Effect of polar nanoregions on giant electrostriction and piezoelectricity in relaxor ferroelectrics

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The role of polar nanoregions in relaxor ferroelectrics of lead magnesium niobate type is investigated in the framework of the spherical random bond–random-field model. Assuming that the interaction between polar nanoregions is modified by a homogeneous lattice stress, an expression for the macroscopic electrostrictive coefficients is obtained. A simple relation between the hydrostatic electrostrictive coefficient and the pressure derivative of the effective transition temperature and the Curie constant is derived.

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Relaxor ferroelectrics are characterized by a large electrostrictive response and a giant piezoelectric effect in the applied electric field. So far, the microscopic origin of these phenomena has not been fully understood. It has recently been suggested that the leading mechanism of electrostriction in Pb(Mg_{1/3}Nb_{2/3})O_3 (PMN) and related systems are the charge-transfer fluctuations occurring in Mg-rich regions on localized pairs and/or triads of Nb and O ions. Meanwhile, nanosized polar regions, which are known to exist in relaxors, are believed to be responsible for the relaxor freezing phenomena observed in the linear and nonlinear dielectric response and in NMR line shape. Thus, the question arises whether the same polar nanoregions may also play a key role in electrostriction and piezoelectricity. To answer this question we use a semimicroscopic approach, which is based on the polar nanoregion picture in the framework of the so-called spherical random bond–random-field (SRBRF) model of relaxors. We derive an expression for the electrostrictive response and a giant piezoelectric effect in the framework of the spherical random bond–random-field (SRBRF) model. Assuming that the interaction between polar nanoregions is modified by a homogeneous lattice stress, an expression for the macroscopic electrostrictive coefficients is obtained. A simple relation between the hydrostatic electrostrictive coefficient and the pressure derivative of the effective transition temperature and the Curie constant is derived.

The starting point of the present discussion is the SRBRF model of relaxor ferroelectrics, which is based on the interacting polar nanoregions picture. The model Hamiltonian is written as

$$\mathcal{H} = - \frac{1}{2} \sum_{\tau \neq j} \sum_{\mu} J_{ij} S_{i\mu} S_{j\mu} - \sum_{\mu} h_{i\mu} S_{i\mu} - g \sum_{ij} E_{\mu} S_{i\mu},$$

where $S_{i\mu}$ ($\mu = 1, 2, 3$) are components of the dimensionless dipole moment field $\vec{S}_i$ subject to the spherical condition $\Sigma_i (\vec{S}_i)^2 = \alpha N$ (here we set $\alpha = 1$). The first term represents random bonds $J_{ij}$, which have a Gaussian distribution with mean value $[J_{ij}]_0 = J_0/N$ and variance $J^2/N$, while the Gaussian random fields $h_{i\mu}$ in the second term have zero mean and variance $\Delta$. Finally, $g$ is the average dipole moment of a polar nanoregion, and $\vec{E}$ the applied electric field.

Under the action of a homogeneous stress field $\vec{X}_{\mu\nu}$ both the dipole moment $g$ and the intercluster coupling $J_{ij}$ will, in general, be modified. Ignoring for the moment the stress dependence for $g$, we can write down an additional stress modulated interaction term

$$\delta \mathcal{H}_J = \frac{1}{2} \sum_{\mu, \nu} m(\mu) \mu \nu \sigma X_{\mu\sigma} S_{\mu},$$

Here the parameters $m(\mu) \mu \nu$ represent stress derivatives of the interaction $J_{ij}$, which are defined by the expansion

$$J_{ij}(\sigma) = J_{ij} \delta_{\mu\nu} + \sum_{\rho \sigma} m(\mu) \nu \sigma X_{\mu\rho\sigma} + \cdots.$$ 

The phenomenological electrostrictive coefficients $Q_{\mu \nu \sigma}$ are defined by the relation between the equilibrium strain $x_{\mu\nu}$ and the dielectric polarization $P_\mu$, namely,

$$x_{\mu\nu} = \sum_{\rho \sigma} Q_{\mu \nu \sigma} P_\rho P_\sigma.$$ 

Note that strains are related to the stress tensor by the elastic compliance tensor $s_{\mu \nu \rho \sigma} = C_{\mu \nu \rho \sigma}^{-1}$, i.e., $x_{\mu\nu} = \sum_{\rho \sigma} s_{\mu \nu \rho \sigma} X_{\rho \sigma}$. Where $C_{\mu \nu \rho \sigma}$ are the elastic constants. In relaxors with average cubic symmetry there are three independent coefficients $Q_{11}$, $Q_{13}$, and $Q_{44}$.

