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Ferroelectrics and the Curie–Weiss law

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Abstract. The electrical properties of ferroelectric substances are investigated and related to the Curie–Weiss law. A cryogenic experiment suitable for students measures the electrical susceptibility of strontium titanate in the 90–300 K temperature range. By measuring the electrical susceptibility of a modified barium titanate ceramic between 273 K and 343 K a phase transition is clearly observed at 304 K.

1. Electrical properties of ferroelectrics

Ferromagnetic substances lose their spontaneous magnetization at temperatures above the Curie temperature, T_C, and become paramagnetic [1]. This involves a phase transition in the crystal structure. Similarly, ferroelectrics lose their intrinsic polarization at temperatures above a transition temperature and become paraelectric. Above the transition temperature the electrical susceptibility, χ, of the substance follows the law

$$\chi = \frac{A}{T - T_C} \qquad (1)$$

where A is a constant [2]. This is the same form of expression as the Curie–Weiss law of magnetic susceptibility. For ferroelectrics, expression (1) is no more than a mean-field approximation applied to the fluctuating local electric fields in the crystal structure.

A simple method of determining electrical susceptibility is to measure the capacitance of a parallel plate capacitor containing the ferroelectric substance as a dielectric [3]. Capacitance, C, is related to susceptibility through the expression

$$C = C_0(1 + \chi) \qquad (2)$$

where C_0 is the capacitance without a dielectric and is determined from

$$C_0 = \frac{\varepsilon_0 A}{d} \qquad (3)$$

where A is the area of the capacitor plate, d is the distance between the plates and $\varepsilon_0 = 8.85 \times 10^{-12}$ Fm^{-1} [4].

2. Electrical susceptibility of strontium titanate

2.1. Interesting properties of strontium titanate

The aim of this experiment is to measure the variation of the electrical susceptibility of the ferroelectric, strontium titanate ($SrTiO_3$) at low temperature. Much research has been carried out into the interesting and unusual properties of $SrTiO_3$ at low temperature including

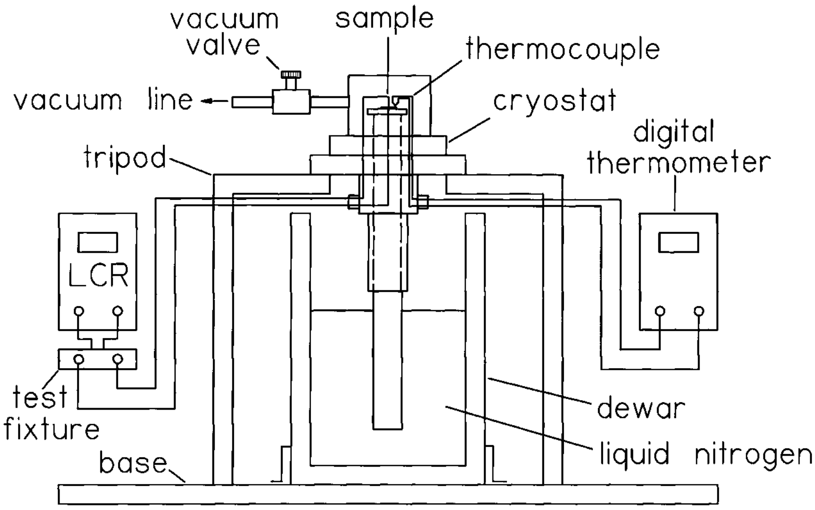

Figure 1. Set-up for measurement of the susceptibility of $SrTiO_3$ at low temperature.

superconductivity with a transition temperature of 0.3 K [5], quantum paraelectric behaviour below 4 K [6], a high level of piezoelectricity at 1.6 K [7] and a structural phase transition at $\sim$ 105 K [8].

Cryogenic apparatus is required to measure the electrical properties of ferroelectric substances at low temperature, and certain precautions have to be taken for the safe handling of cryogenic liquids. In this instance, liquid nitrogen, having a boiling point of 77.4 K, is used. Safety goggles, thermal protective gloves and high-density polystyrene dewars are required by students for handling this liquid.

