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Brillouin-scattering observation of the TA-TO coupling in $SrTiO_3$

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Brillouin scattering from transverse-acoustic modes of $SrTiO_3$ is observed, while the frequencies of the soft polar modes are remeasured with hyper-Raman scattering. It is shown that an anomalous decrease of sound velocities at low temperatures results from the coupling of the strain with the gradient of the electrical polarization fluctuations. The corresponding anomaly in the acoustic width indicates an inhomogeneous broadening of the soft polar mode. [S0163-1829(98)50822-3]

There recently appeared several low-temperature (T) investigations of $SrTiO_3$ and related incipient ferroelectrics.[1–13] Many were triggered by the report that an unexpected, apparently non-symmetry-breaking, transitionlike feature occurs in $SrTiO_3$ at $T_q \approx 37$ K.[14] A reinvestigation of low frequency (ω) and wave-vector (q) modes of $SrTiO_3$ using both Brillouin- and neutron-scattering spectroscopies[3] indeed revealed low-T anomalies, although not necessarily related to T_q. In Brillouin spectroscopy, the most intriguing observations were (i) the existence of an additional broad Brillouin doublet[3,7] and (ii) the appearance of an unusual low-T softening of some shear modes.[3,9] The origin of (i) is still under investigation.[15,16] We present here the explanation for (ii). The early data, complemented by newer results, demonstrate that the anomalous softening is due to a bilinear coupling between the strain and the gradient of the electrical polarization fluctuations. This coupling, already described long ago,[17,18] can lead to the anticrossing of the transverse acoustic (TA) branches with the soft transverse optic (TO) ones. At small q's, the coupling just depresses the TA-frequency proportionally to q^2. The effects of this coupling were identified so far at the large q's of neutron scattering.[18,19] It appears to be the first time that its signature is seen in *any* material at the small q's of Brillouin spectroscopy.

In our experiments, Brillouin scattering was excited with a single-mode argon laser operating at $\lambda = 5145$ Å, and analyzed with a six-pass tandem interferometer.[7] The T region of interest is below the cubic-to-tetragonal structural transition at $T_a \approx 105$ K. It is essential to these measurements that the $SrTiO_3$ crystal be *oriented* in its tetragonal phase below T_a. This is achieved with a moderate uniaxial pressure applied on a (110) face while cooling through T_a. This forces the c axis in the orthogonal [001] direction.[20] In early measurements,[7,9] [results reproduced in Fig. 1(a)], a pressure of ≈ 1 kbar was necessary. For the data in Fig. 2(a), obtained on a new crystal, a pressure below 0.1 kbar was sufficient, provided T was lowered slowly through T_a.[21] In both cases the pressure was released at T below T_a, and the samples maintained their orientation at low T.

We concentrate here exclusively on two TA modes, one propagating along the tetragonal-axis c, and thus polarized in the ab plane, and a second one propagating along the diagonal d of the ab plane and polarized along c. Both modes relate to the *same* tetragonal elastic constant C_{44}.[23] The observed acoustic velocities of these modes, given by $V = \omega / q$, are labeled V_{44}^c and V_{44}^d, respectively. Owing to the particular crystal cut required for the application of the ori-

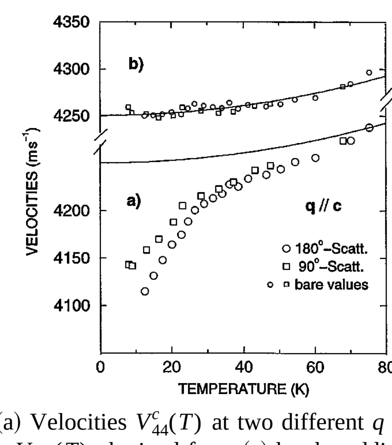

FIG. 1. (a) Velocities $V_{44}^c(T)$ at two different q values; (b) the bare velocity $V_{\mathrm{TA}}(T)$ obtained from (a) by the addition of $|\Delta V|$ as explained in the text. The solid lines are guides to the eye.

