Dmitry Chernyshov*, Vadim Dyadkin, Vladimir Dmitriev and Alexey Bossak

Pressure evolution of $PbMg_{1/3}Nb_{2/3}O_3$ relaxor ferroelectric

Abstract: Diffuse and Bragg scattering of synchrotron radiation on single crystal PMN relaxor has been collected as a function of pressure. The relaxor-specic diffuse scattering (DS) is observed for $p < 40$ kbar and successfully parametrized with the thermal DS-like model of polar correlations. An increase of pressure does suppress the polar correlations in a specic glass-like relaxor state, and above $\sim$40 kbar a new non-polar *R*-phase becomes stable. We propose a phenomenological model accounting for off-center displacements of lead ions; together with previous reports these findings map the relaxor state to a specifc area of phase diagram.

Keywords: relaxor ferroelectrics, diffuse scattering, Landau theory

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1 Introduction

Lead-based relaxors are puzzling ferroelectrics with centrosymmetric perovskite-like average structure and frequency dependent maximum of dielectric permittivity [1]. Albeit the compounds are of technological interest as materials for sensors and actuators, the nature of relaxor response is under debate for more than 50 years.

The average crystal structure of relaxors is simple, but real local structure is much more complex due to the disorder phenomena. A static structural disorder is always present in relaxors due to the chemical composition – different ions are mixed at the same Wyckoff position; the PMN relaxor with composition $Pb(Mg_{1/3}Nb_{2/3})O_3$ may serve as an example. The other component of disorder that could be either static or dynamic is polar displacement of atoms with the leading contribution of Pb as ion having lone electron pair. A dynamic disorder due to the thermal vibrations together with the interaction between different disorder components complements a complex picture of the crystal structure of a seemingly simple perovskite.

The disorder in a structure rarely means a chaos but rather represents certain temporal and spatial correlations between site occupancies and atomic displacements. While sharp Bragg reflections correspond to the average structure, broad diffuse scattering component carries information of the correlation characteristics of a disorder.

Thus for PMN a partial ordering of Mg and Nb is manifested in broad diffuse maxima positioned at *R*-points of the reciprocal lattice. The width of these maxima agrees with the presence of chemically ordered Mg/Nb regions (CORs) with the size $\sim$50 Å [2].

The other diffuse component is located around Bragg reflections and reflects correlated ionic displacements. This relaxor-specific diffuse scattering appears on cooling at so-called Burns temperature and does increase on further cooling [3], at variance with phonon-related thermal diffuse scattering. The relaxor-specific component has been related to the formation of so-called polar nanoregions (PNRs) and their temperature evolution, which are generally accepted to be the core of relaxor response. We have recently shown that an accurate mapping of relaxor-specific diffuse scattering does not agree with any model of polar regions embedded in a non-polar cubic matrix [4]. The accurate mapping implies a fine sampling of reciprocal space, with angular step less than a degree and a consequent reconstruction of reciprocal layers together with the inspection of 3D distributions of diffuse intensity. The relaxor-specific diffuse scattering can be parameterized within the formalism of thermal diffuse scattering with effective parameters related to the correlated distribution of displacements rather than to normal thermal vibrations [4]. We have shown that a glass-like distribution of polar displacements, proposed earlier on the basis of parameterization, agrees well with the accurate data [5]. It has also been shown by molecular dynamics modeling that dielectric properties as well can be reproduced without invoking PNRs interacting via nonpolar matrix [6]. New theoretical model explaining essential physical properties of relaxors has been proposed re-

cently [7]; the nature of relaxor behaviour is linked not to a formation of polar regions but to the extended ferroelectric fluctuations, surviving in a broad temperature range due to the structural disorder and anisotropy of dipolar interactions.

