

elsewhere for an explanation of the large values of  $\delta$  in these metals.

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## Elastic Constants of Strontium Titanate\*

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The elastic constants  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$  of single-crystal strontium titanate have been measured as a function of temperature from 300 to 108°K by determining the velocity of an ultrasonic wave. At 108°K the strontium titanate undergoes a phase transition to a tetragonal structure which causes a marked change of the elastic properties and the appearance of a domain structure, but does not cause a discontinuity of the dielectric constant. The phase transition is free of hysteresis. The dependence of the elastic properties on a dc electric field parallel to the velocity of sound propagation was measured and found independent of the dielectric properties. The implications of this result are discussed.

### I. INTRODUCTION

STRONTIUM titanate is a cubic material above 108°K with the perovskite structure which exhibits paraelectric properties. Its dielectric constant follows a Curie-Weiss law and is dependent on an external electric field.<sup>1</sup> It has been suggested by Cochran<sup>2</sup> and verified by Barker and Tinkham<sup>3</sup> that the high dielectric constant in SrTiO<sub>3</sub> is connected with a "soft mode," an optically active lattice vibration which has a temperature-dependent resonance frequency. The assignment of this mode to a specific type of vibration is still debated.<sup>4,5</sup> The temperature dependence of the effective spring constant for this  $k=0$  mode is believed to be connected with the near cancellation of the short-range repulsive forces with the long-range Coulomb interaction; thus both the long-range and short-range forces are equally important.

For this reason we measured the elastic properties and their field dependence in SrTiO<sub>3</sub> to obtain more information about the short-range forces. As a consequence of the small effective spring constant for the soft

mode, the pertinent ions can move relatively large distances under an external electric field. The ions move into new equilibrium positions with different effective spring constants because of anharmonicities. This is apparent from the nonlinear dielectric behavior. The dielectric constant decreases with electric field,<sup>1</sup> indicating a stiffening of the effective spring constant of the soft mode. Since sound velocity measurements can be carried out relatively accurately, a measurable effect on the elastic properties through the influence of an electric field may be expected although in this case only the short-range forces are involved.

### II. MEASUREMENTS

The elastic constants of a cubic material can be characterized by three stiffness constants,  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$ .<sup>6</sup> These constants are related to the velocity of propagation for longitudinal and transverse waves along various crystallographic directions, so that by measuring velocities for various orientations the elastic constants may be determined. In Table I the equations relating velocities of propagation and elastic constants used for the measurements on strontium titanate are given.

At 108°K where the strontium titanate becomes tetragonal,<sup>7,8</sup> six elastic constants are needed to specify all the elastic properties. When the strontium titanate passes into the tetragonal phase, however, it breaks up into domains which are the order of the wavelength of

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<sup>1</sup> G. Rupprecht, R. O. Bell, and B. D. Silverman, *Phys. Rev.* **123**, 97 (1961).

<sup>2</sup> W. Cochran, *Phys. Rev. Letters* **3**, 412 (1959); W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960), Vol. 9, p. 387.

<sup>3</sup> A. S. Barker, Jr., and M. Tinkham, *Phys. Rev.* **125**, 1527 (1962).

<sup>4</sup> W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, *Phys. Rev.* **126**, 1710 (1962).

<sup>5</sup> J. T. Last, *Phys. Rev.* **105**, 1740 (1957).

<sup>6</sup> W. P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1958).

<sup>7</sup> L. Rimai and G. A. deMars, *Phys. Rev.* **127**, 702 (1962).

<sup>8</sup> K. A. Müller, *Helv. Phys. Acta* **31**, 173 (1958).

TABLE I. Relation of velocity to elastic constants for various modes of propagation.

Orientation of SrTiO <sub>3</sub> sample	Mode of propagation	Relation of velocity to elastic constants	Measured velocity (km/sec) at 20 °C
[100]	Longitudinal	$v_1 = (c_{11}/\rho)^{\frac{1}{2}}$	7.876
[100]	Transverse	$v_2 = (c_{44}/\rho)^{\frac{1}{2}}$	4.910
[110]	Longitudinal	$v_3 = [(c_{11} + c_{12} + 2c_{44})/2\rho]^{\frac{1}{2}}$	8.098
[110]	Transverse	$v_4 = (c_{44}/\rho)^{\frac{1}{2}}$	4.918
[110]	Transverse	$v_5 = [(c_{11} - c_{12})/2\rho]^{\frac{1}{2}}$	4.586
[111]	Longitudinal	$v_6 = [(c_{11} + 2c_{12} + 4c_{44})/3\rho]^{\frac{1}{2}}$	8.141
[111]	Transverse	$v_7 = [(c_{11} - c_{12} + c_{44})/3\rho]^{\frac{1}{2}}$	4.703

the ultrasonic wave. This makes the interpretation of the data difficult, and hence, it was not possible to determine the six elastic constants below the phase transition.

