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Recent progress in relaxor ferroelectrics with perovskite structure

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Relaxor ferroelectrics were discovered almost 50 years ago among the complex oxides with perovskite structure. In recent years this field of research has experienced a revival of interest. In this paper we review the progress achieved. We consider the crystal structure including quenched compositional disorder and polar nanoregions (PNR), the phase transitions including compositional order-disorder transition, transition to nonergodic (probably spherical cluster glass) state and to ferroelectric phase. We discuss the lattice dynamics and the peculiar (especially dielectric) relaxation in relaxors. Modern theoretical models for the mechanisms of PNR formation and freezing into nonergodic glassy state are also presented.

1. Introduction

Relaxor ferroelectrics or relaxors are a class of disordered crystals possessing peculiar structure and properties. At high temperature they exist in a non-polar paraelectric (PE) phase, which is similar in many respects to the PE phase of normal ferroelectrics. Upon cooling they transform into the ergodic relaxor (ER) state in which polar regions of nanometer scale with randomly distributed directions of dipole moments appear. This transformation which occurs at the so-called Burns temperature (T_B) cannot be considered a structural phase transition because it is not accompanied by any change of crystal structure on the macroscopic or mesoscopic scale. Nevertheless, the polar nanoregions (PNRs) affect the behaviour of the crystal dramatically, giving rise to unique physical properties. For this reason the state of crystal at $T < T_B$ is often considered as the new phase different from the PE one.

At temperatures close to T_B the PNRs are mobile and their behaviour is ergodic. On cooling, their dynamics slows down enormously and at a low enough temperature, T_f (typically hundreds degrees below T_B), the PNRs in the canonical relaxors become frozen into a nonergodic state, while the average symmetry of the crystal still remains cubic. Similar kind of nonergodicity is characteristic of a dipole glass (or spin glass) phase. The existence in relaxors of an equilibrium phase transition into a low-temperature glassy phase is one of the most interesting hypotheses which has been intensively discussed. Freezing of the dipole dynamics is associated with a large and wide peak in the temperature dependence of the dielectric constant (ε) with characteristic dispersion observed at all frequencies practically available for dielectric measurements (Fig. 1). This peak is of the same order of magnitude as the peaks at the Curie point in the ordinary ferroelectric (FE) perovskites, but in contrast to ordinary ferroelectrics it is highly diffuse and its temperature T_m ($>T_f$) shifts with frequency due to the dielectric dispersion. Because of the diffuseness of the dielectric anomaly and the anomalies in the temperature dependences of some other properties, relaxors are often called (especially in early literature) the "ferroelectrics with diffuse phase transition," even though no transition into FE phase really occurs.

The nonergodic relaxor (NR) state existing below T_f can be irreversibly transformed into a FE state by a strong enough external electric field. This is an important characteristic of relaxors which distinguishes them from typical dipole glasses. Upon heating the FE phase transforms to the ER one at the temperature T_C which is very close to T_f. In many relaxors the spontaneous (i.e. without the application of an electric field) phase transition from the ER into a low-temperature FE phase still occurs at T_C and thus the NR state does not exist.

Compositional disorder, i.e. the disorder in the arrangement of different ions on the crystallographically equivalent sites, is the common feature of relaxors. The relaxor behaviour was first observed in the perovskites with disorder of non-isovalent ions, including the stoichiometric complex perovskite compounds, e.g.

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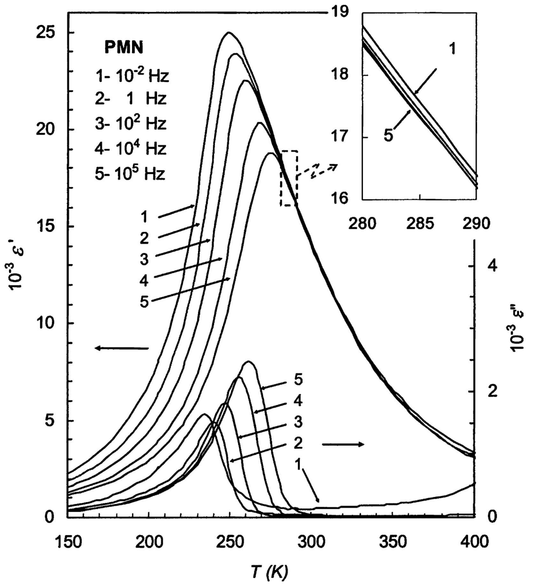

Figure 1 Temperature dependences of the real and imaginary parts of the relative dielectric permittivity measured at different frequencies in a crystal of the prototypical relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$. Enlarged view in the insert shows the universal relaxor dispersion (URD) (after Bokov and Ye, unpublished).

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) [1] or $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) [2] (in which Mg^{2+}, Sc^{3+}, Ta^{5+} and Nb^{5+} ions are fully or partially disordered in the B-sublattice of the perovskite ABO_3 structure) and nonstoichiometric solid solutions, e.g. $Pb_{1-x}La_x(Zr_{1-y}Ti_y)_{1-x/4}O_3$ (PLZT) [3, 4] where the substitution of La^{3+} for Pb^{2+} ions necessarily leads to vacancies on the A-sites. Recently an increasing amount of data reported has shown that many homovalent solid solutions, e.g. $Ba(Ti_{1-x}Zr_x)O_3$ (BTZ) [5, 6] and $Ba(Ti_{1-x}Sn_x)O_3$ [7] can also exhibit relaxor behaviour. Other examples of relaxor ferroelectrics are complex perovskites $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT), $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN), $Pb(In_{1/2}Nb_{1/2})O_3$ (PIN), $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN), $Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) and the solid solutions: $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMN-PT) and $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PZN-PT).

Although relaxor ferroelectrics were first reported nearly half a century ago, this field of research has experienced a revival of interest in recent years. In this paper, we try to provide an overview of the current understanding of the various issues of relaxors. Emphasis is put on the latest developments. For a review of the earlier studies, readers can refer to Refs. [8–11].

2. Compositional order-disorder phase transitions and quenched disorder in complex perovskites

As mentioned above, the disordered distribution of different ions on the equivalent lattice sites (i.e. compositional disorder, also called chemical, ionic or substitutional disorder) is the essential structural characteristic of relaxors. The ground state of the complex perovskites should be compositionally ordered, e.g. in the $A(B'_{1/2}B''_{1/2})O_3$ compounds each type of the cations, B′ or B″, should be located in its own sublattice, creating a superstructure with complete translational symmetry. This is because the electrostatic and elastic energies of the structure are minimized in the ordered state due to the difference in both the charge and the size of B′ and B″ ions. Thermal motion is capable of destroying the order at a certain nonzero temperature (T_t). This occurs in the form of structural phase transition, the order parameter (compositional long-range order, s) of which can be measured by the X-ray or other diffraction methods. Such kind of phase transitions had been known long ago (e.g. in many metallic alloys) and was also discovered comparatively recently at $T_t \sim 1500$ K in PST, PSN [12] and several other complex perovskites. Ordering implies the site exchange between B′ and B″ cations via diffusion. It is a relaxation process with a nearly infinite characteristic time at low temperatures, but at 1500 K it can be quite fast. As a result, in some perovskites (e.g. in PST, PSN, PIN), by annealing at temperatures around T_t and subsequent quenching, one can obtain the metastable states with different s at low temperatures. In some other materials (e.g. in PFN and PMN) the compositional disorder cannot be changed by any heat treatment because the relaxation time of ordering is too long. However in all known relaxors, at T_B and below, the compositional order is frozen (quenched), i.e. cannot vary during practically reasonable time.

In the real complex perovskite crystals and ceramics the quenched compositional disorder is often inhomogeneous, e.g. small regions of the ordered state are embedded in a disordered matrix. These regions can be regarded as a result of incomplete compositional order-disorder phase transformation or as quenched phase fluctuations. In the prototypical relaxor PMN this kind of inhomogeneous structure always exists and cannot be changed by any heat treatment.

In $Pb(B'_{1/2}B''_{1/2})O_3$ perovskites the ordering of B-site ions converts the disordered PE $Pm\bar{3}m$ structure into the ordered $Fm\bar{3}m$ structure in which B′ ions alternate with B″ ions along the ⟨100⟩ directions (1:1 ordering). In the ordered phase of many non-ferroelectric $A(B^{2+}{}_{1/3}B^{5+}{}_{2/3})O_3$ perovskites, B^{2+} ions alternate with two B^{5+} ions along the ⟨100⟩ directions (1:2 ordering). The type of ordering in lead-containing relaxor perovskites, $Pb(B^{2+}{}_{1/3}B^{5+}{}_{2/3})O_3$, has been the subject of debates. In the early works only inhomogeneous ordering (ordered regions within disordered surroundings) was found in the samples studied. High-resolution electron microscopy of PMN revealed nano-size (∼2–5 nm) regions in which the ordering of 1:1 type ($Fm\bar{3}m$) was observed (see e.g. Refs. [13, 14]). These chemical nanoregions (CNR) give rise to weak superlattice reflections (the so-called F-spots). The results of anomalous X-ray scattering measurements [15] showed that the CNRs in PMN exhibit an isotropic shape and a temperature-independent (as expected for the quenched order) size in the temperature interval of 15–800 K. Alternating Mg^{2+} and Nb^{5+} ions, i.e the same type of ordering as in the ordered $Pb(B'_{1/2}B''_{1/2})O_3$ perovskites, were initially supposed to exist in these regions. This structural model was called "space charge model" because it implies the existence of the negatively charged compositionally ordered non-stoichiometric nanoregions, and the positively charged disordered non-stoichiometric matrix. Later, by means of appropriate high temperature treatments, Davies and Akbas [16] were able to increase the size of CNRs and obtained highly 1:1 ordered samples without the disordered matrix in the PMT and modified PMN ceramics. The existence of such ordering in overall stoichiometric samples is obviously inconsistent with the space charge model. The results of X-ray energy dispersive spectroscopy with a nanometer probing size revealed that the Mg/Nb ratio is the same in the CNRs as in the disordered regions of PMN [17], which also disagrees with the space charge model. A charge-balanced "random-site" model has been suggested in which one of the B-sublattices is occupied exclusively by B^{5+} ions while the other one contains a random distribution of B^{2+} and B^{5+} ions in a 2:1 ratio so that the local stoichiometry is preserved [16]. The inhomogeneous compositional disorder, characteristic of the $Pb(B^{2+}{}_{1/3}B^{5+}{}_{2/3})O_3$ perovskites, are shown schematically in Fig. 2.

The degree of compositional disorder can greatly influence the FE properties. For example, the disordered PIN crystals are relaxor ferroelectrics, but in the ordered state, they are antiferroelectrics with a sharp phase transition [18, 19], confirming the general rule that the relaxor behaviour can only be observed in disordered crystals. The possibility for real perovskite samples to have different states of compositional disorder, depending on crystal growth or ceramic sintering conditions, should be taken into account in research work. More detailed discussion on the compositional ordering and its impact on FE properties can be found in Refs. [20–22], and the literature therein.

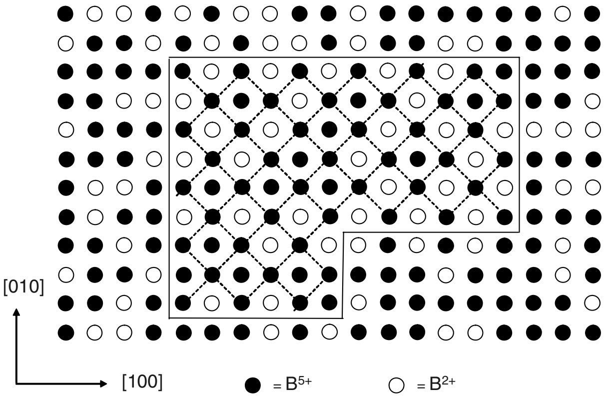

Figure 2 Schematic representation of the ordered chemical nanoregion, CNR (the area delimited by the solid line) within the disordered matrix in $Pb(B^{2+}{}_{1/3}B^{5+}{}_{2/3})O_3$ perovskites according to the random-site model. One of the two sublattices inside CNR (shown by dashed lines) is formed by B^{5+} ions only. Pb and O ions are not shown.

