

LAYERED STRUCTURE IN FERROELECTRIC PHOTOCONDUCTORS

A. I. LARKIN and D. E. KHMEL'NITSKIĬ

Institute of Theoretical Physics, USSR Academy of Sciences

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An explanation is proposed for the occurrence of a periodic structure when a photoconductor is illuminated near the temperature of the first-order phase transition. The temperature region in which a layered structure is formed is determined. The motion of the layers resulting from the flow of current through the sample is considered.

1. INTRODUCTION

IN many semiconductors, illumination can produce a carrier density greatly exceeding the equilibrium value. Near a phase-transition point, the photoelectrons exert an appreciable influence on the character of the transition. In SbSI, for example, a decrease of the temperature of the ferroelectric transition was observed upon illumination<sup>[1,2]</sup>. The explanation proposed by Fridkin<sup>[3]</sup> for this fact is based on the increase of the width of the forbidden bands occurring on going over into the ferroelectric phase.

In addition, an inhomogeneous state of the ferroelectric was observed<sup>[4,5,6]</sup>, consisting of alternating layers of the paraelectric and ferroelectric phases. The occurrence of a layered structure becomes understandable if account is taken of the fact that the carriers can diffuse through the sample. This facilitates the formation of regions with increased carrier density near the transition temperature. These regions remain paraelectric, and the region with the low density becomes ferroelectric. Owing to the finite lifetime of the carriers, the dimensions of the regions cannot greatly exceed the distance over which the carriers have time to diffuse during their lifetime. This gives rise to a periodic structure with a period determined by the diffusion length. In this paper we determine the temperature and carrier-density regions in which such a layered structure is formed.

2. FUNDAMENTAL EQUATIONS

The change of electron energy in the phase transition is the result of the interaction between the electrons and the produced electric field and of the change of the energy spectrum due to the displacement of the ions. The small change of the carrier effective mass is insignificant, and we take into account only the change of the width of the forbidden band  $\epsilon_g = \epsilon_n + \epsilon_p$ . The energy connected with this change can be written in the form

$$\mathcal{E} = \epsilon_n n_n + \epsilon_p n_p, \tag{1}$$

where  $\epsilon_n$  and  $\epsilon_p$  are respectively the energies of the electrons and of the holes, and  $n_n$  and  $n_p$  are their concentrations.

The influence of this energy on the thermodynamics of a ferroelectric substance is appreciable only near the transition temperature. We shall assume that the first-

order transition is close to the critical point and that the free energy can be written in the form

$$F(P) = F_0 + \frac{1}{2}a(T - T_k)P^2 - \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \frac{1}{2}\alpha(\nabla P)^2. \tag{2}$$

Most of the results do not depend on the explicit form of the free energy.

At a fixed electron distribution, the equation determining the polarization  $P(z)$  is obtained by equating the forces  $-\delta F/\delta P$  exerted on the ions by the lattice, to the force exerted on the ions by the electrons. As a result we obtain the equation

$$a(T - T_k)P - bP^3 + cP^5 - \alpha\Delta P + n_n \frac{d\epsilon_n}{dP} + n_p \frac{d\epsilon_p}{dP} - E = 0. \tag{3}$$

The electric field  $E$  is determined by the Poisson equation

$$\text{div}(E + 4\pi P) = 4\pi e(n_n - n_p). \tag{4}$$

When the interaction with the electrons is disregarded,  $F(P)$  has two minima corresponding to the ferroelectric and paraelectric phases. At  $T_0 = T_C + 3b^2/4ac$ , the values of the free energy at the points of the minima coincide, and at this temperature the phases can coexist. In this case there exist, beside the homogeneous solutions, also a solution with a single interphase boundary, in the form

$$P^2(z) = \frac{P_0^2}{2} \left( 1 + \text{th} \frac{z}{r_c} \right), \tag{5}$$

where  $P_0$  is the jump of the polarization at the transition point, and  $r_c = [\alpha/a(T_0 - T_C)]^{1/2}$  is the thickness of the boundary layer.