Rather than trying to calculate the equilibrium strains by minimizing the free-energy functional determined by the above Hamiltonian $\mathcal{H} + \delta \mathcal{H}_J$, we focus on the thermodynamic Maxwell relation $^6,7$

$$Q_{\mu \nu \sigma} = - \frac{1}{2} \left( \frac{\partial X_{\mu \nu}^{-1}}{\partial X_{\mu \sigma}} \right)_{\rho \tau},$$

where $X_{\mu \nu}^{-1}$ are elements of the inverse of the general susceptibility tensor $X_{\mu \nu}$ defined by the relation $P_\mu = \sum_{\nu} X_{\mu \nu} E_\nu$.

The linear susceptibility $X_{\mu \nu}$ can then be calculated from the SRBRF model (1) using the replica approach. In zero external field we obtain the result$^2$

$$X_{\mu \nu} = \delta_{\mu \nu} \left( \frac{g^2}{v_c} - \frac{\beta (1-q)}{1 - \beta J_0 (1-q)} \right),$$

where $\beta = 1/kT$ and $q$ is the spherical glass order parameter. The above expression corresponds to the static field-cooled dielectric susceptibility, to be distinguished from the real part of the low-frequency complex dielectric permittivity, which shows a different behavior below the freezing tem-
temperature. At constant polarization, the stress dependence of $\chi$ will mainly arise from the stress modulation of the coupling parameter $J_0$ resulting from the expansion (3), where it should be kept in mind that the order parameter $q$ is independent of $J_0$ for $T > J_0 k$. An estimate of the stress dependence of the dipole moment $g$ indicates that this effect is of minor importance. Moreover, it would lead to temperature dependent electrostrictive coefficients $Q \approx 1/\chi$, contrary to experiments in PMN. It should be noted, however, that the ferroelectric transition in these systems is of first order and may not be described by a simple mean-field theory. First-principles calculations\textsuperscript{13} show that both fluctuations and strain coupling are required for producing the first-order transition in PbTiO$_3$. In case of a first-order phase transition, the actual transition temperature $T_c$ is generally higher than $T_c$, and its pressure dependence $dT_c/dP$ also differs from $dT_c/dP$\textsuperscript{12}.

To obtain a general form of the susceptibility tensor $\chi_{\mu \nu}$, we derive a stress dependent coupling parameter matrix $J_0(X)_{\mu \nu}$ by performing a random average on Eq. (3) and introducing $m_{\mu \nu \rho \sigma}/N=[m(\mu \nu \rho \sigma)_{\text{av}}]$. This will lead to an expression for $\chi_{\mu \nu}$ analogous to Eq. (6) with $X$-dependent coupling $J_0$. To lowest order, $\chi_{\mu \nu}$ is linear in $X_{\mu \nu}$ and we can easily evaluate the derivative in Eq. (5), leading to the result

$$Q_{\mu \nu \rho \sigma} = \frac{\nu_c}{2g^2} m_{\mu \nu \rho \sigma}. \quad (7)$$

This simple expression relates the macroscopic electrostrictive coefficients $Q_{\mu \nu \rho \sigma}$ to the mesoscopic stress coupling parameters $m_{\mu \nu \rho \sigma}$.

Let us first consider the case of hydrostatic pressure $X_{\mu \nu} = -\rho \delta_{\mu \nu}$ in Eqs. (5)–(7). The corresponding stress derivative is $m_{\mu \nu} = -dQ/dP$, and the appropriate electrostrictive coefficient is given by $Q_h$. The value of $m_{\mu \nu}$ can be estimated from the measured pressure derivative of the static dielectric constant at high temperatures. Since at high temperatures $q \ll 1$, it follows from Eq. (6) that the field-cooled static dielectric constant behaves as $\approx 7,11 e_c \sim C_e/(T-J_0/k)$, where the Curie constant $C_e$ is given by $C_e = g^2/(k e_0 \nu c)$. Thus, we conclude that $J_0/k$ asymptotically plays the role of an effective Curie-Weiss temperature $T_c = J_0/k$, and therefore $m_{\mu \nu}$ is given by the experimental value of the pressure derivative of $T_c$.\textsuperscript{7} Namely, $m_{\mu \nu} = -k(dT_c/dP)$. This leads to the following relation:

$$Q_h = -\frac{1}{2} \frac{dT_c dp}{\varepsilon_0 C_e}. \quad (8)$$

The experimental values of $C_e$ and $dT_c dp$ in PMN are $7,11 C_e = 4.5 \times 10^{10}$ K and $dP dp = -4.8 \times 10^{-9}$ K m$^2$/N. This immediately yields $Q_h = 0.60 \times 10^{-2}$ m$^4$/C$^2$, in perfect agreement with the experimental value of $Q_h$ (see Table I).