The pressure is known to affect strongly behavior of ferroelectrics; the physical reason for that is a coupling between strain and polar displacements via piezoelectric and electrostriction effects. Relaxors are also very responsive for the applied pressure in terms of dielectric properties [8], and also in terms of diffuse scattering [1]. Diffuse intensity under high pressure has been previously probed by synchrotron and neutron scattering [2, 9]. In both cases rather thick sections of reciprocal space have been explored. The pressure dependence of diffuse signal was followed for selected points of reciprocal space, and the observations were interpreted as a suppression of PNRs by pressure. There are few reasons to revisit the diffuse scattering in relaxors as a function of pressure. First, the diffuse scattering is very anisotropic and this anisotropy is partially lost in the thick sections of the reciprocal space; a data collection done with a small angular step improves information content significantly [4]. Second, the proposed parameterization of diffuse scattering without invoking the PNR concept needs verification against good quality data collected as a function of pressure.

Here we present a pressure evolution of the diffuse scattering quantified in form of the reconstructed reciprocal space layers. We show, in agreement with previous observations, that relaxor-specific diffuse scattering disappears under pressure. We also quantify the pressure dependence of anisotropy of diffuse scattering. Finally, we discuss the appearance of new Bragg reflections, superposed with the diffuse maxima at *R*-points and related positioning of relaxor state in the specific region of the perovskite phase diagram.

2 Experimental

The diffraction data were collected at BM01A station of Swiss-Norwegian Beam Lines (European Synchrotron Radiation Facility, Grenoble, France) with help of PILATUS@SNBL diffractometer at $\lambda = 0.694$ Å. The diffractometer is equipped with PILATUS2M area detector and a flexible system for the sample and detector positioning.

The single crystal of PMN of $70 \times 70 \times 25$ mkm^3 size, prepared by polishing and etched by hot concentrated HCl, was loaded into diamond anvil cell together with ruby crystal for pressure measurement. Ethanol/methanol ($^1/_4$) mixture was used as pressure transmitting media. The data were collected with 0.1^0 step by the angular scan of horizontal axis in shutterless mode.

3 Results

At the ambient pressure the diffuse scattering is found to be in full agreement with previously reported for the same sample type [4]. The pressure evolution of scattered intensity is shown in Fig. 1a for *HK0* and in Fig. 1b for *HHL* sections of reciprocal space. In agreement with the previous reports we observe that the pressure gradually suppresses the diffuse scattering. As reported for the neutron scattering [9], diffuse scattering measured near 100 node at unspecified **q**-point located on [−1 1 0] line, disappears between 30 kbar and 35 kbar. According to the X-ray study [2] diffuse scattering taken somewhere near 300 node survives up to 40 kbar. Our data suggest the complete suppression of diffuse component between 30 kbar and 48 kbar (dependence for $\mathbf{q} = [0.025\ 0.025\ 3]$ is shown in Fig. 3a). It is worth noting that if the anisotropy of diffuse scattering is pressure-dependent, the pressure dependence of intensity would defer for different **q**-values.

The distribution of diffuse scattering in the proximity of 300 node can be parameterized on the basis of the similarity between thermal diffuse scattering and relaxor-specific component. Using previously proposed pseudo-dynamical matrix algorithm [5], instead of employing the analogs of acoustic waves we apply here a TO mode formalism [10], which assumes the following shape in *HK0* plane:

$$I(q_x, q_y) = \frac{q_y^2}{q^2\omega_0^2 + S_t q^4 + 2S_a q_x^2 q_y^2} \quad (1)$$

Here $q^2 = q_x^2 + q_y^2$, ω_0 is the virtual frequency in Γ point, S_t and S_a parameters that describe the anisotropy of dispersion. Besides of scaling and background parameters, fit can be reduced to S_a/S_t and ω_0 values. As one can see from the difference map (Fig. 2), the parameterization fits very well the experimental observation. The pressure dependence of the fitted parameters is given in Table 1 and can be further used for modeling the real space distribution of polar displacements. Substantial difference in diffuse scattering distribution, compared to our previous parameterization, appears only in the very proximity of Γ points.