2.2. Measurement of electrical susceptibility at low temperature

In this experiment the $SrTiO_3$ sample (Crystal GmbH, Berlin) was in the form of a (100)-orientated slice (10 mm × 10 mm × 0.27 mm) of a single crystal. Gold electrodes of 6.8 mm diameter were vacuum evaporated on both sides of the slice to form a capacitor. This sample was positioned on a copper platform inside the vacuum container of a cryostat [9] as shown in figure 1. A T-type thermocouple was glued to the edge of the sample. A digital LCR meter (AVO Megger B131) set at 1 kHz was used to measure the capacitance of the sample. A test fixture [10] interfaced the sample leads with the LCR meter. To measure the temperature of the sample, the thermocouple was connected to a digital thermometer (Digitron T208). After evacuating the vacuum container, the copper cold-finger of the cryostat was immersed in liquid nitrogen to bring the temperature down to $\sim$ 90 K. In the interest of safety, the 4-litre high-density polystyrene dewar was clamped securely with an aluminium collar attached to a wide base. After temperature stabilization, the cryostat was removed from the liquid nitrogen and allowed to warm up while readings of capacitance and temperature were taken up to $\sim$ 300 K.

To measure the total stray capacitance of the leads and test fixture, a 270 pF ($\pm 1\%$ tolerance) silvered mica capacitor was substituted for the sample. In the 90–300 K temperature range the average value of the stray capacitance was 80 pF. This was subtracted from the measured capacitance value of the $SrTiO_3$ sample to give the corrected value.

The errors specified for the LCR meter and digital thermometer were $\pm 0.7\%$ and $\pm 0.5\%$ respectively.

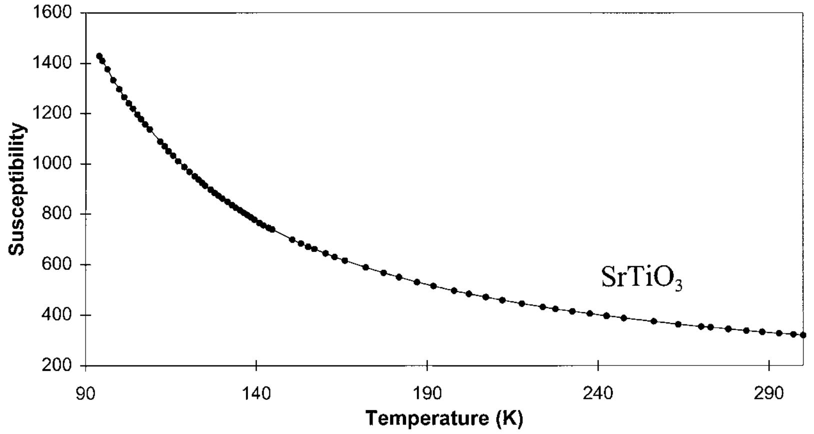

Figure 2. Temperature dependence of the electrical susceptibility of $SrTiO_3$.

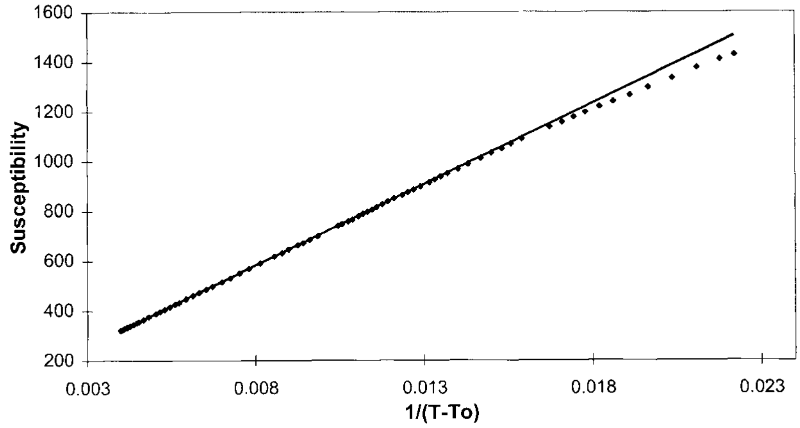

Figure 3. Plot of susceptibility versus $1/(T - T_0)$ for $SrTiO_3$.

