Ferroelectric Semiconductors

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СЕГНЕТОЭЛЕКТРИКИ— ПОЛУПРОВОДНИКИ
В. М. ФРИДКИН

SEGNETOELEKTRIKI-POLUPROVODNIKI
V. M. Fridkin

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Preface to the English Edition

In preparing the book for translation into English, practically no changes have been made either in format or in content except for a small number of brief corrections and comments. The material and the bibliography devoted to the anomalous photovoltaic effect in ferroelectrics and the most recent investigations of the photorefractive effect, which is closely related to our subject, have been left out; the recently published comprehensive book by M. E. Lines and A. M. Glass, entitled *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977), covers the principal aspects of these phenomena. Nevertheless the material on photoferroelectric phenomena (including the photovoltaic and photorefractive effects) is extensive enough to fill a separate volume.

The author would like to thank his American colleagues Professors George Taylor and Issai Lefkowitz, co-editors of the international journal *Ferroelectrics*, for their cooperation and initiative in the publication of the English translation of this book. It is hoped that the English edition of this book will prove interesting and useful to specialists in ferroelectricity as well as to a wider circle of Western readers.

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Preface

Since Kurchatov's discovery of the ferroelectric properties of crystals of Rochelle salt, ferroelectricity has been traditionally considered one of the divisions of the physics of dielectrics. Thanks to the work of Ginzburg, Cochran, Smolenskii, Khokhlov, and others, the physics of ferroelectrics and nonlinear crystals has become in recent years an important branch of solid state physics, a branch in which modern fields such as lattice dynamics, resonance methods of investigation, nonlinear optics and electro-optics, etc., have found application and further development. One could also refer to the recent intensive development of the more traditional fields such as the thermodynamics of phase transitions, atomic structure, crystallographic studies, and crystal physics of ferroelectrics. The latter division touches fields begun classically such as the study of domain structure, the mechanism of polarization reversal, and nonlinear dielectric properties.

A fundamentally new stage in the investigation of ferroelectrics is associated with the discovery of the ferroelectric properties of barium titanate by Vul in 1944 [1, 2]. Barium titanate was the first ferroelectric semiconductor with a not too wide forbidden band ($E_g \simeq 3$ eV), so it appeared possible to use it to investigate electron conductivity and other transport phenomena, the mechanism of carrier scattering, nonequilibrium conductivity and luminescence, intrinsic and impurity optical absorption, band structure, and other semiconductor properties. After the discovery of the ferroelectric properties of barium titanate, the semiconductor properties of other ferroelectrics with the perovskite structure began to be investigated. In 1962, Merz and his colleagues [3, 4] discovered the ferroelectric properties of the relatively high-sensitivity photoconductors of the type $A^{V}B^{VI}C^{VII}$ (for example, SbSI with $E_g \simeq 2$ eV). The class of ferroelectric semiconductors now includes a large number of compounds, among which are both wide-band materials such as lithium niobate, barium and strontium niobate, and compounds of the type $A_2^{V}B_3^{VI}$, as well as narrow-band semiconductors, for example, compounds of the type $A^{IV}B^{IV}$.

Ferroelectric semiconductors, in particular those with a wide forbidden band and low carrier mobility, are not favorable objects of study if one approaches

them from the usual position of semiconductor physics. The indeterminacy of the band structure, the presence in the forbidden band of a complex system of local levels of unknown nature (and the impossibility of alloying related to this), and the large Maxwell relaxation time (which renders difficult the investigation of the kinetics of nonequilibrium electron processes) are a few of the reasons these materials are of little promise in studying elementary processes in semiconductors.

What then is the reason for the great and ever-increasing interest in ferroelectric semiconductors—in investigating and obtaining new materials? It is related first of all to the existence in these materials of ferroelectric and semiconductor properties, and also to the presence of phase transitions of these semiconductors. The contribution of the free energy of the electron subsystem to the free energy of the lattice and the interaction of electrons with the "soft" ferroelectric mode lead to a series of fundamentally new physical phenomena in ferroelectric semiconductors. One of these phenomena is the effect of photoactive illumination and the corresponding nonequilibrium carriers on the Curie temperature, spontaneous polarization, and other macroscopic properties of ferroelectrics. This phenomenon has already had important practical application in holography and optical memory systems (damage effect). The application of ferroelectric semiconductors and, in particular, photoelectric phenomena in ferroelectrics will undoubtedly expand in relation to the development of electrooptics, nonlinear optics, and related disciplines.