In the pressure range where relaxor-specific diffuse scattering vanishes, we observe sharp Bragg scattering

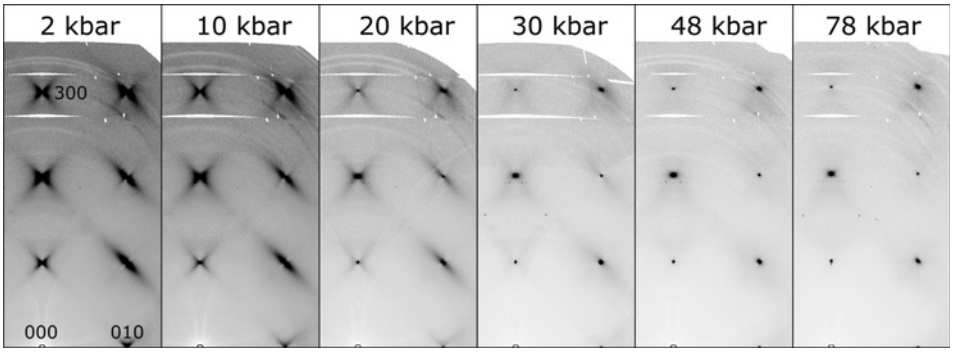

Fig. 1a: Pressure dependence of *HK0* reciprocal space layer in PMN.

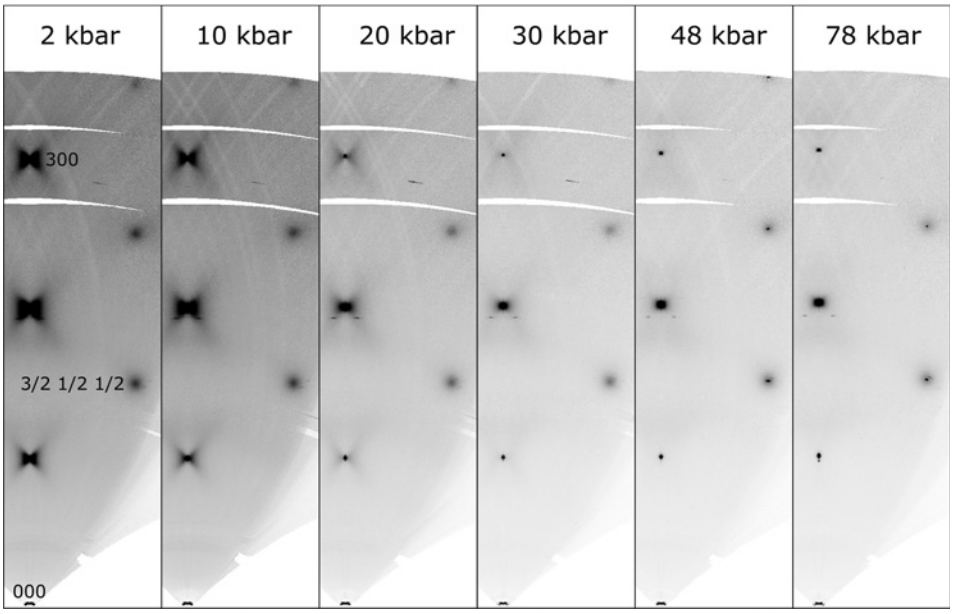

Fig. 1b: Pressure dependence of *HKK* reciprocal space layer in PMN.

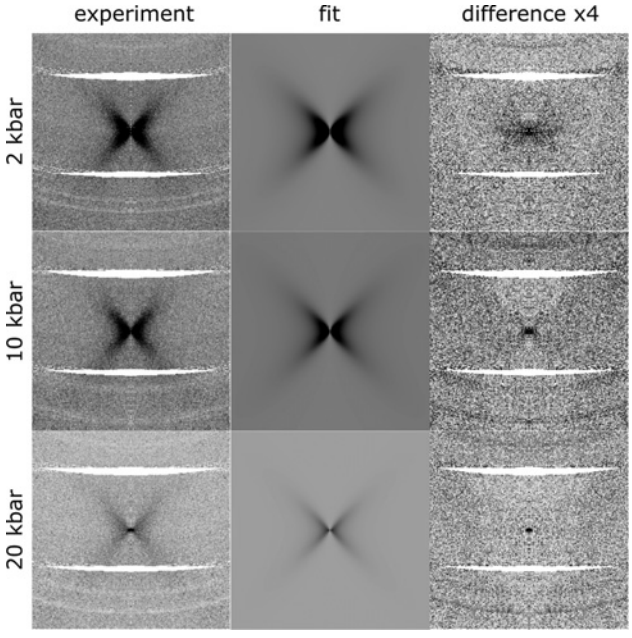

Fig. 2: Experimental, calculated and difference diffuse scattering as function of pressure.

emerging on top of the broad diffuse maxima at *R* points of BZ (Fig. 3). The Bragg intensity increases on pressure, while no significant pressure evolution of the diffuse clouds is noted. Similar observation has been reported before [2] and, together with Raman scattering data [11], is interpreted in favor of an *R*-centered non-polar structure.

