Elastic and Anelastic Properties of Ferroelectric $SrTi^{18}O_3$ in the kHz-MHz Regime

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Resonant ultrasound spectroscopy has been used to follow elastic softening in $SrTi^{18}O_3$ in the frequency range ~0.2–1 MHz. A dramatic softening of C_{44} occurs as the Curie temperature $T_c = 24$ K is approached from above or below, which correlates with the development of a central peak in Raman and Brillouin spectra. This is attributed to strong coupling between the acoustic mode and the central peak mode. A weaker anomaly is seen in a resonance mode which is believed to be controlled by $\frac{1}{2}(C_{11} - C_{12})$. Significant attenuation accompanies this softening and an additional dissipation peak has also been observed at ~80–90 K. This extends earlier work by a factor of 150 000× from the 30 GHz regime and helps address the question as to whether the ferroelectricity is stimulated primarily by a soft mode into a homogeneous ground state or by clustering of rhombohedral nanoregions into an inhomogeneous ground state.

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Strontium titanate is the only material known which becomes ferroelectric when isotopically substituted. 99% O-18 $SrTiO_3$ has a Curie temperature of 24 K [1], whereas O-16 $SrTiO_3$ is not ferroelectric (except under stress), with an extrapolated T_c of around 35 K below absolute zero. Despite this great interest, it has thus far proved impossible to determine the crystallographic symmetry of the low-temperature phase, due to three kinds of nanotwinning: tetragonal ferroelastic nanodomains below 105 K, rhombohedral nanoclusters below around 40 K, and orthorhombic nanodomains below $T_c = 24$ K. The combination of all these produces a structure with overall local triclinic local structure. Despite extensive studies, the exact nature of the ferroelectric phase of $SrTi^{18}O_3$ is not unambiguously determined. This is because of the extensive microtwinning in the low-temperature phase, and because very precise data are seemingly incompatible. In 2005 Blinc *et al.* [2] showed that the ferroelectric ground state was highly inhomogeneous, produced via rhombohedral nanodomain nucleation and growth, resulting in an order-disorder phase transition. But only the next year Takesada *et al.* demonstrated [3] via Raman spectroscopy the existence of an underdamped soft optic phonon branch down to around 1 cm^{-1} (30 GHz) in both ferroelectric and paraelectric phases. This underdamped soft mode is the lowest frequency soft mode known in nature, being slightly lower than that in tris-sarcosine calcium chloride [4]. Such an underdamped soft mode implies that the transition is purely displacive, second order (or very nearly so), and has a homogeneous orthorhombic ferroelectric ground state. Thus there is a paradox regarding the ground state of $SrTi^{18}O_3$. The paradox deepens in light of the Raman and Brillouin studies of Shigenari *et al.* [5–7], which show an incompatibility between the Raman soft-mode symmetry and the acoustic branch, sound velocity instabilities.

The main purpose of the present work was to investigate the elastic properties of $SrTi^{18}O_3$ at much lower frequencies and over a longer length scale than applies for Brillouin scattering, by using resonant ultrasound spectroscopy (RUS). This is not generally easy, because, as shown by Kityk *et al.* [8], the mechanical damping in strontium titanate is very high below its tetragonal-cubic transition near 106 K, due to the presence of ferroelastic twin walls which remain highly mobile down to at least 20 K [8]. This loss mechanism persists to high frequencies, thus affecting much of the elasticity data for tetragonal $SrTiO_3$ [9]. It had previously been reported that the resonance peaks from a parallelepiped of $SrTiO_3$ in RUS spectra become so weak below the transition point, due to dissipation, that no further information could be obtained about the elastic behavior of the tetragonal phase [10]. However, we have been able to observe two resonance modes in a single crystal of $SrTi^{18}O_3$ prepared as a thin plate. One of these persists below ~106 K with only modest damping through the superparaelectric regime near 40–60 K. A second strongly damped mode shows a remarkably steep temperature dependence through the 24 K transition. The latter correlates with the appearance of a quasielastic scattering central peak in Raman and Brillouin spectra.

