

Effect of Thermal Phenomena on a Second-Order Phase Transition in the Landau–Ginzburg Model

A. S. Starkov^a, O. V. Pakhomov^a, and I. A. Starkov^b

^a St. Petersburg State University of Low-Temperature and Food Technologies,
ul. Lomonosova 9, St. Petersburg, 190002 Russia

^b Institut für Mikroelektronik, Technische Universität Wien, A-1040 Wien, Austria

Received February 2, 2010

The influence of electrocaloric and pyroelectric effects on a phase transition in a ferroelectric material has been studied. The difference in the parameters of the Landau model for isothermal and adiabatic processes has been indicated. The temperature dependence of the spontaneous polarization is described by a special function (the probability integral) that results in the disappearance of the second-order phase transition.

DOI: 10.1134/S0021364010100048

INTRODUCTION

One of the most important properties of the ferroelectric crystals used, for example, in the memory storage components is their ability to reverse the polarization direction by the electric field. In this case, the possibility of their investigation is determined by the following most important parameters: (i) the electric field at which the spontaneous polarization is switched, (ii) the polarization switching time, and (iii) the polarization value.

The key characteristic of ferroelectric materials is the dependence of the polarization P on the applied electric field E , whose pronounced nonlinearity manifests itself in the hysteresis. According to the Landau–Ginzburg model, this dependence is polynomial [1],

$$E = aP + bP^3, \quad (1)$$

where a and b are the Landau–Ginzburg coefficients,

$$b = \text{const}, \quad a = a_0(T - T_c).$$

Here, T is the temperature, T_c is the Curie temperature, and a_0 is the Curie–Weiss constant. At $E = 0$, in the ferroelectric phase (at $T < T_c$), the solution of Eq. (1) is $P = \pm P_s$, where

$$P_s = \sqrt{\frac{a_0(T_c - T)}{b}}$$

is the spontaneous polarization.

The square-root singularity in P_s results in the divergence of the pyroelectric coefficient

$$p = \partial P / \partial T$$

at the Curie point; this explains the term “second-order phase transition.” However, this fact contradicts numerous existing experimental data. We also note that recent measurements of the ferroelectric properties revealed a temperature hysteresis. The polarization [2], dielectric permittivity [3, 4], and specific heat capacity [5] of ferroelectrics depend not only on the temperature T but also on whether it increases or decreases. This phenomenon cannot be described within the framework of the Landau–Ginzburg theory. Even if the polarization, temperature, and electric field are related by an algebraic expression more general than Eq. (1), for example, by a higher order polynomial, then any field value corresponds to a certain set of polarizations, each of which is independent of the method we used to obtain it. To describe the hysteresis phenomena, it is necessary to pass from the algebraic to differential equations similar to the passage from the Landau–Ginzburg equation to the Landau–Khalatnikov equation in the description of an ordinary electromagnetic hysteresis [6–8].

We believe that an adequate interpretation of the experimental data requires the joint description of the electric and thermal phenomena. For example, as p increases, in accordance with the electrocaloric effect, the temperature changes and the pyroelectric current increases,

$$j_{\text{pyr}} = p \frac{dT}{dt},$$

and this leads to an increase in the polarization (the pyroelectric effect) and to a decrease in p . Therefore, due to the appearing feedback, the pyroelectric coefficient p remains limited. The qualitative description of the mentioned effects is given below.

TAKING INTO ACCOUNT
THE ELECTROCALORIC EFFECT
FOR THE ADIABATIC PROCESS

The electrocaloric effect is the electric-field-induced temperature variation and can be described by any of the two equations given below [9],

$$\rho C_E dT = -TpdE, \quad \rho C_P dT = T \frac{\partial E}{\partial T} dP, \quad (2)$$

where ρ is the density and C_E and C_P are the specific heat capacities at constant electric field and polarization, respectively. Equations (2) are universal and independent of the explicit form of the equation of state relating P , E , and T . Since all quantities in Eqs. (2) can be experimentally obtained, it is convenient to use them in processing the experimental data.