4 Discussion

In order to parameterize the observed relaxor-specific scattering we apply TO mode formalism that allows accounting for TO-like polar displacements. The distribution of diffuse scattering in reciprocal space for pressures up to 20 kbar fits very well with TDS-like model (Fig. 2) and therefore for this pressure range agrees with previously proposed concept of a specific glass-like polar state [5]. At higher pressures diffuse signal is too weak for the quantitative analysis, however we see no signs of

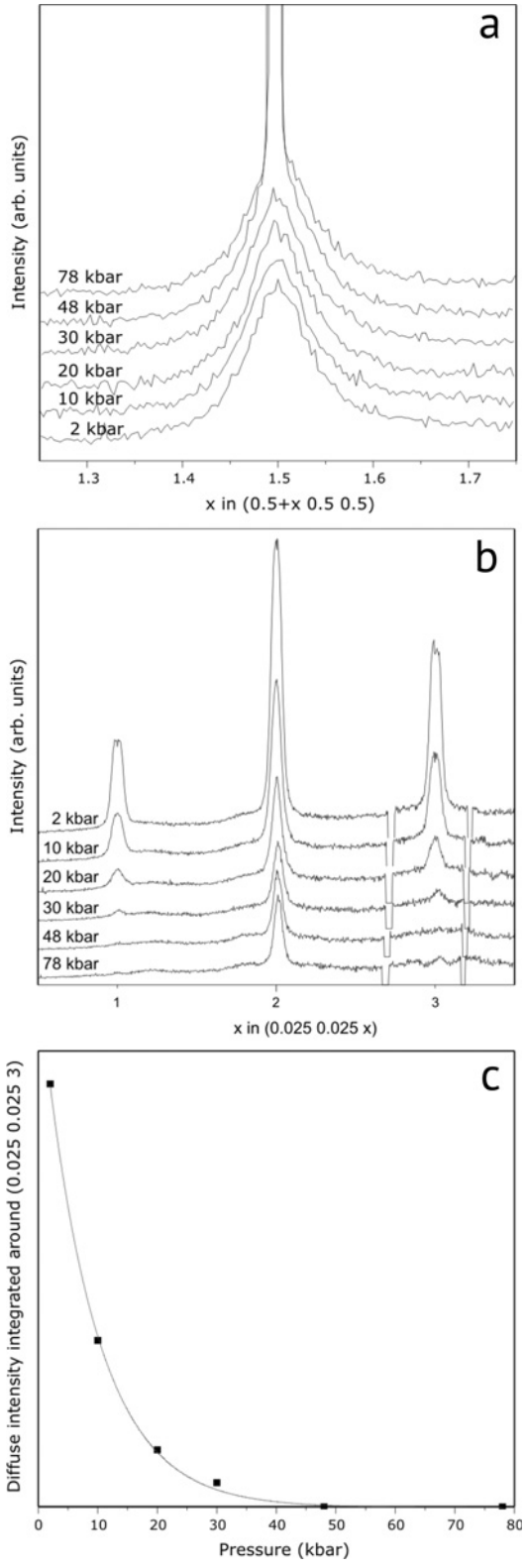

Fig. 3: Left: section through (2.5 0.5 0.5) node along H, note a formation of strong Bragg component at $p = 48$ and 78 kbar on top of the diffuse maximum. Center: linear scan along L through (0.025, 0.025, x) point of reciprocal space showing pressure evolution of diffuse intensity near (0 0 1), (0 0 2), (0 0 3) Bragg nodes. Right: Pressure dependence of the diffuse scattering at (0.025, 0.025, 3) point.

Table 1: Fit parameters for variable pressure, established for the proximity of 300 PMN node.

