Direct evidence of soft mode behavior near the Burns’ temperature in PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\) (PMN) relaxor ferroelectric

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Inelastic neutron scattering measurements of the relaxor ferroelectric PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\) (PMN) in the temperature range 490 K<T<880 K directly observe the soft mode (SM) associated with the Curie-Weiss behavior of the dielectric constant \(\varepsilon(T)\). The results are treated within the framework of the coupled SM and transverse optic (TO1) mode and the temperature dependence of the SM frequency at \(q=0.075\) a\(^*\) is determined. The parameters of the SM are consistent with the earlier estimates and the frequency exhibits a minimum near the Burns temperature (\(\approx 650\)K)

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I. INTRODUCTION

One of the most interesting group of disordered compounds undergoing structural phase transitions is the so-called relaxor ferroelectrics (RF’s) which have ferroelectric-like properties with diffuse phase transitions. Relaxor ferroelectrics (RF) constitute a large group of disordered perovskite-like crystals. The main feature of RF’s is related to the completely or partially random occupation of the equivalent positions by different (usually nonisovalent) ions. This chemical disorder results in the destruction of the normal ferroelectric phase transition and the appearance of new physical properties similar to those of disordered magnets such as spin glasses. There are now hundreds of RF’s and most of them have the simple cubic perovskite structure.

The lead magnoniobate PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\) (PMN) is considered a model system for the cubic RF’s. It has been extensively studied and it was shown that PMN exhibits a glass-like phase transition to a non-ergodic phase at a freezing temperature \(T_\text{g} \approx 230\)K as determined from the appearance of history dependent effects and the divergence of the nonlinear susceptibility \(\chi(T)\). This transition is accompanied by the appearance of the broad frequency dependent peak in the temperature dependence of the dielectric constant, \(\varepsilon(T)\). No apparent symmetry changes were detected either by X-ray or neutron scattering experiments, and no long range ferroelectric order appears at low temperature. It was also demonstrated that besides \(T_\text{g}\) another singular temperature point exists, the so-called Burns temperature, \(T_d\), which in PMN is \(\approx 650\) K. Above \(T_d\) PMN and other relaxors behave like normal ferroelectrics, while below this temperature there are clear indications of the local lowering of the symmetry and formation of some polar nanoregions. In case of Pb(Zr\(_{1-x}\)Ti\(_x\))O\(_3\) (PZT) and related compounds, \(T_d\) can be attributed to a real structural phase transition where the crystal transforms from a cubic to a lower symmetry. However, in the case of PMN, the situation is less clear because there is no reduction in symmetry. It is important to emphasize, that above \(T_d\), \(\varepsilon(T)\) follows Curie-Weiss law with \(T_0=398\) K. In Ref. 9 an analysis of the ultrabroadband dielectric spectroscopy data is presented and demonstrated that the phonon contribution to the permittivity is dominant and determines the Curie-Weiss behavior above \(T_d\).

There exists limited information about the lattice dynamics of RF’s. Several Raman and infrared studies of the \(q=0\) modes of PMN and other relaxors were reported, but no adequate understanding of the lattice dynamics has been achieved. A detailed neutron inelastic scattering experiment on PMN was undertaken. For temperatures above \(T_d\approx 650\) K, there is a broad inelastic response whose intensity increases as the temperature decreases. This scattering was attributed to defect induced optic-like mode, called the quasi-optic (QO) mode, which couples strongly with the transverse acoustic (TA) mode. It was demonstrated that at \(T_d\approx 650\) K a crossover in the critical dynamics takes place, resulting in a cessation of the growth of the inelastic scattering intensity and the appearance of a narrow (resolution limited) central peak. From the analysis of the lineshapes of the phonon resonance related to the coupled TA-QO modes, the estimation of the parameters of the QO mode was made. The authors also predicted that the QO mode should be directly observable in the narrow \(q\)-region near the Brillouin zone (BZ) center. The results of the soft mode search in PMN were reported at room temperature where it was demonstrated that at a small \(q\) there is an increased damping of a transverse optic mode, TO1, which has the appearance of a “waterfall” in the dispersion curve. More recently a weak temperature dependence of the TO1 was observed which varied as \(\omega^2 \sim (T-T_0)\) with negative \(T_0 \approx 330\) K. This mode was earlier assigned as the hard TO branch, but its temperature dependence cannot explain the Curie-Weiss law above \(T_d\) so it is not related to the high-temperature dielectric properties of PMN. The aim of the present paper is to observe directly a soft mode behavior associated with...
the Curie-Weiss law in a PMN single crystal. We shall demonstrate that the QO mode deduced in the earlier experiment is indeed the soft mode (SM) associated with the high-temperature $\varepsilon(T)$ dependence.