2.3. Strontium titanate and the Curie–Weiss law

From equation (3) and the dimensions of the capacitor quoted in the last section, C_0 was determined as $\sim$ 1 pF. Using this and the measured capacitance value at each temperature, the electrical susceptibility was calculated from equation (2). Figure 2 shows the change of electrical susceptibility with temperature for the $SrTiO_3$ sample. A plot of susceptibility versus $1/(T - T_0)$ is presented in figure 3, where T_0 is the critical temperature in the Curie–Weiss law expression. A least-squares method [11] was used to calculate the line that best fitted the data. It was necessary to initially estimate T_0 and then adjust it until the best straight line was obtained. This occurs when the residual sum of squares [12] is minimized. An easy way of doing this was to set up a Microsoft Excel spreadsheet and use the Linest or Polyfit function to obtain the best fit. The experimental expression for the total susceptibility was

$$\chi = 61.7 + \frac{6.48 \times 10^4}{T - 49}. \tag{4}$$

Clearly, from (4), the electrical susceptibility has contributions from two effects

$$\chi = \chi_P + \chi_{CW}. \tag{5}$$

χ_P arises from the polarization of the ions themselves and is temperature independent. χ_{CW} is the contribution from the movement of the ions from their equilibrium position and is temperature dependent [13, 14]. From figure 3, χ_{CW} follows the Curie–Weiss law from $\sim$ 300 K down to 112 K with $T_0 = 49 \pm 0.7$ K. Below 112 K, χ_{CW} departs from the law. For comparison, previous work showed that the electrical susceptibility of a similar sample of $SrTiO_3$ followed the law from 300 K to 105 K with $T_0 = 40 \pm 0.6$ K [15]. Below 105 K it appreciably departed from the Curie–Weiss law. A further study noted a cubic-tetragonal phase transition in $SrTiO_3$ at 105.5 K [16].

3. Phase transition in a modified barium titanate ceramic

3.1. Modification of properties of barium titanate

Using the method described here, the phase transition or Curie temperature, T_C, of a ferroelectric ceramic, modified barium titanate ($BaTiO_3$), can be directly determined. This polycrystalline form of $BaTiO_3$ is widely used as a dielectric in high-permittivity commercial capacitors. In its pure single-crystal form, $BaTiO_3$ has $T_C \sim 393$ K [17]. Above T_C it is paraelectric and has a cubic structure. Below T_C it is ferroelectric with a tetragonal form. The T_C of $BaTiO_3$ can be easily modified by the substitution of small amounts of ions such as Pb^{2+}, Sr^{2+} or Ca^{2+} for the Ba^{2+} ion [18]. Grain-size effects have been observed to alter T_C [19]. Also the susceptibility of ceramic $BaTiO_3$ is strongly dependent on the grain size, the finer the grain the higher the dielectric constant [20].

3.2. Measurement of electrical susceptibility at moderate temperatures

Figure 4 shows the experimental layout. The sample holder was constructed from two copper plates (50 mm × 27 mm × 5 mm) machined to a depth of 3 mm to accommodate the sample, a T-type thermocouple and a standard 470 pF silvered mica capacitor. The sample was in the form of a 0.1 μF ceramic disk capacitor with a modified $BaTiO_3$ dielectric (RS Components Ltd). The dimensions of the capacitor were obtained by filing a section through a similar capacitor and measuring the plate diameter (14 mm) and dielectric thickness (0.15 mm). A 10 Ω, 25 W aluminium-housed wirewound resistor directly attached to the copper block acted as the heating element and was powered by a variable current supply (0–1 A DC). Capacitance was measured at 1 kHz testing frequency using a LCR meter (AVO Megger B131) with a test fixture [10]. For temperature measurements the thermocouple was connected to a digital thermometer (Digitron T208).

Capacitance measurements were taken from 0–70 °C. Initially the sample was brought to 0 °C by allowing some liquid nitrogen vapour to flow over the copper block and then the heater current was adjusted to give a steady rise in temperature.

To estimate the stray capacitance of the test fixture and leads, the capacitance of a silvered mica capacitor was measured over the temperature range and the known 470 pF subtracted from this to give an average stray capacitance value of 35 pF. This was subtracted from the measured capacitance of the sample to give the corrected value.

