

Two notes on ferroelectricity

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Abstract

The hysteresis curves are derived from energy conservation of the coupled polarization (magnetization) and the external field, over a limited range of variation of the latter. The two structural anomalies in the polarization of $BaTiO_3$ are discussed.

1. Hysteresis

Although hysteresis in ferromagnets and ferroelectrics has been associated since long with the existence of domains, and in spite of the existence of two current models of hysteresis,[1, 2] its physical origin has not been revealed yet. The essence of the phenomenon consists in the existence of two branches of the function $P(E)$, where P is the polarization and E is the electric field (or $M(H)$, where M is the magnetization and H is the external field), over a limited range of variation of E (H), whose origin is not elucidated. We present here a model which accounts for this basic feature. Although the discussion is made here for ferroelectrics, the results apply also to ferromagnets, as expected.

The ferroelectric materials consist of interacting molecular dipoles. In the presence of an external electric field E the materials containing dipoles become polarized, *i.e.* they acquire a polarization P which, usually, is proportional to the electric field E , such that we may write $P = \chi E$, where χ is the electric susceptibility (we consider isotropic materials). At high temperature, the susceptibility is proportional to $1/T$, where T is the temperature (this is the Curie-Langevin-Debye law[3]-[6]). The ferroelectric materials exhibit a critical temperature T_c (Curie temperature), where the susceptibility increases abruptly, with a characteristic λ -shaped pattern (the λ -point, Fig. 1); for low temperature the polarization goes to a saturated, constant value, independent of E (at high temperature the susceptibility goes like $1/(T - T_c)$ in this case; just below the T_c the susceptibility has an exponential drop). This is a typical phase transition of the second kind.[7] In the absence of the electric field the polarization is zero above T_c and goes to the saturation value for zero temperature; just below the critical temperature it goes like $(T_c - T)^{1/2}$ (Fig. 2). We say that on passing through T_c from the above, the ferroelectric material suffers a transition to the polarized state. The polarization of the polarized state may have an arbitrary orientation (for isotropic materials), but it is directed along the external electric field, when such a field is applied.

In the polarized state there exists a depolarizing electric field generated by the surface of the body; indeed, we note that the dipole field is oriented in the opposite direction with respect to the direction of the external field. In order to minimize the energy, it is convenient to break the polarized phase in small domains, oriented, in general, randomly. When an external electric field

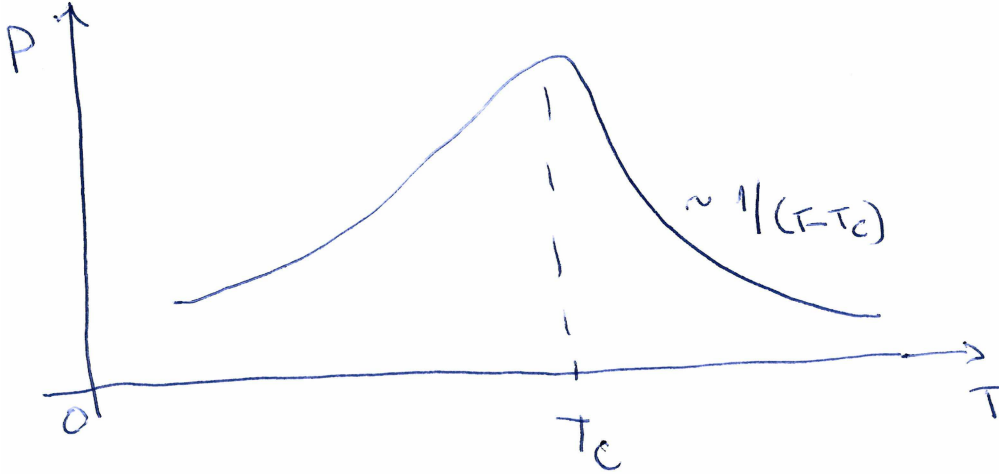


Figure 1: A sketch of the λ -point ($E \neq 0$).

is applied, the domains move (rotate), orient themselves partially along the field, and change, in general, their dimension.[8, 9]

It is worth emphasizing that there exist three distinct notions related to the polarized state. First, there exists the polarization, which is the dipole density; it has the dimension of a field oriented along the external field. Then, there exists the depolarizing field, which is oriented in the opposite direction to the external field. Third, there exists the dipolar interaction, which favours the alignment of the dipoles; this is called internal field. All these quantities are inter-related.

