TABLE I. ZnO multiphonon frequencies (±3 cm^{-1}).

	(cm^{-1})
1 LO	585
2 LO	1165
3 LO	1749
4 LO	2343
5 LO	2928
6 LO	3520
7 LO	4101
8 LO	4678

in LO overtone scattering.[5] Since a is typically less than 1 cm^{-1} in cubic crystals, we ordinarily see[5] multiphonon linewidths dominated by one-phonon lifetimes or spectral slit width and, hence, approximately independent of n, the order of the scattering process.

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[1]R. C. C. Leite and S. P. S. Porto, Phys. Rev. Letters 17, 10 (1966).

[2]R. C. C. Leite, T. C. Damen, and J. F. Scott, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer-Verlag, New York, 1969), pp. 359–368.

[3]R. C. C. Leite and J. F. Scott, Phys. Rev. Letters 22, 130 (1969); K. Nill and A. Mooradian, Bull. Am. Phys. Soc. 13, 1658 (1968).

[4]A. Pinczuk and E. Burstein, Phys. Rev. Letters 21, 1073 (1968).

[5]J. F. Scott, R. C. C. Leite, and T. C. Damen, Phys. Rev. 188, 1285 (1969).

[6]J. F. Scott, T. C. Damen, R. C. C. Leite, and W. T. Silfvast, Solid State Commun. 7, 953 (1969).

[7]J. F. Scott, T. C. Damen, W. T. Silfvast, R. C. C. Leite, and L. E. Cheesman, Optics Commun. 1, 397 (1970).

[8]S. S. Devlin, in *Physics and Chemistry of II–VI Compounds*, edited by M. Aven and J. S. Prener (Wiley, New York, 1967), p. 566.

[9]D. C. Hamilton, Phys. Rev. 188, 1221 (1969).

[10]T. C. Damen, S. P. S. Porto, and B. Tell, Phys. Rev. 142, 570 (1966). Our measured 1-LO frequencies are ~3 cm^{-1} higher.

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Sound Propagation near the Structural Phase Transition in Strontium Titanate†

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Finite ultrasonic velocity changes at the structural phase transition in $SrTiO_3$ are observed for different modes. They are interrelated and correlated by theory. No critical effects are observed.

Ultrasonic waves are an effective probe for studying static and dynamic aspects of phase transitions.[1] Here we would like to present ultrasonic velocity data near the structural phase transition in strontium titanate ($SrTiO_3$). We will interpret and correlate them with recent theories[2,3] and Brillouin scattering experiments.[4] Our results show that this phase transition exhibits characteristic features of a Landau-type displacive phase transition – namely, pronounced but finite velocity changes and the absence of critical effects, such as observed in magnetic phase transitions.[5] Our experiments supersede previous ones[6] in two important aspects: First, our transition occurs ~8 °K lower, probably due to improved crystal quality and, second, due to our special measuring technique,[7] we were able to measure through the transition region for various geometries, which enables us to interpret our data quantitatively.

It is now well established that the $T_a \sim 106$ °K phase transition in $SrTiO_3$ has associated with it a soft optic mode[8,9] and an order parameter ϕ which describes a static rotation of the oxygen octahedra.[10,11] If one also considers the strain–soft-mode interactions, then theory predicts a finite change in the elastic constants at T_a.[2,3,12] Taking the full symmetry of the crystal, theory[2,3,13] predicts for the elastic constants for $T < T_a$

$$c_{11} = c_{11}^c - 1.6D, \quad c_{33} = c_{11}^c - 4D, \quad c_{12} = c_{12}^c - 1.6D,$$

$$c_{13} = c_{12}^c + 2.4D, \quad c_{44} = c_{44}^c - E, \quad c_{66} = c_{44}^c \qquad (1)$$

(c_{ij}^c are cubic elastic constants); i.e., the elastic constant changes at T_a can be represented by two

