Fractal Dynamics in a Single Crystal of a Relaxor Ferroelectric

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We report the high-resolution and broadband light-scattering spectroscopy of a single crystal of a prototypical relaxor ferroelectric, $Pb(Mg_{1/3}Nb_{2/3})O_3$. A self-similar broad central peak, whose intensity is expressed as $I(\omega) \propto \omega^\alpha$ has been observed, indicating the presence of a fractal in the crystal. A strong correspondence exists between the temperature dependence of the exponent α and that of the reported behaviors of *polar nanoregions*. The estimated fractal dimension ($d_f \approx 2.6$) at low temperatures clearly indicates a percolation transition of the polar nanoregions at around 240 K.

In recent years, materials with large response to external fields have been studied widely and intensively in condensed matter physics. Relaxors are a class of disordered crystals that exhibit large piezoelectric and dielectric responses to external electric fields over wide temperature ranges [1], in contrast to the Curie-Weiss behavior of typical ferroelectrics. The large dielectric response and *diffuse* temperature dependence of relaxors are mainly useful for devices such as thermally robust, small capacitors with high dielectric constants, or high-efficiency ultrasonic generators. Regardless of the intensive research efforts aimed at improving the understanding of the nature of relaxors, there remain many unanswered questions regarding the dynamic behavior in wide time scales. It has long been suggested that disorder, which is induced by the frustration between the charge and structure, should be the key, but little information is available regarding its dynamics, in particular.

In this Letter, we report the self-similar quasielastic light-scattering (QELS) spectrum of a single crystal of a prototypical relaxor ferroelectric, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN). The spectrum is self-similar, or of a power-law type, for over three decades of frequency. We also report the temperature dependence of the power exponent, which strongly corresponds to that of the static properties of the so-called *polar nanoregions (PNRs)*. [2–5] We discuss the existence of a *fractal* formed by the clusters of the PNRs in the single crystal of PMN, which is paradoxical with the view that fractals are usually found in noncrystalline disordered systems such as glasses, polymers, or gels. Our analysis suggests that the dynamics of the diffuse phase transition or *freezing* dielectric behavior of relaxors may be characterized by the dynamics of the fractal percolation cluster of the PNR formed within the matrix of a single crystal. An incipient state toward the percolation transition of PNRs is thought to be responsible for the large response of relaxors.

To obtain dynamical information in materials, light-scattering techniques are widely employed [6]. We performed light-scattering spectroscopy with frequencies spanning 1 GHz to 23 THz, combining the spectra obtained with a tandem Fabry-Perot (FP) interferometer and a triple diffraction monochromator. The frequency range covers the Rayleigh, Brillouin, and Raman scattering regimes. The experimental setups for both the Rayleigh-Brillouin and Raman scattering experiments were reported elsewhere [7,8]. Backscattering geometry is adopted in all cases, and the polarization direction of both the incident and scattered light is perpendicular [horizontal-vertical (HV)].

The samples were single crystals of PMN, and were synthesized using the conventional columbite method. The as-grown crystals were $5.0 \times 5.0 \times 0.3$ mm^3 with cubic [100] axes, and the surfaces were polished to optical quality. Other samples with smaller dimensions were also investigated for comparison. The polarization direction of the incident light was along the crystalline [110] direction to minimize the Raman signal around 1350 GHz [8], which can obscure the quasielastic scattering intensity. The samples were placed in cryostats, and the temperature was controlled to within ± 1 K at temperatures above 300 K and to within ± 0.1 K at temperatures below 300 K.

