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Study and Analysis of Transitions in Rochelle Salt

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Abstract - *At the Curie temperature, the properties of dielectrics undergo phase transitions. The Landau's theory is used here to investigate these transitions for a dielectric medium placed between the anode and cathode of a capacitor. In particular, we investigate the variation with temperature of the induced electric current.*

Keywords: *Dielectric, Electric Induction, the Landau's theory of phase transition, nonlinear capacitor*

Nomenclature

P	the polarization of the dielectric.
T	the temperature.
T_c	temperature of Curie
E_s	the electric field.
g_n	coefficients depending on temperature.
A_0 and B	are two constants which depend on the dielectric medium.
ε	the dielectric constant.
ε_0	the permittivity of the vacuum.
ε_r	the relative permittivity of the dielectric.
e	the thickness of the capacitor.
S	the surface of the electrodes of the capacitor.
R	the resistance (Ohms).
L	the inductance (H)
D_0	the induction at thermal equilibrium

I. Introduction

Seignetto- Electric crystals are ferroelectrics that insist of dielectrics with a strong relative permittivity, i.e. $\varepsilon_r \approx 1000$, and varying with temperature.

In this paper, we interested in Rochelle salts, having the chemical formula is: CO_2K-CHOH-CHOH-CO_2Na, $4H_2O$, discovered in 1672 by Seignette. We consider that the salt is placed between the anode and the cathode of a nonlinear capacitor. The latter is part of various electric circuits to appreciate its behaviour with temperature and see the effects of the induced electric current.

Landau's theory [1] is used to explain the phenomenon of phase transition as well as qualitative changes observed in the properties of the dielectric.

II. Characteristics of the Dielectric Medium

II.1. Variation with Temperature of the Electric Polarization

According to Landau's theory of phase transition [1], the free energy of a ferroelectric material can to developed in terms of polarization in the form:

$$F(P,T,E) = -EP + g_0 + \frac{1}{2}g_2P^2 + \frac{1}{4}g_4P^4 + ... \quad (1)$$

The value of the polarization at thermal equilibrium is obtained by minimizing the free energy with respect to P.

Thus spontaneous polarization in an electric field E is obtained by deriving F (P, T, E) with respect to P, as:

$$\frac{dF}{dP} = 0 \Rightarrow -E + g_2P + g_4P^3 + g_6P^5 + ... = 0 \quad (2)$$

To obtain the ferroelectric state we suppose that the term in P^2 of equation (1) is cancelled at the critical temperature of phase transition T_c [2]; one finds:

$$g_2 = A_0(T - T_C) \quad (3)$$

where A_0 function of T_c only.

The spontaneous polarization is obtained by letting E=0 in equation (2), using (3):

$$A_0(T - T_c)P_s + g_4P_s^3 = 0 \quad (4)$$

The relation of equation (4) is:

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$$P_s = 0$$
$$|P_s| = \sqrt{\frac{A_0}{g_4}(T - T_c)} \qquad (5)$$

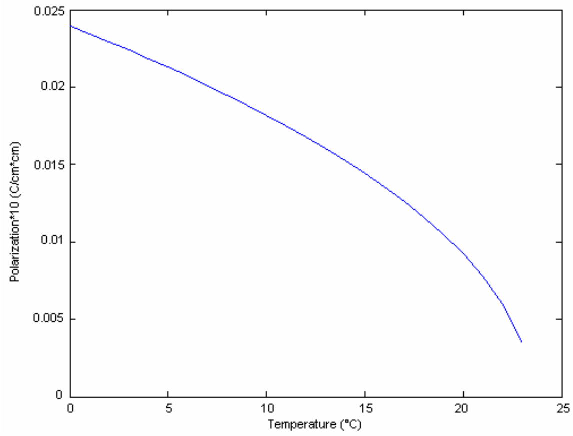

Fig. 1. Spontaneous polarization according to the temperature

We note that Rochelle salt presents a spontaneous polarization even in the absence of the field electric. The polarization tends continuously to zero at T_c=23.5C (temperature of Curie). Therefore, the phase transition of this dielectric is of the second order.

II.2. Variation of the Dielectric Permittivity with Temperature

The Rochelle salt has a critical temperature where its microscopic properties change.

