Eur. Phys. J. B **11**, 13–20 (1999)

THE EUROPEAN PHYSICAL JOURNAL B

EDP Sciences

Inelastic neutron scattering study of the relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$ at high temperatures

A. Naberezhnov[1,a], S. Vakhrushev[1,a], B. Dorner[2], D. Strauch[3,b], and H. Moudden[4]

[1] Ioffe Phys.-Tech. Institute, 26 Politekhnicheskaya, 194021 St.-Petersburg, Russia
[2] Institut Laue-Langevin, B.P. 156, 38042 Grenoble Cedex 9, France
[3] Institut für Theoretische Physik, Universität Regensburg, 93040 Regensburg, Germany
[4] Laboratoire Léon Brillouin (CEA-CNRS), CEA Saclay, 91191 Gif-sur-Yvette Cedex, France

Received 8 February 1999

Abstract. Results of inelastic neutron scattering experiments between 300 K and 900 K on the relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$ are presented. Within a mode-coupling analysis the data are consistent with the observation of a strongly damped quasi-optic excitation. It is demonstrated that below $T_d \approx 650$ K a dynamical crossover takes place manifesting itself by a narrow central peak. This crossover is accompanied by the appearance of strong damping of the transverse acoustic phonons, with the damping constant proportional to q^4. Different physical models of the crossover are discussed.

PACS. 78.70.Nx Neutron inelastic scattering – 77.80.-e Ferroelectricity and antiferroelectricity

1 Introduction

Relaxor ferroelectrics (RF) or ferroelectrics with a diffuse phase transition were first discovered about forty years ago and since that time are under theoretical and experimental study. The main feature of RFs is the random occupation of equivalent positions by different, usually nonisovalent ions. So the RFs are not solid solutions but rather stoichiometric compounds. This chemical disorder suppresses the normal ferroelectric transition. Instead, there appears a broad, strongly frequency-dependent peak in the temperature dependence of the dielectric permittivity $\varepsilon(T)$, and no apparent symmetry change is observed either by X-ray or neutron scattering experiments.

Now hundreds of RFs are known, and lead magnoniobate ($PbMg_{1/3}Nb_{2/3}O_3$, PMN) can be considered as a prototype RF crystal. PMN was extensively studied by a number of different experimental techniques, including dielectric [1–4] and ultrasonic [5] measurements, IR and Raman spectroscopy [6–8], X-ray [9,10] and neutron [11–16] diffraction, high-resolution electron microscopy [17,18], small-angle light scattering [19], etc. It was found that PMN exhibits a diffuse phase transition below room temperature [1]. Later it was shown, that this diffuse phase transition can be considered as a transition to a glass-like state [5,16], and the freezing temperature $T_g = 230$ K was determined from the analysis of the neutron scattering intensity as a function of temperature in field cooled and zero-field cooled regimes [16] and from the results of the nonlinear dielectric [3] and ultrasonic [5] measurements. However, the microscopic origin of this glassy phase transition is far from being understood.

Particularly peculiar are the properties of the high-temperature phase ($T > T_g$). It was found that below 650 K the temperature dependence of the dielectric permittivity $\varepsilon(T)$ does not follow the Curie-Weiss law [1], the distinction being especially pronounced at high frequencies. An empirical expression $\varepsilon = C/(T - T_c)^2$ was proposed [4], but no convincing physical interpretation of this expression was given. Some other deviations from the behavior typical for the paraelectric phase of the "normal" perovskite-like ferroelectrics were reported. Burns and Dacol [6] observed an anomalous behavior of the refractive index n. Below $T \approx 650$ K deviations from the linear proportionality between n and T are observed. In the same temperature region the onset of the softening of the TA and LA phonons was observed in Brillouin scattering experiments [8]. All these anomalies were attributed to the appearance of regions with local polarization below 650 K. This conclusion was supported by the results of X-ray powder diffraction measurements [9]. However, so far there are no data demonstrating whether these polar regions are of static or dynamic origin. To answer the question about the nature of such clusters a detailed study of the PMN lattice dynamics and its variation with temperature is needed. The existing data on the dynamics of PMN and other relaxors are very limited. No inelastic neutron scattering experiment was ever reported for any of these compounds. However, several results of IR and Raman spectroscopy of PMN [7,8] and lead scandotantalate

[a] e-mail: s.vakhrushev@shuvpop.ioffe.rssi.ru
[b] e-mail: dieter.strauch@physik.uni-regensburg.de

$PbSc_{1/2}Ta_{1/2}O_3$ [20] were reported. The IR peaks were shown to be extremely broad due to the compositional disorder. Strong Raman scattering was observed and interpreted as of first order, which is forbidden in the ideal Pm3m perovskite structure. It was shown that this scattering disappears upon heating up to 1000 K. Bismayer *et al.* [20] and Husson *et al.* [7] explained the appearance of this scattering by translational-symmetry breaking. Siny and Smirnova [8] invoked the phase transition from the Pm3m praphase to the Fm3m phase on cooling accompanied by the deformation of the oxygen octahedra, but it seems to us that such an explanation is in contradiction with all structural data. No soft mode was found, but Prohorova and Lushnikov [21] reported for PMN the observation of a rather broad central component and shapeless wings extending for several hundreds of cm^{-1}. The temperature dependence of the central-peak intensity displays a maximum somewhere near T_g [22]. The Brillouin scattering [21] and ultrasonic [5] investigations of the acoustic phonons have revealed softening and broadening of both TA and LA phonons starting at about 650 K and showing minima in the sound velocity and maxima in the damping constant around T_g. Recently [23] a soft optic mode in PMN has been suggested based on the X-ray scattering results, but these data were limited to the low temperature region only. In order to obtain more detailed information about the lattice dynamics of PMN (*i.e.*, about phonon dispersion curves and their temperature evolution and phonon damping) inelastic neutron scattering experiments were carried out.

