Spectra of impurity complexes of the type H^-–H^+ and pseudocrossings of molecular terms in semiconductors

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(Submitted 3 July 1978)
Pis'ma Zh. Eksp. Teor. Fiz. **28**, No. 4, 226–230 (20 August 1978)

It is shown that impurity complexes of the type H^-–H^+, whose optical spectrum reveals pseudocrossings of the ionic and homopolar terms, are produced in semiconductors at low temperatures and under impurity excitation as a result of the hopping of the "extra" carrier over the neutral centers in the direction of the attracting center.

PACS numbers: 71.55.Dp, 72.40. + w

Recent spectral measurements of semiconductors have revealed analogs of the negative hydrogen ion H^- (negative donors D^- and positive acceptors A^+) as well as impurity molecular complexes of the type H_2^+ and H_2, with characteristic distances

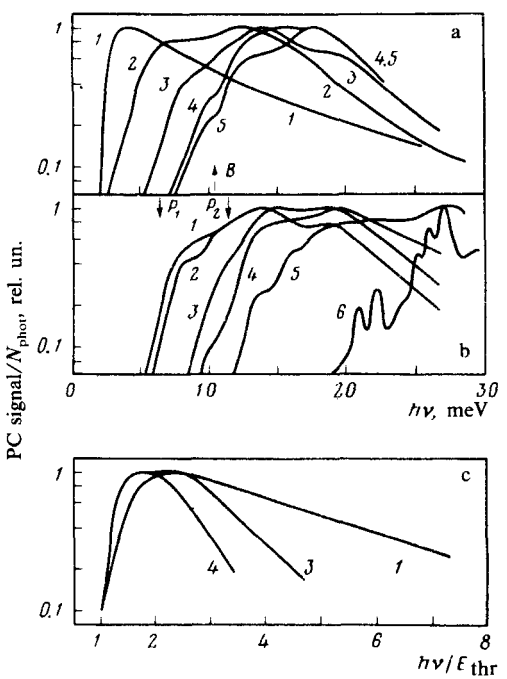

FIG. 1. Photoconductivity spectra: a) Si:B at $T = 2$ K with N, cm^{-3}: 1—8×10^{13}; 2—8×10^{15}; 3—2×10^{16}; 4—6×10^{16}; 5—10^{17}; b)—Si:P with $N = 9\times10^{16}$ cm^{-3} at various T, K:1—2; 2—3.2; 3—4.8; 4—6.8; 5—8; 6—15; c) photoconductivity spectra of Fig. 1a plotted in the $h\nu/E_{thr}$ scale.

 0021-3640/78/160209-04$00.60

between "nuclei" (impurities) that differ generally speaking from the mean value $R_c=(4\pi N/3)^{-1/3}$, where N is the concentration of the impurities (see Ref. 1 and the literature therein). The impurity molecules of type H_2 were observed only in the ground state. It is shown below that in semiconductors there can exist one other impurity complex—the analog of the molecules H_2 in the ionic state H^-–H^+.

The assumption that such complexes can be produced was advanced by us in Ref. 2 to explain the increase of the energy of photodetachement of electrons (E_{ph}) from H^--like centers, observed with increasing N.[2-4] In Refs. 3 and 4, however, this effect is attributed to a manifestation of complexes of the H_2^- type or of the upper Hubbard band. In the present paper we investigate the conditions for the formation of H^-–H^+ complexes and the spectral features that characterize them and are due to the pseudocrossing of the terms. It is shown that the presence of H^-–H^+ complexes explains also the experimental data of Refs. 3 and 4.