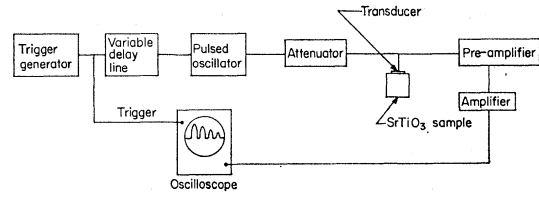
Measurements of the sound velocity were made by two slightly different techniques. In one method a relatively long sample ( $L \approx 1$  cm) was used. A quartz transducer, either  $x$  or  $y$  cut, was applied with Nonaq stopcock grease, and a  $\frac{1}{2}$  to  $1\frac{1}{2}$ - $\mu$ sec rf pulse was applied to the quartz. This excites a slowly decaying ultrasonic pulse which is reflected back and forth between the ends of the sample. Each time the pulse is reflected from the face with the transducer, a small rf pulse is excited which is amplified and applied to the deflection plates of an oscilloscope. Measuring the time delay between successive pulses enables the velocity to be determined. Measurements were generally made at either 10 Mc/sec or 30 Mc/sec. Figure 1 is a block diagram of the experimental setup.

Measurements were also made by applying a relatively long pulse ( $\sim 10 \mu$ sec) to a crystal of strontium titanate approximately 0.2 cm thick. Because of the long pulse and short sample, there is interference between successive reflections which add constructively when<sup>9</sup>

$$U = 2f_n t / (n + \phi / 2\pi), \quad (1)$$

where  $U$  is the velocity of propagation of sound;  $t$  is the sample thickness;  $n$  is an integer;  $f_n$  is the frequency for constructive interference; and  $\phi$  is the phase angle in radians of the reflected wave at the boundary with respect to the incident wave.  $f_n$  can be measured quite accurately and  $n$  can be determined by the difference between two successive resonances, i.e.,  $n \approx f_n / (f_n - f_{n-1})$  if  $\phi / 2\pi \ll n$ . To check this assumption,  $f_n$  was determined and  $2f_n t / n$  was plotted as a function of frequency between 7 Mc/sec and 50 Mc/sec for one sample. From the slight curvature  $\phi \approx 0.06$  rad. If  $\phi$  is neglected, this is an error of less than 0.2% for  $n > 30$  which was the case for most measurements.

The faces of the sample, which was a cylinder, were ground parallel to  $5 \times 10^{-4}$  cm and silver plated with a

FIG. 1. Simplified block diagram of the experimental set up used to measure the elastic constants of SrTiO<sub>3</sub>.

thin coat. The sample was inserted in a holder of Lucite and then cooled by placing over liquid nitrogen. The temperature was measured with a copper-Constantan thermocouple which was in direct contact with the strontium titanate sample. Measurements were made with both increasing and decreasing temperatures. No temperature hysteresis was observed for any measurements.

The frequency of the pulse oscillator was measured by beating the pulse against a variable cw oscillator. The frequency of the oscillator was then measured with a frequency counter.

Measurements were also made of the elastic constants as a function of a dc electric field applied along the axis of the cylinder. Fields up to 30 kV/cm could be applied across the sample.

### III. RESULTS

Table I shows the measured velocities,  $v_i$ , at 20°C for various orientations and modes of propagation. The samples were cut from three different boules of strontium titanate.