3. Relaxors in the ergodic state

3.1. Paraelectric structure

The PE phase of all perovskite ferroelectrics has the cubic $m\bar{3}m$ average symmetry, but locally the ion configuration can be distorted, i.e. the ions are not located in the special crystallographic sites of the ideal perovskite structure. For example, in the classical ferroelectrics $BaTiO_3$, the random displacements of Ti cations along the ⟨111⟩ directions caused by the multiple-well structure of potential surface were found [23, 24]. Such kind of displacements is due to the hybridization between electronic states of cations and the $2p$ states of oxygen (and should not exist in the case of purely ionic bonds). This effect is an important factor in the FE instability [25] and is also expected to occur in perovskite relaxors. Moreover, owing to the different sizes of the compositionally disordered cations and the random electric fields created because of the different charges of these cations in relaxors, all ions are expected to be displaced from special positions. These shifts should exist in the PE phase and also at lower temperatures.

Permanent uncorrelated displacements of ions from the high-symmetry positions of the (fully or partially compositionally disordered) cubic perovskite-type structure were indeed found in relaxors at temperatures much higher, as well as lower, than T_B. They are shown schematically in Fig. 3. The displacements of Pb^{2+} were detected by X-ray and neutron diffraction in PMN [26–28], PZN, PSN, PST, PIN, PFN, PZN-PT and PMN-PT with small x (see Refs. [29–31], and references therein). To describe the Pb distribution, a spherical layer model has been proposed [28] according to which the shifts of ions are random both in length and direction so that they are distributed isotropically within the spherical layer centred on the special Pb site.[1] The typical radius of the sphere is ∼0.3 Å. It decreases slightly with increasing temperature. The off-symmetry displacements of Pb ions in PMN were found to vanish at $T > 925$ K [26] (for other relaxors no data up to so high temperatures are available). The spherical layer model for Pb displacements in PMN was confirmed by the NMR investigations [32] and by the pulsed neutron atomic pair-distribution function (PDF) analysis [33]. Note that the significant random off-centring of Pb ions in perovskites is not the result of compositional

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[1] For PZN the shifts of Pb from the ideal positions along the eight equivalent ⟨111⟩ directions were reported, instead of spherical layer distribution [29].

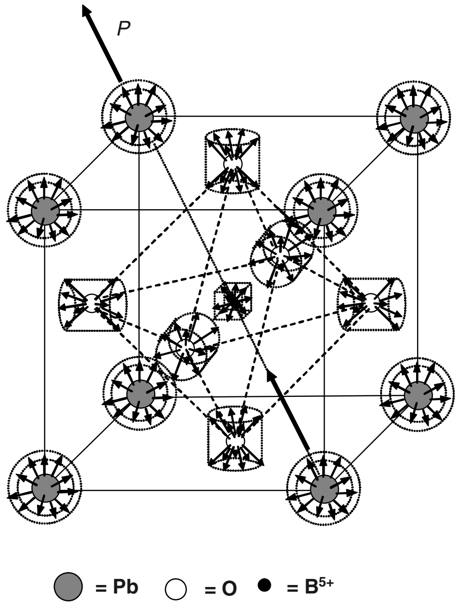

Figure 3 Typical uncorrelated ion displacements (shown by small arrows) in the unit cell of the lead-containing complex perovskite relaxor. Thick arrows show the direction of the local spontaneous polarisation *P* caused by the correlated displacements of ions inside PNRs.

disorder. It was also found in the PE phase of the ordinary perovskite $PbZrO_3$ [34]. On the other hand, in the PMN-PT solid solution with $x = 0.4$ which is still compositionally disordered, the Pb displacements from the special perovskite positions were not observed at $T > T_C$ [31].

According to neutron diffraction data [27, 29, 35] the shifts of oxygen ions in the planes parallel to the corresponding faces of the perovskite cubic cell are isotropic (in PMN the shifts are close to 0.2 Å). The oxygen ions are also shifted (by about 0.06 Å in PMN) in the perpendicular direction so that the distribution of shifts forms two rings parallel to the face of the cube. The displacements of B-site ions (Nb^{5+}, Mg^{2+}, Zn^{2+} etc.) from the ideal positions were not noticed in diffraction experiments [29, 35] (some authors found small seemingly isotropic displacements of about 0.1 Å in PMN [27]). Nevertheless the investigations of the extended X-ray absorption fine structure (EXAFS) and the pre-edge regions of absorption spectra revealed the off-centre random displacements of Nb in the direction close to $\langle 110 \rangle$ in PMN, PZN, PSN and PIN [36]. These displacements are not sensitive to the change of temperature (in the range of 290–570 K), nor to the degree of compositional disorder (in PSN and PIN). The pulsed neutron PDF studies confirm [33] that the Nb displacements (in PMN at room temperature) are comparatively small (much smaller than in $KNbO_3$).

In the canonical relaxors such as PMN, the average crystal symmetry seems to remain cubic with decreasing temperature (see, however, the discussion in Sections 7.1.1 and 7.2), but the local structure changes. In addition to the uncorrelated local distortions described above, the clusters of FE order (i.e. PNRs) appear at $T < T_B$ ($T_B \approx 620$ K in PMN). Due to their extremely small (nanometric) size, these clusters cannot be detected from the profiles of the X-ray and neutron Bragg diffraction peaks. Other experiments are needed to validate their existence.

3.2. Experimental evidence for PNRs

The first experimental (although indirect) evidence for the PNRs came from the temperature dependences of the optic index of refraction (n) which appear to be linear at $T > T_B$, as shown in Fig. 4 [37]. At lower temperatures a deviation from linearity was observed which was attributed to the variation of n induced (via quadratic electrooptic effect) by local spontaneous polarization inside the PNRs. The existence of PNRs was later confirmed by elastic diffuse neutron and X-ray scattering around the reciprocal lattice points [38–41]. In the PMN crystals, significant diffuse scattering appears at $T < T_B$ with the intensity increasing with decreasing temperature. This effect resembles the scattering caused by FE critical fluctuations, but an important difference (found in synchrotron X-ray experiments [41]) is that the shape of wavevector dependence of scattering intensity at large distances from the reciprocal lattice point deviates from the Lorentzian. This means [41] that the PNRs are more compact than the usual FE critical fluctuations and have better defined borders. The correlation length (ξ) of the atomic displacements contributing to the diffuse scattering, which is a measure of the size of PNR, can be derived from the experiment: it is inversely proportional to the width of the

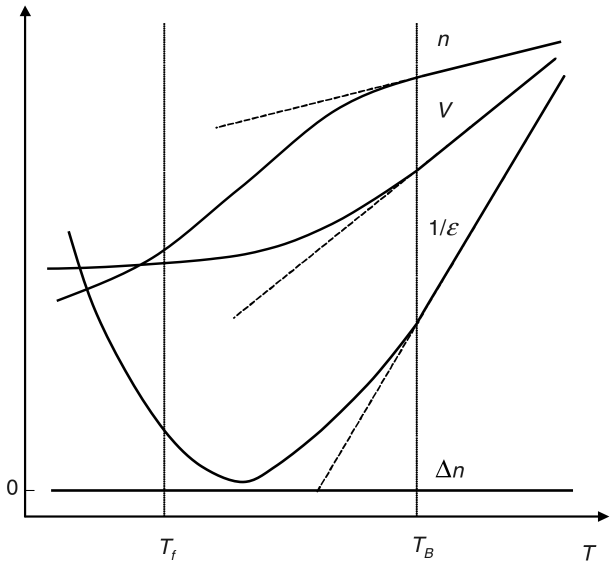

Figure 4 Schematical typical temperature dependences of the refractive index, n, unit cell volume, V, reciprocal dielectric permittivity, $1/\varepsilon$, and birefringence, Δn, in the canonical relaxor.

diffuse (Lorentzian) peak. According to the recent high-resolution neutron elastic diffuse scattering study of PMN [42], the size of the emerging PNRs is very small (ξ is around 1.5 nm) and practically temperature independent at high temperatures (Fig. 5). The perovskite unit cell parameter being ~0.4 nm, each PNR is composed of only a few unit cells. Below about 300 K, ξ begins to grow on cooling, reaching ~7 nm at 10 K. The most significant growth is found around T_f. Qualitatively the same behaviour was observed in the bulk of PZN crystals (the structure of PZN surface layers is different, see Section 7.2) but the size of PNRs is larger: they grow from ~7 nm at high temperatures to ~18 nm at 300 K [43, 44]. From the analysis of the relation between ξ and the integrated intensity of scattering, it was concluded [42] that the number of PNRs also increases on cooling, but in contrast to the temperature evolution of ξ, the increase begins right from T_B and at $T \approx T_f$ a sharp decrease of this number occurs (presumably due to the merging of smaller PNRs into larger ones). Below T_f the number of PNRs remains practically the same at any temperature.

Emergence of PNRs below T_B was also observed in the PMN crystal by means of transmission electron microscopy (TEM) [14], but their size was an order of magnitude larger than that determined from the neutron diffuse scattering, probably because of the influence of electron beam irradiation.

The directions of ionic displacements responsible for the spontaneous dipole moment of PNRs were investigated in several works. By means of dynamic structural analysis of diffuse neutron scattering in PMN crystals it was found that the B-site cations (Nb and Mg) and the O anions are displaced with respect to the Pb cations in the opposite directions along the body diagonal (i.e. the [111] direction) of the perovskite unit cell, forming a rhombohedral polar structure [45]. The rhombohedral $R3m$ symmetry was also derived from the analysis of ion-pair displacement correlations obtained by an X-ray diffuse scattering technique [46], but according to this study, O displacements deviate from the body diagonal and remain parallel to the $\langle 110 \rangle$ direction. The shape of PNR was found to be ellipsoidal [46]. The same shape was revealed by TEM [14].

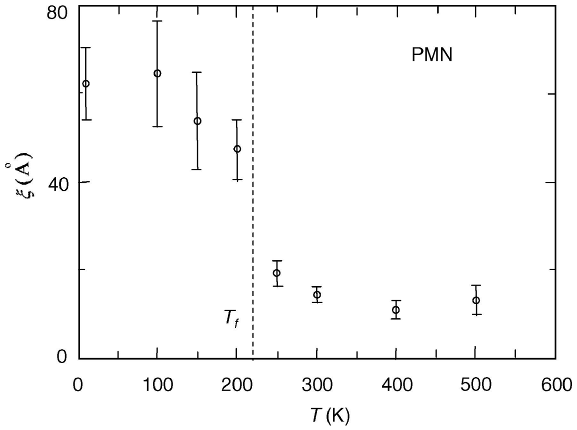

Figure 5 Average size of PNRs in the Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ crystal (determined from diffuse neutron scattering) as a function of temperature. Vertical dashed line corresponds to T_f. (after Xu *et al.* [42]).

Besides the structural features, many properties of relaxors can be adequately explained on the basis of the idea of PNRs. For example, in contrast to ordinary ferroelectrics, where a sharp anomaly of specific heat is known to appear at phase transition, in relaxors such anomaly is smeared over a wide temperature range and thus is hardly distinguishable from the background of the lattice contribution. The excess specific heat (total minus lattice contribution) has been determined in PMN and PMT crystals using precise adiabatic and thermal relaxation techniques [47]. It appears as a diffuse symmetric maximum located within the same temperature interval where PNRs nucleate and grow (between 150 and 500 K in PMN). Therefore the anomaly is likely to be caused by the formation of PNRs and/or by dipolar interactions among them.

Brillouin spectra of PMN-PT at $T \gg T_C$ revealed significant relaxation mode (central peak) which was attributed to the thermally activated fast (10–100 GHz) relaxation of PNRs [48]. The intensity and the width of the peak increase with decreasing temperature, indicating an increase of the number of PNRs and a slowing-down of their dynamics, respectively. The hypersonic damping was also observed. It increases upon cooling, and is attributed to the scattering of acoustic mode by PNRs [48].

PNRs can be thought as unusually large dipoles whose direction and/or magnitude are dependent on an external electric field. Therefore the related properties are expected to be unusual. Indeed, at those temperatures where PNRs exist, relaxors are characterized by giant electrostriction [49–51], remarkable electrooptic effect [50] and extremely large dielectric constant (see Fig. 1 and Section 6).