If the temperature is close to the transition temperature,  $T_0 - T \ll T_0 - T_C$ , then the electrons have little influence on the magnitude of the spontaneous polarization  $P_0$ , but to determine the position of the boundaries and their number. To take into account the influence of the electrons on the phase transition, it is necessary to find their spatial distribution, which is determined by the diffusion equations

$$\begin{aligned} \nabla [D_n \{ \nabla n_n + n_n (\nabla \epsilon_n + eE) / T \}] + G - R &= 0, \\ \nabla [D_p \{ \nabla n_p + n_p (\nabla \epsilon_p - eE) / T \}] + G - R &= 0. \end{aligned} \tag{6}$$

Here  $D_n$  and  $D_p$  are the electron and hole diffusion coefficients, and  $G$  and  $R$  are the numbers of the electron-hole pairs generated by the light or recombining in a unit volume per unit time.

We shall seek below periodic solutions of the system

(3), (4), and (6), with a period larger than the correlation length  $r_c$  and the Debye length  $r_D$ , which are assumed to be small compared with the diffusion length. At small distances from the boundaries it is possible to disregard the last two terms of (6) and to neglect the particle fluxes through the boundary. Then

$$n_n \sim \exp\left[-\frac{\varepsilon_n + e\varphi}{T}\right], \quad n_p \sim \exp\left[-\frac{\varepsilon_p - e\varphi}{T}\right], \quad (7)$$

where  $\varphi$  is the potential of the electric field.

At distances that are large compared with  $r_D$  and  $r_c$ , we obtain from the Poisson equation (4) and from (7) the electroneutrality condition  $n_n = n_p = n/2$ . The ratio of the asymptotic values yields

$$n_s/n_p = \exp[-\Delta\varepsilon_g/2T], \quad (8)$$

where  $\Delta\varepsilon_g = \varepsilon_g^S - \varepsilon_g^P$  is the jump in the width of the forbidden band.

In a region far from the boundary, when the derivatives  $\nabla\varepsilon_p$  and  $\nabla\varepsilon_n$  can be neglected, the equations of (6), when account is taken of the electroneutrality, can be reduced to the form

$$\frac{d^2n}{dz^2} + \frac{1}{D}(G - R) = 0, \quad (9)$$

where  $D = 2/(D_n + D_p)$  is the coefficient of bipolar diffusion. At large photoelectron concentrations, the recombination term can be regarded as linearly dependent on the concentration. Equation (9) then takes the form

$$\frac{d^2n}{dz^2} + \frac{1}{L^2}(n_0 - n) = 0, \quad (10)$$

where  $L = \sqrt{D\tau}$ , and  $n_0$  is the generated carrier concentration, which is proportional to the illumination and to the carrier lifetime  $\tau$ , the latter depending on the phase of carriers. The linearity assumption is immaterial for the obtained qualitative results.

The condition for the equality of the carrier-number fluxes to the boundary

$$D^s \frac{dn_s}{dz} = D^p \frac{dn_p}{dz} \quad (11)$$

is compatible with relation (8) and is the boundary condition for (10) on the interphase boundary.

### 3. EQUILIBRIUM BETWEEN PHASES

Let us obtain the condition for the equilibrium of the boundary in the presence of electrons. To this end, we multiply (3) by the derivative  $dP/dz$  and integrate over  $z$  in a region larger than  $r_D$  and  $r_c$ , but smaller than  $L$ . The electron distribution in this region can be written in the form (7); taking (4) into account, we obtain

$$F_s(P) + Tn_s + E_s^2/8\pi = F_p(P) + Tn_p + E_p^2/8\pi. \quad (12)$$

Here  $E_s$  and  $E_p$  denote the electric field far from the transition region in the ferroelectric and paraelectric phases, respectively. This condition has the simple meaning of the equality of the pressures exerted by the two phases on the boundary. In the derivation of the equilibrium condition (12), the explicit form of the free energy (2) is immaterial.