The investigation of ferroelectric semiconductors is also timely because of the contribution it makes to the study of the nature of ferroelectricity itself. Thus, for example, the development in recent years of the vibron model of ferroelectrics based on the application of the pseudo-Jahn-Teller effect has led to an active investigation of the electron-phonon interaction both in narrow-band as well as wide-band ferroelectrics, previously considered as typical dielectrics. It is within the framework of this theory that the interband electron-phonon interaction is found to be responsible for anharmonicity and the appearance of the soft mode. Another important example is the screening of spontaneous polarization, which both in narrow-band as well as in wide-band ferroelectrics has an electron-hole nature, since it is caused either by a sharp curvature of the bands at the surface or by the participation of electron surface states.

Thus, the application of the basic ideas and methods of semiconductor physics to ferroelectrics has been very fruitful in understanding the mechanism of ferroelectricity. From this point of view, the division of ferroelectrics into dielectrics and semiconductors is very restrictive and arbitrary in a number of cases.

Thus, the effect of the electron subsystem on the generation of ferroelectricity and the ferroelectric properties is one of the aspects of the subject under consideration. Another no less important aspect is the inverse effect of the

dielectric nonlinearity, and the effects of screening and phase transitions on electron processes in ferroelectrics. In this sense, ferroelectrics form a new class of nonlinear semiconductors, a class in which a majority of the phenomena known for electron semiconductors display specific features; moreover, a number of new phenomena are observed (positive temperature coefficient of resistance, a new type of domain instability, "intrinsic" field effect, etc.).

Both of the above-mentioned aspects have been reflected in this book. The author would like to make here some remarks and reservations with respect to its content. The book is written in the form of a systematic consideration of the phenomenological and partially microscopic theory of ferroelectric semiconductors and the classification of groups of phenomena which result from this analysis. The author has tried to avoid a description of the properties of individual compounds, their classification into a series of ferroelectrics, etc. The goal of the book has been to give as complete and systematic a discussion as possible of the theory and experimental results related to the study of the electron processes in ferroelectrics. Thus, the book gives a description of the phenomena, and not a description of the properties of individual or even typical ferroelectric semiconductors. The author has also tried to avoid digressions into related divisions of ferroelectric physics, referring the reader when necessary to the literature. This is justified in view of the recently published monograph of Smolenskii and his co-workers [5] which encompasses all the basic divisions of ferroelectric physics, the book of Vaks on the microscopic theory of ferroelectrics [6], and a number of other very complete monographs, for example [7 - 15].

A decisive contribution to the study of the semiconductor properties of ferroelectrics has been made by a series of Soviet investigators, including the theoretical works of Bonch-Bruevich, Larkin, Guro, Ivanchik, Pasynkov, Kristofel', Bersuker, Sandomirskii, Bursian, Chenskii, Selyuk, and others. In using these works, the author has tried to give as complete and systematic a discussion as possible. Nonetheless, the author accepts responsibility for not having avoided bias by sometimes allotting a disproportionate amount of attention to work done by his colleagues. However, the subject itself is still far from being thoroughly studied, and thus the author was faced with the problem of considering the series of features of electron phenomena in ferroelectrics, instead of a discussion of the subject as a whole.

This monograph generalizes the investigations of the author carried out with his colleagues and students at the A. V. Shubnikov Institute of Crystallography of the Academy of Sciences of the USSR over the past decade. A significant place in the book has been assigned to the results of investigations of photoelectric phenomena in ferroelectrics, which was carried out under the direction of the author in recent years by a group of students and co-workers of the Faculty of Semiconductor Physics of Rostov State University, now directed by

A. A. Grekov. The All-Union seminars on the physics of ferroelectric semiconductors, which are held regularly by the faculty, stimulated this work in many respects. The style of presentation of the book was largely dictated by the lectures read by the author in various years at Rostov State University, at the Karl Marx University (Leipzig, GDR), and at Dejon University (France).

