

Elastic and anelastic relaxations in the relaxor ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$: I.

Strain analysis and a static order parameter

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Abstract

The structural evolution of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ has been reviewed in terms of characteristic temperatures, length scales and timescales, with a view to considering the overall relaxor behaviour from the perspectives of strain and elasticity. A conventional analysis of lattice parameter data in terms of spontaneous strain and strain/order parameter coupling shows that the relaxor ordering process is accompanied by a significant volume strain which follows the pattern of a static order parameter evolving according to that expected for a tricritical phase transition with $T_c \approx 350$ K. This matches the evolution of the intensity of the elastic central peak in neutron scattering spectra and reflects the development of static (or quasistatic) polar nano regions (PNR's) as if by a discrete, mean-field phase transition. It also matches the evolution of shear strain in crystals poled by an electric field. Use of a Landau free energy expansion, which includes Γ_4^- order parameter components to describe ferroelectric contributions and an R_1^+ order parameter to describe cation ordering together with their formal coupling with strain, then allows the pattern of elastic softening

expected for a cubic \rightarrow rhombohedral phase transition to be anticipated. The extent to which observed softening differs from this static mean-field pattern serves to highlight the additional roles of local heterogeneity and relaxation dynamics in determining the relaxor properties of PMN.

1. Introduction

Underlying origins of the distinctive physical properties of relaxor ferroelectrics, such as giant electrostriction, electrooptic effect and large dielectric constant, are usually investigated from the perspective of their response to an applied electric field. Lead magnesium niobate $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) is regarded as a model relaxor phase in this context, and its dielectric properties have been measured over a wide frequency range from $\sim 10^{-3}$ to 10^{14} Hz (e.g. Bovtun *et al* 2006, and many references therein). Real (ϵ') and imaginary (ϵ'') parts of the complex permittivity reveal aspects of the dynamic behaviour of electronic, phonon and relaxational type polarizations over the correspondingly wide range of time scales. The characteristic broad peak of ϵ' through the “diffuse” phase transition in the region of ~ 200 - 300 K together with strong frequency dispersion, in particular, have then been used to inform models of the relaxor behaviour based on the development and freezing of polar nanoregions (PNR's) which are believed to be responsible for the difference from conventional ferroelectric behaviour (Bokov and Ye 2006a). A thermally activated relaxational process with a single relaxation time would be expected to give variations in ϵ' and dielectric loss ($\tan\delta = \epsilon''/\epsilon'$) that depend on the frequency of the applied electric field according to the Debye equation. Instead, the freezing process of PNR's involves a wide spectrum of relaxation times and Vogel-Fulcher dynamics (e.g. for PMN: Viehland *et al* 1990, Dorogovtsev and Yushin 1990, Levstik *et al* 1998, Glazounov and Tagantsev 1998, Bovtun *et al* 2004, 2006, Bokov and Ye 2006a, Pirc and Blinc 2007, Zhao *et al* 2009). The

key parameters of the Vogel-Fulcher equation are a freezing temperature, T_f , and some relaxation time, τ , which are related by

$$\tau = \tau_0 \exp\left(\frac{U}{k_B(T - T_f)}\right). \quad (1)$$

Here τ_0 is the inverse of attempt frequency, U is an effective activation energy and T is temperature. In practice different relaxation times from the total relaxation time spectrum may be extracted in different ways from experimental data (e.g. Glazounov and Tagantsev 1998, Bokov and Ye 2006a, b) and different parts of the spectrum may have different freezing temperatures (Bokov and Ye 2006a).

The relaxation dynamics of PNR's can also be investigated from other perspectives. Most notably, relaxor ferroelectrics display significant electrostriction (e.g. in PMN: Blackwood and Ealey 1993, Zhao *et al* 1998), which is an overt demonstration of the fact that electric polarization is coupled with strain. Polarisation relaxation in a dynamic electric field must depend also on the dynamics of strain relaxation, therefore. The equivalent elastic property to electric polarisation is strain and the equivalent susceptibility to permittivity is elastic compliance. The latter is more usually expressed in terms of the elastic constants for a single crystal or bulk and shear moduli for a ceramic. It follows that, as proposed by Viehland *et al* (1990), interactions between PNR's could occur by both dipole and elastic strain mechanisms. The electric dipole interactions should be relatively strong and short ranging, while correlations via elastic strain fields would be weak but relatively long ranging. Elastic and dielectric responses to external fields will not necessarily be quite the same, therefore. The pattern of strain variations and elastic softening associated with a conventional ferroelectric transition is expected to depend on the evolution of a classical order parameter more or less according to Landau theory. Deviations from this are indicative of the special

characteristics of correlation length scales and relaxational timescales of PNR's as observed from the perspective of strain correlations rather than of electric dipole correlations.

Strain and elastic moduli are second and fourth rank properties, respectively, in comparison with polarisation and permittivity which are first and second rank properties, so that elastic responses have the potential to convey additional information relating to the role of symmetry in some of the coupling processes which determine relaxor behaviour. There will also be acoustic losses in an alternating stress field which can be described by the internal friction or inverse mechanical quality factor, and which will provide specific information on the relaxation properties of boundary regions between the PNR's analogous to the dynamic behaviour of twin walls in ferroelastic materials. The present study was devised with the purpose of investigating the properties and behaviour of PNR's from this perspective of strain and elasticity. PMN was chosen for investigation both because it retains cubic lattice geometry down to low temperatures, without any breaking of macroscopic symmetry, and because of the wealth of experimental data available for its unit cell parameters, dielectric properties and lattice dynamics. In particular, it is already known that there is strong coupling between acoustic phonons and local dynamics of the PNR's (Stock *et al* 2005).

