the condition $\theta - T = \omega\gamma$. The functional dependence of κ on τ and ω in (2) is not unexpected [5], but it is important that (2) contains in explicit form the dependence of κ on the thermodynamic parameters of the crystal.

The reduction of our data for the absorption of sound in the asymmetric phase of the NH$_4$Cl crystal yields $\tau = 1 \times 10^{-9}/(\theta - T)$ sec, which agrees in order of magnitude with the value of τ obtained in [4]. Using the Landau relation (2), we were able to obtain for the first time the value of $d\theta/dp$ from acoustic measurements. The values of ΔC_p and $\mu_{zzzz} = 1/E$ needed for this calculation were taken from [6,7], and we used the value of κ from our measurements for sound of 15 MHz frequency. We obtained $d\theta/d\sigma = 3 \times 10^{-9}$ deg-cm^2/dyne, whereas direct static measurements of the dependence of the phase-transition temperature θ on the pressure p yield 9×10^{-9} deg-cm^2/dyne [6,8]. Recognizing that $d\theta/dp = 3(\partial\theta/\partial\sigma)$, the agreement between values of $d\theta/dp$ obtained by entirely different methods can be regarded as convincing confirmation of Landau's formula (2).

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SEMICONDUCTING PROPERTIES OF FERROELECTRICS

G. M. Guro, I. I. Ivanchik, and N. F. Kovtonyuk
P. N. Lebedev Physics Institute, USSR Academy of Sciences
Submitted 29 September 1966
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Following [1], we assume that the spontaneous induction in BaTiO$_3$ is screened by free carriers flowing from within the crystal. It is shown in [1] that the spontaneous induction of a c-domain BaTiO$_3$ plate can be represented as in Fig. 1. Since the charge density of the free carriers is determined from the equation div$D = 4\pi\rho$, the free-carrier distribution over the thickness of the plate takes the form shown in Fig. 2. Thus, the BaTiO$_3$ crystal in question is similar to a p-n junction (see [2]) in which the regions of high free-carrier density (n and p regions) are separated by a broad dielectric gap. We shall estimate the

free carrier densities in the n and p regions, and the free-carrier and electric-field distributions over the thickness of the plate. The estimates will be made separately for an ideally pure crystal (see [1]) and for a real crystal with impurities.
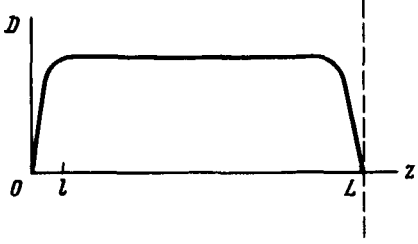

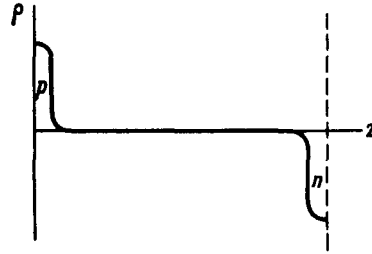Fig. 1. Distribution of spontaneous induction.

Fig. 2. Distribution of free-carrier charge density (broad p-n junction).

In BaTiO$_3$ the forbidden-ban width is $\Delta \sim 3.2$ eV [3], and the intrinsic free-carrier density is [4]

$$n_i = N_c \exp\left(- \frac{\Delta}{2kT} \right), \text{ where } N_c \sim 3 \times 10^{19}. \tag{1}$$

Therefore the Debye radius of an ideally pure crystal is of the order of 10 km. The spontaneous induction is $D_0 \sim 5 \times 10^4$ cgs esu [3], and the coercive field calculated from thermodynamic theory [5] is of the order of 5×10^2 cgs esu. We use, in addition, a length parameter $l \sim 3 \times 10^{-7}$ cm, which coincides [1] with the thickness of a 180° domain wall in BaTiO$_3$. The parameter l is proportional to the gradient energy of the ferroelectric [6] and is equivalent to the length on which the spontaneous induction changes by an amount of the order of D_0. The charge per cm^2 of plate surface needed for total screening of the spontaneous induction is $D_0/4\pi$. Since the spontaneous induction increases from zero to practically D_0 in a layer thickness l, the free-carrier density in this layer will be of the order of

$$n \sim \frac{D_0}{4\pi q l}, \tag{2}$$

where q is the electron charge. Substituting the values of the parameters, we get $n \sim 10^{19}$. On the other hand, under thermodynamic equilibrium we should get $n = n_i \exp(q\varphi/kT)$, where φ is the potential of the internal electric field near the plate surface. From this we obtain for the total potential difference (total bending of the bands in the p-n junction) $q \cdot \Delta\varphi \sim 2kT \ln (n/n_i)$. Substituting here $n_i = N_c \exp(-\Delta/2kT)$ and noting that $n \sim N_c$, we conclude that (Δ is the width of the forbidden band)

$$q \cdot \Delta\varphi \sim \Delta. \tag{3}$$

The dimensions of an ideally pure crystal are always much smaller than the Debye radius, so that inside such a crystal there is no screening of the electric field, which should be practically uniform, except in small regions $\sim l$ near the surface of the plate, where the free-carrier density is high, and the electric field vanishes together with the induction

