# Light Scattering Study of the Coupled Soft-Optic and Acoustic Mode in Hexagonal Barium Titanate

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Low-frequency light scattering spectra of hexagonal barium titanate have been observed in the temperature region from 40 to 300 K. An intense central peak was observed near the phase transition temperature $T_0 = 222$ K and was assigned to be caused by the coupled soft-optic and acoustic mode. The coupled-mode model has been employed to fit experimental data and gives good agreement with the observed spectra. The $\omega_0^2/\Gamma_0$ ratio of soft-optic-mode frequency $\omega_0$ and damping constant $\Gamma_0$ and the bilinear coupling constant $A$ exhibit linear dependence on $T - T_0$ indicating mean-field behavior.

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Hexagonal barium titanate ($h$-$BaTiO_3$) undergoes successive structural phase transitions at $T_0 = 222$ K and $T_C = 74$ K and displays both ferroelectric and ferroelastic properties below 74 K [1,2]. Above 74 K, $h$-$BaTiO_3$ remains paraelectric, but it exhibits piezoelectric properties below 222 K as the crystal symmetry changes to a noncentrosymmetric phase at $T_0$. The results of extensive x-ray, Raman, and hyper-Raman studies have shown that the phase transition at $T_0 = 222$ K is the second-order phase transition from the $6/mmm$ hexagonal phase (phase I) to the 222 orthorhombic phase (phase II) [3–6]. This phase transition possesses unusual characteristics: the silent soft-optic mode at the Brillouin zone center is the trigger of the transition at $T_0 = 222$ K [5], and below $T_0$ paraelectric properties are still observed [1,2]. Furthermore, the soft mode is underdamped until very near the phase transition temperature, very different from the paraelectric cubic–ferroelectric tetragonal phase transition of the classic $BaTiO_3$ perovskite polymorph ($p$-$BaTiO_3$) where the soft-optic mode is largely overdamped well above the phase transition temperature [7,8]. From symmetry considerations, bilinear coupling between the soft mode and the $c_{66}$ transverse acoustic mode is symmetry allowed below $T_0$. However, this coupling is not the piezoelectric coupling that is often found in ferroelectric phase transitions, since in the present case the soft mode is not a polar mode.

We have previously reported the temperature dependence of the frequency shift of the $c_{66}$ acoustic mode observed by Brillouin scattering [9]. Here we present the results for the central peak observed around $T_0$ by a high-resolution wide-range light scattering experiment performed with Sandercock-type tandem Fabry-Pérot. First we discuss the possible coupling between the soft-optic and acoustic modes in $h$-$BaTiO_3$. Next we discuss the progress we have made using light scattering to study the phase transition at $T_0$. High-resolution light scattering experiments are clearly helpful to provide information about the dynamics of the phase transition, from the point of view of both acoustic mode behavior and the aspects of the soft-optic and acoustic mode coupling phenomenon. Finally, we discuss features of the central peak found around $T_0 = 222$ K and the characteristics of the phase transition. This is the first observation of the central peak in hexagonal $BaTiO_3$, identified as the scattering from the coupled acoustic-optic mode.

The light scattering system used in the present study included a Sandercock-type tandem Fabry-Pérot interferometer that allows high resolution (finesse more than 100) in a wide-range measurement [10]. Detailed descriptions of the experimental system and crystal growth are presented elsewhere [2,9].

Light scattering from a coupled acoustic-optic mode was extensively studied, especially in connection with ferroelectric phase transitions [11–13]. For $h$-$BaTiO_3$, it has been found that the soft mode of the phase transition at $T_0$ is the nonpolar $E_{2u}$ optic mode at the Brillouin zone center [5]. In the hexagonal phase, this mode is both Raman and infrared inactive. Further, the existence of inversion symmetry in the hexagonal phase does not allow bilinear coupling between acoustic and optic modes. However, below $T_0$ the soft mode becomes Raman active as the crystal symmetry changes, and bilinear coupling between the soft-optic mode and the acoustic mode is now symmetry allowed. In the $-x(y,x+y)z$ scattering configuration, a phonon propagating in the [101] direction can be observed. The soft mode frequency is decreasing dramatically as it approaches the acoustic shear mode frequency near the phase transition temperature, and, therefore, an anomalous behavior of the coupled optic-acoustic mode can be expected. The shear acoustic mode $\frac{1}{2}(c_{66} + c_{44})$ is polarized in the [010] direction and is propagating in the direction of wave vector $k$ parallel to [101]. The equation of motion for the coupled acoustic and optic mode can be written in terms of the strain defined as $\Delta s = \partial \Delta u_2/\partial r = ik\Delta u_2$ and the normal coordinate of the soft mode $\Delta Q_1$ as