In this first of two papers, the overall relaxor behaviour of PMN is reviewed in terms of characteristic temperatures, length scales and timescales of the structural processes involved. The macroscopic strain evolution is then analysed using a Landau free energy expansion which includes the effects of both ferroelectric displacements and cation ordering. It turns out that the volume strain can be described using normal strain/order parameter coupling as if there is a tricritical phase transition with $T_c \approx 350$ K. This leads to a simple prediction of the form of the elastic anomalies which should be expected to occur. In the following paper (Carpenter *et al* 2011), new data for the elastic properties and acoustic dissipation obtained by Resonant Ultrasound Spectroscopy are combined with elasticity data

from the literature to show the extent to which strain dynamics of the PNR's follow the local dipole dynamics. Deviations from classical strain/order parameter patterns of elastic softening can be understood in terms of coupling between acoustic modes and relaxational modes of the PNR's.

2. Statics and dynamics of relaxor behaviour of PMN

2.1 Characteristic temperatures

With falling temperature, the Burns temperature, $T_d \approx 630$ K, is marked by the onset of changes in refractive index (Burns and Dacol 1983), a change in thermal expansion (e.g. Bonneau *et al* 1989, Zhao *et al* 1998, Dul'kin *et al* 2003, Dkhil *et al* 2001, 2009), together with the appearance of a central peak component in Raman spectra (Siny *et al* 1997, Siny and Katiyar 1998, Svitelskiy *et al* 2003), quasi-elastic scattering in inelastic neutron scattering spectra (Naberezhnov *et al* 1999, Hirota *et al* 2002, Hiraka *et al* 2004, Gvasaliya *et al* 2005), and a peak in acoustic emission (Dul'kin *et al* 2003, Dkhil *et al* 2009). These effects are all understood to originate from the development of dynamic PNR's.

The most overt evidence for a second characteristic temperature, $T^* \approx 500$ K, is provided by a peak in acoustic emission reported by Dkhil *et al* (2009). Acoustic emission arises from the abrupt release of mechanical stress and is commonly associated with phase transitions. In PMN the origin must be due to some local effect since there is no macroscopic symmetry change and Dkhil *et al* (2009) suggested that T^* marks the temperature at which the PNR's acquire a static component. Such a clear anomaly does not seem to show up at 500 K in other properties, though a new peak appears in Raman spectra collected below this temperature (Dkhil *et al* 2009) and elastic diffuse neutron scattering intensity also seems to increase from zero at about the same point (see Fig. 1 of Hiraka *et al* 2004; Fig. 1 and Fig. 8 of Gehring *et al* 2009).

The next characteristic temperature is the Curie temperature, $T_c \approx 400$ K, estimated by extrapolation of dielectric susceptibility data from above T_d according to the Curie-Weiss law (Viehland *et al* 1992). This seems to correspond exactly with the critical temperature for a zone-centre soft optic mode obtained by extrapolation of the square of its frequency to zero from high temperatures, 390 ± 30 K (Al-Zein *et al* 2010, Vakhrushev *et al* 2010). There is also a change in the character of the central peak in neutron scattering spectra at about the same temperature. Immediately below T_d the central peak is broad and due to quasi-elastic scattering. This increases in intensity below ~ 600 K, reaches a maximum at ~ 370 K and then diminishes on further cooling (Gvasaliya *et al* 2005). A narrow component due to elastic scattering increases in intensity steeply below ~ 400 K (Hiraka *et al* 2004, Gvasaliya *et al* 2005, Gehring *et al* 2009, Stock *et al* 2010) and is interpreted as indicating that the PNR's become static, at least on a time scale of greater than 2 ns (Gehring *et al* 2009, Stock *et al* 2010). The elastic central peak remains diffuse, however, indicating that the correlation length of static regions is small. Cowley *et al* (2009) described this overall behaviour in terms of a random field phase transition at ~ 400 K. Svitelskiy *et al* (2003) reported splitting of peaks in Raman spectra below 350 K (see, also, Curecheriu *et al* 2009) and quoted $T^* = 350 \pm 25$ K as the temperature at which “a quasistatic ordering begins to set in, equivalent to one or several underlying or latent structural phase transitions, marked by sharper and split phonon peaks”. Some dynamic component to the ordering remains, however, which from recent neutron inelastic scattering results has its maximum at ~ 300 -350 K and tends to zero at ~ 200 K (Stock *et al* 2010). 350 K is also the temperature below which significant diffuse intensity appears in X-ray diffraction patterns and at which there appears to be a change in thermal expansion of single crystal PMN (Dkhil *et al* 2001).

Finally, the maximum in dielectric permittivity occurs at a frequency-dependent temperature, T_m , which varies between ~ 230 K at $\sim 10^{-3}$ Hz and ~ 370 K at 10^{11} Hz (Bovtun *et*

al 2006). This is usually used to obtain a Vogel-Fulcher freezing temperature, T_{VF} , by fitting to $f = (2\pi\tau_0)^{-1} \exp[-E/(T_m - T_{VF})]$. It does not necessarily follow that the parameters in this expression are identical to those of Equation 1 (Bokov and Ye 2006a) but the frequency f is effectively used to give a relaxation time τ directly as $\tau = 1/2\pi f$ and T_{VF} may be assumed to represent the freezing temperature such that the values of T_f obtained are in the vicinity of ~ 220 K for PMN.