II. EXPERIMENT

All the scattering experiments were performed with the same single crystal used in Ref. [16]. The crystal was grown by the Czochralski technique in the Physical Institute of the University of Rostov-on-Don. It was approximately triangular pyramid shape with a volume of $\approx 0.5 \text{ cm}^3$. The crystal was of good quality with a uniform mosaic spread of less than $40^\circ$. The lattice parameter at room temperature is $4.04 \text{Å}$. The sample was mounted in a vacuum furnace and the measurements performed at temperatures $490 \text{ K} < T < 880 \text{ K}$, i.e. above and below the Burns temperature $T_d$.

The inelastic neutron measurements were performed on the H4M three-axis spectrometer at Brookhaven’s High Flux Beam Reactor. The spectrometer was operated with a fixed final neutron wavevector $k_F = 2.662 \text{ Å}^{-1}$ ($E_F = 14.7 \text{ meV}$). Pyrolitic graphite crystals with a $25^\circ$ mosaic spread were used both as a monochromator and analyzer. The collimations were $40^\circ$-$40^\circ$-$60^\circ$-$60^\circ$, and the resulting energy resolution (Full-width-at-Half Maximum) was $\approx 1.0 \text{ meV}$. The instrument parameters were chosen to obtain a good compromise between scattered intensity, resolution and the possibility to perform the measurements in several Brillouin zones. The sample was mounted with [1 0 0] axis vertical. Scans were performed in the constant-$Q$ mode, i.e. the scattering vector $Q$ was kept constant while the energy was varied.

III. EXPERIMENTAL RESULTS

We have used the previously obtained estimates of the soft mode dispersion and damping to chose the position in reciprocal space for observing the soft mode. Most of the measurements were performed for $Q$ in the [010] direction near the (3,0,0) reciprocal lattice vector. This contrasts with the recently published results where measurements were mostly performed in the Brillouin zone centered at (2,0,0). In the (3,0,0) Brillouin zone, the intensity of the TA phonons is very low which would make observation of the soft mode easier. The TO1 mode with frequency at the zone center of about $7 \text{ meV}$ is also observable in this BZ. Measurements were performed for $q=0$, 0.05, 0.075 and 0.1 in $a^*$ units. Figures 1 and 2 show the inelastic scans near (3,0,0) for temperatures above (a) and below (b) $T_d$. For temperatures above $T_d=650\text{K}$, cooling results in a strong increase of the scattered intensity at the $q=0$ zone center for small energy transfers (Fig. 1a). The arrows in Fig. 1a, taken from Ref. [18], show the positions of the TO1 mode, which changes very little in frequency and intensity over the temperature range shown. The growth of intensity at energies less that TO1 indicate that another mode is present and its frequency is decreasing as the temperature decreases. The spectra measured in this Brillouin Zone are distinctly different than the observations of Ref. [18] measured in the (2,0,0) zone. A similar, but less pronounced effect is observed at $q=0.05 \text{ a}^*$ as shown in Fig. 2a. For larger $q=0.075 \text{ a}^*$ there is barely any temperature dependence in the low energy region (Fig. 3). On cooling below 650K the effect is reversed and the inelastic scattered intensity decreases as the temperature decreases as shown in Figs. 1b and 2b. These results are in good agreement with results reported previously [18], but that experiment had coarser resolution and low energy measurements were only possible for $q=0.05 \text{ a}^*$.

