Permittivity of Strontium Titanate

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Permittivity of Strontium Titanate

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The permittivity of single-crystal single-domain strontium titanate has been measured in detail in the [001], [011], and [111] directions, as a function of temperature (from 4.2 to 300°K), electric field (from −23 000 to +23 000 V/cm, and frequency (from 1 kHz to 50 MHz). The free energy of the crystal is determined as a function of polarization with temperature as a parameter. The Curie-Weiss law is satisfied in the temperature range 60–300°K, giving a Curie temperature of 30±2°K for the three crystal orientations. The Lyddane-Sachs-Teller (LST) relation is satisfied for temperatures between 30 and 300°K and for electric fields between 0 and 12 000 V/cm. A generalized LST relation is used to calculate the permittivity of strontium titanate from zero to optic frequencies. Two active optic modes are important. The lower-frequency mode is attributed mainly to motion of the strontium ions with respect to the rest of the lattice, while the higher-frequency active mode is attributed to motion of the titanium ions with respect to the oxygen lattice. The restoring forces that act on the Ti ions begin to "harden" when these ions are displaced approximately 0.002 Å from their equilibrium positions.

I. INTRODUCTION

Strontium titanate has been studied only relatively recently and is becoming increasingly important as a dielectric material in high-value capacitors.[1] As a member of the peroskvite family of compounds,[2] strontium titanate is cubic in structure at room temperature. The cube structure consists of a small titanium atom at the center, and oxygen atoms in each of the six cube walls forming a cage around the titanium atom, and small strontium atoms at the cube corners.[3] As the temperature is reduced the crystal structure becomes tetragonal at 110 °K, and at 65 °K the structure becomes orthorhombic.[2] The pure crystal is an insulator at room temperature with a band gap of 3.15 eV.[4] Upon reduction by heating in a hydrogen atmosphere, the clear colorless insulating crystal becomes an n-type semiconductor, and the color shifts to a varying shade of blue as a result of the free-carrier absorption.[5]

Although used extensively in capacitors, no systematic study of the relative permittivity of single-domain strontium titanate has been conducted. Reported studies have primarily concerned themselves with multidomain structure strontium titanate crystals, and the published data have been a function of temperature, electrical bias, and frequency of measurement. At room temperature the value for the relative permittivity of [001]-oriented strontium titanate has been determined to be 330±10,[6] independent of frequency of measurement and applied field strength. For [011]-oriented material the relative permittivity was found to be 458 and for [111] orientations 448. At 77 °K the relative permittivity of strontium titanate was found to be 1880 for [001]-oriented material, 2640 for [011]-oriented material, and 2580 for [111] orientation.[6] Rupprecht[7] reports that the relative permittivity is independent of the measurement frequency from 1 kHz to 26 GHz between 93 and 300 °K. Itschner and Gränicher[8] report field strength independence of the relative dielectric constant for fields up to 10^6 V/cm above 110 °K. At liquid-helium temperature (4.2 °K) there is a wide range in reported values of the relative permittivity of strontium titanate[8–13] under a wide range of applied bias field and measurement frequencies. Neville *et al.*[6] have shown that the behavior of the relative permittivity of strontium titanate at liquid-

helium temperatures is consistent with the presence of multiple domains at temperatures below 65 °K, and that suppression of the domains results in a dielectric constant which is frequency independent between 1 kHz and 50 MHz.

We report in this paper on the relative permittivity of single-domain strontium titanate crystals. Crystal samples oriented in the [100], [110], and [111] directions were used. A temperature range from 4.2 to 300 °K was covered for applied dc field strengths from −23 000 to +23 000 V/cm and measurement frequencies from 1 kHz to 50 MHz. A careful search for thermal and electrical hysteresis and other evidences of ferroelectricity[14–16] was made although none was found.

As reported for multiple-domain strontium titanate,[6,10] the observed inverse dielectric constant, for temperatures above 65 °K, follows a Curie-Weiss—law temperature variation[9,10,17,18] with a Curie temperature of 30 °K.[6] The relative permittivity was determined to be a smooth function of temperature and electric field in the vicinity of the Curie temperature. A phenomenological expression was developed for the free energy of the crystal as a function of orientation. The relative permittivity is extrapolated to optical frequencies using a generalized Lyddane-Sachs-Teller relation.[19] Evidence indicates that both the titanium and the strontium atoms contribute to the polarization effects.

II. SAMPLE PREPARATION

Two clear colorless boules of strontium titanate with resistivity in excess of 10^{11} Ω cm were used. The boules, obtained from the National Lead Company, were grown with the same processing.[1] Using a diamond saw, the boules were sliced into 10 thin wafers 1.5 mm thick in a direction parallel to the (100), (110), or (111) face.

One thin wafer from each boule was cut into bars 1×1.5 ×1.5 mm using a diamond saw. These bars were cleaned by etching in phosphoric acid for 10 min followed by immersion in hydrochloric acid for 10 min to remove the phosphates. After 15-min rinse in flowing deionized water, the sample bars were dried in a jet of dry filtered air. One bar from each boule was tested for resistivity by soldering leads on each of the two small

ends and two more leads along one side of the rectangular bar. Using a 4-point method, the resistivity was confirmed to be in excess of 10^{11} Ω cm for both boules.

To determine the purity of the material and confirm the information furnished with the boules by the manufacturer, a sample bar from each boule was submitted to the Geology Department of the California Institute of Technology for an impurity analysis. There, a semi-quantitative analysis was performed using an electron microprobe. Principal impurities were found to be 0.0002% barium, 0.01% calcium oxide, and less than 0.1% tungsten. These data are in agreement with those furnished by the manufacturer.