The photoconductivity (PC) spectra of Si:B and Si:P spectra with $N=10^{14}$–10^{17} cm^{-3} and with compensation $K\lesssim 0.01$ were investigated with the aid of a Grubb Parsons Fourier spectrometer MK-3 at $T=1.5$–20 K under background illumination conditions. Figures 1a and 1b show typical spectra at different N and T. At $N>10^{15}$ cm^{-3}, a structure of several broad peaks appears in the spectra; with increasing N and T, the shorter-wavelength peaks increase relatively. Figure 1c shows some of the spectra of Fig. 1a in $h\nu/E_{thr}$ scale (E_{thr} is the energy of the photoconductivity threshold, assumed to be equal to the radiation energy corresponding to 0.1 of the maximum photoconductivity signal). It is seen that with increasing E_{thr} the spectrum of the photoconductivity becomes relatively narrower, and the short-wave edge becomes steeper. Figure 2

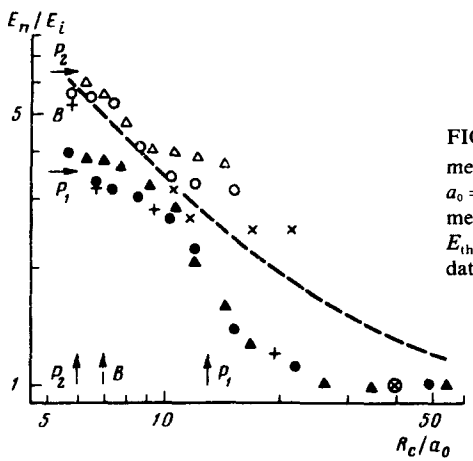

FIG. 2. Plots of E_{thr}/E_i against R_c/a_0 for Si:B ($E_i=2$ meV, $a_0=23$ Å) at T, K: ▲—2, Δ—6; Si:P ($E_i=1.8$ meV, $a_0=20$ Å) at T, K: ●, +—2, ○—6 and Ge:Sb ($E_i=0.62$ meV, $a_0=43$ Å) at T, K: ○—0.38, ×—1.5. The values of E_{thr}/E_i for Si:P (+) and for Ge:Sb were obtained from the data of Refs. 3, 4, and 8.

shows plots of E_{thr}/E_i against R_c/a_0 (a_0 is the radius of the neutral impurity, E_i is the binding energy of the extra electron for the isolated H^--like center), while Fig. 3 shows plots of $E_{thr}(T)$. We note that a weakening of the E_{thr} dependence on N and T is observed at the characteristic values of E_{thr} determined by the form of the impurity.

The results can be explained with the aid of the following models, using an n-type semiconductor as an example. At $K\ll 1$ and $N_D\cdot\ll N_{D^0}$, $N_D\cdot\ll N_{D^0}$, and $N_A\cdot\ll N_{D^0}$ for

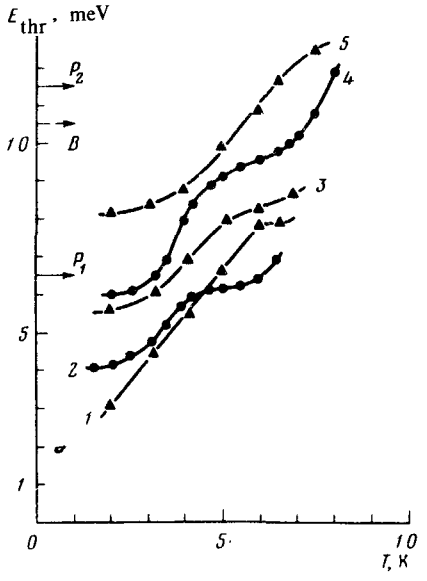

FIG. 3. Plots of $E_{thr}(T)$ for Si:B (▲) and Si:P (●) at the following values of N (cm^{-3}): 1—8×10^{15}; 2—2×10^{16}; 3—2×10^{16}; 4—9×10^{16}; 5—10^{17}.

donors D^0 in a sphere of radius $R_+ \approx R_-$ away from the nearest D^+ or A^- center, we have $E_{ph} > E_i$ and $E_{ph} < E_i$, respectively ($R_+ \approx N_{D^-}^{-1/3} \gg N_{D^0}^{-1/3} \approx R_c$). For the remaining (and most) donors we have $E_{ph} \approx E_i$. The "extra" electrons captured on the D^- levels can hop over the neutral centers to the nearest D^+ center and emit acoustic phonons, with a probability $W_h \sim \exp(-\alpha R_c/a_-)$, where $\alpha \approx 1$ and a_- is the radius of the D^- center. In addition, the D^- centers become thermally depleted with a probability $W_T \sim \exp(-E_{ph}/kT)$. At $W_h \gg W_T$, the D^- centers "approach" the D^+ centers. As a result are produced $D^- - D^+$ complexes (analogous to the molecule H_2 in the ionic state $H^- - H^+$ with distances $R < R_+$ between nuclei and with