In fact, the above derivations are not limited to the SR-BRF model, but are as well applicable to the classical random field model, which is formally described by the same type of Hamiltonian, but with a different constraint on the order parameter field. Our analysis is based on mean-field type arguments, which are valid in random systems with infinite range such as spin and dipolar glasses. As shown in Ref. 7, Eq. (8) is also applicable to ferroelectric perovskites, in which the high temperature dielectric constant obeys the Curie-Weiss law $e_c \sim C_e/(T-T_c)$, where $T_c$ is the Curie-Weiss temperature, for example, in BaTiO$_3$ and PbTiO$_3$.\textsuperscript{12} It should be stressed, however, that the ferroelectric transition in these systems is of first order and may not be described by a simple mean-field theory. First-principles calculations\textsuperscript{13} show that both fluctuations and strain coupling are required for producing the first-order transition in PbTiO$_3$. In case of a first-order phase transition, the actual transition temperature $T_c$ is generally higher than $T_c$, and its pressure dependence $dT_c dp$ also differs from $dT_c dp$\textsuperscript{12}.

In Table I we have summarized the values of $Q_h$ calculated from the published experimental data on $dT_c dp$ and $C_e$ for relaxors PMN and Pb(Zn$_{1/3}$Nb$_{2/3}$)$_2$O$_3$, as well as for normal perovskite ferroelectrics BaTiO$_3$ and PbTiO$_3$. The agreement with the experimental values of $Q_h$ is in all cases rather good.

In analogy to Eq. (8) we can write down the result for the components $Q_{kl}$ of the electrostrictive tensor, i.e.,

$$Q_{kl} = \frac{m_{kl}}{2k e_0 C_e}. \quad (9)$$

From the experimental values of $Q_{11}$ and $Q_{12}$ in PMN (Ref. 7) we can now estimate the values of the corresponding stress coupling coefficients $m_{kl}$. The result: $m_{11}/k = 2.0 \times 10^{-8}$ K m$^2$/N and $m_{13}/k = 7.6 \times 10^{-8}$ K m$^2$/N.

We can now also estimate the magnitude of the interaction term (2) in the Hamiltonian. A typical value of the electrostrictive strain is $x_1 \sim 10^{-4}$,\textsuperscript{6} corresponding to a stress $X_1 \sim 1.6 \times 10^7$ N/m$^2$. This gives an interaction energy $m_{11}X_1/k \sim 3.2$ K, which is small compared to the value of $J_0/k \sim 200$ K.

It should be added that in this approach we have considered only the field induced electrostriction, i.e., the polarization components $P_{\mu}$ in Eq. (4) appear as a response to an applied field. In addition to this effect, random fields contained in the Hamiltonian (1) may give rise to local

<table>
<thead>
<tr>
<th>Substance</th>
<th>$dT_c dp$ ((10^{-8} \text{ K m}^2/\text{N}))</th>
<th>$C_e$ ((10^6 \text{ K}))</th>
<th>$Q_h^{\text{calc}}$ ((10^{-2} \text{ m}^4/\text{C}^2))</th>
<th>$Q_h^{\exp}$ ((10^{-2} \text{ m}^4/\text{C}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td>-4.8, Ref. 12</td>
<td>1.5, Ref. 6</td>
<td>1.8</td>
<td>2.0, Ref. 7</td>
</tr>
<tr>
<td>PbTiO$_3$</td>
<td>-7.1, Ref. 12</td>
<td>1.0, Ref. 6</td>
<td>4.0</td>
<td>3.7, Ref. 6</td>
</tr>
<tr>
<td>Pb(Zn$<em>{1/3}$Nb$</em>{2/3}$)$_2$O$_3$</td>
<td>-5.5, Ref. 7</td>
<td>4.7, Ref. 6</td>
<td>0.66</td>
<td>0.66, Ref. 7</td>
</tr>
<tr>
<td>Pb(Mg$<em>{1/3}$Nb$</em>{2/3}$)$_2$O$_3$</td>
<td>-4.8, Ref. 7</td>
<td>4.5, Ref. 7</td>
<td>0.60</td>
<td>0.58, Ref. 7</td>
</tr>
</tbody>
</table>
strains of different symmetries. It is known, however, that random fields in relaxors are relatively weak compared to dipolar glasses. A typical value of the random-field variance in relaxors is given by $\Delta J^2 = 0.001$. It is possible that random-field-induced distortions are responsible for the recently discovered X phase in Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$, which consists of a nearly cubic lattice with slight tetragonal distortion.