The best values of the elastic constants were determined by minimizing the sum of the square of the deviations of the density times the square of the velocity and the appropriate combination of elastic constants. That is, if

$$\delta = [c_{11} - \rho v_1^2]^2 + [c_{44} - \rho v_2^2]^2 + [\frac{1}{2}(c_{11} + c_{12} + 2c_{44}) - \rho v_3^2]^2 + \dots + [\frac{1}{3}(c_{11} - c_{12} + c_{44}) - \rho v_7^2]^2, \quad (2)$$

then applying the condition

$$\partial \delta / \partial c_{11} = \partial \delta / \partial c_{12} = \partial \delta / \partial c_{44} = 0, \quad (3)$$

gives three equations relating the measured velocities to the values of  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$  which make  $\delta$  a minimum. This was done down to  $-161^\circ\text{C}$  and the results are shown in Figs. 2, 3, and 4. The measurements at room temperature agree with those of Poindexter and Giardini<sup>10</sup> except for  $c_{11}$  which we find 7% lower than their value. In the region around the transition temperature  $c_{11}$  and  $c_{44}$  decreased as  $-1/(T - T_a)$ , while  $c_{12}$  increases as  $1/(T - T_a)$ . The constant  $c_{11}$  as a function of temperature is fit quite well by the expression

$$c_{11}(T) = 3.341 \times 10^{12} [1 - 2.62 \times 10^{-4}(T - T_a) - 0.0992/(T - T_a)]. \quad (4a)$$

<sup>10</sup> E. Poindexter and A. A. Giardini, Phys. Rev. **110**, 1069 (1958).

<sup>9</sup> H. J. McSkimin, J. Acoust. Soc. Am. **22**, 413 (1950).

Similar behavior also was noted for  $c_{12}$  and  $c_{44}$ .

$$c_{12}(T) = 1.049 \times 10^{12} [1 - 1.23 \times 10^{-4}(T - T_a) + 0.1064/(T - T_a)], \quad (4b)$$

$$c_{44}(T) = 1.267 \times 10^{12} [1 - 1.30 \times 10^{-4}(T - T_a) - 0.1242/(T - T_a)], \quad (4c)$$

where  $T_a = 108^\circ\text{K}$  and the elastic constants are in  $\text{dyn}/\text{cm}^2$ .

A detailed analysis of the error has not been made, but the maximum error in the measurement of the length is about 0.05%. The frequency could be determined to 0.05% with little difficulty and neglecting  $\phi$  would give an error of 0.2%. This relatively generous estimate of the error means the velocity should be accurate to  $\pm 0.3\%$  and the absolute value of the elastic constant to  $\pm 0.6\%$  for any one measurement. The actual error is probably much smaller since one set of elastic constants were determined from seven different measurements of the velocity. The relative error from temperature to temperature is quite small being about 1 part in  $10^4$  for  $c_{11}$  and  $c_{44}$ , and 3 parts in  $10^4$  for  $c_{12}$  as estimated from the scatter in the data presented in Figs. 2, 3, and 4.

When a dc electric field was applied, it was found that the elastic constants decrease. Figure 5 shows the dependence of  $\Delta c_{11}/c_{11}$  on an applied dc electric field above the transition temperature.  $\Delta c_{11}$  depends quadratically on the electric field and we have found that the experimental data can be fit quite well by the expression

$$\frac{\Delta c_{11}}{c_{11}} = \frac{1.1 \times 10^{-15}}{(T - T_a)^{1/2}} E^2, \quad (5)$$

where  $E$  is the electric field in volts/meter;  $T_a$  is  $108^\circ\text{K}$ , the transition temperature;  $T$  is the temperature; and  $\Delta c_{11} = (c_{11})_{E=0} - (c_{11})_E$ . A similar expression was found for  $\Delta c_{44}/c_{44}$  with a constant of proportionality of  $0.6 \times 10^{-15}$ .

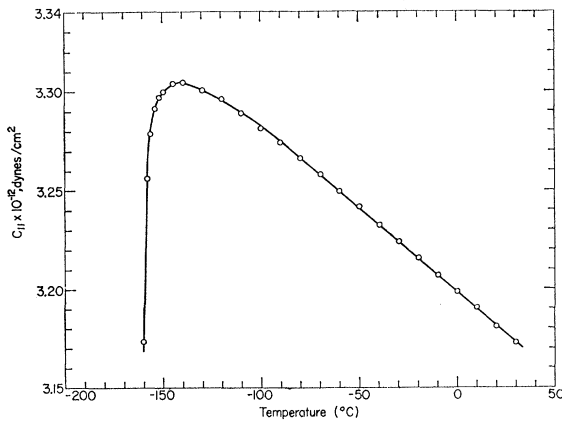


FIG. 2. Temperature dependence of  $c_{11}$  in  $\text{SrTiO}_3$  from  $-161$  to  $30^\circ\text{C}$ .

