Quantum paraelectric behavior of pyrochlore PMN

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Pb$_{1.83}$Mg$_{0.29}$Nb$_{1.71}$O$_{6.39}$ (PMN) crystallizing in a cubic pyrochlore structure exhibits, as the first dielectrics with pyrochlore structure, typical feature of quantum paraelectrics - its permittivity continuously increases on cooling and levels off below ~ 30 K without any signature of a structural phase transition. Broad-band dielectric spectra do not show any dielectric dispersion in the real part of permittivity up to 8.8 GHz. THz and infrared spectra reveal a soft polar optic mode which is responsible for the temperature dependence of the permittivity. The leveling-off of the permittivity at low temperatures obeys the Barrett formula and the fitted vibrational zero-point energy $\frac{1}{2}k_B T_1$ corresponds to the measured soft mode frequency. The number of observed infrared phonons exceeds that predicted from the factor-group analysis which indicates that the structure is at least locally non-cubic.

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I. INTRODUCTION

PbMg$_{1/3}$Nb$_{2/3}$O$_3$ crystallizing in the cubic perovskite structure is one of the most studied dielectrics as the typical representative of relaxor ferroelectrics. It exhibits a high (~10$^4$) and strongly diffused peak in the temperature dependent permittivity whose position remarkably shifts from 245 K (at 100 Hz) to 320 K (at 1 GHz)\footnote{I. The relaxation originates from the dynamics of polar clusters, which develop below the Burns temperature $T_d \approx 620 K$\footnote{II. The broad distribution of relaxation frequencies has its origin in random fields and random forces as a consequence of chemical disorder in the perovskite B sites occupied by Mg$^{2+}$ and Nb$^{5+}$. The local ferroelectric instability in the polar clusters was indicated by an unstable polar optic phonon, which softens to $T_d$ and hardens above $T_d$. Although the dielectric properties of perovskite PbMg$_{1/3}$Nb$_{2/3}$O$_3$ were intensively studied during the last fifty years, not all is completely understood, particularly the complex and broad dielectric dispersion.}}. Its crystal structure remains cubic down to liquid He temperatures. The peculiar dielectric properties are caused by a wide dielectric relaxation which broadens and slows down on cooling.\footnote{II. The related compound Pb$_{1.83}$Mg$_{0.29}$Nb$_{1.71}$O$_{6.39}$ (PMN) with a pyrochlore structure, which frequently grows in the perovskite PMN ceramics and thin films as a second phase and significantly deteriorates its dielectric properties, has been much less studied. The only report known to the authors is that by Shroud and Swartz.\footnote{II. High-frequency dielectric properties, including microwave, THz and infrared frequencies, have not been investigated, although they could be useful for understanding the reported diffused and frequency dependent maximum of the complex permittivity. The present report aims to fill this gap in the literature.}}\footnote{II. We will show that our pyrochlore PMN ceramics does not undergo a diffuse phase transition (reported in Ref.\footnote{II. \cite{ref-2}}, but a quantum paraelectric behavior for which the temperature dependent permittivity is caused only by anomalous polar phonons. In this way, it represents the first quantum paraelectrics with pyrochlore crystal structure.}} The relaxation originates from the dynamics of polar clusters, which develop below the Burns temperature $T_d \approx 620 K$. The broad distribution of relaxation frequencies has its origin in random fields and random forces as a consequence of chemical disorder in the perovskite B sites occupied by Mg$^{2+}$ and Nb$^{5+}$. The local ferroelectric instability in the polar clusters was indicated by an unstable polar optic phonon, which softens to $T_d$ and hardens above $T_d$. Although the dielectric properties of perovskite PbMg$_{1/3}$Nb$_{2/3}$O$_3$ were intensively studied during the last fifty years, not all is completely understood, particularly the complex and broad dielectric dispersion.

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II. EXPERIMENTAL

Pb$_{1.83}$Mg$_{0.29}$Nb$_{1.71}$O$_{6.39}$ pyrochlore ceramic samples were produced by solid state reaction of mixed oxide powders described in details in Refs.\footnote{II. They investigated the dielectric response up to 400 kHz down to liquid He temperatures and observed a diffuse maximum in the complex permittivity below 40 K. The crystal structure of the pyrochlore PMN single crystal (Fd3m space group) was determined in detail by Wakiya et al.\footnote{II. High-frequency dielectric properties, including microwave, THz and infrared frequencies, have not been investigated, although they could be useful for understanding the reported diffused and frequency dependent maximum of the complex permittivity. The present report aims to fill this gap in the literature.}}. PbO (99.5%), Nb$_2$O$_5$ (99.5%) and MgO (97%) powders were mixed and sintered at 880 °C for 8 hours. The pyrochlore cubic structure was verified by the X-ray diffraction.

