

## Soft antiferroelectric fluctuations in morphotropic $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ single crystals as evidenced by inelastic x-ray scattering

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Lattice dynamics of a  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  single crystal with composition close to the morphotropic phase boundary has been investigated by inelastic x-ray scattering. Dispersion curves of the lowest frequency transverse optic and the transverse acoustic phonon modes propagating along the [100] direction have been determined in the high-temperature paraelectric phase as well as in the room-temperature monoclinic phase. The measurement also reveals that upon cooling from the paraelectric to monoclinic phase, the spectral response of the  $M_5$  zone boundary phonon mode associated with antiferroelectric vibrations of lead ions is progressively transforming to a broad central mode. This indicates a crossover from vibrational to relaxational-type dynamics. The existence of this phenomenon previously observed in relaxor materials is a striking result for PZT and it is believed to arise from the nanoscale structural inhomogeneity of these materials.

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The large piezoelectric response of widely used piezoelectric transducer devices based on  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  (PZT) ceramics is known to be related to the competition between the rhombohedral ( $R3m$  or  $R3c$ ) and tetragonal ( $P4mm$  or  $I4cm$ ) ferroelectric structural ground states. Indeed, the piezoelectric performance can be enhanced by tuning the composition close to the so-called morphotropic phase boundary (MPB), separating the thermodynamical stability regions of the tetragonal and the rhombohedral phases ( $x_{\text{MPB}} \doteq 0.48$  at room temperature).<sup>1,2</sup> Although the morphotropic PZT ceramics have been successfully used for 50 years, bulk single crystals with  $x \sim x_{\text{MPB}}$  have been grown only recently.<sup>3,4</sup> This achievement allows to perform an array of basic experiments which were not feasible previously.

One of the unresolved fundamental issues here is the structure of the “morphotropic” compounds with  $0.45 < x < x_{\text{MPB}}$ . The observation by Noheda *et al.* of a threefold splitting of the (220) reflection in the neutron powder diffraction diagram of  $x = 0.48$  PZT cooled below the MPB<sup>5</sup> can be interpreted either as due to a genuine monoclinic ( $Cm$  or  $Cc$ ) structure,<sup>5-10</sup> or as due to a mixed state, e.g., composed of a rhombohedral and a monoclinic structure or a rhombohedral and a tetragonal structure.<sup>3,11-14</sup> Moreover, a further lowering of the symmetry occurs below  $T_{\text{tilt}} \sim 220$  K due to the freezing of the antiphase tilts of oxygen octahedra. The ultimate model for these macroscopic states, denoted here as high-temperature ( $T > T_{\text{tilt}}$ ) and low-temperature ( $T < T_{\text{tilt}}$ ) monoclinic phases, should be established by a structural refinement in which the anticipated<sup>11,14</sup> and observed<sup>7,12</sup> nanoscale twin structures are explicitly taken into account. In any case, the monoclinic symmetry, whether local or macroscopic, plays a central role in current understanding of PZT, as it allows to realize the continuous polarization rotation between the [111] and [001] directions.<sup>5,6</sup>

Another challenging problem is whether the MPB and the vanishing polarization anisotropy are reflected in a critical behavior of some soft lattice modes. As a matter of fact, the *ab initio* lattice dynamics calculations for one of the parent compounds,  $\text{PbZrO}_3$ , show unstable lead ion lattice modes across the whole Brillouin zone.<sup>15</sup> Optical spectroscopy studies<sup>16,17</sup> identified a heavily damped ferroelectric soft mode with a frequency of about 5 meV at room temperature near MPB, but zone-boundary modes were not observed at all, except perhaps for those folded from the zone corner in the low-temperature monoclinic phase.<sup>18</sup> Here we present first results concerning the low-frequency phonon dispersion curves of the monoclinic PZT single crystal by inelastic x-ray scattering (IXS) and demonstrate, in particular, the softening of antiferroelectric vibrations of lead ions in the monoclinic phase. We argue that this softening testifies some similarity with relaxors and that it is most likely caused by its peculiar nanodomain structure.