The eight sample wafers to be used in the dielectric investigation were hand lapped and polished on a succession of silk cloths, starting with an 800-mesh grit, progressing through 1200 and 3200 grits, 1- and 0.3-μ polishing compounds, and finishing with a 500-Å aluminum polishing compound. Final wafer thickness lay between 0.125 and 1 mm with wafer orientation yielding two large flat surfaces in the (100), (110), or (111) planes. At least one wafer from each boule was used for each crystal orientation with a total of four wafers in the [100], two wafers in the [110], and two wafers in the [111] crystal orientation. The wafer surfaces were cleaned by etching in phosphoric acid for 10 min, followed by soaking in hydrochloric acid for 10 min to remove phosphates. The samples were dried in a jet of dry filtered air after a 15-min rinse in flowing deionized water. Capacitors were formed by placing the wafers in an ion-pumped evaporator at a nominal pressure of 8×10^{-7} Torr and evaporating a layer of gold approximately 3000 Å thick from a hot tungsten filament on one side of each wafer. The wafers were withdrawn from the evaporator, inverted, and replaced in the vacuum. Approximately 3000 Å of gold was next evaporated through a large-mesh screen to form a localized contact. Contact diameters from 0.1 to 1.2 cm were used, taking care that the diameter was always much greater than the sample thickness so that the fringe capacitance could be neglected.

III. DOMAINS IN STRONTIUM TITANATE

The strontium titanate crystal lattice is cubic above 110 °K, tetragonal between 110 and 65 °K, and orthorhombic below 65 °K.[2] This means that the three unit-cell angles are rectangular at all temperatures. Above 110 °K the three unit-cell axes are equal. As the crystal is cooled below 110 °K, one of the three unit-cell axes elongates slightly to form the tetragonal c axis. The two remaining unit-cell axes differentiate when the crystal is cooled below 65 °K, thus forming the orthorhombic lattice which has three unit-cell axes of differing lengths. The distortion from a cubic lattice is small. For the orthorhombic lattice, $a:b:c$ $= 0.9998:1:1.0002$.[2]

In the transition from the cubic to the tetragonal lattice at 110 °K, any one of the three cubic unit-cell axes can elongate to form the tetragonal c axis. Thus, tetragonal domains can form with differing c-axis orientations. Similarly, in the tetragonal to orthorhombic transition,

subdomains can form with different a orthorhombic-axis orientations.

We have observed a large anomalous resonance of the permittivity of multidomain crystals. The "resonance" is observed below 65 °K, between 1 and 10 MHz, and will be reported elsewhere. If an electric field of at least 20 300 V/cm is applied to the [100]-, [110]- or [111]-oriented samples while they are cooled through the 110 ° and 65 °K phase transition temperatures, the anomalous resonance is not observed. (We note that the crystal orientations have a one-sigma error of 1°.) It is important to apply the electric field while cooling through both the 110 and 65 °K transition temperatures. If applied solely through the 65 °K transition temperature, the full anomalous resonance is observed. If applied only through the 110 °K phase transition temperature, about 10% of the anomalous resonance is observed, probably indicating the presence of subdomains. These observations lead us to believe that the crystals cooled with a large applied electric field became single domained. (Crystals of KH_2PO_4 have been made single domain by applying an electric field.[20]) For this reason, all crystals measured below 110 °K were cooled past 110 °K (and 65 °K) with an applied electric field of 23 000 V/cm.

IV. EXPERIMENTAL RESULTS

Capacitors with [100]-, [110]-, and [111]-oriented strontium titanate dielectrics were measured as a function of temperature (from 4.2 to 300 °K), dc electrical field (from −23 000 to +23 000 V/cm), and frequency (from 1 kHz to 50 MHz), using Boonton capacitance bridges. The ac test signal was varied from 0.02 to 1 V peak to peak and was always less than 5% of the dc bias.

The sample under examination was placed in a thin twin-walled cryogenic probe for measurements below room temperature. By adjusting the flow of heilum gas at room temperature through the space between the probe walls and immersing the probe in liquids of various boiling points, the temperature of the sample could be varied continuously from 4.2 to 300 °K. The temperature was monitored using a copper-constantan thermocouple at temperatures above 73 °K and a calibrated carbon resistor at temperatures below 100 °K.

The capacitors were measured at discrete temperatures, starting at 300 °K, decreasing in steps to 4.2 °K, and increasing in identical steps back to 300 °K. All temperature changes were made with an applied dc bias corresponding to 23 000 V/cm to avoid multidomain effects. No evidence of thermal hysteresis was detected.

The measurements at each discrete temperature began with an applied dc bias of +23 000 V/cm. The dc bias was then decreased in steps, through zero, to −23 000 V/cm, and finally increased in steps back to the original value of +23 000 V/cm. Capacitance measurements were made with the following applied dc electric fields: 10, 100, 200, 620, 1080, 1550, 6200, 15 500, and 23 000 V/cm. No electrical hysteresis was observed at any temperature from 4.2 to 300 °K.