Formulas (2) are written in the adiabatic approximation and make it possible to adequately describe the electrocaloric effect in the sample under the quasistatic variation of the electric field. In the heat exchange with the environment, the nonuniform temperature distribution appears in it, and Eq. (2) should be replaced by a more intricate heat conduction equation [10–12], which includes the thermal relaxation processes.

We recall that the temperature in the pioneering works by Landau was considered to be constant, and this can be true at a constant field, but both the polarization and temperature in the varying electric field vary. We suggest that Eqs. (1) and (2) should be considered as a system rather than separately as it was done earlier. We write the free energy in the Landau form,

$$F = F_0(T) + a_0(T - T_c) \frac{P^2}{2} + b \frac{P^4}{4} - EP,$$

where $F_0(T)$ is a function of the temperature of an arbitrary explicit form. Hence, we find the entropy

$$S = - \left(\frac{\partial F}{\partial T} \right)_E = -F'_0(T) - a_0 \frac{P^2}{2}$$

and the specific heat capacities

$$C_E = T \left(\frac{\partial S}{\partial E} \right)_E = -TF''_0(T) - a_0 T p P,$$

$$C_P = T \left(\frac{\partial S}{\partial E} \right)_P = -TF''_0(T).$$

According to the above formulas, the specific heat capacities C_E and C_P coincide in the absence of an electric field in the paraphase at $T < T_c$ when $P = 0$. The derivatives with respect to the temperature in Eq. (2) are readily calculated,

$$\left(\frac{\partial E}{\partial T} \right)_P = a_0 P, \quad p = - \frac{a_0 P}{a + 3bP^2}.$$

Therefore, in the Landau–Ginzburg model, the specific heat capacity C_P (in contrast to C_E) is a function of only the temperature, while the derivative

$$\left(\frac{\partial E}{\partial T} \right)_P$$

is a function of only the polarization, and the second equation in Eqs. (2) is a differential equation with separating variables and has the common integral

$$\int_{T_0}^T \rho \frac{C_P(T)}{T} dT = a_0 \frac{(P^2 - P_0^2)}{2},$$

where T_0 and E_0 are the initial temperature and polarization, respectively, in the vicinity of the Curie point. The function $F''_0(T)$ and the density ρ can be considered constant; thus, the notation

$$\rho F''_0(T) = -\kappa$$

can be introduced. The correctness of this notation is supported by the experimental data [13], which demonstrate the linear temperature dependence of the specific heat capacity (away from absolute zero).

As a result, the equation of the adiabatic curve for the ferroelectric material has the form

$$T = T_0 + \frac{a_0}{2\kappa} (P^2 - P_0^2), \quad \kappa = \frac{\rho C_P}{T}. \quad (3)$$

We note that only P^2 enters into Eq. (3), because the polarization P is a vector, and the equations for scalar quantities in the simplest isotropic model can contain only the dependence on the absolute value of P . Substituting relation (3) into formula (1), we obtain the modified Landau–Ginzburg equation

$$E = a_1 P_1 + b_1 P_1^3, \quad (4)$$

where

$$a_1 = a_0 \left(T_0 - T_c - \frac{a_0 P_0^2}{2\kappa} \right), \quad b_1 = b + \frac{a_0^2}{2\kappa}. \quad (5)$$

For the particular case where the electric field is absent at the initial time, the temperature T_0 is specified, and the polarization is equal to the spontaneous one, $P_0^2 = -a/b$, we have

$$a_1 = a_0(T_0 - T_c) \left(1 + \frac{a_0}{2\kappa b} \right).$$

Therefore, if the electrocaloric effect is taken into account, the equation of state (1) is replaced by similar equation (4), where the adiabatic coefficients a_1 and b_1 are related to the isothermal coefficients a and b by expressions (5). The difference in the coefficients results in the difference in the derivatives of the permittivity, pyroelectric coefficient, specific heat capac-

ity, etc. [14]. Naturally, this difference holds also in the approximation of the $E(P)$ dependence by a higher-order polynomial.