The author considers it his duty to thank Academician B. M. Vul, Corresponding Members of the Academy of Sciences of the USSR G. A. Smolenskii and B. K. Vainshtein, and Doctor of Physical and Mathematical Sciences L. A. Shuvalov for their interest in this subject and for their attention and support. The author also would like to express his appreciation to Professor L. M. Belyaev and A. N. Lobachev, the directors of the laboratories at the Institute of Crystallography of the Academy of Sciences of the USSR and the first in our country to develop a series of ferroelectric semiconductor crystals (including $A^{V}B^{VI}C^{VII}$) and the first to investigate their physical properties. The author is grateful to all the colleagues working with him on this subject for many years, in particular to A. A. Grekov, and also to T. R. Volk and K. A. Verkhovskii for carefully reviewing the manuscript of the book. At the request of the author, Section 3.8 was written by B. V. Selyuk and Section 4.6 by A. G. Khasabov, to whom the author expresses his appreciation.

In conclusion, the author expresses the hope that this work will stimulate to some degree the further development of the physics of ferroelectric semiconductors and that future success can be expected in this area, whose beginning was based on the discovery of the ferroelectric properties of barium titanate. B. M. Vul [16] recently wrote: "It was difficult to foresee the ferroelectric properties of barium titanate, but after they were discovered, it was easy to hope that they would have a promising future. The past 25 years have justified this hope."

We hope that the study and practical application of ferroelectric semiconductors as a separate class of compounds will be useful both for solid state physics and for its applications.

Moscow, 1975

V. M. Fridkin

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1

Thermodynamics of Ferroelectric Semiconductors

One of the features of ferroelectric semiconductors is the effect of electrons on the fundamental thermodynamic functions and their behavior near the Curie temperature. As will be shown below, the effect of nonequilibrium electrons on the phase transitions in ferroelectrics is of greatest interest from the experimental point of view. In the literature such phase transitions have been called *photostimulated*, and phenomena related to them in ferroelectrics, *photoferroelectric* [17-24]. Photostimulated phase transitions and the effect of electrons on phase transitions generally are not characteristic of ferroelectrics only, but are typical for all semiconductors experiencing phase transitions. Investigation of ferroelectric semiconductors offers in this respect only the advantage that the photoferroelectric phenomena can be related to the basic phenomenological parameters of ferroelectrics such as the Curie-Weiss constant, spontaneous polarization and heat capacity discontinuity, as well as to other independently measured parameters.

The existence of photostimulated phase transitions in solids and, in particular, in ferroelectrics is of fundamental interest. In considering the mechanism of phase transitions, one usually neglects the contribution of the electron subsystem (or the electron free energy) in the total free energy of the crystal and thereby assumes that the mechanism of phase transitions is not related to electron excitations in the crystal. This assumption is based on the fact that at temperatures above the Debye temperature, the contribution of the electron heat capacity to the total heat capacity of the crystal can be neglected. We will consider this in somewhat more detail. Denoting the free energy by F and the internal energy by E, we write the Gibbs-Helmholtz equation

$$F = E + T\frac{\partial F}{\partial T}. \tag{1.1}$$

After integration, this equation can be represented in the form

$$F = -T\int_0^T \frac{E}{T^2}\,dT. \tag{1.2}$$

The internal energy E, by definition, can be expressed in terms of the heat capacity C_V in the following manner:

$$E(T) = E(0) + \int_0^T C_V(T)\,dT, \tag{1.3}$$

from which, by substituting (1.3) into (1.2), we obtain the final expression for the free energy:

$$F = E(0) + T\int_0^T \frac{dT}{T^2}\int_0^T C_V(\tau)\,d\tau. \tag{1.4}$$

It is seen from (1.4) that the free energy of the crystal is completely determined by the temperature dependence of the heat capacity. It is known from solid state physics that for a nondegenerate semiconductor or dielectric at temperatures above the Debye temperature, the ratio of the electron heat capacity C_V^{el} to the lattice heat capacity C_V^{L} is

