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CRITICAL ATTENUATION OF SOUND BY SOFT MODES IN $SrTiO_3$

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Measurements of acoustic attenuation in $SrTiO_3$ reveal critical scattering behavior near the structural phase transition at $T_a \cong 105$ K. Power laws for the frequency and temperature dependences have been found. By these measurements the behavior of the soft mode frequencies could be studied in a temperature range one order of magnitude closer to T_a than by other methods so far.

It has recently been demonstrated[1-3] that the structural transition taking place in $SrTiO_3$ at $T_a = 105$ K has associated with it a soft optical mode at the R corner of the Brillouin zone for $T > T_a$. The mode in question represents a dynamic rotation of the oxygen octahedra. Below the transition temperature this dynamic rotation is superimposed on a net static rotation[4-7] φ giving rise to a tetragonal distortion and a splitting of the soft mode. The rotation angle φ is the order parameter of the low-temperature phase.

Although the experiments[1-3] have established significant lowering of the soft-mode frequencies $\epsilon_1(T)$ when approaching T_a, they have not revealed the very low frequencies that are to be expected in the range $T_a \pm 5$ K if the condition is truly second order.

This work was undertaken because one expected ultrasonic attenuation to be appreciably more sensitive to the temperature dependence of $\epsilon_1(T)$ in the region where these frequencies become really low: In the presence of coupling[6-9] between optical and acoustic phonons the expected high density of optical phonons when $\epsilon_1(T) \ll kT$ strongly suggests critical scattering of ultrasound at the transition.

In the present note we report the first observations of such critical scattering in $SrTiO_3$. The measurements were performed on a pure Verneuil-grown single crystal obtained from the National Lead Company. Acoustic propagation was chosen along a [100] direction. Double-ended operation with separate transducers for the generation and detection of ultrasonic waves was employed. The sample was mounted in a probe that was in thermal contact with liquid nitrogen through a copper rod. The temperature of the sample could be controlled by adjusting the temperature gradient in the rod. The runs were made using a chart-recording technique by which the ultrasonic signal was continuously monitored as a function of the thermocouple voltage repre-

senting the sample temperature relative to that of liquid nitrogen. The temperature fluctuations in the sample were less than 0.01 K, and the reproducibility better than 0.05 K. Repeated measurements were made at eight different frequencies between 30 and 300 MHz, with longitudinal polarization.

In Fig. 1 we have plotted the data for the frequencies 32.5, 102, 163, and 214 MHz. The curves for the highest three of these frequencies display clearly the critical attenuation taking place at the transition: a strongly peaked attenuation at T_a, falling off rapidly to both sides. On the high-temperature side, the remaining attenuation is reduced to a few per cent at ~6 K above T_a. On the low-temperature side the temperature region available for observation of soft-phonon scattering is more restricted because of the sharply rising absorption edge. We associate this edge with phonon scattering on domain walls, since domain formation is known to occur in the present transition from cubic to tetragonal structure.[10] The lower curve in Fig. 1 displays this aspect of the transition very clearly. The frequency is too low for appreciable coupling to the optical mode, so the peak at T_a is missing. However, well below T_a the attenuation increases strongly. Evidently, the domain scattering is becoming effective here. The temperature dependence of the edge probably reflects directly the temperature variation of the average domain size. In this connection it should be noted that T_a is unambiguously defined in the higher frequency curves. Looking back at these curves, the domain scattering edge is also easily identified there. The qualitative features of the data in Fig. 1 are therefore readily understood. In addition, we can extract the following quantitative information: The frequency and temperature dependence of the attenuation of longitudinal sound along [100] for $T > T_a$ is given by

$$\alpha \propto \omega^n (T - T_a)^{-\eta},$$

where $n = 1.9 \pm 0.15$ and $\eta = 1.25 \pm 0.1$. The power law for the frequency dependence is found for reduced temperatures $t = (T - T_a)/T_a$ between 0 and 3×10^{-2}, while the power law for the temperature dependence is found for $9 \times 10^{-3} < t < 3 \times 10^{-2}$. These results are deduced from measurements at seven frequencies between 90 and 300 MHz.

