

# Investigation of $H^-$ -like centers in semiconductors in submillimeter wavelength range

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Measurements of the submillimeter photoconductivity and of the free-carrier density and mobility were used in a study of carrier recombination and scattering in boron-doped silicon containing  $A^+$  centers, which are analogs of negative hydrogen ions ( $H^-$ ).

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## INTRODUCTION

The problem of negative ions has been attracting interest for decades because creation and annihilation of negative ions (for example,  $H^-$ ) plays an important role in astrophysics, gas-discharge physics, acceleration of charged particles, and elsewhere (see, for example, [1-4]). In semiconductors, where shallow neutral impurities are usually hydrogen-like, the capture of an excess carrier produces  $D^-(A^+)$  centers, which are negatively charged donors (or positively charged acceptors) that are in many respects analogs of negative  $H^-$  ions. Studies of these centers in solids is important not only because of the considerable role played by the  $D^-(A^+)$  centers in various phenomena in semiconductors but also because these centers can be used as model experiments on free negative ions with certain specific advantages.

The possibility of existence of  $D^-(A^+)$  centers in semiconductors formed by the capture of an excess electron by a neutral donor  $D^0$  (or a hole by an acceptor  $A^0$ ) was first discussed in [5]. In some cases the presence of such centers explains conduction between impurities, [7] certain features of the luminescence spectra, [8,9] scattering and recombination of free carriers. [6,10-18] In view of the low binding energy  $\epsilon_i$  of the  $D^-(A^+)$  centers, compared with the ionization energy of neutral centers  $\epsilon_0$  ( $\epsilon_i \approx 0.055\epsilon_0$  [5]), the concentration of the charged centers becomes significant only at fairly low temperatures when  $kT < \epsilon_i$  in the case of intrinsic or impurity optical excitation of free carriers. In the case of Ge and Si the values of  $\epsilon_i$  of various impurities were determined in [19-21] at  $T < 4.2^\circ K$  directly from the long-wavelength photoconductivity edge representing the detachment of electrons (holes) from the  $D^-(A^+)$  centers. These energies are 1-3 meV and they correspond to the submillimeter wavelength range.

The present paper describes an investigation of  $D^-(A^+)$  centers based on the photoconductivity at frequencies close to the binding energy  $\epsilon_i$ , where it is most convenient to observe the effects which are just due to these centers because there are no other photoconductivity mechanisms in this frequency range. The study was carried out on boron-doped silicon (Si:B), in which the  $A^+$  centers had a relatively high binding energy ( $\epsilon_i \approx 2.5$  meV). This made it possible to in-

vestigate, in an accessible temperature range ( $T = 1.4-4.2^\circ K$ ), the characteristic features of the photoconductivity, scattering, and recombination processes resulting from the presence of the  $A^+$  centers. The experiments were carried out under the conditions of impurity optical excitation of free carriers in samples with low acceptor concentrations ( $N_A < 5 \times 10^{14} \text{ cm}^{-3}$ ) and weak impurity compensation ( $N_D/N_A \leq 0.01$ ), which made it possible to avoid secondary effects such as those associated with the interaction between impurities [11] and optical heating of carriers. [22,18]

## SUBMILLIMETER PHOTOCONDUCTIVITY MECHANISM

1. We shall calculate the photoconductivity due to the detachment of electrons (holes) from  $D^-(A^+)$  centers by considering briefly the recombination of free carriers formed as a result of absorption of background radiation ( $kT \approx 300^\circ K$ ) in weakly compensated samples at helium temperatures. Since the experiments were carried out on Si:B, we shall consider specifically a  $p$ -type material, i.e., we shall discuss the photodetachment of holes from the  $A^+$  centers. Holes released from neutral acceptors (transition 1 in Fig. 1) can recombine either at ionized acceptors (transition 2) or they can be captured by neutral acceptors (transition 3), which produces the  $A^+$  centers. At high temperatures ( $\epsilon_i \lesssim kT$ ), the concentration of these centers ( $N_{A^+}$ ) is low because of the strong thermal re-emission of the captured holes (transition 4). When the temperature is lowered, the number of the  $A^+$  centers increases and in a weakly compensated sample it may become greater than the concentration of the compensating impurity  $N_D$ . This increases the concentration of the recombination centers, which are the ionized acceptors:  $N_{A^+} = N_D + N_{A^+}$  and, consequently, reduces the density of free holes  $p$ .

