Ferroelectricity: Measurement of the dielectric susceptibility of strontium titanate at low temperatures

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A cryogenic experiment determining the dielectric susceptibility of the ferroelectric substance, strontium titanate, in the 90- to 300-K temperature range is described. Evidence is presented for a structural phase transition in strontium titanate at 110 K. The experiment is suitable for advanced students. © *2001 American Association of Physics Teachers.*
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I. INTERESTING AND UNUSUAL PROPERTIES OF FERROELECTRICS

Ferroelectricity describes a collection of phenomena which contribute to the generation of a spontaneous electric polarization in materials called ferroelectrics.[1] Spontaneous polarization is a result of the materials having a unique polar axis. The important point is that the direction of the spontaneous polarization can be switched by an external electric field.

Ferroelectrics are an extremely important class of materials used in the electronics industry. The main interest is in the polycrystalline (ceramic) and thin film forms of the materials. These are easier to make than single crystals and their composition can be readily modified. However the physical properties of the ceramic form are different from those of the single crystal and depend on parameters such as doping, grain size, and structural defects.[2] Ferroelectrics are used as dielectrics in ceramic capacitors and in piezoelectric devices. Exciting new possible uses for ferroelectric thin films include nonvolatile memory applications and microelectromechanical systems.[3]

Pray[4] described a method of measuring the dielectric constant of thin films of the dielectric cryolite (Na_3AlF_6) using a parallel plate capacitor technique and a balanced capacitance bridge. Morgan *et al.*[5] measured the pyroelectric coefficient and spontaneous polarization of the ferroelectric triglycine sulfate (TGS) from 25 to 30 °C and observed a phase change at 49 °C. Pyroelectric materials are useful as infrared light detectors because they possess the characteristic of a temperature-dependent spontaneous polarization. All ferroelectric materials are pyroelectric. Ofer and Jodl[6] investigated the electro-optic effects of the ceramic ferroelectric known as PLZT [a modified form of $Pb(Zr, Ti)O_3$]. The transparency of this substance varies under the influence of an electric field. The effect is temperature dependent. Applications for this material include welding goggles and intensity modulation.

A ferroelectric of particular interest because of its unusual properties at low temperatures is strontium titanate, $SrTiO_3$. $SrTiO_3$ belongs to a family of compounds with the general formula ABO_3, where A is a divalent ion and B is a quadrivalent ion.[1] At room temperature $SrTiO_3$ has a cubic perovskite-type structure but at ~105 K undergoes a phase transition to a tetragonal form.[7] Grupp and Goldman[8] observed a giant piezoelectric effect in $SrTiO_3$ at cryogenic temperatures. Its properties at very low temperature also include superconductivity[9] and quantum paraelectric behavior.[10]

Observations of the properties of $SrTiO_3$ have played an important role in the development of the theory of structural phase transitions. It was the first material for which a high static dielectric constant at low temperature was associated with a low frequency (''soft'') optical mode.[11] This gave experimental proof of the Lyddane–Sachs–Teller relation.[12] Indeed, soft modes were first clearly measured in a lattice dynamics study of the $SrTiO_3$ phase transition.[13] $SrTiO_3$ was the first crystal in which a central peak was revealed by neutron scattering.[14] Also x-ray scattering studies of the $SrTiO_3$ phase transition brought into existence the concept of a two-length scale behavior arising from defects and dislocations in the crystal structure.[15]

The aim of this experiment is to measure the dielectric susceptibility[16] of $SrTiO_3$ at low temperature and look for evidence of the structural phase change.

II. DETERMINATION OF THE DIELECTRIC SUSCEPTIBILITY

An easy way of determining the dielectric susceptibility is to measure the capacitance of a parallel plate capacitor containing the ferroelectric substance as a dielectric.[17] The sample is a 100-oriented slice (10 mm × 10 mm × 0.27 mm) of a single crystal of pure strontium titanate.[18] Gold electrodes of 6.8 mm diameter are vacuum evaporated on both sides of the sample to form the capacitor. If vacuum evaporation equipment is not available then 50-μm copper foil can be attached with a thin layer of Opticlean fluid®. Silver paste is used to attach fine enameled copper wire to the electrodes.