The dielectric response was investigated between 400 Hz and 1 MHz from 10 K to 730 K using an impedance analyzer HP 4192A. The TE$_{001}$ composite dielectric resonator method\footnote{II. They investigated the dielectric response up to 400 kHz down to liquid He temperatures and observed a diffuse maximum in the complex permittivity below 40 K. The crystal structure of the pyrochlore PMN single crystal (Fd3m space group) was determined in detail by Wakiya et al.\footnote{II. High-frequency dielectric properties, including microwave, THz and infrared frequencies, have not been investigated, although they could be useful for understanding the reported diffused and frequency dependent maximum of the complex permittivity. The present report aims to fill this gap in the literature.}} and network analyzer Agilent E8364B was used for microwave measurements at 8.8 GHz in 100 - 350 K temperature interval. The cooling rate was 2 K/min.

Measurements at terahertz (THz) frequencies from 7 cm$^{-1}$ to 33 cm$^{-1}$ (0.2 - 1.0 THz) were performed in the transmission mode using a time-domain THz spectrometer based on an amplified Ti - sapphire femtosecond laser system. Two ZnTe crystal plates were used to generate (by optic rectification) and to detect (by electro-optic sampling) the THz pulses. Both the transmitted field
amplitude and phase shift were simultaneously measured; this allows us to determine directly the complex dielectric response $\varepsilon^*(\omega)$. An Optistat CF cryostat with thin mylar windows (Oxford Inst.) was used for measurements down to 10 K.

Infrared (IR) reflectivity spectra were obtained using a Fourier transform IR spectrometer Bruker IFS 113v in the frequency range of 20 - 3000 cm$^{-1}$ (0.6 - 90 THz) at room temperature, at lower temperatures the reduced spectral range up to 650 cm$^{-1}$ only was studied (transparency region of polyethylene windows in the cryostat). Pyroelectric deuterated triglicine sulfate detectors were used for the room temperature measurements, while more sensitive liquid-He-cooled (1.5 K) Si bolometer was used for the low-temperature measurements. Polished disk-shaped samples with a diameter of 8 mm and thickness of $\sim$2 mm were investigated.

### III. RESULTS AND DISCUSSIONS

Temperature dependence of the real and imaginary parts of complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ at various frequencies is plotted in Fig. 1. One can see typical incipient ferroelectric behavior, i.e. increase in $\varepsilon'$ on cooling and its noticeable saturation at low temperatures. It is important to stress that within the accuracy of measurements no frequency dispersion of $\varepsilon'$ was observed between 400 Hz and 8.8 GHz at temperatures below 600 K. The small low-frequency dispersion above 600 K is caused by non-negligible conductivity of our sample. The pronounced $\varepsilon'(T)$ dependence is therefore caused by the softening of an excitation above 10 GHz. To reveal it we measured the THz dielectric spectra (see Fig. 2) and IR reflectivity spectra (Fig. 3) below room temperature (RT). One can actually see very pronounced changes in the THz dielectric spectra (see Fig. 2) and IR reflectivity tails above the phonon frequencies and was assumed to be temperature independent.

The real and imaginary parts of $\varepsilon^*(\omega)$ obtained from the fits to IR and THz spectra are shown in Fig. 4. Parameters of the fits performed at 300 and 20 K are summarized in Table I. One can see a higher number of observed modes at 20 K than at RT. This is due to the reduced phonon damping at low temperatures, which allows to resolve a higher number of modes, which are probably overlapping at RT. One can see in the $\varepsilon''(\omega)$ spectra of Fig. 4 (we remind that the frequencies of $\varepsilon''$ maxima roughly correspond to the phonon frequencies) that the most remarkable frequency shift with temperature is revealed by the lowest frequency mode below 30 cm$^{-1}$, but also the mode near 130 cm$^{-1}$ partially softens on cooling. The temperature dependence of the soft mode frequency $\omega_{SM}$ (left scale) and its dielectric strength $\Delta\varepsilon_{SM}$ are shown in Fig. 5. Mainly this mode causes an increase in $\varepsilon'$ on cooling (see Fig. 4). In the case of uncoupled phonons the oscillator strength $f_j = \Delta\varepsilon_j/\omega^2_{TOj}$ of each phonon is roughly temperature independent so that each softening of phonon frequency $\omega_{TOj}$ is connected with the increase of its dielectric strength $\Delta\varepsilon_j$ given by

$$\Delta\varepsilon_j = \varepsilon_\infty \omega^2_{TOj} \prod_{k \neq j} \frac{\omega^2_{OK} - \omega^2_{TOj}}{\omega^2_{OK} - \omega^2_{TOk}}. \tag{3}$$