Even though no unambiguous structural confirmations for the phase transition at T_B are known, the anomalies of properties at this temperature were reported. The frequency-independent maximum of the dielectric loss tangent was found at this temperature in PMN [52]. In the course of thermal cycling of PMN and PMN-PT crystals unannealed after growth, a narrow maximum of the acoustic emission activity is observed (and decreases with the increase of number of cycles) in the vicinity of T_B [53]. Not only the temperature dependence of the index of refraction deviates from linearity at $T < T_B$ (as discussed above in this section), but the temperature dependences of the reciprocal dielectric constant, lattice parameter [51] (see Fig. 4 and (consequently) thermal strain [10, 53] also do the same.

Little is known about the relation between the CNRs and the PNRs in relaxors, although such relation can *a* *priori* be expected. Based on the TEM data, it was concluded that the PNRs in PMN may contain CNRs inside and in this case the regions in which PNRs and CNRs overlap remain non-polar [14]. In the framework of the theoretical models discussed in Sections 5 and 7.3, the CNRs can be considered as one of the factors influencing the formation and behaviour of PNRs, but not necessarily the determining factor.

4. Lattice dynamics in relaxors

Phase transitions in displacive ferroelectrics (including perovskites) are known to be caused by softening and condensation of transverse optic (TO) phonon mode at the Brillouin zone centre. Since the frequency of this mode (ω_0) is connected to the static lattice dielectric constant (through the Lyddane-Sachs-Teller relation, $1/\varepsilon \propto \omega_0{}^2$), the divergence of ε in ferroelectrics at T_{CW} according to the Curie-Weiss law ($1/\varepsilon \propto T - T_{\mathrm{CW}}$) implies that the mode condenses (its frequency tends to zero) at T_{CW}, too. In relaxors, the Curie-Weiss law also holds in the PE phase, i.e. at $T > T_{\mathrm{B}}$, (see Fig. 4 and Section 6), but the corresponding softening of phonon modes had not been detected until recently. During the last few years neutron inelastic scattering technique was applied to investigate the lattice dynamics in relaxor crystals. In the PE phase of PMN far above T_{B}, the dispersion of the transverse acoustic (TA) and low-energy TO phonons were found to be very similar to that existing in the PE phase of classical displacive ferroelectrics PbTiO$_3$ [39, 54] (see the curves for 1100 K in Fig. 6). On cooling down to $T \approx T_{\mathrm{B}}$, the optic branch softens in the same manner as in displacive ferroelectrics, i.e., the frequency of the mode at wave vector $\vec{q} = 0$ (zone centre mode) follows the Cochran law [54, 55]:

$$\omega_0^2 = A(T - T_0), \qquad (1)$$

with $A > 0$, as shown in Fig. 7. At $T < T_{\mathrm{f}}$, the well-defined TO modes are also observed [55] (see the curve for 150 K in Fig. 6). Once again, the temperature evolution is consistent with the typical behaviour of a FE soft mode below the Curie temperature (Fig. 7), i.e. Equation 1 holds with $A < 0$ (note that T_0 is close to T_{B} in this case). The same dependence is observed at low temperatures in PZN crystal [44]. But in the temperature range between T_{f} and T_{B}, the lattice dynamics is different. The propagating TO modes are observed here only for the wave vectors larger than q_{wf}. For $q < q_{\mathrm{wf}}$, the modes are overdamped. The TO phonon branch drops sharply into the TA branch at q_{wf}, resembling a waterfall (as shown in Fig. 6 for 500 K), and for this reason, the phenomenon is called “waterfall.” It has been observed not only in PMN but also in other relaxor materials for which neutron inelastic experiments were performed, i.e. in PZN [56] and PZNT [57]. In the same temperature range where the TO mode is overdamped (between T_{f} and T_{B}), the damping of TA phonons is also enhanced (e.g. neutron inelastic experiments in PMN revealed a large maximum of the TA-phonon linewidth at ~400 K [55]).

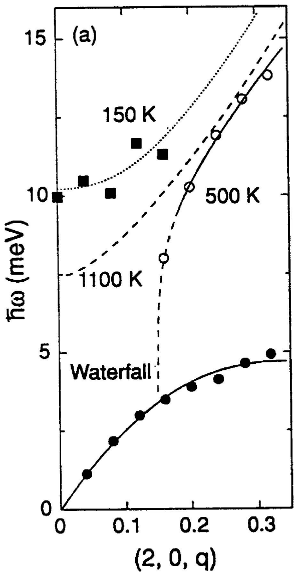

Figure 6 Phonon dispersion curves in PMN crystal for the TA branch at 1100 K (solid circles) and the lowest-energy TO branch at three different temperatures: $T = 1100$ K $> T_{\mathrm{B}}$ (dashed line), $T = 500$ K $< T_{\mathrm{B}}$ (open circles), and $T = 150$ K $< T_{\mathrm{f}}$ (squares). (after Wakimoto *et al.* [55]).

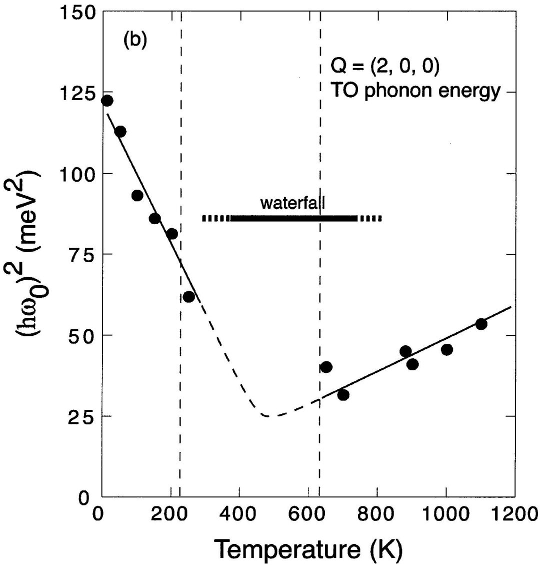

Figure 7 Temperature dependence of TO-phonon energy squared measured at (200) in PMN crystal. Vertical dashed lines correspond to T_{f} and T_{B}. The temperature range in which the waterfall feature appears is indicated by the thick horizontal line. The other dashed and solid lines are guides to the eye. (after Wakimoto *et al.* [55]).

It was initially proposed that the large damping of TO modes is due to the presence of PNRs which prevent the propagation of phonons with wavelength larger than the size of PNR, and thus q_{wf} is the measure of the average size of the PNRs [54, 57]. Later it was shown [58] that q_{wf} depends on the choice of the Brillouin zone and the relation of q_{wf} to the size of PNRs is improbable. The waterfall effect was then explained by the interactions of acoustic and optic branches. It was also noticed that damping of the soft mode near phase transition is not the unique feature of relaxors; similar effect can be found in some ordinary ferroelectrics [58].

An important question arises as to whether the low-energy TO mode found in relaxors is really the FE soft mode, i.e. whether the frozen mode displacements are responsible for the spontaneous dipole moment of PNRs and for the spontaneous polarization of the low-temperature FE phase. Initially the answer to the question was negative. Nabereznov *et al.* [39] compared the correlated atomic displacements in PNRs (found by elastic diffuse scattering experiments) and the TO-mode atomic displacements and concluded that they are incompatible. Besides, Vakhrushev and Shapiro [59] noticed that the value of T_0 derived from Equation 1 does not coincide with T_{CW} found in dielectric measurements and therefore this mode could not be the FE soft mode. They also identified an additional "quasioptic" branch lying significantly lower in energy than the TO branch and having the temperature variation consistent with the Curie-Weiss behaviour of the dielectric constant. The quasioptic mode was proposed to be the true soft mode. This opinion was later disputed. The apparent conflict between diffuse and soft mode scattering experiments was reconciled with the help of the "phase-shifted condensed soft mode" model proposed by Hirota *et al.* [40]. According to this model the total displacement of atoms inside a PNR consists of two components. The first component is created by the TO soft-mode condensation and gives rise to the spontaneous polarisation of PNR. The second one results from a uniform displacement of all atoms leading to the shift of the PNR along their polar direction relative to the surrounding non-polar matrix. Wakimoto *et al.* [60] described the lattice dynamics by a coupling between TA and TO modes without the need for considering any additional quasioptic modes. The concept of soft coupled optic mode was introduced. Being condensed, this mode has the optic component responsible for the dipole moment of PNR and the acoustic component giving rise to the uniform displacement of PNR as a whole. The microscopic origin of the uniform component is not yet clear.

Infrared (IR) spectroscopy of PMN between 20 and 300 K [61] and of PLZT between 10 and 530 K [62] revealed three main zone-centre TO modes as typical of cubic perovskites. High-energy TO modes do not show any pronounced temperature dependence both in PMN and PLZT. The lowest-energy mode (which was also resolved by time-domain THz spectrometry) was found to soften following Equation 1 with $A < 0$ and $T_0 \approx T_{\mathrm{B}}$, i.e. in agreement with the above-discussed neutron scattering data. Nevertheless, in contrast to the neutron data, the mode remains underdamped in the whole temperature range. This discrepancy is related to the fact that phonons with different wave-vectors are probed in IR ($q \approx 10^{-5}$ Å^{-1}) and neutron ($q \geq 10^{-2}$ Å^{-1}) experiments.

Raman scattering, which is known to be an effective tool for studying the optic soft modes in the crystals with normal phase transitions, was also widely applied to relaxors (see Refs. [63–65], for a review), but no soft mode has been found here. Light scattering spectra in relaxors appear to be quite complex and their interpretation is not straightforward. In particular, it is not clear what kind of disorder gives rise to the observed first-order lines that are forbidden by the $Pm\bar{3}m$ (O_h^I) average symmetry of relaxors.

Recently, vibration spectra in PMN were determined theoretically from the first principles [66]. Although the computations were performed for the case of compositionally ordered structure (the real structure is disordered with the inclusions of ordered CNRs, see Section 2), it appeared to be possible to assign the calculated phonons to the main peculiarities of Raman and IR spectra.

5. Origin and evolution of PNRs: Models and theories

Although the very existence of PNRs in relaxors seems to be doubtless, the cause and mechanisms of their formation are not conclusively understood. At temperatures higher than T_{B} the structure and properties of relaxors closely resemble those of normal displacive ferroelectrics. When a relaxor becomes compositionally ordered after high-temperature annealing (without changing the chemical composition), a sharp ferro- or antiferroelectric (AFE) phase transition is observed (see Section 2). These facts seemingly suggest that the relaxor crystal tends to be ferro- or antiferroelectric at low temperatures, but the quenched compositional disorder somehow prevents the normal transition into the phase with macroscopic FE or AFE order from happening. Instead, the PNRs appear. There exist different approaches to explain the formation of PNRs. All of them can be schematically subdivided into two categories. The models of the first category [8, 67–70] consider the PNRs as a result of local "phase transitions" or phase fluctuations so that the crystal consists of nanosize polar islands embedded into a cubic matrix in which the symmetry remains unchanged (as shown in Fig. 8a). The models of the second category assume the transition to occur in all regions of the crystal and the crystal consists of low-symmetry nanodomains separated by the domain walls but not by the regions of cubic symmetry [71, 72] (the example is shown in Fig. 8b). Note that these two situations can hardly be distinguished experimentally by structural examinations [73] because the *local* symmetry of cubic matrix is not expected to be cubic

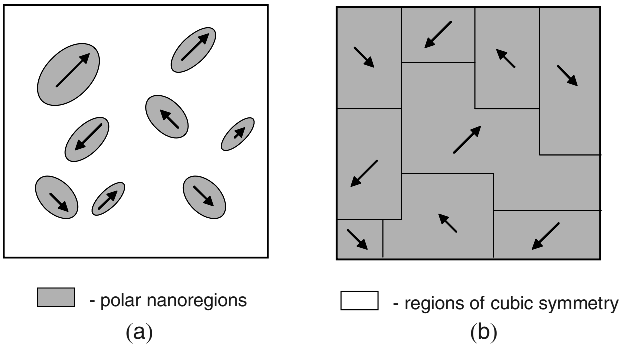

Figure 8 Schematic representation of PNRs in relaxors according to the different models.

and the thickness of domain walls (i.e. the regions where polarization is not well-defined) is comparable with the size of nanodomains.