For the parallel plate capacitor, the polarization **P** induced in the $SrTiO_3$ dielectric is proportional to the applied electric field vector **E**,

$$\mathbf{P} = \chi_e \epsilon_0 \mathbf{E}, \tag{1}$$

where the dielectric permittivity of a vacuum $\epsilon_0 = 8.85 \times 10^{-12}$ F m^{-1}. Relation (1) is valid only for linear material and the dielectric susceptibility χ_e is a dimensionless quantity representing an isotropic medium with a cubic structure. Note, however, that for an anisotropic medium the dielectric susceptibility is a second-rank tensor χ_{ij} (F m^{-1}). Perkalskis and Freeman[19] demonstrated the tensor properties of anisotropic dielectric materials to great effect using a cylindrical capacitor. The dielectric displacement vector **D** represents the total surface charge density induced in the dielectric
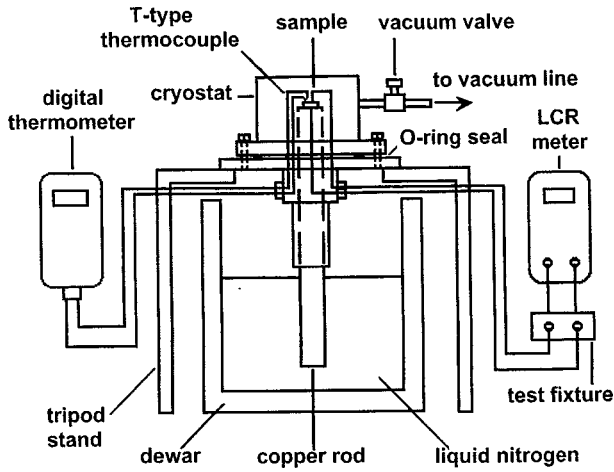
Fig. 1. Setup for determining dielectric susceptibility of SrTiO₃.

Fig. 2. Dielectric susceptibility of SrTiO$_3$ vs temperature.

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}. \tag{2}$$

Substituting the term for **P** in Eq. (2) then

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \chi_e \epsilon_0 \mathbf{E} = (1 + \chi_e)\epsilon_0 \mathbf{E}. \tag{3}$$

If Q is the total charge on the parallel plate capacitor and A is the area of the gold electrode, then $\mathbf{D} = Q/A$. Also $\mathbf{E} = V/d$ where V is the potential difference across the capacitor and d is the thickness of the SrTiO₃ sample. Substituting these relationships for **D** and **E** in term (3), the following equation is obtained:

$$\frac{Q}{A} = (1 + \chi_e)\epsilon_0 \frac{V}{d}. \tag{4}$$

Now the capacitance C of the parallel plate capacitor is defined as the ratio of the charge on either plate to the potential difference between the plates, $C = Q/V$. From this, the relationship between capacitance C and dielectric susceptibility χ_e is expressed as

$$C = \frac{Q}{V} = C_0(1 + \chi_e), \tag{5}$$

where $C_0 = \epsilon_0 A/d$ and is the capacitance with no dielectric.[20] C_0 was calculated as ~1 pF.

Figure 1 shows the measurement setup. The sample is mounted on a copper block inside the vacuum can of a cryostat. By evacuating the can, all air moisture is removed. Moisture solidifying on the sample when the temperature is lowered would interfere with its electrical properties. A T-type thermocouple attached to a corner of the sample and connected to a digital thermometer measures the sample temperature. Capacitance and dissipation factor $\tan \delta$ measurements are taken using a digital LCR meter with an ac test signal of 0.9-V rms amplitude and 1-kHz frequency. A test fixture interfaces the sample leads to the LCR meter.[21]

After evacuating the vacuum can, the copper rod of the cryostat is immersed in liquid nitrogen to bring the temperature of the sample down to ~90 K. The cryostat is then removed from the liquid nitrogen and allowed to warm up. Measurements of C and $\tan \delta$ are taken at frequent intervals from 90 to 300 K.