2 Experimental

All scattering experiments were performed with the same single crystal of roughly triangular pyramid shape of about 0.5 cm^3 in volume. The crystal was grown by the Chochralsky technique in the Physical Institute of the University of Rostov-on Don. The quality of the crystal was checked by the rocking curves measuring on a γ-diffractometer [24], and the mosaic spread was found to be less than 40". The neutron diffraction experiments performed with the DN-2 diffractometer in Dubna have confirmed the persistence of the simple cubic structure at all temperatures down to 50 K with a lattice parameter $a = 4.04$ Å at room temperature.

The inelastic scattering measurements were performed for temperatures 300 K $< T <$ 1100 K. The sample was heated in vacuum, and at high temperatures (above 800 K) it resulted in some oxygen (and probably lead) losses and consequently in a change of the crystal appearance from transparent light yellow (nearly uncolored) to opaque gray. No significant changes of the structure and the electrophysical properties of such a "reduced" crystal were detected.

Three cycles of measurements were carried out with different spectrometers. The first set of data was obtained with the IN20 three-axis spectrometer at the Institute Laue-Langevin. The spectrometer was operated without polarization and with a fixed final neutron wavevector $k_F = 2.662$ $Å^{-1}$. Pyrolitic graphite crystals with 35' mosaic spread were used both as monochromator and as analyzer. The collimations were 35'-40'-60'-60', and the resulting linewidth for the quasielastic line was about 0.25 THz FWHM. This experiment was mainly devoted to the soft mode search. The instrument parameters were chosen to get a good compromise between luminosity, reasonable resolution and the possibility to perform the measurements in several Brillouin zones (BZ). The sample was mounted with the $[1\bar{1}0]$ axis vertical. Most of the measurements were performed for $\boldsymbol{q}$ in the Δ direction, but some additional data were collected at room temperature for $\boldsymbol{q}$ in the Σ and Λ directions.

The measurements were continued with the "Neutron-3" three-axis spectrometer installed on the WWR-M reactor in Gatchina. The aim was to study the lineshape of the acoustic phonons with improved resolution. The spectrometer was operating with fixed incident wavevector $k_I = 2.575$ $Å^{-1}$, a 40' pyrolitic graphite monochromator, and a 20' Cu(111) analyzer. A graphite filter was placed after the monochromator. Collimation was 60'-40'-30'-180'. Both monochromator and analyzer were flat, and together with the large distance from the reactor core to the sample (about 6.5 m) it results in a relatively good vertical resolution reducing the possible lineshape distortions. The crystal was mounted with the [001] axis vertical.

The third series of measurements was performed on the 4F1 spectrometer at the ORPHEE reactor of the Laboratoire Léon Brillouin. The spectrometer was operating with fixed $k_F = 1.97$ $Å^{-1}$, graphite monochromator and analyzer, and 270'-30'-20'-20' collimation. A graphite filter was placed in front of the analyzer. During the measurements we concentrated mostly on the study of acoustic-phonon lineshapes in the region of small q. The wavevector resolution was high enough to enable the TA phonon measurements down to $q = 0.03$ a^* without contamination by the Bragg tails. The sample was mounted with the [001] axis vertical, and measurements were performed for $\boldsymbol{q}$ along the [010] direction around the (200) and (110) reciprocal lattice points $\boldsymbol{\tau}$. The unusual $\boldsymbol{q}$ and $\boldsymbol{\tau}$ arrangement in the latter case (neither parallel nor perpendicular) resulted from the compromise between the necessity to perform the measurements in $(2h\ 2k\ 2l)$ (high Bragg intensity) and $(2h+1\ 2k+1\ 2l)$ (low Bragg intensity) zones under the same experimental condition and to have high q and ω resolution, *i.e.*, k_F as small as possible.

3 Results

3.1 Soft mode and central peak

Attempts have been made to find a soft ferroelectric mode in PMN, which is usually rather easily observable in perovskite ferroelectrics, at least at temperatures much higher than T_c and not too close to the Γ point in the BZ. We have performed preliminary measurements of the intensity of critical scattering by ferroelectric fluctuations at room temperature. The measurements were done with q from 17 different BZs, which allowed us to construct the