Morphotropic PZT single crystals have recently been investigated in Refs. 3 and 4. Dielectric, structural, and optical measurements performed on a  $x \sim 0.46$  single crystal confirmed that ferroelectricity appears below  $T_C \doteq 663$  K, the  $P4mm$  tetragonal phase transforms to the monoclinic phase at around  $T_{\text{MPB}} \doteq 393$  K, and the low-temperature monoclinic phase is stable below  $T_{\text{tilt}} \doteq 220$  K, all in agreement with previous measurements on ceramics and powders. The observations of the crystal of similar composition in crossed polarizers<sup>4</sup> revealed a peculiar optical isotropy of the tetragonal phase, possibly caused by fine, submicron-sized domains, while in the high-temperature monoclinic phase the expected macroscopic monoclinic domain pattern was confirmed. Most strikingly, single crystal neutron scattering experiments of Ref. 3 allowed to investigate separately selected individual Bragg reflections in detail and, among others, to rule out the microscopic  $Cc$

symmetry for the low-temperature monoclinic phase with a doubled unit cell, proposed in previous works.<sup>2,9,10,19</sup>

We have investigated a PZT single crystal with  $x \doteq 0.475$  ( $T_C = 668$  K, and  $T_{MPB} = 338$  K), grown by a top-seeded solution growth technique. A needle-like specimen of about  $250 \times 70 \mu\text{m}^2$  cross section was mounted on a quartz capillary holder in reflection geometry, and heated or cooled by the Heat Blower and Cryostream cooler devices made by Cyberstar S.A. and Oxford Instruments, respectively. This setup allowed to control the sample temperature within about 1 K precision. The experiment itself was carried out at ID28 beamline at the European Synchrotron Radiation Facility, Grenoble. The apparatus was operated with the silicon (999) monochromator configuration at 17.794 keV, leading to an instrumental energy resolution of 3.0 meV.

The IXS spectra were recorded in the cubic, tetragonal, as well as in the high-temperature monoclinic phases. Since the lattice distortions are relatively small and the twinning of the ferroelectric phases could not be avoided in the experiment, we have used the pseudocubic parent structure as a reference in all three phases. An example of a room-temperature IXS spectrum capturing transverse acoustic and transverse optic phonon modes propagating along the [010] pseudocubic direction is shown in Fig. 1. The phonon bands in the measured energy scans were fitted to a damped harmonic oscillator (DHO) response function multiplied by a Bose-Einstein occupation factor and convoluted with a pseudo-Voigt function with parameters fixed to match the independently measured instrumental function. Furthermore, a constant background and an additional pseudo-Voigt peak at zero frequency, representing elastic or quasielastic scattering were included in the fit.

Phonon dispersion curves obtained from the DHO frequencies are traced in Fig. 2. Since the IXS dynamic structure factor is proportional to the electron density associated with moving atoms, the largest contributions are expected to come from the Pb-dominating phonon branches. In fact, the high atomic number of lead compared to other constituents of PZT and the adopted quasitransverse scattering geometry in the recorded

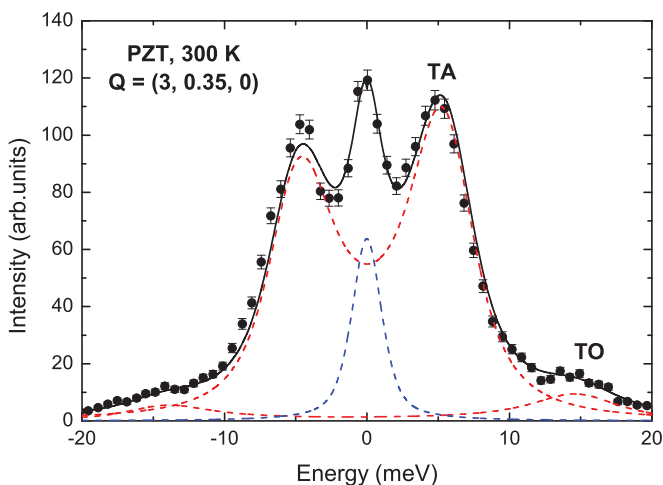


FIG. 1. (Color online) Room-temperature inelastic x-ray spectrum of transverse acoustic (TA) and transverse optic (TO) modes propagating along the pseudocubic [010] direction in the PZT single crystal.