The second category is represented by the random-field model proposed by Westphal, Kleemann and Glinchuk (WKG model) [71, 74], who applied the results of a theoretical work by Imry and Ma [75] to the relaxors. It was shown in Ref. [75] that in the systems with a continuous symmetry of order parameter, a second-order phase transition should be destroyed by quenched random local fields conjugate to the order parameter. Below the Curie temperature the system becomes broken into small-size domains (analogy of PNRs) instead of forming a long-range ordered state. It should be emphasized that this model does not consider the trivial case of the local spontaneous polarization which is directed parallel to the quenched field when the field is strong enough. Instead the situation is determined by the interplay of the surface energy of domain walls and the bulk energy of domains in the presence of *arbitrary weak* random fields [75].

For displacive transitions, continuous symmetry means that the spontaneous deformation is incommensurate with the PE lattice. However, this is not the case for the perovskite ferroelectrics in which the spontaneous deformation and the polarization (order parameter) are aligned along definite crystallographic directions (e.g. the $\langle 111 \rangle$ directions for the rhombohedral phase). Nevertheless, when the number of allowed directions is large (e.g. eight for the rhombohedral phase), the symmetry of order parameter can be considered quasi-continuous and the approach appears to be applicable. The disordered distribution of the heterovalent ions inherent to the compositionally disordered structure (e.g. Nb^{5+} and Mg^{2+} ions in PMN) provides the source for quenched random electric fields.

Ishchuk [72] analysed the thermodynamic potential in the framework of Landau phenomenological theory for the systems in which the energies of the FE and AFE phases are close to each other. It was shown that the state with coexisting FE and AFE domains may have lower thermodynamic potential than the homogeneous (FE or AFE) state. This effect is due to the interactions (electrostatic and elastic) between the FE and AFE domains. It was suggested that relaxors are just the crystals in which this effect occurs. In other words, the nonpolar regions, coexisting with PNRs (FE domains), are the domains of AFE structure.

The best-known model of the first category was developed in the early works by Isupov and Smolenskii [8, 22]. Due to the compositional disorder the concentrations of different ions (e.g. Mg^{2+} and Nb^{5+} in PMN) are subject to quenched spatial fluctuations. As the FE Curie temperature (T_C) depends on the concentration, spatial fluctuations of local T_C are expected. It was suggested that upon cooling, local FE phase transitions occur first in those regions where T_C is higher, whereas the other parts of the crystal remain in the PE phase. Therefore, PNRs are simply the regions with elevated Curie temperature.

Several other models use the microscopic approach and consider the structural evolution and formation of PNRs in terms of interatomic interactions. The FE lattice distortion in the ordinary perovskites is known to be determined by a delicate balance between the electrostatic (dipole-dipole) interactions and the short-range repulsions. Hybridization between the oxygen $2p$ states and electronic states of cations (covalent bonding) is able to change this balance, influencing thereby the phase transition temperature [25]. In the compositionally ordered (translationally symmetric) crystals, exactly the same forces affect all the atoms of a certain type because they have the same coordination neighbourhood. In the case of compositional disorder, the ions of different types may be found in the neighbouring unit cells on the same crystallographic positions (e.g. in the B-sublattice of PMN, both Mg and Nb ions are the nearest neighbours of Nb ions). The interatomic interactions which would cause ferro- or antiferroelectric order in the compositionally ordered state become random in this case, and as a result, the long-range polar order is disturbed. The models described below emphasize the importance of different interactions: the interactions under random local electric fields only (including dipole-dipole interactions) [67], and the dipole-dipole interactions together with random short-range repulsions [9, 68] or random covalent bonding [33].

In the random field theory developed for relaxors by Glinchuk and Farhi (GF model) [67] (see also Ref. [76] in which the related papers are reviewed), the transition is regarded as an order-disorder one, i.e. at high temperature the crystal is represented by a system of reorientable dipoles (dipoles caused by the shifts of ferroactive ions from their ideal perovskite positions, see Section 3.1). These random-site dipoles are embedded in highly polarizable "host lattice" (the high polarizability is due to the transverse optic soft mode existing in relaxors, see Section 4). The dipole-dipole interactions are indirect (they occur via the host lattice) and random. Nevertheless, according to the theory, they should lead to uniformly directed local fields and thus to FE ordering at low temperature (in contrast to *direct* dipole-dipole interactions which can lead to a dipole glass state). Thus to explain the absence of macroscopic FE order in relaxors, additional sources of random local electric fields are considered. These additional fields can be static (coming from quenched compositional disorder, lattice vacancies, impurities and other imperfections) or dynamic (associated with shifts of non-ferroactive ions from the special positions). In contras to the fields considered in the WKG model, these fields should be rather large (larger than critical value) to destroy the long-range FE order. The FE order parameter, phase transition temperature T_C, linear and nonlinear dielectric susceptibilities are calculated within the framework of statistical theory using the distribution function for local fields. It is found that depending on the model parameters (concentration of dipoles, other field sources and the host lattice correlation length), the low-temperature phase can be FE, dipole glass or mixed ferroglass. In the temperature interval between T_C and T_B, the short-range clusters may appear, in which the reorientable dipoles are ferroelectrically correlated (i.e. PNRs). In the ferroglass state these clusters coexist with the macroscopic regions in which the dipoles are coherently ordered.

Note that the GF model for relaxors is the extension of the analogous theory for incipient ferroelectrics with off-centre impurities (e.g. $KTaO_3$:Li, Nb, or Na). In the later case the off-centre impurities are the interacting dipoles. Due to their small concentration the crystal can be considered as a system of *identical* dipoles with random long-range interactions. In the case of complex perovskite relaxors, the dipole concentration cannot be considered small. The random interactions of different (short-range) nature are also involved and thus the dipoles are not identical. It was first recognized in the model proposed by one of the co-authors of the present review [9, 68]. In this model the PNRs are the result of local condensation of the soft phonon mode (which exists in relaxors as discussed in Section 4). The consideration is based on the model of coupled anharmonic oscillators which is often applied to ordinary ferroelectrics. The effective Hamiltonian is given by the sum of Hamiltonians of the individual unit cells:

$$H = \sum_l \left[0.5\Pi_l^2 + A_l\xi_l^2 + B_l\xi_l^4 - \sum_{l'} \upsilon_{ll'}\xi_l\langle\xi_{l'}\rangle \right],$$

where Π_l and ξ_l are the generalized momentum and coordinate of the soft mode displacements, A_l and B_l are parameters of one-particle potential, which are determined by the interactions (mainly short-range repulsive) between ions of the lth unit cell, and υ_{ll}' are parameters characterizing the interactions (long-range dipole-dipole) between the different cells. In the translationally invariant crystal, all the parameters, A_l, B_l, and υ_{ll}', would be the same. In the case of compositional disorder they are different. The distribution function for these parameters is introduced in the model. This distribution gives rise to the spatial distribution of local "Curie temperature" T_C. PNRs appear in the regions with enhanced local T_C. The model parameters are linked to the parameters of real structure (in particular, the size of ions). Based on the crystal composition, this model is able to predict quantitatively the degree of "diffusion" of the transition, i.e. the extent of temperature interval in which the PNRs develop before the crystal transform into the low-temperature nonergodic phase. In particular, the degree of diffusion increases with increasing difference in the radii of ions in the ferroactive sublattice (A or B perovskite sublattice) or with increasing compositional disorder in this sublattice.[2] On the other hand, the diffusion is much less sensitive to the disorder in the non-ferroactive sublattice. The influence of the degree of compositional disorder on T_C is also explained. Based on the arguments similar to those used in the original model [68] it was recently suggested [77] that, because of the randomness of microscopic forces responsible for the onset of spontaneous polarization, each PNR can consist of unit cells polarized in different directions. This model of "soft nanoregions" also implies that, due to thermally activated reorientations of some unit cells inside PNR, not only the direction (as believed before), but also the magnitude of the spontaneous dipole moment of individual PNR can strongly change with time (due to fluctuations or under the external field), while the size of PNR remains the same.

The Hamiltonian considered in the model by Egami [33] consists of two terms,

$$H = H_1 + H_2. \tag{2}$$

The first term is written in a standard form

$$H_1 = -\sum_{ij} J_{ij}\vec{S}_i \cdot \vec{S}_j, \tag{3}$$

where $\vec{S}_i$ is the local polarization caused by the displacement of i-th Pb ion from its special position (as discussed in Section 3.1), J_{ij} describes the random interaction between local polarizations mediated by oxygen and B-site ions. It is explained that in PMN the Pb ions cannot form the covalent bonds with those O ions which are bonded to Nb. On the other hand, Mg ions create purely ionic bonds and do not prevent the Pb–O bonding. Consequently the direction towards Mg is an "easy" direction for Pb displacement. This directional dependence of the energy of Pb displacements resembles the crystalline anisotropy in

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[2] In lead-containing complex perovskites the Nb and Ta cations are supposed to be ferroactive.

magnetic systems. It is random in compositionally disordered crystal and can be described by model Hamiltonian H_2. This model was established to account for the relaxor properties in ER as wall as in NR phases, but the appearance of PNRs was not derived.

Timonin [69] suggested that the ergodic phase in relaxors is an antilog of Griffiths phase theoretically predicted long ago (but not yet experimentally found) for dilute ferromagnetics. Ferroelectric clusters of various sizes (i.e. PNRs) appear in this model at $T < T_C$ (where T_C is the Curie temperature for non-dilute crystal) and specific non-exponential relaxation is predicted.

Specific temperature evolution of PNRs can be explained in terms of the phenomenological kinetic theory of phase transitions in compositionally disordered crystals [70]. The emergence of PNR, i.e. the region of polar crystal symmetry within the cubic surrounding, should be accompanied by the creation of electric and elastic fields around PNR, which increase the total energy of the system. Due to the similar effects in the compositionally ordered crystals undergoing a first-order phase transition, the regions of the new phase (nuclei) are not stable. They tend to grow if their size is larger than the critical one or disappear otherwise. As follows from the theory [70], in disordered crystals the nuclei of the new phase can be stable and the equilibrium size of newly formed nuclei can be arbitrary small. The PNRs in relaxors which are really small (contain several unit cells) and stable can be regarded as such kind of nuclei. The theory predicts that PNRs begin to appear in the PE phase at T_B as a result of local "phase transitions" (e.g. condensation of phonon soft mode). Upon cooling, the number of PNRs increases but the equilibrium size of each PNR remains unchanged within a certain temperature interval just below the temperature at which it appears. Upon further cooling, the PNR grows slowly with decreasing temperature while remaining in a stable equilibrium, and finally at $T = T_\mathrm{C}$, becomes metastable so that the size of PNR increases steeply due to phase instability. In other words, the behaviour predicted by this model is the same as experimentally observed in PMN (see Fig. 5). But this theory is unable to describe quantitatively the real behaviour at $T < T_\mathrm{C}$, because it does not take into account the interactions between different PNRs, which are obviously significant at low temperatures. It was further explained [70, 78] that depending on the model parameters (in particular, the mean T_C and the width of the distribution of local transition temperatures), a sharp phase transition can occur, resulting in large FE domains at $T < T_\mathrm{C}$ (in the case of a small width and a comparatively high T_C) or the transition is diffuse and the low-temperature polar regions are of nanometer size. The dipole-dipole interactions between them can lead to the formation of a glass-type phase at a certain temperature T_f . The intermediate situations are also possible with moderately diffuse transition and mesoscopic polar regions (domains). Note that these different types of behaviour have indeed been observed experimentally in different perovskite materials (see Section 7.2).

6. Dielectric response in relaxors

Small-signal dielectric response has been intensively studied in a large number of relaxor materials, but most investigations were restricted within the frequency range of 10–10^9 Hz or narrower. In the past few years, modern measurement facilities with enlarged frequency range have been applied to relaxors. It has been found that significant dielectric dispersion exists in the whole spectrum starting from the frequency of lattice vibrations down to the lowest practically measurable frequency of $f \sim 10^{-5}$ Hz. The present section will focus on these works.