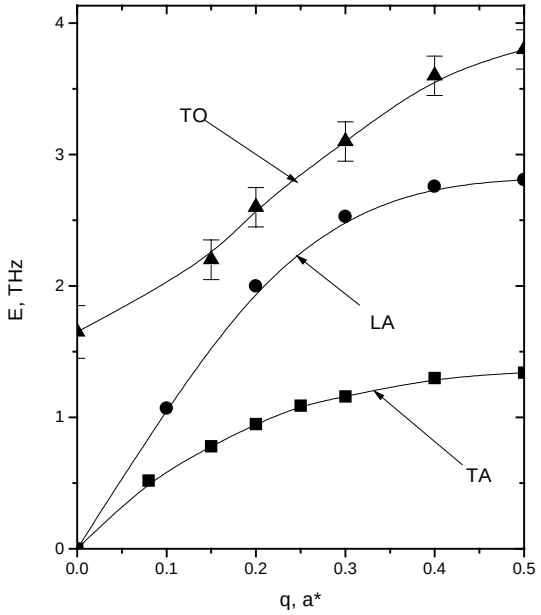

Fig. 1. Dispersion curves of the $\Delta_{\rm TA}$, $\Delta_{\rm LA}$ and $\Delta_{\rm TO1}$ modes in PMN at 800 K. The lines are guides to the eye.

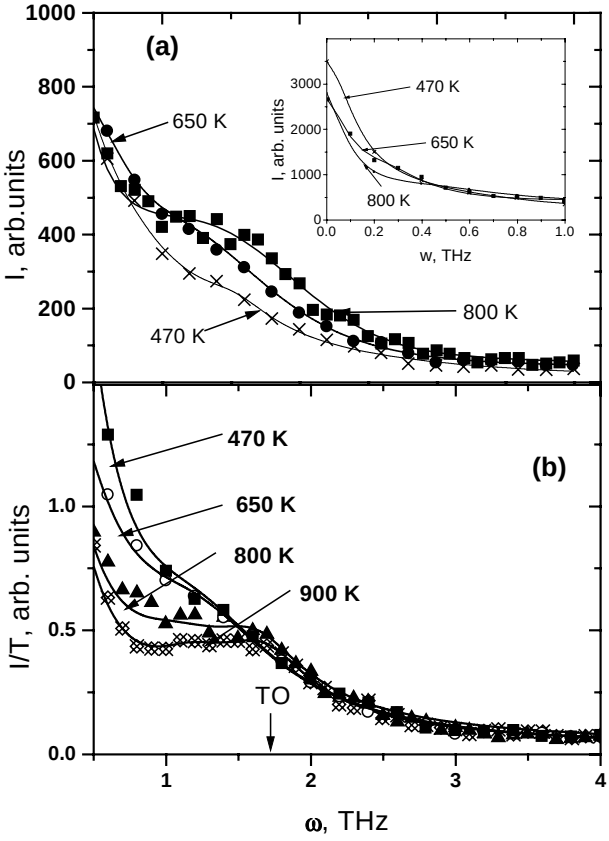

Fig. 2. (a) Neutron inelastic scattering curves at $\boldsymbol{Q} = (2, 2, 0.95)$ for several temperatures; in the insert the quasielastic part is presented. (b) same as (a), but normalized in temperature.

polarization vectors of the ferroelectric mode [25]. These results enabled us to choose the scattering vector for which we expected to have the largest inelastic structure factor of the soft mode. In the case of the IN20 experiments, the optimal point was (221). Moreover we have found an additional advantage of this point for the search of the soft mode because there are the smallest possible inelastic structure factors for the acoustic phonons. Calculations of the inelastic structure factor demonstrate that the intensity of the scattering by acoustic phonons should be approximately 13 times weaker for the (221) point than for the (220) point.

We have performed energy scans at several temperatures from 900 K down to 300 K and at several wavevectors from $q = 0.05\,a^*$ to $q = 0.5\,a^*$ (BZ boundary). No underdamped soft TO mode was observed in the vicinity of the (221) point even at 900 K and at a large q. At the same time we have observed well-shaped signals from the TA and the low-lying TO1 modes in the vicinity of the (220) point. Some dispersion curves at 800 K are presented in Figure 1. The observed TO1 mode cannot be identified with the ferroelectric mode because it shows a $\boldsymbol{Q}$-dependence of its structure-factor absolutely inconsistent with that expected for the ferroelectric fluctuations (nearly no critical scattering was observed around the (220) point close to the transition temperature $T_{\rm g}$). In the (221) zone, in addition to the hard TO1 mode, we have observed broad and shapeless inelastic scattering, see Figure 2. Qualitatively [26], at high temperatures ($T > 650$ K) the intensity of the observed inelastic band was slightly increasing on cooling, contrary to the expected reduction of the intensity due to the reduction of the Bose factor, expected for the hard modes. To make this result even more evident, we show the data, scaled to the same temperature (900 K), in Figure 2b. Below 650 K, the intensity starts to decrease with the simultaneous appearance of a strongly temperature- and q-dependent central peak (CP) with resolution-limited energy width. In Figure 3 the temperature dependence of the CP intensity at $q = 0.05$ and $\omega = 0$ is shown. The temperature independent scattering above 650 K is taken as background, related to the elastic incoherent scattering by the sample and to the unavoidable scattering by the sample environment. The appearance of the CP is usually attributed to the appearance of precursor ferroelectric clusters [27].