If  $p \ll N_D + N_{A^+}$ , this situation is described by the following system of equations

$$N_0 \Phi = p \alpha^- (N_D + \tilde{N}_{A^+}), \quad N_{A^+} \xi = p \alpha^0 N_0, \quad (1)$$

where

$$N_0 = N_A - N_D - 2N_{A^+}.$$

Here,  $N_0$ ,  $N_D$ , and  $N_{A^+}$  ( $\text{cm}^{-3}$ ) are the concentrations of neutral acceptors, neutral donors, and  $A^+$  centers, re-

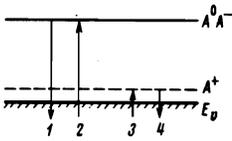


FIG. 1. Energy transition scheme.

spectively;  $\alpha^-$  and  $\alpha^0$  ( $\text{cm}^3/\text{sec}$ ) are the coefficients representing the capture of free holes by ionized and neutral acceptors;  $N_0\Phi$  ( $\text{cm}^{-3} \cdot \text{sec}^{-1}$ ) is the rate of release of holes from neutral acceptors by the background room-temperature radiation;  $N_{A^+}\xi$  ( $\text{cm}^{-3} \cdot \text{sec}^{-1}$ ) is the rate of release of carriers from the  $A^+$  centers; the quantity  $\xi$  is governed by a set of factors which result in the annihilation of the  $A^+$  centers:

$$\xi = T^* + \Phi^* + C^* + E^*,$$

where  $T^* = \alpha^0 N_v \exp(-\epsilon_i/kT)$  is the temperature factor ( $N_v$  is the density of states in the valence band),  $\Phi^*$  is the background-radiation factor,  $C^*$  is the factor governed by the intensity of radiation received from a monochromator, and  $E^*$  represents impact processes in electric fields.<sup>1)</sup>

2. We shall give the solutions of the system (1) for three temperature ranges separated by the values of  $N_D/N_{A^+}$ ,  $\Phi/\alpha^-$ ,  $\xi/\alpha^0$ , in the case when  $N_D/N_{A^+} < 0.01$ , and  $\xi = T^* + \Phi^*$ .

I. The range of a weak dependence  $p(T)$  is observed at high temperatures when  $N_{A^+} \ll N_D$  and  $T^* \gg \Phi^*$ . In this range the solutions are

$$p = \Phi N_{A^+} / \alpha^- N_D, \quad N_{A^+} = N_A \Phi \exp(\epsilon_i/kT) / \alpha^- N_v. \quad (2)$$

II. The range of an exponential dependence  $p(T)$  is observed for  $N_{A^+} \gg N_D$  and  $T^* \gg \Phi^*$ . It corresponds to the solutions

$$p = [N_v \Phi \exp(-\epsilon_i/kT) / \alpha^-]^{1/2}, \quad N_{A^+} = N_A [\Phi \exp(\epsilon_i/kT) / \alpha^- N_v]^{1/2}. \quad (3)$$

III. The range of saturation of  $p(T)$  is observed for  $\Phi^* \gg T^*$ . In this range, we have

$$p = (\Phi \Phi^* / \alpha^- \alpha^0)^{1/2}, \quad N_{A^+} = N_A / [(\Phi^* \alpha^- / \Phi \alpha^0)^{1/2} + 2]. \quad (4)$$

