FERROELECTRICITY

References: Kittel, Introduction to Solid State Physics, Chapter 13

Omar, Elementary SSP, Chapter 8

E. Fatuzzo and W.J. Merz, Ferroelectricity (North-Holland, 1967)

F. Jona and G. Shirane, Ferroelectric Crystals (Pergamon, 1962)

Most insulators have a dielectric susceptibility which is not sensitive to variations in temperature. Although this is true for most substances, there is a class of materials which exhibits a marked departure from this rule: the ferroelectric materials. In these substances, the static dielectric electric constant changes with temperature according to the relation

$$\epsilon = B + \frac{C}{T - T_c}, \qquad T > T_c, \tag{1}$$

where B and C are constants independent of temperature. This relation is known as the Curie-Weiss law, and the parameters C and T_c are called the Curie constant and Curie temperature, respectively.

This behavior is valid in the temperature range $T > T_c$. In the range $T < T_c$, the material becomes spontaneously polarized, i.e., an electric polarization develops in it without the help of an external field. (This phenomenon is analogous to the spontaneous magnetization which takes place in ferromagnetic materials.)

A phase transition occurs at the temperature T_c. Above the transition temperature, the substance is in the paraelectric phase, in which the elementary dipoles of the various unit cells in the crystal are oriented randomly. The dielectric constant is given by (1), whose form is illustrated in Fig. 1.

Below the transition temperature, the elementary dipoles interact with each other, and this gives rise to an internal field, which lines up the dipoles. The direction of this field and the associated polarization lie in a certain favorable orientation in the crystal. Figure 1(b) shows the variation of the spontaneous polarization P_s with temperature for $T < T_c$. This polarization increases gradually as the temperature is lowered.

The second term in (1) is usually much larger than the first. Thus, although typically $B \simeq 5$, $\epsilon \simeq 1000$ or even larger near the transition temperature. We may therefore ignore
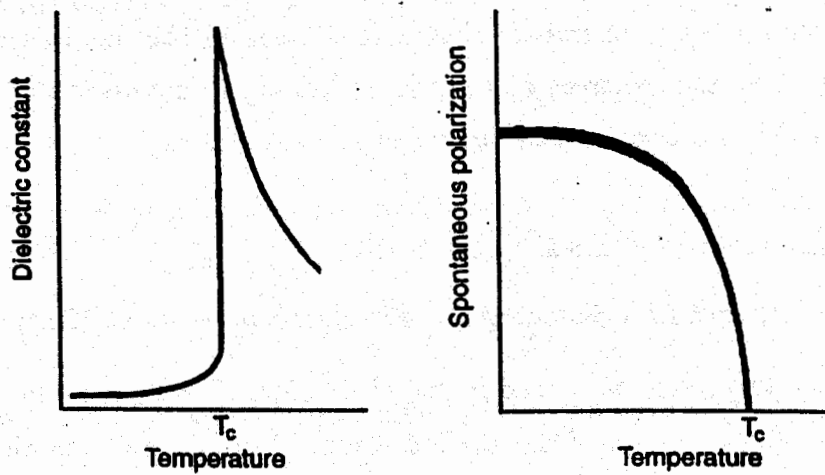
2-F-1

Fig. 1. (a) Dielectric constant versus T. (b) Spontaneous polarization versus T.

B, and write to a good approximation

$$\epsilon \approx \frac{C}{T - T_c} \cdot \qquad (2)$$

In the ferroelectric state the center of positive charge of the crystal does not coincide with the center of negative charge. A typical plot of polarization versus electric field for the ferroelectric state is shown in Fig. 2. The loop is called a hysteresis loop; it is a sign of a ferroelectric state. A crystal in a normal dielectric state usually does not show perceptible hysteresis when the electric field is increased and reversed slowly. In some crystals the ferroelectric dipole moment may not be changed by an electric field of the maximum intensity which it is possible to apply without causing electrical breakdown of the crystal. In these
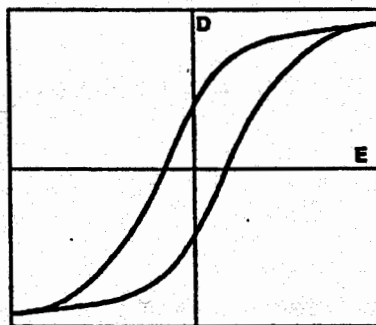

Fig. 2. Ferroelectric hysteresis loop.

