

# H<sup>-</sup>-like impurity centers and molecular complexes created by them in semiconductors

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This review analyzes the status of the problem of H<sup>-</sup>-like centers and the molecular complexes that they form in doped semiconductors. The study of these centers is closely associated with the general problem of the localization of electrons in disordered systems. The existing experimental data are discussed from a unitary standpoint. Models of various impurity complexes are discussed and the pertinent estimates are given. We show that all the fundamental observed regularities at low and moderate impurity concentrations are explained by the formation of either isolated H<sup>-</sup>-like centers or of complexes of the H<sup>-</sup>-H<sup>+</sup> type. At higher impurity concentrations, the number of H<sup>-</sup>-H<sup>+</sup> type complexes declines, impurity clusters are formed, and then a conducting impurity band arises from the H<sup>-</sup>-like states.

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## 1. INTRODUCTION

This review is devoted to elucidating the nature of the states of localized electrons in a system of randomly arranged neutral and charged impurity atoms in doped semiconductors. Considerable interest<sup>1,2</sup> in problems of electronic states in disordered systems has arisen in recent years. One can offer a large number of examples of such systems. In addition to doped semiconductors, they include dense gases,<sup>3</sup> a weakly nonideal plasma,<sup>4</sup> amorphous and glassy materials,<sup>1</sup> solid solutions,<sup>5</sup> etc.

As applied to semiconductors, the literature for a long time had treated only the electronic states of an isolated impurity atom. Recently impurity structures of a molecular type with a distance between the nuclei that depends on the impurity concentration have been found experimentally.

The possibility of realization of molecular impurity systems of various types with a varying distance between the "nuclei" enables one to create models of the

pertinent atomic-molecular systems in semiconductors. Moreover, the large dielectric constant and the small effective mass of electrons (holes) make possible the study of the behavior of impurity molecules under extreme external conditions (electric and magnetic fields, pressure, etc.).

In the theoretical analysis of the states of electrons in disordered systems, two limiting cases have been studied in detail; they have either a Coulomb potential (example: weakly doped semiconductors<sup>6</sup>), or a short-range  $\delta$ -function-like potential (the model of Lifshits<sup>7</sup> for solid solutions).

The Lifshits model deals with a "single electron," taking no account of its interaction with a "hole," and assuming that the distance between the potential wells is considerably greater than the decay distance of the wave function of an electron corresponding to a single well. Consequently the electron is localized either near one well or at two close-lying ones. The simplest realization of a well having a short-range potential in a

plasma and in gases is the neutral hydrogen atom H. As is well known,<sup>6</sup> this atom can attach an "extra" electron to form the negative ion H<sup>-</sup>.

The possible existence of H<sup>-</sup>-like impurity centers in semiconductors that are produced by attaching an extra electron to a neutral donor (D<sup>-</sup>-center) or an extra hole to an acceptor (A<sup>+</sup>-center) was predicted theoretically as early as about 20 years ago.<sup>9,10</sup> Analogy with the H<sup>-</sup> ion<sup>6</sup> implied that these centers must have an affinity energy of the extra carrier of  $E_i = 0.055E_0$  ( $E_0$  is the ionization energy of a hydrogen-like impurity atom). Such centers in weakly compensated semiconductors were actually detected and began to be intensively studied about 10 years ago.<sup>11,13</sup> The study of these centers at different concentrations  $N$  of the neutral impurities is interesting from the standpoint of the theory of disordered systems having short range potentials. Here, as we have noted, a situation is usually rather simply realized in semiconductors that models the phenomenon in other media. The study of H<sup>-</sup>-like centers is also interesting for semiconductor physics *per se*, since they have proved essential in a number of effects. Thus, in a large number of experimental studies performed under conditions of rather low temperatures ( $kT < E_i$ ) with photoexcitation of carriers, a number of features in the luminescence spectra,<sup>13</sup> scattering, and recombination of carriers<sup>12,14</sup> have been attributed to these centers. These centers have also been found to give rise to photoconductivity (PC) of Ge and Si over a broad spectral range.<sup>11,15,1)</sup> Currently the properties of H<sup>-</sup>-like impurity centers from PC spectra are being intensively studied by several research groups in the USSR, the USA, and Japan.<sup>18-32</sup>

In the theoretical analysis of the effects caused by H<sup>-</sup>-like centers in semiconductors, it seemed tempting to treat these centers as a manifestation of the localization of an electron in a disordered system of short-range potentials in line with Ref. 7. However, the experiments have shown the real situation to be more complex.

It has been established that, when  $Na_0^3 \geq 10^{-6}$  ( $a_0$  is the effective Bohr radius), the PC threshold energy  $E_{thr}$  increases considerably (severalfold) with increasing concentration of the neutral impurities.<sup>2)</sup> The shape of the PC spectrum changes at the same time. Moreover, it has turned out that  $E_{thr}$  and the form of the spectrum depend on the temperature, the magnetic field, and on uniaxial compression of the specimens.<sup>23,28</sup> In explaining the results of the experiments, all the authors<sup>18-32</sup> start with the idea that the binding energy and the wave function of the localized electron vary with increasing  $N$ . Here, Refs. 23 and 27 have essentially taken into account only the potentials of the neutral centers and have assumed the existence of molecular complexes of the type of H<sub>2</sub><sup>-</sup> and H<sub>n</sub><sup>-</sup> ( $n > 2$ ). References

19 and 26 have taken into account the fact that, under the experimental conditions, attractive H<sup>-</sup>-like centers exist simultaneously with the neutral centers having a short-range potential. The concentration  $N$ , of the former is of the same order of magnitude as that of the H<sup>-</sup> centers, and is estimated to be  $N_+ \approx 10^{-2}N$ . Here Refs. 19 and 26 have advanced the hypothesis that complexes are formed of the type of H<sup>-</sup>-H<sup>+</sup> analogs of the hydrogen molecule in the ionic state.<sup>33</sup> It was assumed in Ref. 21 that, when  $Na_0^3 \geq 6 \times 10^{-5}$ , the state of the excess electrons are delocalized and an upper Hubbard band is formed, with which the stated effects are associated. We should note that no detailed discussion has been conducted on the hypotheses that have been advanced.

It seems to us that the problem of the existence in semiconductors having neutral and charged impurities of H<sup>-</sup>-like impurity centers and molecular impurity complexes arising from them with an energy of photo-detachment of the weakly bound electron  $E_{ph}$  ( $E_i < E_{ph} < E_0$ ) is of great interest and is closely connected with the general problem of the localization of an electron in disordered systems.<sup>2</sup> Here the various complexes are simply concrete manifestations of this localization.<sup>3)</sup> Moreover, this problem is directly related to the problem of band-type impurity conduction having an activation energy  $\epsilon_2$ .<sup>1</sup> This conduction and a number of accompanying effects are observed in weakly compensated semiconductors when  $Na_0^3 \sim 10^{-2} - 10^{-3}$ . This conduction is qualitatively explained by the formation of a conducting impurity band (D<sup>-</sup>-band) via overlap of the wave functions of D<sup>-</sup>-states. This band is analogous to an upper Hubbard band, though in a disordered system.<sup>37,38</sup> The spacing between the bottom of this band and the ground level (the Mott-Hubbard gap) must decline with increasing  $N$  from  $0.95E_0$  (for  $Na_0^3 < 10^{-6}$ ) to zero for  $Na_0^3 \sim 0.016$  (Mott transition). We should note that this approach neglects the existence of the Coulomb potential that allows states also to exist inside the Mott-Hubbard gap. The PC studied in Refs. 18-32 is directly due to transfer of electrons from states inside the Mott-Hubbard gap into the conduction band.<sup>4)</sup>

This review is organized as follows. Section 2 presents the experimental results<sup>15-32</sup> and their interpretation by the authors. Section 3 points out the physical processes that are fundamental under the conditions of the experiments. It also gives the theoretical models for treating them and the pertinent estimates. These models are generally purely atomic. The semiconductor specifics is taken into account only in Sec. 3c in treating the hopping of the extra electron in the case of anisotropic wave functions. The close of Sec. 3 qualitatively discusses the problems of delocalization of

<sup>1)</sup>This effect is already being employed in designing submillimeter detectors.<sup>16-18</sup>

<sup>2)</sup>The threshold  $E_{thr}$  is taken to mean the minimal quantum energy at which the PC signal amounts to 0.1 times the maximal value.

<sup>3)</sup>We note that several kinds of molecular-type impurity complexes have been already found in semiconductors that do not involve the presence of H<sup>-</sup>-like centers. For example, they include impurity assemblies of the types of H<sub>2</sub><sup>+</sup><sup>34</sup> and H<sub>2</sub><sup>35,36</sup>

<sup>4)</sup>In interpreting optical-absorption data in silicon, Refs. 39-41 have advanced the hypothesis that the features of the spectra involve transition of electrons from the ground states of the impurities to states lying inside the Mott-Hubbard gap.

H<sup>-</sup>-like states with account taken of the Coulomb potential. Section 4 analyzes the experimental data by using the models and estimates of Sec. 3. The Conclusion formulates the fundamental conclusions and problems.

## 2. EXPERIMENTAL DATA ON SUBMILLIMETER PHOTOCONDUCTIVITY OF Ge AND Si

The study of submillimeter PC has advantages over other methods of studying H<sup>-</sup>-like centers, since there are no other mechanisms of PC of germanium and silicon in this wavelength range. The conditions and technique of experimentation have been described in a set of studies.<sup>15,18,23</sup> One usually attains a sufficient concentration of D<sup>-</sup> (or A<sup>+</sup>) centers in specimens cooled to liquid-helium temperature by optical excitation of carriers from the ground impurity states to the conduction band. One employs semiconductor materials having a small impurity compensation *K*. We should note two fundamental lines of study. The first is to study the H<sup>-</sup>-like center itself: to determine the binding energy *E*<sub>1</sub>, the effect on *E*<sub>1</sub> of the many-valley structure of the semiconductor and of the magnetic field, to determine the cross-sections for optical and impact<sup>24</sup> neutralization of the center, etc. The second is to study the interaction of the D<sup>-</sup> (or A<sup>+</sup>) centers with the neutral and charged impurities with increasing *N*.

1. It turned out historically that the necessary conditions of impurity concentration and temperature for observing isolated centers were not always fulfilled in the first experiments to study PC involving D<sup>-</sup> (or A<sup>+</sup>) centers,<sup>11,20,21</sup> etc. Recent studies have shown that the edge of the spectrum and the region *per se* of observing PC are shifted to higher energies with increasing *N* and *T*. This explains the ambiguity in the determination of the values of *E*<sub>1</sub> given by different authors.<sup>11,20,23</sup> At present the value of *E*<sub>1</sub> pertaining to isolated D<sup>-</sup> (A<sup>+</sup>) centers has been determined experimentally in weakly doped specimens at low temperatures ( $N^{1/3} a_0 < 10^{-2}$ ,  $kT < 0.1E_1$ ). In Si it proved to be 1.7 meV<sup>18</sup> and 2 meV<sup>26</sup> for phosphorus (P) and boron (B), respectively. In Ge for arsenic (As) and antimony (Sb), the values of *E* (0.75 meV and 0.625 meV, respectively) have been determined relatively recently. Here the aim was reached by performing the experiment at *T* = 0.38 K,  $N \approx 5 \times 10^{13} \text{ cm}^{-3}$ .<sup>23</sup> Uniaxial compression of the specimens led to an additional small decrease in *E*<sub>1</sub>: to 0.55 for Ge(Sb) and 0.57 meV for Ge(As).<sup>23</sup> All the

TABLE I.

