Bias-field effect on the temperature anomalies of dielectric permittivity in $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ single crystals

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In contrast to ordinary ferroelectrics where the temperature T_m of the permittivity maximum monotonically increases with bias field E in $(1-x)PbMg_{1/3}Nb_{2/3}O_3$-$(x)PbTiO_3$ ($0 \leqslant x \leqslant 0.35$) single crystals, T_m was found to remain constant or to decrease with E up to a certain threshold field E_t, above which T_m starts increasing. The threshold field E_t decreases with increasing x, tending toward zero at approximately $x=0.4$. We explain this dependence in the framework of models which take into account quenched random fields and random bonds. For crystals with $0.06 \leqslant x \leqslant 0.13$, the E-T phase diagrams are constructed. In contrast to PMN, they exhibit an additional, nearly field-independent boundary, in the vicinity of the Vogel-Fulcher temperature. We believe this boundary to correspond to an additional phase transition and the appearing order parameter is likely to be nonpolar.

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I. INTRODUCTION

Solid solutions of $(1-x)PbMg_{1/3}Nb_{2/3}O_3$-$(x)PbTiO_3$ (PMN-xPT) have been in the focus of materials research for almost two decades due to their superior dielectric, electrostrictive, and piezoelectric properties.[1–10] Besides, they serve as model objects for studying relaxor properties. Relaxors represent a class of disordered crystals exhibiting a broad and frequency-dependent temperature maximum of the dielectric permittivity versus temperature instead of a sharp maximum inherent to normal ferroelectrics. At a high temperature usually called the Burns temperature, the relaxors exhibit deviations of the temperature dependence of the refractive index from linear that can be considered as a result of pinning of random Pb thermal displacements to the nearly spherically distributed directions of the random field produced by the charge disorder caused by the difference between the charges of Nb and Mg. The pinned Pb displacements are correlated and organize polar nanoregions (PNR's) at lower temperatures owing to self-assembling. At this stage, the spatial polarization fluctuations are decoupled from the strains because the local polarization follows the direction of the random field, but at lower temperatures, below the so-called Vogel-Fulcher temperature, rhombohedral distortions appear due to freezing. The universality class may change, at this temperature, from the random-field Heisenberg to random-field Ising model.[11]

E-T phase diagrams have been constructed in several studies for [111]-oriented $PbMg_{1/3}Nb_{2/3}O_3$ (PMN)[4,12,13] and PMN-xPT crystals.[3] The main conclusion stemming from experiment[4] is that the phase transition between the relaxor and ferroelectric phases, in PMN, is first order and it happens at a bias field exceeding some critical field. Such a supposition is also supported by the character of the field dependence of permittivity in [111] PMN crystals.[7] This phase transition was modeled by Vugmeister and Rabitz[14] by considering the average polarization as a function of field in the spirit of the Landau mean-field theory. Pirc, Blinc, and Kutnjak[15] modeled a similar phase diagram obtained for $Pb_{1-y}La_yZr_{1-x}Ti_xO_3$ (PLZT) within the spherical random-bond random-field (SRBRF) model supplemented with a field modulation of intercluster coupling. Emelyanov *et al.*[3] have considered the Almeida-Thouless origin of the phase

boundary in the E-T phase diagram. The present study will provide experimental phase diagrams for several compositions of PMN-xPT in the range $0.13 > x > 0$, expanding the conclusion about the first-order phase transition under a bias field.

It is well documented that,[5,8–10] for PMN-xPT compositions within the morphotropic phase boundary (MPB) range, the temperature T_m of the permittivity maximum increases with dc bias field E and the rate of this increase depends on the crystal orientation. Contrary to this, Viehland *et al.*[16] showed that, in PMN-0.1PT ceramics, T_m slightly decreases under small fields and strongly increases only at large fields. Similar observations have been reported for ceramic samples in a $0.1 \leqslant x \leqslant 0.3$ compositional range.[17,18] However, details of the $T_m(E)$ dependence for PMN-xPT crystals remain obscure.

In the present paper, we report experiments on the dc-bias-field effect on the T_m of [001]-oriented PMN-xPT crystals including compositions with low titanium concentrations ($x=0.06$, 0.1, and 0.13) exhibiting relaxor behavior both at zero bias and at bias-field values, up to 5 kV/cm, as well as compositions adjacent ($x=0.25$ and 0.3) and belonging ($x=0.35, 0.4$) to the MPB compositional range, whose properties under the biased condition are similar to normal ferroelectric.

II. EXPERIMENTAL RESULTS

The PMN-xPT single crystals used in this study were transparent plates cut from flux-grown crystals prepared at the Physics Research Institute of the Rostov State University.[3] The large faces of the samples were perpendicular to the [100] direction. Details of dielectric studies have been described elsewhere.[5,7] The majority of our experimental data have been obtained in the 1–100 kHz frequency range. It is well documented in the literature that, in the case of the PMN-PT compositions, this range is wide enough to demonstrate the frequency dispersion of permittivity and the frequency shift of T_m. On the other hand, by using this frequency window, one avoids the influence of conductivity on the experimental results, often observed at lower frequencies, as well as problems with parasitic resonances in the measuring circuit due to a nonoptimal ratio of the samples' capacitance and the inductance of the connecting wires and sample holder, appearing in the MHz frequency range.