3.3. Phase transition temperature

From the dimensions taken from the ceramic capacitor, C_0 was estimated as 10 pF. The susceptibility was calculated using the capacitance value at each temperature and equation (2). Figure 5 is a plot of electrical susceptibility versus temperature for the capacitor. T_C for the modified $BaTiO_3$ was determined as 304 ± 0.3 K from the maximum point on the curve. The curve has the typical features of a high-permittivity ceramic capacitor with a modified $BaTiO_3$ dielectric [21] and clearly shows the ferroelectric-to-paraelectric transition point. It is easy to understand the very high susceptibility values attained at this transition point. The ions

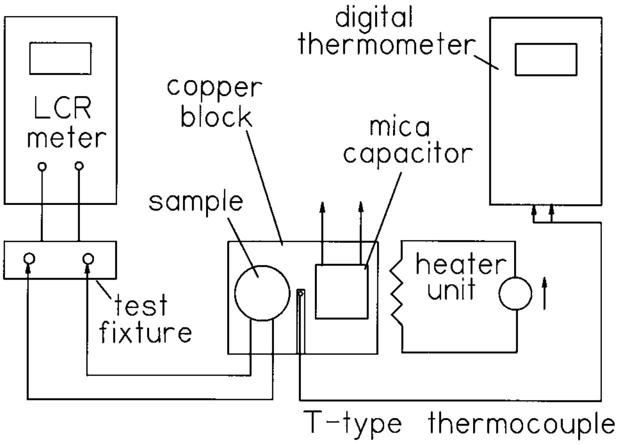

Figure 4. Measurement configuration for determination of the susceptibility of a modified $BaTiO_3$ dielectric at moderate temperatures.

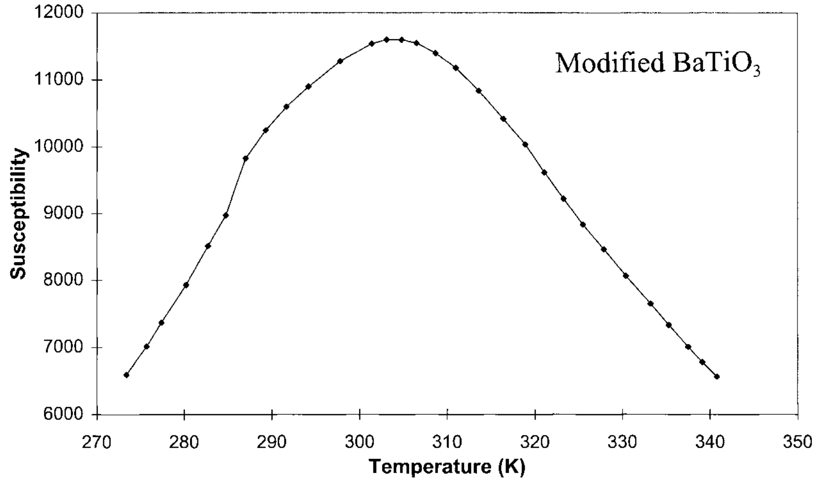

Figure 5. Change in susceptibility versus temperature for a modified $BaTiO_3$ ceramic capacitor.

are on the point of moving into or out of the position corresponding to spontaneous polarization so an applied electrical field is able to produce large shifts in their movement. This motion of the ions produces big changes in the electric dipole moment resulting in a high susceptibility. Below T_C an increasing degree of spontaneous saturation of polarization of the ferroelectric corresponds to a falling susceptibility. Above T_C thermal agitation destroys the ordering of the dipoles, consequently the susceptibility falls.

So in ferroelectric materials, T_C of the ceramic form is different from that of the single crystal and is dependent on parameters like doping and grain size.

4. Conclusions

These experiments have proven to be popular with students. The $SrTiO_3$ experiment is an excellent introduction to the techniques of cryogenics and vacuum systems. Also, students are invited to investigate the electrical properties of ferroelectrics, a class of substances with wide applications in the electronics industry. They can relate their electrical properties to the Curie–Weiss law and directly observe how they change with a structural phase change.

Acknowledgments

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