

# Photoelectric domain structure. Theory

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We construct a phenomenological theory that explains the onset of a steady electrical domain structure in ruby crystals under intense laser illumination. The theory is based on the assumption that the photovoltaic current arising in the centrosymmetric crystal in the presence of an electric field is directed counter to the field. In this case the resistance of the sample in zero field is negative, giving rise to an instability and to the spontaneous appearance of an electric field in the crystal. We study the various types of steady field distributions in the crystal for different values of the applied field and discuss the possible mechanism for the appearance of the negative photovoltaic current. The theoretical conclusions are in complete agreement with the experimental results.

## INTRODUCTION

It was shown by Liao, Glass, and Humphrey<sup>1</sup> that intense laser illumination of concentrated ruby at low temperature gives rise to a strong ( $\sim 10^6$  V/cm) internal electric field in the crystal. This field was detected from the pseudo-Stark splitting which is caused in the luminescence lines. After the illumination was shut off the internal field persisted unchanged over a long period of time at room temperature on account of the extremely low dark conductivity of ruby.

The appearance of an internal field was interpreted<sup>1</sup> as a photovoltaic effect analogous to that observed earlier in ferroelectrics.<sup>2</sup> However, unlike the case of ferroelectrics, the crystal structure of ruby has a center of inversion. In ruby the  $\text{Cr}^{3+}$  impurity ions occupy two noncentrosymmetric positions in the centrosymmetric  $\text{Al}_2\text{O}_3$  lattice; these positions, *A* and *B*, differ by inversion. Therefore, for a uniform distribution of  $\text{Cr}^{3+}$  ions over these positions the ruby crystal has a center of inversion and no photovoltaic current can exist.<sup>1)</sup> For this reason it was conjectured in Ref. 1 that during the growth of the crystal the  $\text{Cr}^{3+}$  ions for unknown reasons preferentially occupy one of the positions, *A* or *B*, so that it becomes possible to have a photovoltaic current *J* parallel to the  $C_3$  axis of the crystal and proportional to the difference in concentrations of chromium in these positions. This current gives rise to an electric field **E** (also parallel to  $C_3$ ) whose time evolution during the illumination is described by the following equation, which expresses the condition that the total current is equal to zero (for an open-circuited sample):

$$\frac{\epsilon}{4\pi} \frac{dE}{dt} + j = 0, \quad (1)$$

where the first term is the displacement current,  $j = \sigma E + J$ , and  $\sigma$  is the electrical conductivity arising during the illumination. Under the experimental conditions of Ref. 1 both  $\sigma$  and *J* depended in the same way on the illumination intensity (provided that it was not too high), so that the steady-state value of the field  $E_s = -J/\sigma$  did not depend on the intensity.

It was recently observed by Basun, Kaplanskii, and

Feofilov<sup>3,4</sup> that the laser illumination of ruby actually gives rise to domains in which the internal electric field  $\pm E_s$ , parallel to the  $C_3$  axis, is equal in magnitude but opposite in direction. The total volume of the domains with fields  $+E_s$  and  $-E_s$  are equal. If at the time of the illumination a field  $E_0$  smaller than  $E_s$  is applied to the crystal along the  $C_3$  axis with the aid of a voltage source, the domain structure persists and fields in the domains remain equal to  $\pm E_s$ . However, the total volume of the domains with field along  $\pm E_0$  increases at the expense of domains with the field in the opposite direction. On the other hand, if  $E_0 > E_s$ , the domain structure does not form, and the internal field does not persist after the illumination is stopped and the voltage source is turned off. It has also been shown<sup>3-5</sup> that the dependence of  $E_s$  on the temperature at which the illumination took place has the characteristic form for a second-order phase transition with a critical temperature  $T_c \approx 150$  K. The effect is observed only if the chromium concentration is sufficiently high and the illumination is not too intense.<sup>1,4</sup>

The results of Refs. 3–5 are at odds with the interpretation offered in Ref. 1. In fact, to explain the existence of domains with fields  $\pm E_s$  from the point of view expressed in Ref. 1, and would have to suppose that the crystal contains regions of equal volume with equal and opposite differences in the chromium concentrations in positions *A* and *B*. Not only is such an impurity distribution improbable, but the hypothesis fails to explain the redistribution of the volumes of the domains in an applied field or the critical temperature dependence of the internal field  $E_s$ .