Two basic observations are in order. First, we note that, in the polarized state, there exist two variables, E and P , which are independent; second, we note that the motion of the domains may allow an "interaction", a relationship, between these two variables. Consequently, we write the change in the (free) energy of the polarized state as

$$\delta\mathcal{E} = \frac{1}{2}A\delta E^2 + B\delta E\delta P + \frac{1}{2}C\delta P^2 = \frac{1}{2}C\left(\delta P + \frac{B}{C}\delta E\right)^2 + \frac{1}{2}\left(A - \frac{B^2}{C}\right)\delta E^2, \quad (1)$$

up to the second-order in powers of δE and δP , with some coefficients A , B , C ; the first-order terms in equation (1) are absent since we assume a change of energy at thermal equilibrium; the applied electric field E and the polarization P it determines in the polarized state (with domains) are equivalent with small variations δE and δP , such that we may replace δE and δP in equation (1) by E and P (for small values of these quantities).

In order to have a minimum for the energy we assume $C > 0$ and $AC > B^2$ in equation (1); then, we note that $P + (B/C)E$ and E are two independent electric fields, so that there is no reason to have distinct coefficients in the energy for their contribution; therefore we assume $C = A - B^2/C$, or $B^2 + C^2 = AC$ (and $A > 0$); equation (1) becomes

$$\delta\mathcal{E} = \frac{1}{2}C\left(P + \frac{B}{C}E\right)^2 + \frac{1}{2}CE^2. \quad (2)$$

Next, we note that $P + (B/C)E$ is an effective field E_e ; it should be related to the depolarizing field; since the latter and E have opposite orientations, it is convenient to change B into $-B$; if we introduce the notation $B/C = \lambda$ (with the new B), the effective field can be written as $E_e = P - \lambda E$; we note that it is similar with the Weiss field $E_w = E + \lambda P$ (different λ); the latter corresponds to the cooperative interaction which leads to the polarized phase.

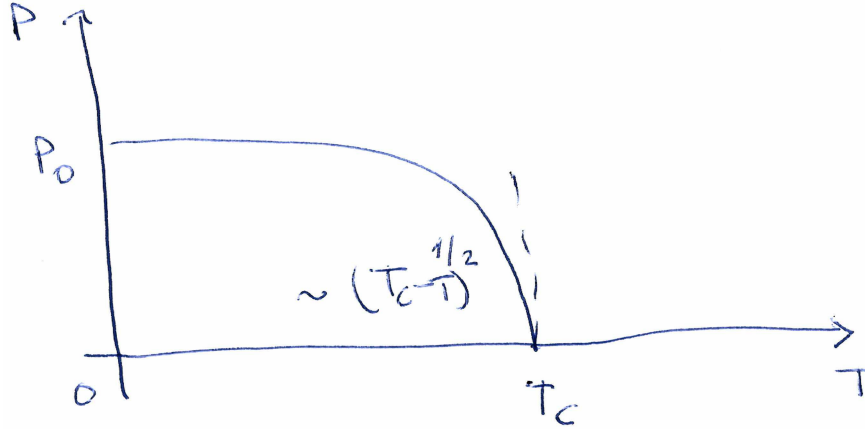


Figure 2: Polarization in the polarized state ($E = 0$).

The energy given by equation (2) should be a constant \mathcal{E}_0 at equilibrium; we denote $2\mathcal{E}_0/C$ by E_c^2 , where E_c is an electric field (coercitive field); equation (2) becomes

$$(P - \lambda E)^2 + E^2 = E_c^2 . \quad (3)$$

This equation shows that there exists a correlation between polarization and the electric field, caused by the motion of the domains, such that their motion may proceed with a constant energy for some limited values of the external field E ; equaton (3) is valid for $E \ll E_c$; for $E \gg E_c$ the energy is not a constant anymore, and we have $P = \lambda E$ (and $E_c = E$). From equation (3) we get

$$P = \lambda E \pm \sqrt{E_c^2 - E^2} , \quad (4)$$

where we can see that the two branches of $P(E)$ appear naturally as a consequence of the energy conservation; the functions $P(E)$ given by equation (4) represent the (electric) hysteresis pattern exhibited by ferroelectrics (or magnetic hysteresis for ferromagnetics) (Fig. 3). The motion of P and E on the hysteresis curve can be parametrized by $E = E_c \sin \varphi$ and $P = \sin(\varphi \pm \theta)$, where $\cot \theta = \lambda$, the sign $+$ corresponding to $-\pi/2 < \varphi < \pi/2$ and the sign $-$ corresponding to $\pi/2 < \varphi < 3\pi/2$. A similar procedure can be used for deriving other forms of hysteresis. Variations of polarization and mechanical strain can be included in an energy variation of the form given by equation (2) for the piezoelectric effect.