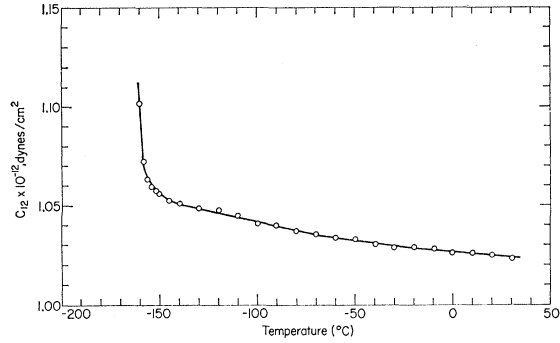


FIG. 3. Temperature dependence of  $c_{12}$  in  $\text{SrTiO}_3$  from  $-161$  to  $30^\circ\text{C}$ .

As the temperature is slowly cooled through the transition region there is a very large increase in the apparent attenuation as well as a marked decrease in the velocity of propagation. Below the transition temperature the attenuation decreases slightly, but the ultrasonic pulses are so badly distorted it is impossible to accurately determine the propagation velocity. It is possible that this distortion is caused by scattering from some type of domain structure whose size is the order of the acoustic wavelength ( $\sim 0.1$  mm). Since the crystal is in a tetragonal phase, not all the  $[100]$  directions are equivalent, so the domain structure could be caused by the crystallites whose  $[100]$ ,  $[010]$ , and  $[001]$  directions are arranged at random along the original cubic axes. X-ray examination shows that the deviations from a cubic structure are extremely small, but the elastic properties are considerably affected. With x-ray diffraction<sup>11</sup> a hysteresis effect has been observed. It should be emphasized that no hysteresis has been visible in our experiments.

Examination of the equations relating the elastic constants to the acoustic velocity shows that only for a longitudinal wave propagating along a  $[111]$  axis would there be no discontinuities of the velocity when passing from crystallite to crystallite with the  $c$  axis along different  $[100]$  directions. When measurements were made on a longitudinal wave along the  $[111]$  axis, it was found indeed that there was only a moderate increase in attenuation at  $T_a$  and little distortion of the ultrasonic pulse so that the velocity could be measured quite easily throughout the entire temperature range. Figure 6 shows  $(v_{\text{long}})_{111}$  as a function of temperature. The data have been taken with increasing and decreasing temperature, but no indication of a hysteresis effect could be detected.

If an electric field is applied along the  $[111]$  axis below the transition temperature, a quadratic decrease of the velocity and therefore of the effective elastic constant is observed.  $\Delta c/c = 4.1 \times 10^{-15} E^2$ , where  $E$  is in

<sup>11</sup> R. S. Krogstad and R. W. Moss, *Bull. Am. Phys. Soc.* **7**, 192 (1962).

volts/meter. The change in elastic constant is independent of the temperature below  $T_a$ .

#### IV. DISCUSSION

Although the exact nature of the phase transition at 108°K is not understood, a number of conclusions can be drawn. The elastic constants undergo a drastic but continuous change in a couple of degree temperature range around 108°K. Since no hysteresis has been observed within the accuracy of our experiment, this phase transition is probably of second order or higher. The lattice changes from a cubic into a tetragonal phase, but the real displacement of the ions seems to be quite small. Krogstad and Moss<sup>11</sup> report a  $c/a$  ratio of 1.003 which is indeed a small deviation from cubic symmetry. This small change in lattice parameters should be contrasted with the change in the elastic constants. In order to be in accord with this observation,

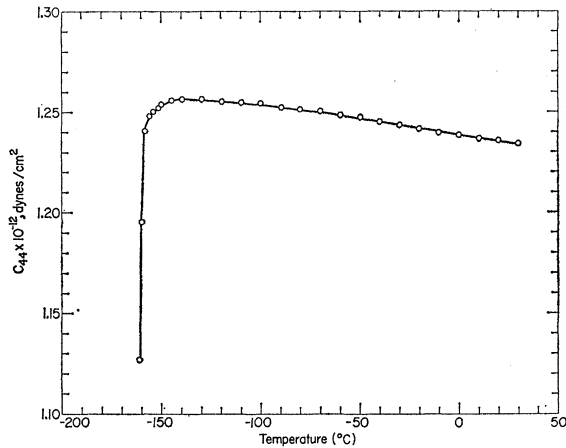


FIG. 4. Temperature dependence of  $c_{44}$  in SrTiO<sub>3</sub> from -161 to 30°C.

we assume that the ions which determine the propagation of sound in SrTiO<sub>3</sub> must be partially covalently bound. This enables a small displacement to lead to a substantial change of the interionic forces.

