Perfect Softening of the Ferroelectric Mode in the Isotope-Exchanged Strontium Titanate of $SrTi^{18}O_3$ Studied by Light Scattering

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The E_u mode of the isotope-induced ferroelectric strontium titanate $SrTi^{18}O_3$ shows a perfect softening at the ferroelectric phase transition temperature T_c, where the frequency of the underdamped mode approaches completely to zero within the instrumental resolution. The spectra of the Raman inactive soft E_u mode have been successfully observed owing to local symmetry breaking and by long-term accumulation of the spectral intensity with a high resolution technique. The mechanism of the phase transition is concluded to be an ideal displacive-type accompanied with perfect softening of the Slater-type polar E_u mode. The difference between the soft mode behavior of $SrTi^{16}O_3$ and $SrTi^{18}O_3$ indicates that the origin of the quantum paraelectric state of $SrTi^{16}O_3$ lies in the quantum fluctuation of the oxide octahedron in the perovskite structure.

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The perovskite oxide strontium titanate $SrTiO_3$ has been considered to belong to the typical quantum paraelectrics, because it keeps paraelectricity until $T = 0$ K by the quantum fluctuation that might depress the occurrence of the ferroelectric order [1]. Indeed, at low temperatures below 4 K, the dielectric constant increases considerably but remains finite even near 0 K without any divergent behavior. The dynamics of the ferroelectric soft mode in the quantum paraelectrics also shows no freezing phenomenon, staying with the finite phonon frequency until 0 K according to the Lyddane-Sachs-Teller relationship [2,3]. Since the effect of quantum fluctuation was first suggested in Ref. [1], many intensive studies have been accumulated to elucidate the dynamics of the quantum fluctuation and also the soft mode behavior related to the quantum fluctuation in $SrTiO_3$ and related materials. There are two types of soft modes in the low frequency region of $SrTiO_3$, as listed in the phonon correlation table [4]: the ferroelectric modes E_u, A_{2u} [2–4] described above and the A_{1g}, E_g modes related to the structural phase transition [5].

Recently, the ferroelectric phase transition in $SrTiO_3$ was discovered at 23 K by exchange of ^{16}O in $SrTiO_3$ to its isotope ^{18}O [6]. Since then, the phase transition mechanism of the isotope-exchanged strontium titanate $SrTi^{18}O_3$ (hereafter abbreviated as STO18 and the ordinary one as STO16) has attracted the intense interest of many researchers in order to elucidate its phase transition mechanism related to the quantum fluctuations. The lowest energy phonon mode in STO18 has been searched for and analyzed to elucidate the soft mode dynamics near T_c by many authors [7–11]. However, any clear softening behavior has not been reported: By Raman scattering studies, the observation of the Raman inactive soft E_u mode has been tried, but the assignment of certain spectral feature to the E_u mode has not been convincing and unambiguous. Inelastic neutron scattering has revealed the temperature dependence of the soft mode of STO18. It shows a small difference with the result reported on STO16 [11]. According to these experimental results about the low energy modes, theoretical and experimental works suggested a nondisplacive phase transition mechanism in STO18 [11,12]. However, quite recently the soft E_u mode observed in Ref. [11] was reassigned to be the A_{2u} mode [13]. The previous works give divergent conclusions due to the insufficient assignment of the soft E_u mode. In this situation we were strongly motivated to elucidate the soft mode dynamics of STO18 with an exact light scattering spectroscopy.

In the present Letter, we report a successful observation of the temperature dependence of the soft E_u mode in the extremely low frequency region using a high resolution technique and an ultrastable optical cryostat. The soft E_u mode demonstrates a perfect softening phenomenon. Here perfect softening means that the frequency of the mode approaches completely to zero value at T_c without any overdamping.

