The modulation of the background can be an indication of the existence of diffuse scattering.

To find out if there is a correlation between the Pb displacements and the diffuse scattering, systematic studies of diffuse scattering as a function of temperature and pressure in PMN (Rotaru et al. (2009)) and as a function of temperature in PMT (Cervellino et al. (2009)) have been performed. In the following, I will present these investigations and their results.

4.1.1 Diffuse scattering as a function of temperature in PMN

The behavior of the diffuse scattering in PMN as a function of temperature has been studied by many groups. It was found that temperature-dependent diffuse scattering occurs close to $T_d$ and increases upon cooling. Figure 4.1 shows the temperature evolution of the static diffuse scattering intensity as measured at $Q = (1,1,0.05)$ by Gvasaliya et al. (2005). One can interpret the scattered intensity as arising from the static polar regions that develop...
below $T_d$. The increase of the intensity can be explained by an increase of
the number and/or volume of the static polar regions upon cooling. Above
$T_d$ only weak diffuse scattering is found, which is hard to distinguish from
the background and can be interpreted as being due to the intrinsic chemical
disorder that exist in PMN. Here, I will present the results of the neutron
diffuse scattering distribution in PMN.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.1.png}
\caption{Diffuse scattering intensity measured at $Q = (1, 1, 0.05)$ as a function
of temperature in PMN.}
\end{figure}

\textbf{Experimental details.}

Diffuse scattering has been measured from a PMN single crystal in two scat-
ering planes $[1, 0, 0]/[0, 1, 0]$ and $[1, 1, 0]/[0, 0, 1]$. The measurements were
performed with $k_f = 2.662$ Å$^{-1}$ fixed on the triple-axis spectrometer TASP.
The collimation was open–80’ – sample – 80’ – 80’. Most of the measure-
ments were done at 100 K as the intensity of the scattering is higher at low
temperatures. The sample was mounted on a niobium holder and placed in
a cryostat. The use of the analyser on the spectrometer helps to improve
Chapter 4. Diffuse scattering in Pb based relaxors

the signal-to-noise ratio. Thus, the diffuse scattering can be better distinguished from the background. Another advantage in using the spectrometer is that the scattering is strictly elastic. Mesh scans were performed around the $(1,0,0)$, $(2,0,0)$, $(1,1,0)$, $(2,2,0)$ reflections with the crystal oriented in the $[1,0,0]/[0,1,0]$ scattering plane and around $(0,0,-1)$, $(0,0,-2)$, $(1,1,0)$ and $(1,1,1)$ in the $[1,1,0]/[0,0,1]$ scattering plane.

![Figure 4.2: Diffuse scattering measured along $<0,0,1>$ in the $(1,1,0)$ Brillouin zone at 450 K and 275 K respectively. The continuous line is the fit and the bold line represents the Lorentzian function that has been assigned to the diffuse scattering.](image-url)
4.1. Introduction

**Results.** Figure 4.2 shows typical scans taken through $(1,1,0)$ in the $<0,0,1>$ direction. A sharp resolution limited peak and a broad diffuse peak can be well differentiated. The two observed components indicate that there are two types of order. The resolution limited peak originates from the long range order, whereas the broad diffuse scattering corresponds to the static short range order.

![Figure 4.2: Typical scans taken through (1,1,0) in the <0,0,1> direction.](image)

**Figure 4.3:** The distribution of diffuse scattering around the $(1,0,0)$ and $(110)$ Bragg reflections in $[1,0,0]//0,1,0]$ and $[1,1,0]//0,0,1]$ scattering planes. Note that the streaks of intensity are along $<1,1,0>$ directions in the first scattering plane and along $<1,1,2>$ in the second.

The distribution of diffuse scattering is found to be anisotropic in the reciprocal space. A particularly complex distribution is found in some zones, for
example (1,0,0) and (1,1,0) Brillouin zones, where the distribution seem to be "butterfly"-shaped (see Fig. 4.3). The intensities appear to be enhanced along the <1,1,0> directions when measured in the [1,0,0]/[0,1,0] scattering plane and along the <1,1,2> directions in the [1,1,0]/[0,01] scattering plane.

4.1.2 Diffuse scattering as a function of hydrostatic pressure in PMN

This section is focused on the evolution of diffuse scattering as a function of hydrostatic pressure. The hydrostatic pressure influences dielectric properties as well as atomic displacements of PMN as has been previously shown in the Chapter 3.3. Since the average structure is centrosymmetric, the origins of the dielectric properties must be found at a local scale. The short range correlations mentioned before were seen in the X-ray and neutron experiments as diffuse scattering.

Previous studies report a suppression of intensity of the diffuse scattering when using X-rays at high pressure (Chaabane et al. (2003)) and the existence of a pressure induced structural phase transitions in PMN at about 4.5 GPa (Chaabane et al. (2003)), (Kreisel et al. (2002)), (Ahart et al. (2009)).

The aim of the present study was to measure the neutron diffuse scattering as a function of pressure in a single crystal of PMN.

**Experimental details.** The measurements were carried out on TASP cold neutron triple-axis spectrometer at SINQ. For this experiment a 3x3x2 mm$^3$ single crystal of PMN was oriented with the [1,0,0] and [0,1,0] crystallographic directions in the scattering plane. The spectrometer was configured to measure the elastic scattering with $k_f = 1.97$ Å$^{-1}$, collimation was set to open−80′ − 80′ − 80′. The energy resolution was about 0.3 meV.

To apply the pressure, the crystal was embedded in a lead matrix and placed into a Cu-Be gasket. With this configuration, lead acts as a pressure-transmitting medium. The crystal - gasket assembly was then loaded in a Paris-Edinburgh cell. The entire pressure cell is mounted in a cryostat.
4.1. Introduction

The lead matrix in which the sample is embedded is also used as a pressure calibrant, the pressure being determined from the change in the volume of the Pb unit cell using the third-order Birch-Murnaghan equation of state (Eq. 3.19). As the diffuse scattering in PMN is most intense at low temperature (Gvasaliya et al. (2005)), the sample was cooled down to 80 K. The spectra were collected in the (1,0,0) Brillouin zone.

**Results.** The distribution of the diffuse scattering has been measured around the (1,0,0) Bragg reflection at 0.5 GPa and 2.2 GPa. Systematic measurements of the diffuse scattering as a function of pressure were performed along the [1,−1,0] direction in the (1,0,0) Brillouin zone. Note that the diffuse scattering exhibits a butterfly shape in the (1,0,0) Brillouin zone (Xu et al., 2004) with the wings elongated along the <1,1,0> directions.

In Fig. 4.4, the distribution of diffuse scattering around (1,0,0) is shown at 0.5 GPa (a) and 2.2 GPa (b). As one can see, the butterfly shape (see Fig. 4.3) is not observed. This is due to the high background resulting from the sample environment that makes the diffuse scattering indistinguishable from the background at $|q|$ larger than 0.1 rlu.

A better understanding of the evolution of the diffuse scattering can be obtained by comparing the $Q$ scans at different pressures. In Fig. 4.5, for clarity, only two scans at 0.5, and 3.2 GPa measured at 80 K are shown. The spectra contain the Bragg peaks reflecting the long range order present at both pressures. The diffuse scattering decreases with pressure such that at 3.2 GPa only the resolution limited peak is left. The data has been fitted assuming a Gaussian function for the Bragg peak and a Lorentzian function for the diffuse scattering. A summary of the evolution of the diffuse scattering intensity as a function of pressure is shown in Fig. 4.6. Although the pressure dependence of the correlation length of the short-range correlations cannot be resolved, there is a decrease of the intensity of the diffuse scattering. Hydrostatic pressure finally suppresses the polar short-range order around 3 GPa.
Figure 4.4: Normalized diffuse scattering distribution in the (1,0,0) Brillouin zone measured at 80 K under 0.5 GPa-(a) and 2.2 GPa-(b). The diffuse scattering intensity is given on a logarithmic scale.
4.1. Introduction

Figure 4.5: Constant-\(Q\) scans around the \((1,0,0)\) Bragg peak in the \([1,-1,0]\) direction measured at 0.5 GPa and 3.2 GPa respectively. The dashed and solid lines correspond to the fit (see text). Notice the pressure induced suppression of diffuse scattering.

Figure 4.6: Diffuse scattering intensity measured along the \([1,-1,0]\) direction in the \((1,0,0)\) Brillouin zone, normalized to the Bragg intensity of the \((1,0,0)\) reflection taken in two-axis mode is plotted as a function of pressure.
Conclusion. These results indicate that there is a strong correlation between atomic displacements, that give rise to the ferroelectric nanoregions, diffuse scattering and the behavior of the dielectric permittivity in PMN. These results combined with the X-ray data, neutron and dielectric studies provide further evidence that the local structure plays an important role in the dielectric properties of PMN.
4.1.3 Diffuse scattering in PMT

In the previous sections of this Chapter, I have shown the influence of temperature and pressure on diffuse scattering in PMN. Another compound that exhibits similar behavior to PMN is PbMg$_{1/3}$Ta$_{2/3}$O$_3$ (PMT). The appearance of the diffuse scattering is also related to the deviation from the linear behavior of the refractive index at $T_d$ that is 570 K for PMT. Studies of the chemical structure as a function of temperature and pressure have shown that the Pb atoms are displaced from the $(0, 0, 0)$ position. The displacements are found to behave in a similar way to those observed in PMN as a function of temperature and pressure.