By substituting for the sample a 270-pF silvered-mica capacitor ($\pm 1\%$ tolerance) the stray capacitance of the leads
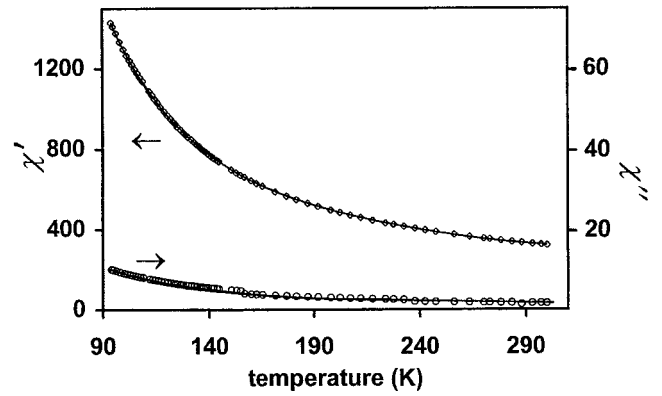
and test fixture can be determined. This was ~80 pF in the 90- to 300-K range. The stray capacitance is subtracted from the measured capacitance to give the corrected value.

The dielectric susceptibility is complex with a real χ' and imaginary component χ'':

$$\chi = \chi' - i\chi''. \tag{6}$$

Equation (5) is used to convert the measured capacitance value to the real dielectric susceptibility. The imaginary dielectric susceptibility is calculated from the dissipation factor, $\tan \delta = \chi''/\chi'$. $\tan \delta$ is a measure of the energy lost per cycle in the form of heat.

A plot of real and imaginary dielectric susceptibility versus temperature at 1 kHz and zero dc bias field is shown in Fig. 2. The χ' values compare well with those measured in other studies.[22] Dielectric spectroscopy studies of SrTiO₃ showed that χ' is almost frequency independent in the range $10^{-3} - 10^8$ Hz at all temperatures.[23] Dec et al.[24] clearly demonstrated the scaling behavior of χ' with respect to dc bias field at temperatures of <65 K. This ability to modify the dielectric susceptibility of ferroelectric materials by an applied electric field has created some excitement in microwave engineering.[25] Neville et al.[17] observed that between 65 and 300 K, χ' is independent of applied dc field. In contrast, van der Berg et al.[26] observed field-dependent permittivity for Nb-doped SrTiO₃ crystals at room temperature. The losses χ'' are very low for SrTiO₃, rising from 0.5% χ' at 300 K to 0.7% χ' at ~90 K. This rise in χ'' near the structural phase transition is due to dielectric relaxation and is frequency dependent.[27] Low loss is a very desirable feature in a dielectric. High loss causes heating of the capacitor which may lead to a destructive breakdown of the dielectric under certain circumstances.

III. THE PHASE TRANSITION IN STRONTIUM TITANATE

The dielectric susceptibility values for SrTiO₃ can be used to derive useful information on its low temperature phase transition. SrTiO₃, like other ferroelectrics, loses its intrinsic polarization above a transition temperature and becomes paraelectric. This involves a cubic-tetragonal phase transition in the crystal structure. Earlier publications[12] quoted a transition temperature of 110 K but more recent research has
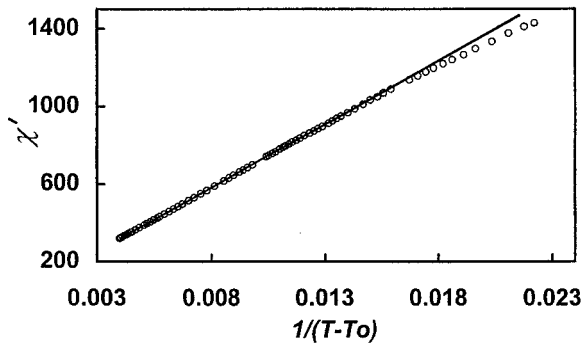
Fig. 3. Dielectric susceptibility χ' vs $1/(T-T_0)$.

