Observation of a Doublet in the Quasielastic Central Peak of Quantum-Paraelectric $SrTiO_3$

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Rayleigh-Brillouin light-scattering spectroscopy performed on oriented samples of tetragonal $SrTiO_3$ reveals the presence of a new doublet at low temperatures. This scattering, also seen in $KTaO_3$, appears in addition to the broad central peak already reported by Lyons and Fleury. The likely origin of this spectral component is second sound, the wavelike propagation of entropy.

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Quantum paraelectrics (QPE's) are dielectric crystals that just fail becoming ferroelectric at low temperatures T owing to the relatively large zero-point motion of their ions [1]. They are characterized by a strong increase of their dielectric constant on cooling, followed by saturation at a high value [2]. There is new interest in QPE's as indications for a novel phase-transition-like anomaly were obtained recently in $SrTiO_3$ by electron paramagnetic resonance [3]. It occurs at a temperature $T_q \approx 37$ K, very close to the Curie-Weiss temperature T_c extrapolated from the high-T dielectric constant. Since there is so far no evidence for a structural change at T_q, the existence of this anomaly prompted theoretical [4] as well as experimental studies, including an investigation of the modes of low frequencies ω and wave vectors $\boldsymbol{q}$ [5]. Given the huge dielectric susceptibility χ of the QPE regime, $\chi > 10^4$ in $SrTiO_3$, one expects fairly large dynamic polarization clusters and related strongly anharmonic interactions. This suggested a careful reinvestigation of light scattering spectra in the Rayleigh-Brillouin range. An earlier study of QPE oxides revealed that, besides the thermal diffusion peak, a broad central peak (BCP) is present [6]. Its intensity and width were reported to decrease linearly with T. In this Letter it is shown that for $SrTiO_3$, and also for $KTaO_3$, the BCP becomes considerably more complex at low T than previously thought. On approaching the QPE regime we find that it contains several components, in particular a T-dependent doublet that can be assigned to second sound. Below T_q, symmetry forbidden scattering is also observed.

The QPE regime of $SrTiO_3$ occurs at T much below the well known cubic-to-tetragonal structural transition which is produced by an instability at the R corner of the Brillouin zone at $T_a \approx 105$ K. The resulting anisotropy in the dielectric properties [7] becomes rather strong near T_q. The related transverse optic (TO) branches split into a high-ω singly degenerated A_{2u} and low-ω doubly degenerated E_u components [7,8]. Below T_a, macroscopic crystals normally form domains with the c axis along any one of the former cubic directions. We found it necessary to orient these tetragonal domains with $\boldsymbol{c}$ along one of these directions, say, [001]. This was achieved by applying a moderate uniaxial pressure (of $\approx$1 kbar for Verneuil-grown crystals) along a cubic $[1\bar{1}0]$ axis while the sample is cooled through T_a. As the ratio of the unit cell parameters c/a is greater than 1, this forces the c axis in the plane perpendicular to the pressure axis [9]. The pressure can be released at lower T, say, below $\approx$50 K, and the domains maintain their orientation as observed in neutron scattering [5]. This procedure orients the domains but does not remove antiphase boundaries. Since 1 kbar affects appreciably the dielectric properties [7], the release of the pressure is significant. Smaller orienting pressures are sufficient for top-seeded-solution grown (TSSG) crystals, but these are generally colored which is unfavorable for optical spectroscopy at low T. The results presented here were mainly obtained on good quality, clear Verneuil-grown samples. However, the remaining internal stresses of these crystals prevent a meaningful optical polarization analysis. The latter was performed on a TSSG crystal.