The search for electrical and thermal hysteresis was repeated at temperatures in the vicinity of the phase
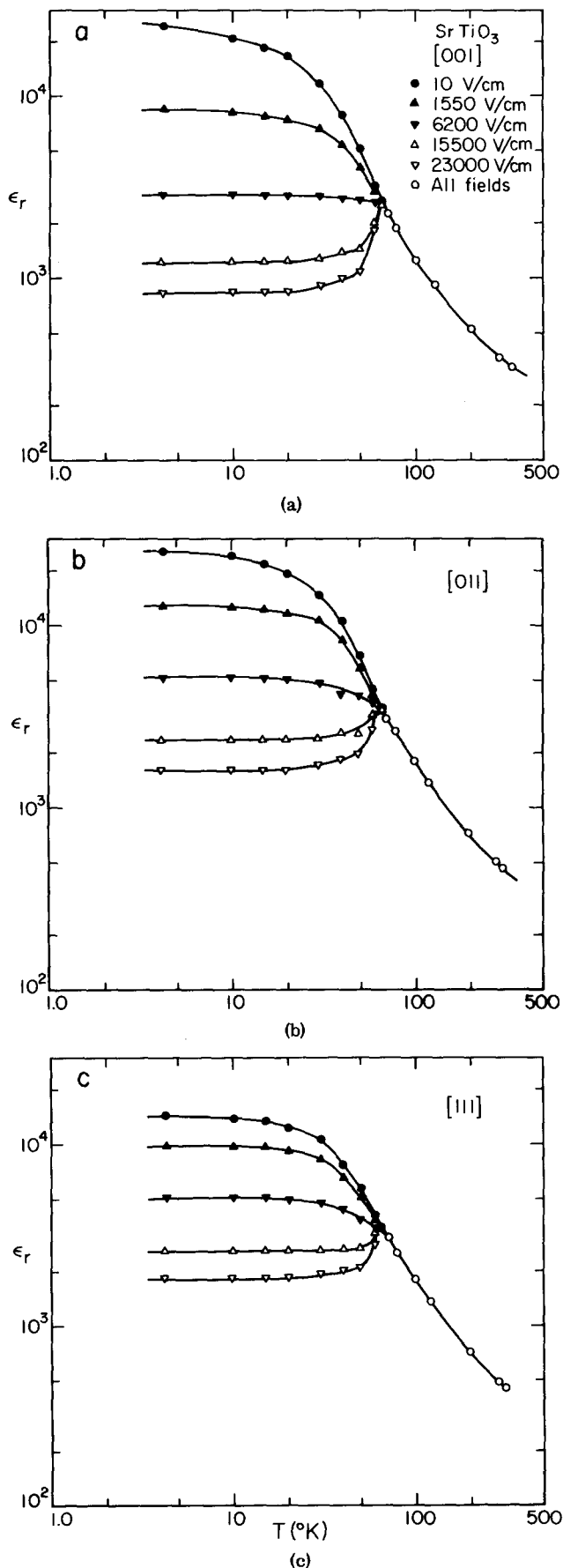
FIG. 1. Relative permittivity of strontium titanate as a function of temperature with applied dc bias field as a parameter: (a) [001] orientation, (b) [011] orientation, and (c) [111] orientation.

transitions at 65 and 110 °K and in the vicinity of the Curie temperature (28 − 44 °K).[6] No evidence of thermal or electrical hysteresis was found.

The capacitance measurements as a function of temperature and dc electric field were made at 1, 5, 10, 20, 50, 100, 200, and 500 kHz, and at 1, 5, 10, 20, and 50 MHz. The permittivity of crystals cooled past 110 and 65 °K with an applied electric field of at least 20 300 V/cm showed no frequency dependence. The dielectric loss factor, $\tan\delta$, of these crystals is less than 10^{-5} in all cases. The permittivity of crystals cooled with no applied electric field shows a large "resonance" and high loss factor between 1 and 10 MHz at temperatures below 65 °K.

The permittivity of the crystals was calculated from the measured capacitance values, contact areas, and sample thicknesses. The relative permittivity of [100]-, [110]- and [111]-oriented samples are presented in Figs. 1(a)−1(c) as a function of temperature, with applied electric field as a parameter. Note that the curves representing the relative permittivity are continuous functions of temperature, and no evidence of thermal hysteresis can be found. Below 65 °K the permittivity is clearly a function of field, while above tetragonal-to-orthorhombic phase-shift temperature of 65 °K the relative permittivity is independent of the electric fields employed. Measured values of the relative permittivity are provided in the Appendix. Notice that at room temperature the "cubic" crystal has anisotropic permittivity. This anisotropy is evidence either of nonlinearities of the ion restoring forces, or that the crystal is "pseudocubic" as suggested by Lytle.[2]

The permittivity below 65 °K could be expressed by $1/\epsilon_r = A(T) + B(T)|E|$. The observed values of $A(T)$ and $B(T)$ which empirically describe the relative permittivity are given as a function of temperature with crystal orientation as a parameter in Table I. In Fig. 2 we present values of $B(T)$ as a function of temperature. Note that the behavior of $B(T)$ is quite different above and below a temperature of 65 °K.

V. DISCUSSION

The high permittivity of strontium titanate and its dependence on temperature, electric field, and frequency can be understood in terms of the electrically active optical phonon. From the data presented in Table I and without a detailed knowledge of the ion displacements it is possible to (a) determine the crystal free-energy−vs−polarization curves at various temperatures, (b) apply the LST[19] relation, and (c) examine the system in light of the Curie-Weiss law.[14] A more detailed knowledge of the crystal structure and chemical bonds is required to determine (d) the ion displacements in the electrically active optical-phonon modes. Each of these topics will now be considered in turn.

A. Free Energy vs Polarization

At constant temperature the increment of free energy per unit volume, F, of a dielectric is given by

$$dF = E\mathbf{e} \cdot d\mathbf{P}, \qquad (1)$$

TABLE I. Relative permittivity of single-domain strontium titanate in the [001], [011], and [111] directions as a function of temperature (from 4.2 to 300°K) and electric field (from $-23\,000$ to $+23\,000$ V/cm). The relative permittivity is given by $\epsilon_r = 1/(A + B|E|)$. B is expressed in m/V. The permittivity is independent of frequency in the measured range from 1 kHz to 50 MHz. The permittivity has one-sigma error of 2%, and the crystal orientation has a one-sigma error of 1°.