The distribution of the diffuse scattering around an extended number of reciprocal points, have been measured for PMT at ESRF using X-rays. Complementarily, the distribution of the scattering intensity around some representative peaks has been measured by neutron scattering. To determine the amplitude and the direction of the Pb displacements a single crystal diffraction experiment has also been performed.

The aim of these measurements was to acquire sufficient information to establish whether or not a microscopic model that takes into account the correlations between Pb displacements can explain the observed diffuse scattering.

In the following the experimental results will be described and then the model that has been developed to analyze the diffuse scattering in PMT.

**Experimental results** The early powder diffraction studies of the chemical structure of PMN and PMT showed that Pb atoms are displaced from the $(0, 0, 0)$ position of the perovskite structure. The displacement $X_{Pb}$ increases with decreasing the temperature, to $\sim 0.22$ Å, in the PMN case, and to $\sim 0.3$ Å in PMT. To determine the Pb displacements, 632 Bragg peaks have been measured at $T=20$ K and $T=300$ K, in a single crystal of PMT on D9 diffractometer at ILL.

As can be seen in Table 4.1 Pb is displaced from the $(0, 0, 0)$ Wykoff position with the displacement being higher at 20 K compared with 300 K.
Table 4.1: Atomic parameters obtained for PMT at $T = 20\, K$. The atomic
displacements are modeled with three split positions for the Pb ions ($\text{Pb}_{<1,0,0>}$ is the
Pb displacements along $<1,0,0>$; $\text{Pb}_{<1,1,0>}$ along $<1,1,0>$ and $\text{Pb}_{<1,1,1>}$ along
$<1,1,1>$). $G$ is the number of ions in the unit cell; $B_{22} = B_{11}, B_{33}$ anisotropic
and $B_{iso}$ isotropic temperature factors in ($\text{Å}^2$).

<table>
<thead>
<tr>
<th>Atom</th>
<th>G</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{11}$</th>
<th>$B_{33}$</th>
<th>$B_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pb}_{&lt;1,0,0&gt;}$</td>
<td>1/3</td>
<td>0.090(4)</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>0.88(7)</td>
</tr>
<tr>
<td>$\text{Pb}_{&lt;1,1,0&gt;}$</td>
<td>1/3</td>
<td>0.056(4)</td>
<td>x</td>
<td>0</td>
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<td>-</td>
<td>0.88(7)</td>
</tr>
<tr>
<td>$\text{Pb}_{&lt;1,1,1&gt;}$</td>
<td>1/3</td>
<td>0.045(3)</td>
<td>x</td>
<td>x</td>
<td>-</td>
<td>-</td>
<td>0.88(7)</td>
</tr>
<tr>
<td>O</td>
<td>3</td>
<td>1/2</td>
<td>1/2</td>
<td>0</td>
<td>1.86(4)</td>
<td>0.960(4)</td>
<td></td>
</tr>
<tr>
<td>Mg/Ta</td>
<td>1</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>0.586(8)</td>
<td></td>
<td>$B_{11}$</td>
</tr>
</tbody>
</table>

$\text{Pb}_{<1,0,0>}$ | 1/3 | 0.076(9) | 0 | 0   | -        | -        | 1.2(2)    |
| $\text{Pb}_{<1,1,0>}$ | 1/3 | 0.05(1)  | x | 0   | -        | -        | 1.2(2)    |
| $\text{Pb}_{<1,1,1>}$ | 1/3 | 0.046(3) | x | x   | -        | -        | 1.2(2)    |
| O          | 3  | 1/2   | 1/2 | 0   | 1.96(7)  | 0.85(7)  |           |
| Mg/Ta      | 1  | 1/2   | 1/2 | 1/2 | 0.62(2)  |           | $B_{11}$  |

The distribution of X-ray diffuse scattering has been measured at the Swiss-
Norwegian Beam Line at ESRF. The measurements have been performed
in the temperature range of 100$<T<$450 K. From the collected data, the
distribution of diffuse scattering in the $[1,0,0]/[0,1,0]$ and $[1,1,0]/[0,0,1]$ scattering planes has been reconstructed. Figure 4.7 shows the reconstruction
of the diffuse scattering at 175 K. We observe an isotropic distribution of the
intensity around the zone boundaries. This scattering is due to the chemical
disorder and is temperature independent. The intensities around the zone
centers are found to be distributed anisotropically. In the $[1,0,0]/[0,1,0]$ scattering plane, the direction of the streaks are along the $<1,1,0>$ directions.
Around the $(H,0,0)$ and $(0,K,0)$ Bragg reflections, the intensity is distributed
along $<1,1,0>$ and $<-1,-1,0>$ directions. In the $[1,1,0]/[0,0,1]$ scattering plane there are streaks of intensities elongated along $<1,1,2>$ (as seen in the
$(1,1,1),(1,1,2)$ Brillouin zones for example) and “butterfly” shaped peaks with
Figure 4.7: The distribution of X-ray diffuse scattering in the \([1,0,0]/[0,1,0]\) and \([1,1,0]/[0,0,1]\) scattering planes as measured at 175 K. Note that the streaks of intensity are elongated along \(<1,1,0>\) in the first scattering plane and along \(<1,1,2>\) in the second scattering plane as indicated by the red lines.
the wings elongated along $<1,1,2>$ and $<-1,-1,2>$ directions respectively (as seen in the (1,1,0) and (0,0,2) Brillouin zones for example).

Let me now compare the distribution of the intensities around some of the reciprocal points that appear in both scattering planes $[1,0,0]/[0,1,0]$ and $[1,1,0]/[0,0,1]$ shown in the Fig. 4.7. Around $(0,0,L)$ one can notice that: i) the direction of the streaks are along $<1,1,0>$ and $<-1,-1,0>$ in the first scattering plane and along $<1,1,2>$ and $<-1,-1,2>$ in the second scattering plane; ii) there is no intensity along the $<1,1,0>$ directions in the second scattering plane.

Around the $(H,H,0)$ reciprocal lattice point we observe that: i) there is only one streak of intensity in the first scattering plane while the intensity is butterfly shaped in the second scattering plane; ii) the intensity is along $<1,1,0>$ in the first scattering plane whereas in the second the wings of intensity are along $<1,1,2>$ and $<-1,-1,2>$ directions; iii) in the second scattering plane there is no intensity along $<1,1,0>$ directions. Therefore, the distribution of the intensity is found to be different along the same direction in the same Brillouin zone in the two scattering planes. Assuming that the intensity arises from the scattering with regions of correlated displacements, previous observations mean that the intensity depends on the direction of the displacements $u$ relative to the orientation of the scattering vector $Q$. The same effect was observed in PMN by Xu et al. (2004), where the diffuse scattering intensity has been considered as proportional with a polarization factor of the form $(Q \cdot u)^2$. This polarization factor is the same as in the phonon scattering, but the neutron measurements revealed that the diffuse scattering is strictly elastic. Consequently, the observed diffuse scattering arises from the correlated static displacements.

**Microscopic model of diffuse scattering.** To model the diffuse scattering it was considered a simplified case in which the polar nanoregions are due to the correlations of the $Pb$ displacements only. The size of the regions can be estimated from the full width at half maximum of the diffuse scattering
peaks. To describe the shape of the polar nanoregions a shape function $S(r)$ has been introduced. The autocorrelation function $G(r)$ of $S(r)$ is

$$G(r) = \int d^3r S(r') S(r - r'), \quad (4.1)$$

and its Fourier transform

$$G(Q) = \int d^3r G(r) \exp(-iQ \cdot r). \quad (4.2)$$

The intensity $I(Q)$ at a given point in the reciprocal point is then given by:

$$I(Q) = |F(Q)|^2 \sum_{\tau} G(Q - \tau), \quad (4.3)$$

where:

$$F(Q) = \sum_j \rho_j(r) \exp(-iQ \cdot r_j), \quad (4.4)$$

is the structure amplitude of one unit cell and $\rho_j(r)$ the scattering density of atom $j$; $\tau$ is a reciprocal lattice vector. For the case of a crystal of limited dimensions, that is not exactly periodic, the total scattering density $\rho(r)$ \footnote{I neglect here Debye-Waller and atomic form factors.} can be decomposed into a mean perfectly periodic structure $\rho_a(r) \propto \delta(r - r_j)$ that has only Bragg peaks and the remaining random density $\rho_b(r) \propto \delta(r - r_j - u) - \delta(r - r_j)$ that gives broad scattering. The atomic distribution in the crystal is therefore:

$$\rho(r) = \rho_a(r) + \rho_b(r). \quad (4.5)$$

If one neglects the interference then $|F(Q)|^2 \approx |F_a(Q)|^2 + |F_b(Q)|^2$. In this approximation the total scattered intensity consists of the superposition of Bragg peaks with broad diffuse components centered around the lattice reciprocal vectors.
Since in the above mentioned approximation only Pb displacements contribute to the diffuse scattering the form factor can be written as:

\[ F_b(Q) = b_{Pb} [e^{-iQ \cdot (r_{Pb} + u)} - e^{-iQ \cdot r_{Pb}}], \]  