If we ignore the reduction in  $N_0$  due to the charging of the centers, the value of  $N_{A^+}$  is given by the simpler formula

$$N_{A^+} = N_A (\Phi \alpha^0 / \alpha^- \Phi^*)^{1/2}. \quad (4')$$

The temperatures of the transitions from range I to range II ( $T_1$ ) and from range II to range III ( $T_2$ ), defined as the temperatures at which the values of  $p$  (or  $N_{A^+}$ ) are equal to those calculated using the formulas for the adjoining ranges can be described by<sup>2)</sup>

$$T_1 = \epsilon_i/k \ln(N_v \alpha^- N_A^2 / \Phi N_D^2), \quad (5)$$

$$T_2 = \epsilon_i/k \ln(N_v / \Phi^*). \quad (6)$$

3. We shall use the above relationships for the calculation of the relative photoconductivity generated by submillimeter radiation  $C^*$ . When the mobilities  $\mu$  of equilibrium and nonequilibrium carriers are equal, the relative photoconductivity is given by the ratio  $\delta p/p$ , where  $\delta p$  is the change in the hole density under the action of the monochromatic radiation  $C^*$ . In ranges II and III, we have

$$p = (\Phi \xi_0 / \alpha^- \alpha^0)^{1/2},$$

where  $\xi_0 = \xi - C^* = T^* + \Phi^* + E^*$ . Therefore, the value of  $\delta p/p$  is given by

$$\delta p/p = (1 + C^*/\xi_0)^{1/2} - 1, \quad (7)$$

where

$$\delta p/p = C^*/2\xi_0, \quad C^*/\xi_0 \ll 1, \quad (7a)$$

$$\delta p/p = (C^*/\xi_0)^{1/2}, \quad C^*/\xi_0 \gg 1. \quad (7b)$$

Thus, in the case of low values of  $C^*$  in range II, we have

$$\delta p/p = C^*/T^* = C^* \exp(\epsilon_i/kT) / N_v. \quad (8)$$

In range III, where  $\xi_0 = \Phi^* + E^*$ , the ratio  $\delta p/p$  is independent of temperature. It follows from Eq. (2) that in range I the value of  $p$  varies weakly with temperature and is independent of  $\xi_0$ . However, even there

$$\delta p/p = C^* \exp(\epsilon_i/kT) / N_v,$$

since the concentration of the  $A^+$  centers absorbing submillimeter radiation and, consequently, the value of  $\delta p$ , increase with rising temperature proportionally to  $C^* \exp(\epsilon_i/kT)$ .

## EXPERIMENTAL CONDITIONS AND METHOD

We determined the dependences of  $\delta p/p$ ,  $p$ , and  $\mu$  on temperature ( $T = 1.4 - 4.2^\circ \text{K}$ ) and electric field ( $E = 0.1 - 200 \text{ V/cm}$ ) in the presence of submillimeter and background radiations of different intensities. A dumbbell-shaped sample ( $2 \times 2 \times 10 \text{ mm}$ ) was connected to a dc circuit and placed in a liquid helium cryostat. Radiation was piped along a polished stainless-steel guide whose diameter was 20 mm and it was concentrated on a sample by a cone. A filter of pure Ge, 0.5 mm thick, was placed in front of the sample; this avoided excitation of free carriers by background radiation of wavelengths  $\lambda < 1.5 \mu$ .

The submillimeter photoconductivity was investigated using either an echelette spectrometer or a backward-wave tube.<sup>[20,23]</sup> The photoconductivity spectrum was determined in the photon energy range 1.5–3 meV using the echelette spectrometer and the spectral distribution of the incident radiation power was measured with an OAP-4 optoacoustic receiver; the photoconductivity signal was normalized to the constant number of photons at each wavelength. The dependences of  $p$ ,  $\delta p/p$ , and  $\mu$  on the submillimeter radiation intensity, and the dependences of  $\delta p/p$  on  $T$  for various values of  $C^*$  and  $E^*$  were obtained using the backward-wave tube. In this case the radiation power was measured with a calibrated attenuator. The photoconductivity was determined by a standard modulation technique employing a V6-2 selective voltmeter and an SD-1 synchronous detector.

