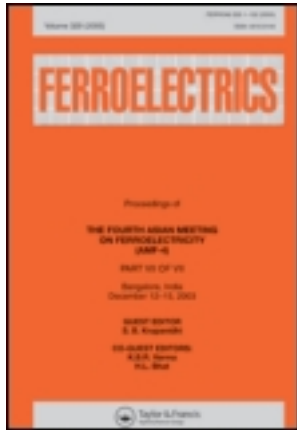


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Ferroelectrics

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gfer20>

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Available online: 13 Jun 2012

To cite this article: Alexander Starkov, Oleg Pakhomov & Ivan Starkov (2012): Impact of the Pyroelectric Effect on Ferroelectric Phase Transitions, *Ferroelectrics*, 427:1, 78-83

To link to this article: <http://dx.doi.org/10.1080/00150193.2012.674413>

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Impact of the Pyroelectric Effect on Ferroelectric Phase Transitions

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The dependence of polarization on the temperature in ferroelectric bulk is investigated. In order to correctly predict the phase transition phenomena, we suggest to pass from the Landau-Ginzburg-Devonshire model to the Landau-Khalatnikov equation with simultaneous consideration of the pyroelectric effect. The developed approach allows us to derive an analytical expression describing the polarization behavior in the vicinity of the Curie point. Additionally, the analysis of obtained equations explains the temperature hysteresis with the difference of physical values at heating and cooling cycles. The model is verified by comparison between experimental data and theoretical results.

1. Introduction

Investigations of the ferroelectric properties carried out during last years have shown presence of the temperature hysteresis. Moreover, the dependence between measurable ferroelectric characteristics and the heating/cooling rate was revealed experimentally as well [6]. Such a phenomenon cannot be described within the framework of classic Landau-Ginzburg-Devonshire (LGD) or Ising [7] theories. The deficiency of these theories is explained as follows: if polarization P , intensity E , and temperature T are linked by any algebraic expression, then a certain set of polarization values P should correspond to any given values of E and T defined by this relation. Note that each value in this set does not depend on the prior history of temperature variations. For the description of the temperature hysteresis phenomenon, algebraic equations have to be changed to the differential ones. This strategy is similar to the method used for the proper treatment of usual electromagnetic hysteresis based on pass from the LGD approach to the Landau-Khalatnikov (LK) technique [8, 9].

According to the LGD theory, the relation between polarization, temperature and intensity for ferroelectrics has the form of

$$E = \frac{aP}{2} + \frac{bP^3}{4} + \frac{cP^5}{6}, \quad a = a_0(T - T_c). \quad (1)$$

Here a, b, c —are Ginzburg-Landau coefficients, a_0 is the Curie-Weiss constant, T_c is the Curie temperature. Equation (1) allows us to describe phase transitions of both the first

Received June 26, 2011; in final form November 30, 2011.

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and second kind. As stated in [7], $b < 0$ for the first-order transition, while $b = 0$ for tricritical point, and $b > 0$ with $c = 0$ for the second-order transition. In case of $E = 0$ and $T < T_c$, the solution of (1) is $P = \pm P_s$, where spontaneous polarization P_s is given by $P_s^2 = (-b \pm \sqrt{b^2 - 4ac})/2c$. The presence of the root singularity in the expression for P_s for the second-order phase transition, or other kind of discontinuity for the first-order phase transition (e.g. delta function,) leads to the infinite value of the pyroelectric coefficient $p = \partial P/\partial T$ at the transition point [7].

Such behavior corresponds to a phase transition of the first and second kinds and results in non-applicability of the LGD theory in the vicinity of the Curie point where the role of fluctuations is crucial [7]. Two main disadvantages of the LGD model, namely an infinite value of parameter p in the phase transition point and the failure to describe the temperature hysteresis, bring out the need for a proper model refinement. As the solution to the problem above, we suggest a new approach based on the LGD model striving to explain experimental data with more precision. For this purpose, it is essential to describe the electric and thermal phenomena simultaneously i.e. to consider pyroelectric (PE) and electrocaloric effects (ECE) together.