At temperatures close to the first-order transition temperature, the difference between the free energies is expressed in terms of the heat of the transition  $\Delta Q$

and the proximity to the transition point  $T_0 - T$ . Neglecting the pressure of the electric field in the condition (12), we obtain

$$\frac{\Delta Q}{T_0^2}(T_0 - T) = n_s \left[ \exp\left(\frac{\Delta\varepsilon_g}{2T}\right) - 1 \right], \quad (13)$$

where we have used the connection between the concentrations  $n_s$  and  $n_p$  (8). The quantity  $n_s$  in (13) should be obtained from the diffusion equation. Its order of magnitude is  $n_0$  and it is determined both by the intensity of the illumination and by the distance between boundaries.

The temperature at which one boundary is at equilibrium is the temperature of the phase transition in the absence of electrons. To determine this temperature, let us find for the diffusion equation (11) a solution satisfying the boundary conditions (7) and equal to  $n_0^S$  and  $n_0^P$  respectively at infinity:

$$n(z) = n_0^s - \frac{n_0^s - n_0^p e^{-\Delta\varepsilon_g/2T}}{1 + \sqrt{\tau_p D^s / \tau_s D^p} e^{-\Delta\varepsilon_g/2T}} e^{-z/L_s}, \quad z < 0;$$

$$n(z) = n_0^p + \frac{n_0^s e^{\Delta\varepsilon_g/2T} - n_0^p}{1 + \sqrt{\tau_s D^p / \tau_p D^s} e^{\Delta\varepsilon_g/2T}} e^{-z/L_p}, \quad z > 0. \quad (14)$$

Assuming that the diffusion coefficients change little in the phase transition,  $D^S = D^P$ , we can simplify (14) and obtain the following expression for the carrier density  $n_s$  near the boundary, which enters into the equilibrium condition (13):

$$n_s = n_0^s \frac{\alpha}{1 + \alpha} \left( 1 + \sqrt{\frac{\tau_p}{\tau_s}} \right), \quad (15)$$

where we put  $\alpha = \sqrt{\tau_p / \tau_s} \exp(-\Delta\varepsilon_g/2T)$ , and use the relation  $n_0^P = n_0^S \tau_p / \tau_s$ . We shall henceforth omit the superscript of  $n_0^S$ .

The transition temperature is determined by formula (13) and equals

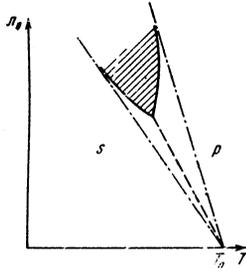
$$T_0' = T_0 - \frac{T_0^2}{\Delta Q} n_0 \frac{\alpha}{1 + \alpha} \left( 1 + \sqrt{\frac{\tau_p}{\tau_s}} \right) \times [e^{\Delta\varepsilon_g/2T} - 1]. \quad (16)$$

Thus, the change of the transition temperature is proportional to the carrier density. The transition line is shown dashed in the figure. When  $\Delta\varepsilon_g \ll T$  and the lifetimes in both phases are equal, formula (16) coincides with Fridkin's result<sup>[2,3]</sup>:

$$T_0 - T_0' = n_0 T_0 \Delta\varepsilon_g / 2\Delta Q. \quad (17)$$

### 4. LAYERED STRUCTURE IN WHISKER CRYSTALS

It is seen from (16) that at a fixed illumination one boundary can be in equilibrium only at a definite temperature. There exists, however, a finite temperature interval, in which a system of boundaries can be in equilibrium. This occurs because the carrier density  $n_s$  near the boundary, which determines the temperature, depends not only on the illumination but also on the distance between boundaries. Such a system of boundaries should form a periodic structure, for only in this case does the diffusion equation have a solution in which  $n_s$  is the same on all boundaries. The condition for the equilibrium of the boundaries (13) gives the relation between the dimensions  $x$  and  $y$  of the ferroelectric and



paraelectric layers. Solving the diffusion equation (10) for the periodic structure, we obtain  $n_S$ , and substituting its value in the equilibrium condition (13), we get