TAKING INTO ACCOUNT THE PYROELECTRIC CURRENT IN THE LANDAU–KHALATNIKOV MODEL

In accordance with the thermodynamics of non-equilibrium processes [15], a natural extension of Eq. (1) to the case of the unsteady state is the Landau–Khalatnikov equation [6],

$$\alpha \frac{dP}{dt} = E - aP - bP^3. \quad (6)$$

The physical interpretation of Eq. (6) is as follows. Since the change in the polarization is equivalent to the presence of the current

$$j = \frac{dP}{dt},$$

this current induces the field $E_{\text{dyn}} = \alpha j$, where α is the “internal” resistance. For an arbitrary (not necessarily adiabatic) process, it is natural to consider the polarization P as a function of two independent variables E and T and to represent the current j as the sum of two terms,

$$j = \frac{\partial P dE}{\partial E dt} + \frac{\partial P dT}{\partial T dt}. \quad (7)$$

The first term on the right-hand side of relation (7) is an ordinary electric current j_{el} , and the second term is the pyroelectric current j_{pyr} , which has not been earlier considered in the Landau model. Taking into account the pyroelectric current is the key objective of this study. We note that the electric component can be written as

$$j_{\text{el}} = \varepsilon_0 \chi \frac{dE}{dt},$$

where χ is the dielectric susceptibility.

Thus, we will consider the following modification of the Landau–Khalatnikov equation:

$$\alpha \left(\frac{\partial P dE}{\partial E dt} + \frac{\partial P dT}{\partial T dt} \right) = E - aP - bP^3. \quad (8)$$

If the left-hand side of Eq. (8) is small, the approximate solution of Eq. (8) away from the Curie point can be represented as

$$P \approx P_0 + P_a, \quad (9)$$

where P_0 is the quasistationary polarization (the solution of Eq. (1)), and

$$P_a = P_E + P_T$$

is the dynamic addition to the polarization, where

$$P_E = -\frac{\alpha}{a + 3bP_0^2} \frac{\partial P_0 dE}{\partial E dt}, \quad P_T = -\frac{\alpha}{a + 3bP_0^2} \frac{\partial P_0 dT}{\partial T dt} \quad (10)$$

are the electric and pyroelectric parts of this addition, respectively. For the Landau–Ginzburg model, the derivatives of the polarization in Eq. (10) can be explicitly calculated,

$$\frac{\partial P_0}{\partial E} = \frac{1}{a + 3bP_0^2}, \quad \frac{\partial P_0}{\partial T} = -\frac{a_0}{a + 3bP_0^2}. \quad (11)$$

The above formulas indicate that, as E increases in the ferroelectric phase, the corresponding part of the addition decreases, and the corrective term P_T increases with T . The first correction P_E was taken into account in [8], where it was shown that this correction explains the difference between the direct measurement of the temperature variation ΔT in the electrocaloric effect and the temperature variation ΔT obtained by recalculating from the polarization measurements. We consider the second particular case where $E = \text{const}$ and the temperature is a linear function of time,

$$T = Vt + T_0,$$

where V is the temperature variation rate and T_0 is the initial temperature of the ferroelectric material. To find the polarization, we have the equation

$$\beta \frac{dP}{dT} + a_0(T - T_c)P + bP^3 = E, \quad (12)$$

where $\beta = \alpha V$. In contrast to Eq. (1), Eq. (12) is differential and allows us to more accurately describe the experimental dependences.

Equation (12) can also be obtained from the condition of the free energy minimum,

$$F = F_0(T) + \frac{\beta}{2} \frac{\partial P^2}{\partial T} + a_0(T - T_c) \frac{P^2}{2} + b \frac{P^4}{4} - EP, \quad (13)$$

which differs from the Landau–Ginzburg free energy by the term

$$\frac{\beta}{2} \frac{\partial P^2}{\partial T}.$$

The introduction of this term can be justified as follows. The temperature effect on the polarization is described in the Landau–Ginzburg model by the factor $T - T_c$. Meanwhile, the Landau–Ginzburg model neglects the effect of the polarization on the temperature (the electrocaloric effect). Therefore, it is reasonable to supplement the Landau–Ginzburg free energy by a term presenting the polarization-induced variation of the thermal (internal) energy. Since the specific heat capacity and entropy depend on the pyroelectric coefficient, it is natural to add the p -containing terms to the Landau–Ginzburg free energy. Since p is small