$$\frac{C_V^{\mathrm{el}}}{C_V^{\mathrm{L}}} = \frac{N_c}{n_0} \ll 1, \tag{1.5}$$

where $N_c = (2\pi m^* kT/h^2)^{3/2}$ is the density of states of electrons or holes in the band, m^* is the effective mass of the electron or hole, and n_0 is the number of atoms per cubic centimeter. For metals at temperatures above the Debye temperature, we have

$$\frac{C_V^{\mathrm{el}}}{C_V^{\mathrm{L}}} \simeq \frac{kT}{E_{\mathrm{F}}} \ll 1, \tag{1.6}$$

where the Fermi energy E_{F} is of the order of several electron volts, while $kT \simeq 0.025$ eV at room temperature. Thus, both for metals and for semiconductors at temperatures above the Debye temperature, the contribution of electrons to the free energy of the crystal can be neglected. The contribution of the electrons can become significant only near $T = 0$, where C_V tends to zero as $\sim T^3$.

Nonetheless, it is found that besides the region of absolute zero, the vicinity of the temperature of phase transitions is also a peculiar temperature region, where the contribution of the electron subsystem to the free energy of the crystal can be significant. The physical meaning of this assertion involves the fact that close to the temperature of a phase transition, the electrons can make a significant contribution not to the heat capacity itself, but to its anomalous part at the phase transition. This conclusion was first reached in [25] for ferroelec-

tric phase transitions within the framework of the phenomenological theory of Landau, Ginzburg, and Devonshire, and is developed in [26, 27]. The effect of electron excitations on phase transitions of a different nature was investigated in a number of subsequent works. We will dwell in this chapter on an analysis of the photoferroelectric phenomena and the effect of electrons on the properties of ferroelectrics on the basis of the phenomenological theory of ferroelectric phase transitions.

1.1. Free Energy of a Ferroelectric Semiconductor

The presence of a relatively high concentration of carriers in a ferroelectric semiconductor makes it necessary to consider the free energy of the electron subsystem in the expression for the free energy of the crystal near the phase-transition temperature. We will then assume that the free energy of the electron subsystem F_2 is small everywhere (except at the vicinity of the Curie point) as compared to the free energy of the lattice F_1, and that the phase transition itself is related to instability of lattice vibrations (in the opposite case, we are dealing with a purely electron phase transition, as, for example, in vanadium oxides). We will also consider the ordinary ferroelectric for which, according to Landau [28], the free energy of the lattice F_1 near the Curie point can be expanded in a series in even powers of the spontaneous polarization P. We will consider separately in Section 1.4 the case of singular ferroelectrics, for which the spontaneous polarization P is not an expansion parameter. Finally, we will consider the thermodynamics of ferroelectric semiconductors neglecting the anisotropy of the dielectric properties by assuming that the polarization of the crystal occurs only in the direction of the spontaneous polarization axis (the c axis). Following [25-27], we represent the free energy of the crystal F as the sum of the free energy of the lattice in the paraelectric region F_0 and in the ferroelectric region F_1 and the free energy of the electron subsystem F_2:

$$F = F_0 + F_1 + F_2, \tag{1.7}$$

where

$$F_0(T) = F \ (P = 0, \ \sigma_k = 0, \ N_i = 0), \tag{1.8}$$

$$F_1 = \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6 - \frac{1}{2}\sum_i \sum_k s_{ik}\sigma_i\sigma_k - P^2 \sum_k \nu_k \sigma_k, \tag{1.9}$$

$$F_2 = \sum_i N_i E_i(T, P, \sigma_k). \tag{1.10}$$

Here, α, β, and γ are the components in the expansion of the free energy in the

polarization P [15, 29, 30], σ_k are the components of the mechanical stress tensor, $S_{ik} = S_{ik}^P = \partial^2 F_1/\partial\sigma_i\partial\sigma_k$ are the components of the elastic compliance tensor, and $\nu_k = \partial^2 F_1/\partial P^2\partial\sigma_k$ are the components of the electrostriction tensor. In expression (1.10) for the free energy of the electron subsystem, E_i and N_i are the energy of the levels and the corresponding concentrations of electrons (holes) in the crystal. For the time being, we will neglect the configuration part of the free energy in equation (1.10), while we assume the polarization to be uniform in equation (1.9) and neglect the correlation term. In the general case, equation (1.9) must be supplemented by the Poisson equation (cf. Chapter 3).