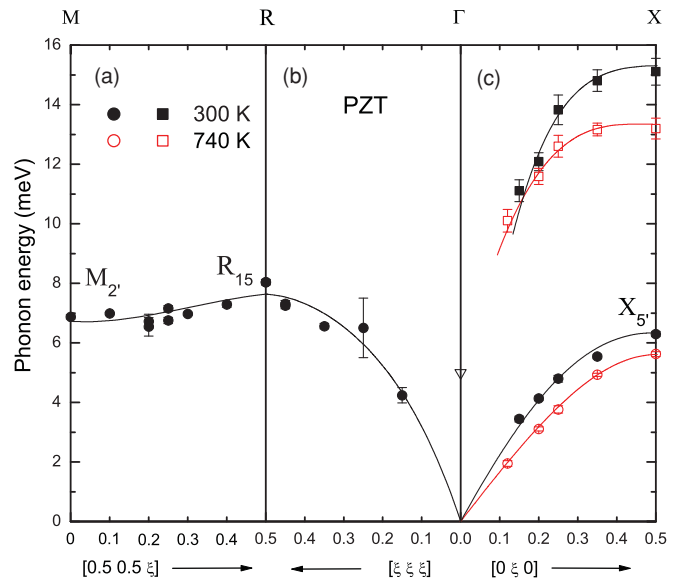


FIG. 2. (Color online) Low-frequency phonon dispersion curves of PZT single crystal with  $x \sim 0.475$  determined from the IXS measurements. Full symbols are phonon frequencies measured at room temperature (high-temperature monoclinic phase), open symbols were taken at 740 K (cubic phase). Data shown in (a), (b), and (c), were determined from measurements with momentum transfers  $(\xi, 0.5, 3.5)$ ,  $(\xi, \xi, 3 - \xi)$ , and  $(3, \xi, 0)$ , respectively. Open triangle stands for the room-temperature soft-mode frequency determined by Raman scattering in Ref. 16, continuous lines are guides to the eye.

spectra [with momentum transfers  $(\xi, 0.5, 3.5)$ ,  $(\xi, \xi, 3 - \xi)$ , and  $(3, \xi, 0)$ ] allow to assign the eigenvectors of the strong low-frequency phonon modes in the zone boundary spectra to the  $M_{2'}$ ,  $R_{15}$ , and  $X_{5'}$  representations, respectively (the notation of Refs. 15 and 20 is adopted here).

A signature of a much weaker TO mode contribution around 10–15 meV was apparent in all transverse scans but its frequency could be reliably determined only in the case of transverse phonons propagating along the [010] direction, where the transverse acoustic mode frequency was lower. Comparison of the room-temperature dispersion curves with those measured in the cubic phase confirms a sizable temperature renormalization of the TO mode frequencies, expected for a soft TO phonon branch. It seems that some softening is transferred to the TA branch, too. On the other hand, phonon frequencies of both  $M_{2'}$  and  $R_{15}$  modes did not show any appreciable change with temperature.

In general, the observed dispersion curves are fairly similar to those measured in other lead-based perovskites by inelastic neutron scattering. In particular, the steep part of the TO ( $\Gamma - X$ ) branch resembles the so-called “waterfall anomaly” discussed originally in the context of relaxor materials.<sup>21–23</sup> Here, however, data points near the  $\Gamma$  point are missing simply because scans taken in the vicinity of the Brillouin zone center were overlapped by strong contributions of the leaking Bragg-scattering processes. We expect that future measurements with a better energy resolution will confirm that this TO branch is directly connected with the zone center TO soft phonon mode observed at around 5 meV in Raman scattering experiments.<sup>16,17</sup> The TA ( $\Gamma - X$ ) branch