One of us has offered an explanation for the effect, attributing the formation of the photoinduced domains in ruby to an electrical instability.<sup>6</sup> It is assumed that the photovoltaic current arising in the centrosymmetric crystal in the presence of an electric field is directed counter to the field. If the absolute value of the photovoltaic current in the low-field region exceeds the conduction current, the resistance of the sample turns out to be negative and the state with zero field is unstable. Under these conditions an electric field should arise spontaneously. The proposed model leads to

conclusions in qualitative agreement with the experimental data.<sup>1-5</sup> A study of the volt-ampere characteristics<sup>5</sup> of an illuminated ruby crystal has shown that under certain conditions the current flowing through the sample is directed counter to the field. This result confirms the basic assumption of Ref. 6.

The mechanism proposed in Ref. 6 for explaining the formation of a photovoltaic current is similar to the mechanism described in Ref. 1. Specifically, the appearance of this current is attributed to a difference in the populations of the excited metastable states  ${}^2E$  of the chromium ions in positions  $A$  and  $B$  (but not, as in Ref. 1, to a difference in the concentrations of chromium ions in these positions). A difference in the populations of the excited states arises in an electric field because the  $A$  and  $B$  positions become nonequivalent. In Ref. 1 it was assumed that the generation of the photovoltaic current occurs in two stages, of which the first is the excitation of the  ${}^2E$  states. Then the photovoltaic current is proportional precisely to the difference in the populations of the  ${}^2E$  states of the chromium ions in positions  $A$  and  $B$ . Here the current can, in principle, be directed either along the field or counter to it. In the latter case the aforementioned instability arises, leading to the spontaneous vanishing of the center of inversion of the crystal and to the appearance of an electric field.

In the present paper we construct a theory of the photoelectric instability on the basis of the hypothesis of Ref. 6. We find the possible types of steady distributions of the electric field in the crystal for various values of the applied field  $E_0$  and show that an electrical domain structure arises for  $E_0 < E_s$ . These field distributions determine the optical and electrical properties of the illuminated crystals. We study the volt-ampere characteristic of the illuminated sample and consider hysteresis effects. In addition, we consider the possible mechanisms for the formation of a photovoltaic current in crystals having a center of inversion in the presence of an electric field.

## 2. QUALITATIVE PICTURE OF THE PHOTOELECTRIC INSTABILITY

The illumination of a crystal having a center of inversion does not give rise to a photovoltaic current. In an electric field, however, such a current does arise. Although the magnitude and direction of the current can in general de-

pend on the relative orientation of the field, the polarization vector of the light, and the crystallographic axes, experiments<sup>1,4,5</sup> imply that there is no polarization dependence in ruby—the current is directed along the  $C_3$  axis and depends solely on the projection of the field onto this axis. Thus in an approximation linear in the electric field  $E$  the expression for the photovoltaic current can be written

$$J(E) = -\alpha n(nE), \quad (2)$$

where  $n$  is the unit vector along the  $C_3$  axis and  $\alpha$  is a photovoltaic coefficient which depends on the intensity and wavelength of the radiation, on the impurity concentration, and on the temperature. The negative sign in (2) corresponds to the basic assumption of the theory—that the photovoltaic current is directed counter to the field.

We shall hereafter consider the one-dimensional situation, assuming that the illuminated sample is a thin slab with surfaces perpendicular to the  $C_3$  axis. Such a geometry corresponds to the experimental conditions of Refs. 1 and 3-5.

The current density in an illuminated sample is given by the expression

$$j = f(E), \quad f(E) = \sigma E + J(E), \quad (3)$$

where  $j$ ,  $E$ , and  $J$  are the projections of the corresponding vector quantities onto the  $C_3$  (i.e.,  $x$ ) axis, and  $\sigma$  is the conductivity arising on illumination.

According to what we have said, in low fields we have  $J(E) = -\alpha E$ . In this case, if  $\alpha > \sigma$ , the contribution of the photovoltaic current is dominant and the net current  $j$  is directed counter to the field. Then the resistance in low fields is negative, giving rise to the photoelectric instability. Since the relationship between the coefficients  $\alpha$  and  $\sigma$  depends on the temperature, impurity concentration, and radiation intensity, the onset of the photoelectric instability will clearly depend on these quantities in a critical manner. In rather large fields the net current should clearly be directed along the field. Thus, for  $\alpha > \sigma$  the  $f(E)$  curve is as shown in Fig. 1a.