Zero-field-cooling (ZF), field-cooling (FC), field-heating after field-cooling (FH), and zero-field-heating after field-cooling (ZFHaFC) protocols were used. After each FC run the samples were heated without bias field (ZFHaFC) up to temperatures exceeding T_m by at least 50–100 K. Such a heat treatment is known to erase effectively the dielectric memory effects in relaxors caused by the previous actions of the bias field. The FH runs, in the present study, always followed the FC runs carried out under a bias field large enough to induce the ferroelectric phase. After such FH runs the samples were annealed for 10–15 min at the maximal temperature reached (50–100 K above T_m).

Figure 1 shows the temperature dependence of the real (ε') part of the complex permittivity measured in the FC mode in the vicinity of the permittivity maximum for some of the crystals studied. For each of the crystals, there exists a critical bias field above which a first-order dielectric anomaly takes place. This critical field vanishes above approximately $x=0.2$: a steplike dielectric anomaly [corresponding to the MPB or to a spontaneous phase transition from the relaxor to ferroelectric or mixed (ferroelectric-relaxor) state (see Refs. 5 and 6 for details)] exists in these compositions even at the zero field. One can conjecture from these data that, in the ZFC procedure and below $x=0.2$, the samples with the [100] orientation remain in the relaxor phase down to the lowest possible temperatures, at least during the measuring procedure.

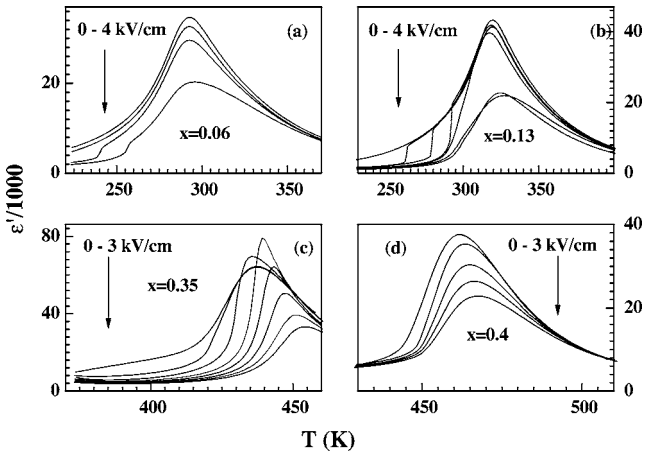

FIG. 1. The $\varepsilon'(T)$ dependence measured at 1 kHz in the FC mode in the vicinity of the permittivity maximum for some flux-grown ([001]) PMN-xPT crystals at different E values: (a) $x=0.06$, $E=0,1,2,4$ kV/cm; (b) $x=0.13$, $E=0,0.25,0.5,1,2,3.5,4$ kV/cm; (c) $x=0.35$, $E=0,0.1,0.4,1,1.5,2,2.5,3$ kV/cm; (d) $x=0.4$, $E=0,0.5,1,1.5,2$ kV/cm.

In the crystals with low titanium content ($x=0.06$, 0.10, and 0.13, in the present study), at large enough bias, field-induced phase transitions from the relaxor to a ferroelectric or mixed state have been observed manifesting themselves in the FC mode by an abrupt drop (step) of dielectric permittivity. The temperature T_S of this step depends on E. Below, we will mainly focus on this dependence as well as on the dependence of T_m on E.

Figure 2 shows the dependence of the reduced temperature $\Delta T_m = T_m(E) - T_m(E=0)$ on E. One can see that T_m increases with increasing E at large E. This is typical of the usual ferroelectrics.

For crystals with $x < 0.4$, at low biases, in contrast to the usual ferroelectrics, T_m remains practically unchanged or even decreases with E first, up to a certain threshold bias E_t, above which T_m increases. It is worth noting that such a type of $T_m(E)$ dependence has been actually observed previously in both single crystals and ceramics of PMN-PT, as is evident from the analysis of the figures published, e.g., in Refs. 4, 5, 8–10, 12, and 16–18. As an example, panel (b) of Fig. 2 shows the $\Delta T_m(E)$ dependence for [111]-oriented PMN-xPT crystals, constructed using the T_m values deduced from the data published in Refs. 4, 9, and 10. The "anomalous" (from the point of view of ordinary ferroelectrics) low-field

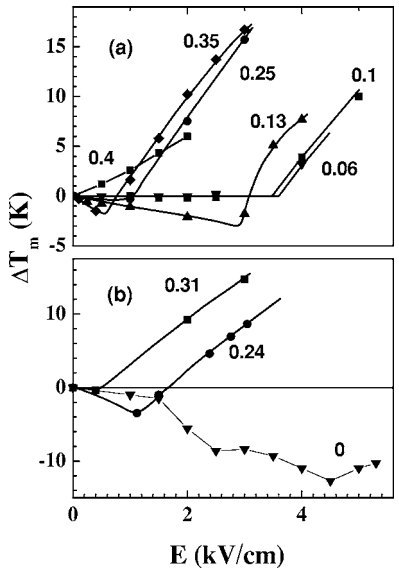

FIG. 2. The dependence of the reduced temperature $\Delta T_m = T_m(E) - T_m(E=0)$ on dc bias E for PMN-xPT crystals. The numbers correspond to x values, and the lines are guides for the eye drawn in the spirit of the Dorogovtsev model: (a) For [001] crystals studied in the present work. (b) For [111] crystals, constructed using the T_m values deduced from the data published in Refs. 4, 9, and 10.

portion of this dependence has not been commented on and has been only scarcely mentioned in the literature yet. The only exceptions are Refs. 17, 19, and 20 where E_t was considered as a field value necessary to overcome the action of random fields. This conception will be discussed in more detail below.