The light-scattering spectra were excited with a single mode argon-ion laser operating at 5145 Å. The samples were places in a He-flow cryostat equipped with a vertical pressure rod similar to that described in Ref. [10]. This geometry allows the study of scattering with momentum exchange $\boldsymbol{q}\|$ to [001] and to [110]. Different samples must be used for 90° and 180° scattering. For 90° scattering, the vertical faces are cut at 45° to the [001] and [110] directions. In that case all vertical faces are antireflection coated with a single quarter-wave layer of Al_2O_3. This precaution is essential owing to the high refractive index of $SrTiO_3$, otherwise reflections superpose scattering from different $\boldsymbol{q}$ directions. The spectra were analyzed with a six-pass tandem interferometer that provides excellent contrast, and suppresses the overlap of orders [11]. This instrument is much superior to the former iodine-filter one [6] for the observation of quasielastic scattering. Furthermore, previous $SrTiO_3$ investigations concentrated around T_a [12], while $KTaO_3$ (for which T_c is $\sim$10 K) was measured only above $\sim$25 K [6]. This explains that the novel features found here escaped previous measurements.

Figures 1 and 2 illustrate the results obtained in backscattering with $\boldsymbol{q}\|$ to [001]. In Fig. 1, the free spectral range (FSR) is 60 GHz, and the instrumental full width is $\sim$0.6 GHz at half-height. The photocounts

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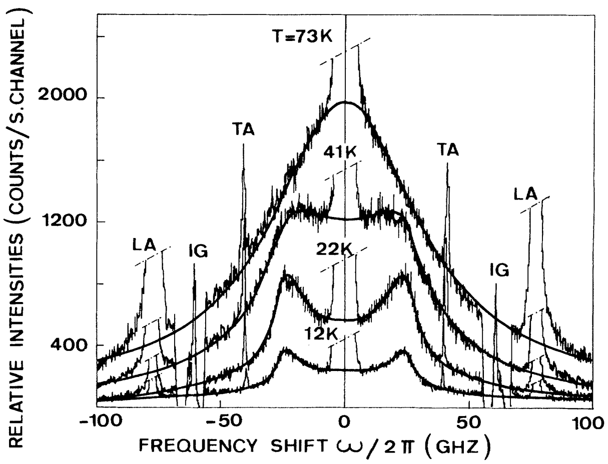

Fig. 1. Typical temperature evolution of backscattering Brillouin spectra of $SrTiO_3$ measured with $\boldsymbol{q}\|[001]$. The FSR is 60 GHz. The instrumental ghosts are marked IG, and the instrumental central peak ICP is off-scale. Besides the broad central component, LA and TA phonons are visible. The solid lines are phenomenological fits.

are recorded in 1024 channels for an integrated duration of the order of 1 s per channel. The features marked ICP and IG are the instrumental central peak and first order ghosts, respectively [11]. The expended vertical scale emphasizes the BCP, the ICP being way off scale. The longitudinal acoustic (LA) phonon peaks are also off scale: They reach 1.4×10^4 at 73 K and 3.3×10^3 at 12 K. Scattering from the transverse acoustic (TA) phonons, forbidden in this geometry, appears weakly.

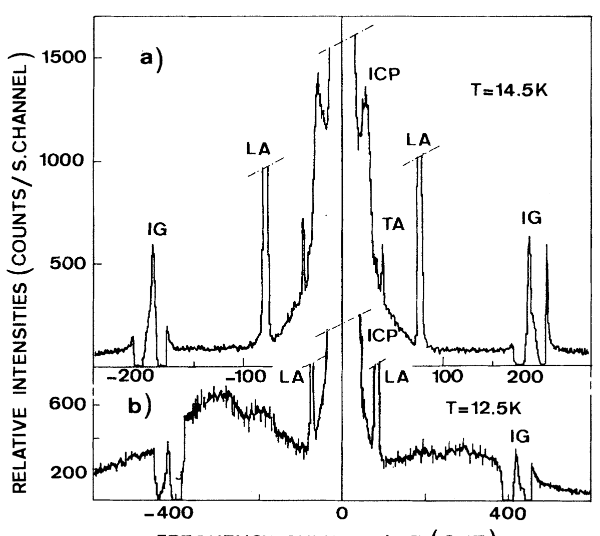

FIG. 2. Spectra as in Fig. 1 but obtained at lower resolutions: (a) with a FSR of 187 GHz, (b) with a FSR of 417 GHz. The Antistokes side is on the right ($\omega > 0$).