2-F-2

crystals we are often able to observe a change in the spontaneous moment when they are heated: changing the temperature changes the value of the dipole moment. Such crystals are called pyroelectric, whereas crystals such that the direction of the spontaneous moment can be altered by an electric field are called ferroelectric.

Mean Field Theory of the Phase Transition

A good reference for this material is Kittel, second edition (1953), Chap. 8.

There are two concepts needed in this discussion. The first is that of local electric field, E_{loc}. This field is the sum of the applied electric field, E, and the electric field due to the polarization charges on the boundaries of the medium. The latter is proportional to the polarization vector of the medium, P, so that E_{loc} is given by,

$$E_{loc} = E + E_{polariz} = E + fP \qquad (3)$$

where f is a constant of proportionality.

Recall that P is defined by the equation,

$$D = E + 4\pi P \qquad (4)$$

which in turn relates the dielectric constant, $\epsilon = D/E$, and the electric susceptibility, $\chi = P/E$:

$$\epsilon = 1 + 4\pi\chi \qquad (5)$$

The local electric field is a function of the polarization and can therefore be expanded in a power series:

$$E_{loc} = g_1 P + g_2 P^3 + g_3 P^5 + ... \qquad (6)$$

Only odd powers are present because even powers would not have the same symmetry as E_{loc} does on reversing the applied electric field. The g coefficients are functions of the temperature, in general.

2-F-3

Put (3) and (6) together to obtain,

$$E = (g_1 - f)P + g_2 P^3 + g_3 P^5 + \dots \qquad (7)$$

Above the Curie temperature, P is very small so P^3 and P^5 can be neglected. As a result,

$$E \approx (g_1 - f)P, \qquad \chi = \frac{P}{E} = \frac{1}{g_1 - f} \qquad (8)$$

One now *assumes* that, for the material in question, g_1 is proportional to the temperature:

$$g_1 = \frac{T}{4\pi C} \qquad (9)$$

Here $1/(4\pi C)$ is the assumed constant of proportionality. (The quantity, 4π, is introduced for convenience.) Next, the constant, f, is rewritten in terms of this number C by introducing a constant T_c, which has the dimensions of temperature. Thus, f is taken to be,

$$f = \frac{T_c}{4\pi C} \qquad (10)$$

Substituting (9) and (10) into (8) gives,

$$\chi = \frac{4\pi C}{T - T_c} \qquad \epsilon = 1 + \frac{C}{T - T_c} \qquad (11)$$

which is the Curie-Weiss law provided T_c is positive. Equation (11) holds only for $T \geq T_c$.

If the temperature is below the Curie temperature, then a spontaneous polarization, P_s, appears in the sample in the absence of an applied electric field. Using equation (7), one obtains,

$$(g_1 - f)P_s + g_2 P_s^3 + g_3 P_s^5 + \dots = 0 \qquad (12)$$

Near the transition temperature $g_3 P_s^5$ and higher terms can usually be neglected, so that

$$P_s^2 = \frac{f - g_1}{g_2} = \frac{T_c - T}{4\pi g_2 C} \qquad (13)$$

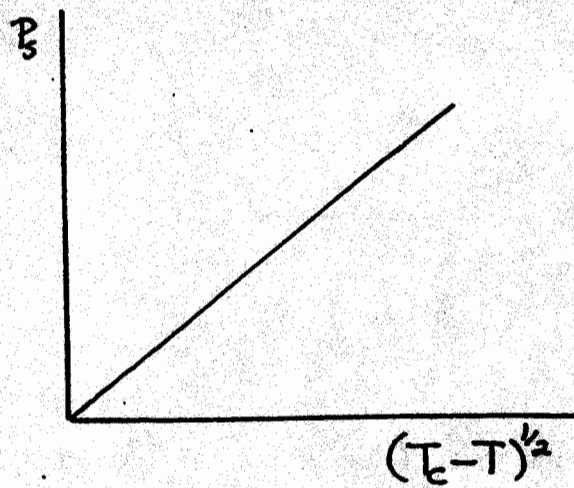That is, P_s is predicted to be proportional to $(T_c - T)^{1/2}$.