(4.6)

where \( b_{Pb} \) is the form factor (including Debye-Waller) of Pb ion in the unit cell. As in our simplified model the cubic unit cell of PMT contains only one ion (Pb) that is displaced from its average site, the form factor of the diffuse intensity reduces to:

\[ |F_b(Q)|^2 = 2b^2_{Pb}[1 - \cos(Q \cdot u)] = 4b^2_{Pb} \sin^2(Q \cdot u/2). \]  

(4.7)

For small values of \( Q \cdot u \), \( |F_b(Q)|^2 \) is proportional with \( (Q \cdot u)^2 \). This dependence differs from the Huang scattering that arises from a small concentration of defects. In this case, the scattering is proportional to:

\[ I_{Huang} \propto (Q \cos(\phi))^2 / q^2 \]  

(4.8)

where \( \phi \) is the angle between the scattering vector \( Q \) and the wave vector \( q \). Figure 4.8 shows the calculated Huang scattering around the (1, 0, 0) Bragg reflection in the [1, 0, 0]/[0, 1, 0] scattering plane. The Huang scattering is enhanced for \( Q \parallel q \) while the diffuse intensity is zero when \( Q \perp q \). As can be seen in the Fig. 4.7, this is not the case in PMT, since the directions of zero intensity are not always perpendicular to the scattering vector.

The expression of the autocorrelation function \( G(r) \) contains the information about the size and the shape of the polar-nanoregions. To describe analytically the shape-function \( S(r) \) is difficult. In the reciprocal space the autocorrelation function determines the line-shape of the scattering.

Figure 4.2 shows the collected spectra taken at 450 K and 275 K are shown. The continuous line describes the fit to the data assuming a sum of Gaussian and Lorentzian line-shapes. The bold line represents a fit of diffuse scattering by a Lorentzian function. Notice that the line-shape of the diffuse scattering is not a Lorentzian. However the line-shape of the intensity follows a \( q^{-\alpha} \) dependence with \( \alpha \) weakly depending on temperature.
Figure 4.8: The calculated Huang scattering intensity around the (1,0,0) reciprocal point in PMT.

The pancake model of Xu et al. (2004) assumes a cylindrical symmetry. The cylinder is oriented along <0,0,1> and is orthogonal to [1,1,0]/[1,−1,0] plane. This model corresponds to ω = 2 along the axis, ω = 3 in the orthogonal plane and higher in the general directions. In our model, we have chosen a more general orthorhombic symmetry with the autocorrelation function given by:

\[ G(r) = e^{-w_1 \cdot r/L_1} e^{-w_2 \cdot r/L_2} e^{-w_3 \cdot r/L_3}, \]  

(4.9)

where \( L_1, L_2, L_3 \) are the average dimensions of the polar nanoregions along the mutually orthogonal directions \( w_i \) (i=1,2,3). The Fourier transform of \( G(r) \), \( G(q) \) is then given by a product of three Lorentzian functions:

\[ G(q) = C \frac{1}{1 + (L_1 w_1 \cdot q)^2} \times \frac{1}{1 + (L_2 w_2 \cdot q)^2} \times \frac{1}{1 + (L_3 w_3 \cdot q)^2}. \]  

(4.10)

\( L_1, L_2 \) and \( L_3 \) can be estimated from the half-width-at-half-maximum of the diffuse scattering peak. Initially it was considered orthorhombic polar regions with the orientation determined by the following unit vectors: \( w_1 = 1/\sqrt{2}[1,1,0], w_2 = 1/\sqrt{2}[1,−1,0] \) and \( w_3 = [0,0,1] \). The displac-
ment has been chosen along $<1,-1,0>$. This model is equivalent with the pancake model of Xu et al. (2004) when $L_1 \ll L_2=L_3$. The model describes well the distribution of intensity in the $[1,1,0]/[0,0,1]$ scattering plane with $L_1 \sim 20\,\text{Å}$, $L_2=L_3 \sim 100\,\text{Å}$. However, in the $[1,1,0]/[0,0,1]$ scattering plane the model does not explain properly the distribution of diffuse intensities e.g. the ”butterfly” shaped diffuse scattering around the $(0,0,1)$ reflection has the wings elongated along $<1,1,1>$ but not along $<1,1,2>$ directions.

The fact that the intensity is elongated along $\pm<1,1,\mp2>$, means that the size of the regions is small in this direction. A simple way to choose the shape of the polar regions with the short size along $<1,1,-2>$ is to take the other two orthonormal vectors along $<1,-1,0>$ (as the intensity is along this direction in the $[1,0,0]/[0,1,0]$) and along $<1,1,1>$. With this choice of shape, the diffuse scattering for $u$ along the $w_1=1/\sqrt{2}[1,-1,0]$, $w_2=1/\sqrt{3}[1,1,1]$ and $w_3=1/\sqrt{6}[1,1,-2]$ axis has been modeled. The best agreement between the model and the experimental observation has been obtained with the displacement along $<1,1,1>$. For this case, there are 12 possible domains given by the Pm$\overline{3}$m space group that contribute to the diffuse intensity. For the displacements along $[1,-1,0]$ and $[1,1,-2]$, the distribution of the intensity around some peaks was incorrect.

Figure 4.9 depicts the calculated diffuse scattering intensities in the two scattering planes in which we have measured. The $Pb$ displacements $u$ has been taken equal to 0.3Å, while $L_1 = 50\,\text{Å}$, $L_2 = 30\,\text{Å}$ and $L_3 = 4\,\text{Å}$.

**Conclusions.** A systematic study of the $Pb$ displacements and of the elastic diffuse scattering distribution in PMT as a function of temperature has been presented. A model that takes into account the correlations between the $Pb$ displacements that leads to the formation of polar nanoregions has been proposed. The model explains well the distribution of the diffuse scattering in the reciprocal space and gives best results when the $Pb$ atoms are displaced in the $<1,1,1>$-type directions.
Figure 4.9: False-color images of calculated diffuse scattering intensities from PMT. (a) in the [H,0,0]/[0,K,0]- and (b) in the [H,H,0]/[0,0,L]-scattering planes. The intensities are given in a logarithmic scale.
Chapter 5

Quasielastic scattering in Pb based relaxors
5.1 Introduction

The investigation of the chemical structure and of the diffuse scattering presented in the previous chapters lead us to the conclusion that mainly the $Pb$ displacements are responsible for the formation of polar nanoregions in the both compounds investigated, namely PMN and PMT. This was evidenced by the evolution of the $Pb$ displacements and of the strictly elastic diffuse scattering as a function of temperature and pressure. The question that arises is whether the polar nanoregions are completely static or there are some dynamic components too. The investigation of the low energy spectra in PMN performed by Gvasaliya et al. (2005) using cold neutrons shows that diffuse scattering has in addition to the strictly elastic component a quasielastic component.

Figure 5.1 shows the inelastic spectra measured in PMN at $Q=(1,1,0.05)$ and 430 K. Strong diffuse scattering can be identified in the spectrum in addition to the transverse acoustic phonon. It consists of two components. The first one is strictly elastic and extended in $q$ as has been described in detail in the previous chapter. It reflects the short-range order of the $Pb$...
atoms that are displaced from the ideal \((0, 0, 0)\) Wyckoff position. The second component is quasielastic (represented by the bold line in Fig. 5.1) and is the result of the scattering with the dynamic polar nanoregions. The temperature dependence of the susceptibility of the quasielastic scattering increases with decreasing temperature and correlates well with the temperature dependence of the dielectric permittivity (see Fig. 5.2). Therefore, the dynamics of the polar nanoregions may play the determinant role to explain the dielectric properties of PMN.

In pure PMN there is no structural phase transition in zero field down to very low temperatures. However, by doping with PT, a structural phase transition occurs. For low concentrations of PT there is a phase transition from cubic to rhombohedral symmetry at low temperature. Upon increasing the amount of PT, a morphotropic phase boundary that separates the rhombohedral phase from a phase with tetragonal symmetry appears at \(x = 0.32\). The term morphotropic refers to the change in the structure due to the change in composition. At this concentration, the dielectric and electrostrictive constants have very high values. For this reason they are used for capacitors and micro-electromechanical applications.

Since these materials are ferroelectric many experiments focused on trying

![Figure 5.2: Temperature dependence of the susceptibility of the quasielastic scattering in PMN measured at \(Q = (1,1,0.05)\). For comparison the real part of the dielectric permittivity of PMN at 1 GHz is also shown. The figure has been taken from Gvasaliya et al. (2005).](image-url)
to identify the soft-mode for the phase transition as found in PT. Gvasaliya et al. (2007) also investigated the diffuse scattering in 0.68PMN-0.32PT. They found a similar behavior as observed in PMN. Diffuse scattering which has an elastic and a quasielastic component occurs. The susceptibility associated with the quasielastic component has a similar behavior as a function of temperature as the real part of the dielectric permittivity.