We emphasize that below $T_d$ not only is the intensity of the low energy part ($2< E < 7 \text{ meV}$) decreasing, but the intensity of the TO1 mode is also diminishing. This effect is especially pronounced at $q=0.05 \text{ a}^*$ (Fig. 2b). The observed temperature dependent behavior is not attributed to the softening of the TO1 mode for the following reasons: i) the experimental curves at $q=0.05 \text{ a}^*$ (Fig. 2a and 0.075 a* (Fig. 2b) cannot be fit with a single
resonance (TO1) or as a sum of a TA or TO resonance. ii) At q=0.075a* an additional excitation is visible at E=4.0 meV. iii) No increase of inelastic scattering intensity of the TO1 mode at q=0 or the central peak was reported in Ref. [18] for (2,0,0) Brillouin zone.

The above results clearly indicate the existence in PMN of a strong temperature dependent intensity associated with a soft excitation. The results at q=0 (Fig. 2) are difficult to analyze because of the contribution of the Bragg peak intensity at $\omega = 0$, which is several orders of magnitude stronger than the inelastic part. The data at q=0.05 and 0.075 a* were analyzed in two different ways. First we fit the data as a sum of 2 gaussians corresponding to the elastic background and the so-called Bragg tail (result of the long axis of the 4-D resolution function touching the q=0, w=0 Bragg point) and 2 independent lorentzians, corresponding to the TO1 and soft mode (the QO mode referred to in Ref. [16]). The fit was successful, but the frequency of the TO1 mode was lower than that determined in Refs. [16,18]. Figure 3 shows the q dependence of the energy of the modes determined in this way and Fig. 4 gives the temperature dependence of the energy of the SM. Such a discrepancy can be attributed to neglecting the coupling between the TO1 and SM. In the next stage we repeated the data analysis using the coupled mode analysis as done previously [16,20]. The scattered intensity can then be written as:

$$I(\omega) = [n(\omega) + 1] \sum_{ik} (2\omega_i)^{1/2} S_i (2\omega_k)^{1/2} S_k \text{Im} G_{ik}(\omega),$$

(1)

with structure factors $S_i$ and the retarded Green’s functions $G_{ik}$ determined by the Dyson equations:

$$G_{ik} = G_{0ik} - \sum_{l,m} G_{0il} \Pi_{lm} G_{mk},$$

(2)

The coupling was considered to be linear and classical harmonic oscillators were used as a zero order approximation. Such choice is well justified for the TO1 mode. In the case of the soft mode (SM) it is not clear if the damped harmonic oscillator represents a proper choice. However, we believe that for our set of experimental data, utilization of a more complicated expression (like Lifshitz tail of the density of states used in Ref. [21]) is not adequate here. Using the self energy in the form used in Ref. [16]:

$$\Pi = \left( \begin{array}{cc} -i \frac{\omega}{\omega_1} \gamma_1 & \Delta_{12} - i \frac{\omega}{\sqrt{\omega_1 \omega_2}} \gamma_{12} \\ \Delta_{12} - i \frac{\omega}{\sqrt{\omega_1 \omega_2}} \gamma_{12} & -i \frac{\omega}{\omega_2} \gamma_2 \end{array} \right).$$

(3)

where $\omega_1$ corresponds to the soft mode (SM) and $\omega_2$ to the TO1 mode are the bare mode frequencies. $\gamma_i$ (i=1,2) are the mode damping constants and $\Delta_{12}$ and $\gamma_{12}$ are the real and imaginary parts of the coupling constants.

This model has 8 parameters, 7 of these are independent and 1 is arbitrary. In the previous study [18] the best
agreement for the description of the coupling between the TA and SM modes has been achieved under the assumption of purely imaginary coupling, i.e. $\Delta_{12}=0$. Following Ref. 22 we treated the present data under the same conditions. The experimental spectra were fit by the sum of a quasielastic component with a gaussian line shape and resolution limited line width, plus a term described by Eq. 1 convoluted with the calculated energy resolution and a Bragg tail. The contribution of the TA phonon was neglected since it is nearly unobservable in this BZ.