Material	Dopant	<i>E</i> <sub>0</sub> , meV	<i>E</i> <sub>0, theor.</sub> , meV	<i>E</i> <sub>1, theor.</sub> , meV	<i>E</i> <sub>1</sub> , meV	$\sigma_0$ , Å	$\sigma_1$ , Å
Si	P	44	31.3	1.72	1.7	17	82
	B	43.5	56	3.1	2	23	105
Ge	Si	10.3	9.8	0.54	0.625	42	168
	As	14.2	9.8	0.54	0.75	35	152

Note. The *E*<sub>0</sub> are the experimental values obtained from optical measurements<sup>6</sup>; *E*<sub>0, theor.</sub> is calculated in the effective-mass approximation<sup>6</sup>; *E*<sub>1, theor.</sub> = 0.055 *E*<sub>0, theor.</sub>. For Si(P) and Ge(Sb, As) we have:  $a_0 = \hbar / \sqrt{2m_d E_0}$ ;  $a_1 = \hbar / \sqrt{2m_d E_1}$ ;  $m_d = (m_1^2 m_{\parallel})^{1/3}$ , where *m*<sub>∥</sub> and *m*<sub>⊥</sub> are the longitudinal and transverse effective masses. For Si(B) we have  $a_0 = \hbar / \sqrt{2m_1 E_0}$ ;  $a_1 = \hbar / \sqrt{2m_1 E_1}$ ; *m*<sub>1</sub> is the effective mass of a light hole.

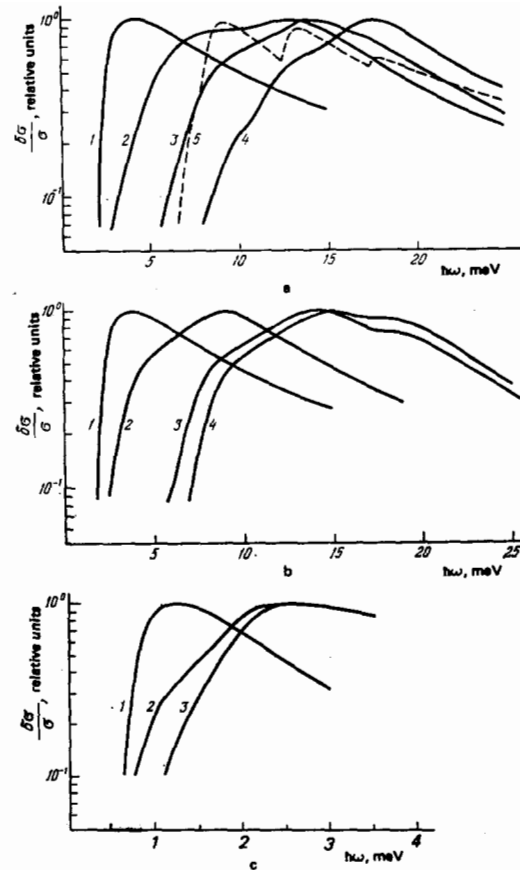


FIG. 1. Photoconductivity spectra at various impurity concentrations. a) Si(B), *T* = 2 K, *N* (cm<sup>-3</sup>) = 8 × 10<sup>13</sup> (1), 8 × 10<sup>15</sup> (2), 2 × 10<sup>16</sup> (3, 4), 9.6 × 10<sup>16</sup>; 5—calculated curve for Si(B) with *N* = 2 × 10<sup>16</sup>; b) Si(P), *T* = 2 K, *N* (cm<sup>-3</sup>) = 3 × 10<sup>14</sup> (1), 5 × 10<sup>15</sup> (2), 9 × 10<sup>16</sup> (3), 1.6 × 10<sup>17</sup> (4); c) Ge(Sb),<sup>27</sup> *T* = 0.38 K; *N* (cm<sup>-3</sup>) = 5 × 10<sup>13</sup> (1), 6.2 × 10<sup>14</sup> (2), 9.9 × 10<sup>14</sup> (3).

values of *E*<sub>1</sub> are given in the table; we see that they are close to the theoretical values. Good agreement was also established between the theoretical curve for the cross-section for detachment of an electron from the free H<sup>-</sup> ion<sup>42</sup> and the submillimeter PC spectra for all the stated materials.<sup>21,23</sup>

However the study of isolated H<sup>-</sup>-like centers in semiconductors has not been exhausted even now. The energy spectrum of a center in a many-valley semiconductor and the effect on it of uniaxial compression and of a magnetic field are being studied theoretically<sup>43</sup> and experimentally.<sup>23,28</sup>

2. In doped specimens the form of the PC spectrum becomes more complicated and depends on *N* and *T*. Figure 1 shows the variation of the PC spectra of Si(B) [Fig. 1(a)], Si(P) [Fig. 1(b)], and Ge(Sb) [Fig. 1(c)] with increasing impurity concentration.<sup>5</sup> We see that the photoconductivity threshold *E*<sub>thr</sub> and the intensity maximum in the spectra are shifted into the higher-energy region; at the same time the spectrum reveals structure. Thus, for Si(B) for  $N > 10^{15} \text{ cm}^{-3}$ , at first there are two weakly marked peaks (curve 2), and then three (curves 3–5).

<sup>5</sup> Here and below we shall present the experimental results of Refs. 18–32 normalized to the number of quanta.

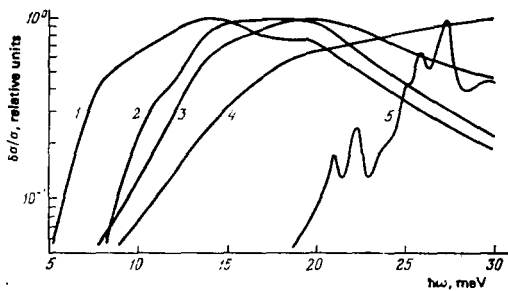


FIG. 2. Photoconductivity spectra in Si(B).  $N = 9 \times 10^{16} \text{ cm}^{-3}$ ,  $T(\text{K}) = 2$  (1), 4.8 (2), 8.0 (3), 9.0 (4), 15 (5).

The features of PC spectra that we have noted are also observed in a single, sufficiently doped specimen as  $T$  increases. Figure 2 shows the variation of the PC spectrum in an Si(P) specimen having  $N = 9 \times 10^{16} \text{ cm}^{-3}$ . For  $T = 2 - 7 \text{ K}$ , the spectra amount to a combination of three peaks. With increasing  $T$ , the relative intensity of the short-wavelength peak increases. For  $T > 10 \text{ K}$  (curve 5), the PC owing to  $D^-$ -centers vanishes and peaks arise from photothermal ionization of donors [the transitions  $1s(T_1)$ ,  $1s(E) - 2p_0$ ,  $2p_x$ , which correspond to the absorption peaks observed in Ref. 44].

In Fig. 3 the curves 1, 3, and 4 of Fig. 2 have been redrawn on the scale of  $\hbar\omega/E_i$ . We see that the PC spectrum becomes narrower with increasing  $N$ , while the short-wavelength edge becomes steeper.

We note that the values of  $E_{\text{thr}}$  exceed  $E_i$  by factors from 2 to 7 in the performed experiments for sufficiently large  $N$  and  $T$ .

3. Uniaxial compression of doped specimens of Ge(Sb)<sup>22,25,27</sup> leads to the same changes in the spectrum as a decreased concentration of impurities does. Pressure elicits a structure (Fig. 4): in addition to the short-wavelength peak, which shifts somewhat to lower energies, a peak appears with a maximum at  $\hbar\omega = 1.1 \text{ meV}$ . With increasing pressure, this peak increases in comparison with the short-wavelength peak, and it proves to dominate in the spectrum at extremely high pressure. The energy  $E_{\text{thr}} = 0.55 \text{ meV}$  proves close to the value obtained for isolated  $D^-$ -centers under condi-

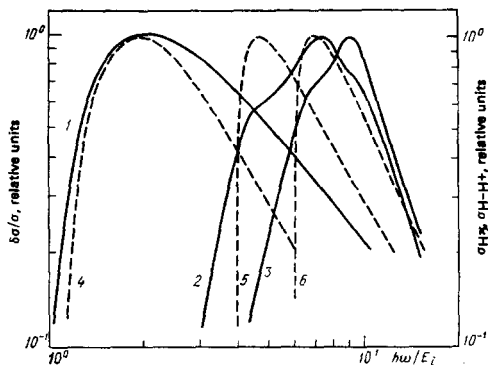


FIG. 3. Photoconductivity spectra of Si(B) at 2 K on the scale of  $\hbar\omega/E_i$ .  $N (\text{cm}^{-3}) = 8 \times 10^{13}$  (1),  $2 \times 10^{16}$  (2),  $9.6 \times 10^{16}$  (3), 4—calculated curve for  $H_2^-$ -type complexes; 5, 6—calculated curves for  $H^- - H^+$ -type complexes for  $R = 9a_0$  (5) and  $R = 5.5a_0$  (6).

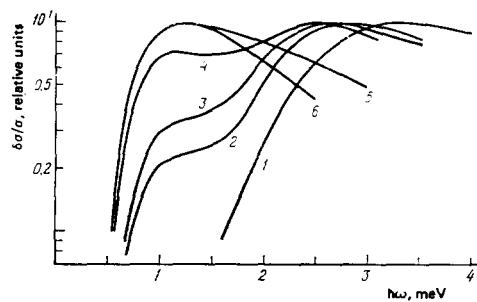


FIG. 4. Photoconductivity spectra in Ge(Sb) with  $N = 9 \times 10^{14} \text{ cm}^{-3}$  under uniaxial compression along [111] at  $T = 1.5 \text{ K}$ .<sup>22</sup> The pressure  $P$  (dynes/cm<sup>2</sup>) is: 0 (1),  $-1.3 \times 10^8$  (2),  $10^8$  (2),  $10^8$  (3),  $2.5 \times 10^8$  (4),  $3.7 \times 10^8$  (5),  $6.0 \times 10^8$  (6).

tions of the same pressure.<sup>23</sup> The action jointly with pressure of a magnetic field with  $H$  up to 25 kOe has practically no effect on the magnitude of the photoresponse.<sup>28</sup> Under the same conditions in a pure specimen of Ge(Sb) ( $N = 5 \times 10^{13} \text{ cm}^{-3}$ ), the PC appreciably declines with increasing  $H$ .