In our case the soft-mode oscillator strength $f_{SM}$ is temperature dependent, it increases twice from $3.3\times10^3$ to $6.5\times10^4$ cm$^{-2}$. This indicates that the soft mode is coupled with some higher frequency mode assuming that

![](image.png)
FIG. 2: (color online) THz dielectric spectra of the pyrochlore PMN at various temperatures. The soft mode frequency shifts down into the THz range on cooling, therefore the sample becomes less transparent at low temperatures (the noise increases) and the accessible spectral range narrows on cooling. Two frequency scales (THz and cm\(^{-1}\)) are given.

FIG. 3: (color online) IR reflectivity spectra of the pyrochlore PMN ceramics at various temperatures below RT. Low-temperature spectra were obtained only below 650 cm\(^{-1}\) (transparency range of the polyethylene windows in the cryostat).

∑\(f_j = \text{const.}\) However, it is difficult to reveal with which mode is the soft mode coupled, because the oscillator strength of the most high-frequency modes is much higher than \(f_{SM}\) and relatively small changes (below the limit of our fitting accuracy) in these modes could explain the increase of the \(f_{SM}\) on cooling.

The static permittivity obtained from the fit of the IR reflectivity is defined as

\[
\varepsilon(0) = \sum_j \Delta \varepsilon_j + \varepsilon_\infty
\]

and is plotted in Fig. 4 in red solid dots. The values of \(\varepsilon(0)\) are slightly lower (by about 20) than the experimental values obtained at and below the microwave range. However, we believe that the disagreement is rather due to the experimental inaccuracy than due to real dielectric dispersion above the GHz range. So we conclude that the temperature dependence of the permittivity below 10 GHz in Fig. 4 is essentially due to anomalous polar phonons.

The temperature dependence of the lowest-mode frequency below 35 cm\(^{-1}\) was fitted with the Cochran law

\[
\omega_{SM}(T) = \sqrt{A(T - T_{cr})}
\]

where \(A\) is a constant and \(T_{cr}\) is the critical softening.
TABLE I: Parameters of the polar phonon modes in the pyrochlore PMN obtained from the fit of IR and THz spectra at 20 and 300 K. Frequencies $\omega_{T\Omega_j}$, $\omega_{L\Omega_j}$ and dampings $\gamma_{T\Omega_j}$, $\gamma_{L\Omega_j}$ of modes are in cm$^{-1}$, $\Delta \varepsilon_j$ is dimensionless, $\varepsilon_\infty = 5.87$.

