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Diffuse scattering in $Pb(Zn_{1/3}Nb_{2/3})O_3$ with 8% $PbTiO_3$ by quasi-elastic neutron scattering

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Abstract

Diffuse scattering (DS) due to the polar nanoregions in perovskite relaxor ferroelectric $Pb(Zn_{1/3}Nb_{2/3})O_3$ with 8% $PbTiO_3$ was investigated by cold neutron scattering with high energy resolution (8 GHz). The anisotropy of DS near the (100) Bragg reflection cannot be explained merely by the polar character of the inhomogeneous displacement field. The occurrence of 'soft' [110]-type directions suggests a close relation to the [110]-type ridges seen in x-ray scattering on $Pb(Mg_{1/3}Nb_{2/3})O_3$. Transverse (quasishear) acoustic phonons with wavevectors near the half maximum of DS density in the 'soft' [110] direction have anomalously large damping but their integrated intensity is small in comparison with the intensity of DS. Since no quasielastic width of the DS was found in this experiment, it is concluded that the characteristic relaxation frequency associated with this DS is less than 1–2 GHz even at 500 K. Results are compared with predictions based on recently proposed models for DS in perovskite relaxors.

1. Introduction

The recent discovery of giant piezoelectricity [1] has attracted great attention to the single crystals of $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), both pure and in solid solution with $PbTiO_3$ (PT). The temperature dependence of the real part of the 1 kHz dielectric permittivity in pure PMN and PZN crystals exhibits a pronounced maximum around $T_{max} = 325$ and 265 K for PZN [2] and PMN [3], respectively, but no macroscopic ferroelectric order is observed in these crystals on cooling (in zero electric field). The maximum is broad and obeys the Vogel–Fulcher-type frequency dependence, indicating a freezing behaviour. A crossover to the glasslike state around temperature $T_g = 220$–230 K in PMN was indeed

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revealed in various history-dependent phenomena [4–6]. Such *relaxor* behaviour is known to be caused by a specific chemical disorder [7, 8], in this case present on the perovskite B-site occupied by Nb^{5+} and Mg^{2+} or Zn^{2+} ions.

Doping by Ti^{4+} gradually reduces the relaxor features and induces a well defined phase transition T_c towards a long-range ferroelectric phase. The order is rhombohedral for weak doping, while Ti rich solid solutions show a transition towards a tetragonal ferroelectric phase as in pure PT. The structure of the crystals with intermediate composition corresponding to the morphotropic phase boundary (around 8 and 33% of PT in PZN and PMN, respectively—for phase diagrams see for example [9–12]) is still under investigation; nevertheless, these crystals are exactly those which reveal the extraordinarily large piezoelectric constants.

Large polarization inhomogeneity, essential for the relaxor behaviour and possibly also for giant piezoelectricity, is often discussed in terms of so-called polar nanoregions (PNRs)—nanometre scale regions with ferroelectric order. Various experiments indicate that these PNRs appear at the so-called 'Burns temperature' [13] T_d which is several hundreds kelvins above the T_{max}. Most direct evidence for PNRs comes from strong diffuse scattering (DS) observed in neutron and x-ray diffraction experiments in both pure and PT doped systems. The intensity of this DS persists at high temperatures and seems to vanish [14, 15] only near T_d.

Detailed analysis of relative intensities of DS associated with distinct Bragg reflections in PMN (both above and below T_g) has confirmed that the local displacements causing this DS are indeed polar: cations (primarily Pb) are displaced against oxygen anions [16, 17]. For polar displacements, one expects strong correlations along the direction of polarization, and the DS should have a pronounced transverse character (the intensity should fall down rapidly in the longitudinal direction of momentum transfer). This was actually observed for DS around the (330) Bragg reflection in a single-crystal neutron scattering study of PMN [16]. The transverse scans across DS obtained by neutron diffraction were reasonably well fitted [16] to Ornstein–Zernike (Lorentzian) profiles, yielding room temperature transverse correlation lengths of the order of 100 Å. Below 500 K, the square of the inverse correlation length seems to decrease linearly with temperature as in the case of ordinary critical scattering, but a few tens of kelvins above the extrapolated 'critical' temperature T_0 ($T_0 = 300$ K for PMN [4], $T_0 = 415$ K for PZN [18]) it saturates, levels off and shows just a very weak decrease, possibly with a small anomaly near T_c in PT doped crystals.

