Dielectric Properties of $SrTiO_3$ at Low Temperatures

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We have measured the temperature dependence of the dielectric constants for single-domain $SrTiO_3$ crystals. Dielectric anisotropies and deviations from the simple Curie-Weiss law have been observed and are discussed in connection with the structural phase transitions at 110 and 65°K.

The structural phase transition at $T_a \approx 110$°K in $SrTiO_3$ is a direct consequence of the condensation of the Γ_{25} optical-phonon mode at the Brillouin-zone boundary.[1-4] The dielectric constant of this crystal was reported to obey a simple form, $\epsilon = C(T-T_c)^{-1}$, with paraelectric Curie temperature $T_c \approx 35$°K. At lower temperatures, an appreciable departure from the Curie-Weiss law was observed, which was ascribed to the quantum effect of ionic polarizability.[5-8]

Hitherto, the dielectric properties were obscured by the presence of multiple domains when the crystal is cooled through T_a. The nonferroelectric structural transitions were generally considered not to affect the dielectric behavior. Recently, it was demonstrated that a uniaxial compressive stress can produce a single-domain crystal at low temperatures.[9,10] We report here dielectric measurements on single-domain crystals produced by this technique.

A tetragonal prism with surfaces of (110), (1$\bar{1}$0), and (001) and of size $2 \times 2 \times 3$ mm^3 was cut from a pure single crystal. Geometries of the crystal axes, electrodes for dielectric measurement, and the direction of compressive stress are shown in Fig. 1. Samples were always cooled from room temperature to liquid-helium temperature under an applied stress higher than 10 kg/mm^2 and the stress was released during dielectric measurement in order to avoid the pressure dependence of the permittivity. This procedure guarantees against recovery of multiple domains.[11]

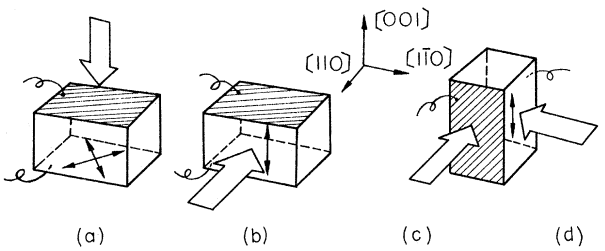

FIG. 1. Geometries of crystal axes, electrodes, external uniaxial stress (thick arrows) and the direction of c axes in the sample (thin arrows), for measuring (a) ϵ_a, (b) ϵ_c, (c) ϵ_{110}, and (d) $\epsilon_{1\bar{1}0}$.

Dielectric permittivity was measured by a three-terminal method using a GR model 1615A capacitance bridge at 10 kHz with a field level of 5 V/cm. Temperature inside the sample cryostat was raised slowly, at the rate of 0.2°C/min.

Components of the dielectric permittivity tensor for crystals subjected to the stress treatment were determined as functions of temperature, with results as shown in Fig. 2. In this figure we notice that the dielectric tensor becomes anisotropic below T_a, with ϵ_a larger than ϵ_c. Furthermore, the dielectric anisotropy in the plane perpendicular to the c axis was found to develop around $T_b \simeq 65$°K[12-14]; that is, [110] and [1$\bar{1}$0] axes

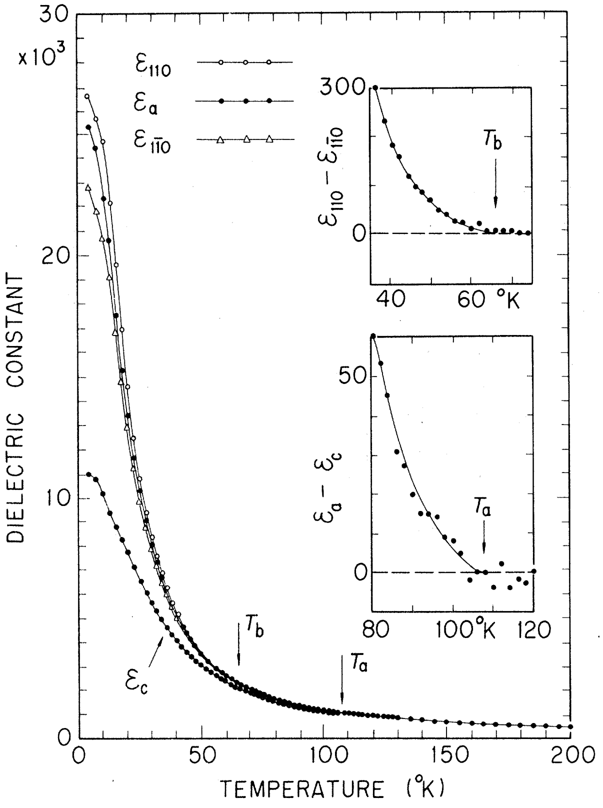

FIG. 2. Temperature dependence of the dielectric constants in $SrTiO_3$ for various orientations (see Fig. 1). The insets show the details of the dielectric anisotropies near T_a and T_b, respectively.