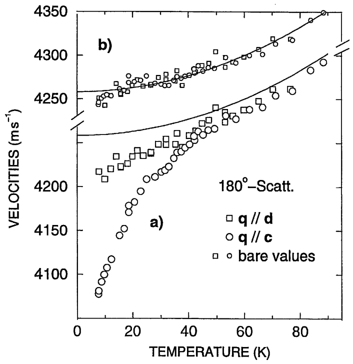

FIG. 2. (a) Velocities $V_{44}^c(T)$ and $V_{44}^d(T)$ measured in backscattering; (b) the corresponding bare velocity $V_{TA}(T)$ obtained from (a) by the addition of $|\Delta V|$ as explained in the text. The solid lines are guides to the eye.

enting pressure, the accessible scattering geometries are restricted. Some early data [Fig. 1(a)] were obtained in 90° scattering.[7,9] For all the other data, it was convenient to use backscattering. Although backscattering from these TA modes is forbidden,[23] there is sufficient leakage to allow the measurement, as shown in Fig. 1 of Ref. 7. An important remark is that the leakage is not T dependent. For any given scattering geometry, the ratio of the forbidden TA intensity to the allowed longitudinal acoustic (LA) one remains constant below T_a. Hence, it is difficult to argue that the T dependent anomalies in V are connected with leakage. Furthermore, since same anomalies are seen in rather different samples (Figs. 1 and 2), their origin can be presumed intrinsic.

Figure 1(a) shows early data for two q values corresponding to 90° and 180° scattering, $q \cong 4.2\times 10^5$ and 6.0×10^5 cm^{-1}, respectively. Here $q = 4\pi n \sin(\theta/2)/\lambda$, where θ is the scattering angle, and $n = 2.47$ is the refractive index whose weak T dependence is neglected. The measured frequency shifts ω, which are approximately 28 and 40 GHz, respectively, were converted to velocities in Fig. 1(a). In these measurements q is parallel to c, so that $V = V_{44}^c$. Uncertainties in the instrument calibration, as well as in the precise value $\theta \cong 90°$, do not allow a direct comparison of the absolute velocities for the two geometries. The data for 90° scattering were thus shifted up by 32 m/s, which is less than its precision, to match it to that for 180° scattering. Above ≈ 35 K the curves nearly overlap, whereas at lower temperatures they are distinct. This implies that V_{44}^c has a T-dependent anomaly that is a function of the *size* of q.

Figure 2(a) shows data obtained in backscattering from two different directions on a recently grown Verneuil crystal.[21] Neglecting the very small birefringence, the same $q \cong 6.0\times 10^5$ cm^{-1} applies to both curves. Whereas there is a large drop in V_{44}^c at low T, just as in Fig. 1(a), the corresponding anomaly on V_{44}^d is much smaller. The actual data points for V_{44}^c were shifted down by 20 m/s to match them to V_{44}^d at high T. The large difference observed at low T demonstrates that the anomaly in V also depends on the *direction* of q.

The fact that V depends both on the size and direction of q is reminiscent of piezoelectric crystals, where this results from the bilinear coupling between strain and electrical polarization.[24] Here however, the symmetry does not allow such a coupling, but rather one between the strain and the *gradient* of polarization. The symmetry further imposes that the acoustic displacement u be parallel to the polarization vector P to which it couples, while the gradient is along q. The displacement u, for $q\|c$, lies in the ab plane, like P for the doubly degenerated softest TO mode of symmetry E_u. On the other hand, for $q\|d$, one has $u\|c$, which is parallel to P for the somewhat harder TO mode of symmetry A_{2u}. A discussion of these TO mode symmetries is given in Ref. 25. With a notation inspired from Vaks,[17] the equations for the coupled displacement and polarization amplitudes for waves at ω and q are written,