reported a value of 105 K.[7] Above the transition temperature, the dielectric susceptibility χ' follows a classical Curie–Weiss-type law

$$\chi' = \frac{C_{CW}}{(T-T_0)}, \tag{7}$$

where C_{CW} is a constant and T_0 is the critical temperature.[2] A plot of dielectric susceptibility χ' vs $1/(T-T_0)$ is shown in Fig. 3. Initially T_0 is estimated and then readjusted until the best straight line is obtained using a least-squares method. From Fig. 3, the dielectric susceptibility of the $SrTiO_3$ sample follows the equation

$$\chi' = 61.7 + \frac{6.48 \times 10^4}{(T-49)}. \tag{8}$$

It is clear from Eq. (8) that there are two effects contributing to the dielectric susceptibility: a temperature-independent susceptibility equal to 61.7 that arises from the polarization of the ions themselves and a temperature-dependent component described by the Curie–Weiss law. The latter is the contribution from the movement of the ions from their equilibrium position.[28] Actually, in effect, relation (7) is no more than a mean-field approximation applied to the fluctuating local electric fields in the $SrTiO_3$ crystal. From Fig. 3, Curie–Weiss-type behavior is observed from 110 to 300 K. Below 110 K, $SrTiO_3$ appreciably departs from the law. This suggests a transition temperature of ~110 K. Dec et al.[24] using a 110-oriented plate sample of $SrTiO_3$ found the best fit to the Curie–Weiss law in the temperature range $110 \leqslant T \leqslant 300$ K with $C_{CW} = 6.6 \times 10^4$ K and $T_0 = 40.5$ K. The same researchers[24] observed that χ' continued to rise to a level of the order 2×10^4 at 4.5 K.

There is some disagreement as to the applicability of mean field theory to $SrTiO_3$ at temperatures below 110 K. Therefore it is important to establish that the behavior of χ' at 110 K is due to a structural phase change rather than departure from mean field theory. Near the phase transition point, many properties of ferroelectrics manifest singularities. For example, in the ferroelectric $BaTiO_3$ the cubic to tetragonal phase change is accompanied by a significant anomaly of the dielectric susceptibility.[29] For $SrTiO_3$ no singularity is observed in χ'. However, other properties, such as elasticity, show significant changes at ~110 K. So the Curie–Weiss law as presented in Eq. (7) is inadequate in describing experimental data over the entire temperature range and the Barrett formula and a generalized quantum Curie–Weiss law

have been introduced to describe χ' at very low temperatures.[30] In support of mean field theory, Hemberger et al.[31] demonstrated excellent agreement between mean field approximations and experimental data for $30 < T < 100$ K.

The phenomena associated with phase transitions and critical points are of great interest to both teachers and researchers. The Curie–Weiss law presented in Eq. (7) is the same form as that for the magnetic susceptibility of ferromagnetic materials. Fisher and Franz[32] demonstrated a ferromagnetic-to-paramagnetic transition in ferromagnetic alloys by measurement of the critical or Curie temperature. Indeed Mata-Mendez[33] draws on the analogy between dielectric and magnetic phenomena and suggests a unified presentation of magnetic and dielectric materials.

A method for a theoretical description of the ferroelectric-to-paraelectric phase transition is provided by the Landau–Devonshire thermodynamic approach.[34] Berezin[35] presented a simple electrostatic model of structural phase transitions between two crystallographically different structures based on the Coulomb law.

IV. CONCLUSIONS

The great variety of observed phenomena and practical applications associated with ferroelectrics makes them very attractive both for theoretical and experimental investigations. The experiment described here has proven to be popular with students and it fits in well with contemporary material physics courses.

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