Holes were excited from neutral acceptors either by background radiation emitted by the warm parts of the guide or by  $\text{CO}_2$  laser radiation ( $\lambda = 10.6 \mu$ ). The background radiation was controlled by crystalline quartz filters of different thickness. The intensity of the laser radiation was varied by a system of diverging KBr lenses and reflecting germanium filters oriented at an

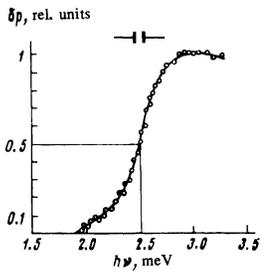


FIG. 2. Long-wavelength photoconductivity edge.

angle of  $45^\circ$  with respect to the beam. In this way the free-carrier density at  $T=4.2^\circ\text{K}$  was varied within the range  $p=10^7\text{--}10^{11}\text{ cm}^{-3}$ . The values of the hole density  $p$  and mobility  $\mu$  were determined from the resistivity and Hall coefficient.

We investigated five Si : B samples with  $N_A=(1\text{--}5)\times 10^{14}\text{ cm}^{-3}$  and  $N_D/N_A=0.01\text{--}0.003$ . The parameters of these samples were deduced from the temperature dependences of the resistivity and Hall coefficient in the temperature range  $T=20\text{--}300^\circ\text{K}$ . These dependences will be given later for a sample with  $N_A=3\times 10^{14}\text{ cm}^{-3}$  and  $N_D/N_A=0.005$ .

### EXPERIMENTAL RESULTS

1. Figure 2 shows the photoconductivity spectrum obtained at  $T=1.4^\circ\text{K}$  in a field  $E=5\text{ V/cm}$ . We can clearly see the long-wavelength photoconductivity edge. The value of  $\varepsilon_i$  deduced from the photon energy corresponding to  $\delta p = \frac{1}{2} \delta p_{\text{max}}$  is  $2.5 \pm 0.1\text{ meV}$ .<sup>3)</sup>

2. Figure 3a shows the dependences of  $\delta p/p$  on  $T$  obtained in a constant electric field ( $E=5\text{ V/cm}$ ) for different values of the submillimeter radiation power  $C^*$ . The curves are normalized to  $T=4.2^\circ\text{K}$ . Figure 3b gives the dependences of  $\delta p/p$  on  $T$  for  $C^*=C_3^*$  and

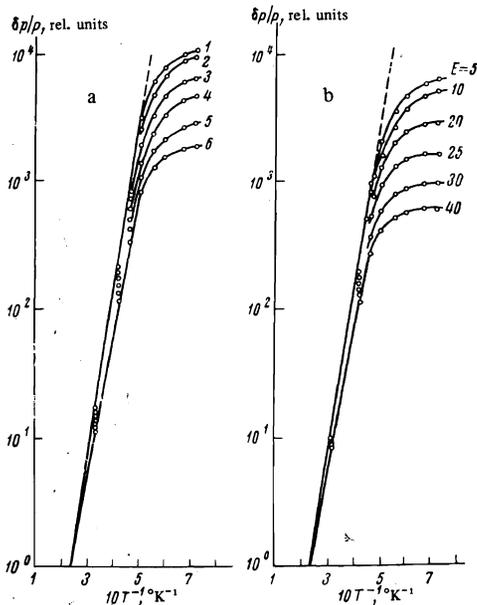


FIG. 3. Dependences of  $\delta p/p$  on  $T$ : a) for  $E=5\text{ V/cm}$  and different intensities of submillimeter radiation  $C^*$ , where  $C_6^*/C_5^*=C_5^*/C_4^*=C_4^*/C_3^*=C_3^*/C_2^*=C_2^*/C_1^*=2$ , where the index refers to the number of the curve; b) for  $C^*=C_3^*$  and different values of  $E\text{ (V/cm)}$ .

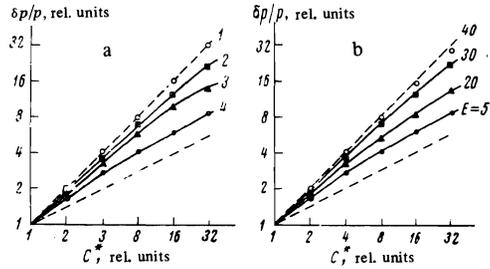


FIG. 4. Dependences of  $\delta p/p$  on  $C^*$ : a) for  $E=5\text{ V/cm}$  at different temperatures: 1)  $4.2\text{--}3^\circ\text{K}$ , 2)  $2^\circ\text{K}$ , 3)  $1.8^\circ\text{K}$ , 4)  $1.4^\circ\text{K}$ ; b) at  $T=1.4^\circ\text{K}$  and for different values of  $E\text{ (V/cm)}$ . The dashed curves represent the dependences  $\delta p/p \propto C^*$  and  $\delta p/p \propto C^{*2}$ .