T (°K)	[001][a] A	B	[011][b] A	B	[111] A	B
4.2	4.097×10^{-5}	4.907×10^{-10}	3.882×10^{-5}	2.466×10^{-10}	7.072×10^{-5}	2.005×10^{-10}
10	4.782×10^{-5}	4.887×10^{-10}	4.142×10^{-5}	2.455×10^{-10}	7.279×10^{-5}	1.996×10^{-10}
15	5.446×10^{-5}	4.848×10^{-10}	4.546×10^{-5}	2.414×10^{-10}	7.477×10^{-5}	1.971×10^{-10}
20	6.175×10^{-5}	4.817×10^{-10}	5.239×10^{-5}	2.391×10^{-10}	8.032×10^{-5}	1.946×10^{-10}
30	8.430×10^{-5}	4.438×10^{-10}	6.735×10^{-5}	2.220×10^{-10}	9.672×10^{-5}	1.809×10^{-10}
40	1.264×10^{-4}	3.777×10^{-10}	9.785×10^{-5}	1.881×10^{-10}	1.266×10^{-4}	1.530×10^{-10}
50	1.958×10^{-4}	3.156×10^{-10}	1.446×10^{-4}	1.578×10^{-10}	1.769×10^{-4}	1.282×10^{-10}
60	3.184×10^{-4}	9.852×10^{-11}	2.290×10^{-4}	5.278×10^{-11}	2.475×10^{-4}	3.879×10^{-11}
65	3.937×10^{-4}	0.0	2.833×10^{-4}	0.0	2.890×10^{-4}	0.0
70	4.484×10^{-4}	0.0	3.247×10^{-4}	0.0	3.300×10^{-4}	0.0
77	5.319×10^{-4}	0.0	3.788×10^{-4}	0.0	3.876×10^{-4}	0.0
100	7.813×10^{-4}	0.0	5.650×10^{-4}	0.0	5.780×10^{-4}	0.0
120	1.099×10^{-3}	0.0	7.299×10^{-4}	0.0	7.463×10^{-4}	0.0
200	1.923×10^{-3}	0.0	1.370×10^{-3}	0.0	1.399×10^{-3}	0.0
280	2.801×10^{-3}	0.0	2.020×10^{-3}	0.0	2.058×10^{-3}	0.0
300	3.030×10^{-3}	0.0	2.183×10^{-3}	0.0	2.232×10^{-3}	0.0

[a] The crystal orientation below 110°K might also be [100] or [010].
[b] The crystal orientation below 110°K might also be [101] or [110].

where e is the unit vector in the direction of the macroscopic electric field E and P is the polarization density. The permittivity of the dielectric in the direction of the macroscopic electric field will be denoted by ϵ. Then, by definition

$$\frac{\partial(\mathbf{e} \cdot \mathbf{P})}{\partial E} = \epsilon - \epsilon_0, \quad (2)$$

where ϵ_0 is the permittivity of free space. From Eqs. (1) and (2)

$$F = \int_0^E (\epsilon - \epsilon_0) E\, dE, \quad (3)$$

and

$$P \equiv \mathbf{e} \cdot \mathbf{P} = \int_0^E (\epsilon - \epsilon_0)\, dE, \quad (4)$$

where

$$\epsilon_r = [A(T) + B(T)|E|]^{-1}. \quad (5)$$

The free energy per unit volume F was calculated as a function of the polarization per unit volume P in the [001], [011], and [111] directions, using the data presented in Table I. The results are presented in Fig. 3. At temperatures of 65 °K and above, the free energy is quadratic in the polarization. Below 65 °K, the free energy for large polarization departs from a P^2 dependence and increases more rapidly.

B. Lyddane-Sachs-Teller (LST) Relation

The LST relation[19] is given by

$$\epsilon(0)/\epsilon(\infty) = w_L^2 / w_T^2, \quad (6)$$

where w_T is the frequency of a long-wavelength transverse optic phonon, w_L the frequency of the corresponding long-wavelength longitudinal optic phonon, and $\epsilon(0)$ and $\epsilon(\infty)$ are the permittivities at frequencies below and above w_T, respectively. The relation (6) can be applied to all the optic-phonon frequencies, yielding the generalized LST relation[21]

$$\frac{\epsilon(0)}{\epsilon(\infty)} = \prod_i \frac{w_{Li}^2}{w_{Ti}^2}. \quad (7)$$

Here $\epsilon(0)$ and $\epsilon(\infty)$ are the permittivities at low and at optic frequencies, respectively. It is expected theoretically and confirmed experimentally[22] that the only opti-
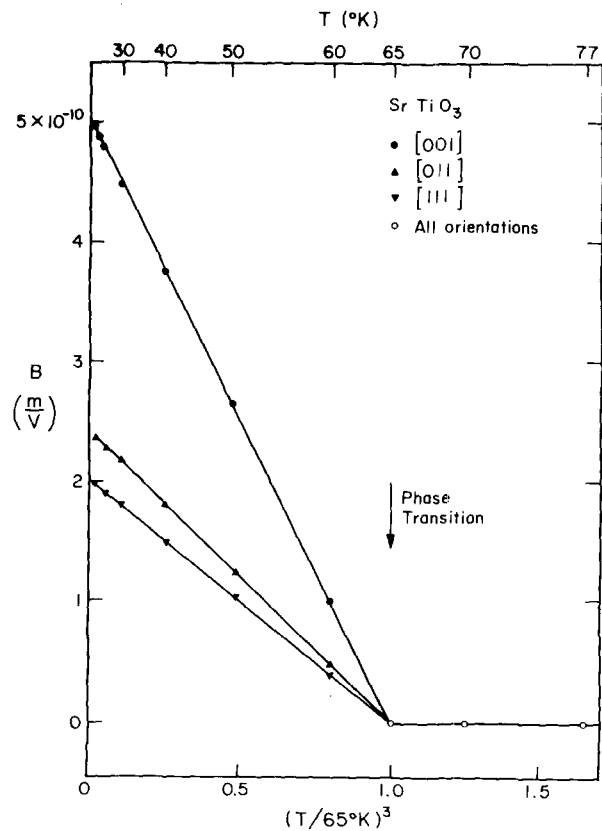