$$(aq^2-\omega^2)u+vq^2P=0, \tag{1a}$$

$$vq^2u+(\Lambda/\varepsilon+sq^2-\omega^2)P=0. \tag{1b}$$

Here, v is the coupling constant, and all indices were dropped. For both TA modes, $a \equiv C_{44}/\rho$. The bare TA frequency is $\omega_{TA}^2 = aq^2$, and the *bare* acoustic velocity is $V_{TA} = \omega_{TA}/q = \sqrt{a}$. The bare TO frequency at $q=0$ is $\Omega^2 = \Lambda/\varepsilon$, where ε is the appropriate dielectric constant. For $q\|c$, P is in the ab plane, $\varepsilon = \varepsilon_a$, and $\Omega = \Omega_a$, the frequency of the softest TO mode of E_u symmetry. For $q\|d$, one has $P\|c$, $\varepsilon = \varepsilon_c$, and $\Omega = \Omega_c$, the frequency of the second-softest TO mode of A_{2u} symmetry. It is this difference in Ω which produces the largely different V's for the two scattering directions in Fig. 2(a), as explained below. The dispersion term sq^2 is added to Fig. 1(b) for completeness. It is not needed for the discussion of Brillouin scattering, as for small q, $\Omega^2 \gg sq^2$. For convenience we define a bare TO frequency at $q\neq 0$ by $\omega_{TO}^2 = \Lambda/\varepsilon + sq^2$. Finally, the coupling term vq^2 was strictly the same for both scattering directions if the crystal remained cubic. However, owing to the tetragonal distortion, v can be slightly different for the two directions. This difference is proportional to the square of the order parameter of the tetragonal phase, the oxygen-octahedron rotation angle squared ϕ^2, and it should be relatively small. It is neglected in the analysis below.

Solving Eq. (1) for the two eigenfrequencies, ω_+ and ω_-, one obtains

$$\omega_\pm^2 = \tfrac{1}{2}\,[(\omega_{TA}^2+\omega_{TO}^2) \pm \sqrt{(\omega_{TO}^2-\omega_{TA}^2)^2+4v^2q^4}]. \tag{2}$$

At small q, the square root in Eq. (2) is expanded and one finds to lowest order in q,

$$\omega_- - \omega_{TA} \equiv \Delta\omega \cong -\tfrac{1}{2}v^2q^4/\omega_{TA}\Omega^2. \tag{3}$$

The anomaly ΔV produced by the coupling is then $\Delta V \equiv V - V_{TA}$, where $V \equiv \omega_-/q$. It is negative, corresponding to a softening. From Eq. (3), it can be written

$$\Delta V/V_{TA} = \Delta\omega/\omega_{TA} \cong -v^2q^2/2V_{TA}^2\Omega^2. \tag{4}$$

Its dependence on q^2 can be verified from the data in Fig. 1(a), and that in Ω^{-2}, from these in Fig. 2(a). In effect, we now determine the value of v such that $|\Delta V|$ added to V leads to a single curve for the bare velocity, $V_{TA}(T)$, as shown in Figs. 1(b) and 2(b). One remarks that the bare velocity V_{TA} can still be weakly T dependent at low T, owing to the combined effects of anharmonicity and of the transition at T_a.

To carry out this plan, one needs accurate values for Ω_a^{-2} and Ω_c^{-2}. These quantities become large and vary rapidly at

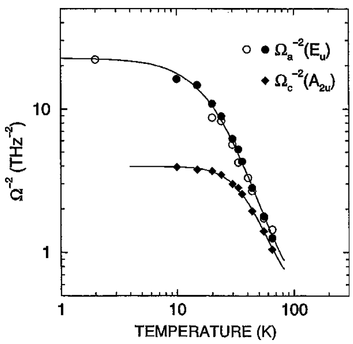

FIG. 3. Hyper-Raman scattering results on the inverse soft-mode frequencies, Ω_a^{-2} and Ω_c^{-2}, for the soft modes of E_u and A_{2u} symmetries, respectively. The ○ are from Ref. 11. The lines are guides to the eye.

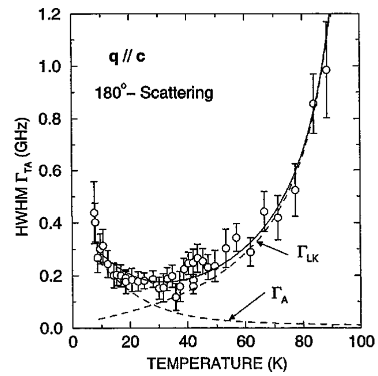

FIG. 4. The HWHM, $\Gamma_{TA}(T)$, of the Brillouin line corresponding to $V_{44}^c(T)$ in Fig. 2. The lines are explained in the text.