The RUS method has been described in detail by Migliori and Sarrao [11]. A rectangular parallelepiped ($2.08 \times 7.01 \times 0.33$ mm^3, mass 0.025 g) specimen used for the RUS measurements described here had previously been used for dielectric measurements and came with thin layers of gold on its largest faces, which were not removed. The largest faces were parallel to (001). Low-temperature

RUS measurements were made with the large faces of crystal parallel to the lead-zirconate-titanate transducers, or with its long edges between the transducers, in the low-temperature RUS head that has been described by McKnight *et al.* [12]. The head was lowered into an "orange" helium flow cryostat, and the sample chamber first evacuated and then filled with ~1–3 mbar of helium exchange gas. Temperature was recorded with a silicon diode inside the sample chamber, through a Lakeshore 340 controller. RUS spectra were collected using Dynamic Resonance System Modulus II electronics, during cooling and heating sequences controlled by software produced in-house. All spectra were analyzed offline within the software package IGOR PRO (Wavemetrics). Values of the mechanical quality factor Q were determined as $Q = f/\Delta f$, where f is the peak frequency and Δf is the peak width at half maximum height, using an asymmetric Lorentzian function (following the approach of Schreuer *et al.* [13] and Schreuer and Thybaut [14]) to fit selected, individual peaks in the primary spectra. Values of elastic constants determining the resonance frequencies of individual distortion modes scale with f^2; i.e., lowering f corresponds to elastic softening.

In the first low-temperature run the sample was oriented so that its longest edges were parallel to the faces of the transducers. Spectra were collected in a cooling sequence, 280 → 10 K, in 30 K steps with a 20 min period for thermal equilibration at each temperature. The heating cycle which followed was 10 → 100 K in 5 K steps, 100 → 112 K in 1 K steps, 112 → 295 K in 5 K steps. A thermal equilibration time of 15 min was included at each temperature before data collection. Spectra were collected in the frequency range 0.05–1.2 MHz, with 50 000 data points per spectrum. Figure 1 contains a selection of the raw spectra collected during the heating cycle. As for the case of $\mathrm{SrTiO_3}$ single crystals with ^{16}O [10], the cubic → tetragonal phase transition is marked by the disappearance of almost all the resonance peaks. Some peaks persist in the vicinity of 1 MHz, but these are due to the transducers. Some persist below 0.2 MHz, and these are a mixture of sample peaks, which show variations with temperature, and instrumental peaks, which do not. The latter are easily recognized from experience of using the same RUS head with many different samples. In addition, there is a very broad peak which first appears at 35 K, softens to a minimum in frequency at 25 K, and then stiffens again with further cooling to 10 K.

Figure 2 contains data for f and Q^{-1} obtained by fitting of selected peaks. In the stability field of the cubic phase all peaks show the same pattern—almost no change in frequency between room temperature and ~120 K, followed by a small degree of softening as $T \rightarrow T_c$. This degree of softening and the temperature interval over which it occurs are significantly less than observed in $\mathrm{SrTi^{16}O_3}$ (cf. Migliori *et al.* [10]). The transition temperature is estimated to be between 107 and 106 K on the basis of the increase in peak widths at 106 K and below. Data for two other peaks at temperatures just above T_c are also shown, to confirm the reproducibility of the softening and Q^{-1} variations. Data for a single peak in the stability field of the tetragonal phase are also given in Fig. 2. The

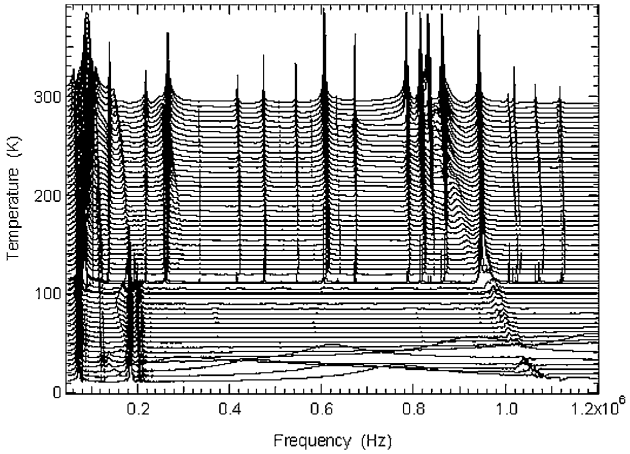

FIG. 1. Selected RUS spectra at approximately 5 K intervals, collected in a heating sequence. The left-hand axis should be amplitude, but the spectra have been shifted in proportion to the temperature at which they were collected and the axis labeled as temperature. The cubic → tetragonal transition is marked by the disappearance of most resonance peaks. The peak which persists near 1 MHz is instrumental in origin, as are peaks below ~0.2 MHz which show little temperature dependence. A sample peak is visible showing variations with temperature between ~0.13 and ~0.18 MHz, and an additional broad resonance peak appears in spectra collected between 10 and 35 K.

