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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 $\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}$ (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.[1] 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.[2–5] We derive an expression for the electrostrictive coefficients in terms of a microsocopic stress coupling term in the Hamiltonian. The field and temperature dependence of piezoelectric coefficients is then calculated using the SRBRF model.

The starting point of the present discussion is the SRBRF model of relaxor ferroelectrics,[2–5] which is based on the interacting polar nanoregions picture. The model Hamiltonian is written as

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

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 $[J_{ij}]_{av}=J_0/N$ and variance J^2/N, while the Gaussian random fields $\vec{h}_i$ in the second term have zero mean and variance Δ. 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 $X_{\mu\nu}$ 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

$$\delta\mathcal{H}_J=-\frac{1}{2}\sum_{i\neq j}\sum_{\mu\nu\rho\sigma}m(ij)_{\mu\nu\rho\sigma}X_{\rho\sigma}S_{i\mu}S_{j\nu}.\tag{2}$$

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

$$J_{ij}(X)_{\mu\nu}=J_{ij}\delta_{\mu\nu}+\sum_{\rho\sigma}m(ij)_{\mu\nu\rho\sigma}X_{\rho\sigma}+\cdots.\tag{3}$$

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

$$x_{\mu\nu}=\sum_{\rho\sigma}Q_{\mu\nu\rho\sigma}P_\rho P_\sigma.\tag{4}$$

Note that strains are related to the stress tensor by the elastic compliance tensor $s_{\mu\nu\kappa\lambda}=C^{-1}_{\mu\nu\kappa\lambda}$, i.e., $x_{\mu\nu}=\Sigma_{\kappa\lambda}s_{\mu\nu\kappa\lambda}X_{\kappa\lambda}$, where $C_{\mu\nu\kappa\lambda}$ are the elastic constants. In relaxors with average cubic symmetry there are three independent coefficients Q_{mn} (in Voigt notation): 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]

$$Q_{\mu\nu\rho\sigma}=-\frac{1}{2}\left(\frac{\partial\chi^{-1}_{\mu\nu}}{\partial X_{\rho\sigma}}\right)_{P,T},\tag{5}$$

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

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

$$\chi_{\mu\nu}=\delta_{\mu\nu}\left(\frac{g^2}{v_c}\right)\frac{\beta(1-q)}{1-\beta J_0(1-q)},\tag{6}$$

where $\beta\equiv1/kT$ and q is the spherical glass order parameter. The above expression corresponds to the static field-cooled dielectric susceptibility,[8] to be distinguished from the real part of the low-frequency complex dielectric permittivity, which shows a different behavior below the freezing tem-

TABLE I. Comparison between calculated values, Q_h^{calc} from Eq. (8), and experimental ones listed in Refs. 6 and 7, Q_h^{exp}, of hydrostatic electrostrictive coefficients in some perovskite-type crystals.

Substance	dT_c/dp (10^{-8} K m^2/N)	C_ϵ (10^5 K)	Q_h^{calc} (10^{-2} m^4 C^{-2})	Q_x^{exp} (10^{-2} m^4 C^{-2})
$BaTiO_3$	−4.8, Ref. 12	1.5, Ref. 6	1.8	2.0, Ref. 7
$PbTiO_3$	−7.1, Ref. 12	1.0, Ref. 6	4.0	3.7, Ref. 6
				2.2, Ref. 7
$Pb(Zn_{1/3}Nb_{2/3})O_3$	−5.5, Ref. 7	4.7, Ref. 6	0.66	0.66, Ref. 7
$Pb(Mg_{1/3}Nb_{2/3})O_3$	−4.8, Ref. 7	4.5, Ref. 7	0.60	0.58, Ref. 7

perature. At constant polarization, the stress dependence of χ 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 $T > J_0/k$.[2] An estimate of the stress dependence of the dipole moment g indicates that this effect is of minor importance.[9] Moreover, it would lead to temperature dependent electrostrictive coefficients $Q \propto 1/\chi$, contrary to experiments in PMN. It should be noted, however, that T-dependent coefficients Q_{11} have been observed in the mixed system 0.9 PMN–0.1PT.[10]

