Theory for Ultrafast Relaxation Dynamics of Ferroelectric Clusters in Paraelectric $BaTiO_3$ Observed with Pump-Probe Speckle Spectroscopy

We develop a theory to clarify the dynamic properties of photo-created ferroelectric clusters observed in the paraelectric $BaTiO_3$ as a real time correlation in the speckle pattern between two soft X-ray laser pulses at just above the paraelectric-ferroelectric transition temperature. It is found that the intensity of the speckle pattern decays as the delay time increases, and the decay rate displays a critical slowing down as the temperature is decreased towards the transition point.

Ferroelectricity refers to the production of a spontaneous polarization (electric dipole moment) at temperatures below the Curie point (T_c). A prototype of the ferroelectric perovskite compounds, barium titanate ($BaTiO_3$) undergoes a transition from the paraelectric cubic to the ferroelectric tetragonal phase at T_c = 395 K. In addition to its extensive applications in technology, there is also an enduring interest in understanding the mechanism of this phase transition. It is generally considered that the transition might be a classic displacive soft-mode type driven by anharmonic lattice dynamics. However, recent studies have also discovered the existence of an order-disorder instability in competition with the displacive transition, and the issue is still controversial.

Direct observations of the creation and evolution of ferroelectric clusters at temperatures around T_c is thus of importance for clarifying the nature of this phase transition. Among the various experimental techniques, soft X-ray laser speckle spectroscopy offers a way of investigating the ultrafast critical dynamics of $BaTiO_3$ [1, 2]. Very recently, Namikawa [3] studied nano-sized polarization clusters in $BaTiO_3$ at just above T_c with plasma-based X-ray laser speckle measurements in combination with pump-probe spectroscopy. In this experiment, schematically illustrated in Fig. 1, the $BaTiO_3$ crystal is subjected to two soft X-ray laser pulses with wavelengths of 160 Å and an adjustable time interval t. After photo excitation by the first pulse, nano-scale ferroelectric clusters are created in the paraelectric $BaTiO_3$, and these tend to be smeared out gradually on the way back to the equilibrium paraelectric state. This relaxation of the clusters thus can be reflected as a variation in the speckle intensity from the second pulse as a function of its delay time from the first one. Hence, by measuring the correlation between two soft X-ray laser pulses, the real-time relaxation dynamics of polarization clusters in $BaTiO_3$ can be clearly represented.

In order to understand the time dependence of the speckle patterns observed in Namikawa's experiment, we propose a theory to describe the optical response of $BaTiO_3$ due to X-ray scattering [4]. We start with a model which consists of the radiation field and the ferroelectric dipole correlation as well as a weak interplay between them. The Hamiltonian reads

$$H = H_p + H_f + H_{pf}\text{, where}$$

$$H_p = \sum_k \Omega_k a_k^+ a,$$

$$H_f = \frac{\omega_0}{2}\sum_l \left(-\frac{\partial}{\partial Q_l^2} + Q_l^2 - c_4 Q_l^4 + \frac{c_6}{3} Q_l^6 \right) - \frac{\omega_0 d_2}{2} \sum_{<l,l'>} Q_l Q_{l'}\text{, and}$$

$$H_{pf} = \frac{V}{N} \sum_{q,q',k} a^+_{k+\frac{q}{2}} a_{k-\frac{q}{2}} Q_{q'-\frac{q}{2}} Q_{-q'-\frac{q}{2}}\ .$$

Here a_k^+ (a_k) is the creation (annihilation) operator of a photon with wave vector k and energy Ω_k. Q_l is the coordinate operator for ionic displacement along the easy axis of $BaTiO_3$ at site l with a dipole oscillatory frequency ω_0. Q_q ($\equiv N^{-1/2}\Sigma_l\, e^{-iql} Q_l$) is its Fourier component for wave vector q, and N is the total number of lattice sites. H_f is based on the extended Krumhansl-Schrieffer model for ferroelectric phonon modes. H_{pf} corresponds to a Raman type bi-linear coupling between the ferroelectric phonon mode and the photons, with V the coupling strength.

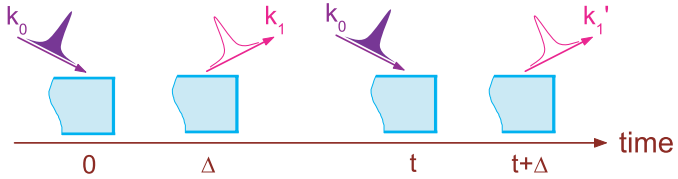

Figure 1
Pulse sequence of the X-ray laser speckle experiment. The pump and probe pulses with wavevectors k_0 create and detect ferroelectric clusters in the sample of paraelectric $BaTiO_3$, and generate new X-ray fields in the directions k_1 and k_1' after a short time interval Δ.

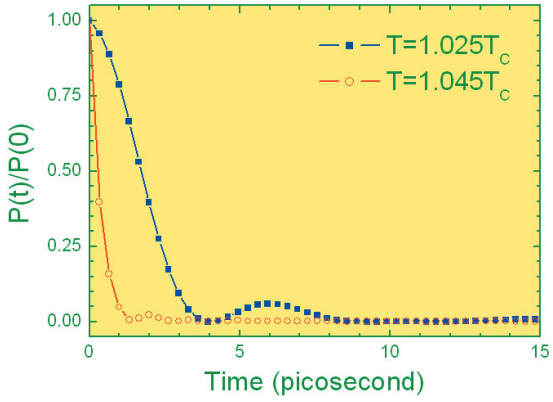

Figure 2
Normalized speckle scattering probability as a function of time for paraelectric $BaTiO_3$ at T=1.025T_c and T=1.045T_c.

In Fig. 2, we show our results for the normalized scattering probability as a function of time at temperatures T=1.025T_c and T=1.045T_c. From this figure we can see that in both cases the probability declines exponentially with time, demonstrating that the photon-created clusters quickly disappear after the excitation, and the system relaxes back to the paraelectric state. At temperatures closer to T_c, a more gentle decay rate is observed, indicative of a critical slowing down of the relaxation time. This is because near T_c, the photo-created clusters are stablized by the strong dipole fluctuation, which appears near T_c as a precursor of the order-disorder transition. Consequently, the relaxation becomes slow. In contrast, at higher temperatures the dipole fluctuation is suppressed, leading to quicker cluster relaxation. These results agree well with Namikawa's experimental discoveries.

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