The polarized scattering light was analyzed by a Sandercock-type tandem Fabry-Perot interferometer on a six-pass stage with an averaged finesse more than 100 in typical free spectral ranges (FSR) of 3.3, 10.0 and 16.7 cm^{-1}. The highest resolution is smaller than 0.04 cm^{-1} in the FSR of 3.3 cm^{-1}. To stabilize the experimental system, an Ar ion laser with a beam-lock system (Beamlok, SP) was used as a light source with longitudinal single mode at an average power of 100 mW and a wavelength of 514.5 nm. The analyzed light was detected by a photomultiplier (R464, Hamamatsu Photonics). The phonon wave vector q was selected to be parallel to the $[001]_c$ axis of the cubic phase. The Raman spectra were observed in the scattering geometries VV, VH shown in the inset of Fig. 1, where V and H mean the polarization of light vertical and horizontal, respectively, to the $(\bar{1}10)_c$ scattering plane, and the former and latter symbols represent the incident and scattering light polarization, respectively. The sample is mounted in an optical cryostat (Optistat CF, Oxford) cooled by liquid helium. It was designed especially in order to keep the scattering position in the sample during the experiment. The temperature was stabilized within an error of ± 0.01 K. However, the observed value of temperature refers to the helium ambient to the sample in order to suppress strain by the contact with the temperature sensor, where we place the significance on the relative temperature of the sample from T_c rather than absolute values. The temperature in terms of absolute value thus includes experimental errors of about 0.5 K. The sample of a single crystal of STO18 was prepared with special high quality in a size of $9 \parallel [001]_c \times 2 \parallel [\bar{1}10]_c \times 0.5 \parallel [110]_c$ to be favorable for a monodomain in the tetragonal phase [6]. The value of isotope concentration x in the sample studied was 95%. T_c is determined to be 25.9 K by the observation of the splitting of the E_g mode into A_2 and B_1 modes at the ferroelectric phase transition.

The Raman spectra of Fig. 1 in the VV geometry have been observed around T_c. The spectra show a drastic change near T_c. The longitudinal acoustic (LA) mode was observed at about 0.7 cm^{-1} as a pair of sharp peaks. Except for the LA mode, the spectra above T_c in Fig. 1 have two components below 5 cm^{-1} and around 10–15 cm^{-1} assigned to be the ferroelectric soft E_u mode and the A_{2u} mode, respectively. The intensity of soft E_u polar mode in Fig. 1 is extremely weak compared to the LA mode at around 30 K because of the Raman inactivity. With decreasing temperature, the spectrum of the E_u mode shifts to the central component critically and a drastic increase of intensity with temperature approaching to T_c. The red points at 25.9 K in Fig. 1 are the spectrum at T_c.

The spectra from 29 K to T_c are well fitted as shown in Fig. 1 by susceptibility $\chi_{E_u(\nu)}$, $\chi_{A_{2u}(\nu)}$, and $\chi_{\mathrm{LA}(\nu)}$ for the E_u, A_{2u}, and LA modes, respectively,

$$I(\nu, T) \sim [n(\nu, T) + 1]\,\mathrm{Im}\Big(\sum_Q \chi_Q(\nu)\Big),$$
$$\mathrm{Im}\chi_Q(\nu) = \frac{\chi_Q(0)\nu_Q^2 \nu \frac{\gamma Q}{2\pi}}{(\nu_Q^2 - \nu^2)^2 + \nu^2(\frac{\gamma Q}{2\pi})^2}, \quad (1)$$

where the sum runs over the three modes, $Q = E_u, A_{2u}$, and LA. The Bose factor $n(\nu, T)$ is $[\exp(h\nu/k_B T) - 1]^{-1}$. The parameters ν_Q, γ_Q represent a frequency and a damping constant for the optical or acoustic mode, respectively. The frequencies ν_{E_u}, $\nu_{A_{2u}}$ are plotted in Fig. 2. The E_u mode in Fig. 2 shows a critical and complete softening at T_c without any increase of damping. Above ~30 K the spectra in Fig. 1 show the feature indicated by a broad ferroelectric microregion (FMR) response [14], which is not well fitted by Eq. (1). We will discuss elsewhere the relation between FMR and the E_u soft mode.