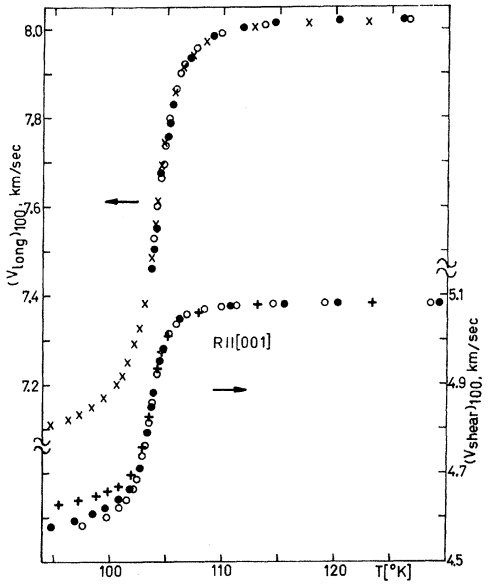

FIG. 1. Velocities for longitudinal and shear waves propagating in a ⟨100⟩ direction. Open circles: 50 MHz; closed circles: 30 MHz; ×: 16 MHz; crosses: 10 MHz. Shear-wave polarization vector $R(001)$.

parameters D and E, which are related to the strain interaction coupling constants and other phase transition parameters.[2,3] It is worth pointing out that E does not depend on soft-mode parameters, whereas D does.

We investigated three single crystals which were purchased from National Lead Co. and oriented along ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions, respectively. The dimensions are 15×5×5 mm. Our velocity measuring apparatus[7] is particularly suitable for measuring strongly modulated echo patterns, because it employs a phase comparison method using only a single echo at constant amplitude. This eliminates systematic errors which one could encounter, for example, using a pulse superposition method applied to such a pattern. We stabilized the temperature to better than 10 mdeg. The temperature gradient along the sample was also kept smaller than 10 mdeg. We noticed that we could not measure "on the fly", since it took very long to reach thermal equilibrium, a typical run lasting ~20 h.

Figures 1 – 3 show our results for the different modes. One notices (see Fig. 3) a flattening in the temperature dependence of the velocity around 130 °K followed by a sharp decrease below 110 °K and again a flattening below 103 °K. Measurements with different frequencies reveal frequency-dependent velocity changes below 103 °K as shown in Figs. 1 and 2. This effect is due to the formation of domains below T_a. It is already present in the temperature region 103–106 °K, but overshadowed by the large velocity changes. Clearly, all our experimental results demonstrate the sort of behavior predicted by theory [Eq. (1)] except that the transition occurs not as a step function, but rather, broadened over a few degrees. This is probably due to residual strains in the crystal which one can observe visually using polarizers. It also prevents us from determining $T_a \sim 106$ °K with any precision.

For a quantitative interpretation of our results we have to define the total velocity change through the transition. This we choose, somewhat arbitrarily, as the velocity change between $T \sim 102.5$ °K, the temperature where the velocity changes for different frequencies visibly flatten, and the intercept (at $T \sim 106$ °K) of the extrapolated straight line from the transition region and the high-temperature extrapolation of the velocity change not associated with the phase transition (which agrees quantitatively with the measurements in Ref. 6). This procedure is illustrated in Fig. 3 by the solid lines. Different methods of obtaining the total velocity change would affect the quoted values for E and D by less than 10%. The measured velocity changes are given in Table I, column 4 for the different modes. In Table I, we have also listed the various measured modes, their effective elastic constants c^c in the cubic phase, and the velocity changes predicted using the elastic constants in Eq. (1). In doing so we made an important assumption concern-

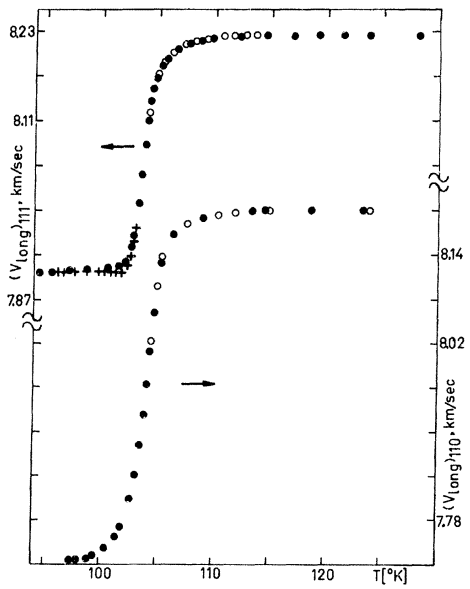

FIG. 2. Longitudinal sound velocities for propagation along the ⟨111⟩ and ⟨110⟩ directions. Symbols are the same as in Fig. 1.