2.2. Characteristic length scales

Although there is no long range order at any temperature in PMN and the structure remains cubic down to 5 K (Bonneau *et al* 1991, de Mathan *et al* 1991a), short range order does develop with distinctive length scales. Firstly, direct observations by transmission electron microscopy (TEM) at room temperature have revealed antiphase domains on a scale of ~ 60 Å associated with B-site cation ordering on the basis of space group $Fm\bar{3}m$ (Hilton *et al* 1989, 1990). Chen *et al* (1989) gave dimensions of $\sim 20 - 50$ Å for the same microstructure, while Yoshida *et al* (1998) and Miao *et al* (2001) gave the dimensions as $\sim 20 - 70$ Å. This chemical ordering gives rise to diffuse intensity in neutron diffraction patterns but the intensity is relatively independent of temperature (Gehring *et al* 2009), indicating that the domains remain unchanged through the interval of PNR formation and freezing. It has been found that there is an increase in intensity of superlattice reflections in X-ray diffraction patterns below room temperature, but this has been attributed to some additional atomic displacements rather than a change in cation order (Gosula *et al* 2000). A constant microstructure associated with the chemical ordering is also consistent with the observations of Hilton *et al* (1990) in relation to limited changes of superlattice reflection intensities and diffuseness between ~ 100 K and ~ 425 K in electron diffraction patterns. Davies and Akbas (2000) reported that heat treatments at temperatures between 700 and 1400 °C failed to

induce any significant structural modification and Farber *et al* (2002) concluded that the equilibrium ordering transition temperature is ~ 950 °C. In this case the antiphase domain texture observed by TEM in samples prepared at higher temperatures arises from short range ordering only.

Diffraction data are consistent with the PNR's having local rhombohedral symmetry (de Mathan *et al* 1991a, Takesue *et al* 2001, Ye *et al* 2003, Jeong *et al* 2005). Diffuse neutron scattering data give correlation lengths for the polar ordering as ~ 10 - 15 Å at 300, 400 and 500 K, with a small increase to ~ 20 Å at 250 K followed by a larger increase to ~ 45 - 60 Å between 200 and 10 K (Xu *et al* 2004). Yoshida *et al* (1998) reported the development of granular strain contrast in TEM images on a scale of ~ 100 Å at 260 K and a few hundred Å at 200 K, together with the appearance of rhombohedral twin walls within individual PNR's below 130 K. An additional domain structure has been observed by piezoresponse force microscopy in $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - PbTiO_3 (PMN-PT) above the ferroelectric-relaxor transition temperature (Shvartsman and Kholkin 2010). The domains appear to be "self-organised agglomerates of static (or quasi-static) PNR's" (Shvartsman and Kholkin 2010) on a scale of ~ 100 - 200 nm. The present authors have not found any reports in the literature of similar features in PMN, but domains in which neighbouring PNR's interact to produce some degree of self alignment of polarisations via dipole/dipole interactions and elastic strain fields clearly might occur. This and the observations of Yoshida *et al* (1998) would fit with the original view of Viehland *et al* (1991) that the freezing process involves correlations between adjacent PNR's up to a length scale of ~ 200 Å in PMN.

Neutron pair distribution analysis implies that the volume fraction of PNR's increases with falling temperature to $\sim 10\%$ at 300 K, then to $\sim 20\%$ at 250 K and $\sim 30\%$ at 15 K (Jeong *et al* 2005). The change near 250 K is consistent with passage through the percolation threshold, which is $\sim 28\%$ for spherical objects in three dimensions and slightly less than this

for ellipsoidal objects (Jeong *et al* 2005, Blinc 2006). The local symmetry of the matrix need not be cubic and the thickness of boundaries between the PNR's is comparable with the size of the PNR's themselves (Bokov and Ye 2006). A distinct pattern of thermal expansion indicates that the development of PNR's is accompanied by a small positive volume strain (e.g. Zhao *et al* 1998, Dkhil *et al* 2001, 2009, Gehring *et al* 2009), which is presumably due to both the increasing volume fraction of PNR's and the contribution of strain relaxation with increasing polarisation within them. Any additional relaxation of the matrix, say to a locally antiferroelectric structure (Ishchuk 2001), would also contribute to this strain.

2.3. Characteristic timescales

An alternative view of the overall relaxor behaviour of PMN is provided by considering the temperature dependence and interactions of phonons. The E_1 soft optic mode described by Al-Zein *et al* (2010) would by itself lead to a conventional ferroelectric transition. The next transverse optic mode (A_1 according to Al-Zein *et al* 2010) has also been shown to soften with increasing temperature below T_f and with decreasing temperature from above T_d (Gehring *et al* 2001, Wakimoto *et al* 2002a, Bovtun *et al* 2004, Vakhrushev *et al* 2010, Al-Zein *et al* 2010, Taniguchi *et al* 2010). Complications of damping close to the Γ point attributed to the influence of PNR's in the temperature interval between T_f and T_d are well documented (e.g. Gehring *et al* 2000, 2001, Wakimoto *et al* 2002a, Shirane *et al* 2005, Bokov and Ye 2006a, Hlinka and Kempa 2008), and a number of analyses of coupling between optic and acoustic modes have also been made (Wakimoto *et al* 2002b, Gvasaliya *et al* 2005 JPCM, Stock *et al* 2005). In one of the most recent analyses (Stock *et al* 2005) it was concluded that this coupling is weak, however.