4. A detailed analysis of the dependences of  $E_{\text{thr}}$  on  $N$  and  $T$  has permitted establishment<sup>26</sup> of the near-constancy of  $E_{\text{thr}}$  over certain ranges of variation of  $N$  and  $T$ . Figure 5 shows the relationships of  $E_{\text{thr}}$  to  $N$  for Si(B) [Fig. 5(a)], Si(P) [Fig. 5(b)], and Ge(Sb) [Fig. 5(c)], as obtained by processing the PC spectra from Refs. 20, 21, 23, and 27. The values of  $E_{\text{thr}}$  that correspond to the plateaus on the  $E_{\text{thr}}(N)$  curves are correlated with the position of the peaks in the PC spectra of Fig. 1. "Shoulders" are observed in Si(B) at  $E_{\text{thr}} = 8$  and  $12.5 \text{ meV}$ , in Si(P) at  $5.8$  and  $9.5 \text{ meV}$ , and in Ge(Sb) at  $E_{\text{thr}} \approx 1.5 - 2 \text{ meV}$ . We note that this is precisely the situation that explains why the value  $E_{\text{thr}} = 1.56$  for Ge(Sb) was assumed for a long time to be the corresponding energy for photodetachment for an isolated  $D^-$ -center.

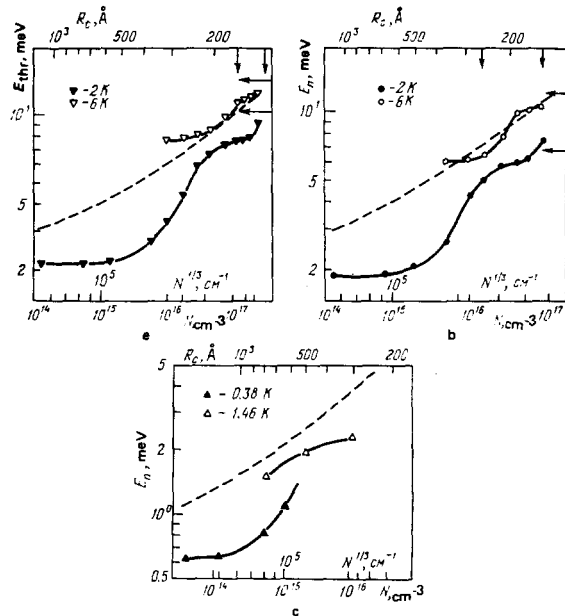


FIG. 5. Dependence of  $E_{\text{thr}}$  on  $N$  for Si(B) (a), Si(P) (b),<sup>19,21</sup> and Ge(Sb) (c)<sup>27</sup> at different temperatures. The dotted curve shows the relationship of Eq. (14).

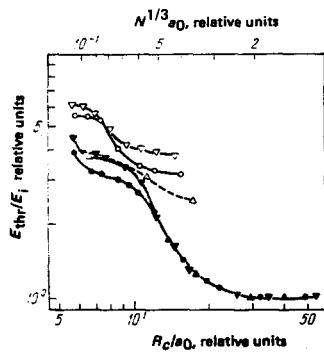


FIG. 6. Dependence of  $E_{\text{thr}}/E_1$  on  $N^{1/3}a_0$  for Si(B) ( $\nabla, \blacktriangledown$ ), Si(P) ( $\circ, \bullet$ )<sup>19,21</sup> and Ge(Sb) ( $\Delta, \blacktriangle$ )<sup>21</sup>.

Figure 6 shows the same relationships in a single graph having the coordinates of  $E_{\text{thr}}/E_1$  and  $N^{1/3}a_0$ . We see that, at low temperature (2 K for Si; 0.38 K for Ge), the PC threshold does not vary, and is determined by  $E_1$  up to concentrations corresponding to  $N^{1/3}a_0 \sim 10^{-2}$ . The value of  $E_{\text{thr}}$  increases with increasing doping. The overall trend of the variations agrees well for the different materials. Figure 7 shows the relationships of  $E_{\text{thr}}$  to  $T$  for several specimens of Si(P) and Si(B). Here also we observe regions having  $E_{\text{thr}} \approx \text{const}$ . These values of  $E_{\text{thr}}$  (except for the low-temperature region of curves 2 and 3) correspond to the shoulders of the curves of Fig. 5.

5. The temperature-dependence of the magnitude of the PC for a fixed frequency, which corresponds to the energy of photodetachment of a hole from an isolated  $A^*$  center, is exponential for  $T > T_c$ . At lower temperatures it becomes weaker—the temperature factor for destruction of  $H^-$ -like centers becomes smaller than the other factors.<sup>19</sup> The lifetimes  $\tau_i$  of the “extra” hole of an  $A^*$ -center having  $E_{\text{ph}} \approx E_1$  were obtained as a function of the impurity concentration (Fig. 8) from the values of  $T_c$  for a wide range of concentrations of B in Si. It turned out that  $\tau_i$  declines exponentially with decreasing distance between the impurities.

The values of  $\tau_i$  for the “excess” electrons in Si(P) having  $N = 8.5 \times 10^{15} \text{ cm}^{-3}$  has been directly measured<sup>20</sup> at  $T = 1.5\text{--}3.9 \text{ K}$  by the decline in the PC that they produce. The lifetime decreases with increasing  $T$ , and varies over the range 115–20  $\mu\text{s}$ .

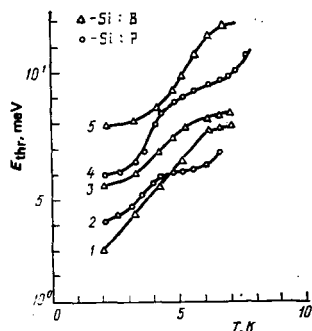


FIG. 7. Dependence of  $E_{\text{thr}}$  on  $T$  for Si(B) and Si(P).  $N \text{ (cm}^{-3}\text{)} = 8 \times 10^{15}$  (1),  $2 \times 10^{16}$  (2),  $2 \times 10^{16}$  (3),  $9 \times 10^{16}$  (4),  $10^{17}$  (5).

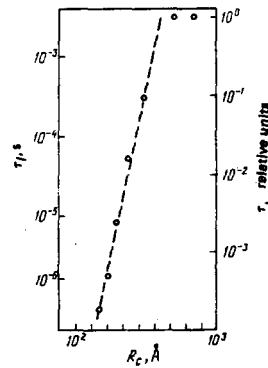


FIG. 8. Dependence of the lifetime of an isolated  $A^+$ -center on the impurity concentration in Si(B) ( $R_c = (4^3 \pi N)^{-1/3}$ ).

6. Figure 9 shows the dependences on  $N$  of the maximal photoresponse  $(\delta\sigma/\sigma)_{\text{max}}$  (i.e., the PC measured at the frequencies corresponding to its maximal values) and of the concentration  $p$  of free holes for Si(B) ( $N = 10^{14}\text{--}10^{17} \text{ cm}^{-3}$ ,  $T = 2 \text{ K}$ ,  $\alpha d < 1$ , where  $\alpha$  is the absorption coefficient and  $d$  is the thickness of the specimen). We see that  $(\delta\sigma/\sigma)_{\text{max}}$  remains practically constant, while the concentration of holes increases, starting at  $N \geq 5 \times 10^{15} \text{ cm}^{-3}$ .

7. In specimens having  $N^{1/3}a_0 > 10^{-1}$ , as  $N$  increases the character of the spectrum changes qualitatively—instead of a peak in the PC, one observes an increase in  $\delta\sigma/\sigma$  with the frequency. Figure 10 shows the transformation of the PC spectra for Si(B) [Fig. 10(a)], Si(P) [Fig. 10(b)], and Ge(Sb) [Fig. 10(c)]. A similar change in the form of the spectrum is also observed with a given particular specimen with increasing  $T$  (see, e.g., curves 3 and 4 in Fig. 2). Increasing  $N$  decreases the temperature  $T_{cr}$  at which the shape of the spectrum changes.<sup>6</sup> Figure 11 shows the PC spectra of an Si(P) specimen for  $N = 3 \times 10^{17} \text{ cm}^{-3}$ . It corresponds to  $T_{cr} \approx 5.2 \text{ K}$ , whereas  $T_{cr} \approx 8 \text{ K}$  for a specimen with  $N = 9 \times 10^{16}$  (see Fig. 2). We see that, when  $T > T_{cr}$ , the slopes of the curves and curve 5 in Fig. 11 ( $T = 6 \text{ K}$ ) resemble curves 4 and 5 of Fig. 10(a).<sup>7</sup>

It is interesting to compare the PC spectra with the absorption spectra under the same conditions. Some recently published papers have studied the variation with concentration of the position of the long-wavelength absorption edge in Ge(As, Sb)<sup>32</sup> and in Si(P).<sup>41</sup> The authors interpret the results of the experiments differently. According to Ref. 32, the absorption edge arises from the transition of an electron from the ground state to the  $D^-$ -band, while according to Ref. 41, it arises from transition to impurity clusters.

<sup>6</sup>We define  $T_{cr}$  as the value of  $T$  at which the exponent in the dependence of the short-wavelength region of the spectrum  $\delta\sigma/\sigma$  on  $\omega$  has declined by 10%.

<sup>7</sup>The results presented in Figs. 9; 10a, b; 11; and 13 (see below) have not previously been published; the data of Figs. 10a, b and 11 were obtained by the authors jointly with V. A. Zayats and Yu. V. Tovmach, members of the Institute of Physics of the Academy of Sciences of the USSR.

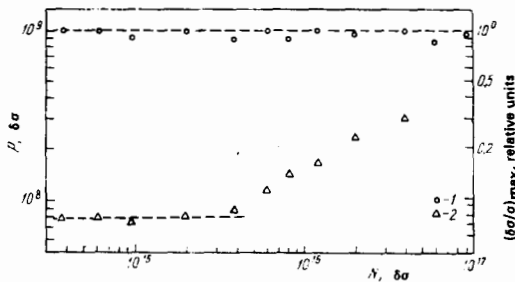


FIG. 9. Dependence of the magnitude of the PC signal at the maximum of the spectrum (1) and the hole concentration (2) on  $N$  in Si(B) at  $T=2$  K.

### 3. MODELS OF COMPLEXES INVOLVING $H^-$ -LIKE CENTERS

#### a) Fundamental physical processes of formation of impurity complexes

Let us examine the processes that affect PC spectra and their dependence on  $N$ ,  $T$ , and other factors. According to the hypotheses of Refs. 15–32, PC spectra can arise from: 1) isolated  $H^-$ -like centers; 2) impurity complexes of the type of the negatively charged hydrogen molecule  $H_2^-$ ; 3) impurity complexes of the type of the hydrogen molecule in the ionic state  $H^-H^+$ ; 4) manifestation of an upper Hubbard band. Here the distance  $R$  between the “nuclei” in the complexes  $H_2^-$  and  $H^-H^+$  and the position of the bottom of the upper Hubbard band must depend on  $N$ .

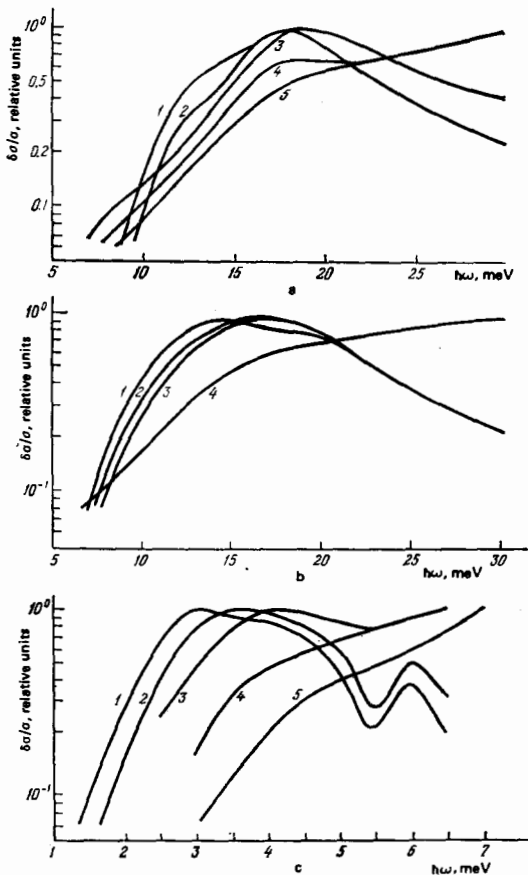


FIG. 10. Photoconductivity spectra.