We have extended the measurements in the (1-x)PMN-xPT family to $x = 0.50$. Moreover due to the similarities between the properties and the phase diagrams of (1-x)PMN-xPT and (1-x)PZN-xPT families we have also investigated the dynamics of the polar nanoregions in (1-x)PZN-xPT with $x = 0.07$ (Rotaru et al. (2008b)) that is close to the morphotropic phase boundary in (1-x)PZN-xPT. In the following, I will first present the results regarding the evolution of quasielastic scattering as a function of temperature in (1-x)PMN-xPT ($x=0.50$) and then the evolution of the quasielastic scattering in (1-x)PZN-xPT ($x=0.07$).

### 5.2 Evolution of quasielastic neutron scattering in 50%PMN - 50%PT

In this section, I will present the results of the neutron scattering investigation in (1-x)PMN-xPT ($x=0.50$). The aim of these measurements was firstly to see whether the diffuse scattering occurs, as observed in the lower -x part of the (1-x)PMN-xPT phase diagram or is absent as in the case of (1-x)PMN-xPT ($x=0.60$) (Stock et al. (2006)). Secondly, we wanted to determine whether the quasielastic susceptibility has a similar temperature dependence as the dielectric permittivity as observed in (1-x)PMN-xPT ($x=0.32$). To address these issues, we have measured the low-frequency portion of the vibration spectrum in (1-x)PMN-xPT ($x=0.50$) in the vicinity of the cubic to tetragonal phase transition at $T_c \sim 520$ K.

**Experimental details.** The experiments were performed with two cold triple-axis spectrometers PANDA and TASP. PANDA is located at the FRM-
II reactor in Munich and TASP at the SINQ spallation source in Villigen. For this experiment, a 10×10×10 mm$^3$ single crystal of (1-x)PMN-xPT (x=0.50) was oriented with the [1,1,0] and [0,0,1] crystallographic directions in the scattering plane. PANDA spectrometer was configured in the constant $k_f$ mode with $k_f = 1.55$ Å$^{-1}$ and the collimation was open−60′−60′−60′. The TASP spectrometer was configured with $k_f = 1.64$ Å$^{-1}$ fixed and the collimation open−80′−80′−80′. A pyrolytic graphite filter was installed in the scattered beam to reduce the contamination by higher-order wavelengths.

Systematic constant-$Q$ scans at $Q=(1, 1, 0.075)$ and constant energy scans at $\hbar\omega=1$ meV have been performed in the temperature range of 373 K to 683 K. At T=523 K we have measured constant-$Q$ scans of the type $Q=(1, 1, q)$, (q=0.05-0.125) in order to determine the q dependence of the diffuse scattering.

**Figure 5.3:** The differential scanning calorimetry spectra measured in (1-x)PMN-xPT (x=0.50). The blue line represents the spectra acquired upon cooling and the red line the spectra upon heating. The arrow indicates the exothermic direction.

Complementary to the neutron scattering experiments, we have measured
the phase transition temperature by using differential scanning calorimetry. Figure 5.3 shows the heat flow dependence as a function of temperature is shown. From the peak position we see that a phase transition occurs at \( \sim 520K \). This temperature is associated with a cubic to tetragonal phase transition.

**Results.** In Fig. 5.4 typical constant-\( Q \) scans measured at \( Q=(1,1,0.075) \) and the constant energy scans at \( h\omega=1\text{meV} \) are shown. As in the 0.68PMN-0.32PT case, in 0.50PMN-0.50PT quasielastic scattering occurs around the zone centers. The quasielastic scattering also has two components originating from the static and dynamic polar regions. In order to extract the information about the changes in the scattering as a function of temperature we have

![Figure 5.4:](image-url) Typical constant-\( Q \) scan and constant energy scan taken at \( T=573 K \) (a, b) \( T=453 K \) (c, d) in 0.50PMN-0.50PT. The bold line emphasizes the contribution of the quasielastic component.
5.2. Evolution of quasielastic neutron scattering in 50%PMN - 50%PT

used a similar approach to that used by Gvasaliya et al. (2007) in (1-x)PMN xPT (x=0.32).

The scattering intensity \( I(Q, \omega) \) at a given temperature is described by the convolution of the scattering function \( S(Q, \omega) \) with the instrumental resolution \( R(Q, \omega) \) plus the background \( B \):

\[
I(Q, \omega) = S(Q, \omega) \otimes R(Q, \omega) + B,
\]

where

\[
S(Q, \omega) = S_{CP}(Q, \omega) + \frac{[n(\omega) + 1]}{\pi} \left[ \chi''_{TA}(Q, \omega) + f_{QE}^2 \chi''_{QE}(Q, \omega) \right]
\]

contains the three spectral components:

1. the resolution limited peak or central peak \( S_{CP}(Q, \omega) \);
2. the transverse acoustic phonon with its imaginary susceptibility \( \chi''_{TA}(Q, \omega) \);
3. the quasielastic scattering with \( \chi''_{QE}(Q, \omega) \).

To model the experimental results we consider a Gaussian function for the central peak and a damped harmonic oscillator function corresponding to the transverse acoustic phonon. The imaginary part of the dynamical susceptibility of the quasielastic scattering has the form:

\[
\chi''_{QE}(\omega, q, T) = \frac{\chi(0, T)}{1 + (q/\kappa)^2} \frac{\omega \Gamma_q}{\Gamma_q^2 + \omega^2},
\]

where \( \Gamma_q = \Gamma_0 + Dq^2 \).

The change in \( \Gamma_q \) as a function of \( q \) is plotted in Fig. 5.5. The fit to the \( \Gamma_q = \Gamma_0 + Dq^2 \) function gives \( D = 23.3 \pm 3.7 \text{ meV } \AA^2 \). To perform the fits \( D \) has been kept constant for all temperatures and both constant-\( Q \) and constant-energy scans were fitted together using Eq. 5.1.
Chapter 5. Quasielastic scattering in Pb based relaxors

Figure 5.5: \( q \) dependence of the full width at half maximum \( \Gamma_q \) of the quasielastic scattering at 523 K in 0.50PMN-0.50PT. The solid line is the fit with \( \Gamma_q = \Gamma_0 + Dq^2 \).

The temperature dependence of the inverse of correlation length \( \kappa \) and of \( \Gamma_0 \) is given in Fig. 5.6. Both \( \kappa \) and \( \Gamma_0 \) decrease as the temperature is lowered from the paraelectric phase, reach a minimum value at the ferroelectric phase transition, and then increase into the ferroelectric phase.

Figures 5.7 - 5.8 show the temperature dependence of the strictly elastic diffuse scattering and of the quasielastic scattering respectively. These spectral components correspond to the scattering from the static and dynamic polar nanoregions respectively. As one can observe, the intensity of the strictly elastic scattering increases as the temperature is lowered in a similar way to that observed in 0.68PMN-0.32PT. However, the intensity is much lower in the 0.50PMN-0.50PT than in the 0.68PMN-0.32PT and no saturation or decrease in the intensity below the phase transition is observed in the temperature range covered. The susceptibility of the quasielastic scattering \( \chi_{QE}(0,T) \) increases upon cooling, reaching a maximum at the cubic to tetragonal ferroelectric phase transition. The intensity then decreases as the polar nanoregions freeze in the ferroelectric phase.

In order to better investigate the changes of the intensity of the quasielastic
5.2. Evolution of quasielastic neutron scattering in 50%PMN - 50%PT

Figure 5.6: Temperature dependence of the line width $\Gamma_0$ and of the inverse of correlation length $\kappa$ in 0.50PMN-0.50PT.

component the intensity at $Q = (1, 1, 0.075)$ and $\hbar \omega = 0.65\text{meV}$ has also been measured as a function of temperature. Figure 5.9 shows the evolution of the intensity measured at this point, together with the evolution of the real part of the dielectric permittivity. This point has been chosen at $(Q = (1, 1, 0.075), \hbar \omega = 0.65\text{meV})$ where the intensity is due to the quasielastic component. It can be expected that the intensity at this point in $(Q, \omega)$-space is a good approximation of the quasielastic scattering behavior.

In conclusion, in (1-x)PMN-xPT (x=0.50) a similar behavior to that in PMN and (1-x)PMN-xPT (x=0.32) was found. Temperature-dependent quasileastic scattering occurs at the zone centers. Its susceptibility has a maximum at a temperature close to the temperature at which the real part of the dielectric permittivity $\varepsilon'$ has the maximum. This is an indication that the quasielastic mode plays an essential role in determining the dielectric properties of (1-x)PMN-xPT (x=0.50) too.
Chapter 5. Quasielastic scattering in Pb based relaxors

Figure 5.7: The temperature dependence of the strictly elastic scattering in \((1-x)\text{PMN}-x\text{PT} \ (x=0.50)\).