3.2 TA phonons

In the course of our IN20 experiment we have also studied the behavior of the noncritical phonons. In particular, the transverse acoustic phonons along the [001] direction ($\Delta_{\rm TA}$) were investigated. The measurements were performed in the (220) and (110) BZs for $0.1\,a^* < q < 0.5\,a^*$. At high temperatures well-shaped neutron resonances related to the scattering by the undamped (within the experimental resolution) TA phonons are observed. However, even at high enough temperature (900 K) some additional "shoulders" are seen with the position and the intensity strongly dependent on the reciprocal-lattice

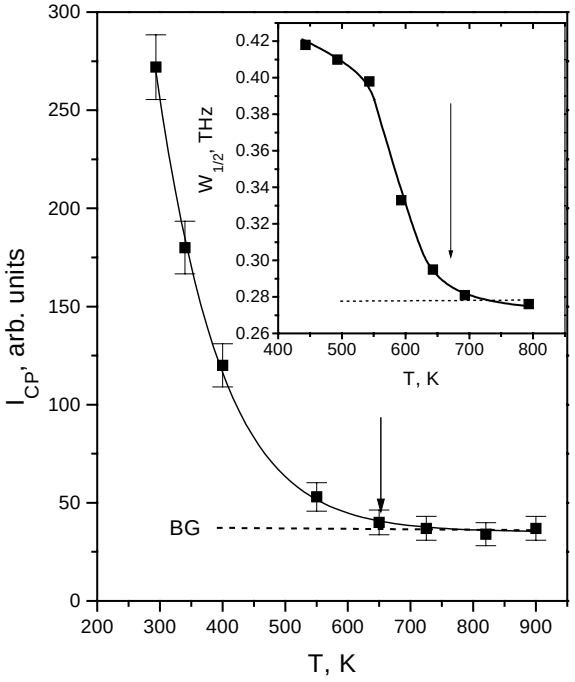

Fig. 3. Temperature dependence of the quasielastic scattering intensity at $\boldsymbol{Q} = (2, 2, 0.95)$ and of the width (FWHM) of the TA phonon at $\boldsymbol{Q} = (2, 2, 0.2)$. The temperature independent value of the background and the resolution limited width of the TA phonon are shown by dashed lines.

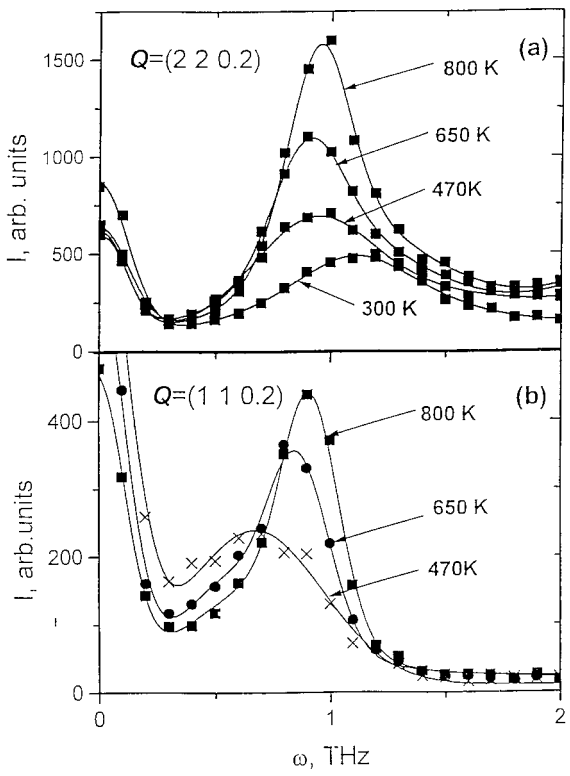

Fig. 4. Experimental neutron groups corresponding to the same $\Delta_{\rm TA}$ phonon with $q = 0.2\ a^*$ in the (220) (a) and (110) (b) BZs at several temperatures.

vector $\boldsymbol{\tau}$. At $\boldsymbol{\tau} = (220)$ the shoulders are observed on the high-frequency side of the TA peaks and at $\boldsymbol{\tau} = (110)$ on the low-frequency side, see Figure 4. These shoulders (or additional peaks) become considerably more pronounced with cooling. At temperatures below 650 K the main TA peaks start to broaden, and at 300 K the main peak and the shoulder merge completely, and just single broad peaks can be seen positioned in the (220) BZ at frequencies slightly higher and in the (110) BZ slightly lower than the high-temperature values. The temperature dependence of the width of the TA phonon resonance for $\boldsymbol{Q} = (2\ 2\ 0.2)$ obtained by the decomposition of the experimental signal into two gaussians without any resolution correction is presented in Figure 3. (The behavior of the resolution corrected intrinsic width will be discussed below.) It is of interest to compare the temperature dependence of the broadening with the appearance of the CP. Both effects starts to become visible below 650 K. We are convinced that the CP is an indication for the formation of precursor ferroelectric clusters and that in turn the short-wavelength acoustic phonons are scattered by these clusters and their signals become broadened.