We presume this is related to internal stresses in the sample, since the strength of this signal depends on the cooling rate, and since it decreases considerably if T is kept constant for several days. For comparison, in 90° scattering with $\boldsymbol{q}\|$ to [001], both LA and TA are allowed, and the strength of the TA mode is about half that of the LA one. The prominent feature in Fig. 1 is clearly the BCP whose shape evolves from approximately a single Lorentzian at 73 K to a well developed doublet below T_q.

Figure 2 illustrates spectra of lower resolution. In Fig. 2(a) one recognizes that several spectral components contribute to the BCP, although they might be difficult to unravel. Moving up in frequency shift ω, and ignoring the thermal diffusion peak [6] that lies within the ICP, there is first the doublet falling off quite sharply as ω approaches ω_{TA}. Its shape, better seen in Fig. 1, is fitted reasonably well with a standard Green function,

$$S_D(\omega) = I_D \omega_D^2 \Gamma_D / \pi[(\omega_D^2 - \omega^2)^2 + \omega^2 \Gamma_D^2]. \quad (1)$$

where I_D is the integrated intensity of S_D. The doublet seems to ride on another signal, whose wings appear in Fig. 2(a) at frequencies between ω_{TA} and ω_{LA}. Inspired by the high-T results [6], we approximated the component, $S_L(\omega)$, with a Lorentzian centered at $\omega = 0$, of width Γ_L, and of integrated intensity I_L. Further, there appears in Fig. 2(a) a very broad background approximately constant at this resolution. Its height is well above the dark counts that contribute only ~5 to that spectrum. This background is absent above T_q, and it increases remarkably strongly below T_q. Figure 2(b) indicates that this signal belongs to the wings of two peaks located at approximately 280 and 200 GHz (≈9 and 7 cm^{-1}), respectively. This is the region of the soft ferroelectric mode of symmetry E_u [7,8], which however should be absent in normal Raman scattering from the paraelectric phase [13]. We conjecture that first-order E_u scattering appears in the strong QPE regime owing to large fluctuations clusters that locally break the symmetry. Their electric polarization, preferably oriented along $\boldsymbol{a}$ or $\boldsymbol{b}$ [7], then splits the doubly degenerated mode. Finally, the trailing foot of the LA phonon seen in Fig. 1 at $|\omega| > |\omega_{\mathrm{LA}}|$ suggests a coupling with the BCP, in fact with the doublet. A coupled-mode expression can be used instead of Eq. (1) to parametrize this feature successfully. However, such fits add more parameters which are not useful to a first discussion. In spite of this coupling, the LA-phonon integrated intensity is found accurately proportional to T over the range of interest.

A series of spectra was fitted using the above expressions. The satisfactory quality of the fits is illustrated by the solid lines in Fig. 1. The main result is that ω_D is nearly constant at low T, as shown for backscattering by the full squares in Fig. 3. The width Γ_D increases approximately linearly with T^2, taking a value of 10 GHz at 15 K and of 50 GHz at 60 K. From there up, the

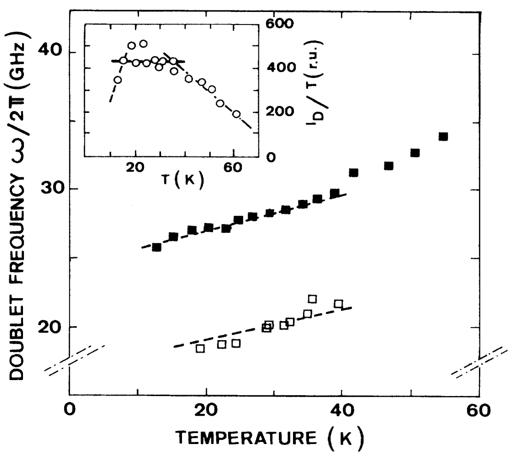

FIG. 3. The doublet frequencies ω_D observed for $q \| [001]$ in 180° (■) and 90° (□) scattering. The corresponding values of q are 6.0×10^{-3} and 4.3×10^{-3} Å^{-1}, respectively. The dashed lines are guides to the eye whose ordinates are separated by $\sqrt{2}$. The inset shows the integrated doublet intensity normalized by T; the lines are guides to the eye.