Key additional features of the relaxor behaviour are the relaxational processes which give rise to the central peak in Raman, IR and Brillouin scattering spectra (Siny *et al* 1997,

Svitelskiy *et al* 2003, Kamba *et al* 2005, Taniguchi *et al* 2010) and to the quasielastic scattering in inelastic neutron scattering spectra (Hirota *et al* 2002, Gvasaliya *et al* 2004a, b, 2005, Gehring *et al* 2009). Siny *et al* (1997) determined that the relaxation times involved are $\sim 10^{-12}$ s for the temperature interval over which the Raman central peak was observed (~ 100 -650 K) and Gvasaliya *et al* (2004b) obtained $\sim 10^{-11}$ s from analysing the peak width of a broad quasi-elastic scattering central peak in inelastic neutron spectra. Essentially the same central peak features have been observed in Brillouin spectra of $0.93\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - 0.07PbTiO_3 (0.93PZN-0.07PT) from which Tsukada *et al* (2008) and Tsukada and Kojima (2008) obtained relaxation times of $\sim 10^{-11}$ - 10^{-12} and $\sim 10^{-12}$ - 10^{-13} s for two separate relaxation processes. Of particular significance in the context of the elastic properties of PMN is the observation that there is strong coupling between the relaxational central peak/quasi-elastic scattering mode(s) and acoustic phonons (Stock *et al* 2005). The same conclusion, that PNR dynamics have a strong influence on acoustic modes, has also been reached for PMN-PT (Ko *et al* 2010) and PZN-PT (Toulouse *et al* 2005, Xu *et al* 2008, Ko *et al* 2008, Tsukada and Kojima 2008, Tsukada *et al* 2008). While the relaxation dynamics occur on a time scale of $\sim 10^{-12}$ s, NMR evidence is that polar clusters exist on a time scale of $\sim 10^{-4}$ - 10^{-5} s (Blinic *et al* 2000).

3. Strain analysis

The starting point used here for considering the relaxor behaviour of PMN from the perspective of strain and elasticity is a conventional Landau treatment for the related ferroelectric transition(s). There are two symmetry-breaking processes: ferroelectric displacements tend to lower the symmetry from $Pm\bar{3}m$ to $R3m$, and cation ordering tends to lower the symmetry from $Pm\bar{3}m$ to $Fm\bar{3}m$. The order parameters transform as irreducible

representations Γ_4^- and R_1^+ , respectively, of $Pm\bar{3}m$. A full Landau expansion for the excess free energy of the combined processes would be

$$\begin{aligned}
G = & \frac{1}{2} a_{\Gamma} \Theta_{s\Gamma} \left(\coth\left(\frac{\Theta_{s\Gamma}}{T}\right) - \coth\left(\frac{\Theta_{s\Gamma}}{T_{c\Gamma}}\right) \right) (q_1^2 + q_2^2 + q_3^2) + \frac{1}{4} b_{\Gamma} (q_1^2 + q_2^2 + q_3^2)^2 \\
& + \frac{1}{4} b'_{\Gamma} (q_1^4 + q_2^4 + q_3^4) + \frac{1}{6} c_{\Gamma} (q_1^2 + q_2^2 + q_3^2)^3 + \frac{1}{6} c'_{\Gamma} (q_1 q_2 q_3)^2 \\
& + \frac{1}{6} c''_{\Gamma} (q_1^2 + q_2^2 + q_3^2) (q_1^4 + q_2^4 + q_3^4) + \lambda_{1\Gamma} e_a (q_1^2 + q_2^2 + q_3^2) \\
& + \lambda_{2\Gamma} \left[\sqrt{3} e_o (q_1^2 - q_2^2) + e_t (2q_3^2 - q_1^2 - q_2^2) \right] + \lambda_{3\Gamma} (e_4 q_3 q_2 + e_5 q_3 q_1 + e_6 q_1 q_2) \\
& + a_{\text{R}} \Theta_{s\text{R}} \left(\coth\left(\frac{\Theta_{s\text{R}}}{T}\right) - \coth\left(\frac{\Theta_{s\text{R}}}{T_{c\text{R}}}\right) \right) q_{\text{R}}^2 + \frac{1}{4} b_{\text{R}} q_{\text{R}}^4 + \lambda_{1\text{R}} e_a q_{\text{R}}^2 + \lambda_{2\text{R}} (e_o^2 + e_t^2) q_{\text{R}}^2 \\
& + \lambda_{3\text{R}} (e_4^2 + e_5^2 + e_6^2) q_{\text{R}}^2 + \frac{1}{4} (C_{11}^0 - C_{12}^0) (e_o^2 + e_t^2) \\
& + \frac{1}{6} (C_{11}^0 + 2C_{12}^0) e_a^2 + \frac{1}{2} C_{44}^0 (e_4^2 + e_5^2 + e_6^2) + \lambda_{\text{TR}} (q_1^2 + q_2^2 + q_3^2) q_{\text{R}}^2
\end{aligned} \tag{2}$$

where a, b, c , etc., are normal Landau coefficients, $\Theta_{s\Gamma}$ and $\Theta_{s\text{R}}$ are saturation temperatures for the Γ_4^- and R_1^+ order parameters, $T_{c\Gamma}$ and $T_{c\text{R}}$ are critical temperatures, e_i are strains, with $e_a = (e_1 + e_2 + e_3)$, $e_o = (e_1 - e_2)$ and $e_t = (1/\sqrt{3})(2e_3 - e_1 - e_2)$, λ 's are strain/order parameter coupling coefficients and C_{ik}^0 are elastic constants of the parent cubic phase. The final term represents direct biquadratic coupling of the two order parameters. Different combinations of non-zero order parameters give rise to different product structures, as listed in full in Table 1. A combination of $R3m$ ferroelectric displacements with $Fm\bar{3}m$ cation order gives a structure with $q_1 = q_2 = q_3 \neq 0$ and $q_{\text{R}} \neq 0$ which has space group $R3m$ and a unit cell expressed in terms of basis vectors $(-1, 1, 0)$, $(0, -1, 1)$, $(2, 2, 2)$ with respect to the parent $Pm\bar{3}m$ structure.