In order to obtain a better insight into the wavevector and temperature dependence of the rather peculiar behavior of the TA phonons we extended the measurements into the small-q region with higher resolution. Therefore we continued our measurements with much higher resolution on the "Neutron-3" and 4F1 spectrometers. The "Neutron-3" spectrometer was used for the measurements of the $\Delta_{\rm TA}$ phonons with $0.05\,a^* \leq q \leq 0.12\,a^*$ in the (200) BZ and the 4F1 spectrometer for the $\Delta_{\rm TA}$ phonons with $0.02\,a^* \leq q \leq 0.12\,a^*$ in both (200) and (110) BZs. (For $q = 0.02\,a^*$ the inelastic part of the spectrum overlapped with the Bragg tail, and therefore these data were not included in the subsequent quantitative analysis.) Again, it was found that at high temperatures narrow TA resonances are observed with shoulders on the high-frequency side for the (200) BZ and on the low-frequency side for the (110) BZ, similar to what is shown in Figure 4. The experimental curves from both the 4F1 and "Neutron-3" spectrometers looked exactly the same. To make sure that the observed lineshapes do not result from some unusually strong anisotropy of the TA phonon dispersion we have investigated the acoustic phonons with $\boldsymbol{q}$ slightly away from [010] direction. In Figure 5 the phonon frequency as a function of the angle between $\boldsymbol{q}$ and the [010] direction is shown. The anisotropy is very weak and so cannot be responsible for the observed effects.

As a first stage of the data analysis the experimental data were fitted by the sum of two damped harmonic oscillators, convoluted with the experimental resolution function. The fit was very good (the χ^2 criterium was close to 1), but the results were not very physical, because in addition to the normal TA branch two additional branches appeared, one above the TA branch and another below it, resulting from the description of the low- and high-frequency shoulders as independent peaks. Therefore

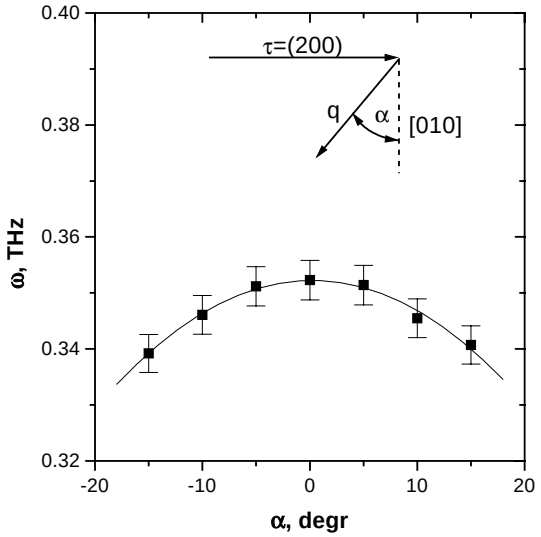

Fig. 5. Experimental dependence of the TA mode frequency on the angle between reduced wavevector $\boldsymbol{q}$ and the [010] direction in the (200) BZ ($\mid \mathbf{q} \mid = 0.05\, a^*$).

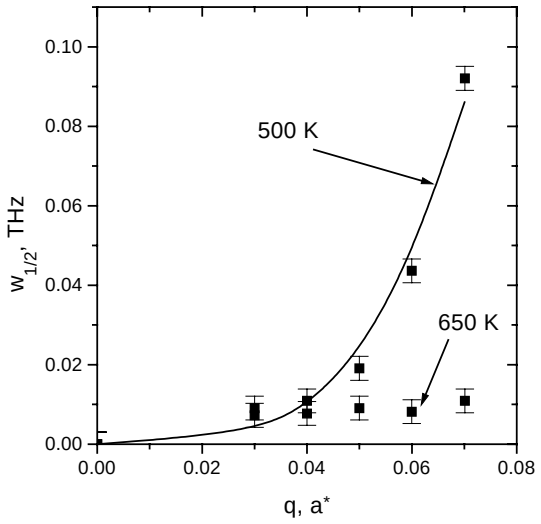

Fig. 6. q-dependence of the TA phonon damping constant $\gamma_{\rm TA} = w_{1/2}$ at 650 K and 500 K.

we did not pursue this approach any further. As far as the TA phonons are concerned one can see from Figure 6 that at high temperatures the above mentioned, practically undamped TA phonons exist (the damping constant $\gamma_{\rm TA}$ is much smaller than the energy resolution and therefore can be neglected). The slope of the linear part of the dispersion curve is in perfect agreement with the sound velocity obtained from ultrasonic measurements [29]. Below 650 K the damping starts to increase and to be strongly q-dependent. At 500 K the $\gamma_{\rm TA}$ dependence follows a power law $\gamma_{\rm TA} \propto q^{\alpha}$ with $\alpha \approx 4$. Below 500 K (at 400 K and 300 K) we were not able to fit the experimental data with two peaks because, in spite of the small q values, the TA peak and shoulders were completely merged. Even at 500 K this procedure worked well only up to $q = 0.08\ a^*$ because at larger values of q the TA peak and the shoulder had nearly the same height and were so broad that the fit remained ambiguous. After the resolution deconvolution the data obtained with both the 4F1 and "Neutron-3" spectrometers at the same temperatures and wavevectors coincided exactly.