Figure 5.8: The temperature dependence of the susceptibility associated with the quasielastic scattering in \(0.50\text{PMN}-0.50\text{PT}\).
Figure 5.9: Temperature dependence of the intensity measured at $Q = (1, 1, 0.075)$ and $\hbar \omega = 0.65$ meV in 0.50PMN-0.50PT. Note that at this point in the ($Q, \omega$) space the scattered intensity comes mostly from the quasielastic scattering. For comparison, the temperature dependence of the real part of the dielectric constant $\varepsilon'$ measured at 10 kHz taken from Kania et al. (2006) is also plotted.
5.3 Evolution of neutron quasielastic scattering in 93%PZN - 7%PT

(1-x)PZN-xPT and (1-x)PMN-xPT families of compounds are very similar. The dielectric permittivities of PMN and PZN have a broad maxima around 265 K and 320 K respectively. This apparent phase transitions occur without changing the average crystal structure that remain centrosymmetric. The most exciting properties for applications occurs at the compositions situated near the morphotropic region in the phase diagram. In the case of (1-x)PZN-xPT this is for x=0.08 while in (1-x)PMN-xPT the morphotropic boundary is at x=0.32.

As seen in the previous chapters the nanoregions in (1-x)PMN-xPT (x=0, x=0.32, x=0.50) are due to the correlation between the Pb displacements. The polar nanoregions are seen in the scattering experiments as diffuse scattering. Using neutron triple axis spectrometry it is found that diffuse scattering in addition to the elastic component has also a quasielastic component. The temperature dependence of the quasielastic component suggested that the dynamics of the polar nanoregions play an important role in the dielectric properties.

As in (1-x)PMN-xPT the dielectric properties of (1-x)PZN-xPT are due to the existence of randomly distributed polar nanoregions below Td. Contrary to what was observed in (1-x)PMN-xPT, Hlinka et al. (2003) reports that the neutron diffuse scattering is entirely static. This observation contradicts the light scattering measurements performed by Jiang and Kojima (2002) in (1-x)PZN-xPT (x=0.09). They reported a relaxation component with a life time in the THz domain, much higher than the resolution of the experiment performed by Hlinka et al. (2003) ~8 GHz.

To address the discrepancy between these studies, the low energy part of the vibration spectrum in (1-x)PZN-xPT (x=0.07) was measured. In the succeeding sub-sections, the experimental details and the results are presented.
Experimental details. A single crystal of $\sim 10 \times 10 \times 10 \text{ mm}^3$ oriented with the $<1\overline{1}0>$ cubic axis vertical to the scattering plane was mounted on a niobium holder. The holder is screwed on a stick that is placed in the furnace. The temperature of the sample was monitored by two thermocouples on two sides of the sample. The experiment was performed on the cold triple-axis spectrometer TASP. The spectrometer operated in the constant $k_f$-mode with $k_f = 1.64 \text{ Å}^{-1}$. A pyrolytic graphite filter was installed in the scattered beam to reduce contamination by higher-order wavelengths. The horizontal collimation was $10'/\text{Å} - 80' - 80' - 80'$. With this setting, the energy resolution was 0.26 meV (0.065 THz).

Systematic constant-$Q$ ($Q = (1, 1, 0.075)$) and constant-energy ($\hbar\omega=1\text{meV}$) scans were performed below and above the ferroelectric phase transition that is $T_c=410\text{K}$. At $T=460\text{ K}$ constant-$Q$ scans of the type $Q = (1, 1, q)$, ($q = 0.0325 - 0.15$) have been measured in order to determine the $q$ dependence of the diffuse scattering.

Data treatment and results. Typical measured scans with $Q = (1, 1, 0.075)$ kept constant and constant energy scans at $\hbar\omega=1\text{meV}$ are shown in Fig. 5.10. The incoherent scattering was measured at high temperature.
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Figure 5.11: The temperature dependences of the damping of the QE scattering $\Gamma_0$ and of the inverse of correlation length $\kappa$ in 0.93PZN-0.07PT.

at $Q = (1, 1, 0.3)$ and subtracted from the data. It has been chosen to measure the constant-$Q$ scans at $Q = (1, 1, 0.075)$ because the line shape allows for an easy identification of the spectral components. Thus, it can be easily modeled. As one can see in Fig. 5.10 (a,b), the inelastic spectra consist of sharp resolution limited peaks centered at the elastic energy transfer, broad quasielastic peaks and the lowest transverse-acoustic phonon.

By comparison of the intensities at the two temperatures at which the scans were acquired: 630 K well above the phase transition and 425 K close to the ferroelectric phase transition, one can see a dramatic difference. At high temperature both the elastic and the quasielastic peaks have a maximum in intensity close to each other while at 425 K the central peak has increased by over an order of magnitude in comparison to the quasielastic peak.

The $q$ dependence of $\Gamma_q$ is obtained from the constant-$Q$ scans taken at 460 K with $q$ varied between 0.0325 to 0.15 rlu.

As previously reported in (1-x)PMN-xPT, $\Gamma_q$ is found to have a $\Gamma_0 + Dq^2$ dependence where $D = 18 \pm 1$ meVÅ$^2$. The parameter $D$ has been kept
constant for all temperatures and both constant-Q and constant-energy scans were fitted together with Eq. 5.1 as described previously in the (1-x)PMN-xPT case.

![Graph](image_url)

**Figure 5.12:** The temperature dependence of the elastic component of the diffuse scattering.

The evolution of the inverse of correlation length $\kappa$ and of $\Gamma_0$ as a function of temperature dependence is given in Fig. 5.11. $\kappa$ is $\sim 0.12 \pm 0.01 \text{ Å}^{-1}$ at 630 K and decreases with decreasing temperature as does the line width of the QE scattering: $\Gamma_0 = 0.48 \pm 0.01 \text{ meV}$ at $T=630$ K and $0.21 \pm 0.01 \text{ meV}$ below $\sim 475$ K, where the dynamics of the polar nanoregions freeze. A similar behavior is observed for the temperature dependence of the width of the central peak in light scattering where $\Gamma_0 \sim 80 \text{ GHz} (\sim 0.3 \text{ meV})$ in the ferroelectric phase. On the other hand, the intensity of the elastic part of the diffuse scattering increases strongly below 600 K and reaches a maximum around $T_c$ (see Fig. 5.12). The temperature dependence of the susceptibility of the QE scattering is shown in Fig. 5.13. $\chi(0,T)$ increases strongly upon cooling below
Figure 5.13: The temperature dependences of the susceptibility $\chi(0,T)$ of the QE scattering and of the dielectric constant $\varepsilon'$ taken from Hosono et al. (2002).

630 K, then reaches the maximum around $T_c$ and finally decreases rapidly in the ferroelectric phase.

In conclusion, diffuse scattering in (1-x)PZN-xPT is found to be similar to that of (1-x)PMN-xPT. The diffuse scattering has two components: an elastic resolution limited component and a quasielastic component. In both families, the susceptibility associated with the quasielastic scattering follows closely the dielectric permittivity. This shows that the quasielastic mode plays an important role in the dielectric properties of the Pb based relaxors.
Chapter 6

Low energy phonons in Pb based relaxors
6.1 Introduction

The appearance of the ferroelectric phase in perovskites that undergo a structural phase transition is described by the soft-mode theory. Spontaneous polarization appears below the Curie temperature. This happens as the ions are displaced and the chemical structure is deformed and loses its center of symmetry. Concomitantly, a structural phase transition occurs at the Curie temperature that results from the condensation of a transverse optic phonon. For example, Fig. 6.1 shows the soft-mode observed in PbTiO$_3$ at the zone center (Shirane et al. (1970)). As the temperature is lowered, the frequency $\omega$ of the transverse optic phonon becomes smaller. The structural phase transition is accompanied by a strong increase of the dielectric permittivity. The dielectric properties are related to the phonon frequencies by the Lyddane-Sachs-Teller relationship:

$$\frac{\omega_L^2}{\omega_T^2} = \frac{\epsilon(0)}{\epsilon(\infty)} \quad (6.1)$$

**Figure 6.1:** Temperature dependence of the soft-mode energy in PbTiO$_3$. $\hbar \omega_0$ at $q = 0$ taken from Shirane et al. (1970).
where $\omega_T$ is the frequency of the lowest transverse optical phonon, $\omega_L$ is the frequency of a longitudinal optic phonon at small wave vectors, $\epsilon(0)$ is the crystal’s static dielectric constant and $\epsilon(\infty)$ is approximately the optical dielectric constant.

From Eq. 6.1 it can be seen that $\epsilon(0) \to \infty$ when $\omega_T \to 0$. In other words one expects that the transverse optic phonon takes small values when the static dielectric constant takes high values. This happens as the crystal goes into the ferroelectric phase from the paraelectric phase.

Based on the Landau theory, Cochran (1959) suggested that the temperature of the frequency soft-mode above the phase transition has the following form:

$$\omega_s^2(q_s, j) = A(T - T_c).$$  \hspace{1cm} (6.2)

where A is a constant that is crystal dependent. This temperature dependence has been found to be correct in $SrTiO_3$ and other perovskites such as $KTaO_3$ and $PbTiO_3$.