Figure 3 shows the concentration dependence of the field E_t at which $\Delta T_m(E)$ has a minimum position or starts abrupt increasing. Surprisingly, the $E_t(x)$ dependences for both

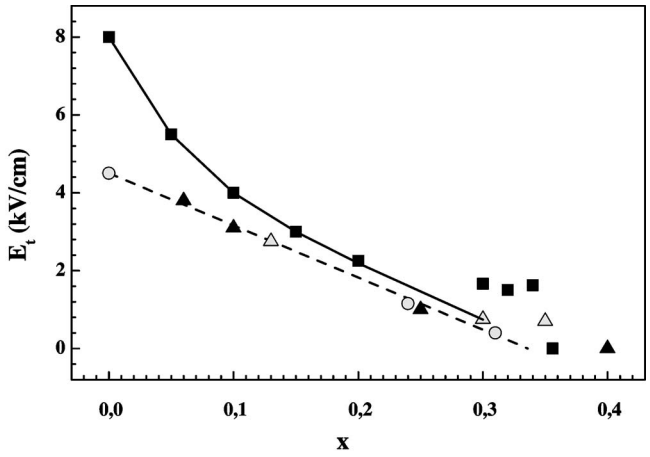

FIG. 3. The concentration dependence of the field E_t at which $\Delta T_m(E)$ has a minimum position or starts abrupt increasing for [001] (triangles) and [111] (circles) PMN-xPT crystals and for ceramics (squares), estimated from the minimum (open symbols) or inflection (solid symbols) in the $T_m(E)$ curves. The data for [111] crystals are deduced from Refs. 4, 9, and 10 and for ceramics from Refs. 17 and 18. The lines are guides for the eye.

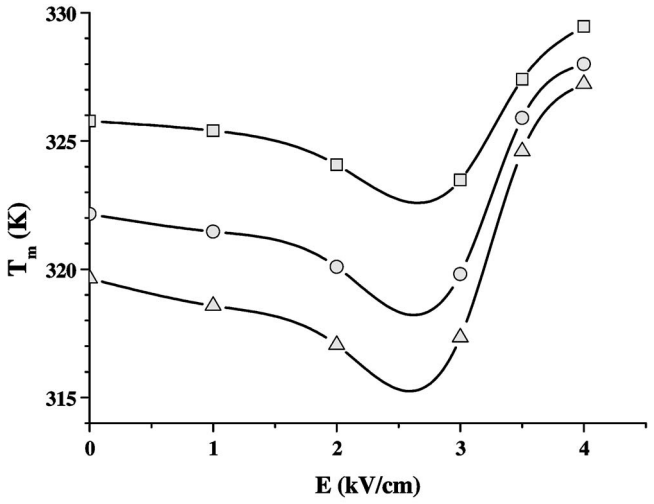

FIG. 4. The $T_m(E)$ dependence for PMN-(0.13)PT crystal measured at different frequencies: 1, 10, 100 kHz (from bottom to the top). The lines are guides for the eye.

[001]- and [111]-oriented crystals scale approximately to one straight line. For comparison, we also plot the E values corresponding to the inflection points in the $\Delta T_m(E)$ curves for PMN-xPT ceramics, deduced from the data of Refs. 17 and 18. One can see that E_t decreases with the increase of x, and the extrapolation of the linear part of $E_t(x)$ dependence both for ceramics and crystals intersects the x axis at about $x = 0.33-0.35$, which is close to the percolation threshold. However, some small, nearly constant values of E_t can be observed in the 0.3–0.35 compositional range. This remaining value seems to be due to compositional fluctuations typical of the PMN-xPT at compositions belonging to the MPB range.[21]

Figures 4 and 5 show the effect of dc bias on the frequency dependence of the T_m and $\varepsilon'(T)$ maximum magnitude (ε_m). In all the crystals studied, the frequency dispersion

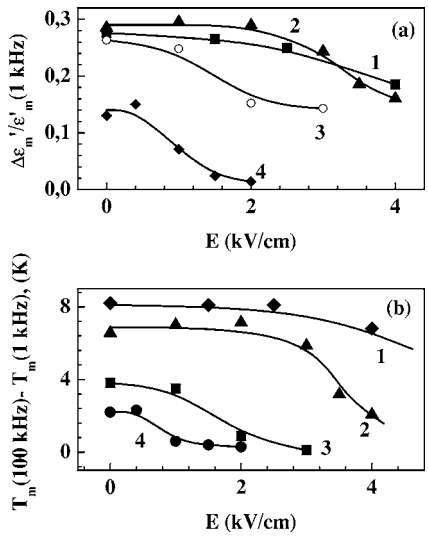

FIG. 5. The effect of dc bias on the frequency dependence of ε'_m (a) and T_m (b) for the PMN-xPT crystals: $x=0.06$ (1), 0.13 (2), 0.25 (3), 0.35 (4) ($\Delta\varepsilon'_m = \varepsilon'_m(100\text{ kHz}) - \varepsilon'_m(1\text{ kHz})$.