| No | $\omega_{T\Omega_j}$ | $\gamma_{T\Omega_j}$ | $\omega_{L\Omega_j}$ | $\gamma_{L\Omega_j}$ | $\Delta \varepsilon_j$ | $\omega_{T\Omega_j}$ | $\gamma_{T\Omega_j}$ | $\omega_{L\Omega_j}$ | $\gamma_{L\Omega_j}$ | $\Delta \varepsilon_j$ |
|----|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 1  | 24.1                 | 19.4                 | 32.5                 | 31.5                 | 110.8                | 33.2                 | 22.6                 | 37.7                 | 30.5                 | 33.7                |
| 2  | 55.8                 | 16.1                 | 63.9                 | 17.7                 | 36.6                 | 56.9                 | 13.5                 | 63.2                 | 16.9                 | 23.9                |
| 3  | 71.7                 | 13.4                 | 80.1                 | 14.5                 | 12.0                 | 71.9                 | 12.3                 | 79.7                 | 18.1                 | 10.8                |
| 4  | 125.9                | 36.1                 | 175.8                | 28.4                 | 46.1                 | 131.9                | 42.9                 | 182.3                | 40.6                 | 40.8                |
| 5  | 179.9                | 28.0                 | 212.0                | 68.7                 | 1.8                  | 186.7                | 36.2                 | 215.3                | 56.3                 | 1.6                 |
| 6  | 216.7                | 49.2                 | 257.3                | 23.2                 | 0.8                  | 217.6                | 41.6                 | 260.1                | 40.2                 | 0.4                 |
| 7  | 271.2                | 26.0                 | 277.3                | 22.0                 | 0.2                  |                      |                      |                      |                      |                     |
| 8  | 293.5                | 23.7                 | 296.0                | 22.0                 | 0.2                  |                      |                      |                      |                      |                     |
| 9  | 329.7                | 29.5                 | 339.8                | 30.7                 | 0.3                  |                      |                      |                      |                      |                     |
| 10 | 348.9                | 23.7                 | 388.1                | 49.2                 | 2.0                  | 338.8                | 41.1                 | 383.5                | 48.9                 | 4.3                 |
| 11 | 389.1                | 36.6                 | 429.5                | 20.6                 | 0.06                 | 386.5                | 40.8                 | 427.7                | 32.4                 | 0.2                 |
| 12 | 449.6                | 28.1                 | 464.1                | 33.6                 | 0.3                  | 448.4                | 31.7                 | 456.3                | 35.0                 | 0.2                 |
| 13 | 490.9                | 19.9                 | 547.6                | 59.5                 | 0.9                  | 486.3                | 41.9                 | 530.7                | 116.5                | 1.0                 |
| 14 | 547.8                | 43.4                 | 551.2                | 55.6                 | 0.001                | 553.1                | 120                  | 586.1                | 120.4                | 0.4                 |
| 15 | 562.6                | 44.8                 | 575.1                | 70.7                 | 0.9                  |                      |                      |                      |                      |                     |
| 16 | 598.9                | 70.5                 | 703.6                | 46.8                 | 0.4                  | 602.6                | 104.9                | 703.6                | 47.6                 | 0.3                 |
| 17 | 862.7                | 80.1                 | 863.0                | 69.1                 | 0.002                | 862.7                | 80.1                 | 863                  | 69.1                 | 0.002               |

FIG. 5: (color online) Temperature dependence of the low-frequency soft mode $\omega_{SM}$ (left scale) and its dielectric strength (right scale). The dashed black line and solid red line show the results of the Cochran and Minaki fit of the soft-mode frequency, respectively (see the text).

Temperature. From the fit we obtained $A = (1.86 \pm 0.01)$ cm$^{-2}$ K$^{-1}$ and $T_{cr} = -285 \pm 11$ K. So, pyrochlore PMN tends to the ferroelectric instability at negative temperatures.

Theoretical critical temperature can be obtained also from the fit of the temperature dependence of permittivity $\varepsilon(T)$, which (for classical paraelectrics) should follow the Curie-Weiss law

$$\varepsilon' = \varepsilon_{\infty} + \frac{C}{T - T_{cw}}. \quad (6)$$

The result of the Curie-Weiss fit is shown in Fig. [4] in dashed line with the following fit parameters: $\varepsilon_{\infty} = 43 \pm 1$, Curie-Weiss constant $C = (47800 \pm 500)$ K and critical temperature $T_{cw} = -202 \pm 8$ K. The Cochran critical temperature $T_{cr} = -285$ K is somewhat lower than the Curie-Weiss critical temperature $T_{cw}$, but if we consider that the extrapolated critical temperatures lie far below the investigated temperature range, the agreement between both values is reasonable.

The Curie-Weiss fit in Fig. [4] deviates from the experimental data below $\sim 50$ K, because $\varepsilon'(T)$ levels off at low temperatures. Similar behavior was observed in incipient ferroelectrics as SrTiO$_3$, KTaO$_3$ or CaTiO$_3$ where the polar soft mode is also responsible for the observed $\varepsilon'(T)$.$^{10,11}$ The soft mode does not soften completely, it levels off at low temperatures (typically below 30 K), mainly due to zero-temperature vibrations of light oxygen ions, which prevents the formation of long-range ferroelectric order and permittivity divergence at low temperatures. Due to this phenomenon the incipient ferroelectrics are also called quantum paraelectrics.$^{12}$ Note that pyrochlore PMN is the first quantum paraelectrics of pyrochlore crystal structure.

