Coexistence of the Phonon and Relaxation Soft Modes in the Terahertz Dielectric Response of Tetragonal $BaTiO_3$

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The dielectric response to infrared waves polarized along the tetragonal axis of a ferroelectric single-domain crystal of $BaTiO_3$ was determined by time-domain THz spectroscopy and Fourier-transform infrared reflectivity techniques. In addition to the three well-known polar lattice modes, the experiment shows an additional mode of the relaxation type in the THz spectral region, which accounts for the Curie-Weiss behavior of the *c*-axis dielectric constant. A comparison of experimental results with *ab initio* based effective-Hamiltonian simulations allows us to elucidate its relation to the order-disorder model of Comes, Lambert, and Guinier [Solid State Commun. **6**, 715 (1968)].

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The nature of certain structural phase transitions is frequently disputed: order-disorder (OD) or displacive one? In the displacive case, atoms remain associated with their average positions, and phase transition occurs as the positional pattern changes its symmetry. In the OD case, the structural model involves partially occupied sites, and the transition occurs as the symmetry of the occupational distribution is broken. Although it has been shown [1] that the purely displacive and OD cases are merely limiting situations, they are typically thought to describe a majority of the known ferroelectric phase transitions [2].

In the spectroscopic community, it is admitted that the transition type is determined by the behavior of the order-parameter spectral response around the phase transition temperature T_c. If the corresponding phonon mode frequency decreases to zero near T_c, it is a signature of a displacive case (''soft mode behavior''). In the OD case, the relevant phonon frequency stays temperature independent, while *another* strongly temperature dependent excitation of the relaxation type (central mode, CM) occurs (''critical slowing down''). Interestingly, the CM and the soft mode (SM) are found to *coexist* in a number of real ferroelectrics [3].

The *coexistence* of displacive and OD features was also advocated by theory [1,4,5], and $BaTiO_3$ is often quoted as an example in this context [6–8]. To which extent do we understand order-parameter dynamics in this textbook substance? In its *cubic* phase, SM was observed by several methods [9]. The possibility of an additional CM was vividly discussed but the considerable damping of the SM did not allow to draw a convincing conclusion. The fit of recent IR reflectivity data [10] was improved if two modes were assumed, but *ab initio* based calculations were needed to prove the relevance of these two modes [10]. As we will see, it turns out that the coexistence is completely obvious in the ϵ_c dielectric response of $BaTiO_3$ in its *tetragonal* phase (probing field parallel to the spontaneous polarization, $\mathbf{E} \parallel \mathbf{P}_S$).

There are three A_1 type polar phonon modes which should contribute to ϵ_c according to the standard factor-group analysis, well known from previous Raman and IR reflectivity studies: it is the so-called Last (*L*), Slater (*S*) and Axe (*A*) mode [11–14]. Frozen displacements in the tetragonal $BaTiO_3$ correspond to the *S*-mode, and frequency of this mode shows indeed some softening [12–14]. Nevertheless, contribution of these modes to the clamped static permittivity ϵ_c given by Lyddane-Sachs-Teller(LST) relation is barely temperature dependent and much smaller than the clamped static permittivity obtained by direct capacitance measurements [13,14]. This discrepancy suggests [13,14] an additional strongly temperature dependent contribution to the ϵ_c spectrum below 2 THz, which was not revealed so far [15].

The present experiments and calculations provide for the first time direct access to the ϵ_c complex dielectric function of $BaTiO_3$ in the THz frequency range, required for observation of this missing CM. The analysis elucidates its intrinsic nature, its relation to the order-disorder phase transition model of Ref. [16] and its coupling to the SM. This Letter thus settles a discussion that lasted over several decades, and suggests a path towards deeper understanding of structural phase transitions in general.