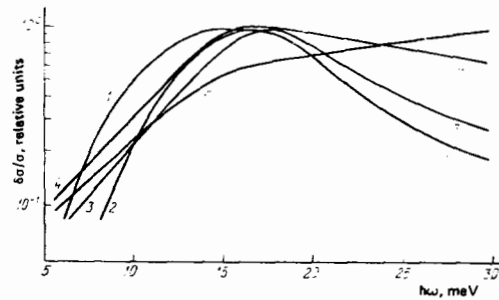


FIG. 11. Photoconductivity spectra of Si(P) with  $N=3 \times 10^{17} \text{ cm}^{-3}$ ,  $T(\text{K})=2$  (1), 4.8 (2), 5.2 (3), 5.6 (4), 6.5 (5).

We shall make estimates to enable us to determine which complexes dominate under different experimental conditions, using the example of an  $n$ -type semiconductor. With a random distribution of the impurities, the shape of the spectrum is determined by the following quantities: the binding energy  $E(R)$  of the “excess” electron at a center or in an impurity complex; the cross-section  $\sigma(\hbar\omega, R)$  for photodetachment of an electron; and the number  $n(R)$  of electrons having a given  $E(R)$  and  $\sigma(\hbar\omega, R)$ . In turn, the value of  $n(R)$  is determined by the lifetime  $\tau_1(E)$  of the electrons and by the number of neutral centers in the interval from  $dE(R)$  to  $g[E(R)] \times dE(R)$ , where  $g(E)$  is the density of states.

Electrons are excited from the impurity levels by optical excitation (e.g., by background illumination) into the conduction band. Then they are trapped by attractive ( $D'$ ) or neutral ( $D^0$ ) centers (Fig. 12). When  $K \ll 1$  and with weak illumination, the concentrations of charged donors  $D'$  and acceptors  $A$  are small:  $N_{D'} \approx N_A \sim KN_{D^0} \ll N_{D^0}$ . The levels of the donors that lie in a sphere of radius  $R$ ,  $\sim R \sim N_{D'}^{-1/3}$  from the nearest  $D'$  or  $A^-$  center (“Coulomb sphere”) are “deepened” or “raised” by the Coulomb field. All the rest of the donors are “weakly displaced.” According to the estimates, they are in the majority for any  $N$  and  $T$ , since the most probable distance<sup>46</sup> to the nearest  $D'$ -center is  $R_s = \Gamma(4/3)[(4/3)\pi N_{D'}]^{-1/3} \approx 0.55N_{D'}^{-1/3}$ . For an electron lying in a  $D^-$ -level, two processes substantially depend on  $N$  and  $T$ : the probability of thermal ejection of an electron into the conduction band is<sup>7</sup>  $W_T \times (E_{pb})$

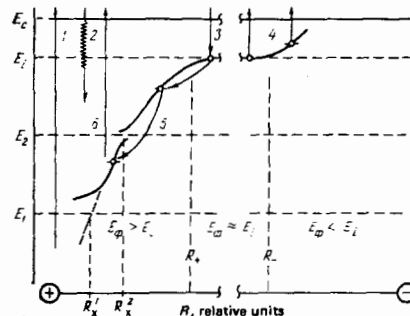


FIG. 12. Fundamental processes that govern the production and breakdown of  $H^-$ -like centers and complexes. 1—photoionization by the “background” illumination, 2—“direct” recombination, 3—trapping of an electron by a neutral center (production of a  $D^-$ -center), 4—thermal detachment, 5—hopping (“sinking”), 6—photodecomposition.

$\propto \exp(-E_{ph}/kT)$ , and the probability  $W_s$  of transition to a deeper energy state (sinking) by hopping via  $D^-$ -states of neutral centers toward an attractive center with preferential emission of acoustic phonons. By analogy with the case of hopping impurity conduction,<sup>6</sup> we should expect for hops via weakly deepened centers that  $W_s \propto \exp(-2\alpha/N^{1/3}a_1)$ . Here  $\alpha \sim 1$  is a parameter, and  $a_1$  is the decay length of the wave function of the  $D^-$ -state. As a result of these hops, the electron approaches a  $D^-$ -center, and complexes of the type  $H^- - H^+$  arise with a distance  $R$  between the nuclei that satisfies the condition  $R_0 \leq R < R_*$ . Here we have  $R_0 \approx 0.55N_{D_0}^{1/3}$ . For weakly shifted donors, the potential difference  $\Delta_{ij}$  between adjacent neutral centers ( $i$  and  $j$ ) is determined by the fields of several charged centers. Whenever  $\Delta_{ij} < kT$ , hops with absorption and emission of phonons are almost equally probable, and  $W_s$  decreases [for estimates, see Sec. 3(d)]. An electron trapped by a weakly shifted donor forms an almost isolated  $D^-$ -center. If the distance  $R_{ij}$  between two adjacent neutral donors is small enough, the electron is collectivized and a  $D_2^-$  complex arises ( $H_2^-$ -type). Its energy level is split by the exchange interaction<sup>34</sup> [see Sec. 3(c)].

We present below some calculations for atomic-molecular systems that we treat as model systems for describing the corresponding impurity assemblies in semiconductors. Here the specific features of the semiconductors (the existence of many valleys in the conduction band, the degeneracy of the valence band, and the interaction with phonons) are not taken into account. We shall take them into account in treating hopping motion of an excess carrier via neutral centers toward an attractive center.

#### b) The negative hydrogen ion $H^-$

In an  $H^-$ -type system, one usually obtains the wave function  $\psi_1$ , the electron affinity  $E_1$ , and the photodetachment cross-section  $\sigma_{H^-}(\hbar\omega)$  of the extra electron by variational calculations.<sup>3,48</sup> Recently models of a potential of finite range ( $r_0$ ) and the model of a  $\delta$ -potential ( $r_0 \rightarrow 0$ ) have been successfully used.<sup>42</sup> Here one assumes that the nucleus and the "inner" electron create a short-range potential of the polarization and screened Coulomb type with a decay length  $\sim a_0$ , while the "outer" electron lies at a distance  $r \gg a_0$  from the nucleus. We shall employ a model of a  $\delta$ -potential, while assuming as usual the binding energy  $E_1$  to be known. Then the wave function of the outer electron has the form

$$\psi_1 = C \frac{\exp(-r/a_1)}{r}, \quad a_1 = \frac{\pi}{\sqrt{2mE_1}}. \quad (1)$$

In calculating the photodetachment cross-section  $\sigma_{H^-}(\hbar\omega)$ , we can describe the wave function  $\psi_k(r)$  of the free electron (the photoelectron) with the plane wave  $\psi_k(r) \sim \exp(ik \cdot r)$ . Then we have

$$\sigma_{H^-} = B^2 \frac{32\pi}{3} \frac{e^2}{\hbar c} a_1^2 \frac{[E_1(\hbar\omega - E_1)]^{3/2}}{(\hbar\omega)^2}, \quad B^2 \approx 2.7. \quad (2)$$

This formula describes well the experimental data on photodecomposition of  $H^-$  ions.<sup>42,48</sup> We note that the cross-section approaches zero for  $\hbar\omega = E_1$  and has a maximum at  $\hbar\omega = 2E_1$ . We can easily see from Eq.

(2) that the relative half-width of the curve is  $\Delta(\hbar\omega)/E_1 \sim 4$ . That is, it is substantially larger than in the case of photoionization of a hydrogen-like atom.<sup>8</sup> The decline in  $\sigma_{H^-}(\hbar\omega)$  for  $\hbar\omega \gg E_1$  is proportional to  $(\hbar\omega)^{-3/2}$ . That is, the decline is far slower than for a hydrogen-like atom.<sup>8</sup>

#### c) The system $H_2^-$

Just like a neutral hydrogen atom, a system of two neutral hydrogen-like atoms whose energy levels are in resonance can attach an extra electron to form the molecular ion  $H_2^-$ . One can represent the wave function of the outer electron for a distance between the nuclei  $R \gg a_0$  in the form<sup>47</sup>

$$\psi_{\pm}(r) = C^{\pm} [\psi(r) \pm \psi(r - R)]. \quad (3)$$

This corresponds to a symmetric and an antisymmetric combination. It yields two energy levels  $E_{\pm} = E_1 [1 \pm 2(a_1/R)e^{-R/a_1}]$ . For example, for  $R/a_1 \approx 2.5$  ( $R/a_0 \sim 10$ ), the splitting  $E_+ - E_-$  amounts to  $0.13E_1$ .

Let us find the photodecomposition cross-section  $\sigma_{H_2^-}$  for the complex  $H_2^-$  in the symmetric and antisymmetric states. We get the following value for the cross-section averaged over the angle between  $k$  and  $R$  ( $k$  is the wave vector of the detached electron) (see the Appendix):

$$\sigma_{H_2^-} \approx \sigma_{H^-} \left( \frac{\hbar\omega - E_{\pm}}{\hbar\omega - E_1} \right)^{3/2} \left( 1 \pm 2 \frac{\Delta_{\pm}}{\hbar\omega} \right) \frac{1}{1 \pm S} \left( 1 \pm \frac{\sin kR}{kR} \right). \quad (4)$$

Here we have  $\Delta_{\pm} = E_{\pm} - E_1$ ,  $|\Delta_{\pm}| \ll E_1$ , and  $S = \exp(-R/a_1)$  is the overlap integral. We see that, whenever both states are occupied with the same probability, the frequency-dependences of  $\sigma_{H_2^-}$  and  $\sigma_{H^-}$  almost coincide. When only the lower state is occupied, then the terms  $2\Delta_{\pm}/\hbar\omega$  and  $\sin(kR)/kR$  cause the cross-section for  $H_2^-$  to have a somewhat steeper short-wavelength tail and a smaller half-width than for  $H$ . Figure 3 shows the curve for  $\sigma_{H_2^-}(\hbar\omega)$  for the value  $R/a_1 = 2.5$ .

An important problem is that of the maximum value of the affinity energy  $E_+$ . According to the data of a variational calculation,<sup>49</sup> it is reached at  $R \sim 5a_0$ , and it exceeds  $E_1$  slightly, by about 20%. When  $R < 3a_0$ , the system  $H_2^-$  becomes unstable with respect to the decomposition  $H_2^- \rightarrow H_2 + e$ .