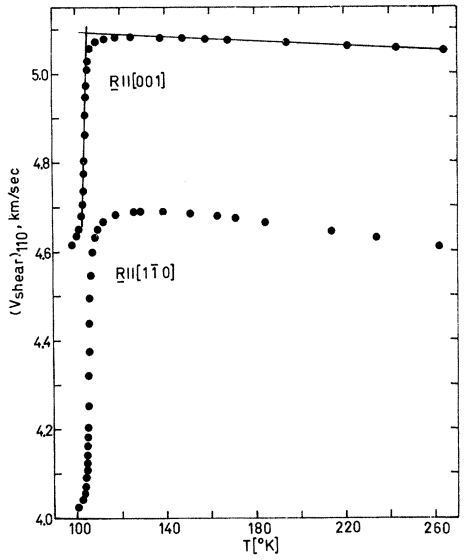

FIG. 3. Shear wave sound velocities for propagation in the [110] direction. Shear wave polarization vectors $\vec{R}\|[001]$ and $\vec{R}\|[1\bar{1}0]$. Symbols are the same as in Fig. 1. The solid lines indicate procedure for estimating total velocity change (see text).

ing the distribution of the tetragonal domains. We assumed that all domains occur with equal probability. Judging from our nicely correlated results and from the fact that we measured three well-annealed crystals grown from different batches, this seems a reasonable assumption. With this assumption one can calculate the velocity changes by averaging over different domains. For example, a longitudinal wave propagating along a ⟨100⟩ direction has a $\frac{1}{3}$ contribution due to c-axis propagation ($v^2 = c_{33}/\rho$) and a $\frac{2}{3}$ contribution due to a-axis propagation ($v^2 = c_{11}/\rho$). This gives a total velocity change $\Delta v/v = -1.2D/c^c_{11}$, etc. From Table I it follows that we have two independent measurements of E, two independent measurements of D, and two coupled determinations of E and D. The results are given in the last two columns of Table I. They show that these values can be determined fairly accurately.

We can compare our results with experimental results from Brillouin scattering experiments.[4] In these experiments the phonon wavelength is usually smaller than a typical domain size. Therefore, no domain averaging is necessary in this case. For shear wave propagation along the c-axis one gets from these experiments[4] $E = 0.31 \times 10^{12}$ erg/cc, in good agreement with our results. From longitudinal waves along a ⟨100⟩ axis the authors quote a 4% shift, which would correspond nicely with a 8% ultrasonic belocity change, using domain averaging. However, the authors[4] do not specify whether the propagation direction was along an a or c axis.

Estimates for D, using c/a ratio measurements[14] and T_a–pressure-dependence data,[15] give values[2,3] of the order $0.04-0.07 \times 10^{12}$ erg/cc, in bad agreement with our results. It should be emphasized, however, that a number of soft-mode parameters enter these estimates as well.

In any case, our experimentally determined parameters E and D are very nicely interrelated for the various modes, indicating that the proposed model[2,3] describes the physical situation rather

TABLE I. Total velocity changes at the structural phase transition in $SrTiO_3$.

Mode ($\vec{R}$ = polarization vector)	Propagation direction	Cubic elastic[a] constant c^c	Theoretically predicted velocity change $\Delta v/v$	Experimentally determined velocity change $\Delta v/v$ (in %)	E (10^{12} erg/cc)	D (10^{12} erg/cc)
(1) Long.	[100]	c_{11}	$-1.2D/c^c$	9.0		0.24
(2) Shear $\vec{R}\|[001]$	[100]	c_{44}	$-E/3c^c$ [b]	7.9	0.30	
(3) Long.	[111]	$\frac{1}{3}(c_{11}+2c_{12}+4c_{44})$	$-(1/9c^c)(0.4D+4E)$	3.8	0.28	0.20
(4) Long.	[110]	$\frac{1}{2}(c_{11}+c_{12}+2c_{44})$	$-(1/3c^c)(D+E)$	5.1	0.30	0.22
(5) Shear $\vec{R}\|[001]$	[110]	c_{44}	$-E/3c^c$ [b]	8.1	0.31	
(6) Shear $\vec{R}\|[1\bar{1}0]$	[110]	$\frac{1}{2}(c_{11}-c_{12})$	$-2.6D/3c^c$	14.3		0.19
					$E_{av} = 0.30 \pm 0.02$	
						$D_{av} = 0.21 \pm 0.03$

[a]The values for c^c_{ij} used here (in 10^{12} erg/cc units): $c^c_{11} = 3.31$, $c^c_{12} = 1.26$, and $c^c_{44} = 1.05$.