$$(-\omega^2 + \omega_a^2 + i\Gamma_a)/k^2\Delta s + (A/\rho)\Delta Q_1 = \sigma/\rho\,, \quad (1)$$

$$(A/m_1)\Delta s + (-\omega^2 + \omega_0^2 + i\Gamma_o)\Delta Q_1 = F_1^Q/m_1\,, \quad (2)$$

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where $\Gamma_a$ and $\Gamma_o$ are the damping constants of the acoustic and optic modes, respectively; $\rho$ and $m_1$ are the mass density and effective mass of the $E_{2u}$ mode; $\sigma = (\sigma_6 + \sigma_4)/\sqrt{2}$ where $\sigma_i$ is the mechanical stress; $F_1^Q$ is the force conjugated to $\Delta Q_1$; the acoustic mode frequency and coupling constant are defined as $\omega_a^2 = k^2(c_{66} + c_{44})/2\rho$ and $A = a/\sqrt{2}$. Details of the derivation can be found in Ref. [11].

Typical light scattering spectra from $h$-$BaTiO_3$ in the hexagonal phase are shown in Fig. 1(a) for $-x(y,x+y)z$ (V-open) and 1(b) for $-x(y,x)z$ (V-H) scattering geometry, where $x$, $y$, and $z$ correspond to the $a$, $b^*$, and $c$ axes, respectively. The light scattering peak in the spectrum obtained in V-H scattering geometry is assigned to the $\frac{1}{2}(c_{66} + c_{44})$ mode according to the polarization selection rules in the $6/mmm$ hexagonal phase, where this acoustic mode is expected to exhibit a depolarized peak. The other two peaks in the spectrum in V-open configuration are the mixed mode peaks, the quasilongitudinal and quasitransverse modes. The double peak around 50 GHz is a "ghost" peak caused by the tandem Fabry-Pérot interferometer. The temperature dependence of light scattering spectra in the $-x(y,x+y)z$ configuration has been studied near the phase transition; three typical spectra are presented in Fig. 2. The intense central peak is clearly observed below $T_0$, and its intensity and shape exhibit substantial changes near the phase transition temperature. The acoustic peak, clearly distinguishable at room temperapture [Fig. 1(a)], is merging with the central peak as the temperature is lowered through the phase transition point. The maximum intensity of the central peak is found below $T_0$, near $T = 217$ K. An intensity dip is clearly seen around 22 GHz. This dip is characteristic of the coupling between the optic and acoustic modes, as has been previously discussed in several papers [11–13]. The principal feature of this anomalous peak is that significant changes in spectral shape are observed below the phase transition temperature $T_0$, as will be discussed further.

On the other hand, in the $x(z,z+x)y$ configuration, the peak near 22 GHz remains discernible as the temperature is lowered through the phase transition point, and it does not show anomalous features of the coupled mode, unlike the spectra in the $-x(y,x+y)z$ configuration. This acoustic mode peak has been assigned to the $\frac{1}{2}(c_{55} + c_{44})$ acoustic mode (Fig. 3). This result can be anticipated from symmetry arguments, which conclude that both $c_{55}$ and $c_{44}$ components cannot couple to the order parameter in the orthorhombic phase. Based on the above considerations, the anomalous central peak in Fig. 2 has been assigned to the scattering from the coupled acoustic-optic mode.