$$\operatorname{th} \frac{x}{2L_s} \operatorname{cth} \frac{y}{2L_p} = \frac{1}{\alpha} \frac{t - \alpha \sqrt{\tau_p/\tau_s}}{1-t}, \quad (18)$$

where

$$t = (T_0 - T)\Delta Q / T_0^2 n_0 [\exp(\Delta \varepsilon_g / 2T) - 1].$$

It is seen from this formula that the periodic structure can exist in the temperature interval

$$\frac{T_0^2 n_0 (e^{\Delta \varepsilon_g / 2T} - 1)}{\Delta Q} > T_0 - T > \frac{T_0^2 n_0 (e^{\Delta \varepsilon_g / 2T} - 1)}{\Delta Q} \alpha \sqrt{\frac{\tau_p}{\tau_s}}. \quad (19)$$

In the figure, this region is bounded by dash-dot lines. The period of the structure can be arbitrary, but a limitation exists on the phase dimensions:

$$\operatorname{th} \frac{x}{2L_s} \leq \frac{1}{\alpha} \frac{t - \alpha \sqrt{\tau_p/\tau_s}}{1-t}, \quad \alpha \sqrt{\frac{\tau_p}{\tau_s}} < t < \frac{\alpha}{1+\alpha} \left( 1 + \sqrt{\frac{\tau_p}{\tau_s}} \right),$$

$$\operatorname{th} \frac{y}{2L_p} \leq \alpha \frac{1-t}{t - \alpha \sqrt{\tau_p/\tau_s}}, \quad \frac{\alpha}{1+\alpha} \left( 1 + \sqrt{\frac{\tau_p}{\tau_s}} \right) < t < 1. \quad (20)$$

The equal sign in the limitations (20) corresponds to the equilibrium of one layer of the ferroelectric phase inside the paraelectric phase and one layer of the paraelectric phase inside the ferroelectric phase.

The condition for mechanical equilibrium, which imposes significant limitations on the equilibrium dimensions of the layers, does not determine these dimensions uniquely. To determine the period, it is necessary to supplement the obtained equilibrium condition (18) with the condition for the stability against fluctuation production and vanishing of the regions. Such a condition, under thermodynamic equilibrium, is equivalent to the condition that the free energy have a minimum. It can be assumed that in this case the fluctuation probability is determined by the minimum work. Then the probability of creation of a new layer is proportional to  $\exp(-2\sigma S/T)$ , and the vanishing probability is  $\exp(-R_{\min} S/T)$ , where  $\sigma$  is the surface tension and  $R_{\min}$  is the minimum work that must be performed against the pressure forces in order to close the boundaries of the layer. Stability corresponds to equality of these probabilities:

$$R_{\min} = 2\sigma. \quad (21)$$

The minimum work is proportional to the carrier concentration  $n_0$ . Therefore, for sufficiently low concentrations,  $R_{\min}$  is smaller than the surface energy at any temperature, the homogeneous state will be the stable one, and the layered structure will be metastable

(see the figure). The boundary of the region in which the layered structure is stable and the homogeneous state is metastable is determined on the  $n_0 T$  diagram from the condition (21) for the case when there is only one layer in the sample. To calculate the minimum work in this case, we find the pressure on the boundary of the layer, which equals the difference between the right and left sides of (12). Finding  $n_S$  from the diffusion equation, we obtain

$$p = T n_0 (e^{\Delta \varepsilon_g / 2T} - 1) \alpha \frac{\sqrt{\tau_p/\tau_s} + \operatorname{th}(x/2L_s)}{1 + \alpha \operatorname{th}(x/2L_s)} - \frac{\Delta Q}{T_0} (T_0 - T). \quad (22)$$