In Figs. 1(a)–1(d), we show the QELS spectrum of PMN at room temperature [9]. The frequency ranges of the four graphs in Figs. 1(a)–1(d) differ by a factor of approximately 4. The QELS spectrum clearly exhibits *self-similarity*, [10], i.e., the spectrum always appears to be an unshifted Lorentzian in any fixed frequency range. Previously, the QELS in relaxors was analyzed by the fitting of a single Lorentzian [11] or the sum of two Lorentzians [12,13], which provided an average relaxation time. However, since the combination of the summation of Lorentzians is arbitrary, the central peak in relaxors should be analyzed over a sufficiently wide frequency range in
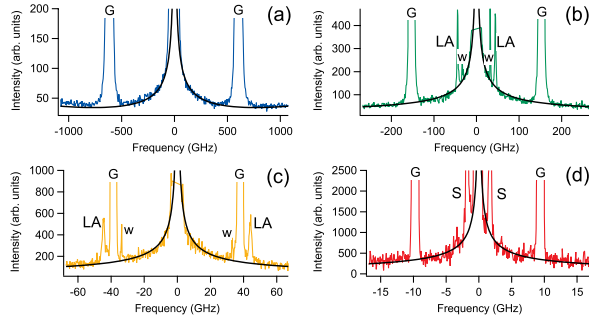
FIG. 1 (color online).   Self-similar quasielastic light scattering observed in PMN at 297 K. The frequency ranges of (a)–(d) are $[-1000, 1000$ GHz$]$, $[-250, 250$ GHz$]$, $[-60, 60$ GHz$]$, and $[-15, 15$ GHz$]$, respectively. The solid black line is a fit of the power-law function; $I \propto \omega^{\alpha}$, with $\alpha = -0.67$. The LA, w, S, and G denote the Brillouin scattering from the longitudinal acoustic phonon, the cryostat window, the surface acoustic wave, and the first order transmission from the interferometer (*ghost* line), respectively.
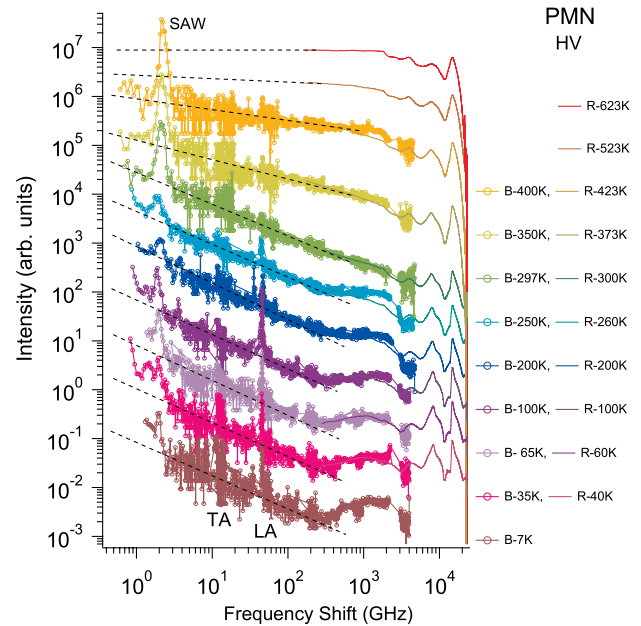

FIG. 2 (color online).   Temperature variation of the power-law light-scattering spectrum observed in PMN. The open circles that are connected by lines represent the spectra recorded by a tandem FP (Brillouin spectra), and the solid lines are the spectra recorded by a triple diffraction monochromator [8]. The temperatures of the Brillouin and Raman spectra (indicated as B- and R-, respectively, in the legend) are not exactly the same, and differ by as much as 10%. The Brillouin spectra above 500 K are not shown because of the poor signal-to-noise ratio. The dashed lines are used as visual guides.

order to discuss the dynamics in detail. Recently, we reported [9] that the intensity distribution of this QELS (or central peak) spectrum obeys a *power-law* as $I(\omega) \propto \omega^{\alpha}$, which is plotted in Figs. 1(a)–1(d) as a solid black line with a power exponent $\alpha = -0.67$.

Figure 2 shows the temperature dependence of the combined light-scattering intensity spectrum obtained with a tandem Fabry-Perot interferometer and a triple diffraction monochromator, which span the frequency ranges from 1 GHz to 4 THz and 0.3 to 23 THz, respectively. In this Letter, we refer to the former and latter spectra as *Brillouin* and *Raman* spectra, respectively. The temperatures at which the Brillouin and Raman spectra are recorded differ by as much as 10% of the absolute value. Therefore, since this figure is intended to show only the spectra over a wider frequency range, our analyses were conducted mostly on the Brillouin spectrum. Slight deviations were observed between the Raman and Brillouin spectra at the frequency shift of around 1.5 THz, where the sample alignment (the angle between the light-polarization direction and crystal-lographic [110] axis) significantly affects the scattering intensity from the F_{2g} phonon mode in $Fm\bar{3}m$ symmetry [8]. However, the lower frequency part of the spectrum was found to be unaffected by a slight misalignment of the sample, and the Raman and Brillouin spectra were successfully connected only by multiplying constants.