FIG. 2. $B(T)$ as a function of the reduced absolute temperature with crystal orientation as a parameter.
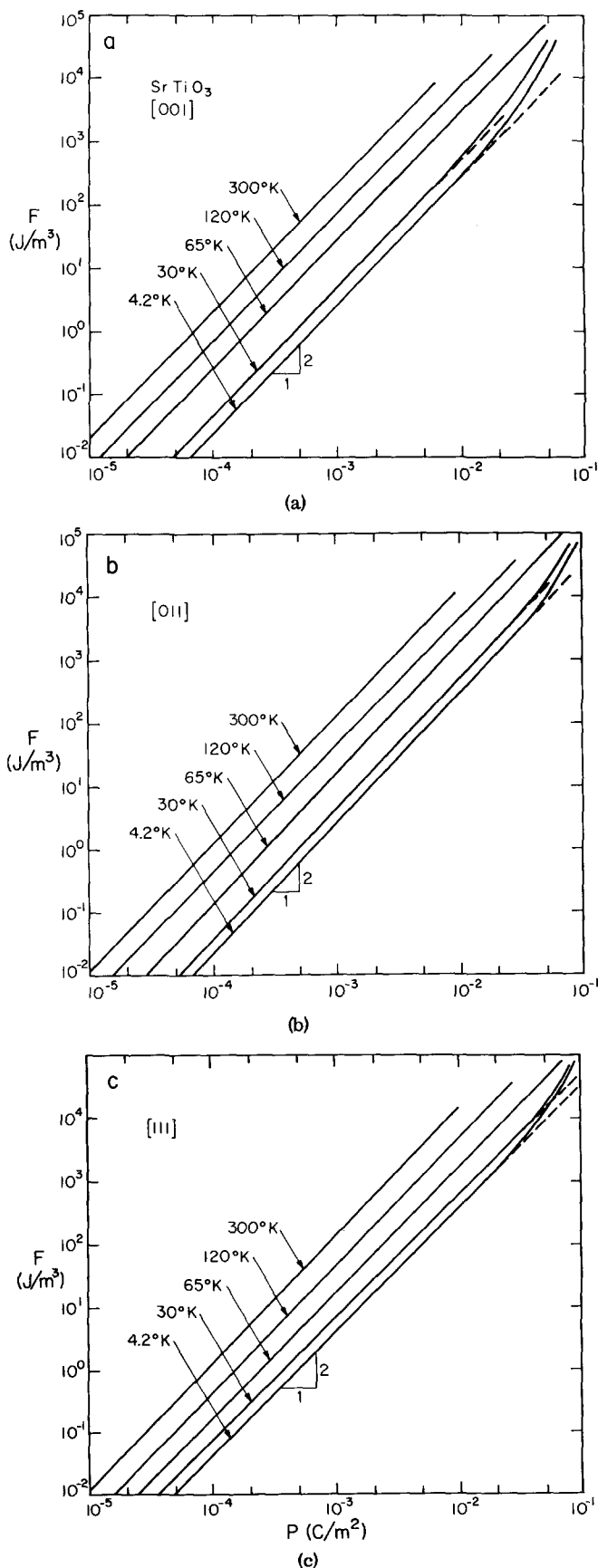
FIG. 3. Free energy of strontium titanate crystals as a function of polarization with temperature as a parameter: (a) [001] orientation, (b) [011] orientation, and (c) [111] orientation. The origins of energy and polarization have been chosen so that $F = P = 0$ when $E = 0$.

cal-phonon frequency strongly temperature dependent is the transverse optic mode of lowest frequency, also called the "soft" phonon mode. Since the permittivities at optic frequencies are not very sensitive to temperature, we expect from Eq. (7) that the product $\epsilon(0)$ $w^2_{T\,soft}$ is independent of temperature. Using the measured permittivities in the [001] direction and the "soft" phonon frequencies measured by Cowley,[22] Worlock and Fleury,[23] Nilsen and Skinner,[24] and Barker and Tinkham,[25] it is found that

$$\epsilon_r(0)w^2_{T\,soft} = 9.65 \pm 0.3 \times 10^{28} \text{ sec}^{-2}, \qquad (8)$$

independent of temperature and electric field in the measured ranges from 30 to 300 °K and 0 to 12 000 V/cm. The [001] direction was chosen because Cowley measured the frequency of phonons propagating in this direction.

Using Eq. (6), it is possible to calculate the permittivity at frequencies above the "soft" phonon frequency. The four transverse and longitudinal optic-phonon frequencies are listed in Table II. The longitudinal modes corresponding to each transverse mode were determined by requiring that $w_{L_i} \geq w_{T_i}$.[14] Note that modes 2 and 3 have $w_L = w_T$, which implies that for these modes the polarization due to ion displacements is zero.[14] This implication is confirmed by the displacements calculated by Cowley for these two modes. The relative permittivity can be calculated from Eqs. (6) and (8), and the data are presented in Table II. Between the "soft" phonon frequency (2.73×10^{12} Hz at 296 °K) and the electrically active phonon frequency at 16.4×10^{12} Hz, ϵ_r is 12.1, and ϵ_r equals 5.35 above 16.4×10^{12} Hz, in good agreement with the permittivity of strontium titanate at optical frequencies. Thus, we have confirmed the generalized LST relation. The permittivity of strontium titanate as a function of frequency is presented in Fig. 4. Note the effects due to the soft phonon frequency.