(see also [1]). It follows therefore that the order of magnitude of the electric field inside the crystal is

$$E \sim \frac{\Delta}{qL} \, , \qquad\qquad (4)$$

where L is the thickness of the plate. In particular, there can be no ferroelectricity when $L < L_{min} - \Delta/qE_{coerc}$, where E_{coerc} is the coercive field [1]. For an ideally pure crystal $L_{min} \sim 10^{-5}$ cm. Thus, the $BaTiO_3$ plate under consideration is similar to a broad p-n junction in which the bands are curved as shown in Fig. 3a.
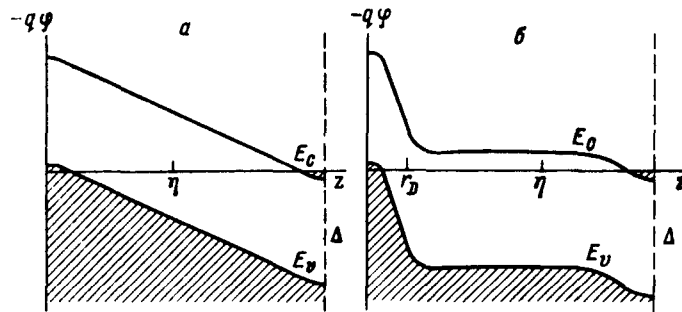

Fig. 3. Band picture of p-n junction: a - in ideally pure $BaTiO_3$ $(r_D \gg L)$, b - in $BaTiO_3$ with impurities $(r_D \gg L$, n-type).

We now determine the degree to which this picture is disturbed by the presence of impurities. Let us consider for concreteness n-type doping. The impurities increase the density n_0 of the free electrons in the conduction band above the Curie point (when there is no electric field inside the crystal). This decreases the Debye radius, which now becomes smaller than the thickness of the crystal. It follows therefore that the electric field inside the crystal will not be homogeneous, and will differ from zero only at distances from the surface on the order of the Debye radius. In addition, in n-type doping the point $\rho = 0$ will shift in the direction of the doping impurity, i.e., toward the electronic surface of the crystal. However, if the doping is not very strong, the total bending of the bands will again be given by (3). Indeed, the total free-carrier charge per cm^2 of the plate surface is qn_0L. Therefore if $qn_0L \ll D_0/4\pi$ the impurity electrons are unable to screen the spontaneous induction. The main bulk of the electrons needed for the screening should be drawn, as before, from the valence band, and to this end the total bending of the bands should be as before equal to the width of the forbidden band, i.e., formula (3) remains in force. In the opposite limiting case, of strong doping, when $n_0 \sim D_0/4\pi q\ell$ (see formula (2)), the total bending of the bands will be small. Thus, if the sample is not too strongly doped, the p-n junction structure described above changes only in that the electric field inside the crystal is screened, and the distribution of the potential becomes asymmetrical with respect to the center of the sample. The bending of the bands in a real $BaTIO_3$ crystal is shown in Fig. 3b. The free-carrier density near the surface is again given by (2), since this density is de-

termined only by the conditions for the screening of the spontaneous induction, and does not depend on the filling of the conduction band.

Let us stop now to discuss the main consequences of the examined picture of the p-n junction.

1) A $BaTiO_3$ crystal connected in an electric circuit will behave like a p-n junction with symmetric current-voltage characteristic. The symmetry of the characteristic is a result of repolarization, which causes the current to flow in one direction relative to the p-n junction.

2) During repolarization, nuclei of the opposite phase grow through the crystal. Non-equilibrium free carriers, with density determined by (2), are concentrated on the ends of these nuclei, in regions on the order of l. At the instant when opposite ends of nuclei meet, recombination takes place and is accompanied by emission of light. The frequency of such emission can be of the order of the width of the forbidden band, corresponding to violet light in the case of $BaTiO_3$. The emission should take place over the entire volume of the crystal and is flash-like. Work aimed at observing this emission is now under way.

3) Thin layers with anomalously high free-carrier density should exist near the surfaces of crystals not equipped with electrodes. Thus, the electric conductivity along the surface should be much higher than in the direction perpendicular to the surface.

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EXCITATIONS OF EXCITON TYPE IN A GAS

A. P. Kazantsev
Institute of Semiconductor Physics, Siberian Department, USSR Academy of Sciences
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In this note we consider collective excitations in a gas, similar in character to Frenkel excitons in molecular crystals.

In a not too rarefied gas, when the emission wavelength at the transition frequency exceeds the distance between particles, the main role in the interaction between atoms is played by dipole-dipole interaction

$$V(r) = (d_1 d_2)/r^3 - 3(d_1 r)(d_2 r)/r^5,$$ (1)