$$E_{ph}(R) = E_i + e^2/\kappa R , \tag{1}$$

where e is the electron charge and κ is the dielectric constant. With increasing N and T, the values of W_h and W_T increase and accordingly an increase takes place in the relative numbers of the $D^- - D^+$ complexes with $R \lesssim R_c \ll R_+$ and $E_{ph} \gtrsim E_c \equiv E_i + e^2\kappa R_c$, and this leads to a shift of the long-wave PC boundary on Figs. 1a and 1b. At the same time, a change should occur in the frequency dependence of the cross section $\sigma(h\nu, R)$ of photodetachment of the electrons from the complex $D^- - D^+$, and this leads to a shrinking of the photoconductivity spectra, Fig. 1c. Our calculation shows that $\sigma(h\nu, R)$ differs substantially from $\sigma(h\nu, \infty)$ of an isolated center already at $R/a_0 \lesssim 30$ [6]: the position of the maximum almost coincides with the threshold, $h\nu_{max} = (1.1\text{–}1.2)\, E_{thr}$, and the short-wave edge falls off more rapidly.

The validity of the development model is confirmed by the presence of a structure in the spectra of Figs. 1a and 1b, and by the deviation of the function $E_{thr}/E_i(R_c/a_0)$ from the Coulomb relation (1) at the characteristic values of E_{thr} (the Coulomb depen-

dence is shown in Fig. 2 by the dashed line). In our opinion, these facts are a manifestation of the pseudocrossings of the ionic and homopolar terms, which are known for molecular systems[5,7] (the electron is in the ground state on one atom and in the excited state on the other), which occur at $R=R_x$, when the values of E_{ph} coincide with the energies of the excited states of the impurity atoms. From qualitative considerations[7] and from variational calculations[5] it follows that in a region ΔR_x near R_x the $E_{ph}(R)$ dependence is weak, the density of states $g(E)$ has a maximum, and the dimension of the region ΔR_x increases with decreasing R_x. The arrows in Figs. 1a, 1b, 2, and 3 mark the positions of the corresponding impurity (atomic) levels of phosphorus (P_1 and P_2) and of boron (B) in silicon, and in Fig. 2 they mark also the values $R_c=R_x$ at which pseudocrossings with the corresponding levels should take place. It is seen that at $7<R_c/a_0<20(E_{thr}/E_i<6)$ the position of the singularities in the photoconductivity spectra correlates with the energy of impurity atomic levels, and the calculated and experimental values of R_c/a_0, corresponding to the pseudocrossings, are in agreement. The plateau observed on the plots of $E_{thr}(R_c)$ and $E_{thr}(T)$ for Si:P ($E_{thr}=9.5$ meV and 5.8 meV) and for Si:B ($E_{thr}=8$ meV) correspond to the levels $2p_0$ ($E=11.5$ meV), $2_{p\pm}$ ($E=6.4$ meV), and $2\Gamma_8^-$ ($E=10.5$ meV).

The temperature region in which the corresponding effects exist likewise does not contradict the developed model: at $T>10$ K the complexes D^-–D^+ are thermally destroyed and only the lines of photothermal ionization of the electrons from the triplet to the doublet levels of the $1s$ states are observed at $h\nu<30$ meV in the photoconductivity spectra.[9]

We note in conclusion that the presence of the complexes D^-–D^+ explains also the results of Refs. 3 and 4 (some of which have been used in Fig. 2), as well as the data on the change of the form of the photoconductivity spectrum and of E_{thr} under uniaxial compression[4]: the compression decreases the overlap of the anisotropic wave functions of the D^- states, the hopping probability W_h,[10] and the fraction of the D^- centers with $E_{ph}>E_i$.

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