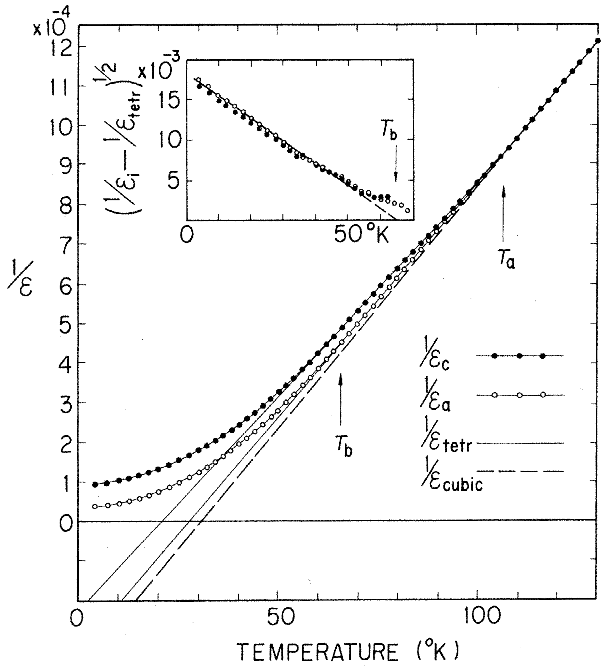

FIG. 3. Inverse dielectric constants as function of temperature. Between T_a and T_b, both ϵ_a^{-1} and ϵ_c^{-1} follow straight lines which are denoted as $\epsilon_{\mathrm{tetr}}^{-1}$. Inset: $(\epsilon_i^{-1}-\epsilon_{\mathrm{tetr}}^{-1})^{1/2}$ versus temperature, open and solid circles corresponding to ϵ_a and ϵ_c, respectively.

become no longer equivalent, which indicates the crystal structure below T_b to be of an orthorhombic or lower symmetry. The dielectric inverse susceptibility[15] χ_i is plotted as function of temperature in Fig. 3, wherein we notice that (1) a slight but distinct knee is observed at T_a in the χ-T characteristics; that is, the χ value ceases to follow the high-temperature Curie-Weiss law, and the difference is proportional to T_a-T; (2) the χ-T curves begin to deviate from the straight lines below T_b; the amount of deviation is proportional to $(T_b-T)^2$ and is not orientation dependent. These characteristics can be summarized by the equation

$$\chi_i = C^{-1}(T-T_c)+\Delta\chi_i, \tag{1}$$

$$\Delta\chi_i = \begin{cases} 0, & T>T_a, \\ A_i(T_a-T), & T_a>T>T_b, \\ A_i(T_a-T)+B_i(T_b-T)^n, & T_b>T, \end{cases} \tag{2}$$

where subscripts $i=1,2,3$ refer to pseudocubic axes and 3 refers to tetragonal c axis. The values of the parameters are $A_1=0.62\times10^5$ deg^{-1} m/F, $A_3=1.58\times10^5$ deg^{-1} m/F, $B_1=B_3=0.90\times10^4$ deg^{-2} m/F, Curie constant $C=0.726\times10^{-6}$ deg F/m, $T_a=107\pm1$°K, $T_b=65\pm2$°K, $T_c=31\pm1$°K, and exponent $n=2$.

Let us now discuss the dielectric behavior below T_a associated with the Γ_{25} soft-mode condensation. We consider, within the framework of phenomenological theory, a free energy G involving polarization P_i, rotation angles of oxygen octahedra φ_i as order parameter of the phase transition, and elastic strains x_{ij}. Adopting the usual convention, we have

$$G=(\pi/C)(T-T_c)\sum P_i^2 + \tfrac{1}{2}\sum c_{ijkl}x_{ij}x_{kl}+G_\varphi+G_{\mathrm{int}}, \tag{3}$$

$$G_\varphi=(a/2)(T-T_a)\sum\varphi_i^2 + (b/4)\sum\varphi_i^4+(c/2)\sum\varphi_i^2\varphi_j^2, \tag{4}$$

$$G_{\mathrm{int}}=\tfrac{1}{2}\sum\left[q_{ijkl}x_{ij}P_kP_l+r_{ijkl}x_{ij}\varphi_k\varphi_l + t_{ijkl}\varphi_i\varphi_jP_kP_l\right], \tag{5}$$

where the first two terms represent usual polarization and elastic energy, and G_φ is the configurational energy due to internal strain φ_i.[4] The interaction energy among the three variables is expressed by G_{int}; the first term is the usual electrostrictive term and the second term represents the interaction between the soft rotational mode and the long-wavelength acoustic phonons.[4] We introduce a new interaction energy represented by the last term of Eq. (5). This term should be responsible for a direct coupling between the two internal strains φ_i and P_i.[16] Symmetry considerations dictate that the nonvanishing elements of the fourth rank tensor, for instance, t_{ijkl}, should be t_{11}, t_{12}, and t_{44} in contracted suffices. Slonczewski and Thomas have derived,[17] minimizing G with respect to x_i and φ_i, an expression for the spontaneous values of φ_i and x_i below T_a as[18]