doublet is not only much broadened, but its intensity decrease to such an extent that ω_D cannot be determined with confidence. The intensity I_D derived from the fits depends of course on the Lorentzian form assumed for S_L. In this sense, the values I_D/T in the inset are only indicative. In 90° scattering, owing to the less efficient light collection, much longer accumulation times were required. For this reason the corresponding values of ω_D could not be determined above 40 K. The dashed lines in Fig. 3 are separated vertically by the ratio of the respective q values. This emphasizes that ω_D is proportional to q. Hence, an effective velocity $v = \omega/q$ can be defined, with $v \approx 2700$ m/s at low T. On the other hand, in accordance with previous results [6], we find that Γ_L is independent of $|\boldsymbol{q}|$.

Spectra were also taken with $\boldsymbol{q} \| [110]$, both in 90° and in backscattering. For that direction down to the lowest temperatures, the doublet does not develop beyond a bulge, not much more pronounced that the one that can be guessed on the top curve of Fig. 1. Spectral intensity is however present, as indicated by the trailing foot of the LA phonon, now located at $|\omega| < |\omega_{\mathrm{LA}}|$. Finally, a light polarization analysis was undertaken in 90° scattering with a TSSG crystal. It confirmed that both the doublet S_D and the underlying signal S_L are essentially polarized, corresponding to VV scattering. A weak and broad depolarized component (VH) might remain at the lowest temperatures, but it appears rather featureless at the resolution of Fig. 1.

The inset of Fig. 3 shows that the doublet strength I_D/T increases as T decreases down to T_q, stabilizes below T_q, and drops below 20 K. Thus it seems appropriate to invoke for S_D the large polarization clusters and the resulting anharmonicities. In particular, the data suggest that the mechanism leading to S_D is related to the one leading to T_q. Several possible explanations come to mind. The doublet must be either a propagative process or a two-phonon difference process. We consider in turn solitons, phonon-density fluctuations, and second sound.

The first idea is that the doublet is caused by solitary waves (SW) propagating along $\boldsymbol{c}$. Such SW's, although possible solutions of the equations of motion [14], do not seem to have ever been observed in ϕ^4 systems. The reason is presumably because they are not genuine solitons preserving their identify in collisions. Thus they have small statistical weight and do not lead to a developed structure in $S(\boldsymbol{q}, \omega)$, as confirmed by well annealed simulations [15]. More quantitatively, the velocity c of such SW's is obtained from the E_u phonon dispersion, $\omega_{\mathrm{TO}}^2 = \Omega_{\mathrm{TO}}^2 + c^2 q^2$ [14], where $c \approx 7500$ m/s [16]. This value appears definitely too high compared to the observed v.

Two-phonon difference scattering on the TA sheet has already been discussed as a tentative explanation for the broad central peak, although it encounters a serious difficulty in accounting for the T dependence of the intensity [6]. For the doublet, one could think of difference scattering from thermal phonons belonging to the soft TO sheet. However, to obtain a doublet, the combined width of the two thermal phonons involved must be appreciably smaller than the observed doublet frequency ($\approx$20 GHz). Hyper-Raman scattering experiments performed on the TO branch show that the phonon width near the zone center is appreciably larger than the doublet frequency [8]. One can safely anticipate larger widths for thermal phonons, which invalidates this mechanism as a likely explanation for the doublet. Further, the strong directional anisotropy which is observed also seems incompatible with such a process.