[b]These two cases belong to different physical situations. The domain averaging gives, however, an identical expression.

well.

Finally, we would like to comment on the absence of any critical effects and on recent ultrasonic attenuation experiments.[16,17] The absence[18] of any critical effects can be due either to the fact that the structural phase transition is a true Landau transition in which fluctuations are rather small or that the strain broadening mentioned earlier masks any critical effects. We were not able to measure ultrasonic attenuation reliably in the transition region due to the strong (strain) modulation of the echo pattern. This has been noticed before.[16] The absence of characteristic critical velocity minima, as observed in magnetic phase transitions,[5] suggests that the observed ultrasonic attenuation maxima are also possibly due to resonant interaction with the soft mode.

Note added in manuscript. Recent Brillouin scattering measurements [D. C. O'Shea, Bull. Am. Phys. Soc. 15, 383 (1970), paper KD6] give the following vlaues for E and D: $E=(0.33\pm0.02)\times10^{12}$ erg/cc, $D=(0.06\pm0.02)\times10^{12}$ erg/cc. Again the shear constant E is in good agreement with our value, whereas D is significantly smaller than our value.

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[1]For an excellent review for various phase transitions see, for example, C. W. Garland, in *Physical Acoustics* (Academic, New York, 1970), Vol. VII.

[2]E. Pytte and J. Feder, Phys. Rev. 187, 1077 (1969); and (to be published).

[3]J. C. Slonczewski and H. Thomas (to be published).

[4]W. Kaiser and R. Zurek, Phys. Rev. Letters 23, 668 (1966); R. Zurek, thesis, Technische Hocschule München, 1969 (unpublished).

[5]B. Lüthi, T. J. Moran, and R. J. Pollina, J. Phys. Chem. Solids (to be published).

[6]R. O. Bell and G. Rupprecht, Phys. Rev. 129, 90 (1963); G. Rupprecht and W. H. Winter, *ibid.* 155, 1019 (1967).

[7]T. J. Moran and B. Lüthi, Phys. Rev. 187, 710 (1969).

[8]P. A. Fleury, J. F. Scott, and J. M. Worlock, Phys. Rev. Letters 21, 16 (1968).

[9]G. Shirane and Y. Yamada, Phys. Rev. 177, 858 (1969).

[10]H. Unoki and T. Sakudo, J. Phys. Soc. Japan 23, 546 (1967); K. A. Müller, W. Berlinger, and F. Waldner, Phys. Rev. Letters 21, 814 (1968).

[11]H. Thomas and K. A. Müller, Phys. Rev. Letters 21, 1256 (1968).

[12]If one takes the free energy in a simple model composed of $F=\frac{1}{2}c_0\epsilon^2+B\epsilon\phi^2+a\phi^2+b\phi^4$, where the first term represents the elastic energy, the second one the strain–order-parameter interaction, and the rest the usual Landau terms, then we get for $T>T_a$, $c=c_0$ and for $T<T_a$, $c=c_0-B^2/2b$ a finite change.

[13]The changes for the elastic constants c_{11}, c_{12}, and c_{13} are different for the two theories (Refs. 2 and 3). Reference 3 assumes no volume change at T_a, whereas Ref. 2 allows for it. In the former case $c_{11}=c_{11}^c-D$, $c_{12}=c_{12}^c-D$, and $c_{13}=c_{12}^c+2D$. These differences in the parameter D as determined from our experiment are $\sim 20\%$.

[14]B. Alefeld, Z. Physik 222, 155 (1969).

[15]B. Pietrass and E. Hegenbarth, Phys. Status Solidi 34, K119 (1969).

[16]R. Nava, R. Callarotti, H. Ceva, and A. Martinet Phys. Letters 28A, 456 (1968); Phys. Rev. 188, 1456 (1969).

[17]B. Berre, K. Fossheim, and K. A. Müller, Phys. Rev. Letters 23, 589 (1969).

[18]The small dip in sound velocity for a ⟨111⟩ propagation direction for 10 MHz at $T\sim102$ °K, which was also observed in Ref. 6, cannot be associated with any critical effects because it is absent for 30 MHz.