Disorder and relaxation mode in the lattice dynamics of PbMg$_{1/3}$Nb$_{2/3}$O$_3$ relaxor ferroelectric

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The low-energy part of vibration spectrum in PbMg$_{1/3}$Nb$_{2/3}$O$_3$ relaxor ferroelectric was studied by inelastic neutron scattering. We observed the coexistence of a resolution-limited central peak with strong quasielastic scattering. The line-width of the quasielastic component follows a $\Gamma_0 + Dq^2$ dependence. We find that $\Gamma_0$ is temperature-dependent. The relaxation time follows the Arrhenius law well. The presence of a relaxation mode associated with quasi-elastic scattering in PMN indicates that order-disorder behaviour plays an important rôle in the dynamics of diffuse phase transitions.

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Enormous attention has been paid to relaxor ferroelectrics for more than 40 years due to their intriguing physical properties. A marking feature observed in relaxors is the frequency-dependent peak in the dielectric permeability $\varepsilon$ which typically extends over a few 100 degrees and does not link directly to the macroscopic changes of symmetry [1]. Since many physical properties of relaxors exhibit anomalies in this temperature range, it was called "diffuse phase transition" [2]. Despite intense investigations, however, the nature of the diffuse phase transition in these compounds remains unclear [3, 4, 5].

The well-known crystal PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN) is a model relaxor. In PMN, the peak in the real part of the dielectric permeability $\varepsilon'$ which typically extends over a few 100 $^\circ$C and does not link directly to the macroscopic changes of symmetry $\varepsilon_3$. Since many physical properties of relaxors exhibit anomalies in this temperature range, it was called "diffuse phase transition" [2]. Despite intense investigations, however, the nature of the diffuse phase transition in these compounds remains unclear [3, 4, 5].

To obtain a theoretical description of a phase transition, an important point is to know whether this transition is primarily of displacement, or of order-disorder type [12]. Since PMN crystallizes in the perovskite structure where the B-site is disordered, it was expected that the diffuse phase transition is of displacement type. Within such a scenario a soft-phonon mode should be observed. Extensive search for the presence of a soft mode in PMN was performed both by light (for a review see [13]) and neutron scattering. From light scattering no soft mode has ever been found. On the other hand, neutron scattering experiments revealed a very complicated behaviour of the phonons in PMN [14, 15, 16]. Firstly, a soft excitation was identified in PMN above $T_d$ [14], which is coupled with transverse acoustic phonon. Later, in Ref. [15] a strong renormalization of the lowest transverse optic (TO) phonon branch was observed starting from T~1100 K. Recently, a soft mode coupled to the lowest TO phonon was reported [16]. Obviously, the identification of a soft mode in PMN has not been definitely settled. In addition to the phonon modes a resolution-limited central peak (CP) is observed by neutron scattering in PMN without [14] and with an applied electric field [17]. The timescale of CP is also at the center of a controversy because it contradicts light scattering data [18], where a broad quasielastic component was observed with a typical width of 2 meV. We note, that the search for a broad quasielastic component in related relaxor PbZn$_{1/3}$Nb$_{2/3}$O$_3+8\%$PbTiO$_3$ was not successful [19] which again is in contradiction with results of light scattering (e.g. [20]). Hence, neutron scattering data speaks in favor of displacement behaviour in relaxor ferroelectrics coexisting with a narrow resolution limited CP. On the contrary, light scattering data suggest order-disorder behaviour in these compounds.