Previously, the observed DS was assumed to originate from either low frequency [4, 16, 19–21] or quasistatic [17, 22] correlations. In fact, the DS has appeared as static in the neutron scattering experiments performed so far. More precisely, previous inelastic neutron scattering experiments [16] have shown that the observed frequency width of DS was given by instrumental resolution (about 1 meV), which shows that the relaxation time associated with this DS is clearly longer than 10^{-11} s.

In order to get more information about temporal correlations associated with the above described DS, we have performed complementary cold neutron scattering investigations with an improved energy resolution of 30 μeV. Prior to our experiment, we speculated that the relaxation frequency associated with the DS may correspond to that of the central peak observed in Brillouin scattering experiments [23], because the temperature dependence of Brillouin CP was strikingly similar to that of inverse correlation lengths determined from neutron scattering. We also wanted to check whether the observed DS is not caused by a coupled acoustic–optic branch of an anomalously low frequency, as could follow from the elegant model of [21]. However, the results reported in this paper show that actually neither of these two plausible scenarios is valid.

The experiment was performed with a morphotropic phase boundary composition PZN–PT system, which was recently investigated by various other techniques, for

example in dielectric [10], infrared [24], Raman [24–28], Brillouin [23, 29], atomic force microscopy [30, 31], optic microscopy [32], x-ray [33], and neutron scattering experiments [34–40]. The solid solution PZN–8% PT with phase transition at [41] $T_c = 435$ K shows both strong relaxor behaviour and giant piezoelectricity [41, 42]. The 3.7 g optically transparent yellowish as-grown single crystal of PZN–8% PT used in our experiment was grown by the high temperature flux technique at the Materials Research Institute, Pennsylvania State University. The measurements were carried out on the IN12 cold neutron three-axis spectrometer at the ILL high flux reactor. The instrument was operated with a fixed energy of scattered neutrons ($k_f = 1.05$ Å^{-1}) and with Soller collimators 43′, 40′ and 60′ in front of the sample, analyser and detector, respectively. The sample was wrapped in a thin Nb foil and mounted in a vacuum furnace, allowing us to reach temperatures up to 1200 K with temperature stability better than 1 K. The sample was oriented with the cubic [001] axis vertical. This geometry allowed us to explore the ($hk0$) scattering plane. Both transverse and longitudinal momentum resolution widths measured on the (001) Bragg reflection were better than 0.01 of a reciprocal lattice unit (rlu), where 1 rlu is $2\pi/a \approx 1.55$ Å^{-1}. The 30 μeV (8 GHz) energy resolution, as given by the energy profile of elastic incoherent scattering from our PZN crystal, was confirmed by an independent measurement on a vanadium reference sample.

2. Results

Due to restrictions imposed by the momentum conservation, the measurements with the 30 μeV energy resolution could be performed only in the vicinity of the (100)-type Bragg reflections. A typical transverse scan across the (100) Bragg peak at 500 K (in the cubic phase) is shown in figure 1. These scan data were fitted by a narrow Gaussian corresponding to the Bragg reflection plus a large Lorentzian tail describing the DS. The FWHM of the Lorentzian shown in figure 1 (0.05 rlu, corresponding to a correlation radius of 25 Å) is close to the FWHM reported for PZN–4% PT and PZN–9% PT in figures 6 and 7 of [39]. The temperature variation of the FWHM and intensity of this DS also agrees with the data reported in [39]. This confirms that we are detecting the same DS signal as described in the previous neutron scattering studies [4, 16, 18, 39].

Figure 2(a) shows the 2D anisotropy of DS in the $hk0$ plane around the (100) Bragg reflection at 500 K. The intensity level marked by 400 corresponds roughly to the half maximum (HM) of the Lorentzian shown in figure 1. For comparison, the ideal polar anisotropy caused by isotropic transverse fluctuations, calculated from the formula

$$I(\boldsymbol{Q}+\boldsymbol{q}) = \frac{|(\boldsymbol{Q}\cdot\boldsymbol{u}_q)|^2}{\kappa^2+q^2} \tag{1}$$

is shown in figure 2(b). Here $\boldsymbol{Q}$ is the momentum transfer corresponding to the (100) Bragg reflection, $\boldsymbol{u}_q \perp \boldsymbol{q}$ is the unit polarization vector corresponding to the transverse fluctuation with wavevector $\boldsymbol{q}$ and the HWHM of the transverse scan $\kappa = 0.25$ rlu was chosen to mimic the 500 K data shown in figure 1. It is obvious that there is an important additional source of anisotropy in this DS, which enhances the intensity along the [110]-type directions. This enhancement is already apparent at the HM level, it becomes more pronounced at larger q-values and it seems to evolve smoothly towards a 'butterfly-like' anisotropy with clear ridges along the [110]-type directions, as observed previously at about one order of magnitude larger q-scale near ($h00$) Bragg reflections in PMN [19, 20], $PbIn_{1/2}Nb_{1/2}O_3$ (PIN) [43] and PZN [15, 22].