P (kbar)	S_a/S_t	$\langle\omega\rangle_0^2$ (arb. units)
2	1.59	1.59
10	1.66	3.80
20	1.75	5.73

distribution of diffuse intensity expected for PNRs [4]. The anisotropy factor, defined within the parameterization, increases with pressure (Table 1); as stated above, that could be a reason for qualitatively different pressure dependences of diffuse scattering reported before.

We have observed an appearance of additional Bragg component at 30 kbar $< p <$ 48 kbar, which can be interpreted as phase transition from $Pm\bar{3}m$ primitive perovskite to an R-type superstructure. Similar conclusion on pressure-induced phase transition has been derived from micro-Brillouin scattering spectroscopy [12] where $R3c$ symmetry has been proposed for the high-pressure phase, being presumably polar. The same anomalies have been interpreted in favor of $R3m$ symmetry with the help of Landau theory [13], in both cases a polar zone-centre distortion has been assumed, in the latter case an order-disorder process in the Mg–Nb sublattice has also been accounted for. However, the hypothesis of Ref. [13] should be considered critically if taking into account a time scales of the corresponding transformation. Indeed, an active symmetry breaking role of an order-disorder diffusive type transformation supposes very slow (much longer than an experiment time) kinetics, which is not the case for observed structure evolution. The kinetic effects and stability of differently ordered structures have been recently discussed for non-relaxor analogue $BaMg_{1/3}Ta_{2/3}O_3$ [14]. It is clear that for PMN the diffusion and re-distribution of B-cations can safely be neglected up to very high temperatures not reached in our experiment. Our data together with the previous report [2] suggest that the high pressure phase is induced by an R-point phonon. In agreement with arguments discussed previously [2] we limit our consideration to rhombohedral non-polar distortions. Irreducible representations (IRs) associated with this point of BZ which are a part of the mechanical (displacive) representation and induced rhombohedral structures are the following:

$$R_4^-(k_{13}, \tau_7) \rightarrow R\bar{3}m \tag{2}$$

$$R_4^+(k_{13}, \tau_8) \rightarrow R\bar{3}c \tag{3}$$

$$R_5^+(k_{13}, \tau_{10}) \rightarrow R\bar{3}m \tag{4}$$

The IR R_4^- corresponds to the antiparallel shifts of Mg/Nb atoms; R_4^+ describes displacements/tilts of oxygen octahedra, and it is conveniently considered as an *R*-point order parameter for the complex tilt transformations in perovskite structures. Finally, R_5^+ distortion contains simultaneous but independent antiparallel Pb–Pb and O–O displacements[1].

The transformation of the cubic lattice to the hexagonal basis is given by the matrix {(−1, 1, 0), (0, −1, 1), (2, 2, 2)}. We note here that at the resolution we have the rhombohedral distortion is too small to be quantified. Also, we have optimized the experiment for observation of weak diffuse scattering features, as a result Bragg intensities are overexposed, especially for very strong reflections, and the intensity information is lost or distorted. This is why no further structural analysis is done on the sole basis of Bragg reflections. Notably, an accurate study of strong Bragg reflections for an analysis of anharmonic thermal vibrations does not report any superstructure spots up to 73 kbar [15]. That could be due to a point detector technique and collection of the data only for Bragg nodes expected for $Pm\bar{3}m$ symmetry, which obviously makes the results over-interpreted. The problem to be addressed in the future is therefore an accurate measurement of both series – very strong main and weak additional Bragg reflections for the solution of a high pressure structure. In particular the role of antiferroelectic displacements of lead ions (R_5^+) has to be clarified [2]. Pressure-induced phase transformations have been observed in $PbSc_{0.5}Ta_{0.5}O_3$ and $Pb_{0.78}Ba_{0.22}Sc_{0.5}Ta_{0.5}O_3$ and interpreted in favor of antiphase tilting of metal-oxygen octahedrons leading to $R\bar{3}c$ structure [16]. However, irrespective of actual combination of rotations of $Mg(Nb)O_3$ octahedra and anti-parallel displacements of lead atoms, a non-polar character of the high pressure *R*-phase has been suggested in agreement with pressure-induced decrease of dielectric constant [17]. It allows us to simplify, without lose in generality, our analysis neglecting a zone-center polar displacement mechanism (Γ_4^-) in a sense that no macroscopic polarization is induced as a function of temperature and pressure.