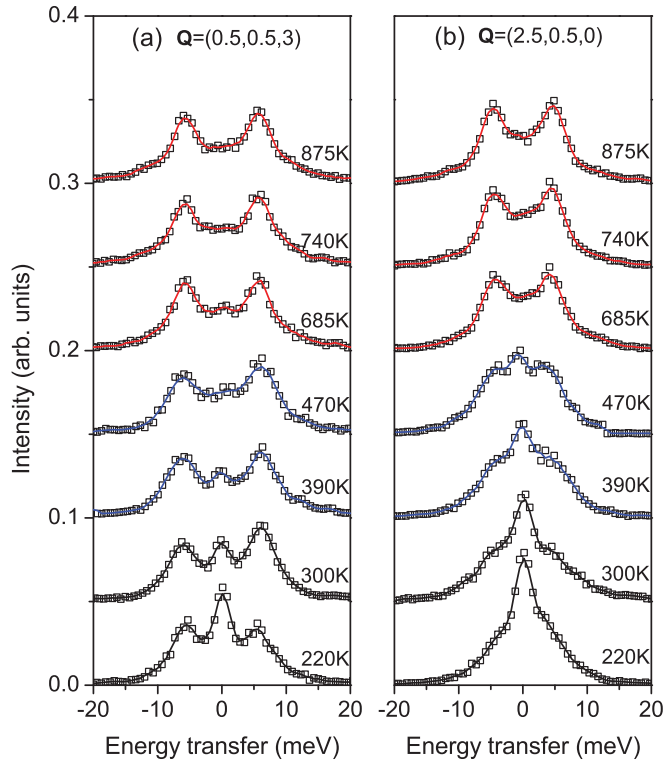


FIG. 3. (Color online) Inelastic x-ray spectra showing (a)  $M_{2'}$  and (b)  $M_{5'}$  zone boundary modes as a function of temperature. Lines are guides to the eye.

is also quite similar to those of lead-based relaxors, it is only somewhat less flat and the  $X_{5'}$  frequency is about 1–2 meV lower than in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{(1-x)}\text{Ti}_x\text{O}_3$  (PMN- $x$ PT) or  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{(1-x)}\text{Ti}_x\text{O}_3$  (PZN- $x$ PT).<sup>21,23</sup>

The most striking result of the present study stems from the comparison of the zone-boundary phonon spectra taken at  $\mathbf{Q} = (0.5, 0.5, 3)$  and at  $\mathbf{Q} = (2.5, 0.5, 0)$  (see Fig. 3). While the spectra taken at  $\mathbf{Q} = (0.5, 0.5, 3)$  show a well-defined resonance near 7 meV at all temperatures, the spectra taken at  $\mathbf{Q} = (2.5, 0.5, 0)$  reveal a dramatic collapse of the phonon side peaks on cooling into a broad central peak. This is correlated with the growth of a resolution-limited central peak in all our spectra, which suggests scattering by static or quasistatic nanoscopic structural inhomogeneity emerging around and below  $T_{\text{MPB}}$ .

Spectra taken at  $\mathbf{Q} = (0.5, 0.5, 3)$  and at  $\mathbf{Q} = (2.5, 0.5, 0)$  are rather similar at high temperatures and without any doubt they show  $M$ -point phonon modes corresponding mainly to the antiphase vibrations of lead ions. For a given  $M$ -point phonon vector  $\mathbf{q} = (0.5, 0.5, 0)$ , two such modes are known to exist in the cubic perovskite lattice—the  $M_{2'}$  singlet mode, in which the ions move along the [001] direction (Fig. 4(a)), and the  $M_{5'}$  doublet, attached to vibrations in the plane perpendicular to [001] (vibrations along  $x$  and  $y$  directions, as shown in Fig. 4(b)). Since the phonon structure factor is always proportional to the scalar product of the momentum transfer  $\mathbf{Q}$  and the dynamic displacements,<sup>24</sup> it is clear that the spectra shown in Figs. 3(a) and 3(b) correspond to the modes shown in Figs. 4(a) and 4(b), i.e., to  $M_{2'}$  and  $M_{5'}$ , respectively.

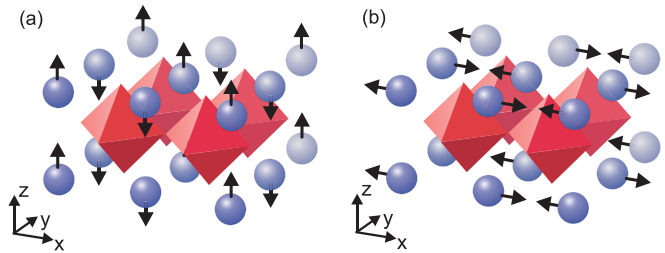


FIG. 4. (Color online) Eigenmodes of the  $M$ -point [ $\mathbf{q} = (0.5, 0.5, 0)$ ] phonons associated with lead ion motions. (a)  $M_{2'}$  singlet mode; (b)  $x$  component of the  $M_{5'}$  doublet.  $\text{Pb}^{2+}$  ions are represented by spheres, oxygen octahedra are shown schematically.

