Polar Nanoclusters in Relaxors: Field Cooled and Zero Field Cooled $^{207}$Pb NMR in PMN

R. Blinc, B. Zalar and V. Laguta

J. Stefan Institute
Ljubljana, SLOVENIA
Perovskite relaxors like PbMg\textsubscript{1/3}Nb\textsubscript{2/3}O\textsubscript{3} (PMN) are intermediate between dipolar glasses and classical ferroelectrics.

They exhibit both substitutional and charge disorder.

Their average symmetry is cubic between 1000 K and 4 K on the macroscopic and microscopic scale, but is broken on the nanoscopic scale.

Burns and Dacol suggested that randomly oriented polar nanoclusters appear below 952 K [PRB 28, 2527 (1983); SSC 13, 423 (1973); Ferroelectrics 104, 25 (1990)] with a size smaller than 500 Å so that they cannot be seen on the profile of X-ray diffraction lines.
FIG. 1. Temperature dependence of the FC quasistatic effective dielectric constant $\varepsilon_{\text{eff}}$ of PMN [111] single crystal at dc bias electric field below critical one and at dc bias electric field just above the critical one. Note the nonlinear increase in $\varepsilon_{\text{eff}}$ at $E < E_c$. Also note the strong discontinuous rise in $\varepsilon_{\text{eff}}$ due to the onset of spontaneous polarization at $T_c$ when $E > E_c$. 

PMN [111]
$E_c = 1.96 \text{ kV/cm}$

FC at
- $E = 0.3 \text{ kV/cm}$
- $E = 0.8 \text{ kV/cm}$
- $E = 1.98 \text{ kV/cm}$
A characteristic difference between dipolar glasses and relaxors is that in relaxors a ferroelectric state appears for $E > E_c$ whereas this is not the case in dipolar glasses.

This difference is obviously due to polar nanoclusters.

Whereas this effect has been so far mainly studied on the macroscopic level, we present here an investigation on the microscopic level by $^{207}$Pb FC and ZFC NMR.
\[ \sigma = \sigma_0 1 \]

Chemical shift is a scalar.

\[ \sigma = \sigma_0 1 + \sigma_a \]

- Chemical shift tensor consists of a scalar part \( \sigma_0 \) and and a traceless second rank tensor \( \sigma_a \).
- For tetragonal or trigonal distortions, \( \sigma_a \) has cylindrical symmetry with largest principal axis parallel to the direction of local polarization \( \vec{p} \); i.e. ion shift.
For a general orientation of the crystal with respect to the direction of the magnetic field \( \vec{B}_0 \) specified by \((\theta, \phi)\) the \(^{207}\text{Pb}(I = 1/2)\) NMR frequencies will be given by:

\[
\nu_{Pb} = \nu_L \left( 1 + \sigma_0 + \sigma_{ZZ}(p, \vartheta, \phi, \theta, \phi) \right)
\]

\( \nu_L \) ... unperturbed Pb nuclear Larmor frequency  
\( \sigma_0 \) ... isotropic part of chemical shift tensor  
\( \sigma_{ZZ} \) ... component of \( \sigma_a \) along magnetic field \( \vec{B}_0 \)  
\( \vartheta, \phi \) ... angles specifying the orientation of \( \sigma_a \) with respect to the crystal fixed frame

\[
\begin{align*}
\sigma_0 &= \sigma_{00} + \sigma_{01} p + \sigma_{02} p^2 + \ldots \quad \text{(no angular dependence)} \\
\sigma_a(p, \vartheta, \phi) &= \sigma_{a0}(\vartheta, \phi) + \sigma_{a1}(\vartheta, \phi)p + \sigma_{a2}(\vartheta, \phi)p^2 + \ldots 
\end{align*}
\]

Generally:

\[
\sigma_{am}(\vartheta, \phi) = C_0^{(m)} + C_4^{(m)} K_4(\cos \vartheta, \phi) + C_6^{(m)} K_6(\cos \vartheta, \phi)
\]

\( K_i(\cos \vartheta, \phi) \) ... cubic harmonic of order \( i \)  
\( p \) ... local polarization  
\( m = 0,1,2 \)

\[
\sigma_{ZZ}(p, \vartheta, \phi, \theta, \phi) = \sigma_a(p, \vartheta, \phi) \frac{4\pi}{5} \sum_{m=-2}^{2} P_{2m}(\theta, \phi) P_{2m}(\vartheta, \phi)
\]