The behaviour of the permittivity [3], a higher temperature than T_c is given by:

$$\varepsilon = \frac{C}{(T - T_c)} \qquad (6)$$

where C is the Curie's constant.

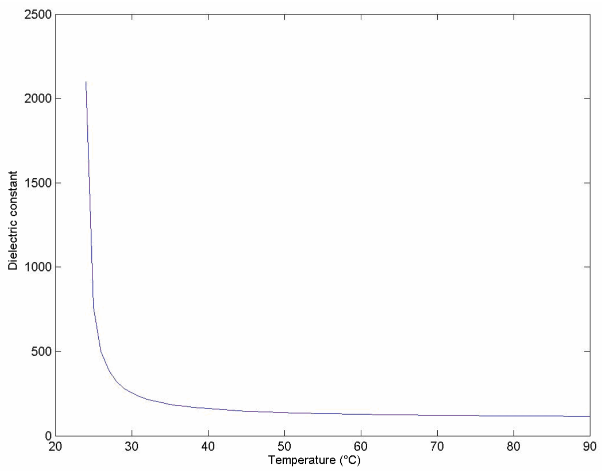

Fig. 2. Variation of the dielectric constant with temperature

This means that the dielectric is paraelecric.

Fig. 2, illustrates the variation of the ε with temperature.

We can also plot the dielectric constant variation with both temperature and time.

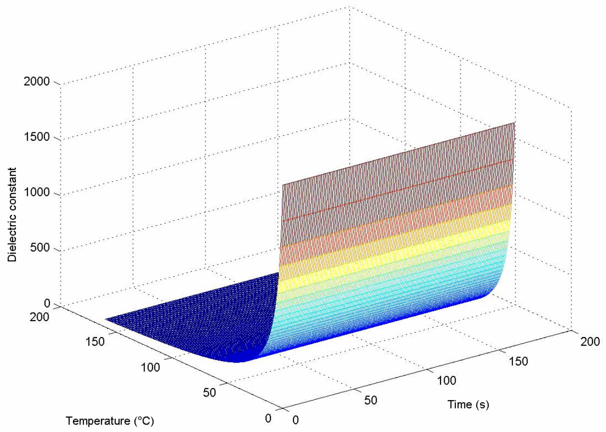

Fig. 3. Variation of the dielectric constant with temperature and time

ε goes to infinity at the temperature of phase transition (T_c=23.5), and falls quickly as T exceeds the critical temperature.

III. Basic Hypothesis of the Study of the Phased Transition in the Dielectric

We place this dielectric between the anode and the cathode of capacitor, so their capacity C becomes to $C = \frac{\varepsilon S}{e}$ where $\varepsilon = \varepsilon_0 \varepsilon_r$ is the dielectric constant.

The fact that the capacity varies means that ε is not constant, and depends on the applied electric field E.

The induction $\vec{D}$ is related to the electric field $\vec{E}$ by:

$$D = \varepsilon_0 E + P = \varepsilon E \qquad (7)$$

The electric charge of the capacitor [1] is:

$$Q = DS \qquad (8)$$

Introduction of this capacitor into a circuit produces a nonlinearity. Therefore, it is proves to be necessary to find a relation between induction and the electric field. For this, two models should be combined; the Landau's model for the free energy in terms of the induced electric current [1] and the gives thermodynamics model of dielectrics which gives the electric field.

The free energy of dielectric can be developed as a function of the induction:

$$G = \frac{A}{2}D^2 + \frac{B}{4}D^4 \qquad (9)$$

with:

$$B>0$$
$$A=A_0(T-T_c)$$
$$A_0>0$$

In thermodynamics [3], the field electric in dielectric is written:

$$dG = EdD \tag{10}$$

Then:

$$E = \frac{dG}{dD} \tag{11}$$

By injecting equation (9) into equation (11), we obtain:

$$E = \frac{dG}{dD} = AD + BD^3 \tag{12}$$

This equation (12) gives the electric field in term of induction D.

IV. Mathematical Model

We place the dielectric between the anode and cathode of a capacitor as shown in the following circuits.