In order to obtain an analogous expression for the layer of the paraelectric phase, it is necessary to replace in (22)  $\operatorname{th}(x/2L_S)$  by  $\operatorname{coth}(y/2L_p)$ . The equilibrium dimension is determined from the condition that the pressure vanish, corresponding to the equal sign in the limitations (20). Integrating the pressure with respect to  $x$  from the equilibrium dimension to zero, we obtain the minimum work. Condition (21) then becomes

$$\sigma = L_s T_0 n_0 (e^{\Delta \varepsilon_g / 2T} - 1) \frac{\alpha}{1-\alpha} \left\{ \left[ \frac{1-\alpha}{\alpha} t + 1 - \sqrt{\frac{\tau_p}{\tau_s}} \right] \right. \quad (23)$$

$$\left. \times \operatorname{arctg} \left( \frac{1-t - \alpha \sqrt{\tau_p/\tau_s}}{1-t} - \frac{1 - \alpha \sqrt{\tau_p/\tau_s}}{1+\alpha} \ln \left[ \alpha \frac{1-2t + \alpha \sqrt{\tau_p/\tau_s}}{\alpha(1-t) + t - \alpha} \right] \right) \right\}.$$

It determines the connection between  $n_0$  and  $T$  on the boundary of the stability region of the layered structure. The second branch of this boundary, corresponding to the loss of stability against transformation into a homogeneous ferroelectric phase, is described by an equation similar to (23). The phase diagram in the  $n_0 T$  plane is shown in the figure. The critical concentration, below which the layered structure is metastable at all temperatures, is obtained from (23) at a temperature equal to the transition temperature:

$$n_c = \frac{\sigma}{L_s T_0 (e^{\Delta \varepsilon_g / 2T} - 1) \alpha (1 - \alpha \sqrt{\tau_p/\tau_s}) \ln(2/(1+\alpha))}. \quad (24)$$

The period of the layered structure is infinite on the boundary of the stability region and decreases towards the inside. It can be determined from Eq. (21). By calculating the work  $R_{\min}$  required to close the boundaries of one layer of the layered structure with a given period, and substituting it in (21), we can determine periods for all other values of  $n_0$  and  $T$  in the stability region.

It must be borne in mind that the times of establishment of the equilibrium period can be large. Therefore a temperature hysteresis of the phase transition is observed in experiment.

## 5. COEXISTENCE OF PHASES IN SAMPLES OF LARGE AND SMALL DIMENSIONS

We considered above, in accordance with the experimental conditions, the phase transition in filamentary samples (whiskers) whose thickness is of the order of the diffusion length. The layered structure could then be regarded as homogeneous, and the bending of the boundaries could be neglected. In a sample of infinite dimensions, this bending cannot be neglected. For example, to determine the limits of the stability region it is necessary to determine the stability of a ferroelec-

tric region surrounded on all sides by a paraelectric phase. Neglecting anisotropy, this region has the form of a sphere. The pressure on its boundary is

$$p = \frac{2\sigma}{r} + Tn_s(e^{\Delta\epsilon_g/2T} - 1) - \frac{\Delta Q}{T_0}(T_0 - T). \quad (25)$$

The first term corresponds to surface pressure, and the two other are analogous to the corresponding terms in (12) and (13). Solving the diffusion equation for the ferroelectric sphere inside the paraelectric phase, we obtain the carrier concentration on the surface of the sphere:

$$n_s = \alpha n_0 \left\{ r + \left[ r \sqrt{\frac{\tau_p}{\tau_s}} - L_s \left( 1 + \frac{\tau_p}{\tau_s} \right) \right] \text{th} \frac{r}{L_s} \right\} \\ \times \left\{ \left[ r - L_s \left( \alpha + \sqrt{\frac{\tau_p}{\tau_s}} \right) \right] \text{th} \frac{r}{L_s} + \alpha r \right\}^{-1}. \quad (26)$$

At a fixed illumination intensity,  $n_s$  decreases with increasing radius. Therefore, if the temperature is sufficiently close to the transition line and the carrier concentrations are sufficiently large, the pressure goes twice through zero as a function of the radius of the sphere. The equilibrium radius corresponds to  $p = 0$  and  $\partial p / \partial r < 0$ . Just as in the one-dimensional case, mechanical equilibrium can be realized in a finite temperature interval. The condition of stability against fluctuation production or vanishing of the ferroelectric region is analogous to the one-dimensional condition (21) and is given by

$$\int_0^{r_0} p(r) 4\pi r^2 dr = 0, \quad (27)$$

where  $r_0$  is the equilibrium radius of the region.