If the ferroelectric transition takes place in a crystal with some fixed degree of cation order, q_{RF} , the effect of the biquadratic coupling term is to renormalise the critical temperature, $T_{c\Gamma}$. Ignoring saturation terms, the new critical temperature would be

$$T_{c\Gamma}^* = T_{c\Gamma} - \frac{2\lambda_{\text{TR}}q_{\text{RF}}^2}{a_{\Gamma}}, \quad (3)$$

where $T_{c\Gamma}^*$ is equivalent to the Curie temperature, T_c , from above. In this case, the evolution of parameters such as the soft mode frequency would give different Curie temperatures between samples that had been prepared with different degrees of cation order. More importantly, the development of ferroelectric displacements within antiphase boundaries of the ordered structure, where $q_{\text{RF}} = 0$, would be different from within the domains, where $q_{\text{RF}} \neq 0$, and heterogeneity would necessarily follow. The difference depends on the sign and magnitude of λ_{TR} . By analogy with $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$, as summarised in Burton *et al* (2005), the ferroelectric transition temperature is expected to increase with increasing $|q_{\text{RF}}|$, implying that λ_{TR} is negative.

There will be two spontaneous strains, e_4 and e_a , defined with respect to the $Pm\bar{3}m$ structure, depending on the order parameters according to

$$e_a = -\frac{\lambda_{1\Gamma}(q_1^2 + q_2^2 + q_3^2) + \lambda_{1\text{R}}q_{\text{RF}}^2}{\frac{1}{3}(C_{11}^0 + 2C_{12}^0)}, \quad (4)$$

$$e_4 = -\frac{\lambda_{3\Gamma}q_2q_3}{C_{44}^0 + 2\lambda_{3\text{R}}q_{\text{RF}}^2}. \quad (5)$$

The only strain contribution arising from cation ordering would be to the volume strain, e_a , and the magnitude of this would in principle be expected to differ locally between antiphase boundaries and antiphase domains. PMN has local rhombohedral domains at low temperatures but retains average cubic lattice geometry, i.e. $e_4 = (a/a_0)\cos\alpha = 0$ since the cosine of the rhombohedral angle, α , over the length scaled averaged by X-ray diffraction is zero. There will still be a volume strain, e_a , from the ferroelectric ordering, however, which should scale with the square of the average ferroelectric order parameter within the PNR's.

Variations of the volume strain can be represented by the variation of e_1 ($e_a = 3e_1$) which is determined from measured lattice parameters in the usual way. Figure 1a shows lattice parameter data from Bonneau *et al* (1991), Zhao *et al* (1998), Dkhil *et al* (2009) measured by neutron and X-ray diffraction, for example. The reference parameter of the parent cubic phase, a_0 , has been obtained by fitting the function (Salje *et al* 1991, Meyer *et al* 2000, 2001, Sondergeld *et al* 2000, Carpenter *et al* 2003)

$$a_0 = a_1 + a_2 \Theta_{s,ao} \coth\left(\frac{\Theta_{s,ao}}{T}\right) \quad (6)$$

to data above 600 K. The resulting extrapolations to low temperatures are illustrated in Figure 1a for data of Bonneau *et al* (1991) and Dkhil *et al* (2009). Following McKnight *et al* (2009), the saturation parameter $\Theta_{s,ao}$ was set at 150 K, which is within the expected range for leveling off of normal thermal expansion in oxide perovskites as $T \rightarrow 0$ K.

Variations of e_1^2 , where $e_1 = (a - a_0)/a_0 = e_a/3$, from all the data in Figure 1a are shown in Figure 1b. Absolute values of e_1 are subject to significant uncertainty from the choice of $\Theta_{s,ao}$ and differ between data sets due to uncertainties propagated from fitting of the baseline to limited number of points for a_0 at high temperatures. The trend with temperature is clearly the same in each case, however. By analogy with the behaviour of PbTiO_3 , the ferroelectric transition might be expected to be close to tricritical in character (Whatmore *et al* 1978), in which case the variation of e_1 is expected to follow

$$e_1^2 \propto q_1^4 \propto \left(\coth\left(\frac{\Theta_{s\Gamma}}{T_{c\Gamma}^*}\right) - \coth\left(\frac{\Theta_{s\Gamma}}{T}\right) \right), \quad (7)$$

as occurs also in the mineral lawsonite (Carpenter *et al* 2003). The only data in Figure 1b that extend to low enough temperatures to clearly include the influence of $\Theta_{s\Gamma}$ are from the neutron diffraction results of Bonneau *et al* (1991). Fitting Equation 7 to data between 5 and 200 K gives $T_{c\Gamma}^* = 342 \pm 38$ K, $\Theta_{s\Gamma} = 91 \pm 45$ K. Keeping $\Theta_{s\Gamma}$ fixed at 91 K for a fit to X-ray

data of Bonneau *et al* (1991) in the interval 73-240 K gives $T_{c\Gamma}^* = 341 \pm 5$ K (Fig. 1b). The data of Zhao *et al* (1998) obtained with a $5\text{kV}\cdot\text{cm}^{-1}$ electric field applied to a ceramic sample show a slightly larger strain for the rhombohedral structure below 220 K, but the raw data overlap with those for the cubic phase (Fig 1a) and it is not clear that the difference is due to the electric field rather than simply being derived from the fitting of a_0 to data at high temperature obtained with zero field.