The field-induced polarization in relaxors can be divided into several qualitatively different parts so that the total relative permittivity in the temperature range of permittivity maximum can be written as

$$\varepsilon = 1 + \chi_e + \chi_{Ph} + \chi_R + \chi_U + \chi_{LF}, \tag{4}$$

where χ_{e}, χ_{Ph}, χ_R, χ_U and χ_{LF} are the susceptibilities (complex numbers) describing the electronic, phonon, "conventional relaxor" (CR), "universal relaxor" (UR) and "low-frequency" contributions, respectively. All the contributions are frequency dependent [in Equation 4 the susceptibilities are ranked in the order of increasing typical characteristic time]. As in any materials, electronic contribution persists in relaxors at all temperatures and at frequencies up to 10^{15}–10^{17} Hz, but at lower frequencies, the value of $\chi'_e = (n^2 - 1) \sim 10$ is small as compared with other susceptibilities.

The phonon (lattice) susceptibility (caused by the mutual displacements of cation and anion sublattices) is active up to the frequencies of 10^{12}–10^{14} Hz. To separate χ_{Ph} from other contributions, measurements at these frequencies are necessary. In relaxors χ_{Ph} has been determined from IR reflectivity spectra at temperatures lower than T_B only. In PMN crystals, χ_{Ph} increases from ~40 at 20 K to ~100 at 300 K [61]. In other words, it constitutes less than 1% of the total low-frequency permittivity measured at T_m (see Fig. 1). This is an important difference of relaxors from ordinary displacive ferroelectrics in which phonon polarization totally accounts for the permittivity peak at the phase transition.

The susceptibilities χ_R and χ_U related to the relaxation-type polarizations are the main contributions giving rise to the peculiar relaxor peaks in the temperature dependences of permittivity (shown in Figs 1 and 9). The real part of χ_R is constant at low enough frequencies and decreases to zero when the frequency reaches the (temperature-dependent) characteristic value. This decrease is accompanied by the peak in the frequency dependence of the imaginary part.[3] Both real and imaginary parts of the UR susceptibility continuously (without any loss peak) decrease in the whole frequency range practically available for measurements according to the power law

$$\chi'_U = \tan(n\pi/2)\chi''_U \propto f^{n-1}, \tag{5}$$

where n is close to but smaller than unity. Note that the same empiric classification (i.e. the monotonic frequency variation versus the variation with loss maximum) applies not only to relaxors, but also to the relaxation processes found in many other solids [79]. Nevertheless, the values of χ_R and χ_U in relaxors are extraordinary large as compared to other dielectrics. The CR dispersion (CRD) is observed at the low-temperature slope of permittivity peak giving rise to the frequency shift of T_m, while the UR dispersion (URD) exists at temperatures lower, as well as higher, than T_m (as shown in Figs 1 and 9).

The last term χ_{LF} in Equation 4 combines all possible relaxation contributions not related to the relaxor ferroelectricity, which may include the polarization of hopping charge carriers [79, 80], Maxwell-Wagner-type polarisation, etc. Typically, these contributions become significant in good-quality samples of relaxor perovskites at comparatively high temperatures and/or low frequencies. In the PMN crystal presented in Fig. 1 the contribution of χ_{LF} at lowest frequency $f = 10^{-2}$ leads to the noticeable increase of ε'' at temperatures above ~300 K.

In the radio- and audio-frequency ranges, where the dielectric properties of relaxors are most often studied, the value of χ'_R is much larger than χ'_U. That is probably the reason why the UR contribution has been discovered only recently with the help of the frequency response analyser that is able to work at ultra-low frequencies [as one can see from Equation 5, χ'_U increases with decreasing f]. The χ_U component was separated from the χ_R one by means of the analysis of dielectric spectra at $T > T_\mathrm{C}$ (or $T > T_\mathrm{f}$) first in PMN-PT [80–82] and then in PMN [77], PSN [83] and BTZ [84]. Since CR is the dominant contribution giving rise to the diffuse $\varepsilon'(T)$ peak, $\chi'_R \approx \varepsilon'$ in the vicinity of T_m (at least for the frequencies that are not very low or very high). Therefore, most of the dielectric investigations of relaxors dealt in fact with the CR contribution, even though it was not identified by the authors.

As shown recently for many relaxors [85, 86], the high-temperature slope of the diffuse $\varepsilon'(T) \approx \chi'_R(T)$ peak can be scaled with the empirical Lorenz-type relation,

$$\frac{\varepsilon_A}{\varepsilon'} - 1 = \frac{(T - T_A)^2}{2\delta^2}, \tag{6}$$

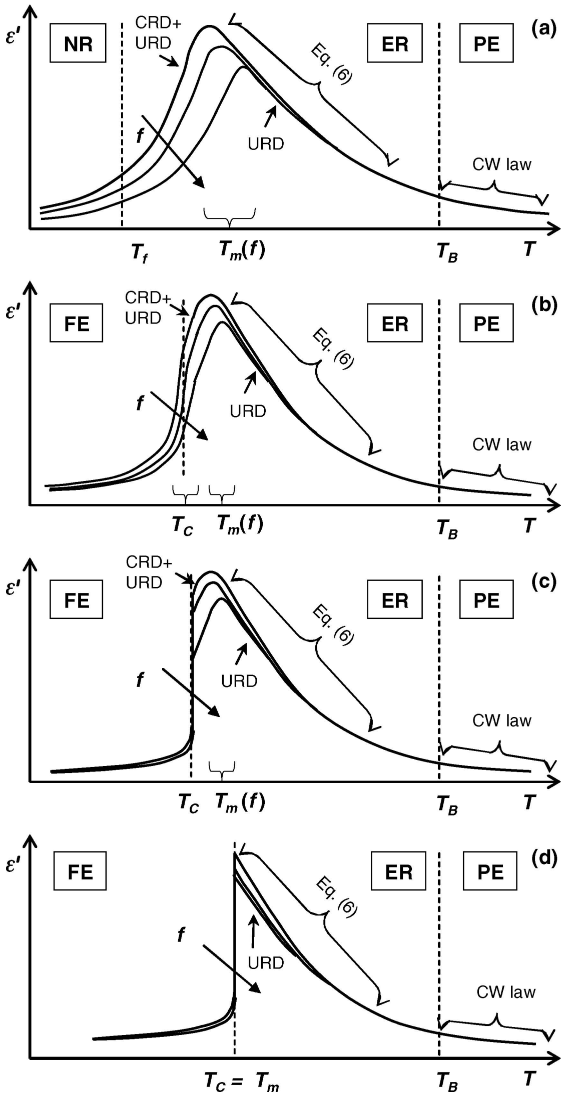

Figure 9 Different possibilities for the temperature evolution of structure and dielectric properties in compositionally disordered perovskites: (a) canonical relaxor; (b) crystal with a diffuse relaxor-to-ferroelectric phase transition at $T_\mathrm{C} < T_\mathrm{m}$; (c) crystal with a sharp relaxor-to-ferroelectric phase transition at $T_\mathrm{C} < T_\mathrm{m}$; (d) crystal with a sharp relaxor-to-ferroelectric phase transition at $T_\mathrm{C} = T_\mathrm{m}$. The temperature dependences of the dielectric constant at different frequencies f are schematically shown. The temperature intervals in which the Lorenz-type Equation 6 and the Curie-Weiss law hold, the regions of conventional relaxor dispersion (CRD) and universal relaxor dispersion (UR) and the types of structure [paraelectric (PE), nonergodic relaxor (NR), ergodic relaxor (ER), ferroelectric (FE)] are identified. Note the similar behaviour at high temperatures in all cases.

where T_A ($< T_m$) and ε_A ($> \varepsilon_m$) are the fitting parameters defining the temperature and magnitude of the Lorenz peak (6), and δ is as a measure of the degree of diffuseness of the peak. This formula gives a more adequate description of the experimental data than the previously used relation, $\varepsilon_m/\varepsilon'' - 1 \propto (T - T_m)^\gamma$ (where $1 < \gamma < 2$, and ε_m is the value of ε' at T_m). Equation 6 holds from temperature T_1, which is typically several degrees higher than T_m, to temperature T_2, which is a few dozens of de-

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[3] The well-known Debye relaxation is an example of such kind of the behaviour.

grees lower than T_B (see Fig. 9). The diffuse peak of $\varepsilon''(T) \approx \chi''_R(T)$ can be scaled with more complex relations (see Refs. [19, 87] for details).

At $T > T_B$, the dielectric constant is described by the Curie-Weiss law,

$$\varepsilon' = C/(T - T_{CW}),$$

where the Curie constant, C, has the same order of magnitude ($\sim 10^5$ K) as in ordinary displacive ferroelectrics and T_{CW} is typically higher than the low-frequency value of T_m (as shown in Fig. 4) but at high frequencies (e.g. in PMN at $f > 20$ GHz) T_m can become larger [52].

The CR contribution can consist of several components in itself involving different polarization mechanisms. Each of the mechanisms gives rise to the corresponding dispersion and can be seen in the $\varepsilon''(f)$ curve as an individual maximum (or an anomaly if neighbouring maxima overlap each other). For example, in PMN crystals three components (dispersion regions) have been found at $T < T_B$ [52, 61, 88], which were resolved simultaneously between 210 K ($\approx T_f$) and 290 K. The first component appears at the (temperature-independent) frequency of $\sim$1 THz and gives rise to a comparatively small input to the static dielectric constant (about 130). The two other dispersion regions become broadened on cooling and their mean relaxation time increases [i.e. the frequency of the corresponding $\varepsilon''(f)$ peak decreases], so that at $T < T_f$ the low-frequency component shifts out of the measurement frequency range and the higher-frequency component develops into a constant (frequency-independent in the range of 10^2–10^{11} Hz) loss. This effect of constant loss is a noticeable property of the low-temperature nonergodic phase in relaxors. It can also be observed in other relaxors, e.g. in the PLZT ceramics [89] and the compositionally disordered PIN crystals [19]. The magnitude of constant loss decreases exponentially on cooling, but still remains measurable at liquid-helium temperature. At extremely low frequencies ε'' in NR phase is no longer constant and slightly increases with decreasing frequency (see Fig. 1).

To describe the CR dielectric spectra, the same empirical expressions as used for other dielectrics were applied. The Kohlrausch-Williams-Watts [80, 90], the Havriliak-Negami [91] and the simpler Cole-Cole [19, 89] formulae have been employed by different authors to fit the experimental $\varepsilon(f)$ data. The alternative way to analyse the dispersion is to find the appropriate function for the distribution of relaxation times. For example, Rychetsky *et al.* [89] fitted the relaxation in PLZT to a uniform distribution that broadens upon cooling.

A remarkable feature which was observed first in PMN [92] and then in many other relaxor ferroelectrics is the Vogel-Fulcher (VF) law connecting the temperature and the frequency of the $\varepsilon'(T)$ peak:

$$f = (2\pi\tau_0)^{-1} \exp\left[-E_a/(T_m - T_{VF})\right], \qquad (7)$$

where f is the measurement frequency, τ_0, E_a and T_{VF} are the fitting parameters. The same relation but with slightly different parameters has also been reported for the peak temperature in the $\varepsilon''(T)$ dependences (T_{mi}). Investigations of PIN crystals showed that the parameters of Equation 7 can be different in different frequency intervals [19]. The VF law was known in structural and spin glasses. When revealed in relaxors, it became one of the main reasons to postulate the existence of a dipole glass phase at $T < T_{VF}$. Equation 7 might (but not necessarily, see below) signify the similar VF relation for the characteristic relaxation time τ of the corresponding relaxation process:

$$\tau = \tau_\infty \exp\lfloor E_b/(T - T_f)\rfloor, \qquad (8)$$

where τ_∞, E_b are the parameters and T_f is the freezing temperature (i.e. the temperature below which the relaxation time becomes infinite). This divergence of τ indicates that the thermally activated reorientations of dipoles responsible for polarization slow down with decreasing temperature and become impossible (consequently dipoles cannot respond to the electric field) at $T = T_f$, but not at $T = 0$ as prescribed by the Arrhenius law for the dynamics of independent dipoles. In dipole glasses the interactions among the dipoles are the cause for such kind of freezing. These interactions (bonds) are frustrated (i.e. can be either FE or AFE but cannot be satisfied simultaneously) and thus favour the configurations with random directions of dipoles, in contrast to the ferroelectrics and antiferroelectrics in which the dipole directions are parallel and antiparallel, respectively.