IV.1. Electrical Circuit RC

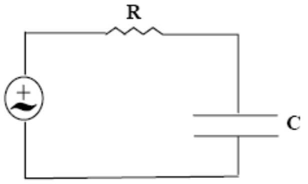

Fig.4. RC circuit

An electrical circuit RC subject to an alternating voltage of pulsation ω and amplitude U obeys to the following equation:

$$RI + \frac{Q}{C} = Ue^{(i\omega t)} \tag{13}$$

$$I = \frac{dQ}{dt} = \dot{Q} \tag{14}$$

Equation (13) takes the form:

$$\dot{D} + \frac{eA}{RS}D + \frac{eB}{RS}D^3 = \frac{U}{RS}e^{(i\omega t)} \tag{15}$$

In the absence of the voltage generator U=0 and we has:

$$\dot{D} + \frac{eA}{RS}D + \frac{eB}{RS}D^3 = 0 \tag{16}$$

This equation (16) has the form of a Bernoulli's equation. Its resolution is made by using the method of the variation of the constant [4].

The solution of the equation (16) gives variation of the induction with temperature respect to time:

$$D(t) = \frac{1}{\sqrt{\frac{b\,exp(-2at)}{a}}}$$

where:

$$b = \frac{eB}{RS},\ a = \frac{eA_0(T-T_c)}{RS}$$

Fig. 5 gives a tridimensional plot of D versus t and T for $T < T_c$.

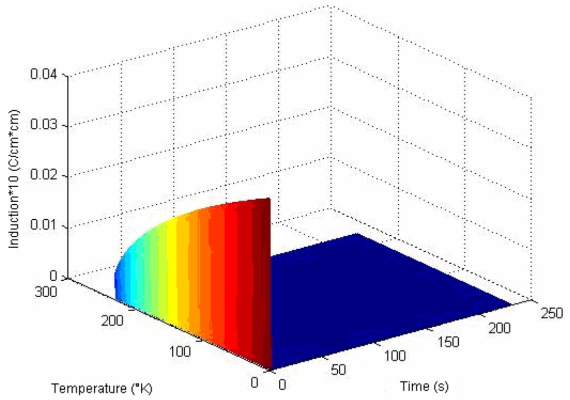

Fig. 5. A tridimensional plot of D versus t and T for $T<T_c$

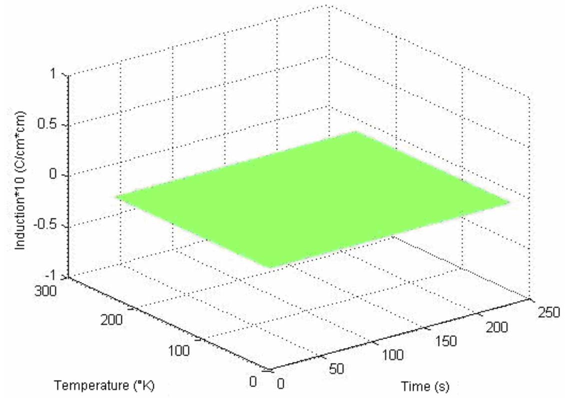

Fig. 6. A tridimensional plot of D versus t and T for $T>T_c$

Figs. 5 and 6, illustrate the phenomenon of phase transition dielectric medium as well as changes of its microscopic properties.

For $T < T_c$, thermal agitation is weak, giving a spontaneous polarisation. But for $T > T_c$, the thermal agitation is strong and the polarization is zero therefore no induced electric takes place because the barycentre of the positive and negative charges of the elementary mesh are distinct [5].

IV.2. To connected RLC Circuit

This circuit is plotted in the Fig. 7.