A poled rhombohedral sample has $\alpha = 89.91 \pm 0.02^\circ$ at 80 K after removal of the electric field (de Mathan *et al* 1991), giving $e_4 = 0.0016 \pm 0.0004$ as the equilibrium strain for the ferroelectric equivalent of the cubic relaxor phase. The sample remained rhombohedral up to ~ 200 K and the limited data of de Mathan *et al* (1991b) have been used to calculate values of e_4 ($\approx \cos\alpha$). Within experimental uncertainties, e_4 follows the pattern expected for

$$e_1^2 \propto e_4^2 \propto q_1^4 \propto (T_c - T) \text{ (Fig. 1b).}$$

4. Discussion

This treatment essentially follows the view of Cowley *et al* (2009) that there is an effective phase transition in PMN. The strain analysis is permissive of the view that the order parameter within PNR's below T_c varies in a manner that is close to tricritical in character. Even excluding the uncertainty of the value of $\Theta_{s,ao}$, the extrapolated transition temperature from e_1^2 (340 ± 40 K) is consistent with the value determined from the evolution of the soft mode frequency at high temperatures ($T_c = 390 \pm 30$ K, Al Zein *et al* 2010; ~ 400 K, Vakhrushev *et al* 2010). Approximately tricritical character for an order parameter, q , is also implied by the variation with temperature of the intensity of the elastic part of a diffuse neutron scattering central peak, I_{CP} , in data of Gvasaliya *et al* (2005). As shown in Figure 2a, I_{CP}^2 , which would be expected to scale with the order parameter as $I_{CP}^2 \propto q^4$, varies in the

same manner as e_1^2 . Equivalent data for elastic diffuse scattering from Gehring *et al* (2009) are also shown and the fit to these has $\Theta_s = 104 \pm 15$ K, $T_c = 342 \pm 5$ K. Separate treatment of the static component of diffuse scattering intensity gives a closely similar result (Fig. 2b, with data from Fig.4a of Stock *et al* 2010). According to Equation 3, there must be differences in the ferroelectric transition temperature between ordered domains and disordered domain walls due simply to renormalisation by the order parameter for cation ordering.

A Landau 246 potential would give slightly higher values of T_c but the implication is still that there is a discrete phase transition and an effective static order parameter which behaves in a manner that is close to tricritical. The overall trend of e_1 and I_{CP} are essentially the same for all the samples represented in Figures 1 and 2, and will be similar to other data sets for thermal expansion that are in the literature. The trend of e_1 is typical of other transitions in perovskites in including a tail in the non-symmetry breaking strain above T_{CF}^* , though this extends to much higher temperatures than in the case, say, of LaAlO_3 (Carpenter *et al* 2010). The absence of a tail in the static component of the diffuse neutron scattering intensity (Fig. 2b) implies that the tail in the strain for PMN is due to the dynamic component of the structural evolution at $T > T_c$. The latter tends to zero at ~ 200 K (Stock *et al* 2010), more or less where the tail in strain meets the mean field fit to the data extrapolated from lower temperatures.

The magnitude of e_1 at 0 K in zero field is ~ 0.0036 implying a total positive volume strain (e_a) of $\sim 1\%$, though this is subject to uncertainties arising from the choice of $\Theta_{s,ao}$. In the freezing interval observed by dielectric spectroscopy, i.e. ~ 230 - 370 K, the dynamic tail of the volume strain is larger than would be implied for the purely static component (Fig. 2b). The effect of increasing pressure at temperatures below ~ 400 K should be first to suppress dynamic aspects of the PNR's, therefore, to give a rhombohedral phase with the enlarged unit cell of a structure which has $q_1 = q_2 = q_3 \neq 0$ and $q_R \neq 0$. Further increases in pressure should

then suppress the ferroelectric order parameter to leave a cubic phase ($Fm\bar{3}m$) with cation ordering only. Chaabane *et al* (2003) have reported a reduction of diffuse X-ray scattering in PMN with increasing pressure, and their limited data for an $h+1/2, k+1/2, l+1/2$ reflection (where h, k, l refer to the cubic P parent structure) are at least consistent with a doubled $R3m$ structure becoming stable above ~ 4 GPa at room temperature. Significant changes in single crystal elastic constants have been observed at ~ 4.5 GPa (Ahart *et al* 2009) but there is uncertainty about the structure of the high pressure phase (Chaabane *et al* 2003, Ahart *et al* 2009). Accurate determinations of both the volume strain and transition pressures would allow this model of the effect of pressure to be tested through the use of the relationship (from Carpenter 2007)

$$P_c = \frac{a_\Gamma \Theta_{s\Gamma} \frac{1}{3} (C_{11}^o + 2C_{12}^o)}{2\lambda_{1\Gamma}} \left(\coth\left(\frac{\Theta_s}{T}\right) - \coth\left(\frac{\Theta_s}{T_{c\Gamma}^*}\right) \right), \quad (8)$$

where P_c is the $R3m \leftrightarrow Fm\bar{3}m$ transition pressure at temperature T .

Even though PMN is a relaxor ferroelectric, the evolution of its macroscopic strain follows a pattern which would be expected at a conventional ferroelectric phase transition associated with a soft optic mode and a critical temperature of between 350 and 400 K. Use of a Landau free energy expansion should then yield predictions of the form of the elastic constant variations which would represent the limiting case of elastic softening due to strain/order parameter coupling alone. The expansion for $Pm\bar{3}m \leftrightarrow R3m$ or $Fm\bar{3}m \leftrightarrow R3m$ (with constant q_R) transitions is the same as for $Pm\bar{3}m \leftrightarrow R\bar{3}c$ (R_4^+), so that expressions for the elastic softening will also be the same. These are given in full by Carpenter *et al* (2010) for the $Pm\bar{3}m \leftrightarrow R\bar{3}c$ octahedral tilting transition in $LaAlO_3$. If the elastic constant matrix for a cubic material is diagonalised, the eigenvalues, $K = \frac{1}{3}(C_{11} + 2C_{12})$, $\frac{1}{2}(C_{11} - C_{12})$ and C_{44} transform as irreducible representations Γ_1^+ , Γ_3^+ and Γ_5^+ respectively. The corresponding