The fit of the data at $q=0.05a^*$ was successful at 880 K, but at lower temperatures the softening resulted in overlapping of the SM component with the Bragg tail at $E\approx1.17$ meV so below 880K all parameters were held fixed except for the intensities of the components. For $q=0.075a^*$ the fits were successful at all temperatures with typical $\chi^2$ between 1.5 and 2. The results are shown in Figs. 4 and 5. In Fig. 4 the frequencies of the TO1 mode and the SM, together with the dispersion curve of the TO1 mode determined in Ref. 16. As can be clearly seen the present results are in good agreement with the data obtained from Ref. 16 determined from the analysis of the coupling with the TA phonons. In Fig. 5, the temperature dependence of the frequency of the SM at $q=0.075a^*$ is shown. Over the temperature range studied the frequency of the SM varies by $\approx20\%$ and shows a minimum at $\approx650$ K which coincides with the Burns temperature determined in this system in Ref. 23. The central peak intensity, also shown in Fig. 5, begins to grow at this same temperature.

### IV. DISCUSSION

The results presented above show that for $T>T_d$ a soft underdamped excitation exists for $q\neq0$. This excitation is clearly resolved for $q=0.075 a^*$ in the temperature region studied: 490K$<T<880$ K. The temperature variation is 20% over this region and it shows a minimum corresponding to the Burns temperature $T_d \approx650 K$. It is important to emphasize that this mode is distinct from the TO1 mode, which is at a higher energy. The main argument against the TO1 mode being the soft mode is the temperature dependence of the dielectric constant, $\varepsilon(T)$. As mentioned above at high temperatures $\varepsilon(T)$ follows Curie-Weiss law with $T_c=398 K$ based upon Lyddane-Sachs-Teller (LST) relationship one expects to see a soft $q=0$ mode with energy, $\omega_0^2$, mirroring the $\varepsilon(T)$ dependence, i.e, $\varepsilon(T) \sim 1/\omega_0^2$. We cannot determine the $\omega_0(q=0)$ temperature dependence quantitatively because the mode is highly damped, Fig. 1a. However, the integrated intensity for phonon scattering in the high temperature limit ($kT >> h\omega$) varies as $I(T) \sim T/\omega_0^2$. If we integrate the intensity for $q=0$ in Fig. 1a (for $\omega >2.0$ meV to eliminate the elastic part) and plot its reciprocal (Fig. 6) we find a linear region above $T_d$ that extrapolates to zero at $T_0 = 340 K$. This is in close agreement with the dielectric measurements which show a Curie-Weiss behavior with $T_0=398 K$. The TO1 mode alone, studied in Ref. 18, cannot account for the dielectric behavior because it is only weakly temperature dependent and the $T_0$ obtained from Ref. 18 is negative. Thus, the inelastic response...
measured about (3,0,0) is the soft mode and can account for the high temperature dielectric behavior via the LST relation.

The hardening of the soft mode below \( T_d \) is also coherent with the results of ultrabroadband dielectric spectroscopy. Below \( T_d \) the dielectric response is determined by the slow polar cluster dynamics and in neutron inelastic scattering data it is observed by the appearance of a central peak which dominates the low-frequency spectra at low temperatures.

The presence of an extra mode is also reasonable in light of the recent important work of Hirota et al. They introduced the concept of a “phase-shifted condensed mode” to explain the observation of strong elastic diffuse scattering below \( T_d \) in PMN around the (3,0,0) zone center and its absence near (2,0,0). Since the diffuse scattering is a result of the condensing of polar nanoregions, it is reasonable to observe precursor dynamical behavior associated with this condensation in analogy with soft mode displacements in normal ordered systems undergoing structural phase transitions. The extra mode reported here is the phase shifted soft mode that is responsible for the high temperature dielectric properties.

The fundamental question remains as to the origin of this extra mode. We speculate that it is due to the inherent disorder in this system due to the mixed occupation of B site by Mg and Nb, which is also the origin of the local polar nanoregions. At small \( q \), in addition to the normal vibrational modes associated with the average lattice, new modes can appear due to the mixed crystal nature, resulting in a situation similar to the two-mode behavior observed in solid solutions. Such a two mode interpretation of the optic measurements was proposed nearly 20 years ago by Burns and Dacol. Moreover, extra modes were recently observed in a mixed crystal of a new superconductor \( \text{Y}_{0.5}\text{Lu}_{0.5}\text{Ni}_2\text{B}_2\text{C} \). Clearly a more complete lattice dynamical study of PMN is necessary.