Let us discuss the consequences of a dependence of this form. First of all, for fields between  $-E_t$  and  $E_t$  there is negative differential conductivity, and therefore the homogeneous state is unstable in a field which lies in this interval. In the particular case of an open-circuited sample, this follows immediately from (1) and (3): the steady state with

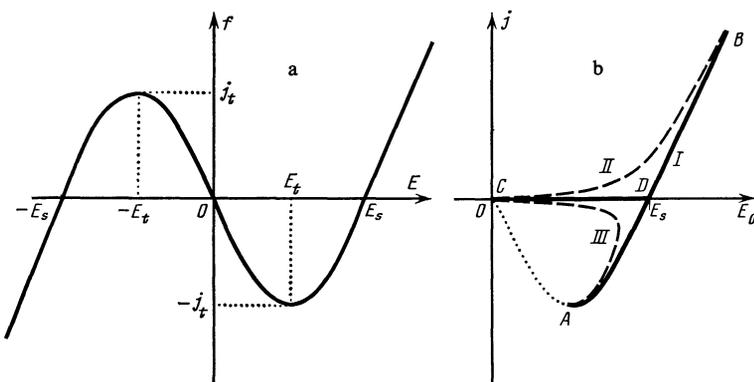


FIG. 1. a) Schematic representation of the function  $f(E)$ ; b) volt-ampere characteristic of an illuminated crystal. Segment  $AB$  corresponds to a homogeneous state, while  $CD$  corresponds to a state with a domain structure. The dashed lines correspond to field distributions of types II and III. Segment  $OA$  is unstable.

$E = 0$  is unstable, while the states with  $E = \pm E_s$  are stable. For  $|E| > E_t$  the homogeneous state is stable and, consequently, the  $F(E)$  curve for  $|E| > E_t$  gives one of the branches of the volt-ampere characteristic of the sample (segment  $AB$  in Fig. 1b).

As is seen from Fig. 1a, values of the current in the interval  $-j_t > j > j_t$  correspond to two stable values of the field, differing in magnitude and sign. This means that at a fixed current  $j$  there are two possible homogeneous states. In addition, the sample can stratify into domains in which these two stable field values alternate. It can be shown that in general the domain boundaries are moving. Stationary walls are possible only for  $j = 0$  (see Sec. 3). Therefore, as can be seen from Fig. 1a, the fields in the stationary domains are equal to  $\pm E_s$ .

If the sample is open-circuited, it can be in a homogeneous state with field  $E = E_s$  or  $E = -E_s$  or in an inhomogeneous state with domains in which these two field values alternate.

Let us now examine the conditions when a fixed voltage  $V = E_0 l$  is applied to the sample ( $l$  is the length of the sample). If  $E_0 > E_t$  a homogeneous state with current  $j = f(E_0)$  is possible (segment  $AB$  in Fig. 1b). If there is a domain structure in the sample, the combined lengths  $l_{\pm}$  of the domains with fields  $\pm E_s$  should satisfy the relation

$$(l_+ - l_-)E_s = E_0 l, \quad (4)$$

which states that the combined voltage across all the domains is equal to the applied voltage. Of course,  $l_+ + l_- = l$ . Obviously, Eq. (4) can be satisfied only if  $E_0 < E_s$ . As we have said, a stationary domain structure is possible only for  $j = 0$ . Thus for  $E_0 < E_s$  the volt-ampere characteristic contains a segment  $CD$  (see Fig. 1b) which corresponds to a state with a domain structure.

It can be seen from Fig. 1b that for fields in the interval  $E_t < E_0 < E_s$  there are two possible steady states (one with a domain structure and one with a uniform field), which differ in the value of the current flowing through the sample. Which of these two states is realized depends on the previous history. If the sample was originally in a homogeneous state with field  $E_t < E_0 < E_s$ , then this state should persist on illumination. If, on the other hand, a domain structure has been produced by a preliminary illumination in a field  $E_0 < E_t$ , then this domain structure persists as the field is increased to  $E_0 > E_s$ . A two-branched volt-ampere characteristic and hysteresis effects due to transitions between the two steady states were observed in Refs. 4 and 5.

The discussion of this section is illustrated by Fig. 2, which shows a schematic representation of the steady field distribution in the sample for various values of the applied field  $E_0$ . For  $E_0 = 0$  there are domains of equal volume with fields  $\pm E_s$  (Fig. 2a). For  $E_0 < E_t$ , the domain wall shifts in accordance with Eq. (4) in such a way that the average field in the sample is equal to  $E_0$  (Fig. 2b). If  $E_t < E_0 < E_s$ , two states are possible; in one of them the field is uniform and equal to  $E_0$ , while in the other there are domains with fields  $\pm E_s$  and dimensions  $l_{\pm}$  determined by formula (4) (Fig.