various values of  $E$ . These dependences are plotted for the  $\lambda=445\ \mu$  radiation obtained from the backward-wave tube. Clearly, in the temperature range  $4.2\text{--}2^\circ\text{K}$  the dependence of  $\delta p/p$  on  $T$  is exponential and at low values of  $E$  and  $C^*$  the argument of the exponential function is  $2.45\text{--}2.6\text{ meV}$ . At  $T \lesssim 2^\circ\text{K}$  there is a saturation of the dependence of  $\delta p/p$  on  $T$ . When  $E$  or  $C^*$  are increased, the deviation from the exponential dependence begins at higher temperatures.

3. Figure 4a shows the dependences of  $\delta p/p$  on  $C^*$  for  $E=5\text{ V/cm}$  at various temperatures. We can see that at  $T > 3.0^\circ\text{K}$  the dependence is  $\delta p/p \propto C^*$ . When the temperature is lowered, the dependence becomes weaker and at  $T=1.4^\circ\text{K}$  it becomes  $\delta p/p \propto \sqrt{C^*}$  at high values of  $C^*$ . An increase in the electric field gives rise to the dependence  $\delta p/p \propto C^*$  (Fig. 4b).

4. Figure 5a shows the experimental temperature dependences of the free-hole density  $p$  obtained in various electric fields, whereas Fig. 5b shows the corresponding dependences  $p(E)$  at several temperatures. It is clear from Fig. 5a that cooling first makes the dependence  $p(T)$  stronger but at lower temperatures it flattens out again. In weak electric fields ( $E \lesssim 0.25\text{ V/cm}$ ) the temperatures of the transitions between the characteristic regions are  $T_1 \approx 2.6^\circ\text{K}$  and  $T_2 \approx 1.8\text{--}1.85^\circ\text{K}$ . When  $E$  is increased, the value of  $T_1$  grows; in fields  $E > 15\text{ V/cm}$ , the value of  $T_2$  also begins to rise so that the exponential region is ob-

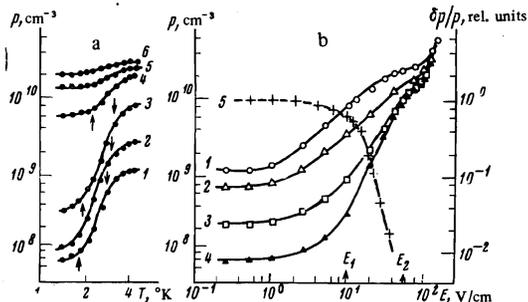


FIG. 5. Dependences  $p(T)$ : a) for different values of  $E\text{ (V/cm)}$ : 1)  $0.25$ , 2)  $2.5$ , 3)  $10$ , 4)  $40$ , 5)  $75$ , 6)  $100$ ; downward arrows denote the transition temperature  $T_1$  and the upward arrows identify  $T_2$ ; b) at different temperatures  $T$ : 1)  $4.2^\circ\text{K}$ , 2)  $2.9^\circ\text{K}$ , 3)  $2.2^\circ\text{K}$ , 4)  $1.4^\circ\text{K}$ ; curve 5 is the dependence of  $\delta p/p$  on  $E$  at  $T=1.4^\circ\text{K}$  for  $C^*=C_1^*$ .