One of the frequent sources of DS is inelastic scattering by low frequency acoustic or soft optic phonon modes. Within this scenario, the observed 'butterfly-like' anisotropy can be

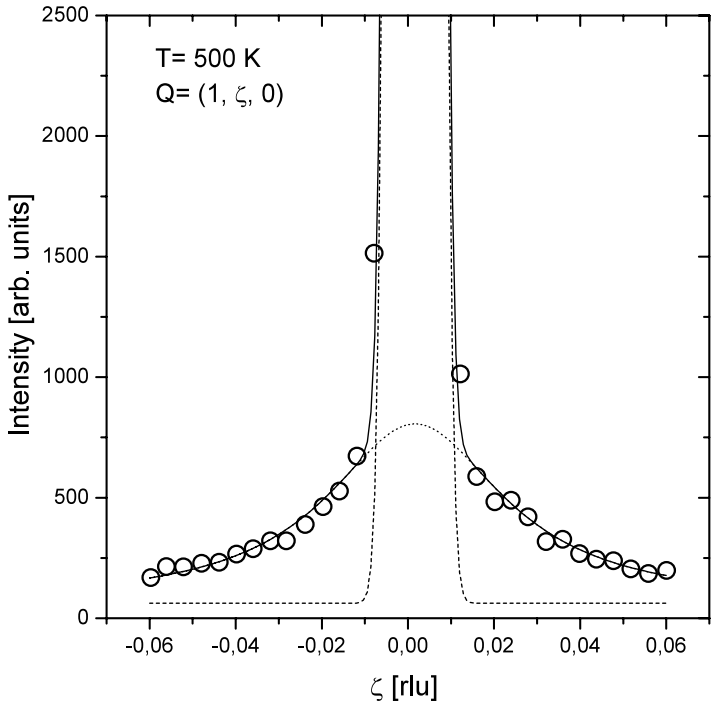

Figure 1. Transverse [010] scan across the (100) Bragg reflection at 500 K in PZN–8% PT. The full curve corresponds to the fit by the sum of a Gaussian (dashed, representing Bragg scattering) and a Lorentzian (dotted, representing DS) superposed on a constant background given mainly by elastic incoherent scattering.

understood assuming that the relevant transverse phonons are particularly soft along the [110]-type directions [19–21]. A number of observations could be explained within the model [21] based on coupling between the soft branch and the lowest frequency acoustic branch. Firstly, the acoustic–optic mode mixing explains [21] the centre of mass shift component [44] in the eigenvector associated with the fluctuations causing the observed DS. Secondly, anisotropy of the transverse acoustic velocity would induce [21] the [110]-type ridges in the corresponding thermal DS. In addition, we notice that the model [21] would explain the absence of the [110] and $[10\bar{1}]$ ridges of DS near (003) Bragg reflections [19]. Indeed, this absence implies that the observed 'soft' fluctuations are polarized in the cube faces [19], and this just happens to be polarization of the quasishear acoustic modes considered in the mentioned model [21].

In order to check whether this model applies to DS observed in our experiment, we have tried to measure quasi-transverse acoustic modes at wavevectors corresponding to the HM of DS. Close to the (100) Bragg reflection, the signal to noise ratio was too small. Therefore, the relevant constant-$\boldsymbol{Q}$ scan was taken near the (110) Bragg reflection (at $\boldsymbol{Q} = (1.02, 0.98, 0)$) and with a more moderate resolution ($k_f = 1.4$ Å^{-1}) (figure 3). We estimate that a larger value of k_f, a larger structure factor of the associated Bragg reflection and the exactly transverse geometry in comparison with a similar $k_f = 1.05$ Å^{-1} measurement near $(1.02, -0.02, 0)$ allowed us to gain almost two orders of magnitude in the acoustic mode counting rate.