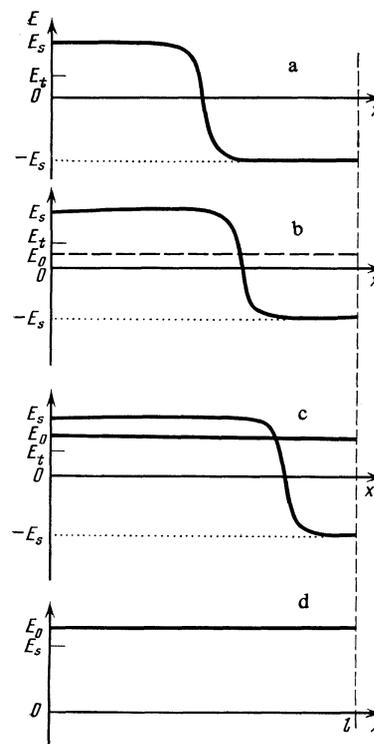


FIG. 2. Field distribution  $E(x)$  in a sample at various values of the applied field  $E_0$ : a)  $E_0 = 0$ , b)  $E_0 < E_t$ , c)  $E_t < E_0 < E_s$  (there are two stable states), d)  $E_0 > E_s$ .

2c). Finally, for  $E_0 > E_s$  the domain structure does not form and the field in the sample is uniform and equal to the applied field (Fig. 2d). In all cases in which there is a domain structure the current through the sample is zero (segment  $CD$  in Fig. 1b). In states with a uniform field we have  $j = f(E_0)$  (segment  $AB$ ).

Let us consider what happens when the illumination is stopped and the voltage source is turned off. We assume here that the sample is short-circuited, as in the experiments of Refs. 3 and 4. The result will vary depending on whether the initial state had a domain structure or a uniform field distribution.

In the first case the charges creating the steady field distribution are located both on the surfaces of the sample and in its interior—on the domain walls. When the sample is close-circuited the charges in the interior remain, since the dark conductivity of the crystal is negligibly small. The surface charges, on the other hand, by flowing through the external circuit, rearrange themselves in such a way as to equalize the potentials of the opposite surfaces of the sample. This gives a new field distribution which differs from the original distribution by an amount  $E_0$  at every point in the sample. Thus the domains persist, with fields  $E_s - E_0$  and  $-E_s - E_0$  and with dimensions  $l_{\pm}$  determined by formula (4).

In the second case, when the initial field distribution is uniform, the surface charges are neutralized and the field in the sample vanishes.

All of these conclusions of the phenomenological theory are in complete agreement with the experimental re-

sults.<sup>3-5</sup> We note that the question of the number of domains and their dimensions has not been studied experimentally. The theory elaborated in the next section, which does not allow for inhomogeneity of the sample, predicts the existence of only two domains (as shown in Fig. 2) or else a few domains, the precise number of which depends on the boundary conditions. However, the inhomogeneity that is actually present can lead to the formation of a large number of domains. All of our results remain valid in this case if  $l_{\pm}$  is taken to mean the optical length of the domains with fields  $\pm E_s$ , respectively.

### 3. STATIONARY DOMAIN STRUCTURE

The complete system of equations describing the field distribution in the crystal includes Poisson's equation and the continuity equations for the charge carriers with allowance for the generation and recombination kinetics. However, nothing is currently known about either the photoconductivity mechanism in ruby or about the nature of the recombination. We shall therefore consider only a very simple model in which it is assumed that there is only one type of mobile charge carrier during illumination (for definiteness, say electrons). In this case the complete system of equations is

$$\frac{\partial E}{\partial x} = -\frac{4\pi e}{\epsilon}(n-p), \quad (5)$$

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x}\left(-\frac{j}{e}\right) + \gamma(np - n_0^2) = 0, \quad (6)$$

$$\frac{\partial p}{\partial t} + \gamma(np - n_0^2) = 0, \quad (7)$$

$$j = e\mu nE + eD\frac{\partial n}{\partial x} + J(E), \quad (8)$$

where  $n$  is the electron density,  $p$  is the density of the immobile holes,  $\gamma$  is a coefficient which determines the rate of recombination,  $n_0$  is the average steady-state electron density, determined by the rate of generation,  $\mu$  is the electron mobility, and  $D$  is the electron diffusion coefficient.

Under steady conditions  $np = n_0^2$  and the system reduces to two equations (5) and (8) for the quantities  $E$  and  $n$ . Further simplification arises if the quasineutrality condition is satisfied:  $|n'| \ll n_0$ , where  $n' = n - n_0$ . In this case  $n - 2n'$  and Eqs. (5) and (8) yield an equation which determines the field distribution for a fixed current  $j$ :

$$j = \sigma E + J(E) - \frac{\epsilon D}{8\pi} \frac{d^2 E}{dx^2}, \quad (9)$$

where  $\sigma = en_0\mu$ . The boundary conditions on Eq. (9) are determined by the physical processes on the  $x = 0$  and  $x = l$  surfaces of the sample (at the contacts). The actual boundary conditions are unknown. However, as we shall see, these conditions are not very important if the sample is large enough.