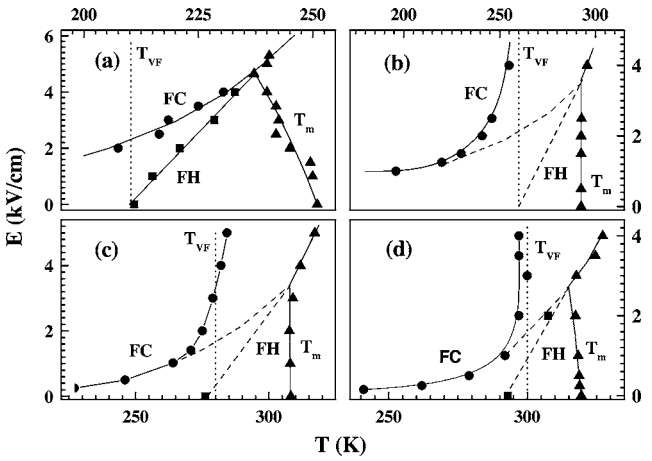

FIG. 6. The position of the dielectric steplike anomaly (FC and FH) and dielectric permittivity maximum measured at 1 kHz (T_m) for some PMN-xPT crystals: (a) [111] PMN (Ref. 4), (b) [001] PMN-0.06PT, (c) [001] PMN-0.1PT, and (d) [001] PMN-0.13PT. The dashed and dotted lines are just guides for the eye.

of ε_m and T_m decreases for the biases exceeding E_t. This effect is the largest for the PMN-xPT crystals in the MPB compositional range. This is consistent with numerous data showing that unpoled PMN-xPT crystals from the MPB compositional range exhibit a relaxorlike behavior, while, at high fields, their properties are similar to ordinary ferroelectrics.[8,9] The new result is that there exists a threshold dc bias value below which the behavior of the crystals is relaxor like, while, above this threshold, it is more or less similar to usual ferroelectrics. The Almeida-Thouless line plotted by using the polarization hysteresis curves[3] lies at higher fields. This can be explained by differences in the experimental procedure (we cooled the samples in the dc field whereas the polarization hysteresis was drawn at fixed temperatures for different ac fields).

Figure 6 shows the tentative E-T phase diagrams for [001] PMN-xPT crystals with low titanium content. For comparison, the E-T phase diagram for a [111] PMN crystal[4] is also presented. The FC and FH lines in the E-T phase diagrams correspond to the step in the $\varepsilon'(T)$ curve in the [001]-oriented crystals and to the additional $\varepsilon'(T)$ maximum in the [111]-oriented crystals appearing when the ferroelectric phase is induced (in the course of cooling) or disappears (in the course of heating). In contrast to the usual practice when $T_m(E)$ is not drawn in the E-T phase diagrams of relaxors, because no structure or phase changes correspond to this line, we do show this line in order to mark the position of the diffuse dielectric maximum at a low frequency. Moreover, above the threshold field, the $T_m(E)$ line converges with the FH one at the end point.

We show the T_m lines corresponding to the FC runs only, in order not to overburden the figure. The T_m lines corresponding to the FH runs are shifted to higher temperatures for a few K while, above the threshold field, they converge with the FC ones.

In the ZFHaFC run, we obtained that the result does practically not depend on the bias field in the FC run if this field is high enough to induce the ferroelectric phase. In the phase diagram, the ZFHaFC line would be a nearly vertical portion of the line above the critical field with its temperature being rather close to the Vogel-Fulcher temperature. This result is in agreement with measurements on ceramic PLZT.[22]

In Fig. 7(a), we show a common E-T phase diagram for a system experiencing a first-order phase transition. There can be different scenarios of the microscopic origin of this phase transition. An ordinary Landau theory assumes that the system can occupy one of two different states (relaxor and ferroelectric) with different temperature dependences of their chemical potentials. The phase transition happens when these chemical potentials become equal. However, the barriers can be macroscopic and this results in a thermal hysteresis controlled by the boundaries of stability of the ferroelectric and relaxor phases.