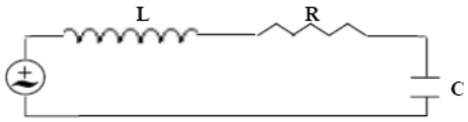

Fig.7. RLC circuit

The equation of state defining this system is:

$$RI + \frac{Q}{C} + L\dot{I} = Ue^{(iwt)} \tag{17}$$

Replacing equations (8) and (14) to (17), we obtain:

$$\ddot{D} + \frac{R}{L}\dot{D} + \frac{eA}{LS}D + \frac{eB}{LS}D^3 = \frac{U}{LS}e^{(i\omega t)} \tag{18}$$

IV.2.1. The case of Small Disturbances

If a sufficiently weak voltage is applied, we can calculate the eigenfrequency of the circuit [1], obtaining:

$$\omega_0^2 = \frac{e}{LS}\frac{d^2G}{dD^2} = \frac{e}{LS}\frac{dE}{dD} = \frac{e}{LS}\left(A + 3BD_0^2\right)$$

where D_0 is the induction at equilibrium, from where:

- for $T<T_c$:

$$D_0 = 0,\ \omega_0^2 = \frac{eA}{LS}$$

- for $T>T_c$:

$$D_0 = \pm\sqrt{-\frac{A}{B}} \text{ and } \omega_0^2 = -2\frac{eA}{LS}$$

If we let $D = D_0 + de^{(i\omega t)}$ where D_0 is the induction at thermal equilibrium, and D will be regarded as small so that the linear approximation remains valid [1].

For $T < T_c$, below the phase transition:

$$D = \frac{U}{\sqrt{\left(\omega^2 LS + 2Ae\right)^2 + \left(\omega RS\right)^2}} \tag{19}$$

and for $T > T_c$, the induction becomes:

$$D = \frac{U}{\sqrt{\left(\omega^2 LS - Ae\right)^2 + \left(\omega RS\right)^2}} \tag{20}$$

The variation of induction with temperature is illustrated in the Figs. 8 and 9.

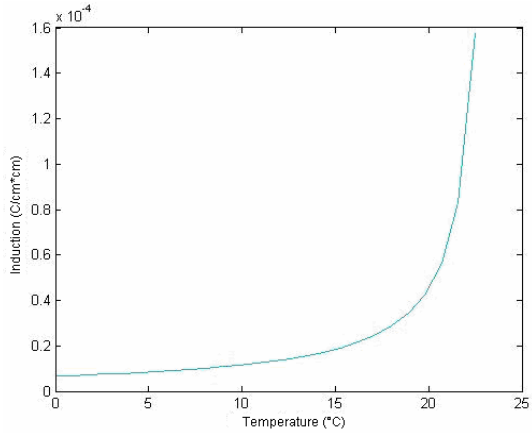

Fig. 8. The induction for $T<T_c$

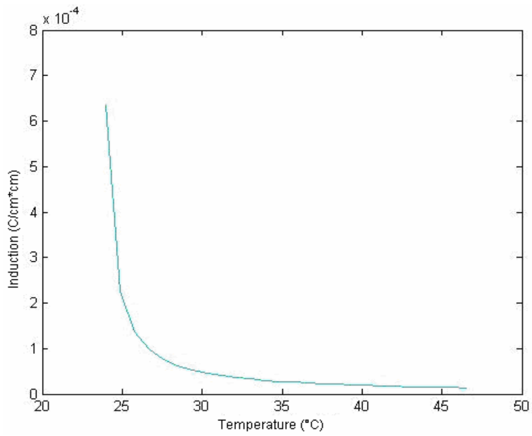

Fig. 9. The induction for $T>T_c$

We can also represent $D(t)$ with time.

We use the fact that the phase transition is given at T=23.5 [6].

The induction is maximum thermal equilibrium because all dipole moments are directed towards the electric field.

IV.2.2. The Case of the Strong Fluctuations

A digital simulation of equation (14) is possible, by using the O.D.E45, a program which belongs to the library of Matlab 7.0, in order to solve our problem. We can plot the induction *D* with temperature and time.