$$\varphi_{1s}=\varphi_{2s}=0,$$

$$\varphi_{3s}^2=\tfrac{1}{2}a\left[2b-(c_{11}-c_{12})^{-1}r_{11}(r_{11}-r_{22})\right]^{-1}\times(T_a-T), \tag{6}$$

$$x_{3s}=-2x_{1s}=r_{12}(c_{11}-c_{12})^{-1}\varphi_{3s}^2.$$

Weak-field dielectric inverse susceptibilities below T_a can be derived, through the relation $\partial G/\partial P_i=\Delta E_i$ and $\chi_i^{\mathrm{eff}}=\lim(\Delta E_i/\Delta P_i)$, as

$$\chi_i^{\mathrm{eff}}=(2\pi/C)(T-T_c)+\Delta\chi_i, \tag{7}$$

$$\Delta\chi_1=t_{12}\varphi_{3s}^2-\tfrac{1}{2}(q_{11}-q_{12})x_{3s}, \tag{8}$$

$$\Delta\chi_3=t_{11}\varphi_{3s}^2+(q_{11}-q_{12})x_{3s}. \tag{9}$$

Since both φ_{3s}^2 and x_{3s} are proportional to T_a

$-T$, it is clear that $\Delta\chi_i$ should also be proportional to T_a-T, which is consistent with the observation. Further, we find that the electrostrictive term should play a minor role, because (1) both $\Delta\chi_1$ and $\Delta\chi_3$ were found to be of the same sign, and (2) the value of $(q_{11}-q_{12})x_{3s}$ estimated from previous experiments[19] is about $3.7\times10^4(T_a-T)$ m/F which is rather small compared with the observed values of $\Delta\chi_i$. Then, as

$$2\Delta\chi_1+\Delta\chi_3=(t_{11}+2t_{12})\varphi_{3s}^2 \tag{10}$$

and $\varphi_{3s}^2=0.22\times10^{-4}(T_a-T)$ rad^2 for $T_b<T<T_a$,[14] we obtain $t_{11}+2t_{12}=1.28\times10^{10}$ rad^{-2} m/F.

Let us now briefly discuss the dielectric behavior below T_b. The phase transition at T_b seems to be still debated, as the anomaly at T_b was previously reported in several experiments,[5, 12-14, 20] but no corresponding anomaly was observed in many other measurements.[2, 21, 22] The onset of orthorhombic dielectric anisotropy below T_b reported here would give support for the phase transition. It is difficult to decide, however, whether the observed $(T_b-T)^2$ term in Eq. (2) would be a consequence of some soft phonon responsible for the T_b phase transition[23] or might be just another expression of the Barrett effect.[7] Recently Saifi and Cross suggested[20] that the crystal should be antiferroelectric below T_b. They observed for annealed crystals a double hysteresis loop which was explained as due to the forced transition from an antiferroelectric state to a paraelectric one. In view of the previous ESR evidence[13] that below T_b the Sr site might become antipolarized along the c axis, their interpretation seems appealing. However, it should be noted that the weak-field dielectric constants for the antiferroelectric and the paraelectric state are, numerically, the same as ϵ_c and ϵ_a in the present study. Therefore, we are left with another possibility that the reported double hysteresis loop might be due to the conversion of the domain configuration in the sample from c plate to a plate. Further observations and analysis are desirable in order to clarify the nature of the T_b anomaly.

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[11] In Ref. 10 it is reported that single-domain crystals subjected to stress above 10 kg/mm^2 did not recover their multiple-domain structure as the stress is released until the sample was again heated above T_a. We have also confirmed this by observing the relative intensities of ESR signals due to different domains (Ref. 1) for a sample containing Fe^{3+} impurity ion.

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[13] H. Unoki and T. Sakudo, J. Phys. Soc. Jap., Suppl. 28, 125 (1970).

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[15] We neglect the difference between the dielectric inverse susceptibility χ_i and the reciprocal dielectric constant $1/\epsilon$ in Fig. 3, except that the χ_i are expressed in mks units.

[16] There should be no term proportional to $\sum\varphi_i P_i$, since φ_i is an axial vector and P_i is a polar vector.

[17] J. C. Slonczewski and H. Thomas, Phys. Rev. B 1, 3599 (1970).

[18] In order to obtain the tetragonal solution, $c>b>0$. They also use the condition $\sum x_{is}=0$ which was verified experimentally by B. Alefeld, Z. Phys. 222, 155 (1969).

[19] From the data on induced piezoelectric measurement [G. Rupprecht and W. H. Winter, Phys. Rev. 155, 1019 (1967)] we estimate $q_{11}=-2q_{12}\sim5.7\times10^9$ m/F. From x-ray diffractometry (Ref. 18), $x_{3S}=(c/a)-1$ $=1.3\times10^{-5}(T_a-T)$.

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[23] It seems difficult to develop a simple theory analogous to the above discussion because (1) the $(T_b-T)^2$ dependence would have to be ascribed to some coupling term involving a higher-than-quadratic interaction, and (2) the first term of Eq. (2) itself might not take a simple form, as the φ_3^2-T curve has a knee at T_b (Ref. 14).