In the lower frequency range, namely, below 1 THz, we observed straight-line spectra over a frequency range as wide as more than three decades in the log-log plot of Fig. 2. This is the *power-law* spectrum, which is expressed as $I \propto \nu^{\alpha}$, where I, ν, and α are the intensity, frequency, and power exponent, respectively. Since $\log_{10} I = \alpha \log_{10} \nu + \text{const}$, the slope of a straight spectrum in the log-log plot equals the exponent of the power-law spectrum. In Fig. 2, we observed that the spectrum at the

highest temperature ($T = 623$ K) is almost horizontal in the low-frequency region ($\lesssim 1$ THz), and it begins to *tilt* to the higher frequency side as the temperature is lowered. The tilting of the slope appears to cease at around 200 K. Note that the intensity of the power-law component decreases on further cooling, but the slope (α) never changes at lower temperatures. As a result, the low-frequency spectrum is clearly decomposed into the power-law and underdamped soft-mode components [8,14].

In the low-frequency region, in addition to the quasielastic intensity distribution, we observed a few inelastic (shifted) peaks in the spectrum, namely, the Brillouin scattering from longitudinal acoustic (LA) phonons, transverse acoustic (TA) phonons, and surface acoustic waves (SAW). Although scattering from the LA and TA phonons is forbidden in the adopted geometry, they are visible owing to leakage from the polarizer and the slight orientation of the sample crystal from the normal incidence of the excitation light. On the other hand, the SAW mode was visible both in HV and horizontal-horizontal geometries. Because the frequency shift of the SAW peak was observed to be proportional to the sine of the light-incident angle, it was confirmed that the observed excitation propagates along the sample surface. Although the observation and analysis of the SAW in a single PMN crystal have not yet

been reported, we will not discuss this since it is outside the scope of this Letter.

The emergence of the power-law spectrum suggests that there is a wide distribution of relaxation times, because a power-law intensity spectrum can be expressed as a superposition of many Lorentzian (relaxational) spectra:

$$\omega^\alpha = C \int_0^\infty [f(\tau)/(1 + \omega^2\tau^2)]d\tau \quad \text{with} \quad f(\tau) = \tau^{-(\alpha+1)},$$

(1)

where τ is the relaxation time and C is a constant defined as $C = \frac{2}{\pi}\cos\frac{\alpha+1}{2}\pi$. Equation (1) represents the Curie-von Schweidler law, which states that the power-law intensity spectrum can be decomposed into an infinite number of relaxational modes with a power-law distribution of relaxation times. This is why the entire spectrum can be reasonably reproduced by the superposition of a few Lorentzians [12,13], and it always appears to be like a Lorentzian in all frequency ranges, as shown in Figs. 1(a)–1(d). Because relaxors are disordered systems formed by the frustration between the charge and structure [1], it is quite plausible that PMN has a wide distribution of relaxation times. The distribution of relaxation times in PMN or related relaxors has been reported by several authors [15–18], and are typically in the lower frequency ranges, namely, the subgigahertz region. However, none of the authors have mentioned the existence of a power-law distribution of τ. It should be noted that there is a formal correspondence between the Kohlrausch function (or socalled *stretched exponential decay*) and the power-law distribution of relaxation times [19].

The self-similarity of the power-law spectrum, or equivalently, the existence of a power-law distribution of relaxation times [Eq. (1)], directly suggests that there is a structural self-similarity [20], which is commonly known as a *fractal*. In fractals, the (mass) density, ρ, scales as a power of the distance r, i.e., $\rho \sim r^{d_f}$, where the exponent d_f is the *fractal dimension*, which is generally a noninteger. Ubiquitous in nature, fractals are also found in disordered systems such as glasses, polymers, and gels. However, this strongly contrasts with the fact that our samples were single crystals. Thus, we need to determine the mechanism behind the formations of the fractal in PMN. One possibility is that it is caused by the disordered arrangement of Mg and Nb ions. It is known that PMN has both chemically ordered (ion arrangement with Mg:Nb = 1:1) and disordered regions [1,14]. However, such an arrangement is independent of temperature, as reported recently [14]. Hence, the fractal structure due to the disordered ionic arrangement is ruled out, and the fractal in PMN is probably formed by *dynamic* objects that exhibit a strong temperature dependence. It has been recognized that nanoscale polarized regions exist, which are referred to as PNRs, in relaxors [1]. In PMN, after cooling from higher temperatures, such polar regions begin to increase in