eigenvectors are the symmetry-adapted strains e_a , e_o and e_t , and e_4 . For a second order transition, eq^2 coupling leads to a discontinuities in C_{44} , $\frac{1}{2}(C_{11} - C_{12})$ and the bulk modulus, K , at $T = T_c$. The rhombohedral phase is expected to be softer than the cubic phase by a fixed amount which depends on the square of the strain/order parameter coupling coefficients, i.e. $\lambda_{1\Gamma}^2$ for the bulk modulus, $\lambda_{2\Gamma}^2$ for $\frac{1}{2}(C_{11} - C_{12})$ and $\lambda_{3\Gamma}^2$ for C_{44} . If the transition is tricritical, the discontinuity is larger and the elastic constants of the low symmetry phase recover in a non-linear manner with falling temperature. These well known patterns are illustrated in Rehwald (1973) and Carpenter and Salje (1998), for example, and the $\beta \leftrightarrow \alpha$ transition in quartz shows the non-linear pattern of softening below the transition point characteristic of a transition which is close to being tricritical (Carpenter *et al* 1998). For LaAlO_3 it was found that RUS measurements on a rhombohedral crystal containing all possible twin orientations could be treated as being cubic, on average, and that the resulting values of C_{44} and $\frac{1}{2}(C_{11} - C_{12})$ which were obtained showed the expected softening due to the cubic \leftrightarrow rhombohedral transition. Thus, a twinned crystal of rhombohedral PMN might be expected to display softening of the form shown in Figure 3 for a tricritical transition. Coupling terms of the form eq^2 and e^2q^2 do not cause softening of elastic constants in the stability field of the high symmetry phase ahead of the transition point. However, softening of elastic constants which have symmetry properties related to the identity representation, in this case K only, can occur above T_c as a consequence of fluctuations due to interactions between phonon modes with k-vectors just away from the critical point of the Brillouin zone (Höchli 1972, Cummins 1979, Lüthi and Rehwald 1981, Yao *et al* 1981, Fossum 1985, Carpenter and Salje 1998, Carpenter 2007). This has been added to the expected form of “classical” softening for a ferroelectric transition in PMN shown in Figure 3. Finally, coupling of the form λe^2q^2 leads to renormalisation of the elastic constants according to $C = C^0 + 2\lambda q^2$ (e.g.

see Carpenter and Salje 1998). Differences in cation order between antiphase domains and antiphase boundaries should, in principle, result in the elastic properties of the domains being different from those of the the domain walls, therefore.

The small size of PNR's in the nonergodic phase of PMN does not appear to hinder the development of volume strain, e_a , since the volume strain of a rhombohedral sample at low temperatures (in a $5\text{kV}\cdot\text{cm}^{-1}$ field) is at most only $\sim 0.3\%$ greater than that of the cubic structure with no field (using e_1 values from Fig. 1b). Softening of the bulk modulus, which scales with $\lambda_{1\Gamma}^2$, would be expected to be comparable to that associated with a normal ferroelectric transition, therefore. Strain contrast associated with the PNR's in transmission electron microscope images (e.g. Viehland *et al* 1995) and the presence of twin walls within individual PNR's (Yoshida *et al* 1998) signify that a degree of local e_4 shear strain also develops, though this could be smaller in magnitude than would occur in larger ferroelectric domains (i.e. $< \sim 0.002$ at 80 K). If the influence of small domain sizes is to reduce the magnitude of the strain by reducing the effective value of the coupling coefficient $\lambda_{3\Gamma}$, the amount of softening of C_{44} would also be expected to be reduced since it scales with $\lambda_{3\Gamma}^2$. On the other hand, shear strains e_o and e_t are strictly zero in the rhombohedral structure so, to a first approximation, the coupling coefficient $\lambda_{2\Gamma}$ should not be renormalized. Softening of $\frac{1}{2}(C_{11} - C_{12})$ should be comparable with the softening which would occur for the true ferroelectric transition.

As set out in the following paper in this series (Carpenter *et al* 2011), the real elastic properties of PMN do not follow the pattern predicted in this way (solid lines in Fig. 3). Rather they show steeper variations with a minimum located between T_f and T_c (dashed line in Fig. 3). Here, the comparison with LaAlO_3 is again instructive. Additional softening of the elastic constants of LaAlO_3 within the stability field of the rhombohedral structure is due to

coupling of acoustic modes with a relaxational mode which gives rise to quasi-elastic scattering in Brillouin spectra (Carpenter *et al* 2010). As with PMN, the relaxation time for the central peak modes ($\sim 10^{-11}$ s) is sufficiently short as to allow strong coupling with acoustic modes. The relaxational processes associated with dynamic and quasistatic PNR's in PMN turn out to dominate the elastic behaviour in comparison with the effects of classical strain/order parameter coupling (Laiho *et al* 1992, Carpenter *et al* 2011).