3.3 Mode coupling analysis

A behavior of lineshapes of acoustic phonons similar to that described above has been observed in perovskites by many authors and has been attributed to the so-called mode-coupling effects. These effects were discussed long ago [30] and have been first considered for the case of neutron inelastic scattering in perovskites by Harada *et al.* [31]. It has been demonstrated that in $BaTiO_3$ the shape of the TA phonons is strongly dependent on the BZ where the measurements are performed. It has been shown that this dependence results from the coupling between the strongly damped soft optic and the acoustic mode. Experimentally observed spectra are mostly analyzed in terms of linearly coupled classical oscillators. The formalism for this case has been well presented in the paper by Wehner and Steigmeier [33]. The scattering intensity of the two coupled modes can be written as

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

where $n(\omega)$ denotes the Bose-Einstein function, S_i, and S_k are the inelastic structure factors, ω_i, and ω_k are the harmonic mode frequencies, and G_{ik} is the retarded Green's function which is obtained by solving the Dyson equation

$$G_{ik} = G^0_{ik} - \sum_{l,m} G^0_{il} \Pi_{lm} G_{mk}\,, \tag{2}$$

where Π_{lm} is self-energy matrix.

In the case of two classical oscillators with linear coupling the problem is reduced to the so-called eight-parameter model with

$$\Pi = \begin{pmatrix} -{\rm i}\dfrac{\omega}{\omega_1}\gamma_1 & \Delta_{12} - {\rm i}\dfrac{\omega}{\sqrt{\omega_1\omega_2}}\gamma_{12} \\ \Delta_{12} - {\rm i}\dfrac{\omega}{\sqrt{\omega_1\omega_2}}\gamma_{12} & -{\rm i}\dfrac{\omega}{\omega_2}\gamma_2 \end{pmatrix}. \tag{3}$$

γ_i is the mode damping, Δ_{12} and γ_{12} are real and imaginary parts of the coupling constant. Currat *et al.* [32] have proposed an explicit formula for such a model, very convenient in practice,

$$I(\omega) = [n(\omega)+1] \left(\frac{CY - BZ}{B^2 + C^2} \right), \tag{4}$$

where

$$\begin{aligned} B &= (\omega_1^2 - \omega^2)(\omega_2^2 - \omega^2) + \omega^2(\gamma_{12}^2 - \gamma_1\gamma_2) - \omega_1\omega_2\Delta_{12}^2, \\ C &= \omega[\gamma_1(\omega_2^2 - \omega^2) + \gamma_2(\omega_2^2 - \omega^2) - 2(\omega_1\omega_2)^{1/2}\Delta_{12}\gamma_{12}], \\ Y &= S_1^2(\omega_2^2 - \omega^2) + S_2^2(\omega_1^2 - \omega^2) - 2S_1S_2(\omega_1\omega_2)^{1/2}\Delta_{12} \\ Z &= \omega(S_1^2\gamma_2 + S_2^2\gamma_1 - 2S_1S_2\gamma_{12}). \end{aligned}$$

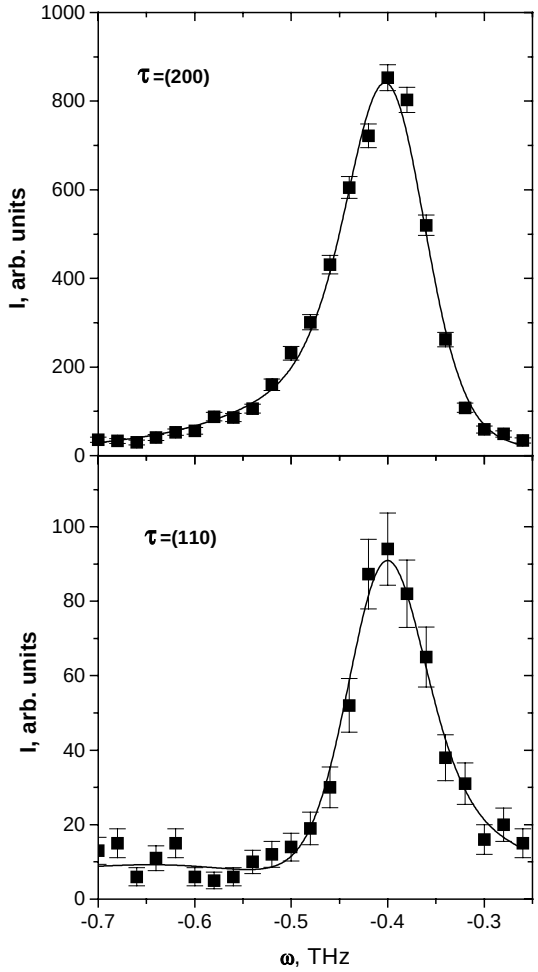

Fig. 7. Results of the coupled-oscillator analysis of the inelastic response at $T = 650$ K for $q = 0.06\ a^*$ in the (200) and (110) BZs.