The relaxor ferroelectrics have the same perovskite structure and the dielectric permittivity also exhibits a peak as a function of temperature. However, the peak in the dielectric permittivity is broad in temperature and depends on the applied frequency and is not sharp and frequency independent as in the classical ferroelectrics. The maximum of the dielectric permittivity observed in the relaxors is not directly linked with a structural phase transition. In order to understand the macroscopic properties of the relaxors, as with the case of classical ferroelectrics, a lot of effort has been focused on trying to identify the soft-mode that would be responsible for the increase of the dielectric permittivity below 400 K (see Fig. 5.2).

The investigation of the low energy phonon spectra in (1-x)PMN-xPT ($x=0$, $x=0.50$) will be presented here.
6.2 Low energy phonons in PMN

The crystal structure of the PMN crystal is cubic down to the lowest temperatures and undergoes a structural phase transition at 210 K under an applied electric field. The dielectric permittivity is broad in temperature, is frequency dependent and has a maximum at $T_m = 420$ K when measured with a frequency $\nu = 10$ kHz.

The soft-mode theory predicts a softening of the transverse optical phonons at a temperature at which the dielectric permittivity has a maximum. Because of this, many groups have studied the low energy part of the vibration spectrum. However, there were no reports of a clear evidence for the existence of a soft-mode.

The determination of the temperature dependence of the lowest transverse optic mode has been proven to be difficult. The difficulty arises from the fact that at small $q$, the transverse optic phonon overlaps with the strong elastic, the quasielastic and the scattering from the transverse acoustic phonon when measured with the constant-$Q$ method. The debate is thus what happens at small $q$. If one measures the region of small $q$ for the dispersion with the data from constant energy scans the transverse optic mode falls precipitously below a certain $q$, so that the dispersion appears to have an infinite slope. This behavior has been called ”waterfall”. There were suggestions that the $q$ at which this effect occurs is related to the size of the polar nanoregions. However this hypotheses has been rejected because in different zones the waterfall appears at different $q$’s.

To observe directly the soft-mode, one needs to monitor the frequency of the transverse optic mode at the zone center as a function of temperature. Figure 6.2 shows such scans that were measured below 300 K. The spectra is broad, which makes it difficult to accurately determine the peak position of the transverse optic mode. By correcting the experimental data for the temperature factor it is possible to observe the contribution from the transverse optic mode. In Fig. 6.2, the spectra have been fitted by a damped-harmonic-oscillator model.
6.2. Low energy phonons in PMN

Figure 6.2: Inelastic scans measured in PMN at zone center at different temperatures. $h\omega$ is the energy of the phonon, $\gamma$ is the damping and $S$ is the scale factor. The line is the fit to a damped-harmonic-oscillator model.

Figure 6.3 shows the temperature dependence of the transverse optic phonon at $q=0$. The squares are the results of the measurements described above, whereas the circles are the results taken from Stock et al. (2006). The vertical lines drawn in the figure correspond to the $T_c$, $T_m$ and $T_d$ temperatures. No softening of the transverse optic mode above $T_c$ can be observed. Therefore, the peak of the dielectric permittivity cannot be explained as in PbTiO$_3$ by the soft-mode theory. Systematic investigation of the low energy range of
the vibration spectrum of PMN has been performed by inelastic cold-neutron scattering.

**Experimental results and data analysis.** We have investigated systematically the low energy phonon spectra in PMN. It was found that in the (1,0,0) and (1,1,0) Brillouin zones, there is strong scattering centered around the Bragg peaks whereas, in the (2,0,0) and (2,2,0) zones the quasielastic scattering is weaker but the transverse acoustic and optic phonons are strongly enhanced when compared to the previous zones.

Figure 6.4 shows typical inelastic spectra in \( SrTiO_3 \). In addition to the phonon the spectra contains strong elastic scattering around the zone boundary. To describe the central scattering, Shapiro et al. (1972) have used a model which introduced an extra decay channel with an inverse relaxation
Figure 6.4: Temperature dependence of the soft-mode on the left-hand side and of the central peak in the right-hand side in SrTiO\textsubscript{3}. Notice the decrease of the soft-mode frequency and the increase of the central peak intensity as the temperature approaches \( T_c \) (taken from Shapiro et al. (1972)).

Time \( \gamma \) and coupling strength \( \delta \). The damped harmonic oscillator response function \( \chi_{DHO}(q, \omega) \) is written in this case as:

\[
\chi_{DHO}(q, \omega) = \frac{1}{\omega_q^2 - \omega^2 - i \Gamma_\omega \omega},
\]

by choosing the damping to be frequency dependent:

\[
\Gamma_\omega = \Gamma_0 + \frac{\delta^2}{\gamma - i \omega},
\]

where \( \omega_q \) is the phonon energy with the damping \( \Gamma_0 \). However, such a model cannot explain the observation in PMN because it predicts a similar behavior in all zones and does not contain \( q \) dependent damping contrary to the observations from PMN.

Another possible explanation of the appearance of the quasielastic scattering is to consider it as a consequence of the coupling between the transverse acoustic and optic phonons. This type of model has been considered by Gvasaliya...
et al. (2005) for PMN. In the following I will be describing the model used by Gvasaliya et al. (2005). The scattering intensity \( I(\mathbf{Q},\omega) \) at a given temperature is given by the convolution of the scattering function \( S(\mathbf{Q},\omega) \) with the instrumental resolution plus a background \( B \):

\[
I(\mathbf{Q},\omega) = S(\mathbf{Q},\omega) \otimes R(\mathbf{Q},\omega) + B. \tag{6.5}
\]

If one chooses for simplicity only the phonon contribution in the spectra then the scattering function is:

\[
S(\mathbf{Q},\omega) = \frac{[n(\omega) + 1]}{\pi} \chi''_{CM}(\mathbf{Q},\omega), \tag{6.6}
\]

where \( \chi''_{CM}(\mathbf{Q},\omega) \) is the imaginary part of the dynamical susceptibility and \( n(\omega) \) is the Bose-Einstein factor.

The dynamical susceptibility for two coupled modes \( \chi_{CM}(\mathbf{Q},\omega) \) is given by:

\[
\chi_{CM}(\mathbf{Q},\omega) = \frac{f_1^2\chi_1 + f_2^2\chi_2 + 2\lambda f_1 f_2 \chi_1 \chi_2}{1 - \lambda^2 \chi_1 \chi_2}, \tag{6.7}
\]

where \( f_1 \) and \( f_2 \) are the wave vector dependent structure factors for the two phonons. \( \chi_i \equiv \chi_i(\mathbf{Q},\omega), i = 1, 2 \) are the dynamical susceptibilities of the uncoupled phonons and \( \lambda \) is the interaction term given by:

\[
\lambda \equiv (\Delta + i\Gamma_{12}) = (\Delta_{12} + i\omega\gamma_{12})\sin^2(\pi q). \tag{6.8}
\]

At small wave vectors the \( q \) dependence of \( \lambda \) is chosen to be proportional to \( q^2 \). The dynamical susceptibilities of the transverse and of the longitudinal phonons are given by the damped harmonic oscillator functions:

\[
\chi_{DHO}(\mathbf{q},\omega) = (\omega_q^2 - i\gamma_q\omega - \omega^2)^{-1}. \tag{6.9}
\]

where \( \gamma_q \) is the damping and \( \omega_q \) is the renormalized frequency of the phonon.
When the damping is neglected the resonance frequency of the coupled modes is:

\[ \Omega_{1,2}^2 = \frac{1}{2} \left( \omega_1^2 + \omega_2^2 \pm \sqrt{(\omega_1^2 - \omega_1^2)^2 + 4\Delta^2} \right), \]  

(6.10)

where:

\[ \omega_1 \equiv \omega_{TA} = d \sin(\pi q), \]  

(6.11)

and

\[ \omega_2 \equiv \omega_{TO} = \omega_{TO}^2(0) + c \sin(\pi q). \]  

(6.12)

The damping of the transverse acoustic phonon was found to have a \( q \) dependence of the form:

\[ \gamma_{TA} = D_{TA}\sin^2(\pi q), \]  

(6.13)

while the damping of the transverse optic phonon is a fitting parameter.

The model has been applied for (1,1,0), (0,0,1), (2,2,0) and (2,0,0) zones. The numerical parameters resulting from the fit to the data of the coupled model in (2,2,0) are given in Table 6.2 and the agreement with the observations is shown in Figs 6.5, 6.6.

