Ionization of shallow impurities by the electric field in a random Coulomb potential

N. G. Zhdanova, M. S. Kagan, E. G. Landsberg, L. V. Levkin, and V. V. Petrishchev

Institute of Radio Engineering and Electronics, Russian Academy of Sciences, 103907 Moscow, Russia

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The ionization of shallow donors in germanium, which are located in the random potential of charged impurities, by an external electric field is found to be attributable to the Poole–Frenkel' effect. © *1995 American Institute of Physics.*

The Poole–Frenkel' effect[1] in extrinsic semiconductors consists of an increase in the rate of thermal ionization of impurity centers[2–6] in an external electric field E (see the inset in Fig. 1). The ionization energy of an attracting impurity decreases by the amount[1,2]

$$\epsilon_{PF}=\alpha\sqrt{E}, \tag{1}$$

where $\alpha=2\sqrt{Ze^3/k}$, e is the elementary charge, Z is the charge multiplicity of the center, k is the permittivity, and the probability of thermal ionization increases by a factor of $\exp(\epsilon_{PF}/kT)$; i.e., the concentration n of free carriers must increase as

$$n\propto\exp(\alpha\sqrt{E}/kT). \tag{2}$$

The Poole–Frenkel' effect has been observed in many semiconductors[3–7] with ionization of deep impurities. In the case of shallow hydrogen-like impurities the Poole–Frenkel' effect ordinarily cannot be observed, since impact ionization of the impurities starts even in comparatively weak fields. In a recent work[7] the Poole–Frenkel' effect was observed in a strong field of the radiation from a powerful far-infrared laser. In this case the high frequency of the electric field prevented the development of impact ionization right up to comparatively strong fields.

In the present study we observed the Poole–Frenkel' effect with ionization of shallow donors in Ge by an electric field in the presence of a random potential. Since at low temperatures most electrons are localized in the valleys of the random potential, impact ionization in this case is impeded, since the electric field can heat only an exponentially small fraction of electrons with energy above the mobility threshold. We studied crystals of n-Ge with deep, multiply charged acceptors (Cu), which were partially compensated for by shallow donors (Sb) in such a manner that the partially filled upper level of copper ($E_c=0.26$ eV) was in equilibrium. Conduction at low temperatures was achieved by optical excitation of electrons from the copper levels. In Ref. 8 it was shown that in the temperature range where the donors are frozen out but are in thermal equilibrium with the conduction band, the stationary population of donors is controlled by direct shallow donor–deep acceptor tunneling transitions. Impurity–impurity recombination makes it