#### d) The probability of phonon hopping and sinking

Now let us take into account the case specific for semiconductors in which, owing to the fields of the charged impurities, the energy difference  $\Delta_{ij}$  between two adjacent atoms is larger than the exchange integral  $I_{ij}$ :

$$\Delta_{ij} > I_{ij} = \frac{2a_1}{R_{ij}} E_1 \exp\left(-\frac{R_{ij}}{a_1}\right). \quad (5)$$

Let us find the probability  $W_{ij}$  of a phonon-stimulated hop of an electron from atom ( $i$ ) to atom ( $j$ ). By analogy with the case of hopping impurity conduction,<sup>45</sup> we obtain (the details of the calculations are given in the Appendix):

$$W_{ij} = \frac{1}{\tau_{\text{pulse}}(T)} \frac{1}{(2mkT)^{3/2}} \frac{2m^2 \Delta_{ij} S_{ij}^2}{(ms)^2} \cdot \frac{1}{4} \varphi^2(q_1 a_1) \begin{cases} N_{q_1} + 1, \\ N_{q_1}. \end{cases} \quad (6)$$

Here  $\tau_{\text{pulse}}(T) \sim T^{-3/2}$  is the equilibrium relaxation time



of a pulse with respect to acoustic phonons,  $q_1 = \Delta_{ij}/\hbar s$ ,  $S_{ij} = S(R_{ij})$ ,  $N_{q_1}$  is the equilibrium number of phonons having the wave vector  $q_1$ ,  $s$  is the velocity of sound, and  $N_{q_1+1}$  and  $N_{q_1}$  correspond to emission and absorption of phonons. The function  $\varphi(q_1 a_1)$  is defined by Eq. (A.5). We see that  $W_{ij}$  and the jump time  $\tau_{ij} \equiv W_{ij}^{-1}$  depend exponentially on the distance  $R_{ij}$  between the donors. We shall discuss the relationship of the characteristic values of  $R_{ij}$  to  $N$  in the next section.

In addition to the hopping time, the time that it takes for the extra electron to change its binding energy, or sinking time  $\tau_s$ , proves important in analyzing the experimental results. Therefore we shall discuss the difference between  $W_{ij}$  and  $W_s \equiv \tau_s^{-1}$ . When  $\Delta_{ij} \ll kT$ , hops with emission and absorption of phonons are almost equally probable, and on the average the electron loses the energy  $\Delta_{ij}$  as the result of  $2N_{q_1} + 1 \approx 2kT/\Delta_{ij} \gg 1$  hops. Then  $W_s \approx W_{ij}(\Delta_{ij}/kT)$ , and the characteristic time for change of the binding energy by an amount  $\sim kT$  is

$$\tau_s(kT) \sim \tau_{ij} \cdot 2 \left( \frac{kT}{\Delta_{ij}} \right)^2 \gg \tau_{ij}. \quad (7)$$

It is difficult to find  $\Delta_{ij}$ . One can only estimate the maximal value of  $\Delta_{ij}$  for fixed  $N$  and  $N$ , under the assumption that it is determined only by the closest charged center and that all three centers ( $i$ ,  $j$ , and the attractive center) lie on a straight line:

$$(\Delta_{ij})_{\max} \approx \frac{e^2}{\kappa R_*} - \frac{e^2}{\kappa(R_* + R_{ij})} \approx \frac{e^2}{\kappa R_{ij}} \left( \frac{R_{ij}}{R_*} \right)^2. \quad (8)$$

Here  $\kappa$  is the dielectric permittivity. An estimate for  $N = 8 \times 10^{15} \text{ cm}^{-3}$ ,  $N_* = 10^{-2} N$ , and  $R_{ij} \sim N^{-1/3}$  yields  $(\Delta_{ij})_{\max} \approx 1.8 \text{ K}$ . For the weakly shifted centers we have  $\Delta_{ij} \ll (\Delta_{ij})_{\max}$ . Therefore an extra electron trapped in such a center apparently loses its energy appreciably through a large number of hops. Sinking by hops (down-hopping) of the extra electrons at weakly shifted centers, in spite of the similarity to hopping movement along a percolation level,<sup>6</sup> has some substantial differences. The first consists of the fact that the pathways of sinking of the extra electron do not pass throughout the entire crystal, but along "narrow channels" made of weakly shifted centers, and whereas they encompass a large number  $(\sim kT/\Delta_{ij})^2$ , yet this number is finite. Here the probability is high of formation of "blocks," i.e., rarefactions in which the centers lie at distances considerably greater than the mean, and the probability of hopping is small. The second difference consists of the need for taking into account the spins of the donor atom and the extra electron (just like acceptor centers, holes are not characterized by their spin, but by their total angular momentum). A hop can occur if the spin of the extra electron is opposite to the spin of the donor electron. This is especially important in the region of "blocks." Since we are interested only in the relationships of  $W_s$  to  $N$ , we shall crudely take both differences into account by replacing  $N$  by  $N_{\text{eff}} = \beta N$  ( $\beta \leq 1$ ) and employ the ideas and formulas of Ref. 6. Then the quantity  $W_s^{-1}$  must be proportional to the hopping resistance  $\rho_{0,s}(\beta N)$ . Then for isotropic wave functions we have

$$W_s^{-1}(N) \propto \rho_{0,s}(\beta N) \propto \exp \frac{1.8}{(\beta N)^{1/3} a_1 v^{1/2}}. \quad (9)$$

For a many-valley band structure, the wave function of the extra electron can be represented in the form of a linear combination of single-valley functions

$$\Psi(r) = \sum_{j=1}^n \Psi_j(r). \quad (10)$$

Here  $n$  is the number of valleys. In the approximation of a short-range potential,  $\Psi_j(r)$  has the form<sup>50</sup>

$$\Psi_j(r) = \left( \frac{1}{2\pi a_1} \right)^{1/2} v^{-1/4} \frac{\exp(-r/a_1)}{r}, \quad r^2 = x^2 + y^2 + z^2/v.$$

(The  $z$  axis lies along the longitudinal-mass axis;  $v$  is the ratio of the "transverse" to the "longitudinal" mass.)<sup>6</sup> The characteristic values of the overlap integral [see (6)] were calculated on a computer<sup>6</sup> for wave functions of this type. For example, for  $n$ -Ge we have

$$\rho_s(\beta N) \propto W_s^{-1}(N) \propto \exp \frac{1.25}{(\beta N)^{1/3} a_1 v^{1/2}}. \quad (11)$$

Now we can estimate the effect of uniaxial compression on  $W_s$  for this material. In the case of compression along the [111] axis of  $\sim 10^9 \text{ dynes/cm}^2$ , the only term essential in Eq. (10) is that corresponding to an ellipsoid with its long axis along the axis of compression. In this case we have

$$W_s^{-1}(N) \propto \rho_{0s}(\beta N) \propto \exp \frac{1.8}{(\beta N)^{1/3} a_1 v^{1/2}}, \quad (12)$$

and  $\tau_s$  increases exponentially in comparison with (11). For  $N = 7 \times 10^{14} \text{ cm}^{-3}$ , taking  $\beta = 1$ , we obtain a relative variation of  $\tau_s$  in the limit of the compression  $P$ :  $\tau_s(P \rightarrow \infty)/\tau_s(P=0) \approx e^{3.15}$ . That is,  $\tau_s$  has increased by a factor of more than 20 and has reached the value characteristic of a material having  $N = 2.3 \times 10^{14} \text{ cm}^{-3}$  in the absence of pressure. We note that the effect of compression is enhanced when  $\beta < 1$ .

### e) Systems of the $H^- - H^+$ type

Let a  $D^-$ -center lie at the distance  $R$  from an attractive ( $D^+$  center, with  $R_0 \leq R < R_*$ ). Then, if we neglect the short-range potential of the nearest neutral centers, we have a  $D^- - D^+$  system analogous to the hydrogen molecule in the ionic state  $H^- - H^+$ .<sup>33</sup>

In the case that the energy of the ionic term  $E_{\text{ion}}(R)$  does not coincide with that of the homopolar terms and we have

$$R \gg a_-(R) \equiv \sqrt{\frac{\hbar^2}{2m E_{\text{ion}}(R)}} \quad (13)$$

then, in the approximation involving a potential of zero range,<sup>42</sup> we have

$$E_{\text{ion}}(R) = E_1 - \frac{e^2}{\kappa R}. \quad (14)$$

Here the wave function of the electron at a distance  $r \ll R$  from a neutral center is spherically symmetric and has the form<sup>51,54</sup>

$$\Psi(r) = \frac{C}{r} \exp\left(-\frac{r}{a_-(R)}\right) \left(1 - \frac{\gamma(R)r}{a_-(R)}\right), \quad \gamma(R) = 1 - \sqrt{\frac{E_1}{E_{\text{ion}}(R)}}. \quad (15)$$

The cross-section  $\sigma(\hbar\omega, R)$  for photodecomposition of an  $H^- - H^+$ -type system differs appreciably from that for an isolated  $H^-$  ion. This arises from the change in the initial state [see (1) and (15)], and more importantly, from the effect of the field of the  $H^+$  ion on the photoelectron.<sup>51</sup> Here the free electron is not de-



scribed by a plane wave, but by a Coulomb wave function of the continuous spectrum  $\psi_{\mathbf{k}}(\mathbf{r})$ .<sup>52</sup> One can derive relatively simple expressions for  $\sigma(\hbar\omega, R)$  in two limiting cases.<sup>51</sup>

1. The cross-section  $\sigma_{\text{thr}}$  near the threshold, i. e., as  $\hbar\omega \rightarrow E_{\text{ion}}(R)$ :

$$\sigma_{\text{thr}}(R) = \frac{32\pi}{3} \frac{e^2}{\hbar c} a_0^2(R) \left( \frac{e^2}{\hbar R E_{\text{ion}}(R)} \right)^{3/2} f(\gamma) \cos^2 \left[ \left( \frac{8R}{a_0} \right)^{1/2} - \frac{3\pi}{4} \right] (1 + 2\gamma)^2, \quad (16)$$

$$f(\gamma) = \left( 1 + \gamma + \frac{1}{2} \gamma^2 \right)^{-1}.$$

It has a finite value, increases with decreasing  $R$ , and undergoes oscillations with the "period"  $\Delta R \approx [(\pi^2/8)a_0 R]^{1/2} \ll R$ . The oscillations are smoothed out when we take into account the small terms of high order in  $a_0(R)/R$ . The oscillations are caused by the behavior of  $\psi_{\mathbf{k}}(\mathbf{r})$  as  $\mathbf{k} \rightarrow 0$ .<sup>52</sup>

2. At values of  $\hbar\omega$  such that  $kR \equiv [2m(\hbar\omega - E_{\text{ion}}(R))\hbar^2]^{1/2} R \gg 1$ , upon employing the asymptotic expression for  $\psi_{\mathbf{k}}(\mathbf{r})$ ,<sup>52</sup> we get

$$\sigma(\hbar\omega, R) = \left( \frac{32\pi}{3} \frac{e^2}{\hbar c} a_0^2(R) \right) \frac{[E_{\text{ion}}(R) (\hbar\omega - E_{\text{ion}}(R))]^{3/2}}{(\hbar\omega)^2} \times f(\gamma) \left\{ \left( 1 + 2\gamma \frac{E_{\text{ion}}(R)}{\hbar\omega} \right)^2 \left[ 1 + \frac{2E_{\text{ion}}(R)(E_{\text{ion}}(R) - E_i)}{\hbar\omega(\hbar\omega - E_{\text{ion}}(R))} \right] \right\}. \quad (17)$$

The first two factors coincide in form with Eq. (2) with the replacement  $E_{\text{ion}}(R) - E_i$ , and the last factor owes its origin to the departure of the function of the final state from a plane wave. It leads to a considerable increase in the cross-section when  $\hbar\omega - E_{\text{ion}}(R) \ll E_{\text{ion}}(R)$  and to a faster decline in the cross-section with increasing  $\hbar\omega$  than in Eq. (2). Figure 3 shows the form of the cross-section for various values of  $R$ . The threshold cross-section has been taken as the average over the period of oscillation. We can see the considerable narrowing of the curve with decreasing  $R$ .