It is of interest to compare the results for $T > T_a$ with those obtained by Pytte[11] on the basis of a model Hamiltonian. In the temperature region

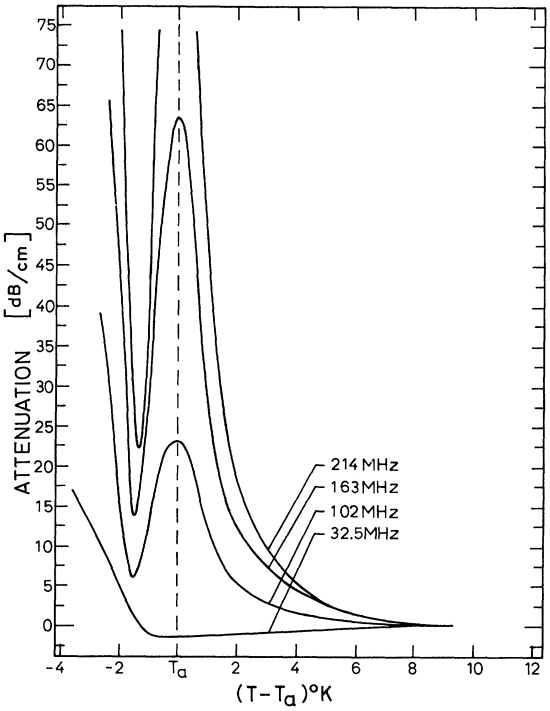

FIG. 1. Critical attenuation of longitudinal sound along [100] in $SrTiO_3$.

where we found a power-law dependence, these calculations give $n = 2$, $\eta = 1.5$ for interaction with overdamped soft modes. On the other hand, underdamped modes in this model correspond to $n = 2$, $\eta = 0.5$. In both cases it is assumed that the ultrasonic frequency is much less than the soft-phonon damping parameter Γ. While the temperature dependence of acoustic attenuation in that model is sensitive to the value of Γ relative to the soft-mode frequency $\epsilon_i(T)$, the frequency dependence ω^2 will always result when $\Gamma \gg \omega$. The latter condition may be assumed satisfied in the frequency region of interest to us.

For $T < T_a$ the situation is more complex both experimentally and theoretically. The presence of domain scattering obscures the experimental picture in the region where one might attempt carrying out an analysis similar to what was done for $T > T_a$. Also, simple power laws may not be expected to hold here since the theory[11] predicts an additional resonant interaction term in the attenuation.

It should be mentioned that the absence of a small peak at T_a in the 32.5-MHz data was somewhat unexpected. A trace of the singularity could have been anticipated here. Possibly this fact should be regarded as connected with the rounding of the curves in the range $T_a \pm 0.9$ K: The

frequency dependence tends to be somewhat stronger in the rounded region than in the region where a power-law temperature dependence is found. As to the cause of the rounding, it is felt that the quality of the sample is directly responsible. First of all, from EPR linewidth measurements of impurity present, Fe^{3+} ions, we have estimated that the order of magnitude of the built-in strains may locally be as high as 100 kg/cm^2 in samples of this type. This may cause a certain smearing of the transition. Furthermore, it has been found in magnetic transitions[12] that impurities have the effect of producing statistical variations in T_a over the sample. Such impurities are present in the Verneuil-grown $SrTiO_3$ crystals in appreciable quantities.

We conclude that our results give evidence for strong mutual interaction between acoustic phonons and soft modes in $SrTiO_3$, below as well as above T_a. The frequency dependence for $T > T_a$ being ω^2 rather than linear in ω shows that the soft modes are indeed damped ($\Gamma \gg \omega$). Furthermore, the temperature dependence for $9\times10^{-3} < t < 3\times10^{-2}$ is close to that predicted for an overdamped soft mode.[11] Our measurements strongly indicate that the transition is not of first order, since hysteresis beyond 0.05 K has not been found. We should also like to point out that the measurements were made in a temperature region where other methods like neutron and Raman scattering and ESR measurements are not easily made with sufficient resolution. This makes ultrasonic measurements even more valuable. The agreement between theory[11] and experiment, in fact, provides the first direct experimental verification of the extreme softness of the optical modes. This occurs down to $T_a \pm 0.5$ K. Earlier the temperature dependence had only been studied to $T_a \pm 5$ K.[2,3] Further results will be given elsewhere.[13]

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