The importance of the competing antiferroelectric instability for lead-based perovskites has been discussed previously<sup>7,25,26</sup> and indications of the enhanced instability of lead-ion  $M_{5'}$  phonon mode in PZT can be found in the first-principles calculations for  $\text{PbZrO}_3$  and  $\text{PbTiO}_3$  lattice dynamics.<sup>15,27</sup> However, the behavior observed here seems to be directly related to the nanoscale inhomogeneity of the structure. In particular, results shown in Fig. 3(b) are strikingly similar to those obtained for a PMN single crystal at an equivalent momentum transfer  $\mathbf{Q} = (0.5, 1.5, 0)$  by inelastic neutron scattering (Fig. 7. of Ref. 28). The analysis performed for PMN shows that the anomalous inelastic scattering observed there is also due to the antiferroelectric fluctuations of lead ions.<sup>29</sup> Since the anomalous  $M_{5'}$  mode was observed in PMN below about 400 K, where the famous “butterfly” diffuse scattering arises, and it was not observed in the tetragonal PMN-60%PT solid solution having a sharp ferroelectric transition and no diffuse scattering, this unusual dynamic effect was proposed to be a signature of the relaxor state.<sup>28</sup>

Moreover, we have realized that the very same  $M_{5'}$  mode shows an anomalous behavior in the field-cooled rhombohedral PZN-4.5%PT single crystal.<sup>30</sup> More specifically, the field-cooling procedure was shown to create an anisotropic nanoscale texture in this crystal. This was evidenced by a strong intensity redistribution between the otherwise equivalent  $\langle 111 \rangle$  arms of the diffuse scattering, associated with the so-called polar nanoregions. The softening of the TA ( $\Gamma - M_{5'}$ ) branch occurs for the modes propagating in the direction parallel to the arms of the enhanced diffusion intensity, but not for the modes propagating in directions associated with the reduced diffuse scattering intensity [note that Fig. 1c and d of Ref. 30 correspond to the ( $\Gamma - M_{5'}$ ) branch]. We believe that these three cases form a sufficient basis for the hypothesis that the anomalous softening of the  $M_{5'}$  mode is a common feature related to nanoscale domain structures of rhombohedral or pseudorhombohedral lead-based perovskites.

In summary, the inelastic x-ray scattering was used to investigate phonon modes of the morphotropic PZT single crystal along several crystallographic directions and in a broad temperature range between 200 and 900 K. The anomalous spectral response of lead-ion antiferroelectric vibrations associated with the  $M_{5'}$ -type eigenvector, spotted in the course of this experiment, indicates that these fluctuations exhibit a relaxational, rather than normal, vibrational dynamics. The

analogy with similar observations reported in the literature for PMN and PZN-4.5%PT crystals led us to conclude that this anomalous dynamics is associated with a characteristic nanoscale inhomogeneity common to lead-based complex perovskite materials.

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<sup>1</sup>B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (Academic Press, New York, 1971).

<sup>2</sup>L. Bellaiche, A. Garcia, and D. Vanderbilt, *Phys. Rev. Lett.* **84**, 5427 (2000).

<sup>3</sup>D. Phelan, X. Long, Y. Xie, Z.-G. Ye, A. M. Glazer, H. Yokota, P. A. Thomas, and P. M. Gehring, *Phys. Rev. Lett.* **105**, 207601 (2010).

<sup>4</sup>A. A. Bokov, X. Long, and Z.-G. Ye, *Phys. Rev. B* **81**, 172103 (2010).

<sup>5</sup>B. Noheda, D. E. Cox, G. Shirane, J. A. Gonzalo, L. E. Cross, and S.-E. Park, *Appl. Phys. Lett.* **74**, 2059 (1999).

<sup>6</sup>R. Guo, L. E. Cross, S.-E. Park, B. Noheda, D. E. Cox, and G. Shirane, *Phys. Rev. Lett.* **84**, 5423 (2000).