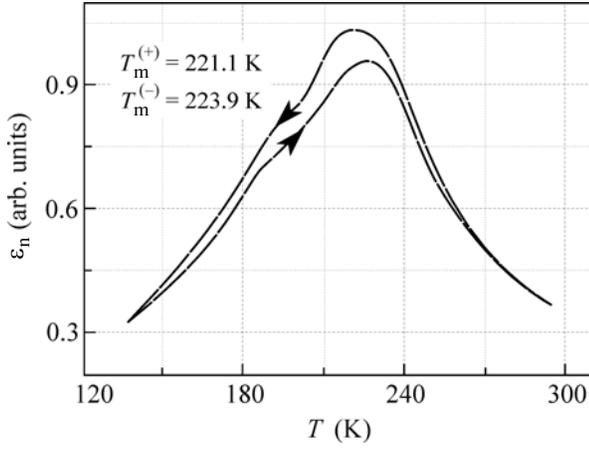


Fig. 1. Temperature dependence of the normalized permittivity during heating and cooling.

and the free energy is a scalar, the only candidate for this term is the scalar product pP .

In most cases, the pyroelectric current is small, and the difference between the polarizations in heating $P^{(+)}$ and cooling $P^{(-)}$ can be described by the formula

$$P^{(+)} - P^{(-)} = \frac{2\beta a_0}{a + 3bP_0^2}, \quad (14)$$

which follows from Eqs. (10) and (11).

Taking into account the equality

$$\varepsilon = \frac{1}{\varepsilon_0} \frac{\partial P}{\partial E} + 1,$$

the difference between the dielectric permittivities in heating $\varepsilon^{(+)}$ and cooling $\varepsilon^{(-)}$ is given by the expression

$$\varepsilon^{(+)} - \varepsilon^{(-)} = -\frac{12\beta a_0 b P_0}{(a + 3b_0^2)^4}. \quad (15)$$

Figure 1 presents the typical curve of the normalized permittivity

$$\varepsilon_n = \frac{2\varepsilon}{\varepsilon_{\max}^{(+)} + \varepsilon_{\max}^{(-)}}.$$

Formulas (13) and (14) are inapplicable near the phase transition temperature, where the contribution of the pyroelectric current in Eq. (13) becomes comparably higher than the remaining terms. The exact solution of Eq. (12) applicable for any temperatures is obtained at $E = 0$. The spontaneous polarization at $\beta > 0$ has the form

$$P_s(T) = \left(\frac{a_0\beta}{\pi b^2}\right)^{1/4} \frac{\exp\left[-\frac{a_0(T-T_c)^2}{2\beta}\right]}{\sqrt{1 + \operatorname{erf}\left(\sqrt{a_0/\beta}(T-T_c)\right)}}, \quad (16)$$

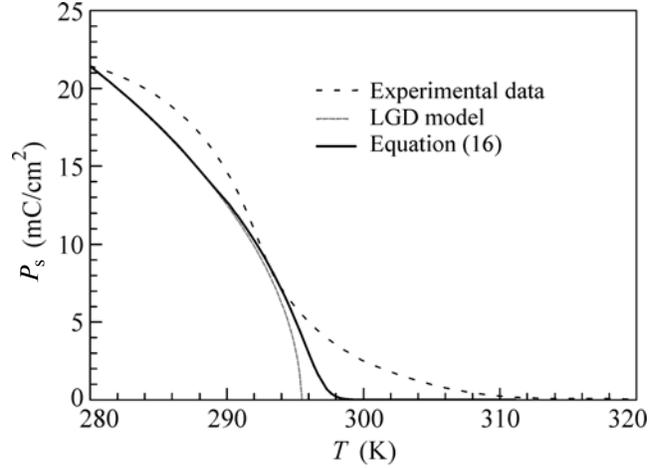


Fig. 2. Spontaneous polarization for 0.87PMV–0.13PT ceramic.

where $\operatorname{erf}(z)$ is the probability integral. Solution (9) is chosen from the condition that the spontaneous polarization in the limit $T \rightarrow -\infty$ tends to a similar value for the Landau–Ginzburg–Devonshire model,

$$P_s \rightarrow \sqrt{\frac{a_0(T-T_c)}{b}}, \quad T \rightarrow -\infty.$$

Above the Curie temperature,

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

i.e., the spontaneous polarization decreases exponentially. Figure 2 shows dependence (16) in comparison with the Landau–Ginzburg–Devonshire model and the experimental data for the 0.87PMV–0.13PT ceramic.