low T. Sufficiently detailed values of Ω^{-2} could not be derived from the literature. Hence, these frequencies were remeasured with hyper-Raman spectroscopy. The apparatus is described elsewhere.[11] The sample is a Verneuil crystal,[21] oriented with a slight vertical (V) pressure on a (1 1 0) face. Near backward scattering along the second [1 1 0] direction is observed. In VH polarization, where the horizontal H is $\parallel c$, one measures the A_{2u} mode, whereas the HV geometry gives the E_u mode. The results, complemented with other recent data on the E_u mode,[11] are shown in Fig. 3 on a scale emphasizing the low-T range. One remarks that $\Omega_c^2-\Omega_a^2=\Lambda(t_{12}^x-t_{11}^x)\phi^2/2\pi$ from Ref. 25, while ϕ^2 can be taken from Ref. 26. From an adjustment of our $\Omega_c^2-\Omega_a^2$ data to ϕ^2 over the entire measured range of T, we obtain $t_{12}^x-t_{11}^x=1.27\times10^{15}$ cgs.[27]

Using the values of Ω^{-2} in Eq. (4), one adjusts the constant v to obtain a single curve for $V_{TA}(T)$ from the two curves in Fig. 1(a), and also a single curve from the two curves in Fig. 2(a). One neglects the weak T dependence of v, and the only important T dependence that needs to be accounted for in Eq. (4) is that of Ω^{-2}. The resulting data points for $V_{TA}(T)$ are drawn in Figs. 1(b) and 2(b), respectively. The smooth T dependences found for $V_{TA}(T)$ in both cases give strong support to this explanation. The solid lines are two-parameter fits to parabolas, as guides to the eye. The same parabolas are traced in the lower parts of the figures to illustrate the strength of ΔV. The shape of $V_{TA}(T)$ is in good agreement with ultrasonic data on pressure-oriented samples,[28,9] as it should be, since in ultrasonics q is so small that ΔV is negligible. From this adjustment we obtain $\sqrt{v}=5300$ m/s, with an estimated accuracy of $\pm 8\%$. This value agrees with a small-q neutron measurement on the coupling of the A_{2u} mode with the TA mode, which gave $\sqrt{v}\approx5500$ m/s (see Fig. 2 of Ref. 3). Interestingly, the v extracted from neutron measurements on $KTaO_3$ (the only other perovskite for which it is known) is nearly the same, $\sqrt{v}=5100$ m/s.[18] However, a Brillouin anomaly was very hard to observe in $KTaO_3$ since Ω^{-2} is an order of magnitude smaller than in $SrTiO_3$.

Finally, it is worthwhile to investigate whether there is a measurable phonon-linewidth anomaly associated with ΔV. Figure 4 shows the Brillouin widths Γ_{TA} derived together with V_{44}^c data of Fig. 2(a). To obtain these widths, the spectra were fitted to Lorentzians convoluted with the instrumental function. The error bars are sizable since the instrumental half-width at half maximum (HWHM) is relatively large, ≈ 0.4 GHz. Nevertheless, one can recognize two obvious contributions to the width. One arises from the structural transition itself, noted Γ_{LK} in Fig. 4, and a second one, noted Γ_A, relates to the anomaly ΔV.

The structural transition produces a bilinear coupling between the strain and the antiferrodistortive displacement of E_g symmetry,[25] owing to the order parameter ϕ. The term in the free-energy expansion responsible for this effect is the one designated by b_{ijkl} in Ref. 25, the component of interest here being b_{2323}. It produces a rapid variation of C_{44} near T_a.[29] Its amplitude, ΔC_{44}, induces a damping by the Landau-Khalatnikov (LK) mechanism.[30] In the simplest phenomenology, the change in complex modulus is $\Delta C=\Delta C_{44}/(1+i\omega\tau)$, where τ is the time constant associated with the critical slowing down of the antiferrodistortive soft mode, $\tau=\tau_0 T/|T-T_a|$. Assuming that $\omega_{TA}\tau\ll1$, the imaginary part of ΔC produces a width $\Gamma_{LK}=\Delta\omega_{tr}\chi_a''/\chi_a'=\Delta\omega_{tr}\omega_{TA}\tau$. Here, $\Delta\omega_{tr}$ is the jump of ω_{TA} near T_a, and χ_a is the susceptibility of the soft mode at frequency ω_{TA}. The condition $\omega_{TA}\tau\ll1$ is satisfied since the measured $\Delta\omega_{tr}\approx6$ GHz is much larger than the width in the region of interest. Then, the only important T dependence in Γ_{LK} is that in τ, which is known from T_a. The adjustment of Γ_{LK} depends on a single prefactor that lumps all the constants. A good agreement is obtained in the higher T region, as illustrated by the dotted line marked Γ_{LK} in Fig. 4. A small constant background was added to the calculated Γ_{LK} value to account for the broadening produced by the finite collection angle in the experiment. This calculated broadening is very small (0.016 GHz HWHM) owing to the backscattering geometry.