Just as in the one-dimensional case, this condition can be satisfied only for sufficiently large carrier concentrations. Equation (27) determines the relation between the temperature and the concentration at which the region of the ferroelectric phase inside the paraelectric phase is in equilibrium. Together with the analogous equation for the paraelectric phase inside the ferroelectric one, Eq. (27) determines the boundary of the stability region of the inhomogeneous state on the  $n_0 T$  diagram; this limit has a form similar to that shown in the figure.

In the opposite limiting case, when all the sample dimensions  $l$  are much smaller than the diffusion length  $L$ , the inhomogeneity of the carrier concentration, due to the short lifetime, can be neglected. In this case the problem can be solved thermodynamically for the case of equal lifetimes.

The free energy of the sample is given by

$$F = \left[ \left( F_s + Tn_s \ln \frac{n_s}{n_0} + \frac{\Delta\epsilon_g n_s}{2} \right) x \right. \\ \left. + \left( F_p + Tn_p \ln \frac{n_p}{n_0} \right) (1-x) \right] V + \sigma S. \quad (28)$$

Here  $x$  is the fraction of the volume  $V$  of the sample occupied by the ferroelectric phase and  $S$  is the area of the boundary. The electron densities  $n_s$  and  $n_p$  are expressed with the aid of (8) in terms of  $x$  and the total number of carriers  $n_0 V$ . From the equilibrium condition

$\partial F / \partial x = 0$  we obtain

$$x = \frac{(T_0 - T)\Delta Q - T_0^2 n_0 (1 - e^{-\Delta\epsilon_g/2T})}{(T_0 - T)\Delta Q (1 - e^{-\Delta\epsilon_g/2T})}. \quad (29)$$

The region of existence of the inhomogeneous state is determined by the condition  $0 < x < 1$ , which assumes, when account is taken of (29), the form

$$\frac{T_0^2 n_0}{\Delta Q} (1 - e^{-\Delta\epsilon_g/2T}) < T_0 - T < \frac{T_0^2 n_0}{\Delta Q} (e^{\Delta\epsilon_g/2T} - 1). \quad (30)$$

To determine the region of temperatures and concentrations in which the inhomogeneous state is stable, it is necessary to compare its free energy with the free energy of the homogeneous ferroelectric and paraelectric phases. As a result we obtain the equation for the boundary of the stability region:

$$\frac{\sigma}{l} + Tn_0 - \frac{\Delta Q(T_0 - T)}{T_0(1 - e^{-\Delta\epsilon_g/2T})} - Tn_0 \ln \frac{\Delta Q(T_0 - T)}{T_0^2 n_0 (1 - e^{-\Delta\epsilon_g/2T})} = 0, \\ \frac{\sigma}{l} + Tn_0 - \frac{\Delta Q(T_0 - T)}{T_0(e^{\Delta\epsilon_g/2T} - 1)} - Tn_0 \ln \frac{\Delta Q(T_0 - T)e^{\Delta\epsilon_g/2T}}{T_0^2 n_0 (1 - e^{-\Delta\epsilon_g/2T})} = 0. \quad (31)$$

Equation (31) can also be obtained, as before, by equating the surface energy to the work required to displace the boundaries.

At a carrier concentration below  $n_c \sim \sigma / l \Delta\epsilon_g$ , the inhomogeneous state is metastable and the stable state is the homogeneous ferroelectric or paraelectric phase. The line of transition between them is obtained by equating the free energy<sup>[3]</sup>

$$T_0 - T_0' = \frac{n_0 T_0 \Delta\epsilon_g}{2\Delta Q}. \quad (32)$$

The diagram in the  $n_0 T$  plane has the form shown in the figure.