In conclusion, the model that takes into account the coupling between the transverse and optic modes explains well the scattering from the transverse acoustic and optic phonons but does not give rise to the quasielastic scattering. Therefore, the quasielastic scattering can be considered as a distinct mode.
Table 6.1: The results of the fits for PMN.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature 750 K</th>
<th>Temperature 300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1 Acoustic stiffness</td>
<td>10.29 ±0.07</td>
<td>12.55 ±0.24</td>
</tr>
<tr>
<td>$\gamma_1$ Acoustic Damping</td>
<td>3.64 ±0.07</td>
<td>3.26 ±0.29</td>
</tr>
<tr>
<td>$f_1$ Acoustic structure factor</td>
<td>426.0 ±3.0</td>
<td>600.3 ±5.9</td>
</tr>
<tr>
<td>$\omega_2(0)$ Optic Frequency</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$c$ Optic Stiffness</td>
<td>367.9±1.6</td>
<td>315.2±8.7</td>
</tr>
<tr>
<td>$D_2$ Optic Damping</td>
<td>4.96 ±0.09</td>
<td>4.72 ±0.12</td>
</tr>
<tr>
<td>$f_2$ Optic Structure Factor</td>
<td>-412.0 ±4.3</td>
<td>-370.0 ±17.7</td>
</tr>
<tr>
<td>$\Delta_{12}$ Real Coupling</td>
<td>122.0 ±1.9</td>
<td>157.2±3.5</td>
</tr>
<tr>
<td>$\gamma_{12}$ Imaginary Coupling</td>
<td>1.40 ±0.05</td>
<td>1.46 ±0.04</td>
</tr>
</tbody>
</table>
Figure 6.5: Typical constant-$Q$ scans measured at 750 K (left column) and at 300 K (right column) in PMN. The solid line is the result of the fit as described in the text.
Figure 6.6: Typical constant-energy scans at 750 K (left column) and 300 K (right column). The solid line is the result of the fit as described in the text.
6.3 Low energy phonons in 50%PMN-50%PT

In this section, I will be presenting the results of the lattice dynamics investigation in (1-x)PMN-xPT, (x=0.50). This study adds to the investigation of PMN described in the previous section and to the analysis of (1-x)PMN-xPT (x=0.32) by (Gvasaliya et al., 2007). As the results in (1-x)PMN-xPT (x=0.32) were similar to that in PMN it was interesting to see how a further increase of the PbTiO$_3$ concentration influences the dynamical properties in (1-x)PMN-xPT family. In Chapter 5.2, I have shown that in (1-x)PMN-xPT (x=0.50) the quasielastic scattering occurs and its associated susceptibility agrees well with the dielectric susceptibility. This observation suggested that the quasielastic mode plays a role in the dielectric properties of (1-x)PMN-xPT (x=0.50) too. So, the open question is whether the transverse optic mode softens, as is observed in PbTiO$_3$. If this is not the case would a similar coupling model, as applied for PMN and for 0.68PMN-0.32PT explain the data?

**Experimental details.** The experiments were performed on the TASP triple-axis spectrometers. The measurements were performed on the same 10×10×10 mm$^3$ single crystal sample of 0.50PMN-0.50PT as used in the investigation of the temperature dependence of the quasielastic scattering.

The crystal was oriented with the [1,1,0] and [0,0,1] crystallographic directions in the scattering plane. The spectrometer was configured with $k_f = 1.97$ Å$^{-1}$ fixed final wavevector. A pyrolytic graphite filter was installed in the scattered beam to reduce contaminations by higher-order wavelengths. The dispersion of the transverse acoustic and optic phonons was measured in the (0,0,2) zone at 750 K well above the ferroelectric phase transition and at 550 K that is just above $T_c = 520$ K as was determined by differential scanning calorimetry.

**Measurements and data analyses.** Figure 6.7 summarizes the observed scattering arising from the transverse acoustic and optic mode. The distribution of the intensity appears to be similar at both temperatures and one cannot determine whether a soft-mode is present or not. The direct observa-
Chapter 6. Low energy phonons in Pb based relaxors

Figure 6.7: The distribution of the inelastic scattering in 0.50PMN-0.50PT in the (0,0,2) Brillouin Zone at 750 K (left) and 550 K (right). The intensity has been corrected for the temperature factor.

tion of the soft-mode can be seen in the constant-\(Q\) scans taken at the zone center. In 0.50PMN-0.50PT as in PMN the intensity becomes broad and the contribution of the acoustic and optic phonons cannot be distinguished from each other. To try to identify the frequency of transverse optic mode the inelastic spectra at the zone centers have been corrected for the temperature factor. Figure 6.8 shows the corrected spectra at the two temperatures that were measured, 750 K and 550 K respectively. The phonons appear to be shifted between the two temperatures.

To gain further insight into the temperature dependence of the transverse acoustic and optic phonons the data have been fitted to the same model that has been used for PMN and was described in the previous section. The results of the fit are summarized in Table 6.3 and the agreement with the observed data is shown in the Figs 6.9 - 6.12. In order to obtain satisfactory fits for all scans acquired at one temperature, coupling is needed. However, the coupling converged to a different value in 0.50PMN-0.50PT compared with that for PMN. This can be due to the fact that this model has too many parameters and therefore fits with similar quality can be obtained for different
6.3. Low energy phonons in 50%PMN-50%PT

![Figure 6.8: Inelastic scans measured with the scattering vector $Q = (0, 0, 2)$ kept constant at 550 K and 750 K respectively. In the inset the data has been corrected for the temperature factor. Note that there is an apparent softening of the phonons as the temperature is lowered.](image)

combinations of the parameters. As can be seen from the parameters given in Table 6.3, the stiffness of the optic phonon converges to the same value at both investigated temperatures. Therefore, this model shows no softening of the transverse optic mode.

To conclude, the low energy phonons in the cubic phase of the 0.50PMN-0.50PT crystal have been studied. The transverse acoustic and optic modes were found to be coupled. As in PMN and in 0.68PMN-0.32PT to identify if the transverse optic mode softens or not is difficult. However, in 0.50PMN-0.50PT one does observe a shift as a function of temperature of the transverse optic phonon energy measured at the zone center.
Table 6.2: The results of the fits for 0.50PMN-0.50PT.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature 750 K</th>
<th>Temperature 550 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1 Acoustic stiffness</td>
<td>6.7</td>
<td>5.57</td>
</tr>
<tr>
<td>$\gamma_1$ Acoustic Damping</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>$\omega_2(0)$ Optic Frequency</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$c$ Optic Stiffness</td>
<td>461.35</td>
<td>461.35</td>
</tr>
<tr>
<td>$D_2$ Optic Damping</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$\Delta_{12}$ Real Coupling</td>
<td>16.9</td>
<td>16.9</td>
</tr>
<tr>
<td>$\gamma_{12}$ Imaginary Coupling</td>
<td>6.941</td>
<td>6.941</td>
</tr>
</tbody>
</table>
Figure 6.9: Inelastic scans measured with the energy kept constant at 750 K in 0.50PMN-0.50PT. The solid line is the result of the fit as described in the text.
Figure 6.10: Inelastic scans measured with the energy kept constant at 550 K in 0.50PMN-0.50PT. The solid line is the result of the fit as described in the text.
6.3. Low energy phonons in 50%PMN-50%PT

Figure 6.11: Inelastic scans measured with the scattering vector $Q = (0.1, 0.1, 2)$ kept constant at 550 K and 750 K in 0.50PMN-0.50PT. The solid line is the result of the fit as described in the text.

Figure 6.12: Dispersion of the lowest transverse acoustic and optic phonon in the (0,0,2) Brillouin zone in 0.50PMN-0.50PT. Red circles the experimental data; solid lines the dispersion resulting from the model.
Chapter 7

Conclusions and Outlook

Relaxor ferroelectrics are of interest due to their broad field of application. Relaxors exhibit a characteristic set of statical and dynamical properties, but their microscopic origin is not yet fully understood. The aim of this work was to investigate the local structure and lattice dynamics of some representative Pb based relaxors using microscopic probes, such as neutron and X-ray scattering.

I have investigated the chemical structure of PbMg$_{1/3}$Nb$_{2/3}$O$_3$ as a function of temperature and pressure by neutron powder diffraction. I found the Pb ions to be displaced from the (0, 0, 0) position in the perovskite structure. The Pb displacements are strongly influenced by temperature and pressure. The eventual displacements of the Mg/Nb ions were taken into account by their temperature factor. As a function of temperature and pressure only a small change is observed. Regarding the O ions there is a distinct evolution as a function of temperature and pressure. The $<1,1,0>$ and the $<0,0,1>$ components of the O temperature factor are approximately constant as a function of temperature. Under hydrostatic pressure the components of the temperature factor are evolving in opposite directions: the component directed from Pb to O increases significantly with decreasing pressure and the Mg/Nb-O bond exhibits a slight decrease. Despite the large change in the magnitude of the displacements, the crystal structure is well described by the Pm$\overline{3}$m symmetry at all temperatures and pressures investigated. However, as the temperature is lowered, the quality of the fits becomes worse and the background is modulated.
To further investigate the local structure of PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\), single crystal investigations of diffuse scattering as a function of temperature and hydrostatic pressure have been performed. To avoid the integration over the energy and to improve the signal-to-noise ratio, the neutron triple-axis method has been used. The elastic diffuse scattering is found to occur around the Brillouin zone centers. This scattering is temperature dependent and has an anisotropic distribution in the reciprocal space. The line-shape of the intensity of the diffuse scattering is not a Lorentzian function. However, it follows a \(q^\alpha\) dependence and \(\alpha\) changes slightly with temperature. A similar decay of the intensity is observed in magnetic systems that exhibit a random field transition.