As a sample we used colorless single-domain crystal plate of $BaTiO_3$, top-seeded solution grown ($T_c = 403.5$ K) at Shanghai Institute of Ceramics. Preliminary THz measurements were performed on an as-received, 120 μm thick, 7×7 mm large, bothside polished plate, with in-plane oriented tetragonal axis. Then the sample was etched in 85% H_3PO_4 acid at 100 °C in order to achieve an optimal thickness for the experiment. Most measurements shown here were done with a 32 ± 1 μm thick sample. THz transmission measurements were performed using a custom-made THz time-domain spectrometer based on an amplified fs Ti:sapphire laser system (Quantronix, Odin) for generation of THz pulses via optical rectification in ZnTe crystal [17]. It allows us to

evaluate the spectrum of complex in-plane dielectric function by a direct procedure, utilizing Fourier transform of the transmitted and reference THz pulse temporal profiles [18], which are detected by electro-optic sampling [17].

Measurements indeed reveal a CM (Fig. 1). Data were first analyzed using a Debye relaxation model

$$\epsilon_c(\nu) = \epsilon_{\mathrm{LST}} + \frac{\Delta\epsilon}{(1 - i\nu/\gamma)}, \tag{1}$$

where γ is the Debye frequency, $\Delta\epsilon$ is the corresponding dielectric step and ϵ_{LST} is the high frequency dielectric contribution including electronic and normal lattice mode contributions. In the fit, ϵ_{LST} was fixed to 33 for all temperatures in agreement with LST estimation from Raman data [14]. On approaching T_c, γ clearly decreases (Fig. 2). The clamped static permittivity $\epsilon(0)$ shows a Curie-Weiss type behavior $\epsilon(0) \approx C/(T_0 - T)$ with $T_0 \approx 420$ K. Data are in a good agreement with the 12 MHz data of Ref. [19]. Low value [2] of the Curie constant $C \approx 4000$ K and the Debye-like frequency response indicate that the ϵ_c critical fluctuations in the tetragonal $BaTiO_3$ are essentially of the OD type.

Existing models suggest [3,4,7] that the dynamics of the CM and of the SM might be interrelated. For this reason, we have also investigated polarized reflectivity spectra in the 30–700 cm^{-1} spectral range, using the spectrometer Bruker IFS 113 v and a thick single-domain $BaTiO_3$ sample of the same origin. Figure 3(a) shows both THz (10–50 cm^{-1}) and far-IR (30–700 cm^{-1}) reflectivity spectra, the former evaluated from the data of Fig. 1 by the Fresnel formula $R = |(\sqrt{\epsilon_c} - 1)/(\sqrt{\epsilon_c} + 1)|^2$. Pronounced temperature evolution of the reflectivity in the whole frequency range up to 300 cm^{-1} suggests that the SM is coupled to the S mode.

To account simultaneously for the three normal lattice modes as well as for the CM, we have assumed a model of three damped harmonic oscillators (DHO's) and one Debye mode (D), defined by

$$\epsilon(\nu) = \epsilon(\nu)' + i\epsilon(\nu)'' = \epsilon_\infty + \mathbf{\Omega}.\mathbf{G}(\nu).\mathbf{\Omega} \tag{2}$$

with Green function $\mathbf{G}(\nu) = (\mathbf{D}'(\nu) - i\nu\mathbf{D}'')^{-1}$, where

$$\mathbf{D}'(\nu) = \begin{pmatrix} 1 & \delta_D & 0 & 0 \\ \delta_D & \nu_S^2 - \nu^2 & \delta_L & \delta_A \\ 0 & \delta_L & \nu_L^2 - \nu^2 & 0 \\ 0 & \delta_A & 0 & \nu_A^2 - \nu^2 \end{pmatrix} \tag{3}$$

$$\mathbf{D}'' = \begin{pmatrix} 1/\gamma_D & 0 & 0 & 0 \\ 0 & \Gamma_S & 0 & 0 \\ 0 & 0 & \Gamma_L & 0 \\ 0 & 0 & 0 & \Gamma_A \end{pmatrix}. \tag{4}$$