Second sound is the wavelike propagation of entropy [17]. It was observed in solid helium, a very anharmonic crystal, and also in exceptionally perfect NaF [18]. Its existence requires thermalization of thermal phonons at the frequency of interest, i.e., $\omega \ll \tau_N^{-1}$, the average *normal* (momentum conserving) relaxation rate. It also requires conservation of quasimomentum, or $\omega \gg \tau_R^{-1}$, where τ_R^{-1} is the *resistive* (momentum nonconserving) relaxation rate, consisting mostly of umklapp, τ_U^{-1}, and impurity, τ_I^{-1}, scattering rates. The "window" condition, $\tau_R^{-1} \ll \omega \ll \tau_N^{-1}$, is very stringent, as repeatedly emphasized by Guyer and Krumhansl [19]. However, in ferroelectrics the simultaneous presence of thermally populated soft and acoustic phonons generates another normal scattering channel which can enhance τ_N^{-1} enormously [20]. Further, the ratio $\tau_U/\tau_N \approx \chi^{1/2}$ is then also large [20]. It results that a *high-ω* window can already open up at relatively high T in QPE's. In particular, it becomes much easier to satisfy the sample quality requirement $\tau_1 \gg \tau_N$. This effect, predicted by Gurevitch and Tagantsev [20], but to our knowledge not observed to this date, seems to be the most reasonable explanation for the doublet.

In this interpretation, the large phonon width of Ref. [8] should be attributed to *normal* phonon-scattering processes. S_D then corresponds to a longitudinal entropy wave, propagating in the $\boldsymbol{c}$ direction, and scattering polarized light as observed. The velocity is given approximately by the group velocity of thermal phonons divided by $\sqrt{3}$ [21]. Using $\omega_{\mathrm{TO}}^2 = \Omega_{\mathrm{TO}}^2 + c^2q^2$, and the known dependence of Ω_{TO}^2 on T [8], one finds $v \approx 3000$ m/s over a large range of low T, in agreement with the observation. The scattering strength should increase with the correlation length ξ [20], consistent with the inset of Fig. 3. The entropy wave also couples linearly to LA phonons. This coupling is proportional to $q\gamma$, where γ is a mean Grüneisen parameter [22]. A fit of our spectra with coupled modes reveals that γ increases considerably as the temperature is lowered in the QPE regime, reaching values above 100. This confirms the strong anharmonicity, consistent with an exceptionally short τ_N. The absence of doublet for $\boldsymbol{q}\|[110]$ suggests a shorter τ_I in that direction. This can be due to scattering of thermal phonons on antiphase-domain walls that are parallel to the $\boldsymbol{c}$ axis. A quantitative comparison with the τ_R extracted from the thermal conductivity κ is not possible at present, as the latter does not seem to have been measured on oriented $SrTiO_3$ in the low-T tetragonal phase.

We have observed a similar doublet on $KTaO_3$ [16]. It develops at lower T, below $\approx$20 K, consistent with the lower T_q of that material. In this case the crystal remains cubic so that a comparison of the value of ω_D ($\approx 2\pi \times 10$ GHz $\approx$60 Gcps in backscattering) with the value τ_R^{-1} extracted from κ is possible. With $\tau_R^{-1} = Cv^2/3\kappa$, where C is the specific heat and v is a typical acoustic velocity, we find $\tau_R^{-1} = 4$ Gcps at 10 K [23], so that $\omega \gg \tau_R^{-1}$ is well satisfied. This supports the second sound interpretation.

In conclusion, we observed for the first time several new spectral features in the QPE regime, the most spectacular being the appearance of a new doublet. It can be interpreted as second sound, confirming an earlier proposal [20]. The fact that this doublet grows as T is lowered toward T_q (inset of Fig. 3) and that it saturates below T_q suggests a connection between the large anharmonicities that allow the doublet and the phase-transition-like anomalies occuring at T_q. This will deserve further investigation.

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