To solve these discrepancies between light and neutron scattering results and to show that order-disorder behaviour plays an important rôle in the lattice dynamics of PMN we have studied the low-energy range of the vibration spectrum in this crystal by inelastic cold-neutron scattering under improved resolution conditions with respect to the previous studies of refs. [14, 15, 17]. The measurements were carried out with the three-axis spectrometer TASP, located at the neutron spallation...
source SINQ at the Paul-Scherrer-Institute, Switzerland. A high-quality single crystal of PMN (~ 8 cm²), mosaic ~ 20° was mounted inside a closed-cycle refrigerator equipped with a small furnace. The crystal was aligned in the (h h l)-scattering plane. The measurements were performed in the temperature range 100 K - 450 K. The (002) reflection of pyrolytic graphite (PG) was used to monochromate and analyze the incident and scattered neutron beams, respectively. The spectrometer was operated in the constant final-energy mode with either \( k_f = 1.64 \text{ Å}^{-1} \) or \( k_f = 1.97 \text{ Å}^{-1} \) using a PG filter to remove higher-order wavelengths. The horizontal collimation was guide ~ 80° – 80° – 80°. With that configuration the energy resolution as measured with a standard Vanadium sample is 0.4 meV for \( k_f = 1.97 \text{ Å}^{-1} \) and 0.2 meV for \( k_f = 1.64 \text{ Å}^{-1} \). Figure 1 shows \((q, \hbar \omega)\) contour-maps of neutron scattering spectra in the vicinity of Bragg positions (0 0 1), (1 1 0), and (0 0 2) at \( T = 300 \text{ K} \), respectively. It is clear that all three figures differ from each other. For example, the intensity distribution in the (0 0 1) Brillouin zone (BZ) consists of a Bragg peak, a rather intense signal which is narrow in energy and broad in \( q \), and a diffuse signal which is broad both in \( q \) and in \( \hbar \omega \). In the (0,0,1) BZ no linear dispersion which could be associated with TA phonons is observed. On the other hand, one can easily see the linear dispersion of TA phonons in the (0 0 2) BZ, in addition to the Bragg peak and to the intense signal narrow in energy. This signal corresponds to the central peak reported before [14, 15]. Qualitatively, the distribution of the intensity in the (1 1 0) BZ lies between what is observed in the (0 0 1) and (0 0 2) zones. The typical peak intensity of a TA phonon measured close the (0 0 2) Brillouin zone center is ~ 5000 counts at room temperature. It is well-known that the neutron intensity of an acoustic phonon scales with the structure factor of the corresponding Bragg peak and with the square of the modulus of the scattering vector \( q^2 \) [23]. The structure factor of the (0 0 2) Bragg peak is 100 times larger than that of (0 0 1). Also, \( q^2 \) increases by a factor of ~ 4 while measuring in the (0 0 2) BZ. Thus, the total decrease of intensity of the TA phonons in (0 0 1) BZ with respect to (0 0 2) amounts to 400. Hence it is impossible to detect the intensity of such a phonon with respect to the diffuse intensity which amounts to ~ 200 counts in the (0 0 1) zone.

In this letter we will concentrate on the properties of the quasielastic intensity found in PMN and not on the behavior of the acoustic phonons as these have been the subject of numerous studies [8, 14, 15, 16, 22]. In order to interpret the data quantitatively we decomposed the neutron scattering spectra \( I(Q, \omega) \) in the following way:

\[
I(Q, \omega) = [S_{CP} + S_{q-el.} + S_{DHO}] \otimes R(Q, \omega) + B
\]

where \( S_{CP} \) refers to the resolution-limited central peak; \( S_{q-el.} \) is the quasi-elastic scattering shown in Fig. 1;

\[
S_{DHO} \text{ describes the phonon scattering. The symbol } \otimes \text{ stands for the convolution with the spectrometer resolution function } R(Q, \omega) \text{ [23]. } B \text{ denotes the background level.}
\]

We found that the data could be modeled using

\[
S_{CP} = A(q)\delta(\omega),
\]

\[
S_{q-el.} = I(q) \frac{\omega}{1 - \exp(-\omega/T)} \frac{1}{\pi \omega^2 + \Gamma_q^2}.
\]
and
\[ S_{DHO} = \frac{\omega}{1 - \exp(-\omega/T)} \left( \omega^2 - \Omega_q^2 \right) + \omega^2 \gamma_q. \] (4)

Here \( \delta(\omega) \) is the Dirac delta function; \( \Gamma_q \) and \( \gamma_q \) are the half-width at half maximum (HWHM) of the Lorentzian and damped-harmonic oscillator function, respectively. \( A(q) \) and \( I(q) \) are the q-dependent susceptibilities of the corresponding excitations and \( W(q) \) is the TA dynamical structure factor. The renormalized dispersion of the TA phonons is given by \( \Omega_q = \sqrt{\omega_q^2 + \Gamma_q^2} \) where \( \omega_q \) is the frequency of a damped oscillation. In our description, \( \Omega_q \) is the physically relevant quantity [24].