It follows from (9) that the characteristic scale of the spatial inhomogeneity of the field is of the order of magnitude of the Debye radius  $r_D$ . We shall assume that the dimensions of the sample are considerably larger than this ( $l \gg r_D$ ). To find the volt-ampere characteristic of the sample one

must [after solving Eq. (9) for a fixed current  $j$ ] evaluate the average field in the sample:

$$E_0 = \frac{1}{l} \int_0^l E(x) dx.$$

One thereby finds the function  $j(E_0)$ . It is clear that  $j(-E_0) = -j(E_0)$ , and therefore it suffices to consider the field distribution for  $j > 0$ .

Equation (9) has the form of Newton's equation describing the one-dimensional motion of a body under an external force if  $E$  and  $x$  are taken as the coordinate of the body and the time, respectively. Let us rewrite this equation in the form

$$d^2 E/dx^2 = -\partial U/\partial E, \quad (10)$$

where  $U$ , which plays the role of a potential energy, is a function such that

$$\frac{\partial U}{\partial E} = \frac{8\pi}{\epsilon D}(j - f(E)). \quad (11)$$

The function  $f(E)$  in (11) is defined by Eq. (3) and is sketched in Fig. 1a.

The functional form of  $U(E)$  implied by (11) is shown schematically in Fig. 3. For  $j < j_c$ , the function  $U(E)$  has two maxima and one minimum, while for  $j > j_c$ , it has one maximum.

The possible trajectories for the motion of the body in the potential field  $U$  correspond to different electric-field distributions  $E(x)$  in the sample. The stay of the body in the equilibrium positions that correspond to the extrema of the function  $U(E)$ , corresponds to a uniform distribution of the electric field.

A nonuniform field distribution corresponds to motion of the body from a certain initial point to a final point, with the sample length  $l$  playing the role of the total time of this motion. Since  $l \gg r_D$ , an arbitrary motion will generally speaking correspond to an enormous value of the field [of the order of  $E_s \exp(l/r_D)$ ] near one of the contacts. Therefore, under reasonable boundary conditions one should consider only motions for which the body either executes oscillations between two maxima of the function  $U(E)$  or spends most of the time near them. Thus the following types of motion are possible: I—motion in which the body spends practically all the time near one of the maxima of  $U(E)$ , II—motion in which the body spends a long time near each of the two maxima, with the greater part of the time near the larger maximum, III—the same as II, but with the body spending the greater part of the time near the smaller maximum, IV—the body executes oscillations between the two maxima without getting too close to them.

Type I corresponds to a practically uniform field in the sample. Such solutions are possible for  $E_0 > E_c$ . Types II and III describe a domain structure with domains which are large in comparison to the width of the domain wall. Such solutions exist only at very small values of the current  $j$ , in which case the heights of the two maxima of the function  $U(E)$  are rather similar. In the type II field distribution the larger domains have the stronger fields, which are in the direction of the current, while in the type III distribution the

larger domains have the weaker fields, directed counter to the current. Type IV describes a structure having domains with dimensions of the order of  $r_D$ .

The stability of the various field distributions is considered in Sec. 4, where it is shown that solutions with a large number of domains are always unstable. In particular, solutions of type IV are unstable.

Let us consider the volt-ampere characteristics for the stable states. Uniform distributions of type I, as we mentioned in the previous section, correspond to segment  $AB$  of the volt-ampere characteristic in Fig. 1b. We shall now show that in the presence of domain structure the current is exponentially small. Since the dimensions of the domains are large compared to the width of the domain wall, as a first approximation let us take one such wall in the sample, which we shall assume to be infinite. In the mechanics problem such a field distribution corresponds to motion beginning at  $x = -\infty$  in one of the maxima of  $U(E)$  and ending at  $x = +\infty$  in the other. Such a motion is obviously possible only if the heights of the two maxima are equal, i.e., for  $j = 0$  (see Fig. 3a). Thus, for  $l/r_D \rightarrow \infty$  the state with the domain structure corresponds to segment  $CD$  of the volt-ampere characteristic in Fig. 1b. It can be shown that this conclusion remains valid when one abandons the quasineutrality approximation used in this Section; in reality this approximation is most likely invalid.

For a real finite sample with a domain structure, one can show that the volt-ampere characteristic is given by

$$j = \pm 2E_s f'(E_s) \exp(-\Lambda) \operatorname{sh}(\Lambda E_0/E_s), \quad (12)$$

where  $\Lambda = l/Na \gg 1$ ,  $N$  is the number of domain walls,  $a = (8\pi f'(E_s)/\epsilon D)^{-1/2}$  is a quantity which determines the width of the domain wall and is of the order of the Debye radius  $r_D$ , and  $f'(E_s)$  is the derivative of  $f(E)$  at  $E = E_s$ . Formula (12) is valid for  $j \ll j_c$ . In addition, it was assumed in the derivation that the boundary conditions at the surfaces of the crystal are symmetric. In this case the number of domains is even, while  $N$  is odd. Structures of type II contain only two domains ( $N = 1$ ). The  $\pm$  signs in (12) correspond to field distributions of types II and III, respectively.

