Brillouin-scattering study of the broad doublet in isotopically exchanged $SrTiO_3$

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A comparative Brillouin-scattering study of the broad doublet and acoustic phonons in isotopically substituted $SrTi(^{18}O_{1-x}{}^{16}O_x)_3$ and ''pure'' $SrTi^{16}O_3$ crystals is presented. The acoustic-phonon frequency is found to decrease as a result of the substitution, but the doublet spectra above 20 K show no obvious differences. The results are examined in connection with the second-sound interpretation of the doublet. Influence of the phase transition on the doublet spectra is discussed.

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Strontium titanate ($SrTiO_3$) is a typical example of quantum paraelectrics (QPE), failing to undergo a ferroelectric phase transition at low temperature.[1] Its low-temperature behavior has become a recent topic of great interest prompted by the discoveries of a large number of novel anomalies, including the most remarkable appearance of a new broad doublet component in light-scattering spectra.[2–5] The origin of the doublet has been discussed in terms of the second sound,[3,6] optical-mode crossing,[7,8] and two phonon difference scattering,[9] however, a closer investigation of the doublet is needed to corroborate its possible explanation. Itoh and co-workers have recently found that isotopically modified $SrTi(^{18}O_{1-x}{}^{16}O_x)_3$, where oxygens are exchanged for their heavier isotopes, exhibits ferroelectric behavior.[10] Light-scattering studies have already begun making contributions to the understanding of the ferroelectric phase transition in $SrTi(^{18}O_{1-x}{}^{16}O_x)_3$, revealing several low-temperature acoustic anomalies.[11,12]

In the present work, we will focus on the effects of the isotopic substitution on the broad doublet spectra. Introduction of the ^{18}O isotope into $SrTiO_3$ crystal increases the mass disorder of oxygen atoms and the rate of the phonon-impurity scattering, an unfavorable condition for the second-sound propagation. An investigation of the doublet in the isotopically substituted crystal can serve as a good test and help clarify the origin of the doublet. In addition, the soft phonon frequency changes largely with temperature near the ferroelectric phase transition. The behavior of the broad doublet near the phase transition can contribute to its more comprehensive understanding. In this study, we have investigated the doublet in $SrTi(^{18}O_{1-x}{}^{16}O_x)_3$ using high-resolution Brillouin scattering and examined its temperature dependence.

Brillouin-scattering experiments were performed on Verneuli-grown single-crystal cubic samples, $3\times3\times3$ mm for $SrTi(^{18}O_{1-x}{}^{16}O_x)_3$ (hereafter STO18) and $5\times5\times5$ mm for $SrTi^{16}O_3$ (hereafter STO16). The final exchange ratio of the ^{18}O isotope was 40.3%. Details of the sample preparation are given elsewhere.[10] The crystal faces were perpendicular to the $[1\bar{1}0]$ direction and at 45° to the [001] and [110] directions. This orientation has enabled us to observe the light-scattering spectra in the 90° scattering geometry with the scattering vector $Q\|[001]$ and $\|[110]$, and with slight uniaxial pressure to the cubic $[1\bar{1}0]$ direction in the entire temperature range, which makes the *c* axis of the tetragonal domains formed below cubic-to-tetragonal phase-transition temperature prefer the orientation in the [001] direction. The sample was mounted in a closed-cycle He-gas refrigerator. Brillouin-scattering measurements were carried out in the temperature range from 300 K to 7 K with the stability within 0.05 K. A highly mode-hop supressed and frequency-jitter stabilized vertically polarized longitudinal single mode Ar^+-ion laser (spectral width within 2 MHz) operated at $\lambda = 514.5$ nm with intensity stabilization was used as a light source. The measurements were made using a Sandercock-type six-pass tandem Fabry-Perot interferometer with the finesse of more than 100.

Figure 1(a) shows the temperature dependence of the Brillouin-scattering spectra of STO18 with the scattering vector $Q\|[001]$. The broad doublet peak around 20 GHz is clearly seen in the spectra at 29.0 and 24.8 K. The c_{33} longitudinal (LA) and c_{44} transverse (TA) acoustic modes are observed at around 53 and 28 GHz, respectively. In Fig. 1, these peaks are off-scaled to emphasize the central component. The peaks around 75 GHz are instrumental ghosts. In the spectra at 88.5 K and 53.8 K, an intense broad central component is observed. With decreasing temperature, the intensity of the central component decreases and the doublet feature is found in the spectra below 40 K.