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 $m_{\mu\nu\rho\sigma}/N = [m(ij)_{\mu\nu\rho\sigma}]_{av}$. This will lead to an expression for $\chi_{\mu\nu}$ analogous to Eq. (6) with X-dependent coupling J_0. To lowest order, $\chi^{-1}_{\mu\nu}$ is linear in $X_{\rho\sigma}$ and we can easily evaluate the derivative in Eq. (5), leading to the result

$$Q_{\mu\nu\rho\sigma} = \frac{v_c}{2g^2} m_{\mu\nu\rho\sigma}. \tag{7}$$

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 $X_{\mu\nu} = -p\delta_{\mu\nu}$ in Eqs. (5)–(7). The corresponding stress derivative is $m_h = -dJ_0/dp$, and the appropriate electrostrictive coefficient is given by Q_h. The value of m_h 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[7,11] $\epsilon_s \sim C_\epsilon/(T - J_0/k)$, where the Curie constant C_ϵ is given by $C_\epsilon = g^2/(k\epsilon_0 v_c)$. Thus, we conclude that J_0/k asymptotically plays the role of an effective Curie-Weiss temperature $T_c \simeq J_0/k$, and therefore m_h is given by the experimental value of the pressure derivative of T_c,[7] namely, $m_h = -k(dT_c/dp)$. This leads to the following relation:

$$Q_h = -\frac{1}{2}\frac{dT_c/dp}{\epsilon_0 C_\epsilon}. \tag{8}$$

The experimental values of C_ϵ and dT_c/dp in PMN are[7,11] $C_\epsilon \simeq 4.5 \times 10^5$ K and $dT_c/dp \simeq -4.8 \times 10^{-8}$ K m^2/N. This immediately yields $Q_h \simeq 0.60 \times 10^{-2}$ 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 SRBRF model, but are as well applicable to the classical random n vector 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 $\epsilon_s \sim C_\epsilon/(T - T_c)$, where T_c is the Curie-Weiss temperature, for example, in $BaTiO_3$ and $PbTiO_3$.[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[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.[12]

In Table I we have summarized the values of Q_h calculated from the published experimental data on dT_c/dp and C_ϵ for relaxors PMN and $Pb(Zn_{1/3}Nb_{2/3})O_3$, 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.,

$$Q_{kl} = \frac{m_{kl}}{2k\epsilon_0 C_\epsilon}. \tag{9}$$

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 is: $m_{11}/k \simeq 20 \times 10^{-8}$ 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 $x_1 \sim 10^{-4}$,[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 the present approach we have considered only the field induced electrostriction, i.e., the polarization components P_ρ 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 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 $\Delta/J^2 \simeq 0.001$.[2,3] It is possible that random-field-induced distortions are responsible for the recently discovered X phase in $\mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3}$,[14] 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_0 proportional to the square of the interaction strength divided by the square of the phonon frequencies. The stress—or strain—dependence of J_0 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 $m(ij)_{\mu\nu\rho\sigma}$.

The piezoelectric coefficients $d_{\mu\nu\rho}$ are defined, as usual, by the relation[6]

$$d_{\mu\nu\rho} = 2\chi \sum_{\sigma} Q_{\mu\nu\rho\sigma} P_{\sigma}. \tag{10}$$

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

$$d_{11} = \frac{m_{11}}{k\epsilon_0 C_\epsilon} \chi^2 E_1. \tag{11}$$

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,[2,3] i.e., by ignoring the extra term $\delta\mathcal{H}_J$ 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 $D_{11} = m_{11} k^2 \epsilon_0 C_\epsilon E_c / J^2 \sim 3.32 \times 10^{-12}$ 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 $E/E_c \lesssim 5$, and falls off with E at larger fields. This behavior is qualitatively similar to that of PMN ceramics.[16]

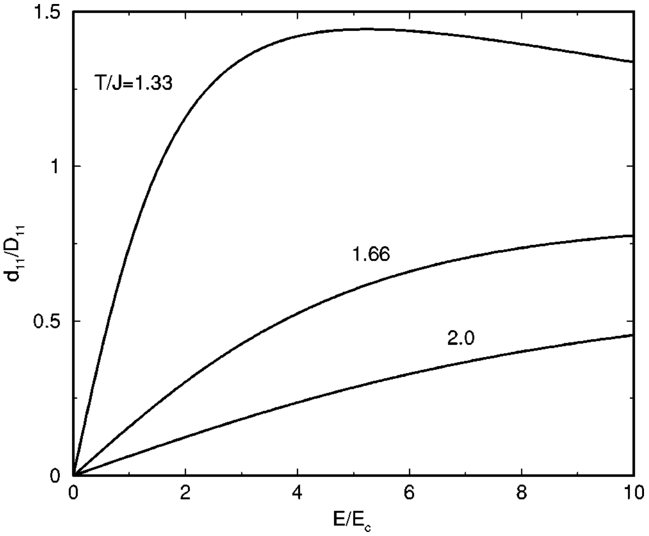

FIG. 1. Calculated electric-field dependence of the piezoelectric coefficient d_{11}/D_{11} for three values of temperature, as indicated.

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 χ 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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