The leveling-off of the low-temperature permittivity in incipient ferroelectrics was explained by Barrett al-
Weiss fit (dashed green line) and the fit with Barrett formula (red solid line). Note the log temperature scale.

ready in the beginning of 1950’s. He derived the formula
\[
\varepsilon'(T) = \frac{M}{T_1^2 \coth(\frac{B}{2T}) - T_0} + \varepsilon_{B\infty}, \quad (7)
\]
where \(M\) is constant, \(T_1\) is the temperature below which the quantum fluctuations start to play a role (\(\frac{1}{2}k_BT_1\) is the zero-point vibration energy\(^{14}\)) and \(\varepsilon_{B\infty}\) marks the temperature independent part of the permittivity (this term was neglected in Ref.\(^ {33}\), because it was very small in comparison to huge low-temperature \(\varepsilon'\) in SrTiO\(_3\) and KTaO\(_3\)). Our use of the the Barrett formula in Eq.( 7) for fitting of \(\varepsilon'(T)\) yields very good agreement with the experimental data (see Fig. 6). We found \(M=\left(4.25\pm0.01\right)\times10^4\) K, \(T_1=\left(96\pm8\right)\) K and \(\varepsilon_{B\infty}=47\pm0.5\). For \(T \gg T_1, \frac{1}{2}T_1 \coth(\frac{B}{2T})\) asymptotically approaches \(T\) and Eq.( 7) becomes a Curie-Weiss law. Therefore also \(\varepsilon_{B\infty}=47\) is close to \(\varepsilon_{CW\infty}=43\). It is worth to note that the zero point vibration frequency \(\frac{1}{2}k_BT_1=1\) THz=33 cm\(^{-1}\) corresponds very well to the soft mode frequency (see Fig. 5). Note also that the \(T_1\) parameter as well as the soft-mode frequency in the pyrochlore PMN qualitatively agree with analogous parameters obtained for SrTiO\(_3\) and SrTi\(_\text{18O}_3\), although the values of permittivity in these materials are two orders of magnitude higher\(^{34,35,36,37}\) which is the consequence of different \(M\) parameters.

In the only published dielectric data below 400kHz Shrout and Swartz\(^ {2}\) observed similar essentially dispersionless increase in \(\varepsilon'\) on cooling down to 50 K as we did in Fig. 1. We believe that the small dispersion below 50 K and small decrease in \(\varepsilon'\) below \(\sim 30\) K observed by Shrout and Swartz could be due to some defects (e.g. vacancies) in the crystal lattice of pyrochlore Pb\(_{1.83}\)Mg\(_{0.29}\)Nb\(_{1.71}\)O\(_6\).39, which is substantially non-stoichiometric.

It is clear that the soft mode frequency cannot follow the Cochran law (Eq. 5) in the case of low-temperature quantum fluctuations. The correct low-temperature dependence of the soft mode frequency derived from the Barrett formula for permittivity can be found e.g. in the paper of Minaki et al.\(^ {16}\)

\[
\omega_{SM}(T) = \sqrt{A\left[\left(\frac{T_1}{2T}\right)\coth\left(\frac{T_1}{2T}\right) - T_0\right]}, \quad (8)
\]

where \(A\) is constant and \(T_1\) and \(T_0\) have the same meaning as in Eq.( 7). Note that Eq.( 8) follows from Eq.( 7) and Lyddane-Sachs-Teller relation under assumption that the temperature dependence of static permittivity is caused just by softening of the soft TO mode. Result of the soft mode fit with Eq.( 8) is shown by solid line in Fig. 5 where one can clearly see the level-offing of the soft-mode frequency at low temperatures (unlike the Cochran fit). The fitting parameters are the following: \(A = \left(2.03\pm0.05\right)\) cm\(^{-1}\)K\(^{-1}\), \(T_1 = \left(96\pm9\right)\) K and \(T_0 = \left(-240\pm11\right)\) K. The fit parameters could be significantly improved if we would have more points in Fig. 5 especially below 50 K. Nevertheless, one can see reasonable agreement of both Cochran and Barrett fits above 50 K as well as \(T_0\) and \(T_1\) parameters obtained from the Barrett fits of permittivity (Eq. 5) and the Minaki model of the soft mode frequency (Eq. 8).

Let us compare the IR reflectivity spectra of pyrochlore PMN (Fig. 3) with those of perovskite PMN. The latter was first published by Burns and Dacol\(^ {14}\) together with the temperature dependence of the optical index of refraction \(n(T)\), which shows deviation from the linear dependence below \(\sim 600\) K. They explained the unusual \(n(T)\) dependence by formation of polar nanoregions. Surprisingly, the published IR spectrum of the perovskite sample corresponds to our pyrochlore spectrum in Fig. 3. In later papers of other authors (Refs.\(^ {17,18,19,20}\)) the mutually similar (but different from Burns and Dacol’s spectra\(^ {14}\)) IR reflectivity spectra of perovskite PMN consisted of three distinct reflection bands typical for all cubic perovskite oxides. We stress that the infrared spectra in Refs.\(^ {17,18,19,20}\) were obtained independently on ceramics, single crystals as well as on thin films. It appears that the IR spectrum by Burns and Dacol\(^ {14}\) belongs to pyrochlore PMN. The rest of their data (\(n(T)\) and \(P(T)\)) were obviously obtained on perovskite PMN, because the peculiarities near the Burns temperature in the perovskite PMN were later confirmed in many experiments.