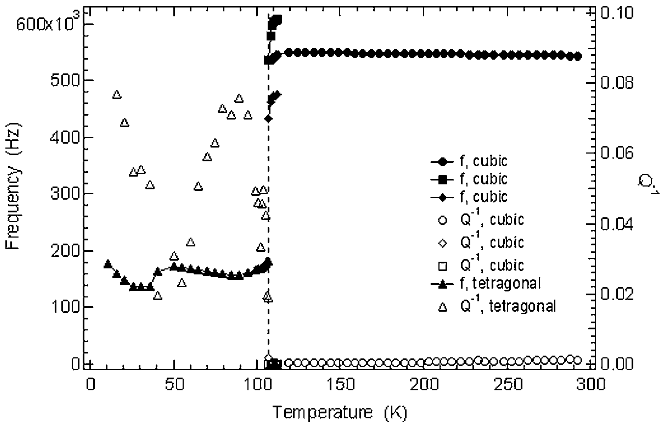

FIG. 2. Data for resonance frequency f and inverse quality factor Q^{-1} obtained by fits to the sample peak near 0.15 MHz in the stability field of the low symmetry structure and to peaks near 0.45, 0.55, 0.6 MHz from the stability field of the cubic phase. The broken line represents the transition point, which has been placed at 106.5 K in view of the steep increase in Q^{-1} which occurs below 107 K. In comparison with $\mathrm{SrTi^{16}O_3}$, elastic softening as $T \rightarrow T_c$ from above is limited both in magnitude and the temperature range over which it occurs.

peak in question is the one with significant temperature dependence between 0.13 and 0.18 MHz in Fig. 1. It shows a pronounced minimum in Q^{-1} near 40 K and a drop in f between 35 and 40 K.

Figure 3 contains frequency (plotted as f^2, since this scales with the elastic constant for the resonant mode) and Q^{-1} data for the broad peak which appears below 40 K. The peak is unlike most normal resonance peaks with respect to both its extreme width ($Q^{-1} \approx 0.3$), about 20× that studied via RUS in other materials, and strong temperature dependence. No equivalent peak has been seen in experiments carried out on many other materials in the same RUS instrument, however, so there is no immediate reason to suppose that it is an artifact. The ratio of slopes from linear fits to f^2 above and below 25 K is 2.4:1.

Spectra collected in the second low-temperature run, with the sample plate held horizontally between the transducers, confirmed the pattern of evolution of peaks in the stability field of the cubic phase and of the weak, low frequency peak in the stability field of the tetragonal phase. The broad resonance peak was not observed, however, presumably because the distortional mode was not excited in this orientation.

In summary we have presented RUS data for SrTi^{18}O$_3$ that show remarkably steep elastic softening as $T_c \approx 24$ K is approached from above or below, together with evidence of dissipation effects at two different temperatures. From Brillouin scattering results it is known that C_{44} decreases steeply at the 24 K transition [15–17], so it is likely that the resonance mode observed here is determined by C_{44} also. It should be noted that this same softening was not observed by Takesada *et al.* [3] in their Brillouin spectra, and they suggested that it is not intrinsic to the transition. The softening of the bulk sample is real enough in the present study, but an extrinsic origin could conceivably arise from highly mobile microstructures associated with the transition. This, in itself, would be a remarkable result, however. The ratio of slopes above and below T_c for a pseudoproper ferroelastic transition would be the reverse of what is observed here (i.e., steeper on the low-temperature side than the high-temperature side), so bilinear coupling of an acoustic mode with a soft optic mode can be ruled out as the driving mechanism. On the other hand, correlation of the steep softening with the development of a central peak in optical spectra [3,7] suggests that the softening mechanism is coupling with the central peak mode. Equivalent softening is not seen in the other elastic constants so, if it is intrinsic, it is possible that the central peak mode has a component with the appropriate symmetry for bilinear coupling with the C_{44} acoustic mode. The origin of the central peak mode is likely to be associated with the polar nanoclusters, and strong attenuation (large Q^{-1}) of the RUS mode is also consistent with a dynamic origin. The more normal looking softening and attenuation shown in Fig. 2 must be related to elastic constant combinations which depend only weakly or not at all on C_{44}. For a crystal with all possible tetragonal twin domains such that average cubic geometry is maintained, the effective elastic constant would be $\frac{1}{2}(C_{11} - C_{12})$. Softening below 50 K (Fig. 2) also appears to be related to the 24 K transition, though the effect is much smaller than for C_{44}. If the softening mechanism again involves coupling with the central peak mode, the smaller magnitude could be indicative of biquadratic, rather than bilinear, coupling. Attenuation continues to increase below the transition as if it is related to a transformation microstructure.