C. Curie-Weiss Law

It can be seen in Fig. 5 that the permittivity of strontium titanate with a very small applied dc bias field follows the Curie-Weiss relation[14] $1/\epsilon_r \propto (T - T_c)$ from 65 to 300 °K, with a Curie temperature of $T_c = 30 \pm 2$ °K. The Curie temperature is the same from the three crystal orientations. Departures from the Curie-Weiss law occur at temperatures below 40 °K with small applied dc electric field, and below 65 °K with applied fields as shown in Fig. 1.

D. Ion Displacements

If a static electric field is applied to strontium titanate, the strontium and titanium ions are slightly displaced

TABLE II. Frequency (in units of 10^{12} Hz) of long-wavelength transverse optical phonons, and frequency of the corresponding long-wavelength longitudinal optical phonons. Data from Cowley (Ref. 22) and others (Ref. 23).

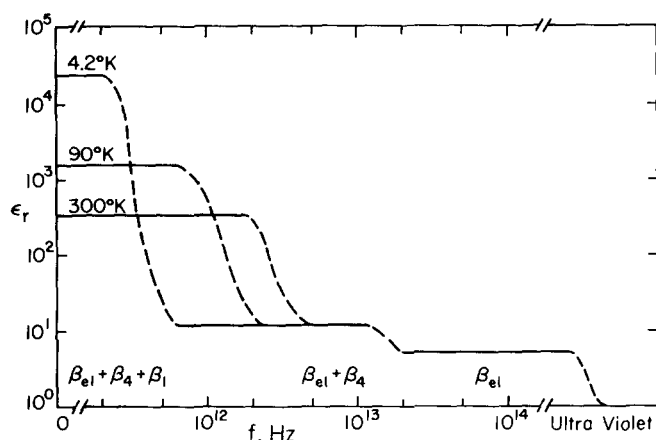| Mode	Transverse	Longitudinal
1	2.73 at 296°K	14.2
2	5.10	5.10
3	7.95	7.95
4	16.4	24.7

FIG. 4. Permittivity of strontium titanate as a function of frequency with temperature as a parameter for [001]-oriented material.

with respect to the oxygen ions. The displacement of each of the five ions in the unit cell is, in general, different and cannot be obtained from permittivity measurements alone.[22] There is some debate whether the "soft" transverse phonon is mainly due to motion of the strontium ions or the titanium ions. Cowley[22] favors titanium ion displacements while Bell and Rupprecht,[3] Last,[26] and Spitzer et al.[27] favor strontium ion displacements.

Let us consider the crystal structure of perovskite strontium titanate. The unit cell is a cube with a Ti^{4+} ion at the body center, surrounded by O^{2-} ions at the face centers and Sr^{2+} ions at the cube corners. The charge indicated for each ion is correct only if the crystal bonds are purely ionic. The charges are smaller if the bonds are partially covalent. The atomic weights and approximate ionic radii are summarized in Table III. If the ions are assumed to be solid spheres, the lattice constant would be 4.00 Å if determined by the O-Ti distance, 3.45 Å if determined by the O-Sr distance, and 3.73 Å if determined by the O-O distance. The lattice constant is thus determined by the O-Ti bond. The actual unit-cell cube edge is 3.9 Å.[2] If the ions were solid spheres, the Sr^{2+} ion would be free to move at least 0.3 Å from its equilibrium position. This freedom of motion of the Sr ion might give rise to the "soft" phonon mode. We shall see, however, that the ion displacements are quite small, so that Ti ion motion might also be important.

The greatest polarization density indicated in Fig. 3 is 9.87×10^{-2} C/m^2, which is obtained by applying an electric field of 23000 V/cm in the [011] direction at 4.2°K. Taking into account the electronic polarizability,[14] this polarization density corresponds to a 0.075 Å displacement of the Sr^{2+} ions, or to a 0.037-Å displacement of the Ti^{4+} ions with respect to the rest of the lattice.

Let us consider the free-energy—vs—polarization curves of Fig. 3. At low polarization densities, $F \propto P^2$ which is characteristic of linear restoring forces. At higher polarization densities, there is departure from $F \propto P^2$, indicating a "hardening" of the restoring forces. The nearest-neighbor Ti-O distance decreases fastest if the Ti ion is displaced in the [001] direction, and least if the Ti ion is displaced in the [111] direction.
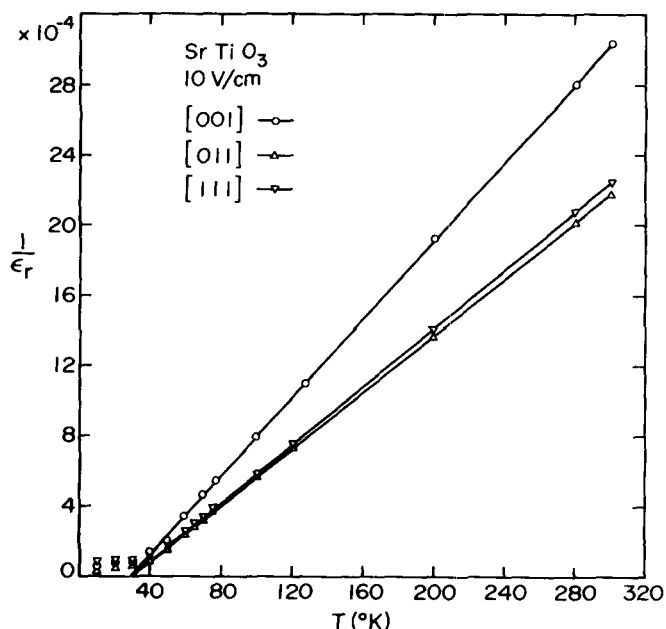

FIG. 5. Inverse relative permittivity of strontium titanate as a function of temperature with crystal orientation as a parameter for an applied dc bias field of 10 V/cm.