In the spectra taken with $Q\|[110]$, the intensity of the central component decreases with decreasing temperature similar to the spectra with $Q\|[001]$, however, the doublet is not observed in this direction and the central peak shows a plateaulike shape between the stokes and antistokes TA mode frequencies [Fig. 1(b)]. This anisotropy is consistent with results reported for $SrTiO_3$ and is attributed to the antiphase boundaries formed below the cubic-to-tetragonal phase

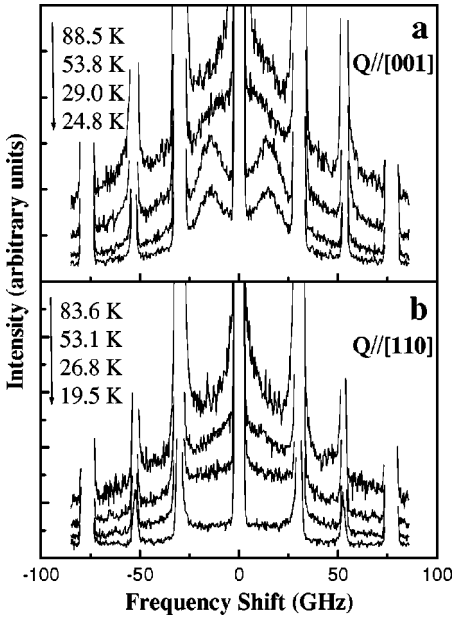

FIG. 1. Temperature dependence of the light-scattering spectra of STO18 above 20 K taken with (a) $Q\|[001]$ and (b) $Q\|[110]$, where Q is the scattering vector.

transition.[3] The trailing foot of the LA modes in the high-frequency sides is not observed in this direction, in contrast with Fig. 1(a), suggesting anisotropic nature of the broad central component.

Figure 2 shows the Brillouin-scattering spectra of STO16 at various temperatures taken with (a) $Q\|[001]$ and (b) $Q\|[110]$. The doublet feature appears with decreasing temperature at around 40 K in the $Q\|[001]$ configuration and the plateaulike spectra are observed with $Q\|[110]$. These

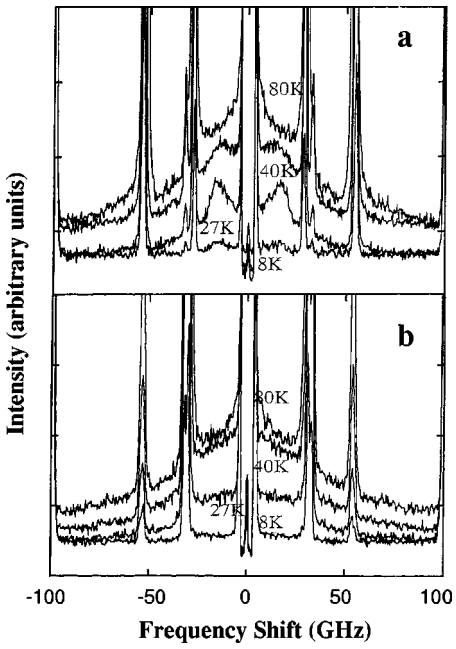

FIG. 2. Temperature dependence of the light-scattering spectra of STO16 taken with (a) $Q\|[001]$ and (b) $Q\|[110]$.

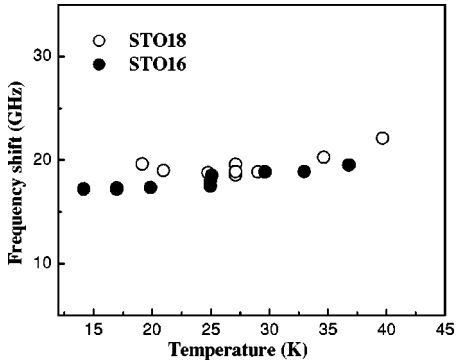

FIG. 3. Temperature dependence of the doublet frequency shifts for STO18 and STO16.

temperature-dependent spectral features found for STO16 agree with the previous studies.[3] The temperature dependence of the spectra in Fig. 2 does not show significant differences from the STO18 spectra above 20 K. Below 20 K, new features appear in the spectra of STO18 as a result of the ferroelectric phase transition, as will be discussed later. Let us now focus on the effects of the isotopic substitution above 20 K.