If the external field is oscillating in time, $E = E_0 \sin \omega t$, then, for $E_0 \ll E_c$ and fast oscillations, the mean values of the polarization are $\overline{P^2} = E_c^2 - E_0^2$ and $\overline{P} = E_c^2 - (1 + \lambda^2)E_0^2$, two relations which offer access to the parameters E_c and λ ; they correspond to the switching back and forth of the domains between the two hysteresis curves. If $E_0 = E_c$, then we have the parametric motion with $\varphi = \omega t$ (the oscillating motion takes place along the hysteresis loop).

2. Structural anomalies in $BaTiO_3$

The effective field in ferroelectrics

$$E_w = E + \lambda P \quad (5)$$

includes the internal field λP beside the external electric field E ; this is the Weiss molecular field, where the parameter λ remains to be determined (λ in equation (5) is different from λ introduced in the previous section).[10, 11] Indeed, it has been shown in Ref. [12] that the dipolar interaction between two dipole moments is $-nd^2$ (up to an immaterial numerical factor), where n is the density of dipoles. In the polarized phase this interaction leads to an interaction energy $-nz\bar{d}d$ of the dipole d , where z is the number of nearest neighbours and \bar{d} is the mean value of the dipole

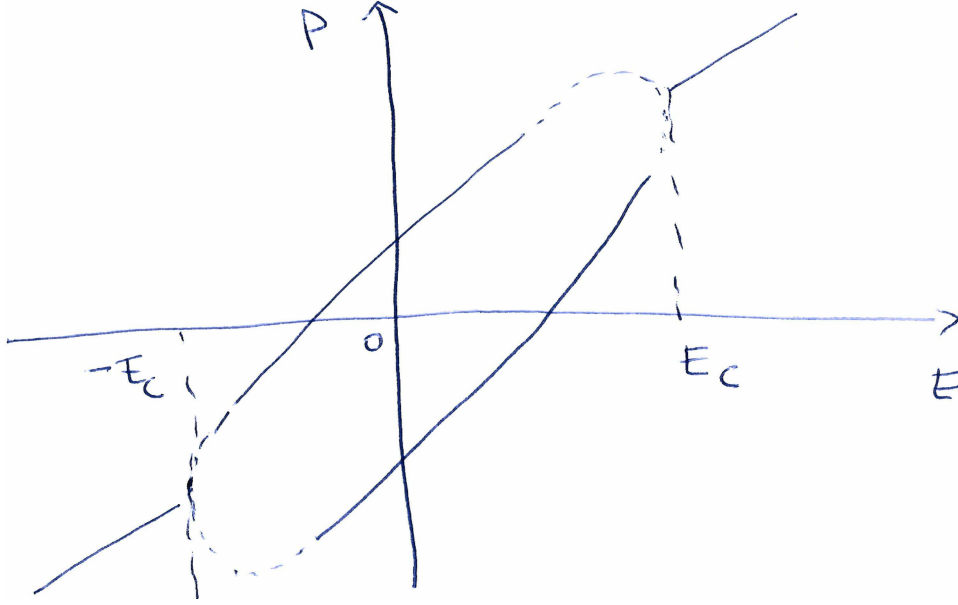


Figure 3: A sketch of the hysteresis curve.

moment; since $n\bar{d}$ is the polarization P , we may write this internal field as zP , which is precisely the Weiss field with $\lambda = z$ (up to a numerical factor).

For a distribution of dipoles $\pm d_0$, we get the polarization

$$P = n\bar{d} = nd_0 \tanh \beta d_0 (E + \lambda P) , \quad (6)$$

where $\beta = 1/T$ is the inverse of the temperature T . For $E = 0$ this equation gives the transition temperature (Curie temperature)

$$T_c = \lambda n d_0^2 ; \quad (7)$$

indeed, the dipolar interaction nd_0^2 may generate ferroelectricity.[12] For $T > T_c$ the polarization is zero, while for $T < T_0$ the polarization increases from zero (where it goes like $(T_c - T)^{1/2}$) to the saturation polarization $P_0 = nd_0$. For $E \neq 0$, equation (6) gives the λ -shaped curve of the polarization as a function of temperature (and the Curie law of the susceptibility $\chi \sim 1/(T - T_c)$ for $T \gg T_c$). For $T \ll T_c$ we may neglect E in equation (6) and the polarization is given approximately by

$$P \simeq nd_0 + \frac{CT}{d_0\lambda} , \quad (8)$$

or

$$P = P_0 + \frac{Cd_0}{a^3 T_c} T , \quad (9)$$

where a is the mean separation distance between dipoles ($n = 1/a^3$), λ is substituted from equation (7) and the constant C ($C > 0$) is undetermined (it is different from C used in the previous section); equation ([9]) is valid over a limited range of variation of the temperature, and C depends on this range; more exactly, P_0 should also be viewed as a fit parameter. These parameters (C and P_0) can be determined by fitting the curve given by equation (9) to the experimental data.