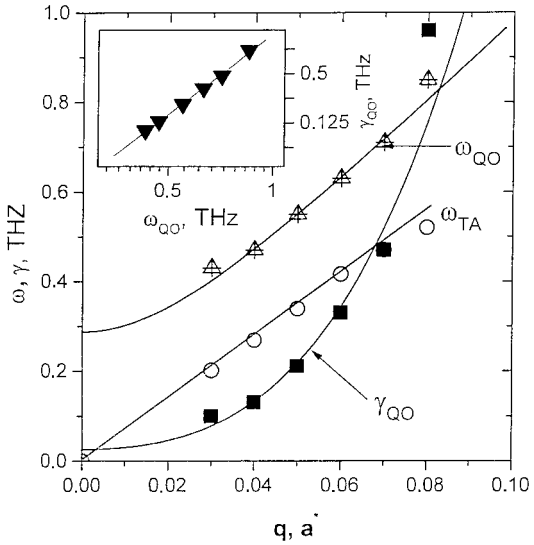

Fig. 8. q-dependence of the TA-mode frequency $\omega_1 \equiv \omega_{\rm TA}$ (open circles), of the frequency $\omega_2 \equiv \omega_{\rm QO}$ (triangles), and of the damping constant $\gamma_2 \equiv \gamma_{\rm QO}$ of the additional quasioptic (QO) mode (see text), derived from the coupled-oscillator analysis. The straight line connecting the data for $\omega_{\rm TA}$ is obtained from the sound velocity. For the QO data, see text. The insert shows a double logarithmic plot of $\gamma_{\rm QO}$ as a function of $\omega_{\rm QO}$.

In this model there is one more parameter than can be determined uniquely from the spectrum [33,32]. In the early paper [31] the coupling was considered to be real ($\gamma_{12} = 0$), whereas Currat *et al.* have demonstrated that in $KNbO_3$ the coupling is predominantly imaginary. Some other choices are also possible.

We used equation (4) with imaginary coupling ($\Delta_{12} = 0$) convoluted with the experimental resolution. Phonon resonances for the (200) and (110) BZs were fitted by the least-squares method simultaneously with the same set of parameters, except for S_1 and S_2 which depend upon the reciprocal-lattice vector $\boldsymbol{\tau}$. As an example, the results of the coupled-oscillator fit for $T = 650$ K and for $q = 0.06\,a^*$ in both zones are shown in Figure 7. One can see a good agreement between the experimental and fitted data. All parameters (except γ_{12}) were found to be practically temperature independent. The q-dependence of ω_1, ω_2, and γ_2 is shown in Figure 8. Within the model of coupled anharmonic oscillators we did not observe any significant intrinsic damping of the TA phonons in the range of small q's for temperatures either above or below 650 K. Above 650 K, γ_{12} is temperature independent and exhibits just a weak q-dependence, see Figure 9. Below 650 K, γ_{12} significantly increases, and a strong q-dispersion is observed.

4 Discussion

The results of the mode-coupling analysis indicate the existence of a low-frequency excitation with optic-like dispersion ${\omega_2}^2 = \omega_0^2 + Dq^2$ with $\omega_0 = 0.287$ THz, and $Da^{*2} = 88.5$ THz^2. This expression can be rewritten in the form ${\omega_2}^2 = \omega_0^2(1 + r_{\rm c}^2 q^2)$, where $r_{\rm c}$ is the correlation length of the excitation at $q = 0$ [34]. This analysis leads to an unexpectedly large correlation length of about 21 Å. Our mode-coupling calculations do not allow any conclusion about the physical origin of this excitation (real optic mode, disorder-induced local mode, etc.), and for the following discussion we shall call it quasioptic (QO) mode. This QO mode can explain the nature of the broad inelastic wing in the vicinity of the (221) reciprocal lattice point. We have failed to find any temperature dependence of the frequency of the QO mode from our fit of the data. But, as was already mentioned, the observed temperature dependence of the inelastic wing at $\boldsymbol{Q}$ =(2 2 0.95) ($q = 0.05$) leads us to the conclusion that the mode softens upon cooling for temperatures above 650 K. The QO mode is strongly damped at all q. Its damping constant γ_2 obeys a power law $\gamma_2 = b\omega_2^{\beta}$ (see insert in Fig. 8), with $b \approx 0.616$ and $\beta \approx 3.3$. The mode is underdamped ($\gamma_2^2 < 2\omega_2^2$) close to the Γ point and becomes overdamped at $q > 0.09\,a^*$. In order to observe the QO mode directly special

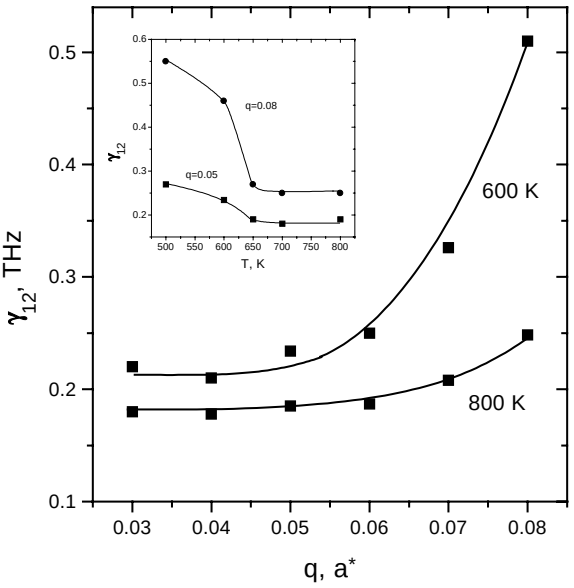

Fig. 9. Dispersion of γ_{12} at several temperatures, derived from the coupled-oscillator analysis. The insert shows γ_{12} as a function of temperature for $q = 0.05\ a^*$ and $q = 0.08\ a^*$.

experiments should be performed with even higher resolution both in q and ω.