volume at around 600 K, which is often referred to as the Burns temperature [21]. As the temperature is lowered, the volume of the PNRs increases, and a percolation transition is believed to occur, leading to the formation of an infinite percolation cluster, which is generally a fractal with a noninteger fractal dimension [22,23]. The fractals in relaxors have been mentioned by some authors [24–26], and the percolation scenario in relaxors has been proposed theoretically [27]. However, to the best of our knowledge, convincing observations of fractal dynamics, e.g., a power-law spectrum as wide as three decades, have not been presented to date.

To study the fractal dynamics in PMN, instead of analyzing the intensity spectrum, we consider the *reduced intensity* [28], which is defined as $\mathcal{I}(\nu) \equiv \nu I(\nu)/[n(\nu) + 1] = \nu\chi''(\nu)$, where $n(\nu) = [\exp(h\nu/k_BT) - 1]^{-1}$ is the Bose-Einstein factor, χ'' is the imaginary part of the susceptibility. It is known that the reduced intensity, $\mathcal{I}$, is proportional to the density of states of excitations in disordered systems [28]. In Fig. 3, we show the temperature dependence of the reduced intensity spectrum in a log-log plot for selected temperatures. Again, we observe that all spectra have clear power-law distributions over three decades, i.e., $\mathcal{I}(\nu) \propto \nu^\mu$, where μ is the power exponent for the reduced-intensity expression [29]. The temperature dependence of μ is plotted in Fig. 4. At around 600 K, we observe that μ is close to 2, while it decreases on cooling, and approaches a constant at $T \lesssim 240$ K. The high-temperature asymptotic value $\mu \to 2$ corresponds to the spectrum of a phonon mode(s) because a damped harmonic oscillator whose intensity is expressed as $S(\omega) = \omega_0^2\Gamma/[(\omega_0^2 - \omega^2)^2 + \omega_0^2\Gamma^2]$ yields a reduced intensity with ω^2-dependence as $\omega \to 0$. Because there are always a few phonon modes at $\omega/2\pi \gtrsim 1000$ GHz, as can be seen in the
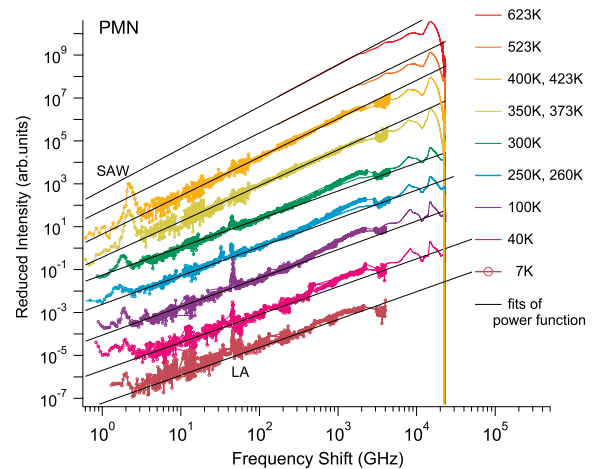

FIG. 3 (color online). Temperature variation of the reduced intensity, $\mathcal{I}(\nu) \equiv \nu I(\nu)/[n(\nu) + 1]$, for selected temperatures. The spectra are vertically shifted only by the multiplication of constants for visual clarity. The solid straight lines represent the least-square fits of the power function, $\mathcal{I} = A\nu^\mu$.
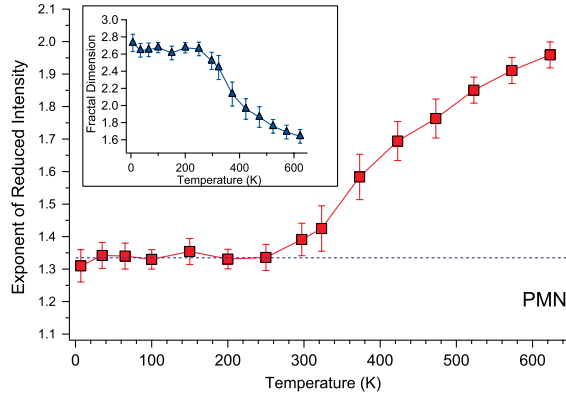
FIG. 4 (color online).   Temperature dependence of the power exponent of the reduced intensity obtained in PMN. The dashed straight line is the fitted asymptotic value (≈ 1.33) obtained by constant-line fitting to the data points below 200 K. The inset shows the temperature dependence of the estimated fractal dimension, d_f, assuming constant values for d_ϕ and d_s.