Ferroelectricity is often associated with structural transitions.[13] For instance, the Curie transition in $BaTiO_3$ is accompanied by a structural transition from a cubic symmetry to a tetragonal symmetry. Moreover, there exist in this material two temperatures $T_{1,2} < T_c$ where structural modifications associated with first-order phase transitions appear (Fig. 4).[14] They have the

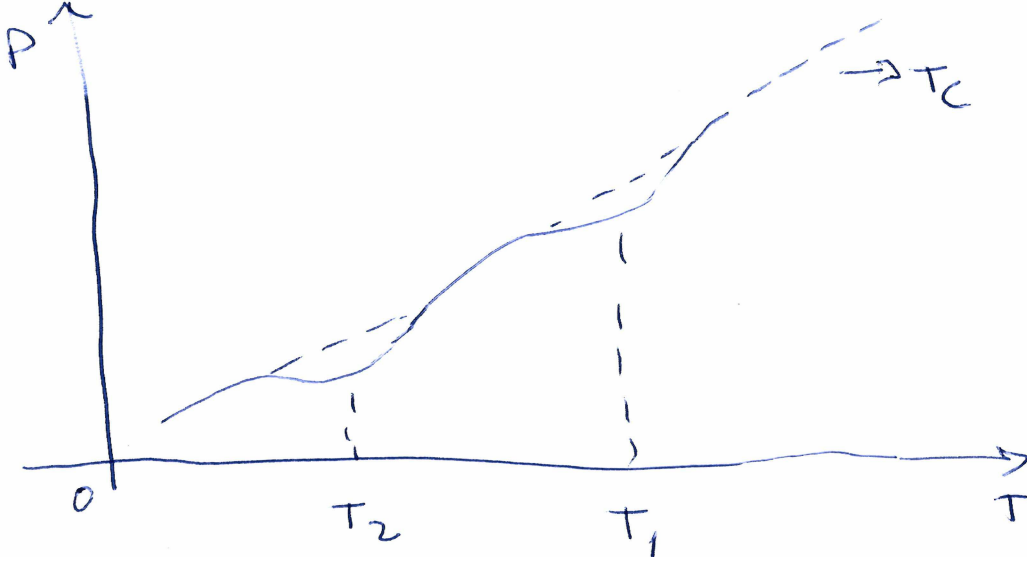


Figure 4: Two anomalies in $BaTiO_3$.

form of two δ -shaped anomalies of the polarization occurring at two temperatures $T_{1,2} < T_c$ (the polarization current may have two δ' -shaped anomalies, slightly shifted due to a temperature hysteresis). In this case, the deviation from a monotonous T -function in equation (9) is provided by a change

$$\delta a = a_1 \Delta T_1 \delta(T - T_1) + a_2 \Delta T_2 \delta(T - T_2) \quad (10)$$

in the lattice constant (dipole density), where $a_{1,2}$ are two undetermined constants and $\Delta T_{1,2}$ are the widths of the two anomalies; indeed, any structural modification proceeds by a variation in the magnitude of the lattice constant in one direction followed by a variation in the opposite direction; we assume here that the two variations are equal; equation (10) describes two such changes, which generate two changes in the polarization (equation (9)) given by

$$\delta P = -\frac{3Cd_0}{a^4 T_c} [a_1 T_1 \Delta T_1 \delta(T - T_1) + a_2 T_2 \Delta T_2 \delta(T - T_2)] \quad (11)$$

This equation may serve to determine the parameters $a_{1,2}$ from experimental data. There exists an exchange of heat $Q_{1,2}$ between dipoles and the lattice, due to these anomalies, given by $Q_{1,2} = 3(a_{1,2}/a)P_{1,2}^2$, where $P_{1,2}$ are the polarizations at $T_{1,2}$. We can see that this inference agrees with the internal energy given in the previous section ($\sim P^2$). On this occasion, we should note that there exists an electrocaloric effect associated with hysteresis, given by

$$\Delta T = \frac{1}{c} \oint T(\partial P / \partial T) dE \quad , \quad (12)$$

where c is the heat capacity and equation (9) is used; integration in equation (12) is extended to the whole hysteresis curve. We note that the heat exchanged with the external field in a hysteresis loop is

$$Q = \oint P dE = 2 \int_{-E_c}^{E_c} dE \sqrt{E_c^2 - E^2} = \pi E_c^2 \quad . \quad (13)$$

Finally, we note that the structural anomalies given by equation (11) are expected to be associated with anomalies in specific heat, piezoelectric response and optical spectra (the latter arising from the dipole modes called dipolons in Ref. 10).

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