In disordered media, the nucleation of the polar phase is a subtle point especially under the condition of large electrostriction coefficients.[25] The boundaries of stability of the phases can be substituted by the boundaries of stability of the

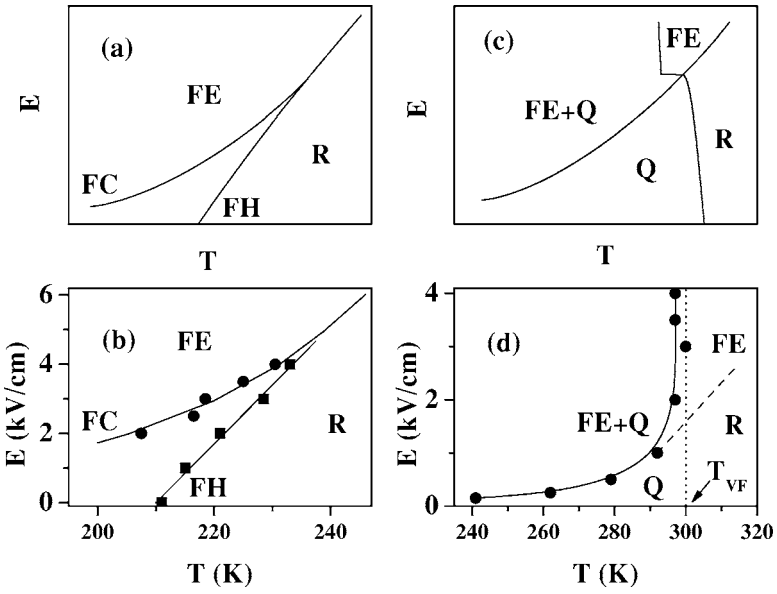

FIG. 7. Theoretical modeling and comparison with experiment: the position of the dielectric anomaly in the FC and FH modes for a system experiencing a first-order phase transition described within a Landau theory (a) and corresponding experimental data for [111] PMN crystals (Ref. 4) (b). The theoretical E-T phase diagram including the relaxor (R), ferroelectric (FE), and Q phases, where Q is a scalar order parameter coupled to polarization P (c), and experimental data on the position of the dielectric steplike anomaly for the PMN-0.13PT crystal in the FC mode (d). The dashed and dotted lines are guides for the eye.

nuclei. The electrostriction is at the origin of the first-order phase transition also in the SRBRF model.[15]

Villain developed a microscopic model of the phase transition by using a random-field Ising theory.[23] This theory considers two possible states of a PNR, with the polarization along the fluctuation of the random field or in the direction of the mean polarization. The correlation length in the theory of Villain, in the former state, saturates below some temperature (cf. Ref. 24). In the ferroelectric phase, such a saturation is absent. Switching the polarization requires one to overcome a large potential barrier that results in a logarithmic relaxaton of the relaxor phase below the temperature where these two states have equal energies. This relaxation can be rather long because the ferroelectric phase, in this theory, is hardly attainable at the fields below the threshold one. This theory can be fitted to experiment. However, the validity of the random-field Ising model in the considered temperature interval has not been proven yet.

The FH (FC) line corresponds to the disappearance (appearance) of *macroscopic* metastable states. The points on the FH line correspond to the FH (or, in the case of $E=0$, ZFH) runs after FC at fields high enough to induce the ferroelectric phase. This inclined line shows a boundary of stability of the metastable ferroelectric phase. The sample is depolarized at this boundary. Thermal hysteresis decreases with the increasing field and vanishes on the end point where the FH and FC lines converge. Above this point, the ferroelectric phase is indistinguishable from the relaxor phase and the dielectric permittivity has only a diffuse maximum. Its temperature T_m depends little on frequency (see, e.g., Fig. 4), but at higher fields, T_m becomes frequency independent.[16] The phases appearing on FC in different regions separated by solid lines are denoted in Fig. 7(b).

It is seen from the plotted experimental phase diagrams that, in the FC mode, for PMN-xPT crystals ($x>0$), there appears a nearly vertical portion, above the relaxor-ferroelectric boundary, which has not been observed in pure PMN. This portion looks like an additional vertical line in the E-T phase diagram and, in order to check this possibility theoretically, we consider an additional scalar order parameter Q, which is coupled to the square of the polarization P with a positive coupling constant (cf. Refs. 3 and 26) and with other constants assuming a first-order phase transition under a bias field [Fig. 7(b)]. The experimentally observed vertical portion in the phase diagram looks similar to the vertical line in Fig. 7(b) although we have not found experimental evidence of the phase transition below the relaxor-ferroelectric boundary. It is possible that this is because random fields smear this phase transition at small bias fields.

A similar nearly vertical line exists also in the data obtained on the basis of the studies of the polarization hysteresis loop[3] for $x=0.13$. This study considers a "mixed" ferroelectric-glass phase sandwiched between the pure glass and pure ferroelectric phases. In this study, the boundary of the stability of the "mixed" phase coincides with the nearly vertical line.

It is important that coupling between P and Q changes the FC line and, in particular, there appears a critical field,[27] below which there are no phase transitions in agreement with experiment.

The meaning of the order parameter Q is not clear, for the moment. We assume a close relationship to the dynamic behavior of PNR's, which are believed to be at the heart of the relaxor behavior.[1,28] We should notice that the nearly vertical line is close to the Vogel-Fulcher temperature T_{VF}, where the PNR's size strongly changes[29] and above which the PNRs are dynamic (T_{VF} is always close to the ZFHaFC line, which marks the disappearance of macroscopic metastable ferroelectric states). At low bias fields, the phase transition is diffuse due to coupling between Q and random fields.[15] Thus, Q might refer to the average size of PNR,[29] the Edwards-Andersson parameter,[30,31] or any other scalar order parameter with the above-described properties.