## 6. MOTION OF LAYERS

Motion of a layered structure under the influence of an electric field was observed experimentally in<sup>[7]</sup>. As noted by Fridkin, this fact can be explained by recognizing that heat is released or absorbed when current flows through the boundary (Peltier effect). Therefore the dependence of the temperature on the coordinates is a sawtooth function—the left and right boundaries of one layer have different temperatures. The carrier concentration, on the other hand, is determined only by the location of the boundaries. We see therefore that it is impossible to satisfy the equilibrium condition (13) on both boundaries, and the boundaries are acted upon by forces proportional to the difference between the boundary temperature and the mean temperature. As a result of the dielectric losses, the motion of the layers has a finite velocity. In order to determine this velocity, it is necessary to take into account in (3) the dependence of the polarization  $P$  on the time, and to add to it the term  $\gamma \dot{P}$ . The coefficient  $\gamma$  as expressed in terms of the tangent of the loss angle and is connected with the dielectric constant in the paraelectric phase by the relation

$$a(T - T_c) + i\omega\gamma = 4\pi / \epsilon. \quad (33)$$

Multiplying the obtained equation for the polarization by  $dP/dx$  and integrating over the coordinate, we can obtain, in analogy with the derivation of (12), an equation of motion for the boundary. Recognizing that in the case

of uniform motion  $P$  depends on the combination  $z - vt$ , we have

$$\gamma v \int_{-\infty}^{+\infty} dz \left( \frac{dP}{dz} \right)^2 = - \frac{\Delta Q}{T_0} (T_0 - T) + T n_s (e^{\Delta \epsilon_g / 2T} - 1). \quad (34)$$

The slow motion of the boundary has little influence on its structure. Therefore, we can use formula (5) for the  $P(z)$  dependence. It is also necessary to recognize that the distance between the boundaries, and consequently also  $n_s$ , is established in such a way that the velocities of all boundaries are equal. On different boundaries of the same layer, the left sides of (34) have different signs, and the right ones have different temperatures. As a result we get

$$v = \frac{\Delta Q \Delta T \sqrt{2} r_c}{2 T_0 P_0 \gamma}. \quad (35)$$

For a quantitative comparison with experiment it is necessary to know the difference  $\Delta T$  of the boundary temperatures of one layer; this difference enters in formula (35) and is proportional to the Peltier heat, which in turn is equal to the product of the current by the contact potential difference.

## 7. CONCLUSION

The considerations advanced above allow us to state that in ferroelectric semiconductors in which the carrier density exceeds a critical value  $n_c$ , an inhomogeneous state is produced in a temperature interval close to the transition temperature. In whiskers, this state is realized in the form of a periodic layered structure. At concentrations on the order of the critical value, the period of the structure coincides with the diffusion length and decreases with increasing concentration. At sufficiently high concentrations, the temperature interval in which the layered structure is stable is proportional to the concentration, and as  $\Delta \epsilon_g \sim T$  it coincides in order of magnitude with the shift of the transition.

The described phenomena are apparently observed in SbSI. For this substance, the diffusion length of the electrons is  $L_n \approx 0.03$  cm. If the diffusion length of the holes does not differ greatly from  $L_n$ , then the typical period of the layered structure has the same order 0.01 cm, in good agreement with experiment. As shown by estimates of the surface energy, presented in the appendix,  $\sigma \approx 5 \times 10^2$  erg/cm<sup>2</sup> for SbSI. From this we can obtain by means of formula (24) the critical concentration  $n_c \sim 10^{17}$  cm<sup>-3</sup>, which also agrees with the observed value. The authors thank E. I. Rashba and V. M. Fridkin for numerous discussions.