For a quantitative analysis of the doublet spectra, a damped oscillator model was employed, which describes the line shape of the doublet as

$$I(\omega)=\frac{I_D}{\pi}\frac{\omega_D^2\Gamma_D}{(\omega^2-\omega_D^2)^2+(\omega\Gamma_D)^2}, \tag{1}$$

where I_D, Γ_D, and ω_D are the integrated intensity, damping constant and frequency shift of the doublet, respectively. The broad central peak[13] and a broad background originated from the soft ferroelectric E_u mode[3] were also included in the fitting, similarly to the previous works.[3,5] The soft ferroelectric E_u modes are Raman inactive from the symmetry considerations in the tetragonal phase, however, they are often observed in the quantum paraelectric regime.[3,14] The spectral shape of the doublet has been fitted reasonably well with the damped oscillator function.

Figure 3 shows the temperature dependence of the frequency shift obtained from the fitting. Both STO16 and STO18 have similar frequency values in this temperature range, although STO18 has slightly larger frequency shifts, and the frequency decreases with temperature. It has been reported that the frequency of the doublet, ω_D, shows an acoustic-mode-like dispersion relation, $\omega_D=v_DQ$, where v_D is effective velocity and Q is scattering vector.[3] The effective velocities were estimated to be 2778 m/s for STO18 and 2657 m/s for STO16 at 25 K. They are slightly smaller than previously reported values,[3] possibly due to crystal differences. In the present study, both crystals were obtained from the same source.

Figure 4 shows the temperature dependence of the acoustic-mode frequencies for both STO16 and STO18. Frequency shifts were measured in the 90° scattering configuration with the Q vector parallel to c axis. Both c_{33} and c_{44}

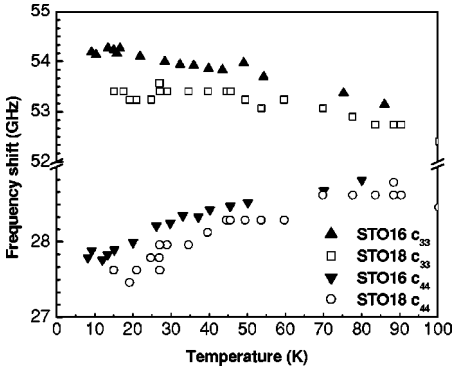

FIG. 4. Temperature dependence of the frequency shifts of the c_{33} and c_{44} acoustic modes for STO18 and STO16.

mode frequencies in STO18 show smaller values below the phase-transition temperature. For example, at 27 K, the c_{33} frequency shifts for STO16 and STO18 are 54.0 and 53.2 GHz, respectively, and the c_{44} frequency shifts are 28.3 and 27.8 GHz, respectively. The ratio of the acoustic-mode frequencies for STO18 and STO16 is about 1.02 for both c_{33} and c_{44} modes. It has been reported that the lattice constants for STO16 and STO18 in the tetragonal phase show no differences within experimental error.[10] The density ratio for STO16 and STO18 can be estimated and the expected change of the frequency shifts of c_{33} and c_{44} modes can be obtained as $\omega_{16}/\omega_{18}=(\rho_{18}/\rho_{16})^{1/2}\simeq 1.01$. Similarly, the ratio of the acoustic-mode frequencies is 1.01 for both c_{33} and c_{44} modes at 45 K. The observed changes of the acoustic-mode frequency are of the same magnitude as expected from the density changes. The small temperature dependence of the ratio can be a result of the temperature-dependent dielectric constants.