The relations between Equations 7 and 8 in relaxors were studied by several authors. In the case of Debye relaxation (which can be expected in the system of identical non-interacting dipoles) this relation should be simple: τ follows the Arrhenius law [which is the same as the VF law (8), but with $T_f = 0\rfloor$ and this automatically means that law (7) also holds for T_{mi} with the same parameters, i.e. $\tau_0 = \tau_\infty$, $E_a = E_b$ and $T_{VF} = 0$. The relaxation in relaxors is much more complex and can be characterized by a wide spectrum for the distribution of the relaxation times. Simple relations between the parameters of Equations 7 and 8 are not evident. Furthermore, different relaxation times from the spectrum may have different freezing temperatures. It was also shown theoretically that the situations are possible in which Equation 7 holds with $T_{VF} \neq 0$, but no freezing at a non-zero temperature really takes place [93], i.e. the VF relationships for T_m and T_{mi} do not necessarily imply glass-type dipole dynamics. The problem seems to be solved in some relaxors by means of a special analysis of the frequency-temperature dependences of the real part of permittivity. It was shown that the longest relaxation time in the spectra of PMN [94, 95], PST [94] and PLZT [96] diverges according to the relationship (8) with $T_\mathrm{f} = T_{VF}$ (≈220 K in PMN), while the bulk of the distribution of relaxation times remains finite even below T_f [95, 96]. The divergence of the longest relaxation time means that, at least empirically, the behaviour of relaxors in small-signal electric field is similar to the behaviour of dipole glasses. However, a microscopic interpretation of this fact is not so clear. In contrast to ordinary dipole (or spin) glasses in which the susceptibility can by unambiguously attributed to the reorientation of certain permanent dipoles (spins), the structure of relaxors is more complex and the polarization mechanisms responsible for the large and diffuse $\varepsilon(T)$ peak have not been definitely identified.

Most of the existing explanations relate the dielectric relaxation in relaxors to the PNRs. The PNRs are very small and can be considered as individual thermally activated dipoles giving rise to the orientational polarization. Thus, the dominant contribution to the measured $\varepsilon(T)$ relaxor peak (i.e. the CR contribution according to the classification described above) may be attributed to the thermally activated reorientation of dipole moments of PNRs (local spontaneous polarization vectors). Many authors proceeded upon this assumption when analysing the dielectric data (see e.g. Refs. [97–99]). The dipole moments of PNRs are considered in many models as interacting (directly or via surrounding matrix) entities constituting a glassy system (see Sections 5 and 7.3). The reorientations may be affected by the random anisotropy and (in contrast to magnetic spin glasses) by an environment of random electric and elastic fields.

The second possible mechanism associated with PNRs is the side-way motion of their boundaries without the change of the orientation. In the course of such motion, the volume (and thereby the dipole moment) of the polar region changes, giving rise to the characteristic polarization response. This looks like breathing of PNRs and therefore, the corresponding model developed by Glazounov and Tagantsev is called "breathing" model [100]. The model considers the vibrating PNR boundaries in terms of the theory of randomly pinned interface, which was developed earlier for magnetic materials. In the case of relaxors the internal random local fields induced by charge disorder act as the pinning centres. Another approach was used by Rychetsky *et al.* who proposed a thermodynamic model for the polarization reversal near the PNR boundary, which is equivalent to the displacement of the boundary [89]. In particular, this model describes well the constant loss effect at low temperatures. From the analysis of the behaviour of PMN crystals in large dc and ac electric fields, it was suggested [101] that the dielectric response in the ergodic phase [i.e. in the vicinity of the $\varepsilon(T)$ maximum] is controlled by the vibration of PNR boundaries, rather than by the thermally activated reorientations of PNRs.

Note that in PMN and some other relaxors two main components determine the CR dielectric response in the ergodic phase (see above in this section). The low-frequency component may result from the reversal of the spontaneous dipole moments of PNRs and the high-frequency one may originate from the PNR boundary motion [88].

The value of the universal susceptibility [i.e. the susceptibility whose dispersion is described by Equation 5 at all frequencies] in relaxors is several orders of magnitude larger than in non-relaxor materials with the same n [80]. Thus it is reasonable to suggest that the UR polarization mechanism is also connected with PNRs which are inherent only in relaxors. Within the scope of the soft nanoregions model (see Section 5), the UR response has been attributed to the thermally activated reorientations of dipole moments of individual unit cells inside PNRs [77].

The Curie-Weiss law in relaxors can be treated in two different ways, depending on the polarization mechanism which is supposed to be valid in the temperature range of the law (i.e. at $T > T_\mathrm{B}$). The first way (see e.g. Refs. [52, 59, 60, 88, 102]) implies that, as in the case of normal perovskite (displacive) ferroelectrics, the field-induced polarization is due to the phonon contribution. The second approach suggests that the polarization mechanism in the temperature range of the Curie-Weiss law is qualitatively the same as at T_m (by analogy to order-disorder ferroelectrics and spin glasses) and involves the relaxation of individual dipoles (see e.g. Ref. [103] in which the Sherrington-Kirkpatrick model was used to analyze the susceptibility in PMN). To determine which way is adequate, the experimental investigation of high-frequency (IR) dispersion at $T > T_\mathrm{B}$ is needed.

7. Relaxors at low temperatures: A glassy state or a ferroelectric phase

In the previous sections we have mainly considered the relaxors at comparatively high temperatures, i.e. in the PE and ER phases. We have also discussed some basic aspects of the low-temperature behaviour of canonical relaxors, i.e. those in which the structure remains macroscopically cubic at all temperatures and the FE phase can be achieved only by poling (e.g. by applying an external electric field). In the canonical relaxors (e.g. PMN, PMT, PLZT with large x), a nonergodic (glassy) state appears at low temperatures. In many other materials (e.g. PSN, PST, PLZT with small x, and PMN-PT with large x) that exhibit relaxor properties and related structural features (e.g. PNRs) at high temperatures, a spontaneous (i.e. without poling) structural phase transition into the FE phase occurs. These two different paths of temperature evolution are shown schematically in Fig. 9. In this Section, we describe the low-temperature behaviour of relaxors in more detail.

7.1. Glassy nonergodic relaxor phase

7.1.1. Structure

As mentioned in Section 4 the soft mode in the prototypical relaxor PMN recovers below T_f so that the temperature dependence of the mode frequency shows the behaviour characteristic of a normal ferroelectric phase [i.e. follows Equation 1 with $A < 0$]. A sharp peak of hypersonic dumping was observed at T_f [104]. However, no other evidence of the structural phase transition at T_f has been detected. The average cubic symmetry of PMN at low temperatures was confirmed in many structural studies by the absence of any splitting of X-ray and neutron Bragg reflections (which means that the shape of unit cell is cubic) as well as by the analysis of the intensities of the reflections (which are sensitive to the positions of atoms in the cell). For instance, in Refs. [27, 73], the unit cell was determined to be cubic by X-ray and neutron powder diffraction experiments performed down to 5 K, but due to the limited number of reflections analysed, the positions of atoms and the thermal parameters could not be refined simultaneously. In Refs. [105, 106], the analysis of a large number of reflections obtained from X-ray diffraction of PMN single crystals confirmed the $Pm\bar{3}m$ space group in the range of 100–300 K. The cubic structure is also confirmed by the absence of birefringence [107, 108].[4]

Even though the structural phase transition in PMN is not definitely observed, some important structural changes not affecting the average symmetry are still found. With decreasing temperature, the average size of PNRs increases significantly around T_f (Fig. 5). The synchrotron X-ray scattering revealed the emergence of very weak and wide 1/2(hk0) superlattice reflections (α spots) in the vicinity of T_f [110]. These reflections were attributed to the antiferroelectric nanoregions (AFNR) formed by the correlated anti-parallel (static or dynamic) displacements of Pb ions along the $\langle 110 \rangle$ directions with a magnitude of $\sim$0.2 Å. Significant enhancement of the intensity of α spots below T_f is believed to arise from an increase in the total number of the AFNRs, whose average size of $\sim$30 Å (determined from the width of reflections) remains constant down to the lowest measured temperature of 10 K [110]. AFNRs appear to be different from PNRs and CNRs, and unrelated to either of them [110].

7.1.2. Broken ergodicity in relaxors

Relaxors show nonergodic behaviour resembling the behaviour of spin (or dipole) glasses. In the high temperature (ergodic) phase of glasses, the spins (or dipoles, which can be considered as pseudospins) are weakly correlated and free to rotate, so that after any excitation (e.g. after application and removal of an external field) the system quickly comes back to the state with the lowest free energy, i.e. the state with zero total magnetization. It is always the same state regardless of the initial conditions (i.e. the strength and direction of the field in our example). At lower temperatures, due to the correlations between spins, the free energy surface has very many minima of almost the same depth separated by energy barriers of different heights (each minimum corresponds to a specific configuration of spins). In the glass phase, some of these barriers are so high that the time needed to overcome them is larger than any practically reasonable observation time. Therefore, during this time the system cannot reach all the configuration states, and consequently, the usual thermodynamic averaging and the time averaging give different results, i.e. the system is in a nonergodic state. On its way to a new state of minimum free energy required by the changed external conditions, the system should pass many barriers of different heights. This leads to a process with a wide distribution of relaxation times. The maximum relaxation time from this distribution may be so large (infinite for an infinite crystal) that the system cannot effectively reach the equilibrium. As a result, the state and the physical properties of the material depend on the history (i.e. the external field applied, the temperature variations, the observation time, etc.). In particular, substantial ageing effects should be observed, i.e. the change of properties with time spent by the sample at certain fixed external thermodynamic parameters (temperature, field, etc.).

All the main (mutually related) characteristics of nonergodic behaviour typical of spin glasses, i.e. anomalously wide relaxation spectrum, ageing, dependence of the thermodynamic state on the thermal and field history of a sample, are observed in relaxors at temperatures around and below T_f. The slowing-down of dipole dynamics was already discussed in terms of small-signal dielectric response in Section 6. Slow relaxation manifests itself also in other properties related to the local and/or macroscopic polarization. In particular, the relaxation of optical linear birefringence induced in PMN by a weak ($E < E_{cr}$) external electric field was studied [107] (E_{cr} is the critical field needed to induce the transition to the FE phase). The Kohlrausch-Williams-Watts-type and the Curie-von Schweidler-type relaxations were found in the temperature intervals of $180 < T < 210$ K and $210 < T < 230$ K, respectively. The results were successfully described in terms of Chamberlin's approach to dynamic heterogeneity [111], implying a broad relaxation spectrum. Application of a strong ($E > E_{cr}$) d.c. field to the PMN crystal at $T < T_\mathrm{f}$ results in a nearly logarithmic decay of dielectric permittivity [112] and a slow evolution of X-ray Bragg

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[4] While most researchers agree that the average structure of PMN is cubic, the rhombohedral structure was also reported [109]. The possible reason for this discrepancy will be discussed in Section 7.2.