5. Conclusions

Spontaneous strains determined from published lattice parameter data contain information on both static and dynamic aspects of the relaxor ferroelectric behaviour of PMN. Specifically:

1. The volume strain evolves as if there is a discrete phase transition which is tricritical in character with $T_c \approx 350$ K. This matches with the Curie temperature for the soft optic mode and the characteristic temperature for the development of the static part of PNR formation. The static component of the relaxor behaviour thus appears to conform to a simple mean field model.
2. Although the characteristic length scale of PNR's in PMN remains small, the volume strain provides a measure of the effective order parameter within them. This is matched by data for the shear strain in samples poled in an electric field. The discrete (\sim tricritical) phase transition thus appears to occur within the PNR's on a length scale of ~ 10 -50 Å.
3. Additional strain, beyond that expected from coupling with a static order parameter, occurs in the temperature interval of freezing indicated by dielectric measurements, and is interpreted in terms of dynamic contributions down to the freezing temperature, T_f .
4. There is no direct evidence for an anomaly in the evolution of the strain near T^* , unless this corresponds with the first appearance of a dynamic component of the volume strain. Data

from the literature generally do not extend to high enough temperatures to be able to discern exactly how this onset might actually be associated with the Burns temperature, T_b , however.

5. Predictions of the pattern of variations for elastic constants based on a conventional Landau description of the ($Fm\bar{3}m - R3m$) ferroelectric phase transition do not match up with observations, signifying that the elastic softening arises predominantly as a consequence of dynamic aspects of the relaxor behaviour. As is taken up in the companion paper (Carpenter *et al* 2011), relaxational mode(s) accompanying the PNR formation occur on a sufficiently short time scale to allow strong coupling with acoustic modes.

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Table 1. Space groups, non-zero order parameter components, and lattice vectors for (origin = (0,0,0)), for combined R-point ordering and gamma-point ferroelectric displacements, as obtained from ISOTROPY (Stokes *et al* 2007).

Space Group	Order parameter components		Relationships between order parameter components	Lattice vectors
	R_1^+	Γ_4^-		
$Pm\bar{3}m$	0	000		(0,0,0)(0,0,0)(0,0,0)
$P4mm$	0	q_100		(0,1,0)(0,0,1)(1,0,0)
$Amm2$	0	q_1q_20	$q_1 = q_2$	(0,0,1)(1,-1,0)(1,1,0)
$R3m$	0	$q_1q_2q_3$	$q_1 = q_2 = q_3$	(1,-1,0)(0,1,-1)(1,1,1)
Pm	0	q_1q_20	$q_1 \neq q_2$	(0,1,0)(0,0,1)(1,0,0)
Cm	0	$q_1q_2q_3$	$q_1 = q_2 \neq q_3$	(1,1,0)(-1,1,0)(0,0,1)
$P1$	0	$q_1q_2q_3$	$q_1 \neq q_2 \neq q_3$	(1,0,0)(0,1,0)(0,0,1)
$Fm\bar{3}m$	q_R	000		(2,0,0)(0,2,0)(0,0,2)
$I4mm$	q_R	q_100		(0,-1,1)(0,-1,-1)(2,0,0)
$Imm2$	q_R	q_1q_20	$q_1 = q_2$	(1,-1,0)(0,0,2)(-1,-1,0)
$R3m$	q_R	$q_1q_2q_3$	$q_1 = q_2 = q_3$	(-1,1,0)(0,-1,1)(2,2,2)
Cm	q_R	q_1q_20	$q_1 \neq q_2$	(-2,0,0)(0,0,2)(-1,1,0)
Cm	q_R	$q_1q_2q_3$	$q_1 = q_2 \neq q_3$	(-1,-1,-2)(-1,1,0)(1,1,0)
$P1$	q_R	$q_1q_2q_3$	$q_1 \neq q_2 \neq q_3$	(1,0,1)(1,1,0)(-1,1,0)

Figure captions

Figure 1. Strain analysis of transformation behaviour associated with T_c . (a) Lattice parameter data from the literature showing the well known change in thermal expansion in the vicinity of 400 K. Lines through the neutron diffraction data of Bonneau *et al* (1991) and X-ray diffraction data of Dkhil *et al* (2009) represent the variation of the reference parameter, a_0 , as given by fits of Equation 6 for temperatures above 600 K. (b) Solid lines through data for e_1^2 are fits of Equation 7 which show that the strain evolution below ~ 350 -400 K can be represented as a Landau tricritical evolution of the order parameter. Data for $\cos\alpha^2$ are from a sample initially cooled in an electric field to induce transformation to the rhombohedral ferroelectric structure.

Figure 2. Comparisons of strain evolution with intensity data from central peaks in neutron scattering spectra. (a) The square of the intensity of central peak data from Fig. 8a of Gehring *et al* (2009), and Fig. 15 of Gvasliya *et al* (2005) shows the same evolution with temperature as e_1^2 . (b) Data from Figure 4a of Stock *et al* (2010) for the static part of the intensity, I_{static} , also vary in a manner that is indistinguishable from the variation of e_1^2 , apart from in the temperature interval ~ 250 -450 K where there is a distinct tail in e_1 but almost none in I_{static} .

Figure 3. Schematic comparison of the form of elastic softening expected from coupling between strain and a classical static parameter (solid curves) with the form of observed variations (dotted curves), following Laiho *et al* (1992). The horizontal broken line represents the evolution of single crystal elastic constants for the high temperature structure in the absence of any relaxor or ferroelectric ordering, excluding the normal influences of thermal expansion. The solid curve above T_c represents the form of softening that would be expected

for the bulk modulus, K , ahead of the transition due to interactions between phonon modes with k -vectors just away from the critical point. The solid curve below T_c represents the form of softening/stiffening of bulk and shear moduli that would be expected for a normal ferroelectric transition with tricritical character. The observed softening (summarised in Carpenter *et al* 2011) is distinguished by steeper softening over a wide range of temperatures as $T \rightarrow T_c$ from above, in both shear and bulk moduli, a frequency-dependent minimum at $T_f < T < T_c$, followed by an approximately linear recovery of the shear modulus and saturation as $T \rightarrow 0$ K.