The experimental observations collected so far do not allow a complete mapping of the phase diagram. The tentative phase diagram is presented at Fig. 4. Burns

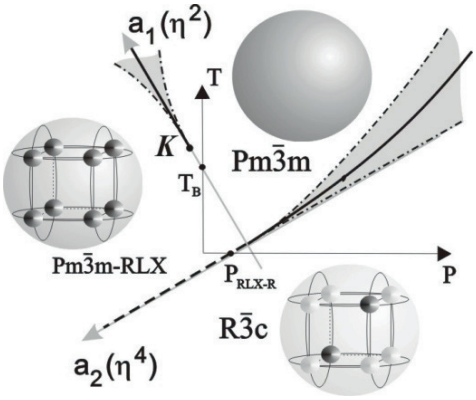

Fig. 4: Tentative phase diagram for PMN in (*T*; *p*) plane. Burns temperature is set to 620 K according to [21]. Solid, dashed and dashed-dotted lines represent first-order, second-order transitions and stability limit lines, respectively. Schematic probability distribution for lead atoms around the lattice nodes is shown in each phase as a sphere of an equal probability in paraelectric $Pm\bar{3}m$, a multi-minimum distribution in the relaxor phase, and a long range correlated antiferroelectic displacement of lead ions along [111] cubic direction. *K* is a critical end point of the gas-liquid type.

temperature signifying a crossover between relaxor and non-polar primitive perovskite structure set the border for the relaxor state at ambient pressure. Pressure p_{RLX-R} where the diffuse scattering is suppressed and new Bragg component appears at *R*-points separates relaxor and new non-polar phase. In spite of very limited information, a certain predictions can be done, for example a phase transition between two non-polar phases on heating at high pressures must exist. Moreover, in agreement with diffuse scattering behavior, the relaxor state can be seen as specific polar fluctuations related to correlated displacement of lead ions distributed over a sphere in the average non-polar structure. At variance with normal fluctuations increasing close to the transition temperature, relaxor-specific fluctuations are suppressed in the vicinity of the transition to non-polar *R*-phase, thus indicating a negative coupling between polar and non-polar fluctuations.

The experimental data accumulated to the date allow us suggesting a generalized structure model which consistently describes effects observed in PMN compounds. The corresponding perovskite type parent structure contains two kinds of disorder mentioned in the introduction. First one is an intrinsic feature of all $A(B'_xB'_{1-x})O_3$ solid solutions including end members ($x = 0$ and $x = 1$) with A ions having lone electron pair: A ions are not localized in the *1b:* (0.5 0.5 0.5) position of the $Pm\bar{3}m$ space group but it is dynamically distributed on a sphere centered at the above *1b* [18]. A disorder-order process in the system of such atoms shows fast kinetics due to its dis-

1 The notations correspond to A-cation at 1b Wyckoff position according to ISODISTORT software, for more detailes see B. J. Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, ISODISPLACE: a web-based tool for exploring structural distortions," Journal of Applied Crystallography, **2006**, *39*, 607

placive nature. Short range correlations of A ions positioned over a sphere would give diffuse scattering, long-range ordering would modify the Bragg scattering pattern.

Another kind of disorder exists in solid solutions ($0 < x < 1$) and relates to a static distribution of B' and B″ atoms occupying the *1a:* (0 0 0) position. Ordering process in this subsystem needs an atomic diffusion through the crystal lattice and demonstrates, therefore, very slow kinetics not normally observable at experimental times typical for diffraction and spectroscopic methods. In the absence of a special long-time annealing procedure, crystals of solid solutions at "ambient conditions"l; (internal energy k_BT is less than a diffusion activation energy barrier) demonstrate a mesoscopic structure revealed in diffraction experiments. The latter show existence of regions of typical linear size of few tens of Å with small dispersion of the disorder rate inside a domain but differing in the rate in different domains. It results in a diffuse component of the corresponding diffraction patterns. Due to a slow kinetics this type of disorder and corresponding mesoscopic structure are not affected by pressure variation and survive, in our experiment also after onset of a new superstructure with rhombohedral symmetry. It results in a conservative component of the diffuse scattering pattern observed above 40 kbar (Fig. 3).