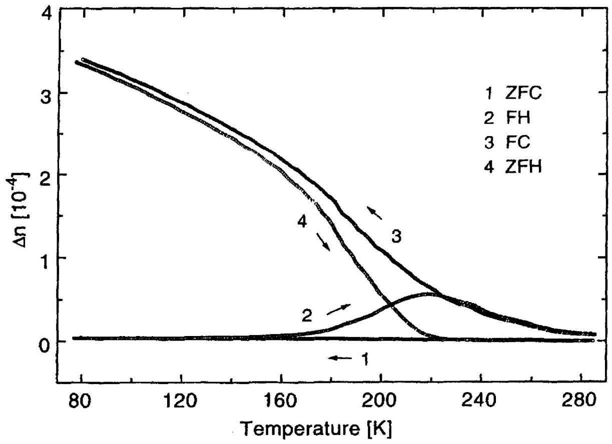

Figure 10 Linear birefringence measured subsequently as a function of temperature on zero-field cooling (ZFC), field heating with $E = 1.2$ kV/cm $< E_{cr}$ (FH), field cooling (FC) and zero-field heating (ZFH), illustrating the nonergodic behaviour of PMN crystal. (after Kleemann *et al.* [107]).

peaks reflecting the change of crystal symmetry [113].[5] The effects of ageing of susceptibility in the NR phase of PMN and in the typical spin glass phase were found to be very similar (and much stronger than in typical dipole glasses) [114]. The example of the dependence of properties on the thermal and electrical history of sample is shown in Fig. 10. The other examples are the splitting in the temperature dependences of the field-cooled and zero-field-cooled quasistatic dielectric constants in PMN and PLZT [95, 96] and the $P(E)$ hysteresis loops (see Section 7.1.3),

The ergodicity is clearly broken in relaxors at low temperatures, but this does not necessarily mean that relaxors are really dipole glass systems. Many other systems may also be nonergodic [115]. In particular, an ordinary FE phase is also nonergodic, but its potential landscape contains only a few minima (which are symmetric and correspond to the different directions of spontaneous polarization). As a result, the properties are easily distinguishable from those of nonergodic spin glass (or relaxor) phase. Wide relaxation spectrum and ageing phenomena are absent in the ideal FE crystal. But in the compositionally disordered perovskite crystal the situation is very different and different explanations for the nonergodic behaviour are possible. For instance, the above-mentioned Kohlrausch-Williams-Watts-type relaxation of birefringence was explained by domain wall displacements, rather than by the reorientations of dipoles [107]. Furthermore, some peculiarities of the relaxor behaviour have never been observed in spin and dipole glasses. In particular, the Barkhausen jumps during poling process (detected optically in PMN) are not compatible with the glassy reorientation of dipoles, which takes place on a microscopic length scale and hence should be continuous and monotonic [71]. Field-induced FE phase and FE hysteresis loops have not been observed in typical dipole glasses. Thus, the nature of the nonergodic phase in relaxors remains the subject of intensive discussion. In particular, the WKG model suggests that the low-temperature phase of canonical relaxors is a ferroelectric state, but broken into nanodomains by quenched random fields. We will discuss the origin of nonergodic phase in more detail in Section 7.3.

Note also that in terms of compositional disorder, relaxors are frozen in a metastable state, as discussed in Section 2. The degree of compositional disorder can depend on thermal prehistory. This is also an effect of nonergodicity.[6] However, at temperatures around T_B and below, the compositional disorder remains unchanged on the experimental time scales (i.e. frozen), and at the same time, the motion of dipoles (at $T > T_f$) is fast. Thus, when considering the subsystem of dipoles at $T > T_f$, one can believe that the crystal reaches the equilibrium[7] and the phase is effectively ergodic. On the other hand, if the sample has been annealed during experiment at high temperatures (~700 K or higher) the possible effects of nonergodicity related to the compositional disorder should be taken into account.

7.1.3. Electric-field-induced ferroelectric phase in relaxors

An important feature of the NR state is that, it can be irreversibly transformed to the phase with the FE dipole order when poling by an electric field larger than the critical strength (in PMN the minimal E_{cr} is about 1.7 kV/cm at $T_C \simeq 210$ [108]). This feature points to the common nature of relaxor and normal ferroelectrics. The FE hysteresis loops, which are known to be the determinative characteristic of FE phase, are observed in relaxors with the values of remnant polarization and coercive field typical of normal ferroelectrics. Pyro- and piezoelectric effects are also observed after poling. X-ray diffraction [113, 117] and optical [108] investigations of poled PMN crystals showed that the field-induced phase has the rhombohedral 3m symmetry, i.e. the same symmetry as in several normal perovskite ferroelectrics. On the other hand, locally the structure is inhomogeneous, i.e. different from normal ferroelectric structure. The traces of cubic phase were observed at low temperature by X-ray diffraction experiments in poled PMN crystal [113]. The NMR investigations of PMN crystal poled by a field almost two

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[5] After a long (several hours) waiting time the entire crystal suddenly transforms to the FE phase via a first-order transition.

[6] In contrast to spin (dipole) or FE state where the relaxation time is expected to become infinite in infinite crystal, the rate of compositional ordering does not depend on a crystal size. The corresponding relaxation time at nonzero temperature can be very large, but not infinite.

[7] According to Feynman [116], a system is in equilibrium if "all the fast things have happened and all the slow things have not".

times as large as E_{cr}, revealed that only about 50% of Pb ions are displaced parallel to the [111] poling direction in a FE manner, while the other 50% exhibit spherical layer-type displacements characteristic of PE phase [32]. The size and number of AFNRs found in PMN in the unpoled state (see Section 7.1.1) remain unchanged in the FE phase [110].

Upon heating, the FE phase transforms to the cubic (ER) phase at a well-defined temperature, T_C (≈210 K in PMN). This first-order phase transition is accompanied by a step-like drop of spontaneous polarization (as determined from pyroelectric current), sudden vanishing of birefringence, and sharp peak of dielectric constant. A more detailed description of the field-induced transition and FE phase in relaxors is given in Ref. 11.

7.2. Spontaneous relaxor-to-ferroelectric phase transition

The transition from the ER to the FE phase typically takes place at temperature T_C, which is several degrees or several dozens of degrees lower than T_m, as schematically shown in Fig. 9b and c. Usually the transition is observed in those relaxors where the $\varepsilon'(T)$ peak is not very diffuse (i.e. the diffuseness parameter δ is relatively small). X-ray and neutron diffraction experiments unambiguously indicate the change of symmetry at T_C from the high-temperature cubic to a low-temperature tetragonal or rhombohedral (in most cases) one [118, 119]. The symmetry breaking is also confirmed by the appearance of Brillouin scattering peaks which are forbidden in cubic phase [48], the appearance of optical birefringence [120], and the formation of FE domains which are clearly observed by optical polarizing microscopy [121, 122], electron microscopy [123] and scanning force microscopy [124–126]. The FE phase in relaxors exhibits typical FE properties, namely the large dielectric constant, the FE hysteresis loops [118, 121, 127], the pyro- [128] and piezoelectric (see below) effects, etc. At temperatures slightly above T_C, double hysteresis loops can be observed [118], as is typical of normal ferroelectrics.

The spontaneous relaxor-to-ferroelectric phase transition can be accompanied by significant anomalies in the temperature dependences of structural parameters [118, 119, 128], dielectric [4, 82, 118], optical [4, 120, 128], thermal [118, 128] and other properties. The transition can be very sharp: e.g. in PFN crystals, the related jump of $\varepsilon(T)$ occurs in a temperature interval smaller than 0.1 K [130]. In many other cases, it is smeared for different reasons. The change of $\varepsilon(T)$ in ceramics is usually not as sharp as in single crystals, probably because of the inhomogeneity related to the existence of grains and boundaries [131]. Another type of inhomogeneity that can smear the transition in the relaxor-based solid solution crystals (e.g. PMN-PT, PZN-PT) is the macroscopic variation of x across the sample [120, 132]. Besides, some "intrinsic" causes for the smearing of phase transition also exist so that a clear boundary between the canonical relaxors (in which the anomalies of structure and properties are diffuse or absent) and the relaxors with a sharp FE transition cannot be defined. The intermediate behaviour can appear in different ways. X-ray diffraction studies of PZN crystals revealed the coexistence of the mesoscopic domains of FE phase and the regions of cubic (relaxor) phase in a temperature range of about 70 K around the mean T_C [78, 133]. The concentration of the cubic phase gradually decreases on cooling, i.e. the transition is highly diffuse. The size of FE domains in PZN (40–200 nm) [78, 133] and in disordered PST (25–75 nm) [123] is smaller than in a normal FE phase, but larger than the size of typical PNRs. The average domain size (at room temperature) in the $(1-x)$PMN$-x$PT solid solutions was found, by scanning force microscopy, to gradually increase from ~40 nm in the rhombohedral phase with $x = 0.1$, to ~2 μm (which is comparable to the domain size in ordinary ferroelectrics) in the tetragonal phase with $x = 0.4$ [126].

Because of the similarity between the FE phase in ordinary ferroelectrics and the FE phase in relaxor ferroelectrics, the transition at T_C was initially called "spontaneous relaxor-to-normal ferroelectric transition," but later investigations showed that the low-temperature phase in relaxors is not exactly a "normal" ferroelectric phase, even in those relaxors where the FE transition is relatively sharp and FE domains are large. In particular, in the PMN-PT crystals with $x = 0.35$, the central peak in the Brillouin spectra, which is related to the relaxation of PNRs, was observed not only at $T > T_C$ (see Section 3.2), but also at $T < T_C$, indicating that the PNRs persist in the FE phase [48]. Furthermore, macroscopic (1–2 μm) areas of average cubic symmetry were found alongside with the areas of FE phase [48]. In PMN-PT crystals with $x = 0.20$, the piezoresponse force microscopy revealed a continuous distribution of the sizes of polar regions starting from ~5 nm (resolution limit). The complex structure of the micron-size FE domains with the PNRs of the opposite polarity embedded in them was observed [125]. A mixture of the rhombohedral domains and the domains of a different low-symmetry (presumably monoclinic) phase was observed by synchrotron X-ray diffraction in the FE phase of PZN crystal [78]. Unlike the plane walls in ordinary ferroelectrics, the domain walls in relaxor ferroelectrics are usually diffuse and irregular [122, 124]. The IR spectroscopy of PZN-PT and PMN-PT crystals (with $x = 0.08$ and $x = 0.29$, respectively) did not reveal any phonon softening that was expected for normal FE phase transitions at T_C and below [134]. Accordingly, the phonon contribution to the dielectric constant at these temperatures is small (~100), i.e. much less than the low-frequency value that reaches $\sim 5 \times 10^4$ at $T = T_C$ and $\sim 5 \times 10^3$ at $T << T_c$. Therefore, similarly to the case of canonical relaxors (and in contrast to ordinary displacive ferroelectrics), the dielectric response is determined by the relaxation polarization at all temperatures around and below the dielectric peak. It was concluded that the transition into the FE phase consists in a stepwise increase in the size of PNRs which transform into FE domains [134].

Another phenomenon, which is unusual for ordinary ferroelectrics, is the specific macroscopic phase inhomogeneities discovered recently in good-quality crystals of some relaxor ferroelectrics. Diffraction experiments performed in PZN with X-ray of different energies (and thus different penetration lengths) revealed that the outer layer (an estimated thickness of ~10–50 μm) undergoes a structural phase transition into the FE phase while the lattice inside the crystal maintains the cubic unit cell [135, 136].[8] Another interesting point is that at all temperatures the lattice parameter of the outer layers is slightly (~0.2%) smaller than that of the bulk (inside) [136]. The same feature, i.e. a FE "skin" (observed by low-energy X-ray diffraction) and a cubic phase in the bulk (observed by high-energy X-ray or neutron diffraction), was also found in PZN-PT [137, 138] and PMN-PT [139] crystals with small x. It was suggested that this cubic phase (named X-phase) is similar to the average cubic phase in pure PMN [140], i.e. it is a NR phase. As a typical NR phase, the X-phase can be irreversibly transformed into the FE phase by poling [137].

Using spatially resolved neutron diffraction technique, it was found that even in PMN crystals, where the rhombohedral phase has not been detected, the near-surface layer (of ~100 μm thick) has the lattice constant noticeably smaller than the bulk structure [141]. It was supposed [140] that a very thin rhombohedral skin possibly exists in PMN also, with a thickness much smaller than the penetration length of X-rays, so that the skin could not be detected in the usual diffraction experiments. Note in this connection that, as reported in Ref. [109], the Rietveld refinement of neutron diffraction data collected on PMN powder revealed a rhombohedral macroscopic symmetry, namely $R3m$ at 300 K (i.e. above T_f) and $R3c$ at 10 K. Second harmonic generation signal was also detected, indicating a non-centric symmetry. In these experiments, very fine powder (of 4–5 μm particle size) synthesized by a special route was used, so the whole material can be considered a near-surface region. This is the possible reason why the rhombohedral phase was found instead of the cubic phase usually observed by other authors in crystals and large-grain powders of PMN.