III. DISCUSSION

A widely accepted model of relaxors[27] considers dipoles under the action of random bonds and in random fields, which were introduced into the discussion of relaxor behavior previously.[32,33] In the present study, we concentrate on the bias-field dependence of the diffuse peak. Below, we will test different models considering nonlinear dielectric permittivity in PMN in connection with our experimental results.

Vugmeister and Rabitz described the frequency and bias-field dependence of FC dielectric susceptibility[14,34] in relaxors by considering the average polarization produced by PNR's in the spirit of the Landau mean-field theory. The main expression can be also obtained from the theory of nonlinear susceptibility of coupled dipoles:[35]

$$\varepsilon = \varepsilon_\infty + \frac{\chi_s}{1-\lambda^2 n \chi_0 F}, \tag{1}$$

where

$$\chi_0 = \left\langle \frac{1}{\alpha + 3\beta P^2 + 5\gamma P^4 + 7gP^6} \right\rangle, \tag{2}$$

$$F = \frac{1}{4k_B T \cosh^2(u/k_B T)} \left\langle \frac{1}{1+i\omega\tau} \right\rangle. \tag{3}$$

The polarization P can be found from the equilibrium condition

$$\alpha P + \beta P^3 + \gamma P^5 + gP^7 = E + e, \tag{4}$$

where e is a random field given by one of the following two distribution functions:

$$g(e) = \frac{1}{2}[\delta(e-e_0) + \delta(e+e_0)], \tag{5}$$

$$g(e) = \frac{1}{\sqrt{\pi}} e^{-ae^2}. \tag{6}$$

The angular brackets in expression (2) mean averaging over the random-field magnitude while the angular brackets in expression (3) imply averaging over the barriers.

In expressions (1)–(3), $u=2\mu E+\lambda P$, μ is the dipole moment, λ is a constant coupling the dipole moment to the

polarization P, n is the concentration of dipoles, χ_s is the low-frequency susceptibility without coupling to the average polarization, ε_∞ is the high-frequency dielectric permittivity, and $\tau=\tau_0 \exp[U/k_B(T-T_{VF})]$. The Landau coefficient α is assumed to depend on T in the manner which has been described by Potts-type model computations of PMN (Ref. 36) as well as by the SRBRF model and experiment:[24,27] it decreases linearly with decreasing temperature and saturates at low temperatures without crossing zero. Correspondingly, due to random fields and random bonds, the correlation length increases as temperature decreases and, then, saturates at low temperatures.

Our analysis has shown that the main factor influencing the direction of the shift of T_m under bias field is the direction of the shift of the susceptibility maximum (2). If $\beta>0$, as in ferroelectrics with a second-order phase transition, and random fields were absent, then the maximum of $\chi_0(T)$ would shift upward in small fields. This would contradict experiment. If $\beta<0$, then this maximum shifts downward, first, and upward, above some threshold field. So one can see that the result seems to depend crucially on the sign of β.

Experiments[37] show that β is strongly anisotropic with respect to the main axis. For PMN at about 250 K, β is small for the [111]-oriented crystals, but it is comparatively large and positive for [001] orientation. Indeed, our experiment exhibits a dip for [111]-oriented PMN, but for most of the [001]-oriented PMN-xPT, T_m is kind of insensitive to the field below the threshold. At first glance, it seems that the positive sign of β contradicts the experimentally observed first-order phase transition between the relaxor and ferroelectric phases. Pirc, Blinc, and Kutnjak[15] assumed that the parameter, which is responsible for the average interaction among the dipoles, J_0 increases with the increasing bias field and just this makes the relaxor-ferroelectric phase transition possible at finite fields in PMN. Vugmeister and Rabitz[14] used in their model a positive value of β, but γ was negative. We computed the dependence $\chi_0(E)$ without averaging over random fields at different reasonable values of β and found that β does not play a significant role at $T=T_m$ in PMN (because $3\beta P^2$ is comparatively small with respect to α at actual fields) and χ_0 is approximately constant until about 3 kV/cm. This fact would correspond to the silence of T_m to bias field in this range. Above 3 kV/cm, T_m becomes strongly inclined in the direction of the end point in the phase diagram if one supposes a first-order phase transition. Above the end point, the dependence of $T_m(E)$ changes again and $T_m(E)$ starts increasing. At comparatively high fields, this dependence is consistent with our experiment, but at low E, the experiment performed for PMN shows the existence of a dip that is not fully reproduced by the considered theory. We found that taking into account the random-field distribution (5) reproduces this dip [Fig. 8(a)], while distribution (6) provides the dependence, which is insensitive to E [Fig. 8(b)]. A similar effect of random fields on $T_m(E)$ at second-order phase transitions was discovered earlier by Dorogovtsev[19] (cf. the result of averaging of polarization with the same distribution function[38]).