We now turn to the anomalous contribution Γ_A that develops at low T. This contribution is specific to the mode whose velocity is V_{44}^c. For the TA mode of velocity V_{44}^d, we find $\Gamma_{TA}\cong\Gamma_{LK}$, where Γ_{LK} is the same LK damping as above, with no appreciable additional broadening at low T. Since the anomaly in velocity is much weaker for the mode propagating along d, Γ_A must be related to the anomaly $\Delta\omega$ given in Eq. (4), in which case it cannot be derived from a standard calculation of the damping.[31] To estimate Γ_A, one might first attempt to use an expression inspired from the LK theory. Replacing $\Delta\omega_{tr}$ by $|\Delta\omega|$, and using for χ the complex susceptibility χ_ε of the soft polar mode at ω_{TA}, one finds $\Gamma_A=|\Delta\omega|\chi_\varepsilon''/\chi_\varepsilon'=|\Delta\omega|\tan\delta$. We note that $|\Delta\omega|$ is less than 2 GHz at the lowest T. The value of tan δ at 8 K and 10 GHz is known from microwave measurements.[32] Using $\tan\delta \tilde{\propto} \omega$, the loss factor extrapolates to less than 10^{-3} at $\omega_{\mathrm{TA}} \approx 40$ GHz. Hence, one estimates that $\Gamma_A < 2$ MHz from this mechanism, which is much too small to account for the observations in Fig. 4. A likely explanation for the large value of Γ_A is that the width of the soft TO mode of E_u symmetry, Γ_Ω, which is known from hyper-Raman scattering,[33] arises from a spatial spread of the soft-mode frequency. Then the spread in ω_- is also inhomogeneous, and Γ_A must be calculated from the derivative of Eq. (3). This gives

$$\Gamma_A \cong |\Delta\omega| \frac{2\Gamma_\Omega}{\Omega}. \tag{5}$$

The value of Γ_Ω has been measured for several samples in Ref. 33, and it was indeed found to be sample dependent. The full width $2\Gamma_\Omega$ shown in Ref. 33 refers to the ''best'' sample i.e., the one that exhibited the weakest hyper-Rayleigh signal together with the smallest Γ_Ω. The dotted line marked Γ_A in Fig. 4 is obtained using that $2\Gamma_\Omega$ in Eq. (5), and multiplying it by a constant equal to 1.6, which is reasonably close to 1. Preliminary measurements of the width of our own hyper-Raman signal indicate, however, that our sample is somewhat better than the best sample in Ref. 33, as it shows a smaller Γ_Ω. We presume that there might be an increase of Γ_A over the value (5) owing to the fact that the observed TA scattering arises from the leakage of a forbidden process, meaning that it is likely to originate from regions of the crystal forbidden process, meaning that it is likely to originate from regions of the crystal that are more disturbed than average. The sum of the two dotted lines in Fig. 1 gives the solid line marked Γ_{TA}, in satisfactory agreement with observations. We are aware that a simple summation of Γ_A and Γ_{LK} might not be strictly correct, but the low accuracy of the data does not justify a more elaborate treatment. This quantitative analysis implies that fairly large scale inhomogeneities in the soft-mode frequency lead, via the coupling-induced changes in the TA mode frequency, to the apparent width of the dressed TA mode propagating along c.

In conclusion, we have established that the Brillouin-scattering anomalies observed at low temperatures on the TA modes of $SrTiO_3$ are produced by the coupling of the shear strain to the gradient of the electrical polarization. These anomalies are neither related to T_q,[14] nor to the crossing of the soft E_g and E_u modes.[15] This appears to be the first time that this coupling is observed at Brillouin frequencies. The observation is made possible by the exceptionally low soft-mode frequency.

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