Theoretical and experimental spectra obtained with the $-x(y,x+y)z$ scattering geometry are presented in

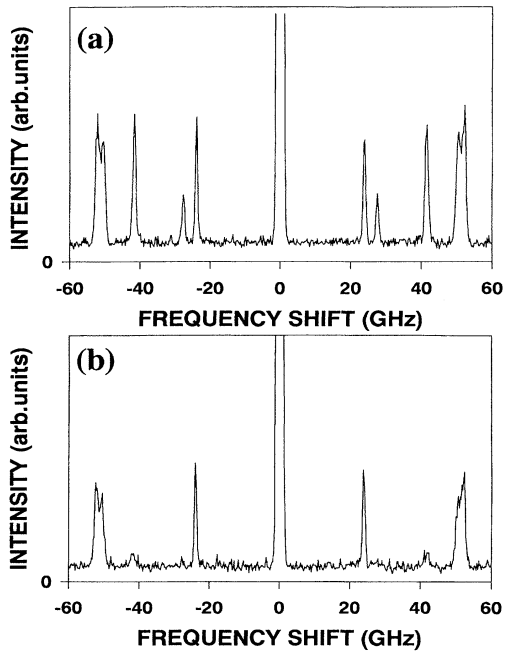


FIG. 1. Light scattering spectra of $h$-$BaTiO_3$ in hexagonal phase ($T = 243$ K) in (a) $-x(y,x+y)z$ (V-open) and (b) for $-x(y,x)z$ (V-H) scattering configuration.

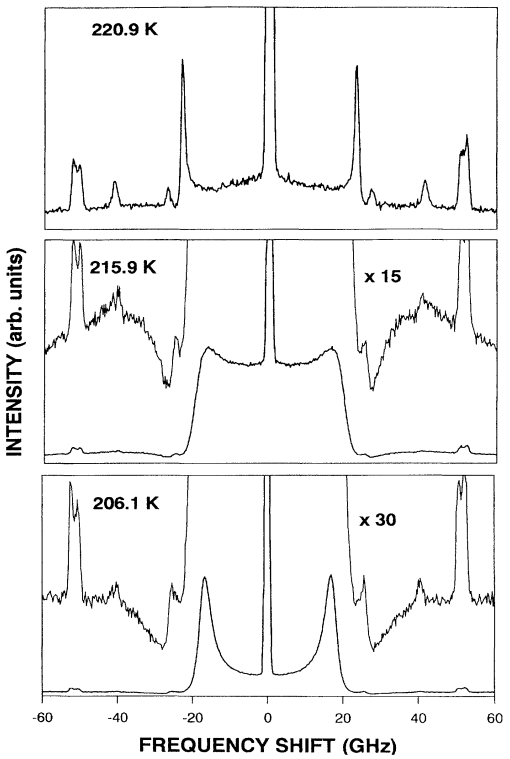


FIG. 2. Light scattering spectra obtained in $-x(y,x+y)z$ scattering geometry at several temperatures near $T_0$.

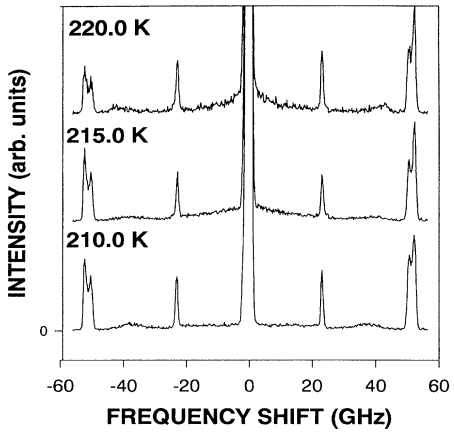


FIG. 3. Light scattering spectra obtained in $x(z, z + x)y$ geometry near $T_0$.