Below T_c, we have clearly observed the characteristic spectra with strong intensity in the frequency range below 5 cm^{-1}, as seen in Fig. 1. This shows that the soft mode becomes Raman active due to the symmetry change at T_c. The spectra near T_c are composed of three phonon modes except for the LA mode, since it is necessary for a well-fitting function to add another overdamped harmonic oscillator to the function of the paraelectric phase above T_c, as shown in the right inset in Fig. 1. With decreasing temperature, the lowest frequency phonon in Fig. 2 shows

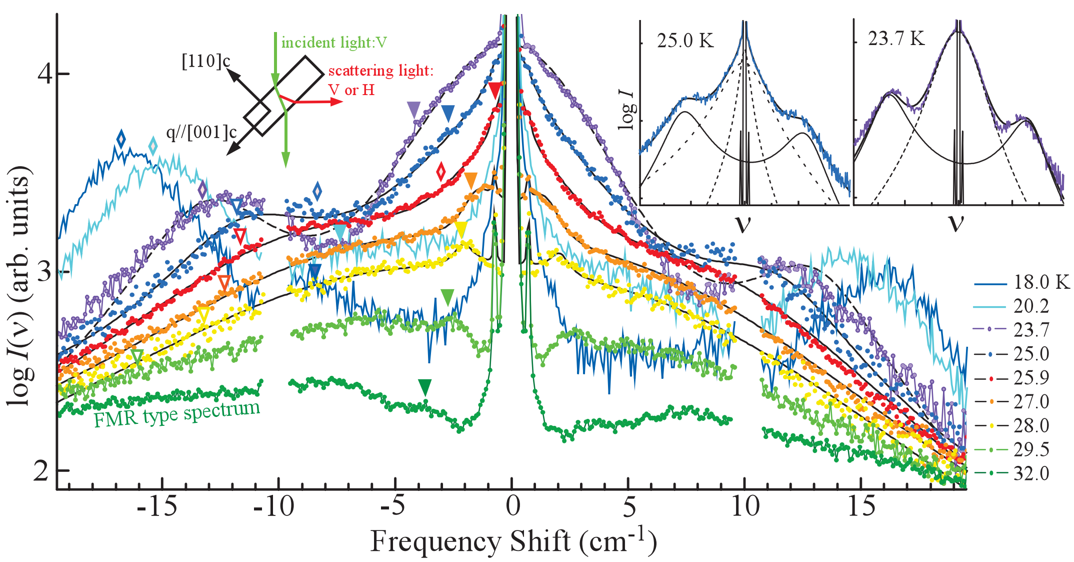

FIG. 1 (color). The low frequency Raman spectra with the VV geometry on FSR of 10.0 cm^{-1} in $SrTi^{18}O_3$. The black solid curves were determined by a least-squares fit. The lack of spectra around 10.0 cm^{-1} of FSR shows the experimental blind region for the tandem Fabry-Perot interferometer. The symbols represent the position of $\nu_{E_u(A_1)}$ (▼), $\nu_{A_{2u}(B_1)}$ (▽) and ν_{B_2} (◆). The values of ν_{B_2} and $\nu_{A_{2u}}$ are much larger than the spectrum peak position due to the large γ. The left inset shows the scattering geometry. The right inset is a fitted result. The spectrum at 25.0 K includes two overdamped modes $A_1(E_{u1})$ (inner dashed line), $B_2(E_{u2})$ (outer dashed line), and two underdamped modes $B_1(A_{2u})$ and LA (solid curves). One of the modes disappears at around 24 K.

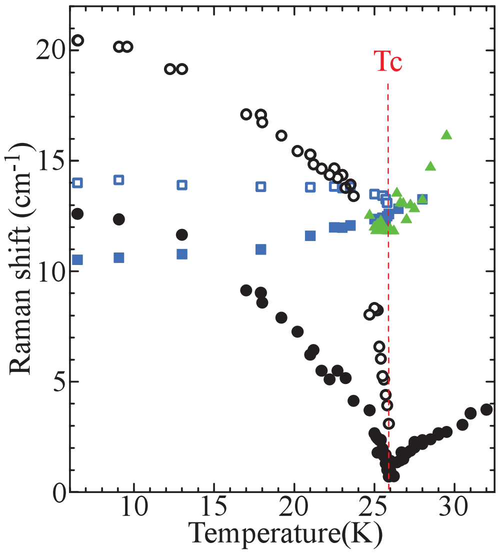

FIG. 2 (color). The temperature dependence of E_u (●), A_{2u} (▲), and E_g (■) modes above T_c, and $A_1(E_{u1})$ (●), $B_2(E_{u2})$ (○), $B_1(E_{g1})$ (■), $A_2(E_{g2})$ (□), and $B_1(A_{2u})$ (▲) modes below T_c in $SrTi^{18}O_3$. The E_g, $B_1(E_{g1})$, and $A_2(E_{g2})$ modes are observed in the VH geometry (see Fig. 3).