Here $\mathbf{\Omega} = (0, \Omega_S, \Omega_L, \Omega_A)$ is an array of mode plasma frequencies [11], and ν_S, ν_L, ν_A and Γ_S, Γ_L, Γ_A are quasiharmonic frequencies and damping constants of S, L and A modes [11]. The three real constants δ_A, δ_L and δ_D stand for coupling of the soft mode S to the other three modes. Two of them (δ_A and δ_L) account for the characteristic line shape asymmetry of A and L modes (see, e.g., Refs. [12,14]). Mode D is specified by its *bare* relaxation frequency γ_D and the D-S coupling constant δ_D which induces its effective dielectric strength (vanishing strength of the bare Debye mode ensures convergence of the integral in the conductivity sum rule [11]). In order to deter-

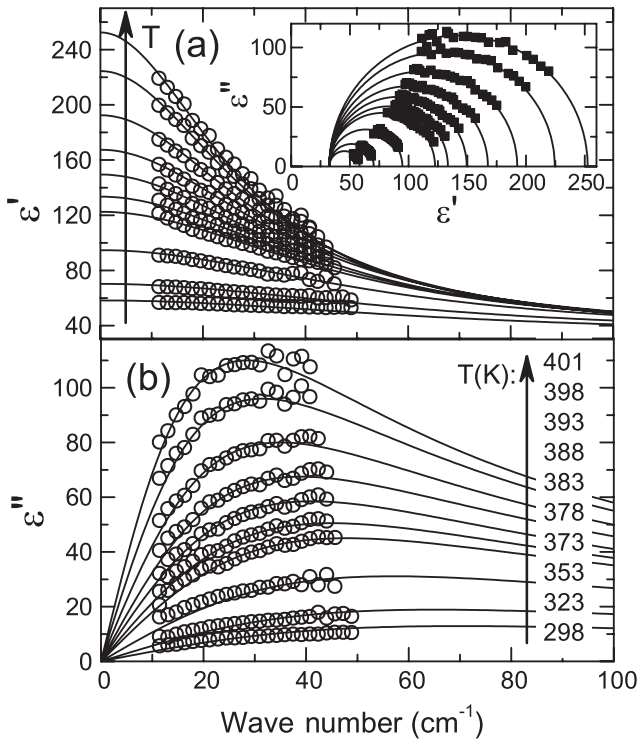

FIG. 1. Frequency dependence of real (a) and imaginary (b) part of complex permittivity ϵ_c in the tetragonal phase of $BaTiO_3$ as obtained by THz spectroscopy technique. Continuous lines comes from the Debye model [Eq. (1)] adjusted to the data. Inset: Same data in Cole-Cole representation.

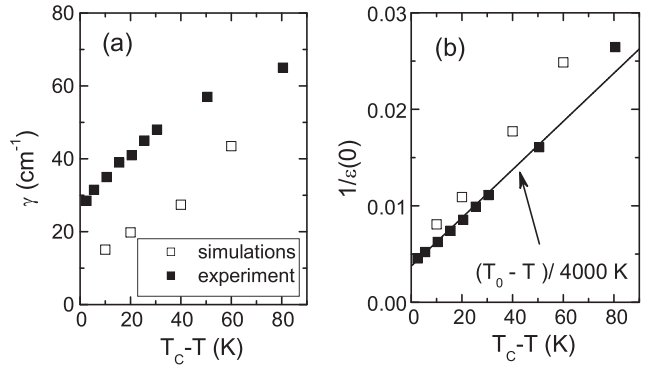

FIG. 2. Temperature dependence of (a) Debye mode frequency and (b) inverse static permittivity. Full symbols are from the THz experiment, open symbols are derived from MD simulations described in the text.