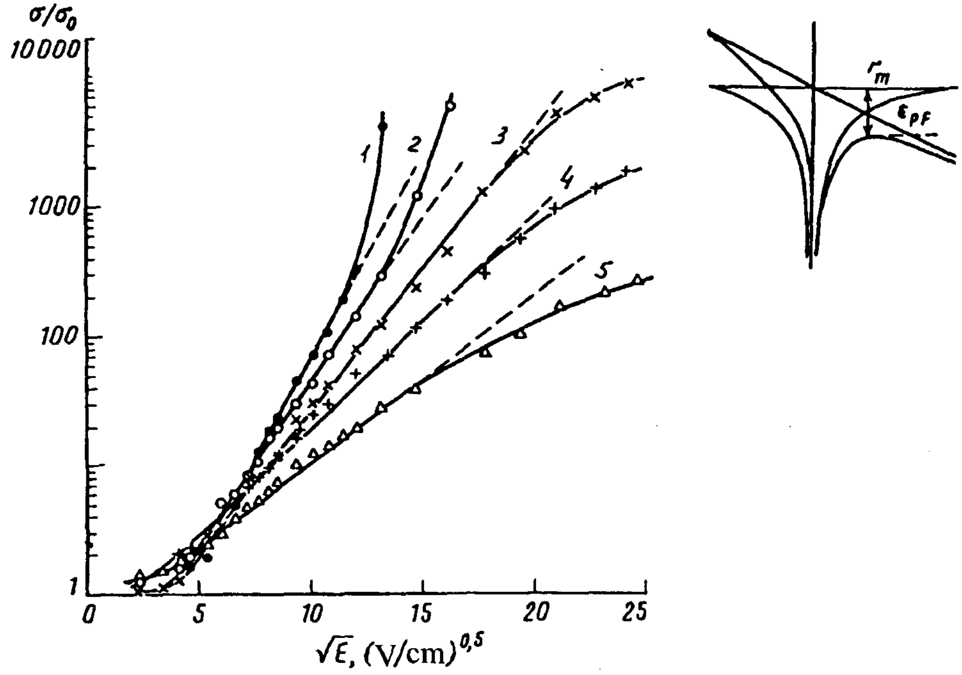

FIG. 1. Log(σ/σ_0) versus $\sqrt{E}$ for different temperatures T (K): curve *1* — 8, 2 — 10, *3* — 12, *4* — 16, *5* — 20. Inset: Diagram of the Poole–Frenkel' effect.

possible to vary over wide limits the filling of the donors by changing the rate of optical generation from the acceptors. As a result of the smearing of the donor levels by the random potential of the charged impurity ions, the quasi Fermi level for donors, which strongly changes with a change in the intensity of the optical excitation of the acceptors, can lie much deeper in the band gap than the ionization energy of an isolated donor center.[8]

The field dependence of the conductivity of samples in the pulsed regime was measured. To eliminate the influence of electron recombination at copper ions, short voltage pulses with durations of 1–10 μs, much shorter than the trapping times on copper, were investigated. Figure 1 shows curves of the conductivity σ, normalized to the conductivity σ_0 in a weak field, plotted as log(σ/σ_0) versus $\sqrt{E}$. It is evident that in some range of fields there is a linear section at all experimental temperatures. The slope of this linear section was found to be proportional to $1/T$ (Fig. 2). Therefore, the field dependence of the conductivity is described well by the law (2); i.e., the donors are ionized by the Poole–Frenkel' effect. In strong fields, saturation due to exhaustion of the donors is observed. At low temperatures and/or high intensity I of optical excitation with deep acceptors (i.e., with increasing filling of the donors) a sharp intensification of the field dependence of σ (curves *1* and *2*) is observed immediately prior to saturation of the current. This increase could be associated with tunneling of electrons through the barrier of the center (see, for example, Ref. 2) or with impact ionization.

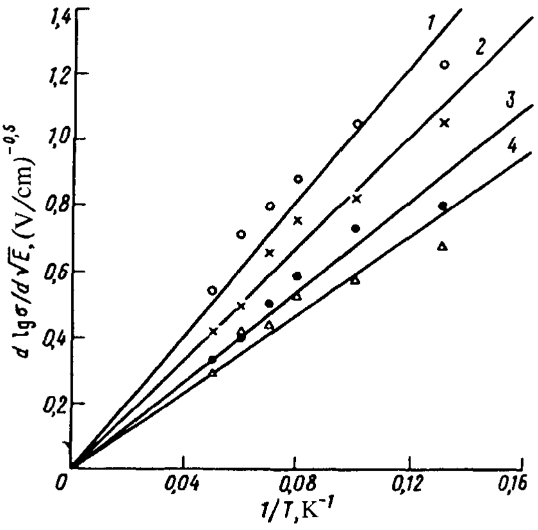

FIG. 2. Slope of the curves in Fig. 1 versus the inverse temperature for different illumination intensities.

Let us now consider some peculiarities which are not described by the standard Frenkel' formula. First, as one can see from the curves in Fig. 1, there exists a threshold field in which the concentration grows exponentially. On the other hand, according to Eq. (2), $\log(\sigma/\sigma_0)$ should be proportional to $\sqrt{E}$ for arbitrarily weak fields. (The fact that the square-root dependence on the electric field starts in some threshold field has also been observed in other studies.[3-7]) Second, the coefficient α in the exponent in the exponential function (2) should correspond to $Z=1$ for a hydrogen-like donor. In general, expression (2) is valid only for the one-dimensional case, since the ionization energy decreases by the amount (1) only in the direction of the field. For this and other reasons (see, for example, Ref. 9), α can only be less than $2\sqrt{e^3/k}$, as is usually observed experimentally.[3-7,9] In our case, however, this coefficient was found to be unexpectedly large. It corresponds to a charge with $Z=10-30$ at the center, depending on the position of the quasi Fermi level of the donors.