Raman spectra, the ω^2 slope appears as a superposition of such phonon modes if the power-law component in the lower-frequency region is substantially weaker. Therefore, at the highest temperature (> 600 K), there is little spectral contribution from the power-law quasielastic component. As the temperature decreases from above 600 K, the spectral weight of the power-law component becomes dominant. In Fig. 3, we observe that the slope of the reduced intensity becomes less steep at temperatures lower than 600 K. The temperature change of μ is most rapid at temperatures slightly above 300 K, as we can also see clearly in Fig. 4. The variation in the temperature of μ ceases at around 240 K, and remains constant until the lowest temperature is reached. The asymptotic value at the lowest temperature is found to be 1.33 ± 0.02 (shown by the dashed line in Fig. 4) from line fitting to the data points at and below 200 K. This overall temperature dependence of μ is in strong agreement with those reported for the volume fraction [2,3] and the correlation length of the PNRs [4,5].

Because no theory that is specific to relaxors has been reported, we make a tentative comparison between our data and the existing dynamic scaling theory for disordered systems [20]. According to the percolation theory for disordered systems [20,23,30–32], the reduced intensity of the light-scattering spectrum from an infinite percolation cluster is given as

$$I(\omega) \sim \omega^\mu, \quad \text{with} \quad \mu = d_s\left(\frac{2d_\phi}{d_f} + 1\right) - 1, \quad (2)$$

where d_s and $d_\phi \geq 1$ are the *spectral* or *fracton* dimension and the super-localization exponent, respectively. Equation (2) relates the static exponents (d_ϕ and d_f) of a percolation fractal to the dynamic ones (μ and d_s). Assuming a nonlocalized excitation, and using the value of d_s calculated for a three-dimensional (3D) space, namely,

$d_\phi = 1$ and $d_s = 1.32 \pm 0.01$ [23], we obtain a fractal dimension in PMN at $T \lesssim 200$ K (where $\mu = 1.33 \pm 0.02$) of $d_f = 2.61 \pm 0.09$, which is in good agreement with that obtained theoretically for an infinite percolation cluster in a 3D space, $d_f = 2.53 \pm 0.02$ [23]. Therefore, in PMN, the percolation transition of the PNRs at around 240 K is very likely. This explains the glass-like freezing or the so-called *Vogel-Fulcher* behavior [27] of the temperature dependence of the characteristic relaxation time in relaxors, which has been a long-standing controversial issue. The inset of Fig. 4 shows the temperature dependence of the fractal dimension estimated from Eq. (2) assuming constant d_ϕ and d_s (1.0 and 1.32, respectively).

It should be noted that, in the temperature range in which the large dielectric responses of PMN are found, namely $200 \lesssim T \lesssim 350$ K, μ has values greater than 1.33, which gives $d_f < 2.5$. In such a case of the *incipient* state toward percolation transition, the PNRs should be sufficiently large to strongly respond to the external field, and still be able to freely rotate or vibrate because there should still be space between the adjacent PNRs. Therefore, the situation as it approaches the percolation transition, i.e., a fractal dimension slightly larger than 2, may be an important condition that leads to large responses in relaxors and other systems. Real-space microscopy or small-angle neutron scattering that detect self-similar structures in relaxors are strongly desired to directly determine the fractal dimension. Theories specific to fractal dynamics in relaxors are also desired.

In summary, we reported the temperature dependence of the power-law quasielastic light-scattering spectrum of a single crystal of a relaxor PMN. The frequency of the power-law spectrum was observed to be distributed for at least three orders of frequency, ranging from below 1 GHz to 1 THz. The temperature dependence of the power exponent of the reduced intensity clearly indicated the percolation transition of the PNRs at around 240 K. This also indicated the existence of a fractal formed by the PNRs in the single crystal. The fractal dimension at low temperatures was estimated to be 2.61, whereas that for the *responsive* temperatures was found to be slightly greater than 2. The consideration of such an incipient state toward the percolation transition may be useful in the design of more responsive materials.

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