In the region of applicability of formula (12), while  $E_s - E_0 \gg \Lambda^{-1} E_s$ , the current is exponentially small and the volt-ampere characteristics are very close to the straight line  $CD$  in Fig. 1b. Outside this region the type II and type III field distributions go over to practically uniform distributions of type I. Therefore, the volt-ampere characteristics of types II and III approach segments  $DB$  and  $DA$ , respectively, as is shown in Fig. 1b.

Which of the two types of domain structure, II or III, is actually realized depends on the boundary conditions on the surface of the sample. However, for  $1 \gg r_D$  the boundary conditions play only a minor role, and so, as we have shown, the field distributions and volt-ampere characteristics of these two types are practically indistinguishable. It is possible, in fact, that the domain structure is determined by inhomogeneities in the sample. In that case, if the domains are large compared to the width of the domain wall, as is found in experiments,<sup>3-5</sup> all of the above conclusions remain in force.

#### 4. STABILITY OF THE STEADY STATES

At a given current  $j$  through the sample the evolution of the field distribution is described by the equation

$$j = f(E) - \frac{\epsilon D}{8\pi} \frac{\partial^2 E}{\partial x^2} + \frac{\epsilon}{4\pi} \frac{\partial E}{\partial t}, \quad (13)$$

which differs from (9) in that it contains a displacement current. Equation (13) is valid if the recombination time of the carriers is considerably shorter than the characteristic time for changes in the field.

The stability of the steady states can be analyzed by the standard method used, for example, in the study of the domain instability in semiconductors.<sup>7</sup> Let  $E(x)$  be some standard solution of Eq. (13). Writing a small correction to this field distribution in the form  $\psi(x)\exp(-\lambda t)$  and linearizing Eq. (13), we obtain the equation

$$-\frac{D}{2} \psi'' + V(x)\psi = \lambda \psi, \quad V(x) = \frac{4\pi}{\epsilon} f'(E(x)). \quad (14)$$

The steady state is stable if all the eigenvalues  $\lambda$  determined from Eq. (14) are positive.

If the voltage across the sample and not the current is given, then the stability problem also reduces to Eq. (14) but in this case one should consider only those fluctuations of the field which leave the voltage across the sample unchanged. In other words, the function  $\psi(x)$  should be subject to the condition

$$\int_0^l \psi(x) dx = 0.$$

Let us first consider the case  $1 \rightarrow \infty$ . Then the steady field distributions are periodic. Equation (14) has the form of a Schrödinger equation for a particle in a periodic potential  $V(x)$  with minima at the locations of the domain walls. We note that the function  $\psi_0 = E'(x)$  is a solution of Eq. (14) with the eigenvalue  $\lambda = 0$ . With increasing domain size the distance between adjacent potential wells increases. In the limiting case, when this distance is infinitely large, the value  $\lambda = 0$  determines the ground state in a single well, since the corresponding eigenfunction  $\psi_0$  has no nodes in this case. For a finite distance between wells the ground state will obviously be lower, i.e., eigenvalues  $\lambda < 0$  appear. Thus in the present case of an infinite sample, any domain structure is unstable on account of the interaction of the domain walls. An exception is a structure with a single domain wall, which is found in a state of neutral equilibrium ( $\lambda = 0$ ).

In the real case of a finite sample the stability of the steady field distributions depends on the boundary conditions. It is clear, however, that a structure with a large number of domains is still unstable, since the interactions between domain walls is more important than the influence of the sample boundaries. If, on the other hand, the sample has only a few domains, then the boundary conditions can stabilize such a structure. A structure with a single domain wall in a finite sample can be either stable or unstable depending on the boundary conditions. For example, in the case of the simple boundary conditions  $dE/dx = 0$  at  $x = 0$  and  $x = 1$  one can show the following. In the case of a fixed