As estimated in [10], the expression describing the ECE is $dT \sim -pdE$. Thus, even a small change of the field intensity leads to a significant change in temperature which, in turn, involves growth of the pyrocurrent. As a result, an increase in polarization (just pyroelectric effect) and, therefore, a reduction of p occur. Thus, taking pyrocurrent into account allows us to limit the pyroelectric coefficient. In this work we demonstrate a quantitative description of this effect.

2. Pyrocurrent Influence on Ferroelectric Characteristics

According to the thermodynamics principles of nonequilibrium processes, natural generalization of (1) in case of unsteady condition is the LK equation (also known as Time Domain Ginzburg-Landau-Devonshire) [8]

$$\alpha \frac{dP}{dt} = E - a_0(T - T_c)P - bP^3 - cP^5, \quad (2)$$

where the coefficient α has the meaning of the “internal” resistance [8]. On the basis (2) it is natural to consider the polarization P as a function of two independent variables E and T , i.e. the current j containing two components

$$j = \frac{dP}{dt} \equiv \frac{\partial P}{\partial E} \frac{dE}{dt} + \frac{\partial P}{\partial T} \frac{dT}{dt} = j_{el} + j_{pyr}. \quad (3)$$

The impact of “electrical” current j_{el} on the polarization and the ECE is investigated in [9], where it has been shown that taking j_{el} into account allows us to explain the distinction in ECE values obtained by measurements of the sample temperature and calculated through polarization [11, 12].

Let us now discuss the impact of pyrocurrent component j_{pyr} on polarization. We consider the case of $E = \text{const}$ and assume linear temperature evolution with time: $T = V \cdot t + T_0$, where V is the rate of change of temperature and T_0 is the initial temperature. In order to find polarization, one should use the equation

$$E = \beta \frac{dP}{dT} + a_0(T - T_c)P + bP^3 + cP^5, \quad \beta = \alpha \cdot V. \quad (4)$$

It is important to note that we chose the linear dependence between α factor and the rate of heating because it was predicted by the LK theory in spite of a rather complicated relation between α and β obtained experimentally [6]. Assuming a more complex dependence between these two values, we can easily eliminate the aforementioned deficiency. Unlike (1), the Equation (4) is differential and describes the dependences received experimentally more precisely. Note that (4) can be obtained from the free energy minimum condition

$$F = F_0(T) + \beta p P + \frac{a_0(T - T_c)P^2}{2} + \frac{bP^4}{4} + \frac{cP^6}{6} - EP, \quad (5)$$

which differs from the LGD free energy \tilde{F} [7] by term $\beta p P$.

The influence of temperature on the polarization in the LGD model is described by the multiplier $(T - T_c)$. At the same time, the reciprocal impact on temperature (like in ECE) is not considered in the LGD model. Therefore, it is reasonable to add this free energy LGD-term, taking into account the change of thermal energy in the expression for polarization. Considering the entropy and thermal capacity dependence on the pyroelectric coefficient, one should add a term containing p . The free energy is a scalar while p and P are vectors, and therefore the only imaginable form of this term has to be proportional to the scalar product $p \cdot P$. In the common case, the pyrocurrent is small and the approximate solution of (4) could be presented in the form

$$P \approx P_0 + P_{\text{pyr}}, \quad (6)$$

where P_0 is the quasistationary polarization (the solution of (1)) and P_{pyr} is the pyrocurrent additive to polarization

$$P_{\text{pyr}} = - \frac{a_0 \beta}{(a_0(T - T_c) + 3bP_0^2 + 5cP_0^4)^2}. \quad (7)$$

For a temperature increase, the additive polarization is negative $P_{\text{pyr}} < 0$, while for a decrease it is a positive $P_{\text{pyr}} > 0$. The formula for the description of the polarization difference for heating $P^{(+)}$ and for cooling processes $P^{(-)}$, following from (6), (7) is

$$P^{(+)} - P^{(-)} = - \frac{2a_0 \beta P_0}{(a + 3bP_0^2 + 5cP_0^4)^2}. \quad (8)$$