We propose the following picture of the QO mode: The QO mode displays "normal" softening above 650 K, where the Curie-Weiss law is obeyed [35]. Unfortunately this softening could not be measured with the given resolution. In this way the QO mode is responsible for the dielectric behavior above 650 K. Below $T_\mathrm{d} \approx 650$ K the softening ceases, and a narrow (resolution limited in energy) CP appears. We relate the appearance of the central peak to the formation of short-range ferroelectric clusters. There are several evidences in favor of this conclusion. The structure-factor analysis of reference [25] at room temperature has lead to the conclusion that the main role in the ferroelectric displacements is played by the Pb^{2+} ions, and the center of mass of the unit cell is shifted from its original position. Such a shift cannot correspond to optic-like lattice vibrations, but rather to the slow relaxation of superparaelectric clusters. Another evidence is the appearance of the strongly q-dependent broadening of the TA phonons. This broadening cannot be explained by the standard anharmonicity, which results in $\gamma_\mathrm{TA} \propto q^4$ only in the low-temperature limit $k_\mathrm{B}T \ll \hbar\omega_\mathbf{q}$. In the high-temperature limit one has $\gamma_\mathrm{TA} \propto q$ [28]. We attribute the appearance of the q^4 damping of the TA phonons to their scattering by the slowly relaxing superparaelectric clusters forming below T_d. Thus, there is sufficient evidence for a well-defined temperature T_d at which there is an essential change of the dynamical properties of PMN.

There are several models describing specific types of precursor phase transitions at temperatures above the thermodynamic transition temperature. Schwabl and Täuber [36] have considered the influence of a finite concentration of defects, which locally increases the transition temperature of the distortive phase transition. They have found a new phase transition at temperatures higher than the transition temperature of a pure crystal. In many respects the results of reference [36] resemble our experimental data. Nevertheless, there are still several differences. The most essential one is that there is no evidence of the divergence of the static susceptibility predicted in reference [36]. The lineshape of the transverse response function $(1/q^2)$ obtained in reference [36], corresponding to the hydrodynamic dispersion, is different from the experimentally observed Lorentzian lineshape $(1/(q^2 + \kappa^2))$ [15]. Thus, the results of [36] cannot be directly used for the interpretation of our data.

A different approach to the anomalous behavior observed in many systems with a structural phase transitions above the transition temperature was proposed by Aksenov *et al.* [37,38]. They used the mode-coupling theory, originally proposed for the description of the dynamical glass transition [39], to explain the appearance of precursor clusters in crystals undergoing a structural phase transition. The dynamical phase transition, accompanied by the formation of finite long-time correlations of the local displacement, was predicted to occur at $T_\mathrm{c}^* = T_\mathrm{c} + \Delta T$ with $\Delta T \approx 50$ K. In reference [38] the frequency and temperature dependence of the dynamical susceptibility near the dynamic phase transition was calculated. One can find some qualitative resemblance between their results and the properties of PMN in the vicinity of T_d. On the other hand, the difference ΔT between $T_\mathrm{d} \approx 650$ K and the freezing temperature $T_\mathrm{g} \approx 230$ K is much larger than expected from the mode-coupling theory. Also, as far as we know, no sharp peak in the temperature dependence of the imaginary part of the susceptibility, as predicted in reference [38], was ever observed in PMN.

Rather recently, a new approach to the properties of PMN in the vicinity of T_d was presented [40]. It was proposed to consider T_d as an analog to the Griffiths [41] temperature T_G in dilute ferromagnets. In the framework of this theory it is supposed that at T_G the condensation of the modes, localized due to disorder, starts with those which have the largest localization lengths. This condensation results in the formation of ferroelectric clusters (ferromagnetic in the original theory [41]) of various sizes, including sufficiently large ones. In the dynamic response such a transition should result in the appearance of a narrow central peak, related to the possibility to find arbitrarily large clusters with an arbitrarily low relaxation rate [40]. Still the theory in its present state does not provide the possibility of a quantitative comparison with the experimental data.

In conclusion, our experiments have demonstrated the existence of a soft excitation in PMN above $T_\mathrm{d} \approx 650$ K. The coupled-anharmonic oscillator analysis of the TA phonon lineshape enabled us to estimate the parameters of this excitation. It was demonstrated that this excitation can be considered as some quasioptic mode with strongly frequency-dependent damping. Below 650 K the character of the critical dynamics changes substantially. Mode softening ceases, and a strong central peak appears. The

observed changes can be attributed to some kind of phase transition into a superparaelectric phase, which is corroborated by the appearance of the strongly q-dependent damping of the TA phonons. In order to make a final conclusion about the origin of the observed soft excitation and the physical mechanism of the transition at $T_{\rm d}$, additional measurements with high resolution both in q and ω are asked for.

It is a pleasure to acknowledge B.P. Toperverg and R. Currat for helpful discussions. The measurements in LLB were performed with support of the research grant of the Ministry de Recherche et Technology of France, and the work at the Ioffe Institute was supported by the Russian Fund for Basic Researches grant 95-02-04065, and by the National Program "Neutron scattering study of Condensed Matter". S.V. is sincerely grateful to all colleagues from the ILL and LLB for their valuable help during his visits as well as to the Graduiertenkolleg "Komplexität in Festkörpern" (Deutsche Forschungsgemeinschaft GRK 176) for a guest lecturership.

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