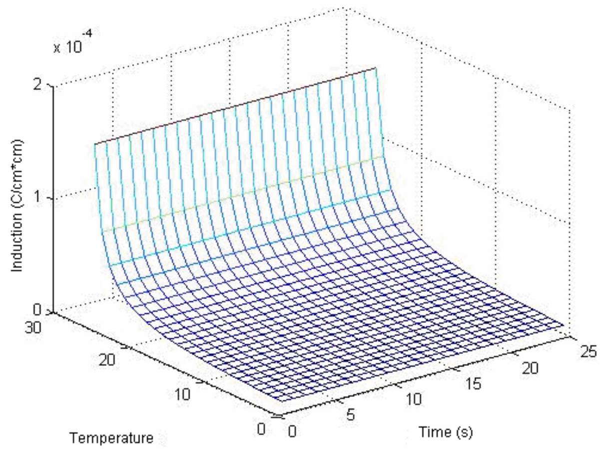

Fig. 10. Induction for $T<T_c$

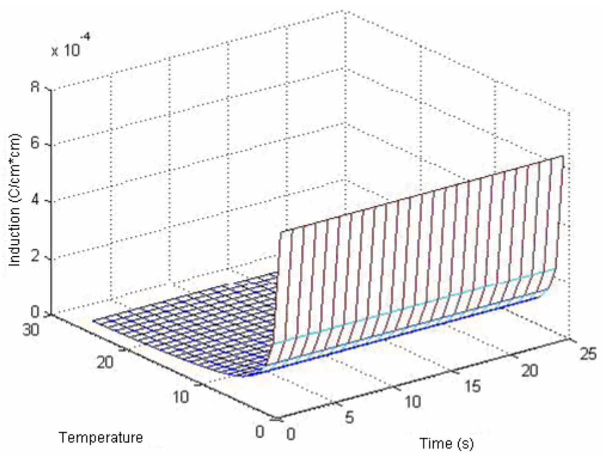

Fig. 11. Induction for $T>T_c$

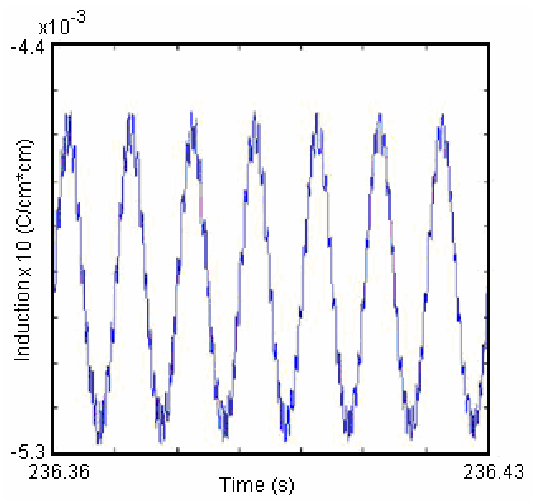

Fig. 12. Induction for $T<T_c$

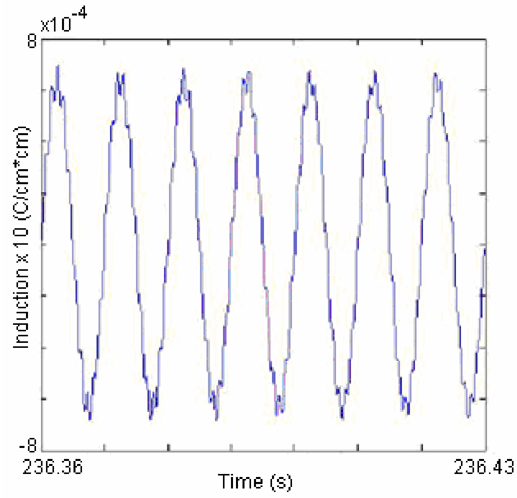

Fig. 13. Induction for $T>T_c$

According to the above figures, the induction changes at the critical temperature. When $T < T_{c,}$ it oscillates around a non zeros value, above the temperature of phase transition, the induction will oscillate around a zero value. We conclude that the dipole moment will change the physical state of the dielectric).

V. Conclusion

The crystalline structure of Rochelle Salt changes at T_c. For a temperature lower than the temperature of Curie, it has a monoclinic structure. It has a dissymmetry which yields permanent dipole moment. Since like these dipole moments are directed in the same way, a spontaneous polarization i.e. induction

Although this induction is not zero, but when the temperature exceeds the temperature of phase transition the structure becomes orthorhombic, It is symmetrical and its spontaneous polarization disappears. In this case the induction oscillates around a zero value. For a temperature above the critical temperature, the induction electric tends towards zero and as the charge of the capacitor is connected to this induction, in a linear way, this will cause a discharge in our capacitor. It was a problem for electronicians (manufacturers of the no volatiles memory FRAM).

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