continuous hardening below T_c from zero frequency. This mode is assigned to be the A_1 (E_{u1}) mode, where the symmetry in the parentheses indicates the one in the paraelectric phase. Both of the temperature dependences of the squared frequency of soft E_u and A_1 (E_{u1}) modes obey the Curie-Weiss law near T_c. The E_u and A_1 modes in Fig. 2 show the soft mode behavior expected in a typical displacive-type mechanism of a ferroelectric phase transition. The present results are completely different from the previous ones observed above 5 cm^{-1} in STO18 [7–11]. The damping constant γ_{E_u} keeps a small value even just above T_c. Below T_c, the damping constant γ of the A_1 mode shows a drastic increase with decreasing temperature and reaches a peak at about 2 degrees below T_c. The anomalous behavior of γ_{E_u} will be discussed below.

The temperature dependence of spectral intensity below 5 cm^{-1} in Fig. 1 shows a peak at about $T_c - 2$ K different from T_c. The asymmetry of the spectra around zero frequency becomes remarkable with the temperature approaching to 0 K. The ratio of the observed intensity between Stokes and anti-Stokes spectra is well described by the Boltzmann factor. The A_{2u} mode in Fig. 2 softens with decreasing temperature above T_c and transforms continuously into the $B_1(A_{2u})$ mode below T_c, though it is observed only near T_c. The $B_1(A_{2u})$ mode is not expected to be observed from the selection rule. Such a behavior of the $B_1(A_{2u})$ mode could be observed if the dynamic clusters with the structure above the T_c or with two (or more) polarization orientations exist in a narrow temperature range near the T_c. Disappearance of the $B_1(A_{2u})$ mode with further cooling away from T_c seems to support this dynamical cluster model. Another different mode from $A_1(E_{u1})$ shows hardening from zero frequency below T_c in Fig. 2. The mode is assigned as the $B_2(E_{u2})$ mode. The temperature dependence of $B_2(E_{u2})$ mode around 24 K in Fig. 2 shows an anomalous behavior, which might be recognized as an effect of mode coupling.

In VH geometry, the observed spectra below T_c in Fig. 3 are composed of five phonons including the LA mode. From the temperature dependence of phonon frequencies, they are assigned to be $B_1(E_{g1})$, $A_2(E_{g2})$, $A_1(E_{u1})$, and $B_2(E_{u2})$ modes as denoted in Fig. 2. The $B_1(E_{g1})$ and $A_2(E_{g2})$ modes are consistent with previous works [8,9].

Here we have to consider the reason why the Raman inactive E_u mode is observed. The reason is discussed from the viewpoint of noncentrosymmetric clusters induced by defects in the crystal [14,15]. However, the structure of the cluster should not be restricted to the symmetry of the low temperature phase. The perovskite oxide crystals of STO18 and STO16 have defects caused, e.g., by oxygen vacancies. The local breakdown of crystal lattice symmetry occurs around the defects. The local symmetry breakdown region accompanied by a small lattice distortion might be extended to submicrometer scale region especially near T_c, because of the coupling with the critical ferroelectric fluctuation. From this viewpoint, the Raman inactive E_u mode can be observed reasonably. The observation of Raman scattering by inactive A_{2u} and E_u modes above T_c was reported in $SrTi(^{18}O_x{}^{16}O_{1-x})_3$ [15].

An anomalous behavior of the acoustic c_{44} mode has been reported around T_c by Brillouin scattering [8,16]; the drastic decrease of the value of frequency shift and the anomalous increase of intensity were presented. However, we have not observed such anomalous behavior in the c_{44} mode in the high quality STO18 samples of 95% and 96% concentrations in the present study. The difference indicates that the reported anomalous behavior of the c_{44} mode is not intrinsic for the transition, though it might be related to coupling effects induced by a sample-depending internal stress created from the transition at 105 K [3] or FMR [14].