## APPENDIX

### SURFACE ENERGY OF BOUNDARY

The energy of the boundary separating two phases consists of the pure lattice energy, the energy of the electric field, and the energy of the carriers. The lattice energy results from the fact that the polarization in the transition layer assumes not only its equilibrium values, but also all the intermediate values, while the free energy is not equal to its minimal values, but exceeds them slightly. The additional energy per unit area

is equal to

$$\sigma_0 = \int_{-\infty}^{+\infty} [F(z) - F_0] dz. \quad (A.1)$$

Using expression (2) for the free energy and taking (3), (5), and (33) into account, we obtain

$$\sigma_0 = \frac{2\pi P_0}{\epsilon} r_c. \quad (A.2)$$

The contribution from the electric field to the surface energy is connected with the fact that in a layer of thickness  $r_D = (T\epsilon/4\pi e^2 n_0)^{1/2}$  the carrier density is not equal to its equilibrium values, and the field differs from zero. Assuming that  $r_c \ll r_D \ll L$ , we obtain in the self-consistent field approximation<sup>[8]</sup> the system of equations

$$\begin{aligned} \frac{d^2\varphi}{dz^2} &= - \frac{4\pi e}{\epsilon} (n_n - n_p), \\ T \ln \frac{n_n}{n_0} + e\varphi - \epsilon_n(z) &= 0, \\ T \ln \frac{n_p}{n_0} - e\varphi - \epsilon_p(z) &= 0, \end{aligned} \quad (A.3)$$

where

$$\epsilon_n = (U + \Delta \epsilon_g / 2) \theta(z), \quad \epsilon_p = (-U + \Delta \epsilon_g / 2) \theta(z),$$

and  $U$  denotes the change of the energy corresponding to the middle of the forbidden band. The boundary conditions are of the form

$$\frac{d\varphi}{dz}(\pm\infty) = 0, \quad \varphi(0+) = \varphi(0-), \quad \frac{d\varphi(0+)}{dz} - \frac{d\varphi(0-)}{dz} = - \frac{4\pi P_0}{\epsilon}. \quad (A.4)$$

Solving (A.3) with the aid of (A.4) and choosing  $\varphi(-\infty) = 0$ , we obtain for the potential on the boundary

$$\exp\left(\frac{\Delta \epsilon_g}{4T}\right) \text{sh} \frac{e\varphi(0) - U}{2T} + \text{sh} \frac{e\varphi(0)}{2T} = \frac{\pi P_0}{\sqrt{2\pi\epsilon T n_0}}. \quad (A.5)$$

In formula (A.1) for the surface energy we can take into account the dependence of the free energy on the electric field and on the carrier density. In the self-consistent field approximation, with allowance for (A.3), we have

$$\sigma = \sigma_0 + \frac{\epsilon}{8\pi} \int_{-\infty}^{+\infty} \varphi \frac{d^2\varphi}{dz^2} dz. \quad (A.6)$$

Substituting in (A.6) the solution (A.3) subject to the condition (A.4), we obtain finally

$$\sigma = \sigma_0 + \frac{1}{2} P_0 \varphi(0) - \frac{2T}{\pi e} \sqrt{2\pi\epsilon T n_0} \left[ \text{sh}^2 \frac{e\varphi(0)}{4T} + \exp\left(\frac{\Delta \epsilon_g}{4T}\right) \text{sh}^2 \frac{e\varphi(0) - U}{4T} \right]. \quad (A.7)$$

In the case of SbSI considered here, it can be assumed that  $U \sim \Delta \epsilon_g \sim T$  and  $P_0 \gg e n_0 r_D$ . Then the surface energy is

$$\sigma = \sigma_0 + \frac{TP_0}{e} \left[ \ln \frac{2\pi P_0}{\sqrt{2\pi\epsilon T n_0} \{1 + \exp[(\Delta \epsilon_g - 2U)/4T]\}} - 1 \right]. \quad (A.8)$$

In the other limiting case  $U \ll T$ ,  $\Delta \epsilon_g \ll T$ ,  $P_0 \ll e n_0 r_D$ , and

$$\sigma = \sigma_0 + \frac{3\pi P_0^2 T}{16e\sqrt{2\pi\epsilon T n_0}} + \frac{UP_0}{4e} - \frac{U^2}{16\pi e T} \sqrt{2\pi\epsilon T n_0}. \quad (A.9)$$

According to this expression, the surface energy can become negative at sufficiently high carrier density and

when  $U \neq 0$ . The case considered in this paper corresponds to positive surface energy. A negative surface energy should lead to an inhomogeneous state with a characteristic dimension on the order of  $r_D$ .

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