The data shown in figure 3 allow us to draw three important conclusions. Firstly, the quasishear mode frequency is indeed lower than the expected pure shear ([001]-polarized) acoustic mode frequency (0.65–0.7 meV, extrapolated from $(2, -0.2, 0.2)$ measurements [40]

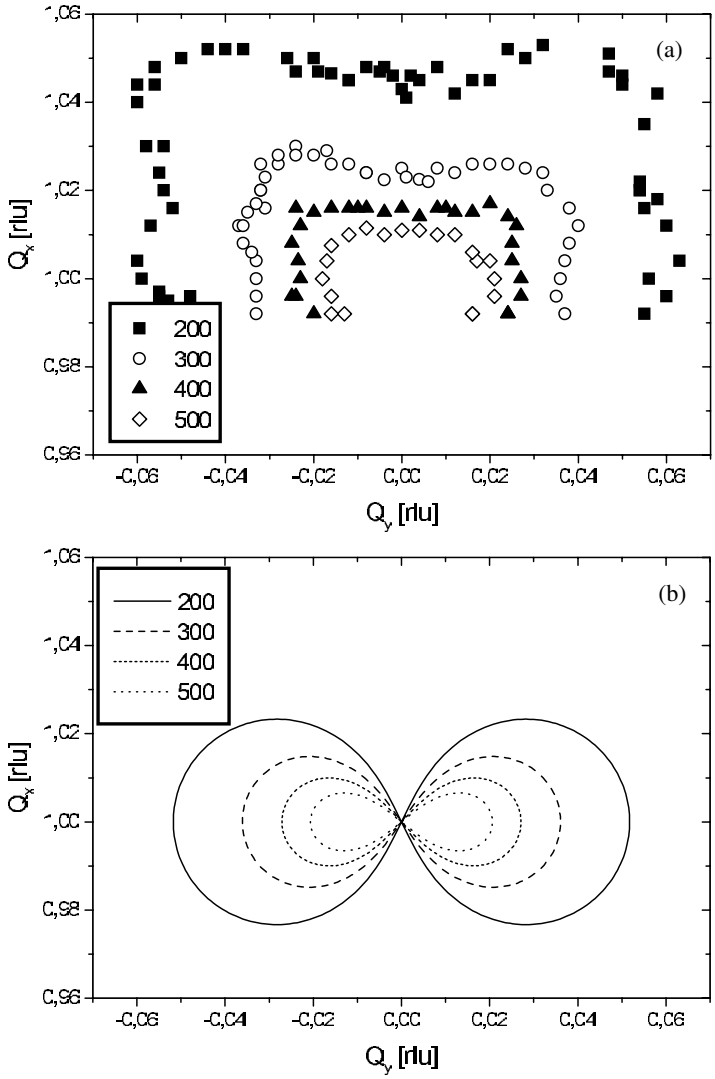

Figure 2. Equidistant constant-intensity levels describing the anisotropy of DS in the $hk0$ plane around (100) Bragg reflection. (a) Elastic neutron scattering data (30 μeV resolution) for PZN–8% PT at 500 K. (b) Ideal polar anisotropy caused by isotropic transverse fluctuations with transverse correlation length taken from the experiment (details in the text).

on PZN–9% PT at 600 K). We have not observed any sign of a really drastic softness. Nevertheless, assuming that the frequency corresponds to the bare elastic constant, the anisotropy factor $A = 2c_{44}/(c_{11} - c_{12})$ would be about 1.55–1.8, which is still larger than the value $A \approx 1.4$ assumed in the model of [21]. Secondly, the ratio of damping versus frequency $\Gamma/v \approx 1$ is quite high for an acoustic mode with such a small wavevector, indicating that its anharmonicity, presumably indicating coupling with the optic mode, is much more important than the anharmonicity of the pure shear acoustic modes measured previously at larger q-values [39, 40, 45]. Third, the temperature (540 K) and wavevector $\boldsymbol{q} = (0.02, -0.02, 0)$ were chosen purposely to ensure that the DS measured at zero frequency has more than half of its maximum intensity at this $\boldsymbol{q}$-vector. Obviously, the Lorentzian-like peak of the quasishear