The high value of Z is due, in our opinion, to the fact that the electrons bound on the donors are located in clusters of positive ions. Indeed, in our case the filling of tin is low [it varies from 10^{-3} to 10^{-1} for different values of I and T (Ref. 8)] and the quasi Fermi level of the donors lies much deeper than the energy of an ionized center; i.e., electrons with the Fermi and lower energy are bound on clusters of positively charged donors. The binding energy of an electron on a typical fluctuation cluster (optimal fluctuation) is of the order of $\epsilon\approx Ze^2/kr_s$ (Ref. 10), where r_s is the screening radius. Assuming that electrons with the Fermi energy ϵ_F make the main contribution to the Poole–Frenkel' effect, we have $Z\approx\epsilon_F kr_s/e^2$. The values of ϵ_F, which were measured from the unperturbed ionization energy of a donor, under the conditions of the present experiments fall in the range 3–10 meV, depending on the illumination; $r_s\approx N_t^{1/3}/N_s^{2/3}$ (Ref. 10), where N_t is the total concentration of charged centers, and N_s is the concentration of screening

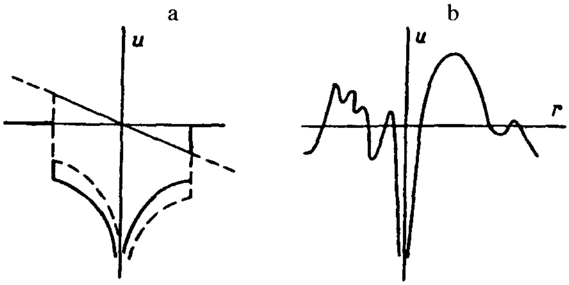

FIG. 3. Schematic diagram of the potential of an attracting impurity center in the presence of screening (a) and a random potential (b).

charges. In our case $N_t = N_2 + N_3 + N_D^+ = 2N_D$, $N_s = N_3$, where N_2 and N_3 are the concentrations of doubly and triply charged copper ions, N_D is the donor concentration, and for the sample whose data are shown in Figs. 1 and 2, we have $r_s \approx 3 \times 10^{-5}$ cm. We thus find $Z \sim 10-30$. These values of Z show that in typical fluctuations with a binding energy of 3–10 meV there are $\sqrt{Z} \approx 2-3$ excess charges within the average spacing between the impurities.

Substituting Z into expression (1), we obtain

$$\epsilon_{PF} = 2\sqrt{\epsilon_F eEr_s}. \tag{3}$$

With an increase in ϵ_F (the intensity of optical excitation of the acceptors decreases), the value of ϵ_{PF} should then increase. However, the slopes of the straight lines in Fig. 2, which are proportional to the ϵ_{PF}, decrease as ϵ_F increase. We do not understand this contradiction.

There are two possible reasons for the appearance of a threshold field. The first reason is screening. Equation (1) is valid only in the case where the distance from the center at which the potential has a maximum $r_m = \sqrt{Ze/kE}$ (see the inset in Fig. 1) is less than the screening radius r_s. If $r_m > r_s$, then the decrease of the ionization energy will not be proportional to $\sqrt{E}$. In the simplest case, if it is assumed that for $r > r_s$ the potential $U(r) = 0$ (see Fig. 3a), then for small E, we have $\epsilon_{PF} \propto E$. The square-root dependence of $\log n$ starts at $r \leq r_s$, i.e., in fields higher than the threshold field, $E_c \sim Ze/kr_s^2$.

Second, in the presence of a random potential with a small amplitude γ, the Poole–Frenkel' effect can be observed only for $\epsilon_{PF} > \gamma$. Indeed, as long as $\epsilon_{PF} < \gamma$, the thermal ionization energy must be equal to the splitting between the Fermi energy and the mobility threshold and it should not depend much on the electric field (see Fig. 3b). Apparently, this is the case that is realized in our experiments, since substituting the experimental values of the threshold field into expression (1) and using the experimentally determined values of α, we obtain an energy close to the amplitude of the random potential.[8]

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