Fig. 4. The theoretical curve was fitted to the experimental spectra using the last squares method [14]. The Rayleigh peak, mixed mode peaks around 25 and 41 GHz, and the ghost doublet peaks around 50 GHz were not included in the theoretical fit. Despite the fact that the experimental spectra change their shapes remarkably near the phase transition temperature, all the spectra are fitted very well in the framework of the coupled-mode model (Fig. 4). Therefore we can conclude that the coupled-mode model is an adequate theoretical model for the phase transition at $T_0$. From the fitting analysis we can obtain the parameters necessary to discuss the nature of the phase transition at $T_0 = 222$ K. Figure 5 is a plot of the temperature dependence of the bilinear coupling constant between acoustic and soft-optic modes obtained from the theoretical fit. The coupling constant is zero at $T_0$, and its value increases at lower temperatures. The bilinear coupling constant is related to the coupling constant between the strain and the square of $Q_i$ in the mean-field theory in the following manner:

$$A \sim \alpha_3 Q_s \sim (T - T_0)^{1/2} \qquad (T < T_0), \qquad (3)$$

where $\alpha_3$ is the coupling constant between strain $s_6$ and the product of $Q_1$ and $Q_2$ [15]. By definition, the order parameter $Q_s$ is zero above $T_0$; therefore the coupling constant has a nonzero value only at $T < T_0$. A theoretical curve proportional to $(T - T_0)^{1/2}$ has been fitted to the experimental data (Fig. 5). The theoretical and experimental data agree fairly well in the temperature region down to about 20 K below $T_0$, indicating the mean-field behavior of the coupling constant in this temperature region. As we pointed out above, the substantial changes in spectral shape occur mainly below $T_0$. Generally, the amplitude of the soft-optic mode is maximum at the phase transition temperature; however, in our case the bilinear coupling constant is zero at $T_0$ and the coupled-mode feature is not expected. As the temperature is lowered from $T_0$, the amplitude of the soft mode becomes smaller, but the coupling constant becomes much larger, and thus the effects of the soft mode coupling to the acoustic mode become notable. As a result of the competition of these two tendencies, the coupled-mode feature appears

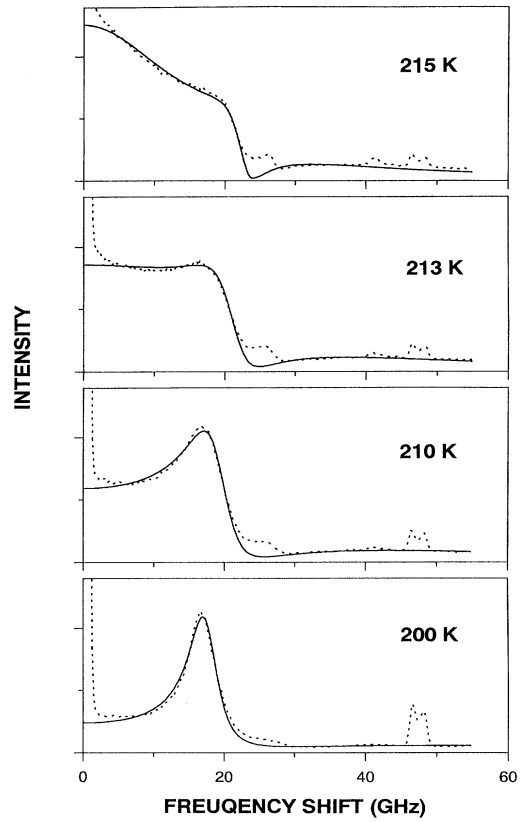


FIG. 4. Theoretical and experimental light scattering spectra in $-x(y, x + y)z$ configuration near $T_0$. Solid lines represent theoretical curves; dotted lines represent experimental spectra.

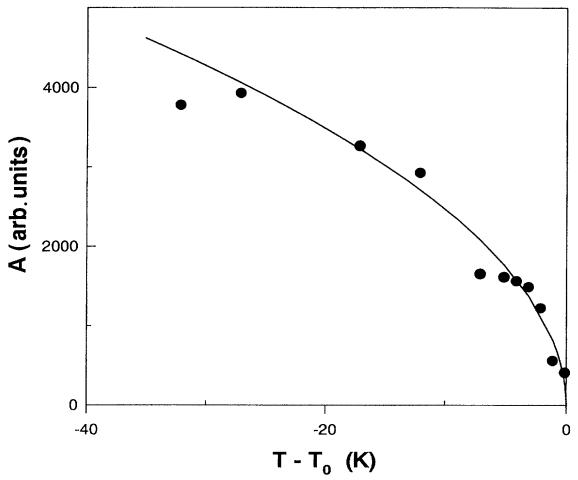


FIG. 5. Temperature dependence of the bilinear coupling constant $A$ below $T_0$. Solid line is the theoretical curve proportional to $(T - T_0)^{1/2}$.

stronger below $T_0$ than at $T_0$. On further decreasing temperature, the soft mode frequency becomes much higher than that of the acoustic mode and the coupled-mode features disappear at approximately 30 K below $T_0$.