#### f) Pseudocrossing of terms of the impurity molecule. Energy of photodetachment and density of states near a pseudocrossing

One of the characteristic features of an  $H^- - H^+$  system is the existence of pseudocrossings of ionic ( $H^- - H^+$  type) and homopolar [ $H(n=1) - H(n=2, 3)$  type] terms of the impurity molecule.<sup>9)</sup> The effect of pseudocrossings arises at the distances  $R = R_{xn}$  where  $E_{\text{ion}}(R)$  coincides with the energy of the homopolar term  $E_n$ .<sup>42</sup> Here the extra electron can simultaneously be on two atoms, and one must take into account the exchange interaction, which can lead to "repulsion" of the terms and formation of a symmetric ( $E_n^{(+)}$ ) and an antisymmetric ( $E_n^{(-)}$ ) state. Since the accuracy of the variational calculation and that of the method of zero-range potential are similar in the region  $R \gg a_0$ , we shall give the expressions for  $E_n^{(+)}(R)$  and  $E_n^{(-)}(R)$  obtained by the latter method for  $R \approx R_{xn}$ :<sup>54</sup>

$$E_n^{(\pm)}(R) \approx E_n \pm \sqrt{\frac{8\pi}{a_1}} |\psi_n(R_{xn})| \pm \frac{1}{4} \frac{E_{\text{ion}}(R_{xn}) - E_{\text{ion}}(R)}{8\pi/a_1 |\psi_n(R_{xn})|}. \quad (18)$$

The energy values are given in rydbergs, and  $\psi_n(R)$  is the normalized function of the atomic level at the point

<sup>9)</sup>The symbol  $H(n=1) - H(n=2, 3, \dots)$  means that the electron of one atom is in the ground state and that of the other is in an excited state.

$r = R$  where a neutral atom is situated.

The difference between the terms is minimal at the point  $R = R_{xn}$  and is equal to twice the exchange-interaction energy  $\Delta E_n$ :

$$E_n^{(+)} - E_n^{(-)} \approx 2\Delta E_n \approx 2 \sqrt{\frac{8\pi}{a_1}} |\psi(R_{xn})|. \quad (19)$$

In the case of an  $m$ -fold degenerate level (wave functions  $\psi_{ns}$ ,  $s = 1, 2, \dots, m$ ), the splitting is increased<sup>55</sup>:

$$\Delta E_n = \sqrt{\frac{8\pi}{a_1}} \sqrt{\sum_{s=1}^m |\psi_{ns}(R_{xn})|^2}. \quad (20)$$

Thus Eqs. (18)-(20) imply that the exchange interaction is manifested most strongly for sufficiently deep atomic levels with small  $R_{xn}$ . As  $R$  approaches  $R_{xn}$  from the direction of larger  $R$ , the  $E_{\text{ion}}(R)$  relationship weakens and has a minimum at  $R = R_{xn}$ . This is also confirmed by a variational calculation for the  $H_2$  molecule.<sup>56</sup> An estimate of  $\Delta E_n$  for a hydrogen-like level with  $n=2$  yields  $\Delta E_2/E_2 = 6.4 \times 10^{-2}$ . For  $n=3$  the relative level shift  $\Delta E_3/E_3$  is  $3 \times 10^{-3}$ , i. e., substantially smaller.

Now let us point out some possible consequences of pseudocrossing of terms of impurity molecules in semiconductors. First, as the distance between the "nuclei" approaches  $R_{xn}$ , the energy of photodetachment from the ionic state approaches  $E_n^{(-)}$ , and it remains almost constant in some region  $\Delta R_{xn}$ . We can estimate  $\Delta R_{xn}$  by equating the change in  $E_{\text{ion}}(R)$  at the distance  $\Delta R_{xn}$  to the exchange-interaction energy. Second, with a random distribution of distances between the "nuclei" in the molecules, the number of states

$$g(E(R)) dE(R) \propto 4\pi R^2 (E_{\text{ion}}(R)) \frac{dR}{dE_{\text{ion}}(R)} dE(R) \quad (21)$$

has a sharp maximum in the pseudocrossing region. These effects must be manifested at impurity concentrations  $N_{xn}$  such that the most probable distance between impurity centers is close to  $R_{xn}$ . No estimate has yet been made of the exchange-interaction energy for impurity molecules in semiconductors whose atomic levels differ from hydrogenlike levels. We can expect the exchange interaction for Ge and Si to be larger than is given by the hydrogen-like model: the energies of the levels are determined by the greatest of the masses (the longitudinal mass of an electron for donors, and the mass of a heavy hole for acceptors), while the decline of the wave functions at large distances from the center is determined by the light mass.

#### g) Delocalization of $H^-$ -like states. Upper Hubbard band

The treatment that we have conducted above of  $D^-$ -centers,  $D_2^-$  and  $D^- - D^+$  complexes, and the hopping mechanism of formation of the latter is valid as long as the overlap of the wave functions of the  $D^-$  states of adjacent centers is small, i. e., when  $N^{1/3} a_1 \ll 1$ .<sup>2</sup> When  $N^{1/3} a_1 = \lambda$ , where  $\lambda \sim 1$ , the  $D^-$  states must become delocalized. This gives rise to a conducting impurity band (upper Hubbard band).<sup>2</sup> This is precisely the band in which the so-called  $\sigma_2$  conduction arises, which is characterized by the activation energy  $\varepsilon_2$ .<sup>36</sup> The theoretical value of the parameter  $\lambda$  is not known. For

specimens with a small compensation (i.e., when there are almost no charged centers), the experimental data on the static conductivity of Ge and Si reveal  $\sigma_2$  conduction in Ge(Sb) at  $N \geq 2.9 \times 10^{16} \text{ cm}^{-3}$ , i. e., when  $N^{1/3} a_i > 0.55$ ,<sup>57</sup> and in Si(P) at  $N > 1.2 \times 10^{16}$ , i. e.,  $N^{1/3} a_i > 0.9$ .<sup>58</sup> We should expect an upper Hubbard band to be created at somewhat smaller values of  $N$ .

Under the physical conditions stated above [see Sec. 3(a)], delocalization must occur first of all in the states of the weakly shifted centers and the centers whose energy positions correspond to pseudocrossings. Here finite clusters can be formed<sup>6</sup> whose dimensions increase with increasing number of resonance centers. The creation of clusters weakens the hopping mechanism of formation of  $H^- - H^+$ -type complexes. Moreover, the possible phototransition of an electron from a cluster or an upper Hubbard band to the conduction must alter the form of the PC curve, since the short-wavelength decline of the cross-sections of (2), (4), and (17) is characteristic only of a transition from localized states.

#### 4. ANALYSIS OF THE EXPERIMENTAL RESULTS ON PHOTOCONDUCTIVITY

##### a) The role of complexes of the $H^- - H^+$ type

Let us compare the discussed models of  $H^-$ -like centers and of the molecular complexes that they produce with the experimental results.

For weakly doped specimens with a small compensation of impurities at low temperatures ( $Na_0^3 < 10^{-6}$ ,  $K \ll 1$ ,  $kT < 0.1E_i$ ), the model of an isolated  $H^-$ -like center is quite applicable—the experimental and calculated photodetachment cross-sections agree, as do the values of the binding energy. The effect of the many-valley band structure on  $E_i$  is relatively small: uniaxial compression of pure specimens of Ge ( $N \leq 5 \times 10^{13} \text{ cm}^{-3}$ ) yields a change of  $E_i$  by only 10–20%.<sup>23</sup>

To analyze why the spectra vary with increasing impurity concentration and temperature in specimens having  $10^{-6} < Na_0^3 < 10^{-3}$ , let us single out the most essential facts:  $E_{mr}$  can exceed  $E_i$  by a factor of 2 to 7 (see Figs. 6, 7); the PC spectra become relatively narrower and their short-wavelength edge becomes steeper (Fig. 3); and the spectra manifest a structure (Figs. 1, 2). It is important that these changes have the same character for different materials and are governed only by the magnitude of  $Na_0^3$ . Therefore we should not seek to explain them by the features of the band structure.

References 18 and 27 have explained the increase in  $E_{mr}$  with increasing  $N$  by the formation of  $H_2^-$ -type complexes. The model of  $H_2^-$ -complexes allows a maximal increase in  $E_{mr}$  by 20% [see Sec. 3(e)], and it yields a  $\sigma_{H_2^-}(\hbar\omega)$  relationship that differs insignificantly from  $\sigma_{H^-}(\hbar\omega)$  (see Fig. 3). Thus the fundamental experimental results do not involve the formation of  $H_2^-$ -type complexes.

In Ref. 21, the variation of  $E_{mr}$  with  $N$  for Si(P) specimens with  $N > 3 \times 10^{15} \text{ cm}^{-3}$  ( $Na_0^3 > 1.5 \times 10^{-5}$ ) is explained by formation of an upper Hubbard band. How-

ever, at these values of  $N$ , the overlap of the wave functions of the  $D^-$  states does not yet suffice for formation of an impurity band [see Sec. 3(g)]. Moreover, in this model one cannot explain the observed structure and relative narrowing of the spectrum.

As we see it, the noted experimental facts can be explained by a model that includes the following points:

1) The existence of attractive centers ( $D^+$  in an  $n$ -type semiconductor) gives rise to  $H^- - H^+$  complexes with a distance between the nuclei  $R \geq R_0$  and a binding energy of the extra electron  $E_{ph} = E_i + (e^2/\kappa R)$ .

2) The complexes are produced mainly by hopping movement of the extra electron over neutral centers toward the attractive center.

3) Quantum effects substantially influence the energy and photodetachment cross-section of the electron from an  $H^- - H^+$ -type complex even when  $R \gg a_0$ : pseudo-crossing of terms [see Sec. 3(c)] and narrowing of lines [see Sec. 3(e)].

##### b) Comparison of the experimental data with calculations from the $H^- - H^+$ model

In addition to the photodetachment cross-section [see Sec. 3(e)], a detailed comparison of the theory with the experimental data requires that one should know the density of states  $g(E)$  and their occupancy. The  $g(E)$  relationship is known approximately only in the case in which  $E_{ph}(R)$  is governed only by the nearest charged center. The occupancy of the  $D^-$  states is determined by equating the rates of arrival of carriers into a given state and of exit from it. In addition to the processes mentioned in Sec. 3, we must take into additional account under the experimental conditions: 1) the breakdown of  $D^-$  centers by the background radiation with the probability  $W_{ph}$  and via annihilation, i. e., the transition of a carrier from a  $D^-$ -center to a  $D^+$  to form two neutral centers ( $W_A$ ); 2) the processes that alter the binding energy of a  $D^-$ -center (photoionization of a neutral center or the formation of another  $D^-$ -center near it, as well as trapping of a free electron by the  $D^- - D^+$  complex under study).