Remaining, low barrier transition mechanisms are the following: (i) a tilt (displacive) type distortion R_4^+ reducing the symmetry from cubic $Pm\bar{3}m$ ($Z = 1$) to rhombohedral $R\bar{3}c$ ($Z = 4$); (ii) totally symmetric ordering mechanism hindering "free" movement of A-atoms on the sphere and replacing dynamical disorder by (quasi)static one without changing the cubic symmetry. This mechanism implies that the sphere of averaged distribution of the lead ions is deformed to set of many minima preserving the same site symmetry $m\bar{3}m$. Such an ordering process corresponds to the transformation the crystal to a relaxor state, a correlated character of lead off-center displacements appears in the relaxor-specific diffuse scattering and also manifest itself in the other experimental probes, for example polarised Raman scattering [1, 19]. Since in the relaxor state the average displacement of the lead ion from *1b* position is zero, $\langle u \rangle = 0$, but its second moment is not, $\langle u^2 \rangle \neq 0$. Let ξ be the totally symmetric ordering type OP Γ_1^+, $\langle u^2 \rangle$ serves as a measure of this order parameter, and ξ^2 is therefore proportional to the intensity of relaxor-specific diffuse scattering.

An effective phenomenological model corresponding to the above symmetry conditions were analyzed recently in Ref. [20]. It operates two single-component order parameters of necessary symmetry, and starts from the Landau potential:

$$F(\eta, \xi) = a_1\eta^2 + a_2\eta^4 + b_1\xi + b_2\xi^2 + b_3\xi^4 + y_1\eta^2\xi + y_2\eta^2\xi^2 \quad (5)$$

In our case, effective OP η represents the three-dimensional tilt mechanism R_4^+ belonging to the *R*-point. A section of the multi-dimensional theoretical phase diagram is shown in Fig. 4. It generalizes experimental observations, accumulated so far, in a logical scheme. Indeed, following this scheme, PMN solid solutions may transform from a parent paraelectric state (phase $Pm\bar{3}m$) to a cubic relaxor state ($Pm\bar{3}m$ – RLX) either via an isomorphic phase transition or, beyond the critical point *K*, via a crossover process. Any of these structures can transform to the $R\bar{3}c$ phase by the octahedron tilt mechanism. The displacive tilt mechanism reducing the crystal symmetry, both rotational and translational, suppresses the disorder in the A-atoms sublattice and that results, at certain pressure, in disappearance of relaxor-specific diffuse component and onset of superstructure Bragg reflections localized in the *R*-points of primitive cubic BZ.

5 Conclusion

New data of diffuse and Bragg scattering in PMN relaxor as a function of pressure have been collected with help of synchrotron radiation. The data are in perfect agreement with previously proposed TDS-like parameterization and at no pressure show a signature of polar nanoregions. The pressure does suppress polar correlations in a specific glass-like relaxor state, and above ~40 kbar new non-polar *R*-phase becomes stable.

The transition between non-polar $Pm\bar{3}m$ and relaxor phases is considered as an isostructural crossover between uncorrelated and correlated displacements of lead ions. Taken together experimental observations and phenomenological analysis imply a complex coupling between ferroelectric and antiferroelectric displacements of lead ions with rotations of BO_3 octahedrons. Complimentary neutron diffraction measurtements would help to evaluate the tilting of BO_3 and solve the actual structure of the *R*-phase. Neutron diffraction may also help to elucidate a disorder component related to tilting distortions in the relaxor phase. The generic phase diagram proposed here calls for additional experiments as a function of pressure in 300–600 K temperare range that would map the border between non-polar $Pm\bar{3}m$ and the *R*-phase.

Acknowledgements: Authors like to thank Prof. Sergey Vakhrushev for numerous discussions on the relaxor phenomena. SNBL team also like to thank Geir Wicker for his technical help in setting up high pressure diffraction experiment.

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Received April 9, 2013; accepted October 30, 2013
Published online January 7, 2014