2-F-4

Fig. 3. Predicted dependence of P_s versus $T_c - T$ for T close to T_c.

Now if an external electric field, ΔE, is applied, the polarization will change by an amount, ΔP. Use equation (7) again:

$$\Delta E = (g_1 - f)(P_s + \Delta P) + g_2(P_s + \Delta P)^3 + ... \tag{14}$$

Dropping terms in ΔP^2 and using (12), one obtains,

$$\Delta E = (g_1 - f)\Delta P + 3g_2 P_s^2 \Delta P + ... \tag{15}$$

Now use (13):

$$\Delta E = 2(f - g_1)\Delta P \tag{16}$$

The susceptibility is defined for this situation by the equation,

$$\chi = \frac{\Delta P}{\Delta E} \tag{17}$$

that is, the full polarization, P, is not used, only the increment, ΔP. The reason is that one wants the suseptibility to measure the effect of the applied field, ΔE, on the sample. To that end, the spontaneous polarization, P_s, is removed from the definition.
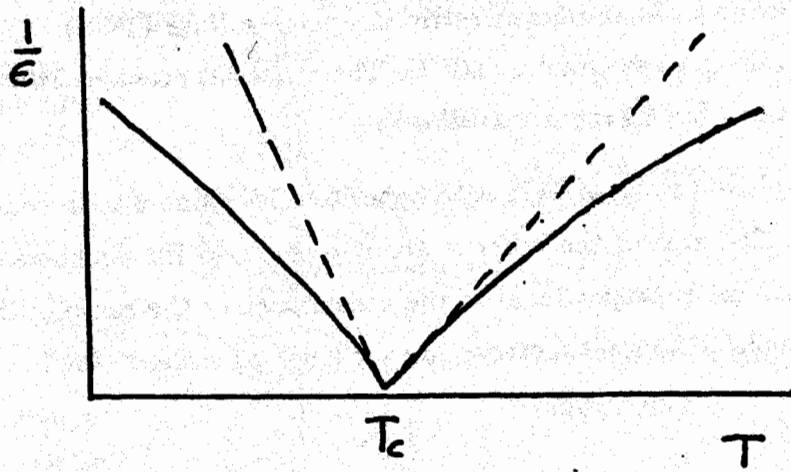
2-F-5

50

Fig. 4. Plot of inverse dielectric constant versus temperature.

Using (16) and (17), one obtains,

$$\chi = \frac{1}{2(f - g_1)} = \frac{2\pi C}{T_c - T} \qquad \epsilon = 1 + \frac{C}{2(T_c - T)} \tag{18}$$

for $T < T_c$.

Expanding equations (11) and (18) about $T = T_c$, one obtains,

$$\frac{1}{\epsilon} = \frac{1}{C}(T - T_c), \qquad T > T_c \tag{19}$$

$$\frac{1}{\epsilon} = \frac{2}{C}(T_c - T), \qquad T < T_c \tag{20}$$

These equations show that close to T_c, $\frac{1}{\epsilon}$ should be two straight lines, one on each side of T_c, and the slopes of these lines should differ by a factor of two, as shown in Fig. 4. Note that these equations emphasize the need for taking careful data near T_c.

Measurement of T_c

2-F-6

In this experiment one measures temperature dependence of the dielectric constant $\epsilon(T)$ above and below T_c in the ferroelectric triglycine sulfate (TGS). T_c for this second-order phase transition is approximately 50° C. This material provides an excellent example of a phase transition obeying mean-field theories.

The sample is a wafer of TGS with opposite sides painted with conducting paint to form a cacapitor. The area of the wafer is about 1 cm^2 and its thickness is about 1 mm. The dielectric constant is proportional to the capacitance of the sample; this is measured using a Simpson model 2795 multimeter set on the 0.001 μf scale.
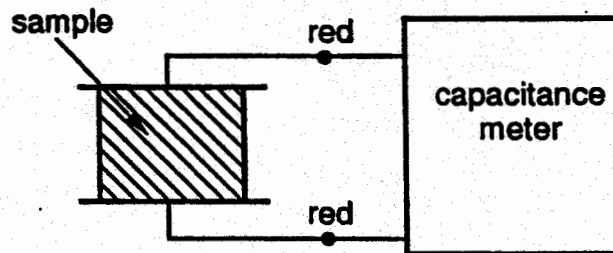

Fig. 5. Measuring the sample capacitance.