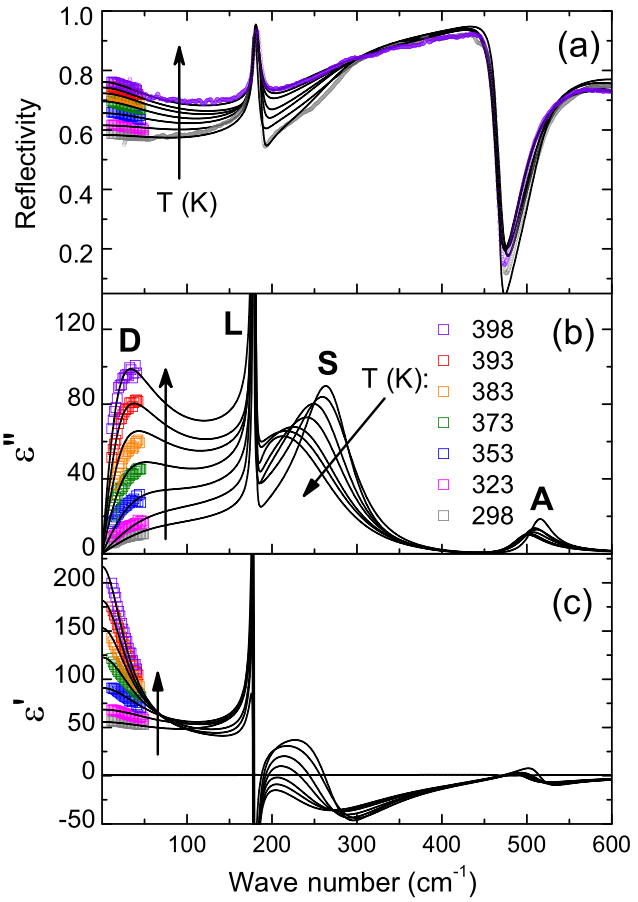

FIG. 3 (color online). Dielectric response of A_1-symmetry modes of tetragonal $BaTiO_3$. From top to bottom: reflectivity spectra (a), imaginary (b), and real (c) part of the dielectric function, respectively. Continuous lines are obtained from the simultaneous fitting of THz and far-IR data to the model of Eqs. (2)–(4). For clarity, far-IR data are shown for highest and lowest temperatures only. Maxima in the loss spectrum correspond to the Debye (D), Last (L), Slater (S), and Axe (A) modes.

mine the 13 parameters of this model, additional constraints were needed. Full details of our analysis will be given elsewhere. However, we can indicate that the temperature behavior of the DHO parameters is essentially those reported in Ref. [14] and γ_D is of the order of 100 cm^{-1}.

Imaginary and real parts of the adjusted dielectric function are shown in Fig. 3(b) and 3(c). At room temperature, there are three maxima in the loss spectrum [Fig. 3(b)], corresponding to transverse optic (TO) frequencies of the L, S, and A modes. As the temperature is increasing, the extraneous D peak arises from the low frequency tail of the soft S mode. It becomes clearly separated from the three regular lattice modes near T_c.

Let us note that if L and A modes are neglected, the above model would reduce to the famous formula for a single DHO with an extra self-energy term $-\delta_D^2/(1 - i\nu/\gamma_D)$ describing an additional channel [20] for decay of phonon fluctuations with frequencies lower than the characteristic frequency γ_D. Could this decay be associated with defects or with an additional degree of freedom? To confirm its intrinsic origin, we have carried out molecular dynamics (MD) simulations with a model of $BaTiO_3$ that possesses only a *single* polar degree of freedom per unit cell [10]: the computational technique employed here to treat the case of ferroelectric phase is an extension of the one used in Ref. [10]. It is based on the effective Hamiltonian with parameters derived from first principles, and its only dynamical degrees of freedom are inhomogeneous and homogeneous strain variables and "local soft modes" (associated with the lowest optical phonon modes). Classical molecular dynamics (MD) simulations are typically performed with a $14 \times 14 \times 14$ supercell at fixed number of particles, volume and energy (NVE-ensemble), using about 11×10^6 individual MD steps with 1 fs duration. The initial state is prepared using equilibration cycle with 20000 MD steps at constant number of particles, pressure and temperature and 5000 MD steps within a NVE-ensemble. The dielectric response is calculated using Fourier transform of the total dipole moment autocorrelation functions as described in Ref. [10] and references therein.

The ϵ_c dielectric response obtained from MD simulations indeed reveals two loss bands, a broad vibrational band around 300 cm^{-1} and a Debye-like mode critically slowing down from about 40 cm^{-1} to about 15 cm^{-1} as T approaches T_c from below. Moreover, there is a remarkable agreement between the predicted and the measured Curie-Weiss constant [see Fig. 2(b)]. Thus, both experimentally observed anomalous modes (D and S) find their counterparts in this model, which automatically implies that such modes are associated with the dynamics of the *same* polar degree of freedom per unit cell.