In the first case [distribution (5)], the quenched fields are up and down, and the main contribution to the shift of T_m stems from the random fields, which are opposite to external field. T_m has a dip in this case until the field reaches the magnitude of the random field, $e=e_0$, and, then, T_m increases as happens in normal ferroelectrics with a second-order phase transition ($\beta>0$, $\gamma>0$). In the case if $\gamma<0$ (see Ref. 14), the dip continues until coming close to the end point in the phase diagram (the lower the frequency, the closer is T_m to the end point), and only then does T_m start increasing. This behavior suits qualitatively our experiment and explains not only the existence of the dip in some cases but also the fact that $T_m(E)$ is directed towards the end point for all considered concentrations. Thus, our results are in favor of distribution (5), at least for pure PMN with [111] orientation. Also, Monte Carlo computations performed for a two-dimensional set of dipoles with random fields and random bonds gave a shallow dip in $T_m(E)$ until a threshold field above which T_m started increasing.[20] These data emphasize the necessity of using the random-field–random-bond idea in order to explain the low-field dependence of T_m in PMN-xPT.

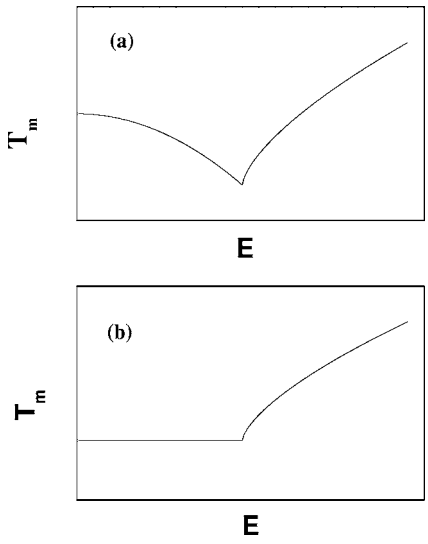

FIG. 8. The dependence of $T_m(E)$ obtained within a model, which takes into account random fields. Panels (a) and (b) correspond to different distribution functions of random fields (see text).

The inverse dielectric permittivity (stiffness) of ferroelectrics depends on the bias field linearly because the polarization fluctuation caused by the field can be coupled with the mean polarization. In relaxors, such a dependence has also been observed above some threshold field, and it was explained by the divergence of the transverse susceptibility.[7]

Poplavko[39] assumed that the average relaxation time in relaxors decreases with the increase of bias field. Tagantsev and Glazounov[38] suggested that the vibration of PNR's can be described by the following field dependence of the relaxation time: $\tau=\tau_0 \exp[(U-VPE)/k_BT]$ where V is the PNR's volume and P the polarization magnitude inside PNR's. These suggestions lead to a decrease of the relaxation time with E. Though they would be in line with $T_m(E)$ found by us, experiments performed on ceramics[16] do not confirm the decrease of the relaxation time in PMN below the threshold field. As another example, in the SRBRF model,[15] the

frequency-dependent part of the dielectric permittivity is expressed over $z+i\omega\tau$ where z is a model parameter, which can be found as a function of the average dipole-dipole interaction energy J_0 and average dispersion of this interaction, J. When z increases, the relaxation time decreases and $T_m(E)$ moves downward. Our analysis has shown that z only slightly increases at small fields but this increase becomes rather strong at the relaxor-ferroelectric boundary. Thus, this model predicts that the relaxation time only slightly changes at small fields, which is consistent with experiment.[16]

IV. SUMMARY

Our experiment has shown that, in all studied PMN-xPT single-crystal compositions, there is a FC line in the E-T phase diagram separating the relaxor and ferroelectric phases. A first-order phase transition happens at this line. In contrast to pure PMN, this line has a portion which does not depend on the bias field (nearly vertical line), which we attribute to a first-order nonpolar phase transition. In PLZT, the same line has been observed on ZFHaFC and it was shown that the depolarization takes place at this line.[22,40] This implies that the ferroelectric phase becomes unstable above this line. Below this line, the ferroelectric phase is metastable but it can nucleate above the threshold field. We connect the nearly vertical line with the appearance of a macroscopic state, which is due to the onset of freezing of large PNR's.

The dielectric peak temperature T_m was found to be insensitive to the bias field or even slightly decreasing, at small fields but increasing at large fields. Our analysis of different models of relaxors has shown that, in order to explain this effect, a first-order phase transition at the relaxor-ferroelectric phase boundary has to be taken into account as well as quenched random fields and random bonds. The quenched uncorrelated fields, which are at the origin of the generic random-field model,[32] relate in relaxors to their inherent charge disorder.[33] The Dorogovtsev effect extended to the relaxor systems provides a good qualitative description of the dependence of $T_m(E)$ at small fields. At large fields, both the Vugmeister-Rabitz model[14] supplemented with a temperature dependence of quasistatic dielectric permittivity and the Pirc-Blinc-Kutnjak model[15] explaining both the quasistatic dielectric permittivity, frequency, and the bias field dependences provide a reasonable explanation of our experiment.