The field dependence of the elastic forces also seems to indicate that the binding forces are not strictly ionic. We have found that an external electric field decreases the elastic constants  $c_{11}$  and  $c_{44}$ . A change is expected since even in cubic materials the electrical and mechanical properties are connected via electrostrictive constants. Using an ionic model for SrTiO<sub>3</sub>,<sup>12</sup> it can be shown that for large dielectric constants the internal field,  $F_n$ , at the  $n$ th ion is related to the external field,  $E$ , by the dielectric constant,  $\epsilon$ :

$$F_n \approx \phi_n \epsilon E,$$

where  $\phi_n$  are constants that depend on the lattice sites. The internal field will displace the ions to new equi-

<sup>12</sup> J. C. Slater, Phys. Rev. **78**, 748 (1950).

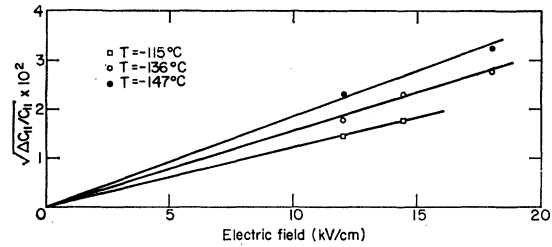


FIG. 5. The dependence of  $\Delta c_{11}/c_{11}$  on a dc electric field applied parallel to the direction of propagation for SrTiO<sub>3</sub>.

rium positions which have slightly different binding forces. One would expect that these changes in the elastic forces can be expressed in a power series expansion of the internal fields with terms of the form  $(\epsilon E)^m \sim E^m / (T - T_c)^m$ . Since from experiment  $\Delta c_{ik}/c_{ik}$  is proportional to  $E^2$ , the temperature dependence of the constant of proportionality should behave as  $1/(T - T_c)^2$  or at least be connected in some way with the Curie temperature. The experimental data, however, show that this is not the case. Rather the change of the elastic properties behaves as  $1/(T - T_a)^{1/2}$  above  $T_a$  and is independent of temperature below  $T_a$ . This indicates that the use of an ionic model is inadequate for SrTiO<sub>3</sub>.

As was noted in the Introduction, the high dielectric constant in SrTiO<sub>3</sub> is believed to be related to the low frequency of a fundamental lattice vibration caused by the partial cancellation of the short-range repulsive force by the long-range Coulomb interaction. In a spring constant mode, the behavior of the soft mode can be introduced by an effective spring constant proportional to  $(T - T_c)$  which goes to zero at the Curie temperature,  $T_c$ .

The dielectric constant is field dependent,<sup>1</sup> and the relative change with application of an external field is given by  $\Delta(1/\epsilon) \sim E^2 / (T - T_c)^2$ . Since the application of an electric field decreases the dielectric constant, we can assume that the spring constant becomes stiffer,

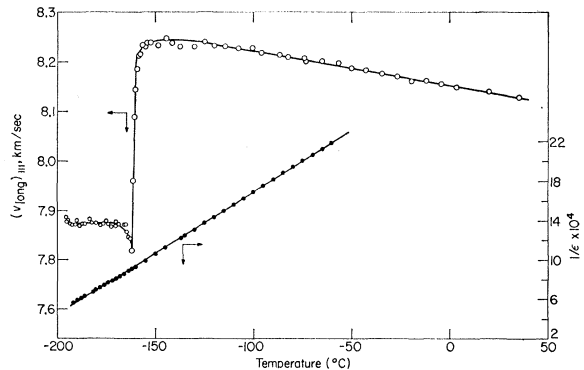


FIG. 6. Temperature dependence of the velocity of sound propagation along the [111] crystallographic axis from -190 to 30°C for SrTiO<sub>3</sub>. Also shown is the reciprocal of the dielectric constant in the temperature range around the phase transition.

but  $c_{11}$  and  $c_{44}$  decrease which indicates a softening of the short-range repulsive forces. The result means that the short-range forces responsible for sound propagation are not connected with the dielectric properties.

Further evidence for this point is indicated by the behavior of the dielectric constant in the vicinity of the phase transition at 108°K. If the particular short-range lattice forces that determine the elastic properties are also connected with the forces that determine the frequency of the soft mode, a discontinuity of the dielectric constant would be expected. No discontinuity or even a change in slope of the dielectric constant is observed (Fig. 6).