Thus, if Ti ion displacements are significant, we expect the greatest departure from $F \propto P^2$ for electric fields applied in the [001] direction and the smallest departure for fields applied in the [111] direction. This is in fact observed in Fig. 3. If only the Sr ion were displaced with respect to the rest of the lattice, we would expect the greatest departure from $F \propto P^2$ in the [011] direction and the smallest departure in the [001] direction. The "hardening" of the restoring forces is therefore indicative that the Ti ion motion is significant.

Verification of the theory of ionic dielectrics[14] is complicated in strontium titanate by the fact that there are two important active optic modes (modes 1 and 4 of Table II). The theory for cubic lattices with two ions per unit cell can be generalized in a simple manner by making the important approximation that the local electric field is the same at all ion sites. To test the theory we shall make the following additional simplifying approximations: (a) The lattice formed by the oxygen ions is rigid, (b) mode 1 of Table II is assigned to oscillation of the strontium ions with respect to the rest of the lattice as indicated by Last,[26] and (c) mode 4 is assigned to oscillation of the titanium ions with respect to the oxygen lattice as indicated also by Last.

With these approximations, the permittivity of the crystal is given by

$$\epsilon = \epsilon_0 (1 + 2\beta)/1 - \beta), \qquad (9)$$

where ϵ_0 is the permittivity of free space, $3a^3 \epsilon_0 \beta$ is the

TABLE III. Approximate ionic radii and atomic weights of Ti^{4+}, O^{2-}, and Sr^{2+}. [a]

	Ti^{4+}	O^{2-}	Sr^{2+}
Radius (Å)	0.68	1.32	1.12
Atomic weight	47.9	16.0	87.6

[a]Obtained from Handbook of Chemistry and Physics, 51st ed. edited by Robert C. Weast (The Chemical Rubber Co., Cleveland, Ohio, 1970).

TABLE IV. Relative permittivity for single-domain strontium titanate, as a function of temperature with applied dc bias as a parameter. The crystal surfaces are (100) planes.

E(V/cm) ±	10	100	200	620	1080	1550	6200	15 500	23 000
T (°K)									
4.2	24 123	21 600	20 163	13 900	10 560	8450	2925	1240	855
10	20 700	19 200	17 193	12 705	9880	8019	2840	1240	855
15	18 200	16 700	15 510	11 800	9310	7689	2810	1235	855
20	16 070	14 900	14 025	10 900	8790	7342	2780	1240	855
30	11 800	11 190	10 692	8840	7550	6510	2772	1290	905
40	7890	7690	7474	6682	5963	5410	2760	1400	1005
50	5098	5050	4970	4670	4372	4100	2757	1455	1085
60	3140	3140	3140	3100	3036	3010	2640	2110	1835
65	2540	2540	2540	2540	2540	2540	2540	2540	2540
70	2230	2230	2230	2230	2230	2230	2230	2230	2230
77	1880	1880	1880	1880	1880	1880	1880	1880	1880
100	1280	1280	1280	1280	1280	1280	1280	1280	1280
128	910	910	910	910	910	910	910	910	910
200	520	520	520	520	520	520	520	520	520
280	357	357	357	357	357	357	357	357	357
300	330	330	330	330	330	330	330	330	330

polarizability of the unit cell (see Ref. 14), and a^3 is the unit-cell volume. At frequencies below the "soft" transverse optic mode, β has three contributions: β_{e1} due to electron displacements;

$$\beta_4 \equiv q_4^2/3C_4 a^3 \epsilon_0 \qquad (10)$$

due to titanium displacements, and

$$\beta_1 \equiv q_1^2/3C_1 a^3 \epsilon_0 \qquad (11)$$

due to strontium displacements. C_1 is the restoring force constant acting on each Sr ion, defined by $C_1 x_1 = q_1 E_{loc}$, where q_1 is the charge of the Sr ion, x_1 is its displacement with respect to the oxygen lattice, and E_{loc} is the local electric field. C_4 is the restoring force constant acting on the Ti ion, and q_4 is its charge. At frequencies between the "soft" mode and 16.4×10^{12} Hz (see Table II—transverse modes), $\beta = \beta_{e1} + \beta_4$, and at optic frequencies $\beta = \beta_{e1}$, as indicated in Fig. 4. Applying Eq. (9) to the three frequency ranges, we obtain $\beta_{e1} = 0.592$, $\beta_4 = 0.195$, and $\beta_1 = 0.204$ at 300 °K.[28] Since $\beta_4 \approx \beta_1$, the two active optic modes give approximately the same contribution to the low-frequency permittivity of strontium titanate, i.e., if a static electric field is applied to the crystal, then $x_1 q_1 \approx x_2 q_2$.

The frequency of the long-wavelength longitudinal mode 4, W_{L4}, is given by

$$\mu_4 W_{L4}^2 = C_4[1 + 2\beta_4/(1 + 2\beta_{e1})], \qquad (12)$$

and for mode one

$$\mu_1 W_{L1}^2 = C_1\{1 + 2\beta_1/[1 + 2(\beta_{e1} + \beta_4)]\}. \qquad (13)$$

The reduced mass of the Sr ion oscillating against the rest of the lattice is $\mu_1 = 45.8 m_0$ and that of the Ti ion oscillating against the oxygen lattice is $\mu_4 = 24.0 m_0$, where m_0 is the proton rest mass (see Table III). From Eqs. (12) and (13) and the values of w_{L1} and w_{L2} in Table II, we obtain $C_1 = 525$ N/m and $C_4 = 820$ N/m.