A detailed account taken of the mentioned processes is complicated, but the estimates show that they are not all essential in producing the spectrum—without down-hopping, one cannot obtain the observed variation of  $E_{mr}$  with  $N$  and  $T$ . The determining role of the hopping mechanism of sinking is directly implied by the exponential decrease in the lifetime  $\tau_i$  of isolated  $H^-$ -like centers with increasing  $N$  (see Fig. 8). Upon assuming that the experimental  $\tau_i(R_c)$  relationship can be described by the formula  $\tau_i \sim \exp(-\alpha/N^{1/3} a_i)$ , where  $\alpha \sim 1$ , one can determine the decay length of the wave function  $a_i$  (to the accuracy  $\alpha$ ) from the slope of the curve in Fig. 8. If we assume that the sinking of the extra carrier arises as the result of a large number of hops, then we can employ the calculations of percolation theory,<sup>6</sup> which gives  $\alpha \sim 1.8-1.9$  and  $a_i = 65 \text{ \AA}$ . Whenever an appreciable energy change arises from the first hop to a nearest center lying at the most probable radius  $R = 0.55N^{-1/3}$ , then we find  $\alpha \approx 1.1$  and  $a_i = 110 \text{ \AA}$ .

Thus the values of  $a_1$  obtained from the experimental  $\tau_1(R_c)$  curve agree reasonably with calculation from Eq. (1). However, the values of  $W_s$  found according to Sec. 3(d) for  $110 > a_1 > 65 \text{ \AA}$  prove far larger than the experimental values of  $\tau_1^{-1}$ . Apparently this discrepancy involves both the approximate nature of the estimates and the neglected effect of the direction of the spin of the adjacent centers on the probability of a hop.

The action of uniaxial compression on the form of the PC spectra can be easily explained in terms of down-hopping. As was shown in Sec. 3(d),  $W_s$  is decreased by uniaxial compression. Consequently the number of  $H^- - H^+$ -type complexes should decline. Here the number of weakly perturbed  $H^-$  centers increases, as well as the number of  $H_2^-$ -like complexes.

We see from Figs. 5 and 6 that the  $E_{thr}(N^{1/3})$  relationship is stepwise. When  $N^{1/3}a_0 > 0.05$ , the regions in which  $E_{thr}$  changes are described well by Eq. (14), where  $R \approx R_0$ . This implies that the characteristic distances in the complex are close to  $R_0$ . As we see it, the flat regions in the  $E_{thr}(N)$  relationship manifest the pseudocrossings of the ionic and homopolar terms. Apparently the following impurity levels participate in them:

$$\begin{aligned} \text{Si(B)} \quad E_{thr} &\approx 8; \quad 12 \text{ meV} - 2\Gamma_2^-(10.5); \quad 1\Gamma_2^-(14.5); \\ \text{Si(P)} \quad E_{thr} &\approx 5.8; \quad 9.5 \text{ meV} - 2p_{\pm}(6.4); \quad 2p_0(11.5); \\ \text{Ge(Sb)} \quad E_{thr} &\approx 1.5 - 2 \text{ meV} - 2p_{\pm}(1.73); \quad 3s(2.14). \end{aligned}$$

The energies of the impurity levels and the corresponding [see Sec. 3(f)] values of  $N$  are marked in Fig. 5 by the indexed arrows. We see that the experimental values of  $N$  and  $E_{thr}$  are close to the calculated values.

Let us examine the region of the  $E_{thr}(N^{1/3})$  relationship in Fig. 6 that corresponds to  $N^{1/3}a_0 > 10^{-2}$ . When  $kT < 0.1E_i$ , the experimental curves of Fig. 5 coincide well for the different materials when redrawn on the scale of  $N^{1/3}a_0$ . That is, they are governed only by the parameter  $R_c/a_0$ . Here the values of  $E_{thr}$  prove to be smaller than  $E_{ph}(R_c)$  (dotted curves). That is, they correspond to the complexes for which  $R > R_c$ . Under these conditions, in spite of the determining role of down-hopping, we can reasonably assume that not all the  $D^-$ -centers lie at the closest distances to a  $D^+$ -center.

When  $kT > 0.2E_i$ , the experimental values of  $E_{thr}$  lie above the dotted curve. That is, under these conditions complexes exist having  $R \approx R_c$ , owing to thermal decomposition. Section 3(f) indicates that the dependence of the density of states on the energy  $g(E)$  is nonmonotonic and has the form of diffuse peaks whose positions are shifted with respect to the impurity levels by the amount  $\Delta E_n/E_n \approx 20\%$ . The number of these peaks, their intensity, and the occupancy of the states near the maxima are determined by the distribution  $w(R)$  of the  $D^- - D^+$  complexes with respect to the distances between the nuclei. If a  $D^-$  and a  $D^+$  center prove to be closest neighbors (e.g., owing to hopping), then we have

$$w(R) = 4\pi R^2 \exp\left[-\left(\frac{R}{R_c}\right)^3\right]. \quad (22)$$

Owing to the difference in the values of  $R$ , several maxima of the density of states can prove to be simul-

taneously occupied. The relative intensity of the PC peaks corresponding to them is determined by the parameters  $R_c/R_c$  and  $T$ . The value of  $E_{thr}$  remains constant with increasing  $N$  and  $T$ , while the number of complexes having  $E_{ph} \approx E_n^{(c)}$  does not prove to be small, owing to the removal of carriers by the Coulomb field at the centers closer to the attractive center, or by thermal ejection.<sup>9)</sup> Figure 1(a) compares the experimental and calculated PC spectra for a specimen having  $N = 2 \times 10^{18} \text{ cm}^{-3}$ . The calculation was performed under the assumptions that the distances in the complexes correspond to the distribution of (22), the photodetachment cross-section  $\sigma(\hbar\omega, R)$  is given by Eq. (17), and the  $E(R)$  relationship for  $R > 220 \text{ \AA}$  and  $R < 85 \text{ \AA}$  is given by Eq. (14). For the values of  $R$  for which one should expect pseudocrossing of terms, the corresponding constant values of  $E(R)$  were employed in the calculation: 8 meV for  $150 < R < 220 \text{ \AA}$ , 12 meV for  $100 < R < 150 \text{ \AA}$ , and 17 meV for  $85 < R < 100 \text{ \AA}$ .

The calculated spectrum proves to be close enough to the experimental: the values of  $E_{thr}$  and the half-widths of the curves hardly differ. The existing features (peaks) coincide in position. A certain disagreement of the relative intensities of the peaks and of the slopes of the curves in the short-wavelength region apparently stem from the inapplicability of the expression (17) for  $\sigma(\hbar\omega, R)$  under conditions of pseudocrossing. As we see it, the deviation of the curves in the long-wavelength region of the spectrum can involve a number of circumstances. Thus, for example, the direction of approach of the carriers to the attractive center may not coincide with the direction to the closest  $D^0$  center. That is, the distribution of (22) is not fully applicable to the problem being treated.

The discussion that we have carried out shows that the fundamental results of the experiment can be naturally explained within the framework of the model of  $H^- - H^+$  complexes formed by hopping. However, other structures can also prove essential under certain, specially chosen conditions. Thus, in a narrow range of  $N$  and  $T$ , uniaxial compression increases the role of  $D_2^-$  complexes in the PC spectra. This has been detected in experiments<sup>18</sup> to observe PC that were performed in a magnetic field. Apparently, at very small compensations and at low temperatures, also more exotic complexes can be manifested, e.g.,  $H^- - H^+ - H^-$  and  $H_2^- - H^+$ .

### c) On the problem of annihilation of complexes of the $H^- - H^+$ type

The problem of the time of existence of  $H^- - H^+$ -type complexes and of their annihilation has not been discussed in the literature. It seems to us that annihilation is not significant at low enough temperatures ( $kT < 0.1E_i$ ), and the main process is the destruction of  $H^- - H^+$  complexes by the background radiation ( $W_{ph} > W_A$ , where  $W_A$  is the probability of annihilation). This hypothesis explains the absence of a dependence

<sup>9)</sup>The  $T$ -independence of  $E_{thr}$  for curves 2 and 3 of Fig. 7 is explained by the fact that  $W_T \ll W_{ph}$  at these temperatures.

of the PC on  $N$  (see Fig. 9). Actually, under the conditions of experiment ( $W_{ph} > W_T$ ), any extra electron rapidly arrives by hopping at a distance  $R \sim R_c$  from a  $D^+$  center. Here the free electrons are no longer trapped at isolated charged centers, as in pure specimens ( $Na_0^3 < 10^{16}$ ),<sup>15</sup> but at a dipole  $D^- - D^+$  having the trapping coefficient  $\alpha^+(R) < \alpha^-(R \rightarrow \infty)$ . The expressions for  $n$ ,  $N_{D^-}$ ,  $N_D$ , and  $\delta\sigma/\sigma$  prove analogous to those given in Ref. 15:

$$n = \sqrt{\frac{W_{ph}W_{ph}}{\alpha^+\alpha^0}}, \quad \frac{N_{D^-}}{N_D} = \sqrt{\frac{W_{ph}\alpha^+}{W_{ph}\alpha^+}}, \quad \frac{\delta\sigma}{\sigma} \propto \frac{1}{W_{ph}}.$$

Thus,  $n$  and  $N_{D^-}/N_D$  vary by the same law with varying  $\alpha^+(R)$ , while the quantity  $\delta\sigma/\sigma$  remains constant, in agreement with the experimental results. The increase of  $n$  with  $N$  observed when  $N > 5 \times 10^{15} \text{ cm}^{-3}$  can be explained by the dependence of  $\alpha^+$  on  $R$ .<sup>59</sup> We note that the inverse inequality  $W_A > W_{ph}$  would lead to a decline in  $\delta\sigma/\sigma$  with increasing  $N$ .

At higher temperatures ( $kT > 0.1E_i$ ) and in materials having  $Na_0^3 > 2.5 \times 10^{16}$  [for Si(P) we have  $N > 5 \times 10^{16} \text{ cm}^{-3}$ ], the situation becomes more complicated and one can no longer rule out a possible effect of annihilation of  $H^- - H^+$ -type complexes. Actually, one cannot quantitatively describe the variation of  $E_{thr}$  with  $T$  (see Fig. 7) solely by the thermal ejection of carriers into the empty band, since the estimates yield  $W_T \ll W_{ph}$  even for complexes having  $E_{ph} \approx E_{thr}$ . Thus, for an Si(P) specimen having  $N = 9 \times 10^{16} \text{ cm}^{-3}$ , we find  $E_{thr} \approx 6 \text{ meV}$  at  $T < 2 \text{ K}$ , and this quantity begins to increase even at  $T \approx 3 \text{ K}$ . Thermal ejection of an electron from a complex under these conditions requires  $W_T$  to exceed the calculated value by a factor of about  $10^3$ . Apparently, under these conditions, also other processes of resolution of  $H^- - H^+$ -type complexes whose probability increases with the temperature can prove essential. It is difficult to assume that direct annihilation could fulfill this. More likely, a two-step process can involve breakdown of a center with ejection of the electron into an intermediate state having a smaller binding energy, with subsequent annihilation.