The damping of the QE component is found to behave like \( \Gamma(q) = \Gamma_0 + Dq^2 \). At \( T = 450 \) K the parameters are \( \Gamma_0 = 0.28 \pm 0.01 \) meV and \( D = 24.5 \pm 7.3 \) meV\( \cdot \)\( \text{Å}^2 \) and at \( T = 225 \) K we obtain \( \Gamma_0 = 0.02 \pm 0.01 \) meV and \( D = 21.3 \pm 8.9 \) meV\( \cdot \)\( \text{Å}^2 \). The absence at all \( q \) of an intrinsic energy width of CP implies that the associated fluctuations are very slow. Further, the intensity of the QE scattering does not scale with the narrow CP. In the \((0 \ 0 \ 2)\) BZ (Fig. 1) bottom the CP is very intense, but we were unable to detect QE component in this BZ. On the contrary, in the \((0 \ 0 \ 1)\) BZ the narrow CP is significantly weaker and the QE component is clearly seen. The different \( q \)-dependences of the energy widths and behavior of the relative intensities of the CP and quasi-elastic scattering indicate that these processes are of different origins.

We now turn to the temperature behaviour of the relaxation time \( \tau = 1/\Gamma \) of the QE-mode measured in the \((0,0,1)\) and \((1,1,0)\) BZ, respectively, and shown in Fig. 3. It is obvious, that the temperature dependence of \( \tau \) is very similar in both zones. We found that \( \tau \) is well described by the Arrhenius law \( \tau(T) = \tau_0 \cdot \exp [E_a/k_B \cdot T] \).

The solid line in Fig. 3b corresponds to the parameters \( \tau_0 = 8.6 \pm 0.1 \cdot 10^{-12} \) (s) and \( E_a = 0.023 \pm 0.0002 \) (eV). While these parameters are reasonable, they have to be taken with care as quantities like the refraction index, the specific heat [23] and the diffuse scattering [3] exhibit anomalous behaviours in this temperature range. This implies that the structure of PMN undergoes significant changes on a local scale, which in turn should affect the value of \( E_a \). Despite this uncertainty, the fact remains that \( \tau(T) \) is connected to a thermally activated behaviour, which allows us to speculate about the origin of the relaxation mode. It is well-known, that in relaxors, Pb ions are shifted from their ideal positions in the perovskite structure [24]. Recently it was shown that the probability density function \( \rho(R) \) for Pb in PMN has more than a single maximum below \( T_d \) [27]. Therefore, it is reasonable to assume that at high temperature the Pb ions move between maxima of \( \rho(R) \). In that case when the temperature is low enough with respect with the potential barrier, the hopping frequency \( 1/\tau \) becomes small. This gives rise to a narrowing in the energy-width of the QE component, which, within the limitations of the present experiment, is resolution limited at \( T = 100 \) K in PMN.

There is a number of models which describe the presence of a central peak in the vicinity of a structural phase transition (for a review of earlier papers see [28]). However, PMN does not undergo any structural phase transition without application of an electric field. To link the coexistence of a central peak with quasi-elastic scattering in a broad temperature range might be of importance to understand the diffuse phase transition in relaxor ferroelectrics.

