III.9. THE HYSTERESIS CYCLE OF FERROELECTRIC SUBSTANCES

1. Work purpose

The analysis of the behaviour of a ferroelectric substance placed in an external electric field; the dependence of the electrical polarisation upon the external field, \( P = P(E) \).

2. Theory

Ferroelectric substances are insulators that have a spontaneous polarisation and a domain structure. In each domain of such a substance, the molecular dipoles have the same orientation, but this orientation is different for different domains and can be influenced by an external electrical field.

For ferroelectric substances, spontaneous polarisation occurs only for a certain temperature range. In most of the cases, ferroelectric crystals may experience changes of their structure, thus loosing their spontaneous polarisation. The structure change of such crystals, followed by the appearance or disappearance of spontaneous polarisation, is called a phase transition, and the corresponding temperature is called transition temperature or Curie point.

The crystals KH₂PO₄, BaTiO₃, LiTaO₃ and others are ferroelectric if \( T < T_C \) and paraelectric if \( T > T_C \).

In the transition temperature neighbourhood, almost all the properties of the crystal (electrical, optical, mechanical, thermal etc.) abruptly change and present several anomalies.
The domain structure influences several non-linear properties of such substances, among which there is the non-linear dependence of the electrical polarisation on the external field $P = P(E)$.

The image below (Fig. 1) shows the hysteresis curve of a ferroelectric substance, which proves that the influence of an external electrical field causes the rearrangement of domains (pieces). The different rates at which the domains and the electrical field change lead to a phase difference between the electric field intensity and the polarisation, hence the non-linear variations.

![Hysteresis curve of a ferroelectric substance](image)

**Figure 1.**

When an electric field influences the crystal, the domains having a polarisation parallel to the external field increase on the account of those domains having a different polarisation; thus, the polarisation increases and the dependence $P = P(E)$ is shown by the curve a-b-c in Figure 1. When all the domains have become oriented parallel to the external electric field, the polarisation reaches a saturation level $P_s$; we may say that the crystal has became a single domain. The value of the spontaneous polarisation is obtained by the extrapolation of the linear part in the point c. The value of $P_s$ that was obtained is obviously similar to the polarisation that existed in
each domain in the initial state corresponding to the point a. Therefore, when we refer to “spontaneous polarisation”, we mean the polarisation of each separate domain, not the total polarisation of the whole crystal.

When the intensity of the electrical field decreases, so does the polarisation. If the field intensity becomes zero, there will still be a remnant polarisation \( P_r \) in the crystal, represented by the curve c-d. In order to destroy this remnant polarisation, a good part of the crystal must be polarised in the opposite direction by applying an opposite electric field. This electric field, which is needed to counteract the polarisation, is called coercive field; its intensity is quoted \(-E_c\) and its application is represented in Figure 1 by the curve d-e. Afterwards, the polarisation of the substance sample changes its sense according to the orientation of the domains corresponding to the new direction of the electrical field; it will eventually reach its maximum value \(-P_s\), represented by the point f in Figure 1.

The subsequent variation of the electrical field towards positive values will generate a dependence \( P = P(E) \) similar to that already described previously; this dependence is represented by the curve f-g-h-c.

The ferroelectric substance that we will be using in this experiment is a Rochelle salt crystal. The Rochelle salt was proven to have ferroelectric properties in 1921. It is a salt of sodium and potassium resulting from tartric acid. Its chemical formula is \( \text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O} \).

The Rochelle salt has ferroelectric properties only in the temperature range \(-18^\circ\text{C} \text{ – 24 }^\circ\text{C}\). This means that it has 2 transition temperatures: the lower Curie point at \(-18^\circ\text{C}\), and the upper Curie point at \(24^\circ\text{C}\). In the temperature range below \(-18^\circ\text{C}\) and above \(24^\circ\text{C}\), the crystal has an orthorhombic structure. When it becomes ferroelectric, the crystal is monoclinic. The Rochelle salt has only one polar axis and only two
possible polarisation directions, that is, parallel or anti-parallel to the axis. Consequently, the domain structure of the Rochelle salt is very simple.

3. Experimental Set-up

We will analyse the non-linear dependence of the electrical polarisation \( P(E) \) in an electric field that oscillates as:

\[
E = E_0 \sin(2\pi vt),
\]

where \( E_0 \) is the amplitude of the field and \( v \) is its frequency.

The draft of the experimental device is represented in Fig. 2:

![Diagram of the experimental device]

**Figure 2.**

The voltage \( U_g \) adjusted by the self-transformer ST, is applied to the transformer TR, whose function is to galvanically separate the generator from the rest of the device. From its secondary, the generated voltage \( U \) is applied to the circuit. The central piece of this circuit is the differential amplifier DA (supplied by the source SD) which generates a voltage \( U_f \) given by:

\[
U_f = U_2 - U_1.
\]

\( U_1 \) is the voltage obtained at the jacks of the divider \( P_1(R_1), C_V, C_0 \), and can be computed by this formula:

\[
U_1 = \frac{1}{C_0} \int i_1 dt = \frac{1}{C_0} \left( \frac{1}{R_1} \int U dt + C_V U \right),
\]
where $R_1$ is the variable resistance and $C_V$ is an adjustable air capacitor; both elements are considered ideal, without any electric charges. The capacitor $C_0$ is the circuit element that collects the electrical charge of the sample; this capacitor must satisfy the conditions $C_0 >> C_x, C_V$, so that most of the voltage $U$ will be distributed on $C_x$ and $C_V$, respectively. The ferroelectric sample, represented by the parallel system $C_x - R_x$, is placed in the divider $C_x, R_x, C_0$. The obtained voltage ($U_2$) will be:

$$U_2 = \frac{Q_2}{C_0} = \frac{1}{C_0} \int i_2 dt = \frac{1}{C_0} \left( \int \frac{U dt}{R_x} + C_x U + Q_f \right),$$

where $Q_f$ is the sample ferroelectric charge, $R_x$ its resistance and $C_x$ its non-ferroelectric capacitance.