In turn, for the difference in the dielectric permittivity at heating $\varepsilon^{(+)}$ and cooling $\varepsilon^{(-)}$, accounting for equality $\varepsilon = \frac{1}{\varepsilon_0} \frac{\partial P}{\partial E} + 1$, one obtains

$$\varepsilon^{(+)} - \varepsilon^{(-)} = - \frac{8a_0 \beta P_0 (3b + 10cP_0^2)}{(a + 3bP_0^2 + 5cP_0^4)^2}. \quad (9)$$

Formulae (6)–(9) are inapplicable near the phase transition temperature, because in this case the pyrocurrent can be too large (infinite in the LGD theory). From the mathematical point of view [7], the denominator in (7)–(9) becomes 0 and

$$\left. \frac{\partial^2 \tilde{F}}{\partial P^2} \right|_{P=P_0} = 0. \quad (10)$$

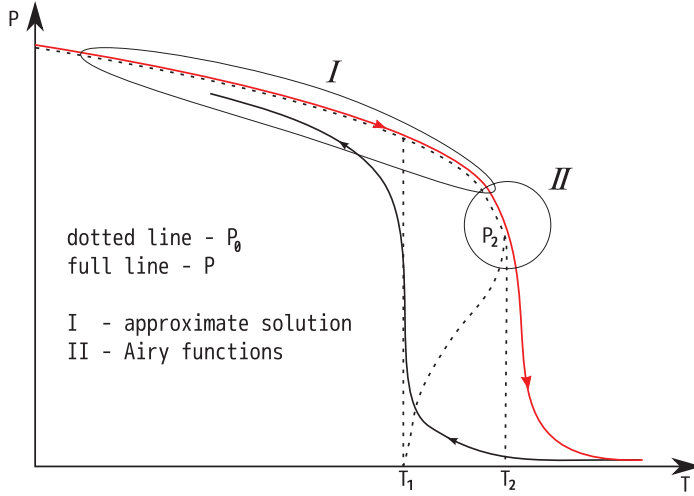


Figure 1. The temperature dependence of the polarization at different temperature cycles for first-order phase transition (Figure available in color online).

2.1. First-Order Phase Transition

In Fig. 1, the dependence between polarization and temperature at different temperature cycles is schematically presented. Values T_1 and T_2 correspond to temperatures of phase transition for cooling and heating ($T_2 > T_1$), respectively. For the phase transition of the first kind, the relation (10) is satisfied at T_1 and T_2 while Equation (1) has multiple roots [7]. In case of heating for $T < T_2$, i.e. in the area I (Fig. 1), the approximate solution (6) is valid. However, at the temperature T_2 the polarization P_0 abruptly changes from the value $P_2 = P_0(T_2)$ to 0. In this region, the solution of (4) will be sought in the form of $P = P_2 + \delta P$ with δP having to satisfy following Equation

$$\beta \frac{\partial \delta P}{\partial T} = K_1 (\delta P)^2 + K_2 (T - T_2) \quad (11)$$

$$K_1 \equiv \left. \frac{\partial P^3}{\partial^3 \tilde{F}} \right|_{P=P_2} = 6bP_2 + 20cP_2^3, \quad K_2 \equiv \left. \frac{\partial^2 \tilde{F}}{\partial P \partial T} \right|_{P=P_2} = a_0 P_2^2.$$

The solution of derived Equation (12) has the form [9]

$$\delta P = \sqrt[3]{\frac{\alpha K_2}{K_1^2} \frac{u'(\sqrt[3]{a_2/K_1 K_2}(T_2 - T))}{u(\sqrt[3]{a_2/K_1 K_2}(T_2 - T))}},$$

where $u(z)$ is the Airy function. Further, as it was shown in [9], for temperatures outside areas of I and II the polarization exponentially decreases to zero. This means that the total solution of (4) for the phase transition of the first kind is now obtained.