An interesting problem, which will be left for future investigations, is the microscopic origin of Eq. (2). As shown in Ref. 15, one can derive an effective intercluster coupling $J_{ij}$ by considering the dipole-phonon interaction. After transforming away the phonon coordinates, one obtains an expression for $J_{ij}$ proportional to the square of the interaction strength divided by the square of the phonon frequencies.

The stress—or strain—dependence of $J_{ij}$ is expected to be mainly due to lattice anharmonicity, which results in a shift of phonon frequencies under applied stress. An analogous mechanism could then be responsible for the coefficients $m(i)_{\mu\nu\rho}$.

The piezoelectric coefficients $d_{\mu\nu\rho}$ are defined, as usual, by the relation

$$d_{\mu\nu\rho} = 2\chi \sum_{\sigma} Q_{\mu\nu\rho\sigma} P_{\sigma}.$$  

Substituting the electrostriction coefficients from Eq. (8) and using the relation $P_{\sigma} = \chi E_{\sigma}$, we have for $d_{11} = d_{111}$ in a cubic system:

$$d_{11} = \frac{m_{111}}{k_e C_e} \chi^2 E_1.$$  

An analogous relation holds for $d_{13}$.

The field dependence of $d_{11}(E)$ can now be obtained by calculating $\chi(E)$ from the SRBRF model. To lowest order of perturbation theory this can be done in the usual manner, i.e., by ignoring the extra term $\partial H_j / \partial e$ in the Hamiltonian. To illustrate the behavior of $d_{11}(E)$ at different temperatures, we plot in Fig. 1 the dimensionless ratio $d_{11}/D_{11}$ versus $E/E_c$, where $D_{11} = m_{111} k_e^2 C_e / J^2 \sim 3.32 \times 10^{-12}$ m/V for PMN, and $E_c \sim 0.2 \times 10^6$ V/m is the critical field, which induces a relaxor-to-ferroelectric transition. At small values of the field, $d_{11}$ increases quasilinearly with $E$; for $T/J = 1.33$ it reaches a maximum at $E/E_c \leq 5$, and falls off with $E$ at larger fields. This behavior is qualitatively similar to that of PMN ceramics.

A similar result for $d_{11}$ as a function of field and temperature has been obtained earlier from a local mechanism based on the charge-transfer fluctuations (CTF’s) in isolated pairs and triads of Nb and O ions occurring in Mg rich regions in

PMN.$^1$ The same CTF mechanism predicts that $Q_{13} = -Q_{11}/2$ and $d_{13} = -d_{11}/2$, whereas no such constraints appear in the present mechanism based on stress modulation of the interaction between polar nanoregions.

In the present approach, the strong piezoelectric effect is simply due to the large value of the dielectric susceptibility $\chi$ in relaxors. It has been shown, however, in a microscopic first-principles study$^{17}$ that a polarization rotation mechanism$^{18}$ is responsible for the ultrahigh piezoelectric response observed in mixed single crystals such as PZN-PT and PMN-PT. It is not clear at present whether local effects or long-range dipolar interactions are a key factor in the polarization rotation mechanism.

In conclusion, polar nanoregions seem to play an important role in electrostriction phenomena in relaxors. The main effect is due to the interactions between polar nanoregions, which are modified by the local stress tensor. A simple formula relating the hydrostatic electrostrictive coefficient with the stress derivative of the effective critical temperature and the Curie constant has been obtained, which does not contain any adjustable parameters and is also applicable to other perovskite-type systems.

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Assuming that the strain derivative of the dipole moment \( g' \) yields the main contribution to \( Q \), we find \( g' = gC_{el}Q \), where \( C_{el} \) is the elastic constant. It follows that the logarithmic derivative \( g'/g \) should have a colossal value \( \sim 560 \) in order to reproduce the observed value of \( Q \) at \( T = 200 \) K.


G. A. Samara, Ferroelectrics 2, 277 (1971). Note that we write \( T_c \) and \( T'_c \) for \( T_0 \) and \( T_c \) of Samara, respectively.