To be specific, we will consider an n-type ferroelectric semiconductor, whose band energy diagram is presented in Figure 1.1. Let there exist in a crystal having a width of the forbidden band E_g and a concentration of free electrons n, one type of electron-trapping levels (with energy u_1, concentration M, and electron concentration in these levels N) and one type of hole-trapping levels (with energy u_2 and hole concentration in the levels p). Neglecting the contribution of the recombination levels and assuming that $N, p >> n$, as usually occurs in high-resistance semiconductors, we can represent the free energy F_2 in the form

$$F_2 = nE_g + N(E_g - u_1) - pu_2 \simeq N(E_g - u_1 - u_2) = N\tilde{E}, \quad (1.11)$$

where the condition of electrical neutrality $p = n + N$ is used and the notation $\tilde{E} = E_g - u_1 - u_2$ is introduced. Thus, N in (1.11) should be understood as the concentration of electrons (holes) in the trapping levels, which exceeds by many orders of magnitude the concentration of free electrons (holes), while $\tilde{E}$ should be understood as the width of the forbidden band with an accuracy to the energies of the trapping levels. Assuming further than the function F_2 must be invariant with respect to the same symmetry transformation as the function F_1, we expand the energy $\tilde{E}$ near the phase transition temperature in a series in P and σ_k:

$$\tilde{E}(T, P, \sigma_k) = \tilde{E}_0(T) + \frac{1}{2}(\tilde{E}_P^{II})_0 P^2 + \frac{1}{4}(\tilde{E}_P^{IV})_0 P^4 +$$

$$+ \frac{1}{6}(\tilde{E}_P^{VI})_0 P^6 + \sum_k \tilde{E}_k'\sigma_k + \frac{1}{2}\sum_k\sum_i \tilde{E}_{ki}''\sigma_k\sigma_i + P^2\sum_k \tilde{E}_k'''\sigma_k, \quad (1.12)$$

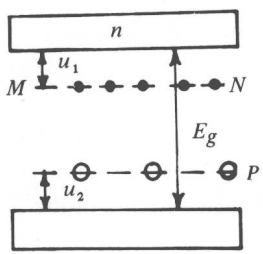

Figure 1.1. Band diagram of a ferroelectric semiconductor.

where the following notation is assumed:

$$(\tilde{E}_P^{II})_0 = \left(\frac{\partial^2 \tilde{E}}{\partial P^2}\right)_0 = a, \quad (\tilde{E}_P^{IV})_0 = \left(\frac{\partial^4 \tilde{E}}{\partial P^4}\right)_0 = b,$$

$$(\tilde{E}_P^{VI})_0 = \left(\frac{\partial^6 \tilde{E}}{\partial P^6}\right)_0 = c,$$

$$\tilde{E}_k' = \left(\frac{\partial \tilde{E}}{\partial \sigma_k}\right)_0, \quad \tilde{E}_{ki}'' = \left(\frac{\partial^2 \tilde{E}}{\partial \sigma_k \partial \sigma_i}\right)_0, \quad \tilde{E}_k''' = \left(\frac{\partial^3 \tilde{E}}{\partial P^2 \partial \sigma_k}\right). \tag{1.13}$$

Combining (1.8), (1.9), (1.11), and (1.13), we obtain the final expression for the free energy of the ferroelectric semiconductor:

$$F(T, P, \sigma_k, N) = F_{0N} + \frac{1}{2}\alpha_N P^2 + \frac{1}{4}\beta_N P^4 + \frac{1}{6}\gamma_N P^6 +$$

$$+ N\sum_k \tilde{E}_k' \sigma_k - \frac{1}{2}\sum_i \sum_k s_{Nik}\sigma_i \sigma_k - P^2 \sum_k \nu_{Nk}\sigma_k. \tag{1.14}$$