The theory can now be checked by calculating the charges of the Sr and Ti ions using Eqs. (10) and (11). The results are $q_1 = 2.56$ electronic charges for the strontium ion and $q_4 = 3.14$ electronic charges for the titanium ion. Considering the approximations made in this analysis, the calculated charges are in reasonable agreement with the expected ion charges in the strontium titanate crystal.

VI. CONCLUSIONS

The permittivity of single-crystal single-domain per-

TABLE V. Relative permittivity for single-domain strontium titanate, as a function of temperature with applied dc bias as a parameter. The crystal surfaces are (110) planes.

E(V/cm) ±	10	100	200	620	1080	1550	6200	15 500	23 000
T (°K)									
4.2	25 600	23 960	22 700	18 400	15 180	12 936	5230	2380	1650
10	24 000	22 600	21 400	17 530	14 619	12 474	5170	2370	1650
15	21 880	20 823	19 990	16 550	13 920	12 000	5110	2370	1665
20	19 000	18 645	17 850	15 150	13 000	11 286	5010	2370	1660
30	14 800	14 322	13 800	12 300	10 923	9800	4890	2430	1730
40	10 200	9960	9800	9075	8430	7850	4165	2574	1885
50	6910	6864	6780	6470	6190	5910	4140	2580	1970
60	4366	4366	4360	4310	4273	4230	3860	3290	2854
65	3530	3530	3530	3530	3530	3530	3530	3530	3530
70	3080	3080	3080	3080	3080	3080	3080	3080	3080
77	2640	2640	2640	2640	2640	2640	2640	2640	2640
100	1770	1770	1770	1770	1770	1770	1770	1770	1770
120	1370	1370	1370	1370	1370	1370	1370	1370	1370
200	730	730	730	730	730	730	730	730	730
280	495	495	495	495	495	495	495	495	495
300	458	458	458	458	458	458	458	458	458

TABLE VI. Relative permittivity for single-domain strontium titanate, as a function of temperature with applied dc bias as a parameter. The crystal surfaces are (111) planes.

E(V/cm) ±	10	100	200	620	1080	1550	6200	15 500	23 000
T (°K)									
4.2	14 100	13 700	13 350	12 000	10 800	9790	5110	2620	1880
10	13 700	13 350	13 000	11 700	10 580	9610	5080	2620	1880
15	13 340	13 000	12 680	11 480	10 380	9487	5060	2610	1894
20	12 420	12 128	11 850	10 800	9850	9010	4960	2620	1894
30	10 320	10 180	10 000	9300	8600	8020	4800	2656	1950
40	7887	7870	7720	7350	6980	6630	4520	2673	2090
50	5650	5610	5560	5400	5240	5080	3894	2656	2120
60	4040	4040	4040	4010	3990	3950	3680	3238	2970
65	3460	3460	3460	3460	3460	3460	3460	3460	3460
70	3030	3030	3030	3030	3030	3030	3030	3030	3030
77	2580	2580	2580	2580	2580	2580	2580	2580	2580
100	1730	1730	1730	1730	1730	1730	1730	1730	1730
120	1340	1340	1340	1340	1340	1340	1340	1340	1340
200	715	715	715	715	715	715	715	715	715
280	486	486	486	486	486	486	486	486	486
300	448	448	448	448	448	448	448	448	448

ovskite strontium titanate has been measured in detail in the [001], [011], and [111] directions as a function of temperature (from 4.2 to 300 °K), electric field (from −23 000 to +23 000 V/cm), and frequency (from 1 kHz to 50 MHz). From this data the free-energy—vs-polarization curves were calculated. The Curie-Weiss law is satisfied in the temperature range 40−300 °K, giving a Curie temperature of $30 ± 2$ °K for the three crystal orientations. The LST relation is satisfied for temperatures between 30 and 300 °K and electric fields between 0 and 12 000 V/cm. A generalized LST relation was used to calculate the permittivity of strontium titanate from zero to optic frequencies. The calculated optic frequency permittivity is in excellent agreement with the literature. It was concluded that only two of the long-wavelength optic modes propagating in the [001] direction generate dipole moments.

The perovskite strontium titanate crystal is formed of a tightly bound oxygen-titanium lattice which leaves ample spaces for the strontium ions. The O-Ti lattice determines the lattice constant and, most likely, the mechanical characteristics of the crystal. Each small Ti ion is tightly surrounded by six half-oxygen ions. Thus, the lattice formed by the oxygen ions screens the Ti ions from the Sr ions. We are led to believe that the two electrically active modes are mainly due to strontium motion and to titanium motion, respectively. The low-frequency active optic mode is attributed to motion of the heavy loosely bound Sr ions with respect to the rest of the lattice, and the high-frequency active mode is attributed to motion of the lighter and more tightly bound Ti ions with respect to the oxygen lattice, as indicated by Last. These assumptions are seen to be consistent with the theory of the permittivity of ionic crystals. The two active optic modes give approximately equal contributions to the low-frequency permittivity of strontium titanate. It was seen that departures of the free energy from $F \propto P^2$ indicate Ti ion motion. The restoring force that acts on a titanium ion begins to "harden" when this ion is displaced by approximately 0.002 Å from its equilibrium position.

APPENDIX: CALCULATED VALUES OF RELATIVE PREMITTIVITY FOR SINGLE-DOMAIN STRONTIUM TITANATE

Tables IV−VI contain typical values of the relative permittivity of single-domain strontium titanate as a function of temperature with applied dc field as a parameter. The measurement frequency lies between 1 kHz and 50 MHz. The accuracy of measurement, in all cases, is ±2%.

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