Figure 5 shows the polarization dependence of the doublet in STO18 at 27 K. Both the doublet and the central peak and background components have stronger polarized components. The depolarization ratio for the doublet is about 10/47 for STO18 from the fitting analysis. The high-frequency tail of the LA mode peak shows the trailing feature in VV configuration similar to STO16, which is attributed to the coupling between the doublet and LA phonon mode.[3]

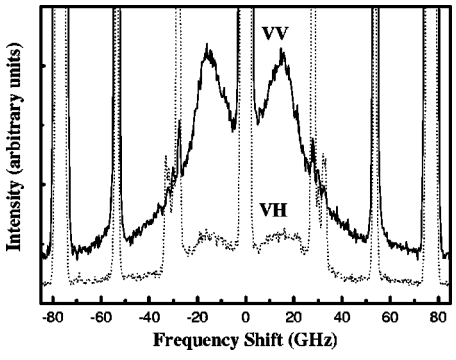

FIG. 5. Polarization dependence of the light-scattering spectra of the broad doublet in STO18. VV indicates vertical polarization of both incident and scattered light, VH indicates vertical polarization of incident light and horizontal polarization of scattered light with respect to the scattering plane.

The second-sound velocity, v_{II}, of the multiple-polarized-phonon gas in the Debye approximation is expressed in terms of the sound velocities as

$$v_{II}^2=\frac{1}{3}\sum_{\lambda} v_{\lambda}^{-3}\left(\sum_{\lambda} v_{\lambda}^{-5}\right)^{-1}, \tag{2}$$

where v_{λ} ($\lambda=t_1$, t_2, or l) is the sound velocity of each acoustic branch (two transverse modes and longitudinal acoustic mode, respectively).[15]

The second-sound velocities obtained from Eq. (2) are 2475 m/s for STO16 and 2385 m/s for STO18, and the change expected from the isotopic substitution is the approximately 4% decrease. The experimental values of v_D obtained from the doublet frequencies are slightly smaller than those estimated from Eq. (2) and they increase, instead of decreasing, by 4%. On the other hand, the acoustic-mode frequencies decrease as a result of the substitution owing to the increase in density, as was discussed previously.

For the second-sound propagation, a weakly damped temperature wave,[16] the "window condition" given by $\tau_U^{-1}, \tau_I^{-1} \ll \omega_D \ll \tau_N^{-1}$ has to be satisfied, where τ_U^{-1}, τ_N^{-1}, and τ_I^{-1} are the rates for the umklapp and normal processes, and phonon-impurity scattering. Gurevich and Tagantsev have shown that in ferroelectric crystals with the soft optical phonons in the low-frequency region, the interaction between the acoustic phonons and anharmonic soft optical phonons enhances the rate of the normal collision process and makes the upper limit of the window condition τ_N^{-1} higher than in ordinary dielectric crystals.[16] Substituting the ^{18}O isotope into $SrTiO_3$ crystal increases the mass disorder of oxygen atoms and increases the rate of isotope scattering of phonons, thus the lower limit of the window condition

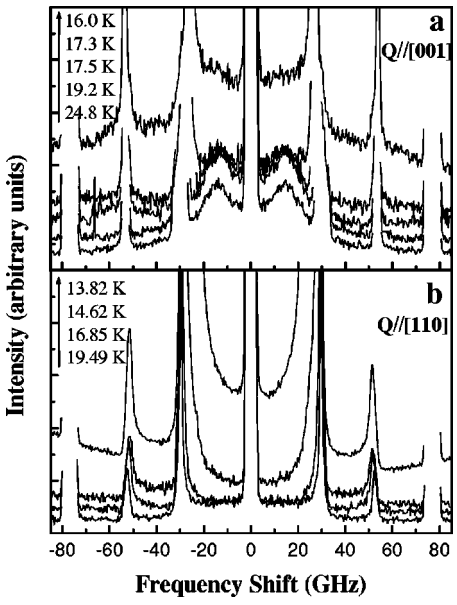

FIG. 6. Temperature dependence of the light-scattering spectra of STO18 near the ferroelectric phase-transition point T_C with (a) $Q\|[001]$ and (b) $Q\|[110]$.

increases. If the lower limit becomes as high as the higher limit (τ_N^{-1}), the window will no longer be open and there will be no second-sound propagation. The doublet spectra are expected to change significantly if it is second sound. However, our experimental results do not show such effects of the isotopic substitution.