We discuss the consequences following from the change of Eq. (1) to Eq. (12). First, the pyroelectric coefficient p calculated by formula (16) is limited at $T = T_c$; i.e., the phase transition in the strict sense disappears. The dielectric permittivity is also limited. Second, the spontaneous polarization in the paraphase is nonzero within a small, of the order of $\sqrt{\beta/a_0}$, vicinity of the Curie point. Third, Eq. (12) allows us to describe the temperature hysteresis, and the difference between the physical quantities in heating and cooling appears to be proportional to the parameter β . Fourth, the maximum of the pyroelectric effect shifts from the Curie point to higher temperatures.

We are grateful to A.I. Dedyk and Yu.A. Pavlova for the presented experimental results. This work was supported by the Federal Agency for Education, Ministry of Education and Science of the Russian Federation (project no. 2.1.2/5063, program “Development of the Potential of Higher Education for 2009–2010”).

REFERENCES

1. V. L. Ginzburg, *Usp. Fiz. Nauk* **38**, 490 (1949).
2. V. V. Gladkii, V. A. Kirikov, T. R. Volk, et al., *Fiz. Tverd. Tela* **45**, 2067 (2003) [*Phys. Solid State* **45**, 2171 (2003)].
3. M. E. Guzhva, V. V. Lemanov, and P. A. Markovin, *Fiz. Tverd. Tela* **43**, 2058 (2001) [*Phys. Solid State* **43**, 2146 (2001)].
4. K. A. Verkhovskaya, A. A. Plakseev, A. M. Lotonov, et al., *Fiz. Tverd. Tela* **51**, 1297 (2009) [*Phys. Solid State* **51**, 1370 (2009)].
5. E. D. Yakushkin, *Fiz. Tverd. Tela* **46**, 325 (2004) [*Phys. Solid State* **46**, 335 (2004)].
6. L. D. Landau and I. M. Khalatnikov, *Dokl. Akad. Nauk SSSR* **96**, 469 (1954).
7. A. S. Starkov and O. V. Pakhomov, *Vestn. Mezhdunar. Akad. Kholoda* **12**, 30 (2009).
8. A. S. Starkov and O. V. Pakhomov, *Pis'ma Zh. Tekh. Fiz.* **36**, 3 (2010) [*Tech. Phys. Lett.* **36**, 1 (2010)].
9. J. F. Nye, *Physical Properties of Crystals* (Oxford Univ. Press, Oxford, 1957).
10. M. Marvan, A. K. Jonscher, and J. Fahnrich, *J. Eur. Ceram. Soc.* **21**, 1345 (2001).
11. A. S. Starkov, S. F. Karmanenko, O. V. Pakhomov, et al., *Fiz. Tverd. Tela* **51**, 1422 (2009) [*Phys. Solid State* **51**, 1510 (2009)].
12. S. F. Karmanenko, O. V. Pakhomov, A. M. Prudan, et al., *J. Eur. Ceram. Soc.* **27**, 3109 (2007).
13. A. M. Aliev, Sh. V. Abduvagidov, A. B. Batdalov, et al., *Pis'ma Zh. Eksp. Teor. Fiz.* **72**, 668 (2000) [*JETP Lett.* **47**, 464 (2000)].
14. E. V. Milov and B. A. Strukov, *Fiz. Tverd. Tela* **43**, 495 (2001) [*Phys. Solid State* **43**, 513 (2001)].
15. S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962; Mir, Moscow, 1964).

Translated by E. Perova