By adjusting $R_1 = R_x$ and $C_V = C_x$, the voltage $U_f$ is obtained at the terminals of the differential amplifier AD; this voltage controls the oscilloscope OSC on the vertical, and is proportional only to the ferroelectric charge of the sample:

$$U_f = U_2 - U_1 = \frac{Q_f}{C_0} = \frac{AP}{C_0},$$

where $A$ is the sample area and $P$ its polarisation.

A signal proportional to the electric field intensity $E$ in the sample is applied to the horizontal plates of the oscilloscope, $E$ being related to $U$ as:

$$E = \frac{U}{d},$$

where $d$ is the thickness of the sample, and $U$ is the voltage measured by the voltmeter V (For a correct fitting onto the screen, the voltage $U$ is applied to the plates through the potentiometer $P_2$).
4. Working Procedure

The following tasks will be executed in this exact order:

1. Adjust the self-transformer ST and the source SD to a voltage equal to 0 V.
2. Plug in the source SD and adjust the voltages of the two channels to 10 V (this value should be marked red on the display).
3. Plug in the self-transformer and the oscilloscope. Turn on the oscilloscope and the source SD.
4. Examine the curves $P = P(E)$ on the screen of the oscilloscope and centre them, if necessary. In order to obtain the largest possible image that still fits the screen, adjust $P_2$ for the appropriate horizontal dimension of the cycle.
5. Adjust $P_1$ and $C_V$, in order to obtain a correct hysteresis curve.

In Figure 3 below we have represented several possible dependencies $P = P(E)$. In order to obtain a correct curve (that has horizontal and pointed saturation sides, as seen in fig. 3.e), you must adjust $P_1$ to correct distortions 3a and 3b, and $C_V$ to correct distortions 3c and 3d.

![Figure 3](image-url)
5. Experimental Data Processing

The adjustments suggested previously must be done for each value of the voltage applied to the sample: 100, 150, 200, 250, and 300 V.

For each voltage, you must read on the screen positions $n_1$, $n_2$, $n_3$, and $n_4$ corresponding to the maximum electric intensity $E$, the coercive electric field intensity $E_c$, the remnant polarisation $P_r$ and the maximum polarisation $P_m$, respectively.

The collected data are written in Table 1:

<table>
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<tr>
<th>$U$ (V)</th>
<th>$n_1$</th>
<th>$n_2$</th>
<th>$n_3$</th>
<th>$n_4$</th>
<th>$E$</th>
<th>$E_c$</th>
<th>$P_r$</th>
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The values of $E$ are computed using the formula (6). Since horizontal displacements are proportional to the electric field, it follows that:

$$E_c = \frac{n_2}{n_1} E = \frac{n_2}{n_1} \cdot \frac{U}{d}.$$  \hspace{1cm} (7)

From equation (6), we obtain:

$$P_m = \frac{U_f \cdot C_0}{S} = K_y C_0 \frac{n_4}{S}, \hspace{1cm} P_r = K_y C_0 \frac{n_3}{S},$$  \hspace{1cm} (8)

where $K_y$ is the vertical sensitivity of the oscilloscope at the terminal X3 (1/1 range).

The values of the parameters that are used in this experiment are $d = 4$ mm, $K_y = 1$ V/div, $C_0 = 10^{-7}$ F, $A = 1$ cm$^2$. 

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Plot the dependencies \( P_r(E), P_m(E) \) and \( E_c(E) \). Observe the tendency towards saturation of these quantities as the intensity of the electrical field increases and estimate their limit values.

When computing a quantity that is not directly measured, one must apply the error propagation method. According to this method, any quantity \( X = f(x,y,z...) \) can be determined by applying the following equations:

\[
X = \overline{X} \pm S_X,
\]

where

\[
\overline{X} = f(\overline{x}, \overline{y}, \overline{z}, ...), \quad \overline{x} = \frac{1}{N} \sum_{i=1}^{N} x_i, \quad ...
\]

and the dispersion or the mean square root deviation is:

\[
s^2_X = \left( \frac{\partial f}{\partial x} \right)_{x=\overline{x}}^2 s^2_x + \left( \frac{\partial f}{\partial y} \right)_{y=\overline{y}}^2 s^2_y + \left( \frac{\partial f}{\partial z} \right)_{z=\overline{z}}^2 s^2_z +..., \tag{11}
\]

with

\[
s^2_x = \frac{\sum_{i=1}^{N} (x_i - \overline{x})^2}{N(N-1)}, \quad ...
\]

For this particular experiment, you must determine the values of the coercive field intensity \( E_c \), the remnant polarisation \( P_r \) and the maximum polarisation \( P_m \) by applying the above method. For the first quantity: \( X = E_c; x_i = n_{1i}; y_i = n_{2i}. \) In order to compute the average values and the mean square root deviations, you must make 10 independent measurements for each voltage value. The final result will have the form \( E_c = \overline{E_c} \pm S_{E_c}. \)

Similarly, you will obtain \( P_r = \overline{P_r} \pm S_{P_r}, P_m = \overline{P_m} \pm S_{P_m}. \)