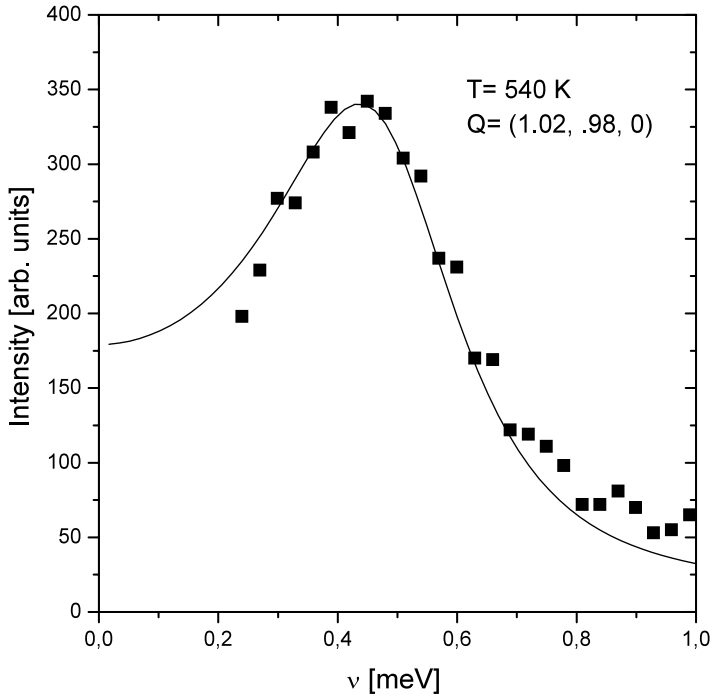

Figure 3. Constant-$\boldsymbol{Q}$ scan at $\boldsymbol{Q} = (1.02, 0.98, 0)$ showing the $\boldsymbol{q} = (0.02, -0.02, 0)$ quasishear acoustic mode for PZN–8% PT at 540 K. The full curve is a standard response of a damped harmonic oscillator with frequency 0.52 meV and damping constant 0.4 meV.

mode shown in figure 3 does not contribute to the (1.02, 0.98, 0) DS intensity at zero frequency at all. Thus, we may conclude that the diffuse signal shown in figures 2 and 3 is surely not caused by scattering by quasishear acoustic phonon modes; it appears *in addition* to the scattering by quasishear acoustic phonon modes. Moreover, we estimate that the integrated intensity of quasishear acoustic modes in figure 3 is about 10% of the integrated intensity around zero frequency (DS). In other words, in the standard neutron scattering measurements with resolution of the order of 1 meV, this TA mode would contribute to elastic scattering at (1.02, 0.98, 0) by merely 10%. The ratio of DS versus TA phonon integrated intensities is even higher near the (100) Bragg reflection and at lower temperatures.

Finally, we have undertaken a search for a finite quasi-elastic width of the DS itself at several temperatures and wavevectors, which has not given any positive results. A typical constant-Q scan across the DS signal at $\boldsymbol{Q} = (1.03, 0.0225, 0)$ and 500 K is shown in figure 4. The elastic incoherent scattering by our sample (measured independently at $\boldsymbol{Q} = (0.99, 0.04, 0)$) represents only a few per cent of the intensity shown in figure 4 and can be neglected. The spectrum is perfectly fitted by a single Gaussian with an FWHM corresponding to the instrumental resolution, showing that the intrinsic relaxation frequency of this DS at 500 K is not higher than a few gigahertz. Therefore, we can also safely exclude all scenarios ascribing the DS to an overdamped soft phonon mode. At the same time, the relaxation frequency of DS is clearly below that of the Brillouin central peak [23] (which is about 50 GHz in PZN–9% PT at 500 K). It also implies that the relaxation frequency of DS does not correspond to the relaxation frequency observed in dielectric spectroscopy, because the 500 K dielectric data indicate that the maximum of dielectric loss in PMN is above 50 GHz [46].