The temperature of the sample is monitored by means of a thermocouple (copper-constantan) glued to the TGS. the thermocouple is connected to a regulator, which has two displays. The upper display is the temperature, obtained from the thermocouple. The lower display is the set temperature, which can be adjusted with the up and down arrows. The regulator works to make the two temperatures the same.

DO NOT EXCEED TEMPERATURES OF 100° C, or sample and can will self-destruct!!

Cooling of the sample is done by filling the dewar with ice water up to the level indicated by a mark inside the dewar. A copper rod conducts heat from the sample to the ice water. With ice water cooling and the heater, temperatures from about 10 °C to 90 °C can be obtained. Note: if too much liquid nitrogen is placed in the dewar, the wiring will get wet and the capacitance values will be in error.
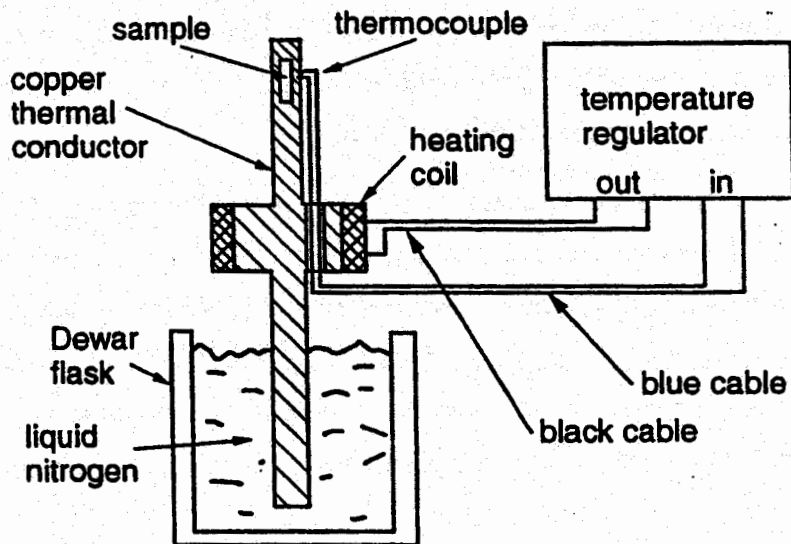
2-F-7

Fig. 6. Measuring the sample capacitance.

Measure the capacitance of the sample at temperatures above and below T_c. Make plots both of the capacitance versus temperature and the reciprocal of the capacitance versus temperature. Find T_c and determine whether the slopes of the reciprocal capacitance plot differ by a factor of two, as required by equations (19) and (20).

Measurement of the temperature dependence of P_s

To measure temperature dependence of the spontaneous polarization P_s, the charge on the conducting electrodes on the surface of the sample is monitored with an electrometer.

There are in fact two kinds of charges present. The first are free charges on the electrodes bonded to the sides of the sample. The second are charges on the faces of sample due to the presence of polarization in the sample. For these latter charges to be observed, the sample must be in a single-domain state, i.e., all the polarization must point the same direction in the crystal.

This is achieved by heating the sample above T_c, say to 55 °C, (but not above 60°C), then applying 50 volts DC to the sample capacitor faces with a DC power supply, and finally cooling slowly down to 10° C.

When the sample is cold, the 50 volt polarizing voltage is removed. and the two leads coming from the sample are shorted together. (That means, a single wire with banana plugs

2-F-8

53

on both ends is used; one end is plugged into one of the red connectors, the other end into the other connector.) Now the sample capacitor has a free charge on its conducting faces that exactly equals the polarization charge, so that the total charge on the sample and the total voltage across the sample are both zero.