Finally, we discuss the anomalous behavior of the damping constant γ_{E_u} as follows: γ_{E_u} does not increase even

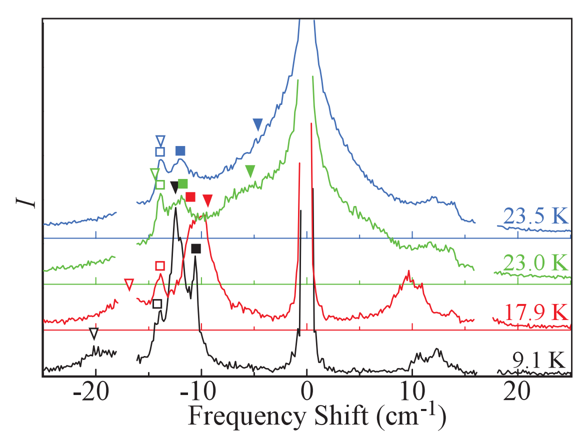

FIG. 3 (color). The Raman spectra with the VH geometry on FSR of 16.7 cm^{-1} in $SrTi^{18}O_3$. The symbols represent the $B_1(E_{g1})$ (■), $A_2(E_{g2})$ (□), $A_1(E_{u1})$ (▼), and $B_2(E_{u2})$ (▽) mode.

near T_c to keep the E_u mode in an underdamped state at T_c, in contrast to the case of an ordinary ferroelectric transition in the high temperature region where an extremely large value and/or anomalous increase of γ near Tc were reported in many cases, e.g., in $BaTiO_3$ and $PbTiO_3$ [17]. In the case of STO18, the ferroelectric transition takes place at the low temperature. A decrease of the number of thermally activated phonons suppresses the damping related to the mode coupling. However, an anomalous increase is still expected because of anharmonicity caused by the increase of the amplitude of the E_u mode upon approaching T_c. An adequate candidate for this mechanism which controls the behavior of γ_{E_u} is a new coherent phonon state of the E_u soft mode.

If the soft E_u mode takes a coherent state near T_c, the damping driven by a dephasing between each mode in the E_u phonon branch should be reduced, where the coherent phonon state could be related to a quantum coherence [18] on oxide octahedron in the perovskite structure. This can be a possible origin of the perfect softening of the ferroelectric E_u mode in STO18. Below T_c, γ_{A_1} shows a drastic increase and a peak. These behaviors might be explained by the existence of dynamical clusters and a breakdown of the coherent phonon state just below the T_c, which disturbs the lattice vibrations associated with the soft phonons. However, there has been no report to establish the physical description for the origin of γ obtained from the spectroscopic analysis even in the typical ferroelectrics. More research is needed to elucidate conclusively the origin of the behavior of γ in STO18.

In the present Letter, the perfect softening of the ferroelectric soft E_u mode is found in the isotope-induced ferroelectric STO18. The mechanism of the ferroelectric phase transition in STO18 is concluded to be an ideal displacive-type associated to the Slater-type polar soft mode. Kozlov *et al.* have reported the ideal softening of the polar mode in the proper ferroelectric tris-sarcosine calcium chloride by the submillimeter monochromatic spectroscopy [19]. The present Letter is for the first time on a perfect softening of the Slater-type polar mode in the quantum ferroelectric STO18 [6]. If the transition is recognized as a second order one associated with the E_u soft mode, the structure of the ferroelectric phase is concluded to be orthorhombic, C_{2v}, with the polar axis along the $[100]_c$ cubic direction according to theory based on the free energy function and the selection rules of the observed phonons, the $A_1(E_{u1})$, $B_2(E_{u2})$ modes for the VV geometry and the $A_1(E_{u1})$, $A_2(E_{g2})$, $B_1(E_{g1})$, $B_2(E_{u2})$ modes for VH. From the viewpoint of the difference of the soft phonon dynamics between STO18 and STO16, the quantum fluctuations of oxygen octahedra in perovskite-type crystals are considered to be at the origin of the quantum paraelectric state of STO16. Furthermore, the recently observed photoinduced cooperative phenomena with isotope effect might originate in the vibronic coupling between the soft phonon mode and excited electrons [20].

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