Figure 6 shows the temperature dependence of the doublet spectra of STO18 near the ferroelectric phase-transition temperature (12 K). In this temperature region, the intensity of the spectra observed for STO18 increases with decreasing temperature, in contrast to the spectra observed above 20 K for both STO18 and STIO16. In the central peak region, new features appear in the spectra in addition to the doublet component [Fig. 6(a)]. The spectra show anomalous behavior near the phase transition. The spectral shape shows anisotoropy and different character in the two directions of the scattering vector *Q*. No such behavior was observed in the spectra of STO16. With $Q \| [001]$, the broad doublet feature is clearly seen down to 17 K, where the intensity of the spectra in the high-frequency region shows anomalous behavior, indicating that the low-frequency optical-phonon spectrum is changing with temperature. The frequency and intensity of the doublet are not affected by the phase transition in this temperature region. The doublet spectra should be largely affected by the frequency changes of the low-frequency optical phonons in the second-sound scenario since the interaction between the acoustic and soft optic phonons governs the higher limit of the window condition.[16] This relative unresponsiveness of the spectral shape to the soft mode frequency was also observed in STO16 under electric field.[5] With $Q \| [001]$, the intensity and line shape of the central part of the spectra (plateaulike part between the TA modes) show no obvious changes down to 17 K, while the acoustic peak shape changes in the same temperature region.

In conclusion, the elucidation of the Brillouin-scattering spectra of STO18 and STO16 has revealed new features of the broad doublet. The results do not support the second-sound interpretation of the doublet, providing experimental incentive for further study of its origin.

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[1] K.A. Muller and H. Burkard, Phys. Rev. B **19**, 3593 (1979).
[2] E. Courtens, G. Codeens, B. Hennion, B. Hehlen, J. Pelous, and R. Vahcer, Phys. Scr., T **T49**, 430 (1993).
[3] B. Hehlen, A.-L. Perou, E. Courtens, and R. Vacher, Phys. Rev. Lett. **75**, 2416 (1995).
[4] B. Hehlen, L. Arzel, A.K. Tagantsev, E. Courtens, Y. Inaba, Y. Yamanaka, and K. Inoue, Phys. Rev. B **57**, R13 989 (1998).
[5] M. Watanabe, M. Yamaguchi, and T. Yagi, Ferroelectrics **218**, 169 (1996).
[6] E. Courtens, B. Hehlen, E. Fahri, and A.K. Tagantsev, Z. Phys. B: Condens. Matter **104**, 641 (1997).
[7] J.F. Scott, A. Chen, and H. Ledbetter, J. Phys. Chem. Solids **61**, 185 (2000).
[8] J.F. Scott and H. Ledbetter, Z. Phys. B: Condens. Matter **104**, 635 (1997).
[9] E. Farhi, A.K. Tagantsev, B. Hehlen, R. Currat, L.A. Boatner, and E. Courtens, Ferroelectrics **239**, 25 (2000).
[10] M. Itoh, R. Wang, Y. Inaguma, T. Yamaguchi, Y.-J. Shan, and T. Nakamura, Phys. Rev. Lett. **82**, 3540 (1999).
[11] M. Yamaguchi, T. Yagi, R. Wang, and M. Itoh, Phys. Rev. B **63**, 172102 (2001).
[12] T. Yagi, M. Kasahara, Y. Tsujimi, M. Yamaguchi, H. Hasebe, R. Wang, and M. Itoh, in Proceedings of the 10th International Meeting on Ferroelectronics, 2001 (to be published).
[13] K.B. Lyons and P.A. Fleury, Phys. Rev. Lett. **19**, 161 (1976).
[14] H. Uwe, K.B. Lyons, H.L. Carter, and P.A. Fleury, Phys. Rev. B **33**, 6436 (1986).
[15] C.C. Ackerman and R.A. Guyer, Ann. Phys. (Leipzig) **50**, 128 (1968).
[16] V.L. Gurevich and A.K. Tagansev, Zh. Eksp. Teor. Fiz. **94**, 364 (1988) [Sov. Phys. JETP **67**, 206 (1988)].