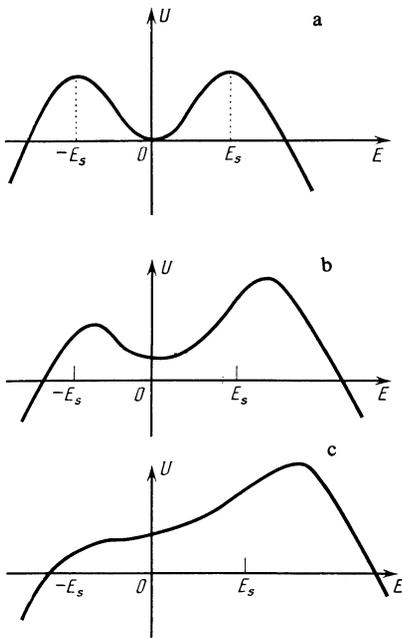


FIG. 3. Schematic representation of the "potential energy"  $U(E)$  at different values of the current  $j$ : a)  $j = 0$ , b)  $0 < j < j_c$ , c)  $j > j_c$ .

current any domain structure is unstable, and only homogeneous states with  $E > E_c$  are stable. In the case of a fixed voltage there is, in addition to these homogeneous states, a stable structure consisting of two domains with fields  $\pm E_s$ . All structures having a greater number of domains are unstable.

The actual boundary conditions, as we have mentioned, are unknown. However, on the basis of the arguments presented above it can be concluded that in any case only structures with a small number of domains can be stable.

The stability analysis in this Section does not allow for the presence of inhomogeneities in the crystal. In this case, when the size of the domain is much larger than the width of the domain wall ( $\Lambda \gg 1$ ), the growth increments of the fluctuations are extremely small:  $\lambda \sim \sigma \exp(-\Lambda/2)$ . Therefore, inhomogeneities actually present in the sample might stabilize structures having a large number of domains.

## 5. ON THE NATURE OF THE BACKWARD PHOTOVOLTAIC CURRENT

The photovoltaic effect arises in crystals lacking a center of inversion.<sup>2</sup> In the presence of a center of inversion this effect cannot occur. However, in an electric field the center of inversion vanishes, and so a photovoltaic current should appear. (Here we are speaking, of course, not about the direct action of the electric field on the photoexcited charge carriers (the effect responsible for the photoconduction current), but about a photoexcitation asymmetry which gives rise to an average carrier velocity.) General principles admit any direction of the photovoltaic current, both with the field and against it. In fact, in ferroelectrics, where the photovoltaic current is due to an internal field, the direction of this current varies depending on the optical excitation conditions.<sup>8</sup>

Let us discuss the possible mechanism for the appearance of photovoltaic current in crystals having a center of inversion in the presence of an electric field. First of all, the field directly affects the wave functions of the states between which the transitions that lead to photoionization occur. As a result, the probabilities for carriers to be excited with velocities directed with the field or counter to it are not the same. This effect is clearly proportional to the ratio of the applied field to the atomic field. In the case of photoionization of impurities occupying centrosymmetric positions in the crystal, this mechanism is the only one present.

If a crystal having a center of inversion contains impurities distributed uniformly over equivalent noncentrosymmetric positions (such as the chromium ions in ruby crystals), there is also another mechanism, which derives from the fact that the levels of impurities occupying different positions are shifted differently in an electric field. If all the impurities occupied positions of only one type, then the crystal would in fact be a ferroelectric and would support a photovoltaic current.

In the case of a uniform distribution of the impurities over all the positions the contributions to the photovoltaic current from impurities occupying positions which differ by inversion precisely cancel each other and there is no net current. In an electric field, however, positions which differ by inversion become nonequivalent, and so there is a preferential photoionization of the impurities in one type of position. As a result, the compensation of the currents breaks down and a photovoltaic current appears in the crystal. The difference in the photoionization probabilities for the impurities in different positions is due to the difference in the shifts of the energy levels in an electric field.

For single-photon excitation such a selectivity can be particularly pronounced near the photoionization threshold. If the photoionization process has a two-photon character (as was assumed in Ref. 1), then the difference in the populations of the intermediate excited states of the impurities occupying different positions becomes an important consideration. This difference, in turn, can be due to two causes. One is the selective pumping of the excited state of the impurity in one type of position in the case when the first stage of the photoionization has a resonance character.<sup>2)</sup> The other possible cause involves the establishment of a Boltzmann distribution between the excited states of the impurities in different positions through a transfer of excitation.

Let us consider in more detail the formation of a photovoltaic current in an electric field for the case of two-photon excitation. If it is assumed as in Ref. 1, that the formation of mobile carriers in ruby occurs in two stages, the first of which is the population of the metastable  ${}^2E$  level of chromium, then the photovoltaic current is proportional to the difference in the populations of the chromium ions  $A^*$  and  $B^*$  (in positions  $A$  and  $B$ ) that have been excited to this state:

$$J(E) = k(A^* - B^*), \quad (15)$$

where  $k$  is a proportionality coefficient.