#### d) Manifestation of delocalization of $H^-$ -like states

The qualitative variation of the form of the PC spectrum with increasing impurity concentration (see Fig. 12, where one observes a monotonic increase in PC with frequency) is associated<sup>27</sup> with the appearance of a conducting impurity band ( $D^-$ -band). This is proved by the coincidence of the concentration thresholds  $N_{thr}$  at which the spectrum changes [see Fig. 12(c)] and at which a conducting impurity band is manifested in the static conductivity ( $\sigma_2$ ). One notes the possible appearance of new optical transitions when  $N > N_{thr}$ —from localized ground states to the  $D^-$ -band and between delocalized states, i. e., from the  $D^-$ -band to the conduction band. The latter contribute to the PC, owing to the large mobility of the electrons in the conduction band, with this contribution assumed to be dominant. The same group in a subsequent paper<sup>32</sup> has made a further study of the absorption spectra. They state that transitions of the former type are the most important in this case.

It seems right to adduce a  $D^-$ -band to explain the discussed set of phenomena. Yet substantial refinements are required in a number of details.

First we must note that the absorption cross-section for transitions of carriers from the  $D^-$ -band to the conduction band must increase monotonically with the quantum energy, just as for ordinary interband transitions. Therefore we believe that the qualitative variation of the form of the PC spectrum that we have discussed above proves *per se* the delocalization of the  $H^-$ -like states. In this regard we must note that the decreased slope of the short-wavelength tail [see Fig. 12(c)] indicates the simultaneous existence of delocalized states. In line with Sec. 3(g), these can be states in finite clusters, where the energy levels of the centers are slightly displaced and the  $H^-$ -like states overlap, and  $H^- - H^+$ -type complexes. In the clusters, the exchange interaction arising from the overlap of the  $H^-$ -like states exceeds the energy spread of the levels arising from the random arrangement of the neutral centers and from the Coulomb field of the charged centers. The "extra" electrons existing in a cluster are almost delocalized and do not participate in the hopping movement toward the attractive centers. As the concentration  $N$  increases, the dimensions of the clusters and the number of states in them increase, and the number of  $H^- - H^+$ -type complexes relatively diminishes. As we see it, the change in the slope followed by appearance of a rise in the short-wavelength region of the PC spectrum, is a manifestation of the delocalization of states.

It is evident from what we have said that  $H^-$ -like states can become delocalized at lower impurity concentrations than those manifested by measuring the static conductivity. In dc experiments, the band-type impurity conduction is observed only when it becomes comparable in magnitude with the jumpwise and the ordinary band conductivity. In PC experiments performed under conditions of background illumination and occupation of the  $D^-$ -states by electrons from the conduction band, the delocalized "extra" carriers can be detected almost immediately after delocalization. Figures 2 and 12 imply that a PC spectrum characteristic of transitions between delocalized states can be observed in Si specimens having  $Na_0^3 \approx 5 \times 10^{16}$ , where the  $\sigma_2$  conduction does not yet exist and the value  $\epsilon_1$  of the activation energy of the electrons from the ground states into the conduction band corresponds to the ionization energy of isolated neutral centers ( $\epsilon_1 = \epsilon_0$ ).

Apparently the coexistence of localized and delocalized states is also manifested in another group of experiments in which temperature changes affect the form of the PC spectra. In Si(P) having  $N = 9 \times 10^{16} \text{ cm}^{-3}$ , and PC spectrum characteristic of transitions from localized states is observed at  $T < 8 \text{ K}$  (see Fig. 2). At a higher concentration of P ( $N = 3 \times 10^{17} \text{ cm}^{-3}$ ), such a spectrum exists at a lower temperature  $T < 5.2 \text{ K}$  (see Fig. 11). The transformation of the spectrum with increasing temperature is analogous to its variation with the concentration.

The influence of the temperature on the degree of de-

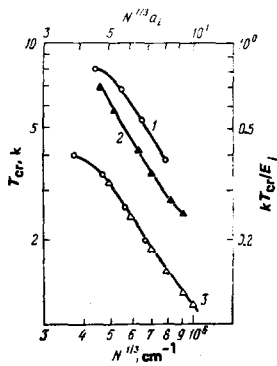


FIG. 13. The  $T_{cr}(N^{1/3})$  relationship. 1—Si(P), 2—Si(B), 3—relationship of  $kT_{cr}/E_1$  to  $N^{1/3}a_0$ .

localization is illustrated in Fig. 13, which shows the dependence of the critical temperature of the effect  $T_{cr}$  (see Sec. 2) on the impurity concentration for Si(B) and Si(P). The same diagram shows the relationships of  $kT_{cr}/E_1$  to  $N^{1/3}a_0$ . We see that the variations are very similar for the two materials. This indicates the influence of temperature on delocalization to be general in nature. The existing correlation between the variations of the spectra with temperature and with concentration qualitatively seems natural (by analogy to a Mott transition<sup>1,3a</sup>). However, the concrete mechanism of the influence of temperature still remains open.

#### e) Conditions for existence of $H^- - H^+$ - type complexes

The set of models that we have examined and the experimental results allow us to state the conditions for existence of isolated  $H^-$ -like centers and of complexes based on them.

When  $kT < 0.1E_1$  and  $Na_0^3 \leq 10^{-6}$ , the spectra mainly arise from  $H^-$ -like centers close in energy to isolated centers. Down-hopping is not substantial, and the number of  $H^- - H^+$ -type complexes is small.  $H_2^-$ -type complexes can be present in small amount.

An increase in  $N$  ( $10^{-6} < Na_0^3 < 10^{-3}$ ) leads to an increased probability of down-hopping and an increased role of  $H^- - H^+$ -type complexes in the PC spectra. The relative concentration of isolated  $H^-$ -like centers that are weakly shifted in energy diminishes. The binding energy of the extra electrons in the  $H^- - H^+$ -complexes increases. Upon increase in the temperature ( $kT > 0.1E_1$ ), the  $H^-$  and  $H_2^-$  complexes are practically absent.

The disappearance of  $H^- - H^+$ -type complexes with the appearance of clusters and delocalization occurs at higher concentrations for lower temperatures. For example, in Si at  $T \approx 1.5$  K, the complexes cease to be manifested when  $N \geq 10^{18} \text{ cm}^{-3}$ , and in Ge they do so at  $T = 0.38$  K and  $N \geq 3 \times 10^{16} \text{ cm}^{-3}$ .

## 5. CONCLUSION

The set of results that we have presented indicates that several forms of localization of electrons can exist in a system of neutral and charged impurity centers in semiconductors: isolated  $H^-$ -centers and molecular

complexes of the type  $H_2^-$  and  $H^- - H^+$ . The distances between the "nuclei" in the complexes are determined by the concentration  $N$  of neutral impurities.  $H^- - H^+$ -complexes predominate for sufficiently large  $N$ , and their mechanism of formation is by hopping. The range of binding energies of the "extra" electrons lies inside the Mott-Hubbard gap, and extends from  $0.05$  to  $0.5E_1$ . A broad set of phenomenon in semiconductors at low temperatures is governed by the existence of these complexes.

The existence of an  $H^- - H^+$ -type complex in systems having a Coulomb potential implies that one must take this potential into account also in studying the conditions for delocalization and disappearance of the Mott-Hubbard gap upon further increase in  $N$ .

The estimates given in the review are mostly mode-based and they enable one to describe the observed regularities qualitatively. For a more detailed analysis of the actual situation, it seems necessary to treat a number of theoretical and experimental problems, both "atomic" and specifically solid-state problems. The form of the wave functions of the ionic term near pseudocrossings with the fact taken into account that the charged center is not hydrogen-like is of great interest. The problem remains open of the effect of spin on the hopping movement of an "extra" electron. Undoubtedly, it is important to study the conditions for delocalization in semiconductors at different temperatures and degrees of compensation, as well as the probabilities of radiative and radiationless transitions in  $H^- - H^+$ -type complexes and of annihilation of complexes.

## APPENDIX

1. Let us explain the derivation of Eq. (4). The normalized wave function of Eq. (3) is given by the expression

$$\psi_{\pm} = \frac{(2\pi a_1)^{-1/2}}{\sqrt{2} \sqrt{1 \pm S}} \left( \frac{\exp(-r/a_1)}{r} \pm \frac{\exp(-|r-R|/a_1)}{|r-R|} \right). \quad (\text{A.1})$$

Here  $S$  is the overlap integral:  $S = \langle \psi(r_a) | \psi(r_b) \rangle$ . We can represent the matrix element  $M$  of a dipole transition from the state of (A.1) to that described by the plane wave  $\psi_k \sim e^{ik \cdot r}$  in terms of the matrix element  $M_{H^-}$  for an  $H^-$  ion:

$$M = \frac{1 \pm e^{ik \cdot R}}{\sqrt{2} \sqrt{1 \pm S}} \frac{\hbar \omega}{\hbar \omega \mp \Delta_{\pm}} M_{H^-}, \quad (\text{A.2})$$

$$|M|^2 = \frac{1 \pm \cos(kR)}{1 \pm S} \frac{(\hbar \omega)^2}{(\hbar \omega \mp \Delta)^2} |M_{H^-}|^2. \quad (\text{A.3})$$

Upon averaging (A.3) over the angle between  $k$  and  $R$  and assuming that  $\Delta \ll E_1$ , we obtain the formula (4) for the cross-section.

2. In calculating the probability  $W_{ij}$  of a hop stimulated by phonons, the wave function of the extra electron has been taken in the form<sup>42,48</sup>:

$$\psi = B \sqrt{\frac{1}{2\pi a_1}} \frac{e^{-r/a_1} - e^{-\gamma r/a_1}}{r}, \quad B^2 = \frac{\gamma(\gamma+1)}{(\gamma-1)^2}, \quad \gamma \approx 3.2. \quad (\text{A.4})$$

The function of (A.4) describes the state of the electron near the nucleus better for  $r < a_1$  than Eq. (1) does. In calculating the frequency-dependence of the photo-decomposition cross-section, the difference between (A.4) and (1) is not essential; it must be taken into ac-

count in calculating the probability of a phonon transition. The function  $\varphi(q_1, a_1)$  that enters into (6) has the form

$$\varphi(q_1, a_1) = \frac{\gamma(\gamma+1)}{(\gamma-1)^2} \cdot \frac{2}{q_1 a_1} \left( \tan^{-1} \frac{q_1 a_1}{2} + \tan^{-1} \frac{q_1 a_1}{2\gamma} - 2 \tan^{-1} \frac{q_1 a_1}{1+\gamma} \right). \quad (\text{A.5})$$

The function  $\varphi$  decreases with increasing  $q_1$ . Thus, when  $q_1 a_1 = 2$ , we have  $\varphi^2 = 0.25$ ; when  $q_1 a_1 = 4$ ,  $\varphi^2 = 0.036$ , and when  $q_1 a_1 = 3$ ,  $\varphi^2 \approx 4 \times 10^{-4}$ . In Si the value  $q_1 a_1 = 2$  corresponds to  $\Delta_{ij} \approx 1.2$  meV, and in Ge to  $\Delta_{ij} \approx 0.3$  meV.

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