It is of interest to compare the number of observed polar modes in the reflectivity spectra with the prediction of factor-group analysis: pyrochlore PMN crystallizes in \(Fd\bar{3}m\) space group with 8 formula units per conventional unit cell\(^ {8}\), i.e. 2 formula units per primitive unit cell. This means that on the whole, 66 lattice vibrational branches are expected. Pb ions are in 16d positions while Mg and Nb ions are in 16c positions\(^ {8}\), both sites having \(D_{3d}\) symmetry, while the O cations are in positions 48f and 8b of \(C_{2v}^d\) and \(T_d\) symmetry, respectively. The mode symmetries and their activities in IR and Ra-
man spectra can be obtained using standard tables with the following result for the Γ-point of the Brillouin zone (factor-group analysis):

\[
\Gamma_{d3m} = 3A_{2u}(-) + 3E_u(-) + 8F_{1u}(x) + 4F_{2u} + 4F_{2g}(xy, yz, xz) + 1A_{1g}(x^2, y^2, z^2) + E_g(x^2 + y^2 - 2z^2, \sqrt{3}x^2 - \sqrt{3}y^2) + 2F_{1g}.
\]

(9)

It means that after subtraction of 1F1u acoustic mode, 7F1u modes should be IR active, 4F2g, 1A1g and 1Eg should be Raman active, the rest of modes being silent. Table I shows that our fit of IR spectra required 17 modes, much more than expected. The analysis in Eq. 9 assumes one effective ion in 16c positions instead of statistically distributed Mg and Nb ions. Since the ions strongly differ in the mass, one could expect splitting of the modes in which these ions take part. If we take into account different Mg and Nb vibrations, the factor group analysis yields:

\[
\Gamma_{d3m} = 4A_{2u}(-) + 4E_u(-) + 10F_{1u}(x) + 5F_{2u} + 4F_{2g}(xy, yz, xz) + 1A_{1g}(x^2, y^2, z^2) + E_g(x^2 + y^2 - 2z^2, \sqrt{3}x^2 - \sqrt{3}y^2) + 2F_{1g}.
\]

(10)

In this case 9 polar F1u modes are expected, which is still less than 17 modes observed at low temperature (see Table I). If we assume that the Pb cations and some of the oxygen anions are dynamically disordered among more equivalent positions with the average structure remaining cubic like in isostructural Bi1.5ZnNb1.5O7, then 14 modes could be IR active close to our experimental result.

The problem with the excess IR active modes is also known from the perovskite PMN, where only 4F1u polar modes are allowed in Fm3m structure, although 7 modes were observed. The excess modes in the perovskite PMN were explained by polar clusters, which locally break the cubic symmetry into a rhombohedral one. In the case of pyrochlore structure similar local symmetry breaking, if present, should probably be non-polar, because there is no indication for the existence of polar clusters. There is also no dielectric dispersion below the polar phonon range, in contrast to the PMN perovskite, where the huge dielectric dispersion appears just due to polar cluster dynamics. Therefore it appears that new structural studies of pyrochlore PMN are needed to detect either a dynamical disorder of some atoms in the lattice or a non-cubic crystal symmetry.

IV. CONCLUSION

Our dielectric studies of pyrochlore PMN indicate quantum paraelectric behavior, i.e. the permittivity increase on cooling following the Barrett formula in the whole investigated temperature range. The permittivity shows no dispersion up to the microwave range and its temperature dependence can be explained by the softening of polar optic modes. The zero-point vibrational energy \( \frac{k_B T_1}{3} \) obtained from the Barrett formula corresponds very well to the soft mode frequency observed near 30 cm\(^{-1}\). It is worth to note that the pyrochlore PMN is the first quantum paraelectrics with pyrochlore crystal structure. Our IR spectrum of pyrochlore PMN corresponds to IR spectrum by Burns and Dacol, whose paper concerns the perovskite PMN. By comparing it with the later results, it becomes clear that Burns and Dacol published (by mistake) the IR spectrum of the pyrochlore PMN. Since the IR experiment revealed more modes than expected from the factor-group analysis, we suggest that the structure should have at least locally lower symmetry than the cubic one.

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