Now one measures the changes in the charge with the electrometer as the sample is heated to T_c. To accomplish this, connect one side of the sample to the ground terminal of the electrometer and use the other to read out changes in the sample's charge on the electrometer. <u>DO NOT APPLY 50 VOLTS TO THE ELECTROMETER INPUT!!</u> Before you change the temperature, zero the meter reading by pushing the "zero" button on the electrometer. Now heat up the sample slowly and read the change in charge across the sample on the
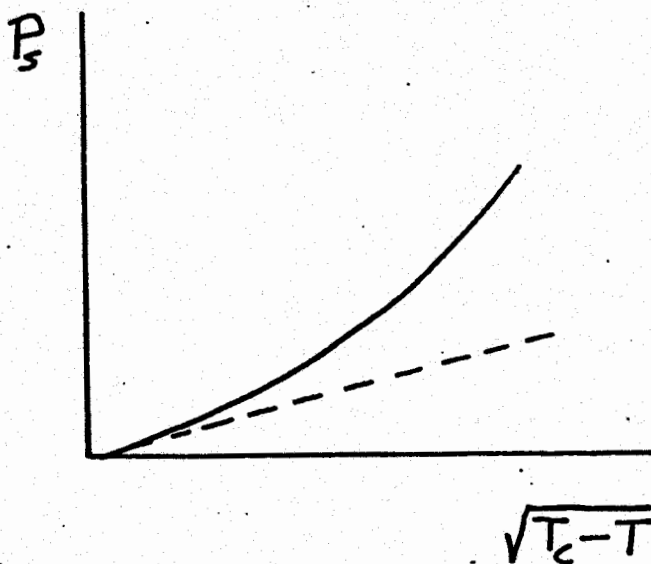
Fig. 7. P_s vs $\sqrt{T_c - T}$.

The charge should increase as the temperature is raised, up to the temperature T_c, after which it should stay constant. However, the polarization, P_s, is expected to be zero at T_c. Your observation of the charge present at temperature T_c then gives the initial free charge on the conducting electrodes. You should subtract the charge you measured at each temperature T from this value to obtain the charge due to the polarization, P_s. This charge will in fact be proportional to the polarization, so your result should look like Fig. 6.

2-F-9

54

Compare your data for this polarization charge to the prediction (13). You may find it useful to plot the logarithm of the charge due to the polarization, P_s, against $\log (T_c - T)$ and see that it approaches a straight line with slope 1/2 as $T \to T_c$. Alternatively, you could plot the charge due to P_s against $(T_c - T)^{1/2}$ and see if it approaches a straight line.

Hysteresis Loops

Hysteresis loops of P_s vs. E can be observed on the oscilloscope by means of a modified Sawyer-Tower circuit, shown below:
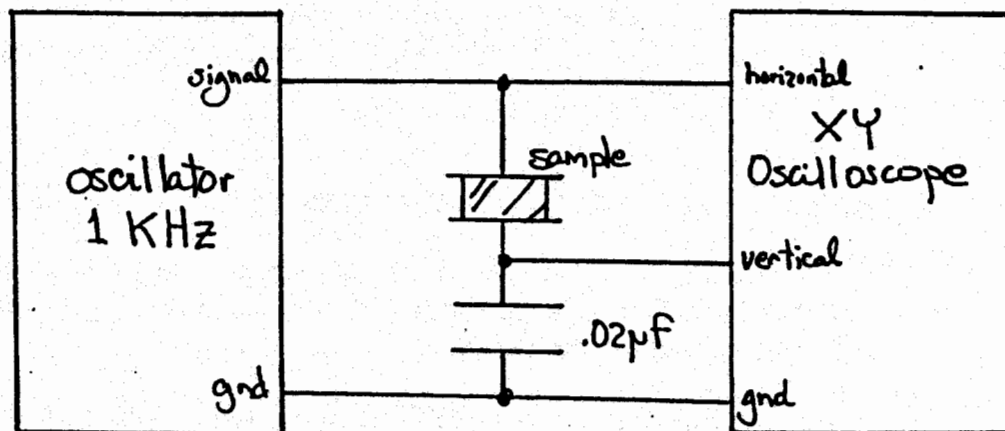

Fig. 8. Modified Sawyer-Tower Circuit.

The voltage across the ferroelectric crystal C_x is applied to the horizontal plates of the oscilloscope. The capacitor C_o is in series with C_x. The voltage across C_o is proportional to the polarization of C_x and is applied to the vertical plates.

Observe the hysteresis loops at a frequency of 1 kHz at a temperature of 43 °C .Include a sketch of the observed hysteresis loops with your report.

2-F-10