Renormalization of the coefficients in (1.9) leads to the following relations:

$$F_{0N} = F_0 + N\tilde{E}_0, \quad \alpha_N = \alpha + aN, \quad \beta_N = \beta + bN,$$
$$\gamma_N = \gamma + cN, \quad \nu_{Nk} = \nu_k - \tilde{E}_k''' N, \quad s_{Nik} = s_{ik} - \tilde{E}_{ik}'' N. \tag{1.15}$$

Equation (1.14) must be supplemented by the two equations of state

$$\frac{\partial F}{\partial P} = \mathcal{E} = \alpha_N P + \beta_N P^3 + \gamma_N P^5 - 2P\sum_k \nu_{Nk}\sigma_k, \tag{1.16}$$

$$\frac{\partial F}{\partial \sigma_k} = -u_k = N\tilde{E}_k' - \frac{1}{2}\sum_i s_{Nik}\sigma_i - P^2 \nu_{Nk}, \tag{1.17}$$

where $\mathcal{E}$ is the electric field; u_k are the components of the deformation tensor.

1.2. First- and Second-Order Phase Transitions

Before turning to an analysis of equations (1.14), (1.16), and (1.17) and the effect of electrons on the phase transition and the ferroelectric properties, we recall the principal consequence of the thermodynamic theory of ferroelectrics [15, 28-30]. For this, it is sufficient to analyze equations (1.14), (1.16), and (1.17) for $N = 0$. For simplicity, we will also assume $\sigma_k = \mathcal{E} = 0$. We will then consider separately the cases of first- and second-order phase transitions.

According to [15, 29], in the expression for the free energy (1.14) for a second-order phase transition, it is sufficient to retain the first two terms in the expansion in the polarization:

$$F = F_0 + \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4. \tag{1.18}$$

The equilibrium condition corresponds to the minimum of the free energy, i.e.,

$$\frac{\partial F}{\partial P} = \alpha P + \beta P^3 = 0, \tag{1.19}$$

$$\frac{\partial^2 F}{\partial P^2} > 0. \tag{1.20}$$

It follows from (1.19) that the paraelectric phase corresponds to the solution $P = 0$, while the ferroelectric phase corresponds to

$$P^2 = -\alpha/\beta.$$

It follows from condition (1.20)

$$\alpha + 3\beta P^2 > 0 \tag{1.21}$$

that the paraelectric region ($P = 0$) corresponds to $\alpha > 0$, while in the ferroelectric region ($P^2 = -\alpha/\beta$) α is negative. By denoting the phase-transition temperature (the Curie point) by $T = T_0$, expanding α in a series near $T = T_0$, and retaining the linear term, one can represent α in the form

$$\alpha = \alpha'_T (T - T_0) = \frac{2\pi}{C}(T - T_0), \tag{1.22}$$

where the Curie–Weiss constant is denoted by C. According to (1.21), $\beta > 0$ everywhere below the Curie point. We will assume that β does not depend on the temperature. Thus the temperature dependence of the spontaneous polarization near the Curie point is given by the relation

$$P^2 = \frac{\alpha'_T}{\beta}(T_0 - T), \qquad T < T_0. \tag{1.23}$$

We determine the behavior of the entropy S and heat capacity C_p near the Curie point:

$$S = -\frac{\partial F}{\partial T} = S_0 + \frac{(\alpha'_T)^2}{\beta}(T - T_0), \tag{1.24}$$

where $S_0 = -\partial F_0/\partial T$ is the entropy of the paraelectric phase. One can determine from (1.24) the discontinuity of the heat capacity $C_p = T(\partial S/\partial T)_p$ for a phase transition of second order:

$$\Delta C_p = \frac{T_0}{\beta}(\alpha'_T)^2. \tag{1.25}$$

In accordance with the general nature of second-order phase transitions, a finite discontinuity of the heat capacity occurs at the Curie point, while the latent heat of transition equals zero.

Assuming that $\mathfrak{E} \neq 0$ in (1.16), one can determine the temperature depen-