Above the Burns temperature, \(T_d\), the diffuse scattering is rather low. From the analyses of the distribution in the reciprocal space, it was possible to conclude that above \(T_d\), diffuse scattering is actually Huang scattering. Below \(T_d\), the diffuse scattering starts to increase rapidly and eventually saturates. For example, in PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\) the strong increase of the diffuse scattering occurs at about \(\sim 420\) K and saturates at about \(\sim 100\) K. This behavior can be related to polar nanoregions that cause the nonlinearity of the refractive index below \(T_d\) in the relaxor ferroelectrics. In other words, the intensity of the elastic diffuse scattering evolves as the number and/or size of the static polar nanoregions change with temperature.

In order to better understand the origin of the diffuse scattering in \(Pb\) based relaxors, the distribution of diffuse scattering in PbMg\(_{1/3}\)Ta\(_{2/3}\)O\(_3\) has been systematically measured by X-ray scattering. The diffuse scattering in PbMg\(_{1/3}\)Ta\(_{2/3}\)O\(_3\) has a similar distribution to that found in PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\). The distribution of the intensity was measured in two scattering planes: \([1,0,0]/[0,1,0]\) and \([1,1,0]/[0,0,1]\). To explain the observed diffuse scattering, a model based on the correlations between the \(Pb\) displacements has been proposed. The model assumes an orthorhombic symmetry for the polar nanoregions. To simulate the diffuse scattering a sum over the contributions of all equivalent domains was considered. The comparison of the simulation with the observed data led to a choice of the shape of the polar regions with the short size along \(<1,1,-2>\) and two long lengths along
<1,-1,0> and along <1,1,1> respectively. The best agreement between the observed and simulated distribution of the diffuse scattering is obtained when the Pb is displaced along <1,1,1> direction.

The dependence of the diffuse scattering as a function of hydrostatic pressure has been measured in PbMg$_{1/3}$Nb$_{2/3}$O$_3$ at 80 K. Diffuse scattering was also found to be strongly influenced by hydrostatic pressure. It decreases with pressure such that at 3.2 GPa, only the resolution limited peak is left. The behavior of the diffuse scattering can be related to that of the peak in the dielectric permittivity and of the Pb displacements under hydrostatic pressure which also decrease with pressure.

The low energy energy part of vibrational spectra in PbMg$_{1/3}$Nb$_{2/3}$O$_3$ was also investigated by neutron inelastic scattering. The measurements revealed that in addition to the strictly elastic scattering previously described, quasielastic scattering occurs around the Brillouin zone centers. In order to understand the origin of this scattering as well as to investigate the changes in the lattice dynamics as a function of temperature, the lowest transverse acoustic and optic phonons were measured. To explain the data, a model that considers the coupling between the acoustic and the optic modes has been used. With such a model it was possible to describe the evolution of the lowest transverse acoustic and optic phonons. The first conclusion of this investigation was that there is no softening of the transverse optic mode when the temperature is lowered from above $T_d$ to the temperature at which the dielectric permittivity has its maximum (as observed in the classical ferroelectric). Hence, the soft mode theory that relates the dielectric permittivity to the frequencies of the longitudinal and transverse optic phonons through the Lyddane-Sachs-Teller relationship, cannot be applied to explain the temperature behavior of the dielectric permittivity of PbMg$_{1/3}$Nb$_{2/3}$O$_3$.

The model of two coupled modes that describes the phonon spectra does not explain the quasielastic scattering. So, this scattering can be considered as a distinct mode, resulting from the scattering from the dynamic nanoregions. To describe the diffuse scattering with the two components, the strictly elastic component and the quasielastic component, the intensity was expressed in
terms of the neutron scattering function which is proportional to the imaginary part of the dynamical susceptibility:

$$\chi''_{QE}(\omega, q, T) = \frac{\chi(0, T)}{1 + (q/\kappa)^2} \frac{\omega \Gamma_q}{\Gamma_q^2 + \omega^2},$$

(7.1)

The full width at half maximum of the quasielastic scattering $\Gamma_q$ and the inverse of the correlation length $\kappa$ were found to diverge at a temperature close to $T_m$. Moreover, the quasielastic susceptibility follows well the temperature dependence of the dielectric permittivity. These results show that the quasielastic mode in PbMg$_{1/3}$Nb$_{2/3}$O$_3$ plays the role of the soft mode in classical ferroelectrics.

In addition to the investigations of the PbMg$_{1/3}$Nb$_{2/3}$O$_3$ model relaxors, the low energy spectra in the solid solutions of PbMg$_{1/3}$Nb$_{2/3}$O$_3$ and PbZn$_{1/3}$Nb$_{2/3}$O$_3$ with PbTiO$_3$, 50%PbMg$_{1/3}$Nb$_{2/3}$O$_3$-50%PbTiO$_3$, and 93%PbZn$_{1/3}$Nb$_{2/3}$O$_3$-7%PbTiO$_3$ were also measured. In these compounds, a similar behavior to that observed in PbMg$_{1/3}$Nb$_{2/3}$O$_3$ was found. Temperature dependent diffuse scattering that has two components, a strictly elastic component extended in $q$ and a broad quasielastic component. The susceptibility associated with the quasielastic scattering follows as well the temperature dependence of the dielectric permittivity. Therefore the quasielastic scattering seems to carry out an important role in the dielectric properties of the Pb based relaxors.

The above results show that relaxors exhibit a complex behavior and that the phase transition is not conventional. However, it can be related to the properties of the static and dynamic (quasielastic) diffuse scattering that arises from the scattering by polar nanoregions. Diffuse scattering observed in relaxors has some similarities to what is observed in magnetism in compounds with random field transitions. The effect of the random field on the phase transition of diluted antiferromagnets has been extensively studied. The random fields in this case can be obtained by applying an uniform external magnetic field (Fishman and Aharony (1979)). In relaxors, the random field may originate from intrinsic random distribution of two ions with different valencies (e.g. in PbMg$_{1/3}$Nb$_{2/3}$O$_3$ is +2 whereas Nb is +5) on the B site of the ABO$_3$
perovskite structure. In a three-dimensional system (as is the case in relaxors), the random field inhibits the realization of the long range order and only finite clusters are formed. Therefore, diffuse scattering will be observed in the random field state. One of the important signatures of the random field transition is the line-shape of the diffuse scattering. If in the conventional phase transitions the line shape of the diffuse scattering is a Lorentzian, in the random fields transition the line-shape is a Lorentzian square (Cowley et al. (1986)). As I have mentioned, we do observe in relaxors a non Lorentzian shape of the diffuse scattering. However, to determine the exact line-shape in relaxors is difficult as other factors are involved (e.g. shape of the polar nanoregions, instrumental resolution). Another feature of the diffuse scattering that suggests that a random field state is realized below the maximum of the quasielastic scattering is the temperature dependence of the correlation length. The correlation length has a history dependent temperature dependence below the random field transition and is expected to diverge at the random field transition. In relaxors the correlation length is found also to diverge at a temperature close to the maximum of the quasielastic scattering. In PbMg$_{1/3}$Nb$_{2/3}$O$_3$, the inverse of the correlation length $\kappa$ saturates below the maximum of the quasielastic susceptibility whereas in 68$\%$PbMg$_{1/3}$Nb$_{2/3}$O$_3$ - 32$\%$PbTiO$_3$, 50$\%$PbMg$_{1/3}$Nb$_{2/3}$O$_3$ - 50$\%$PbTiO$_3$ and 93$\%$PbZn$_{1/3}$Nb$_{2/3}$O$_3$ - 7$\%$PbTiO$_3$ it decreases. The random field scenario also accounts for other phenomena that were observed in relaxors, such as the history dependent phenomena. Therefore, the experimental results presented in this thesis show evidences that the relaxors may exhibit a random field transition. The fluctuations that occur below $T_d$ have slowed down and freeze in the random field state.

As I have discussed, there have been extensive experimental studies of the properties of relaxors properties. Here, I have described the investigation in some key materials with relaxor properties and show that the relaxors may be examples of compounds with a random field transition. Until a theoretical description is available, there will be many experimental aspects left to be explored. First of all, more effort have to be directed towards a more detailed characterization of the phase diagrams as a function of different parameters such as concentration, temperature, pressure and electric field. In
the (1-x)PMN-xPT family of compounds the strictly elastic diffuse scattering have to be characterized as a function of temperature for several more PbTiO$_3$ concentrations. The evolution of diffuse scattering as a function of hydrostatic pressure has been characterized only for PbMg$_{1/3}$Nb$_{2/3}$O$_3$. It will be useful to extend the measurements to other compositions as well as to determine the influence on the dynamics of the polar nanoregions as a function of pressure. Another task will be to measure the evolution of the line shape of the strictly elastic diffuse scattering and of the quasielastic susceptibility as a function of electric field for different concentrations of PbTiO$_3$. This should bring further information about the dynamics of the polar nanoregions. Similar characterization can be extended to other families of relaxors such as (1-x)PZN-xPT and (1-x)PMT-xPT.
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