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[1] L. E. Cross, Ferroelectrics **151**, 305 (1994).
[2] S.-E. Park and T. R. Shrout, J. Appl. Phys. **82**, 1804 (1997).
[3] S. M. Emelyanov, F. I. Savenko, Yu. A. Trusov, V. I. Torgashev, and P. N. Timonin, Phase Transitions **45**, 251 (1993).
[4] E. V. Colla, S. B. Vakhrushev, E. Yu. Koroleva, and N. M. Okuneva, Phys. Solid State **38**, 1202 (1996).
[5] E. V. Colla, N. Yushin, and D. Viehland, J. Appl. Phys. **83**, 3298 (1998).
[6] M. El Marssi, R. Farhi, and Yu. I. Yuzyuk, J. Phys.: Condens. Matter **10**, 9161 (1998); L. S. Kamzina, I. P. Raevski, S. M. Emelyanov, S. I. Raevskaya, and E. V. Sakhkar, Fiz. Tverd. Tela (S.-Peterburg) **46**, 881 (2004) [Phys. Solid State **46**, 908 (2004)].
[7] S. A. Prosandeev, I. P. Raevski, A. S. Emelyanov, E. V. Colla, J.-L. Dellis, M. El Marssi, S. E. Kapphan, and L. Jastrabik, J. Appl. Phys. **98**, 14103 (2005).
[8] J. Han and W. Cao, Phys. Rev. B **68**, 134102 (2003).
[9] X. Zhao, J. Wang, H. I. W. Chan, C. I. Choy, and H. Luo, J. Phys.: Condens. Matter **15**, 6899 (2003).
[10] X. Zhao, J. Wang, Z. Peng, H. I. W. Chan, C. I. Choy, and H. Luo, Mater. Res. Bull. **39**, 223 (2004).
[11] C. Stock, R. J. Birgeneau, S. Wakimoto, J. S. Gardner, W. Chen, Z.-G. Ye, and G. Shirane, Phys. Rev. B **69**, 094104 (2004).
[12] Z-G. Ye, Key Eng. Mater. **155–156**, 81 (1998).
[13] R. Sommer, N. K. Yushin, and J. J. van der Klink, Phys. Rev. B **48**, 13230 (1993).
[14] B. E. Vugmeister and H. Rabitz, Phys. Rev. B **65**, 024111 (2001).
[15] R. Pirc, R. Blinc, and Z. Kutnjak, Phys. Rev. B **65**, 214101 (2002).
[16] D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttig, J. Appl. Phys. **69**, 414 (1991).
[17] E. A. Bikyashev, Ph.D. thesis, Rostov State University, 1999.
[18] E. A. Bikyashev, D. A. Taranin, and L. A. Litvinova, in *Proceedings of the International Conference "Piezoelectronics-95"*, edited by V. P. Sakhnenko (Rostov University Press, Rostov-on-Don, Russia, 1995), Vol. 2, p. 50 (in Russian).
[19] S. N. Dorogovtsev, Sov. Phys. Solid State **24**, 948 (1982).
[20] H. Gui, B. Gu, and X. Zhang, Phys. Rev. B **52**, 3135 (1995).
[21] Z.-G. Ye and M. Dong, J. Appl. Phys. **87**, 2312 (2000).
[22] V. Bobnar, Z. Kutnjak, R. Pirc, and A. Levstik, Phys. Rev. B **60**, 6420 (1999).
[23] J. Villain, Phys. Rev. Lett. **52**, 1543 (1984).
[24] A. Levstik, Z. Kutnjak, C. Filipic, and R. Pirc, Phys. Rev. B **57**, 11204 (1998).
[25] V. G. Bariakhtar, I. M. Vitebskiy, and D. A. Yablonskiy, Fiz. Tverd. Tela (Leningrad) **23**, 1448 (1981).
[26] A. K. Tagantsev and A. E. Glazounov, Appl. Phys. Lett. **74**, 1910 (1999).
[27] R. Pirc and R. Blinc, Phys. Rev. B **60**, 13470 (1999).
[28] G. Samara, J. Phys.: Condens. Matter **15**, R367 (2003).
[29] I.-K. Jeong, T. W. Darling, J. K. Lee, Th. Proffen, R. H. Heffner, J. S. Park, K. S. Hong, W. Dmowski, and T. Egami, Phys. Rev.

Lett. **94**, 147602 (2005).
[30] E. V. Colla, E. Yu. Koroleva, N. M. Okuneva, and S. B. Vakhrushev, J. Phys.: Condens. Matter **4**, 3671 (1992).
[31] B. Dkhil and J. M. Kiat, J. Appl. Phys. **90**, 4676 (2001).
[32] Y. Imry and S.-K. Ma, Phys. Rev. Lett. **35**, 1399 (1975).
[33] V. Westphal, W. Kleemann, and M. D. Glinchuk, Phys. Rev. Lett. **68**, 847 (1992).
[34] B. E. Vugmeister and H. Rabitz, Phys. Rev. B **57**, 7581 (1998).
[35] S. A. Prosandeev, Phys. Solid State **43**, 1948 (2001).
[36] H. Qian and L. A. Bursill, Int. J. Mod. Phys. B **10**, 2027 (1996).
[37] A. K. Tagantsev and A. E. Glazounov, J. Korean Phys. Soc. **32**, S951 (1998).
[38] A. K. Tagantsev and A. E. Glazounov, Phase Transitions **65**, 117 (1998).
[39] Yu. Poplavko, *Fizika dielektrikov* (Vyshcha Shkola, Kiev, 1980).
[40] M. El Marssi, R. Farhi, and D. Viehland, J. Appl. Phys. **81**, 355 (1997).