\( P_{2m} \) ... Legendre polinom of order \( l = 2 \)
$^{207}$Pb NMR Lineshapes in PMN

1) Cubic sites:  
   \[ T > T_B \]
   - $\sigma_a = 0$, no static displacements
   - no local polarization $\rho$
   - no angular dependence of NMR line
   - $\delta$-function type lineshape

2) Spherical type distortion  
   (Spherical glass, of Pb shifts  
   SRFRB-model)
   - $\sigma_a \neq 0$
   - distribution of local polarization $W(\rho)$
   - spherical distribution of directions of principal axes of $\sigma_a$
   - no angular dependence of NMR line
   - STATICALLY broadened NMR lineshape

1) Pb shifts in a given direction only \{e.q. [111]\}  
   ("FE cluster" line)
   - $\sigma_a \neq 0$
   - direction of the largest principal axis of parallel to the shift direction $\sigma_a$
   - strong angular dependence of NMR line $P_2(\cos \vartheta, \varphi)$
NMR Intensities and Transition to FE State for $E > E_c$

- The NMR method also allows for a determination of the relative intensities of these two entities.

a) The intensity of the anisotropic NMR line corresponding to “ferroelectric-like” clusters with a Pb shift parallel to [111] in the field cooled data strongly increases for

$$E > E_c = 1.8 \text{kV/cm}, \quad T < T_c = 210 \text{K}$$

b) This increase which is accompanied by a dielectric peak at $T_c$ demonstrates the occurrence of a first order phase transition to a ferroelectric state.

c) About 50% of the crystal volume still remains in the spherical glass matrix state.

d) With decreasing $T$ the volume percentage of the [111] ordered polar clusters remains constant but the size of the domains along [111] increases so that they become visible by X-ray - orientational percolation transition?
Incipient FE transition in PMN

- A similar though smaller increase in the intensity of the anisotropic “FE cluster” line occurs also in ZFC data at $T_c$.

- The concentration of “FE-like clusters” is however below the threshold for a “percolation transition”.

- PMN is thus an incipient ferroelectric.
Evidence for Polar Clusters

1) STATICALLY broadened $^{207}$Pb NMR line below $T_B$
   - spherical distribution of $^{207}$Pb shifts and directions of the largest principal axes of
   - exchange between different directions of Pb-shifts on all time scales
   - isotropic $^{207}$Pb NMR spectrum od Gaussian shape

2) $T_f \approx 250 \text{ K}$: “Freeze-out” of exchange ($T_2$ minimum)

3) Below 205 K:
   - an “anisotropic” component appears in the NMR spectrum in addition to the “spherical” one
   - Pb-shift parallel to [111] direction
   - effect strongly increases if $E > E_c \parallel [111]$ and signals transition to FE state.

4) second $T_2$ minimum at $\approx 140 \text{ K}$ for $E > E_c$
   - evidence for orientational domain wall motion
$T_2$ and Nanocluster Dynamics

- $T_2(\omega \to 0)$ is by three orders of magnitude shorter than $T_1(\omega = 79.4 \text{ MHz})$ but has the same $T$-dependence. Cluster fluctuations on all time scales.

- $T_2$ minimum occurs around $T_f = 255 \text{ K}$ where the maximum of dielectric susceptibility occurs - same mechanism for $T_2$ and dielectric losses. Orientational fluctuations of the nanocluster polarization.

- Above 250 K, $T_2$ only weakly depends on the frequency off-set. Nanocluster dynamics similar in different parts of the crystal, fast exchange, no difference between FC and ZFC data.

- Below 250 K, $T_2$ depends on the frequency off-set. Freezing of polar clusters, two-component system.

- Below 200 K, a difference between Fc and ZFC data appears related to “ferroelectric-like” [111] Pb shifted clusters.

- Abound 140-150 K a $T_2$ minimum appears in the Fc data in the FE phase. Motion of domain walls of [111] clusters of the orientational percolation transition. It is absent in the ZFC data.
Dynamics of Polar Nanoclusters

1) $T > T_B$
   - no static polar clusters exist
   - purely dynamic correlations
   - no static Pb shifts

2) $T_B > T > T_f$
   - quasi-dynamic phase
   - condensation of polar clusters for $T \leq T_B$
   - static Pb shifts
   - reorientational dynamics possible between different equivalent cluster orientations on all time-scales
   - distribution of local polarization of spherical type

3) $T < T_f$
   - frozen phase
   - most of cluster reorientational motion has stopped
   - spherical glass (static)