We should note that \( \text{Nb}^{5+} \) is a ferroelectric active ion while \( \text{Mg}^{2+} \) is not. Thus one can imagine a soft polar mode in which only \( \text{Nb}^{5+} \) ions participate. Such a collective mode cannot exist at large \( q \). A first approximation of \( q_{\text{max}} \), above which such a Nb mode disappears (becomes localized), can be the inverse correlation length of chemical order in PMN of about 0.06\( a^* \), i.e. of the same order of magnitude as estimated from the observability of the soft mode. Such an assumption is in agreement with the results of the present work, where this mode is observed at \( q=0.075a^* \), but not at \( q=0.1a^* \).

The presence of a minimum of the frequency and the appearance of a narrow central peak at \( T_d \) indicates either a special phase transition or a change of dynamics from soft-mode to cluster regime since it is clear that below \( T_d \) clusters of the polar phase arise. Different models for the origin of this phenomenon have already been discussed. Probably the main unsolved question is topological: are there infinite clusters below the Burns temperature? In the framework of the present study we can make no conclusion on this topic.

**Summary**

The main results of the present study are:

For the first time in a relaxor ferroelectric we have directly observed a soft ferroelectric mode associated with the high temperature Curie-Weiss law. This mode is clearly distinct from the TO1 mode.

The temperature dependence of the soft mode frequency measured at finite \( q \) passes through a minimum at the Burns temperature, \( T_d \), at the same time a narrow central peak develops in the spectra.

Our results confirm the earlier speculation that at \( T_d \) a real or local phase transition occurs, resulting in a crossover of the critical dynamics. Above \( T_d \) the dynamics is of displacive type, while below it is governed by a relaxation of the large polar clusters.

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1. G. A. Smolensky et al., Ferroelectrics and Related Materials (Gordon and Breach, New York, 1981).
2. L. E. Cross, Ferroelectrics 76, 241 (1987).
3. S. B. Vakhrushev, A. Nabereznov, N. Okuneva, and B. Toperverg, Ferroelectrics 90, 173 (1989).
4. E. V. Colla, E.Yu Koroleva, N. M. Okuneva, and S. B. Vakhrushev, J. Phys.: Condens. Matter 4, 3671 (1992).
5. M. de Mathan, E. Husson, G. Calvarin, J. R. Gavarri, A. Hewat, and A. Morell, J. Phys.: Condens. Matter 3, 8159 (1991).
6. S. B. Vakhrushev, B. E. Kvyatkovskii, R. S. Malysheva, A. A. Naberezhnov, N. M. Okuneva, and P. P. Syrnikov, Izv. Akad. Nauk SSSR (ser. Phys.) 51, 214 (1987) (in Russian).
7. G. Burns and B. A. Scott, Solid State Commun. 13, 423 (1973).
8. D. Viechland, S. J. Lang, L. E. Cross, and M. Wuttig, Phys. Rev. B 46, 8003 (1992).
9. V. Bovtun, J. Petzelt, V. Porokhonskyy, S. Kamba, and Yu. Yakimenko, J. Eur. Cer. Soc. 21, 1307 (2001).
10. I. G. Siny, T. A. Smirnova, Ferroelectrics 90, 151 (1990).
11. E. Husson, I. Abello, and A. Morell, Mat. Res. Bull. 25, 539 (1990).
12. I. G. Siny and T. A. Smirnova, Ferroelectrics 90, 191 (1989).
13. I. G. Siny, S. G. Lushnikov, and R. S. Katiyar, Phys. Rev. B56, 7962 (1997).
14. I. G. Siny and R. S. Katiyar, Ferroelectrics 206-207, 307 (1998).
15. I. G. Siny and R. S. Katiyar, Ferroelectrics 223, 35 (1999).
16. A. Naberezhnov, S. Vakhrushev, B. Dorner, D. Strauch, and H. Moudden, Eur. Phys. J. B11, 13 (1999).
17. P. M. Gehring, S. B. Vakhrushev, and G. Shirane, in Fundamental Physics of Ferroelectrics 2000, edited by R. E. Cohen (American Institute of Physics, Melville, NY, 2000), Vol. 535, p. 314.