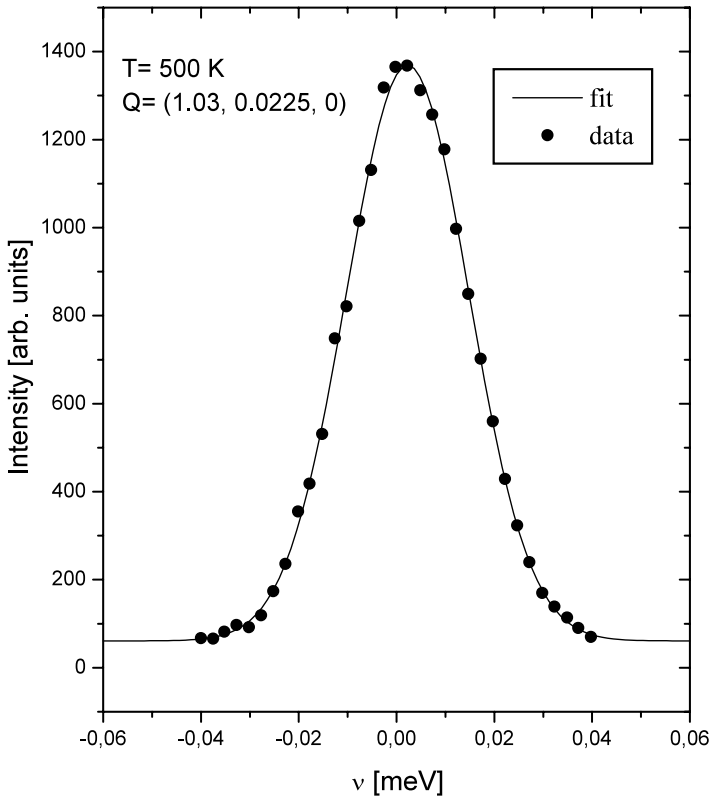

Figure 4. Constant-Q scan at $Q = (1.03, 0.0225, 0)$ showing that DS in PZN–8% PT at 540 K appears as elastic. The full curve is a Gaussian fit with FWHM corresponding to 30 μeV instrumental resolution.

3. Discussion and conclusions

In order to understand correctly the influence of PNRs on various properties of relaxors, the dynamics of PNRs is obviously as important as spatial correlations. For example, it was pointed out [21] that the so called 'waterfall' [34, 47–49] damping of the soft branch can hardly be explained merely as due to the presence of static PNRs. In fact, dynamical processes closely related to PNRs were observed in various experiments and on various timescales, for example in NMR, dielectric, microwave and Brillouin, as well as in IR, Raman and neutron scattering experiments. The difficult problem is how to identify and to characterize the corresponding motions and their role in a sufficient detail. By inelastic neutron scattering, one can in principle directly investigate the frequency profile of the DS and determine directly the corresponding relaxation time.

So far we have focused on the DS related to the ferroelectric fluctuations (static or dynamic PNR). This DS [4, 5, 16, 18, 44] has by definition a mainly transverse character, corresponds to a correlation radius smaller than about 100 Å and appears near the main Bragg reflections. It is obviously distinct from the DS observed near $(1/2, 1/2, 0)$ and $(1/2, 1/2, 1/2)$, which is related to the antiferrodistortive structural ordering and to the chemical ordering, respectively [7, 8, 50–52]. Probably, elastic deformation associated with these fluctuations may contribute to a Huang scattering (HS) close to the main Bragg peaks, too; but neither of these contributions

is expected to be strongly temperature dependent in the region between T_{max} and T_d. In order to distinguish our DS signal from the temperature independent HS, seen [53] around the $(2h, 2k, 2l)$ type reflections in previous neutron studies [16], we have checked that all intensity shown in figure 2(a) is strongly temperature dependent (in fact, in the same experimental conditions, the DS vanished at 600 K in the whole 2D region shown in figure 2(a)). On the other hand, the anisotropy seen in figure 2(a) strongly suggests that this DS may be directly related to the [110]-type ridges seen in x-ray experiments up to the zone boundaries.

In this study, we were able to show that the DS related to ferroelectric fluctuations is not a thermal DS by low frequency optic and/or acoustic phonons, at least not in the q-range comparable with FWHM of this DS. The fact that the intensity of [110]-type ridges could be followed up to $q = 0.3$ rlu also by neutron scattering (in PIN [43] and PZN [15]), indicates that the thermal DS scenario does not hold for [110]-type ridges either.

In addition, we have shown that the apparent quasielastic width of this DS remains resolution limited even in the present 8 GHz resolution experiment. This allows us to discard models in which the DS stems from overdamped phonon modes, as well as the possibility that the relaxation time corresponds directly to the critically temperature dependent relaxation frequency seen in the Brillouin experiments.

The DS could be understood as a part of the phonon response only in the sense of the central peak, as introduced e.g. in [54]. Within this concept, an additional narrow central peak may develop in the spectral response of the soft mode due to an extra term in phonon self-energy describing a special low frequency channel for phonon decay. Another quite probable possibility is that this DS is indeed quasistatic and that the correlations are not related to phonon spectral response at all. Further investigations are thus required.

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