It is surprising to us that such a marked change in the elastic properties can occur with little or no observable

effect on the dielectric properties. From the dependence of the elastic constants on electric field and on temperature, it appears that SrTiO<sub>3</sub> is not completely ionic. One possible interpretation is that the TiO<sub>3</sub> octahedra, which are the building blocks of the perovskite lattice, are partially covalently bound.<sup>13</sup> At the transition temperature they undergo a slight rearrangement which cause the change in elastic properties. The soft mode, on the other hand, if assigned to the vibration of the strontium ion against the TiO<sub>3</sub> octahedron (Last), does not "notice" the rearrangement of the TiO<sub>3</sub> complex. The masses involved in this vibration and the total charge of the TiO<sub>3</sub> octahedron as seen by the strontium ion are not altered.

<sup>13</sup> H. D. Megaw, *Acta Cryst.* **5**, 739 (1952).

## Far Infrared Dielectric Dispersion in KTaO<sub>3</sub>

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The room-temperature reflectivity of single-crystal KTaO<sub>3</sub> has been measured from 5000 to 77 cm<sup>-1</sup>. These data have been analyzed by a Kramers-Kronig relation and by classical dispersion theory. The three infrared-active fundamental vibrations allowed by the lattice symmetry have been observed. The strength of the lowest frequency mode accounts for the large low-frequency dielectric constant of the material. The lattice band contribution to the microwave loss tangent at 3 cm is estimated to be about  $2 \times 10^{-3}$ . Attempts to fit the reflectivity data with dispersion theory show that a frequency-dependent damping constant for the low-frequency resonance is necessary in order to obtain a good fit between the calculated curve and the data. The required variation of the damping constant is by more than an order of magnitude. The present results are compared with similar measurements reported earlier on barium and strontium titanates.

### INTRODUCTION

SEVERAL recent papers, both experimental<sup>1,2</sup> and theoretical,<sup>3,4</sup> have emphasized the essential role played by a single, long-wavelength, optical mode of vibration in accounting for the large values of the low-frequency dielectric constants observed in several materials containing the TiO<sub>6</sub>-octahedra structure. In the case of the three crystals for which experimental data have been obtained, namely, BaTiO<sub>3</sub>,<sup>2</sup> SrTiO<sub>3</sub>,<sup>1,2</sup> and TiO<sub>2</sub>,<sup>2</sup> the low-frequency (microwave and lower frequency portions of the electromagnetic spectrum) dielectric constants  $\epsilon_0$  are of the order of hundreds or thousands, and the high-frequency or optical dielectric

constants  $\epsilon_\infty$  are less than 10. Analyses<sup>1,2</sup> of the near and far infrared reflectivity of these three crystals showed that of all the infrared-active vibrations allowed by symmetry, the lowest frequency mode in each case accounts for the large low-frequency dielectric constant. This mode is believed<sup>2</sup> to be primarily associated with TiO<sub>6</sub>-octahedra vibrations. The unusually large damping constant characteristic of the low-frequency modes was consistent with the observed microwave loss tangents. For all three crystals investigated, attempts to fit the reflectivity data with classical dispersion theory were not completely satisfactory. The analyses suggested that to fit the experimental data accurately, a frequency-dependent damping constant was required for the low-frequency resonance.

Measurements and analyses similar to those described above have now been made on single-crystal KTaO<sub>3</sub>. This material is in some ways quite similar to the titanates. Like SrTiO<sub>3</sub>, it is cubic and paraelectric at room temperature.<sup>5</sup> The ferroelectric Curie point is reported<sup>5</sup>

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<sup>1</sup> A. S. Barker and M. Tinkham, *Phys. Rev.* **125**, 1527 (1962).

<sup>2</sup> W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth *Phys. Rev.* **126**, 1710 (1962).

<sup>3</sup> W. Cochran, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960-61), Vol. 9, p. 387; Vol. 10, p. 401.

<sup>4</sup> P. Anderson, in *Fizika dielektrikov*, edited by G. I. Skanavi (Akad. Nauk S.S.S.R. Fizicheskii Inst. im P. N. Lebedeva, Moscow, 1960).

<sup>5</sup> J. K. Hulm, B. T. Matthias, and E. A. Long, *Phys. Rev.* **79**, 885 (1950).