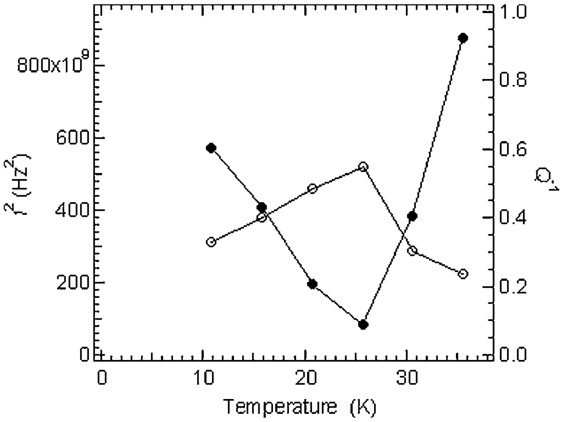

FIG. 3. Variations of f^2 (filled circles) and Q^{-1} (open circles) from fits to the broad peak which is clearly visible in low-temperature spectra shown in Fig. 1.

The second dissipation peak occurs at ~80–90 K. It could be related to the development of microstructure below the 106 K transition, but it also corresponds closely to the onset of splitting in the ^{87}Sr NMR lines. In the NMR data this begins at around 75 K and is manifest as an onset of asymmetry parameter in the ^{87}Sr lines, which then increases by 50% at $T_c = 25$ K. In addition to the asymmetry parameter, the NMR linewidth also increases by 100% below T_c, reaching 0.16 at 20 K. And the NMR frequency undergoes a 0.2 kHz splitting at T_c beginning at 80 K [18].

Our results help to reconcile two previously incompatible models: the rhombohedral nanocluster order-disorder model of Blinc *et al.* [12] with its inhomogeneous ground state and the soft-mode displacive transition model with homogeneous ground state of Takesada *et al.* [3]. Shigenari [7] have previously pointed out that the soft-mode model would predict an orthorhombic state below T_c. However, their Brillouin and Raman data conflict with that. By comparison the rhombohedral nanocluster model of Blinc *et al.* [2] and Laguta *et al.* [18] states two things: (1) The local disorder at the Sr site is purely rhombohedral, and combined with the orthorhombic soft-mode distortion gives a resultant triclinic structure for ferroelectric SrTiO$_3$; (2) the local disorder never reaches the percolation level; therefore it in itself does not produce ferroelectricity. From

RUS we see that there is strong softening and acoustic dissipation which is consistent with the development of dynamic nanoclusters which have symmetry lower than tetragonal. We also see a good correspondence with the temperature at which the second-harmonic generation signal shows clear evidence of polar nanoclusters [19].

There is no established terminology for the unique kind of phase transition we infer in $SrTi^{18}O_3$. In magnetism for historic reasons an analogous structure is termed ''mictomagnet'' (e.g., [20,21]). One might also refer to it as a ''percolative'' transition, although Laguta *et al.* [18] emphasize that the percolation threshold of connectivity is probably not reached. The structure also has similarities with some incommensurate insulators, such as $Ba_2NaNb_5O_{15}$, where van Tendeloo *et al.* [22] showed short-range $2q$ discommensurations nucleating from the sides of long-range $1q$ discommensurations in a $1q$-$2q$ transition that lowers local symmetry; like this incommensurate structure, $SrTi^{18}O_3$ technically does not belong to any (3D) space group symmetry. The short-range order is also not like most relaxor ferroelectrics because there is no local compositional nonstoichiometry. We modestly refrain from specifying a label here, since that may be premature, but, in fact, the structure is basically that of a highly compact ''high-density glass,'' and is closest to metamictization in zircon. The process of metamictization of zircon and whether this is a proper phase transition is analyzed by Salje *et al.* [23]. Although all previous attempts (e.g., by x-ray techniques) at determining the crystallographic symmetry of $SrTi^{18}O_3$ in its ferroelectric phase have failed, we note that neutron structural studies are scheduled by one of the current authors to determine the oxygen ion positions and help with the semantic choice of label for this unique transition. Optimum terminology depends upon the interfaces between rhombohedral nanoclusters. If they are well separated, a brick-wall model is appropriate and implies significant elastic softening, whereas if they nestle closely, a Hashin-Shtrikman [24] model of space-filling bubble domains is more appropriate but implies little softening. Our data favor the former.

While RUS measurements do not give direct information in relation to the symmetry of $SrTi^{18}O_3$ at low temperatures, our overall conclusion is that the ferroelectric state is probably triclinic, dominated by rhombohedral nanoclusters embedded in an orthorhombic matrix. The rhombohedral clustering exhibits a mechanical loss peak with onset near 80–85 K, in agreement with NMR data, but does not reach the percolation level required for a phase transition. Instead the transition is triggered by a soft mode (Takesada *et al.* [3]), with a resulting triclinic (not orthorhombic) local structure. This helps explain the Raman spectra reported by Shigenari *et al.* [7]. $SrTi^{18}O_3$ must therefore be regarded as an example of a phase transition which is neither purely displacive nor purely order-disorder.

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