The balance equations for the populations of the excited states (under weak pumping) are of the form

$$\begin{aligned} dA^*/dt &= G_A - A^*/\tau - W_{AB}A^* + W_{BA}B^*, \\ dB^*/dt &= G_B - B^*/\tau + W_{AB}A^* - W_{BA}B^*, \end{aligned} \quad (16)$$

where  $G_A$  and  $G_B$  are the rates of pumping of the  ${}^2E$  states of the chromium ion in positions  $A$  and  $B$ , respectively,  $\tau$  is the lifetime of the excited state, and  $W_{AB}$  and  $W_{BA}$  are the probabilities for excitation transfer from position  $A$  to position  $B$  and vice versa.

The difference between  $G_A$  and  $G_B$  and between  $W_{AB}$  and  $W_{BA}$  is due to the nonequivalence of positions  $A$  and  $B$  in an electric field. The energies of the excited states of the ions in positions  $A$  and  $B$  differ by an amount of  $2Ed$ , where  $\pm d$  are the dipole moments of the  ${}^2E$  states for the  $A$  and  $B$  ions. Here the ratio of the probabilities  $W_{AB}$  and  $W_{BA}$  is given by the Boltzmann factor:  $W_{BA}/W_{AB} = \exp(2Ed/T)$ , where  $T$  is the temperature in energy units.

The steady solution of Eqs. (16) is of the form

$$\begin{aligned} A^* - B^* &= \mathcal{N}^* \frac{\xi \tau^*(E) + \tau \operatorname{th}(Ed/T)}{\tau + \tau^*(E)}, \\ \mathcal{N}^* &= (G_A + G_B) \tau, \quad \xi = (G_A - G_B) / (G_A + G_B), \quad \tau^*(E) \\ &= (W_{AB} + W_{BA})^{-1}, \end{aligned} \quad (17)$$

where  $\mathcal{N}^*$  is the total concentration of excited chromium ions,  $\xi$  is a measure of the selectivity of the excitation,  $\tau^*(E)$  is the characteristic excitation-transfer time, which depends on the chromium concentration, the temperature, and the size of the energy gap  $2Ed$ .

If the ratio  $\tau^*/\tau$  is sufficiently large, than the selectivity of the excitation is the most important factor. In small fields,  $\xi$  is clearly proportional to the field:  $\xi = CE$ . The photovoltaic current is directed counter to the field if the product of  $Ck$  of the coefficients is negative.

If  $\xi \tau^*/\tau \ll Ed/T$ , the population difference is governed by the tendency toward the establishment of a Boltzmann distribution. In this case, assuming  $|Ed| \ll T$ , we can use Eqs. (16) and (17) to write the expression for the photovoltaic current as

$$J(E) = -\sigma E \frac{T_c}{T} \frac{\tau + \tau^*(0)}{\tau + \tau^*(E)}, \quad (18)$$

where we have introduced the critical temperature

$$T_c = (-kd\mathcal{N}^*/\sigma) (1 + \tau^*(0)/\tau)^{-1}.$$

The photovoltaic current is directed counter to the field if  $kd < 0$ .

If the ratio  $\tau^*(E)/\tau$  increases substantially in the field interval where  $|Ed| \ll T$ , then the saturation field  $E$  is determined by an equation which follows from the condition  $f(E) = \sigma E + J(E) = 0$ :

$$(\tau + \tau^*(0)) / (\tau + \tau^*(E_s)) = T/T_c. \quad (19)$$

In the opposite case, when the ratio  $\tau^*(E)/\tau$  depends weakly on the field,  $E_s$  is determined by the equation

$$\operatorname{th} y = (T/T_c) y,$$

where  $y = E_s d / T_c$ .

The function  $E_s(T)$  has the form characteristic for a second-order phase transition at  $T + T_c$ . The currently available experimental data do not permit a definite conclusion as to the specific mechanism for the formation of the photocurrent in ruby. For this reason it is not possible to do a quantitative calculation of  $T_c$  and  $E_s$ .

In conclusion we note that the phenomenological theory which we have elaborated here for the photoelectric domain instability is in complete agreement with the experimental results. It can thus be considered firmly established that ruby supports a current directed counter to the electric field. However, the specific microscopic mechanism which gives rise to this current is still unknown.

The spontaneous vanishing of the center of inversion in the crystal, the presence of negative resistance in zero field, and the resulting instability which leads to the formation of a static domain structure in the absence of electric field are new effects which merit further study.

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<sup>1</sup>In this paper the term photovoltaic current is used everywhere to mean the current due to the absence of a center of inversion in a crystal (the current which leads to an anomalous photovoltage in ferroelectrics<sup>2</sup>), as distinct from the currents which arise in the Demer or drag effects.

<sup>2</sup>This idea has been expressed by S. P. Feofilov.

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