The behaviour unusual for relaxor as well as for ordinary ferroelectrics was recently found in PMN-PT crystals with large x (~0.5) [132]. The dielectric properties typical of the ER phase are observed at $T > T_m$, namely the deviation from the Curie-Weiss law at $T < T_B$ (where $T_B \gg T_m$) according to Equation 6 and the behaviour permittivity, indicating the UR dispersion. Nevertheless, the CR dispersion is absent, and consequently, T_m coincides with the temperature of the FE phase transition, T_C. This is shown in Fig. 9d. Both the deviation from the Curie-Weiss law and the UR dispersion are believed to result from the existence of PNRs, so the high-temperature phase is the ER state. PMN-PT with high x seems to be the first examples of relaxor without the characteristic CR dispersion. To confirm this opinion, more direct identification of PNRs (e.g. by neutron scattering) is desirable.

While an external electric field transforms a NR state to a FE one, the hydrostatic pressure is able to induce the reverse transformation. In the crystals exhibiting the relaxor-to-FE phase transition, the FE phase does not appear if the sample is cooled under a high enough pressure and the behaviour typical of the canonical relaxors is observed. The pressure-induced crossover from a ferroelectric to a relaxor state was discussed in detail in the recent reviews by Samara [142, 143].

Excellent piezoelectric properties were found near the morphotropic phase boundary in PMN-PT, PZN-PT and some other solid solutions of complex perovskite relaxors with $PbTiO_3$. The transition from FE to ER phase is observed in these crystals at temperatures much higher than room temperature. Thus, they are considered and investigated as promising materials for practical applications. This field of research, currently very active, has been reviewed in a number of recent papers [144–148].

7.3. Theoretical description of nonergodic phase in relaxors

Early works on relaxors (e.g. the composition fluctuations model by Smolenskii and Isupov [8, 97] and the superparaelectric model by Cross [10]) considered the PNRs to be relatively independent noninteracting entities. It was later understood that the specific nonergodic behaviour of relaxors at low temperatures cannot be explained without taking into account the interactions among PNRs and/or quenched random local fields existing in the compositionally disordered structure. The interactions among PNRs may lead to anomalous slowing-down of their dynamics (nonergodicity effects) or, when becoming frustrated, even to the formation of the glass state in which the dipole moments of individual PNRs are randomly fixed in different directions. Note that these interactions are of dipole-dipole nature and can be considered as dynamic local fields. Additionally PNRs can be influenced (or probably even fixed) by quenched local random fields stemming from the compositional disorder or other types of lattice defects.

In Section 5 we have already discussed the modern theories explaining the formation of PNRs. Some of these

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[8] A tetragonal unit cell was initially reported [135], but more elaborate investigations [136] later showed that it is indeed cubic.

theories can also explain the transition from the ergodic to nonergodic relaxor state. In particular, in the GF model, the PNRs naturally appear in the temperature interval between the PE and the low-temperature dipole glass or mixed ferroglass phase. In the WKG model, the formation of PNRs as well as the transition to the NR state is ascribed to the quenched random fields exclusively.

However, the mechanisms leading to the formation of PNRs at high temperatures are not necessarily responsible for their freezing and for the development of the low-temperature nonergodic state. The formation and freezing of PNRs are possibly two distinct phenomena requiring different approaches. The "semi-microscopic" models [98, 149, 150] of glass state in relaxors describe only the latter phenomenon, while PNRs are believed to be already-existing objects and the mechanisms of their formation are not examined.

In the spherical random-bond-random-field (SRBRF) model proposed by Pirc and Blinc [149, 150], the Hamiltonian is formally written with Equations 2 and 3, but the meanings of the parameters are different from those discussed in Section 5. Pseudospins $\vec{S}_i$ proportional to the dipole moments of PNRs are introduced so that the relation

$$\sum_i (\vec{S}_i)^2 = 3N \tag{9}$$

is satisfied (N is the number of pseudospins in the crystal). It is assumed that each component of $\vec{S}_i$ can fluctuate continuously and take any value,[9] i.e.

$$-\infty < S_{i\mu} < +\infty. \tag{10}$$

J_{ij} in Equation 3 are the random interactions (bonds) between PNRs which are assumed to be infinitely ranged. The second term in the Hamiltonian in Equation 2 describes the interaction of pseudospins with quenched random electric fields $\vec{h}_i$,

$$H_2 = -\sum_i \vec{h}_i \cdot \vec{S}_i.$$

Both random bonds J_{ij} and random fields $\vec{h}_i$ obey the (uncorrelated) Gaussian probability distributions with an rms variance of $J/\sqrt{N}$ and Δ, respectively. The mean value of the distributions equals J_0/N (for random bonds) and zero (for random fields). In the absence of random fields ($\Delta = 0$), if $J < J_0$, the theory predicts the transition from the PE phase (in the model this phase is equivalent to the ER phase) into an inhomogeneous FE phase with a nonzero spontaneous polarization; if $J > J_0$, the system transforms, at a well-defined temperature $T = J$, from the PE to a spherical glass phase without long range order, and the glass order parameter (which is equivalent in this model to the well-known Edwards-Anderson order parameter, q_{EA}) decreases linearly from 1 at $T = 0$ to zero at $T = J$. The presence of random fields ($\Delta \neq 0$) destroys the phase transition so that q_{EA} remains nonzero at $T = J$, and approaches zero when the temperature further increases. Fig. 11a shows the temperature dependence of q_{EA} determined experimentally from the NMR data of PMN (q_{EA} is shown to be proportional to the second moment, M_2, of the frequency distribution corresponding to the narrow ^{93}Nb NMR line) [150]. The solid line represents the fit with the parameters $J/k = 20$ K and $\Delta/J^2 = 0.002$, confirming the applicability of the model. The local polarization distribution function $W(\vec{p})$ (where $\vec{p} = < \vec{S} >$) predicted by the model and determined experimentally from the NMR lineshape also appears to be the same as shown in the inset of Fig. 11a [150]. The $W(\vec{p})$ shape observed in dipolar and quadrupolar glasses look very different, as shown in Fig. 11b. These results suggest that the NR phase in PMN cannot be described as a dipolar or quadrupolar glass. It is a new type of glass which can be called "spherical cluster glass" [151]. The SRBRF model is also able to explain the dielectric non-linearity in PMN. The dynamic version of SRBRF model describing the dispersion of liner and nonlinear dielectric susceptibility has been developed [152]. In the coupled SRBRF-phonon model [99], the coupling of PNRs with soft TO phonons leads to the modification of interactions among PNRs. The effect of pressure on the relative stability of different phases in relaxors are explained.

Vugmeister and Rabitz [98, 153] considered in their model the hopping of PNRs in multi-well potentials. The PNRs exist in a highly polarizable PE host lattice with a displacive dielectric response. The theory takes into account the broad distribution of the potential barriers controlling PNR dynamics and the effect of interactions between PNRs mediated by highly polarizable host. These two aspects are described in terms of the local field distribution function. In this model, the dipole glass freezing is believed to be accompanied by the critical FE slowing-down. It is shown that the true glass state in which all dipoles (PNRs) are frozen is not achieved in relaxors: the degree of the local freezing is rather small even at low temperatures.[10] The role of the critical slowing-down is shown to be significant in the dynamics of the system due to the closeness of FE instability. In other words, relaxors can be considered incipient ferroelectrics. This explains their very large dielectric constant. In the framework of this model, the shape of the frequency-dependent permit-

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[9] Models in which the order parameter satisfies conditions (9), (10) are called "spherical" models. Due to these conditions the model is exactly solvable by the replica method.

[10] This is in agreement with the experimental finding that in relaxors only the longest relaxation time diverges at T_f, while the bulk of the relaxation spectrum remains active at low temperatures (see Section 6).

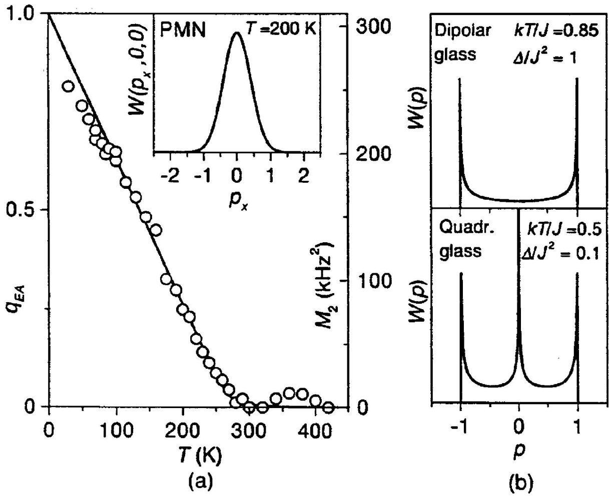

Figure 11 (a) Temperature dependence of the Edwards-Anderson glass order parameter q_{EA} in PMN. The solid line is the fit to the "spherical random bond random field" (SRBRF) model. The inset shows the local polarization distribution function $W(\vec{p})$ along the p_x axis according to the SRBRF model. (b) Examples of the $W(p)$ functions for dipolar and quadrupolar glasses are shown for comparison (after Blinc *et al.* [150]).

tivity as a function of temperature in typical relaxors is explained qualitatively. The glasslike freezing of the dynamics of PNRs is characterized by the non-equilibrium spin-glass order parameter, the temperature behaviour of which is consistent with the NMR experiments (shown in Fig. 11). The kinetics of the electric field induced transition from the NR to FE phase was also successfully reproduced [154] (while the glass models experience difficulties in explaining this transition).

The behaviour of PNRs can be influenced by the electronic subsystem. In particular, the thermo-localization of charge carriers on the defects in the temperature range of phase transition can change the relaxation dynamics. The direction of spontaneous polarization of PNRs can be pinned by localized charge carriers, preventing the alignment of PNRs in the external electric field. The related phenomena are studied in Refs. [155, 156].

As mentioned above, the models so far discussed in this Section consider PNRs (pseudospins) to be already-existing entities. In order to describe the process of their formation and development (which begins from $T_{\mathrm{B}} \gg T_{\mathrm{f}}$), other models are needed. Recently, it has been proposed that quenched random fields give rise to the formation of PNRs in the PE phase, as prescribed by the WKG model, and then, upon further cooling, the crystal undergoes a transition into the spherical cluster glass state due to random interactions between PNRs [151]. Alternatively, some other models can be used to describe the formation of SRBRF pseudospins, in particular, the soft nanoregions model [77] [which justifies the fulfilment of condition (10)] together with the kinetic model [70] (as discussed in Section 5).

Let us now discuss the mechanisms of the spontaneous relaxor-to-ferroelectric phase transition. There are two ways to explain the formation of FE phase at T_{C} from the system of disordered PNRs in relaxors. The first one suggests that the dipole-dipole interactions between PNRs (or individual ions) lead to their FE-type arrangement (as, e.g., in the SRBRF model discussed above). The second mechanism arises from the kinetic model of phase transitions in compositionally disordered crystals [70] (see Section 5) and suggests the thermally activated growth of PNRs at T_{C}. It is not easy to discriminate these two mechanisms from each other. In fact, it is also possible that both mechanisms contribute to the process of the formation of FE phase.

8. Conclusions

In this paper we have analyzed the peculiar behaviour of relaxor ferroelectrics that occurs in compositionally disordered perovskites. The quenched compositional disorder in these compounds gives rise to another type of disorder, i.e. the glassy nonergodic state that can be observed at low temperatures, instead of a FE or AFE ordering that exists in many simple perovskites. The research in this field has undergone such a tremendous growth that it was not possible to review all the important works in this short paper. Some subjects were discussed only briefly just to give the examples characterizing the peculiarities of the behaviour. Some other important topics have been left out, in particular, the materials technology of crystals, ceramics and thin films and applications of relaxor ferroelectrics.

Despite the remarkable progress achieved in the recent years, fundamental physics of the relaxors remains a fascinating puzzle. Some key questions, such as what the origin of relaxor behaviour is, still have no definite answers. Several theoretical models have been proposed; some of them contradict each other. Further experiments need to be performed in order to prove or reject these models, while new and more satisfactory theories are yet to be worked out. With their complex structures and intriguing properties, relaxors represent truly a frontier of research in ferroelectrics and related materials, offering great opportunities both for fundamental research and for technological applications.

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