<sup>7</sup>D. I. Woodward, J. Knudsen, and I. M. Reaney, *Phys. Rev. B* **72**, 104110 (2005).

<sup>8</sup>G. Frayssé, J. Haines, V. Bornand, J. Rouquette, M. Pintard, P. Papet, and S. Hull, *Phys. Rev. B* **77**, 064109 (2008).

<sup>9</sup>D. M. Hatch, H. T. Stokes, R. Ranjan, Ragini, S. K. Mishra, D. Pandey, and B. J. Kennedy, *Phys. Rev. B* **65**, 212101 (2002).

<sup>10</sup>D. Pandey, A. K. Singh, and S. Baik, *Acta Crystallogr. Sect. A* **64**, 192 (2008).

<sup>11</sup>G. A. Rossetti, A. G. Khachatryan, G. Akcay, and Y. Ni, *J. Appl. Phys.* **103**, 114113 (2008).

<sup>12</sup>K. A. Schonau, L. A. Schmitt, M. Knapp, H. Fuess, R.-A. Eichel, H. Kungl, and M. J. Hoffmann, *Phys. Rev. B* **75**, 184117 (2007).

<sup>13</sup>H. Yokota, N. Zhang, A. E. Taylor, P. A. Thomas, and A. M. Glazer, *Phys. Rev. B* **80**, 104109 (2009).

<sup>14</sup>A. G. Khachatryan, *Philos. Mag.* **90**, 37 (2010).

<sup>15</sup>Ph. Ghosez, E. Cockayne, U. V. Waghmare, and K. M. Rabe, *Phys. Rev. B* **60**, 836 (1999).

<sup>16</sup>D. Bauerle, Y. Yacoby, and W. Richter, *Solid State Commun.* **14**, 1137 (1974).

<sup>17</sup>D. Bauerle and A. Pinczuk, *Solid State Commun.* **19**, 1169 (1976).

<sup>18</sup>D. Wang, J. Weerasinghe, L. Bellaiche, and J. Hlinka, *Phys. Rev. B* **83**, 020301(R) (2011).

<sup>19</sup>I. A. Kornev, L. Bellaiche, P.-E. Janolin, B. Dkhil, and E. Suard, *Phys. Rev. Lett.* **97**, 157601 (2006).

<sup>20</sup>R. A. Cowley, *Phys. Rev.* **134**, A981 (1964).

<sup>21</sup>P. M. Gehring, S.-E. Park, and G. Shirane, *Phys. Rev. Lett.* **84**, 5216 (2000).

<sup>22</sup>J. Hlinka, S. Kamba, J. Petzelt, J. Kulda, C. A. Randall, and S. J. Zhang, *Phys. Rev. Lett.* **91**, 107602 (2003).

<sup>23</sup>I. Tomeno, S. Shimanuki, Y. Tsunoda, and Y. Ishii, *J. Phys. Soc. Jpn.* **70**, 1444 (2001).

<sup>24</sup>J. M. Perez-Mato, M. Aroyo, J. Hlinka, M. Quilichini, and R. Currat, *Phys. Rev. Lett.* **81**, 2462 (1998).

<sup>25</sup>S. A. Prosandeev, M. S. Panchelyuga, S. I. Raevskaya, and I. P. Raevskii, *Phys. Solid State* **53**, 147 (2011).

<sup>26</sup>I. Grinberg, V. R. Cooper, and A. M. Rappe, *Phys. Rev. B* **69**, 144118 (2004).

<sup>27</sup>U. V. Waghmare and K. M. Rabe, *Phys. Rev. B* **55**, 6161 (1997).

<sup>28</sup>I. P. Swainson, C. Stock, P. M. Gehring, G. Xu, K. Hirota, Y. Qiu, H. Luo, X. Zhao, J.-F. Li, and D. Viehland, *Phys. Rev. B* **79**, 224301 (2009).

<sup>29</sup>As clear from our argument, the  $M$ -point soft columns of PMN are mistakenly assigned as  $M_2'$  phonons in Ref. 28.

<sup>30</sup>G. Xu, J. Wen, C. Stock, and P. M. Gehring, *Nat. Mater.* **7**, 562 (2008).