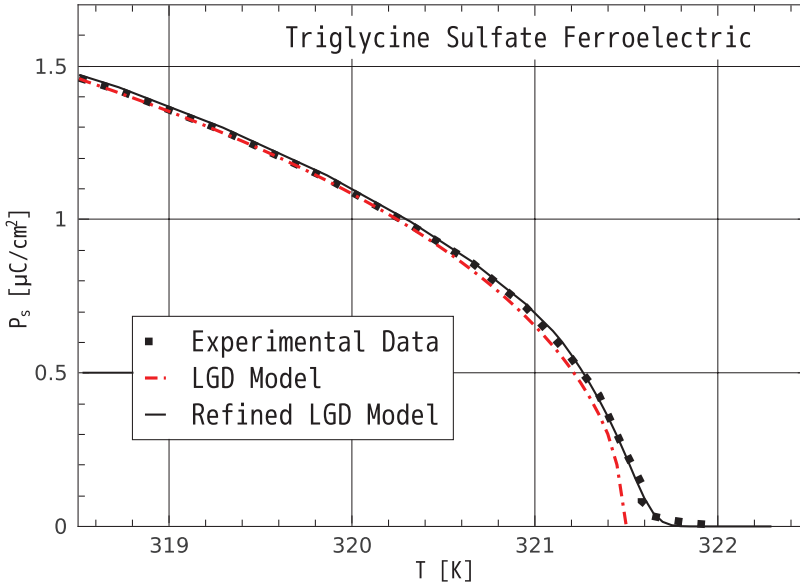


Figure 2. The temperature dependence of the spontaneous polarization for the TGS crystal: comparison between experiment, standard LGD model, and our refined approach (Figure available in color online).

2.2. Second-Order Phase Transition

For the second-order phase transition it is possible to obtain the exact solution of (4) at $E = 0$. The spontaneous polarization for $\beta > 0$ and $c = 0$ is

$$P_s(T) = \left(\frac{a_0 \beta}{\pi b^2} \right)^{\frac{1}{4}} \frac{\exp \left[-a_0 (T - T_c)^2 / (2\beta) \right]}{\sqrt{1 + \operatorname{erf} \left(\sqrt{a_0 / \beta} (T - T_c) \right)}}, \quad (12)$$

where $\operatorname{erf}(z)$ is the error function. The asymptotic behavior of (12) for $T > T_c$ gives

$$P_s \cong \left(\frac{a_0 \beta}{\pi b^2} \right)^{\frac{1}{4}} \exp \left[-\frac{a_0 (T - T_c)^2}{2\beta} \right],$$

which allows us to conclude on the exponential character of the spontaneous polarization decrease. As an example for the model verification, we used a thoroughly investigated Triglycine Sulfate (TGS) ferroelectric. Corresponding calculations performed using the LGD model and our refined version—Equation (11)—are compared against the experiment in Fig. 2. The developed approach demonstrates a rather better agreement between experiment and theory as compared to the LGD model.

3. Results

Detailed analysis of (4) makes it possible to draw the following conclusions: First, the pyroelectric coefficient p calculated by the formula (12) is limited at $T = T_c$, i.e. the phase transition of the second kind is diffused. In addition, the dielectric permittivity is also limited and the sharpness of $\varepsilon(T)$ peak is defined by the parameter β . Second, for

the second-order transition, the spontaneous polarization at $T = T_c$ does not turn to zero but deviates in the vicinity 0 bounded by $\sqrt{\beta/a_0}$ at the Curie point. Third, the Equation (4) allows us to describe the temperature hysteresis. The difference of physical values at heating and cooling cycles appears proportional to the parameter β .

4. Conclusion

Our work is derived from the conventional Landau-Khalatnikov model for ferroelectric materials which is known to describe a wide range of experimental data. Comparing experimental results with findings from classical LGD theory and with those obtained by means of our refined model, we have shown that the latter better represents the matter. In other words, we have proved that if the ferroelectric behavior can be described within the framework of the LK theory, then the dependence between temperature and polarization will be adequately described by the theoretical model we have proposed.

Acknowledgments

The authors would like to thank Dr. A.I. Dedyk from the Saint-Petersburg State Electrotechnical University for presented experimental data. The work was performed with support of the “Development of Scientific Potential of Higher Education 2009–2011” state program of the Ministry of Education and Science of the Russian Federation, project no.2.1.2/5063.

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