The ratio of the square of the frequency of the soft mode and the damping constant, $\omega_0^2/\Gamma_0$, obtained from the theoretical fit is plotted against the temperature in Fig. 6. In the coupled-mode model, $\Gamma_0$ and $\omega_0$ are treated as independent parameters. However, the soft mode is overdamped near the phase transition and does not have perceptible oscillatory features; therefore $\omega_0$ alone is no longer a feasible quantity to specify the state of the soft mode. It is known in such situations that the shape of damped oscillator spectra does not depend considerably on $\Gamma_0$ and $\omega_0$ independently except for the small difference in the spectrum's shoulder [16]. Instead, it depends substantially on the ratio $\omega_0^2/\Gamma_0$, which now represents the quantity of immediate experimental interest. Physically, this ratio corresponds to the inverse of relaxation time, $\sim 1/\tau$, in systems that show the order-disorder type of phase transition. In Fig. 6, $\omega_0^2/\Gamma_0$ clearly exhibits a linear dependence on temperature. Curie-Weiss behavior of $1/\tau \sim \omega_0^2/\Gamma_0$ is observed within 20 K below $T_0$. The results of hyper-Raman scattering have previously shown that the square of the silent soft $E_{2u}$ mode frequency above $T_0$ depends on temperature as $\omega_0^2 \sim (T - T_0)$ [5], which is in good agreement with mean-field theory. On the other hand, Raman scattering experiments [4] have proposed the dependence $\omega_0^2 \sim (T - T_0)^{2/3}$ to be held in a wide temperature range down to 100 K below $T_0$, and we consider the deviation from mean-field behavior as evidence of the critical region, as is often seen in nonferroelectric structural phase transitions [16]. In the present work we have performed the analysis in a temperature range closer to $T_0$ than in the Raman scattering study and have found that both the bilinear coupling constant $A$ and

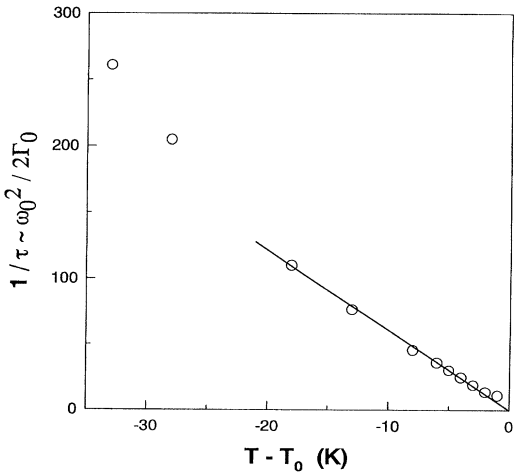


FIG. 6. Temperature dependence of $\omega_0^2/\Gamma$ ratio of soft-optic mode frequency and damping constant obtained from theoretical fit.

$1/\tau \sim \omega_0^2/\Gamma_0$ show linear dependence on $T - T_0$, thus providing good confirmation of the mean-field behavior. These results do not support the previous statement of the existence of critical behavior down to 100 K below $T_0$. It is not yet clear why the frequency of the soft-optic mode in the temperature region below $T_0$ where the mode is underdamped shows deviation of the temperature dependence from $\omega_0^2 \sim T - T_0$, although the elastic stiffness constant exhibits mean-field behavior in that range [9]. Light scattering measurements in the region below $T_0$ are now in progress.

A coupled-mode analysis based on the phenomenological theory of light scattering from coupled modes gave good agreement with the results of light scattering experiments for $h$-$BaTiO_3$ near the phase transition at $T_0 = 222$ K. The intense central mode is found to be caused by scattering from the coupled soft-optic and acoustic modes, with the bilinear coupling constant showing mean-field behavior below $T_0$.

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