X-ray diffuse scattering and phase transition sequence of $BaTiO_3$ were beautifully explained by the famous Comes-Guinier-Lambert model, based on chainlike correlated $\langle 111 \rangle$-type off-center Ti displacements [16]. In this purely OD model, the tetragonal state with spontaneous polarization $P_S \parallel (001)$ corresponds to the preferential occupation of the 111, $1\bar{1}1$, $\bar{1}11$, and $\bar{1}\,\bar{1}\,1$ quadruplet, obviously privileged by the established (001) molecular field. The eight-minima local potential was later confirmed by several other experimental and theoretical techniques [6,21,22]. Thus, it is natural to suspect that the CM is due to hops between a privileged ("ground") and an "excited" minimum. Such hops can be indeed seen in our MD simulations. It is indicated in Fig. 4 showing the p_z component ($z \parallel P_S$) of the local dipole moment *vs* time. Moreover, the hops of p_z in the nearest-neighbor unit cells along the z-axis occurs at practically the same instants, as expected [16,23]. If $p_z < 0$ is considered as a signature of the excited state, the average lifetime is about $\tau_e = 40$ fs in the excited state and about $\tau_g = 900$ fs in the privileged

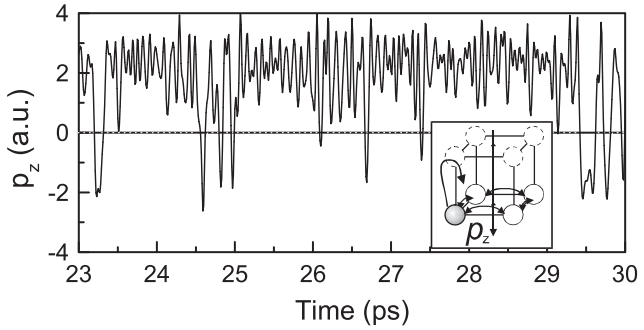

FIG. 4. Dipole moment p_z of an arbitrarily chosen unit cell as a function of time in MD simulations at $T = T_c - 10$ K. The inset shows the 8 possible off-center Ti sites. The Ti ion mostly fluctuates around and among the 4 sites preferred by the molecular field (full circles, $p_z > 0$). Occasionally, it also hops towards the excited site (dashed circles, $p_z < 0$). These hops correspond to the few negative spikes encountered on the p_z trajectory.

one. The resulting average hopping rate $f_{\mathrm{hop}} = 1/(2\pi\tau_e) + 1/(2\pi\tau_g) \cong 4$ Thz ($\sim$135 cm^{-1}) is comparable with the experimental hopping frequency γ_D. In this way, MD simulations confirm the relation of the relaxation mode D with the genuine OD dynamics of the eight-site model.

We have checked that the coupled CM—SM model is equally well applicable to the simulated ϵ_A response ($\mathbf{E} \perp \mathbf{P}_s$) and to the measured and simulated cubic-phase dielectric spectra [10]. Thus, the coexistence of two distinct fluctuational modes associated with the same normal coordinate is a generic feature. The need for both modes is obvious in the OD case: a small-amplitude intrawell vibrational mode has to coexist with large-amplitude interwell hops. Our results indicate that such split modes are present also in situations that are intermediate between displacive and OD cases.

In summary, we have found a pronounced CM in the ϵ_c dielectric response of tetragonal $BaTiO_3$, which (i) is clearly separated from the response of the partially soft S-phonon mode, (ii) accounts for OD dynamics associated with stochastic interwell hops, (iii) shows a critical slowing down tendency near the tetragonal-cubic-phase transition, and (iv) leads to a Curie-Weiss behavior of the clamped static permittivity with a Curie-Weiss constant of about 4000 K. We hope that our analysis will help to elucidate the enigmatic CM paradigm observed near structural phase transitions of the ''ambivalent'' character.

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