To summarize, we have carried out high-resolution neutron scattering measurements in the relaxor ferroelec-

FIG. 2: Typical examples of constant-Q scans in different BZ. The bold line shows the results of data analysis as described in the text. The solid line shows the contribution of the quasielastic component, the dash-dotted line the narrow central peak and the dotted line the TA phonon.
(squares) and of damping (triangles) of the QE component at relaxation mode follows a of thermally activated character. The damping of this quasi-elastic and appears to be related to ionic motion resolution-limited central peak. The other component is components associated with two different timescales. One is the tric PMN. The low-energy spectra exhibit two compo-
ents. The solid line is a fit to the data with the Arrhe-

FIG. 3: a and b q-dependence of integrated intensity (squares) and of damping (triangles) of the QE component at \( T = 450 \, \text{K} \) and \( 225 \, \text{K} \), respectively. c Temperature dependence of the relaxation time \( \tau \) associated with the quasielastic component. The solid line is a fit to the data with the Arrhenius law.

tric PMN. The low-energy spectra exhibit two components associated with two different timescales. One is the resolution-limited central peak. The other component is quasi-elastic and appears to be related to ionic motion of thermally activated character. The damping of this relaxation mode follows a \( q^2 \) dependence. The presence of a relaxation mode associated with quasi-elastic scattering in PMN indicates that order-disorder behaviour plays an important rôle in the dynamics of diffuse phase transitions. It will be interesting to see if this relaxation mode, which was also observed in PMT [1], is a common feature of all relaxor ferroelectrics.

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[1] L.E. Cross, Ferroelectrics, 76, 241 (1987).
[2] G.A. Smolenskii et al., Ferroelectrics and Related Materials, (Gordon and Breach, NY, 1984).
[3] V. Westphal, W. Kleemann, and M. D. Glinchuk, Phys. Rev. Lett. 68, 847 (1992).
[4] D. Viehland et al., Phys. Rev. B 46, 8003 (1992).
[5] R. Blinc et al., Phys. Rev. Lett. 83, 424 (1999).
[6] G. Schmidt et al., Krist. und Tech. 15, 1415 (1980).
[7] G. Burns and B.A. Scott, Solid State Commun. 13, 423 (1973).
[8] K.Hirota et al., Phys. Rev. B 65, 104105 (2002).
[9] S. Wakimoto et al., Phys. Rev. B 66, 224102 (2002).
[10] D. La-Orauttapong et al., Phys. Rev. B 64, 212201 (2001).
[11] S.N. Gvasaliya, B. Roessli, and S.G Lushnikov, Europhys. Lett. 63, 303 (2003).
[12] R.A. Cowley, Adv. in Phys. 29, 1 (1980).
[13] I.G. Siny et al., Ferroelectrics 226, 191 (1997).
[14] A. Naberezhnov et al., Eur. Phys. J. B 11, 13 (1999).
[15] P. M. Gehring et al., Phys. Rev. Lett. 87, 277601 (2001).
[16] S. B. Vakhrushev and S. M. Shapiro, Phys. Rev. B 66, 214101 (2002).
[17] Yu.O. Chetverikov et al., Appl. Phys. A 74, 5989 (2002).
[18] I.G Siny et al., Phys. Rev. B 56, 7962 (1997).
[19] J. Hlinka et al., J. Phys.: Condens. Matter 15, 4249 (2003).
[20] F. Jiang and S. Kojima, Ferroelectrics 266, 19 (2002).
[21] e.g. S.W. Lovesey, Thermal neutron scattering, (Oxford University Press, UK, 1984).
[22] S. Wakimoto et al., Phys. Rev. B 65, 172105 (2002).
[23] M. Popovich, Acta Cryst. A 31, 507 (1975).
[24] B. Fäk and B. Dorner, Physica B 234, 1107 (1997).
[25] Y. Moriya et al., Phys. Rev. Lett 90, 205901 (2003).
[26] B. Dkhil et al., Phys. Rev. B 65, 024104 (2002).
[27] S. B. Vakhrushev and N.M. Okuneva, AIP Conference Proceedings 626, 117 (2002).
[28] A.D. Bruce and R.A. Cowley, Adv. in Phys., 29, 219 (1980).