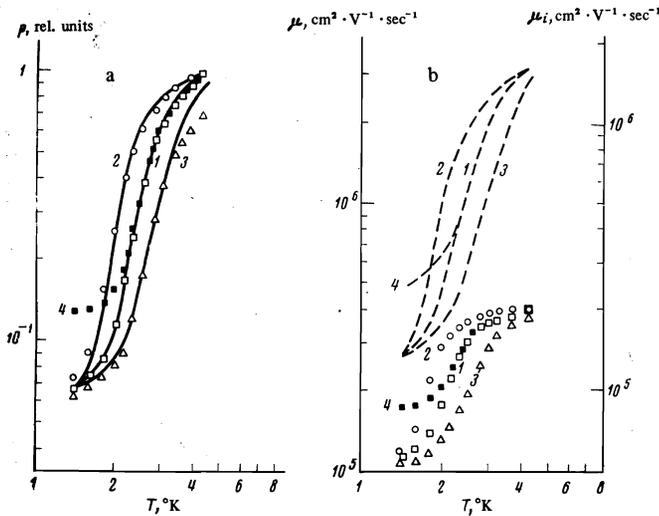


FIG. 6. a) Dependences  $p(T)$  obtained by varying the rates of optical excitation of holes from neutral acceptors: 1)  $\Phi_1 = \Phi$ , 2)  $\Phi_2 = \Phi/10$ , 3)  $\Phi_3 = 10\Phi$ , 4)  $\Phi_4 = \Phi$ ,  $C^* = C_6^*$ ; the continuous curves are calculated; b) Dependences  $\mu(T)$ ; the dashed curves are the calculated dependences  $\mu_i(T)$ .

served in fields  $E < 40$  V/cm; in the range  $E > 70$  V/cm, there is no strong dependence  $p(T)$ .

The nature of the dependences  $p(E)$  in Fig. 5b varies with temperature. At  $T = 4.2^\circ\text{K}$ , the region of constant  $p$  is followed by a relatively uniform increase of  $p(E)$  ending with a steep rise of  $p$  due to the breakdown of neutral acceptors. At  $T = 1.4^\circ\text{K}$  the region of weak variation of  $p(E < E_1)$  changes to a region of steep variation of  $p(E > E_1)$ , which ends at  $E \approx E_2$ , and then the dependences  $p(E)$  at  $T = 4.2$  and  $1.4^\circ\text{K}$  are close to one another. The value of  $\delta p/p$  at  $T = 1.4^\circ\text{K}$  decreases with rising  $E$  and a steep fall corresponds to the onset of a strong rise of  $p$ , i.e., it begins in the field  $E \approx E_1$ .

5. We have quoted so far the results relating to the rate of excitation of holes from neutral acceptors and from the  $A^+$  centers, governed by the background radiation from the warm parts of the guide. Figure 6 compares the dependences  $p(T)$  (Fig. 6a,  $E = 1$  V/cm) and  $\mu(T)$  (Fig. 6b,  $E = 0.25$  V/cm) under the same conditions (curves denoted by 1), when the rate of excitation is reduced by a factor of 10 by filters (curves denoted by 2), and when this rate is increased by a factor of 10 (laser radiation, curves denoted by 3), compared with the usual rate. It is evident from Fig. 6a that the change in the rate of excitation does not alter the nature of the dependence  $p(T)$  and simply shifts the region of the strong temperature dependence in accordance with the actual values of  $T_1$  and  $T_2$ . The dependences  $\mu(T)$  are governed by similar relationships. Illumination of a sample with additional unmodulated submillimeter radiation ( $\lambda = 445 \mu$ ,  $C^* = C_6^*$ ) under conditions of normal background excitation increases  $T_2$  and reduces the fall of the values of  $p$  and  $\mu$  in the temperature range under discussion (curves denoted by 4).

## DISCUSSION

The photoconductivity signal in the submillimeter range and its rise with decreasing temperature in ac-

cordance with an exponential law whose argument contains  $\epsilon_i$  (Figs. 3a and 3b), which is the binding energy of the  $A^+$  centers determined directly from the long-wavelength photoconductivity edge (Fig. 2), is in full agreement with our analysis of the relationships governing the photoconductivity associated with the  $A^+$  centers.

The  $p(T)$  dependences (Fig. 5a) are also in good qualitative agreement with the proposed model: the region of a weak  $p(T)$  dependence changes to strong and this ends in saturation. In quantitative comparison of the calculated and experimental values in the case of a known ratio  $N_D/N_A$  for a given sample, we have to determine the values of  $\epsilon_i$ ,  $\Phi/\alpha^-$ ,  $\Phi^*/\alpha^0$ , and the dependence  $\alpha^-(T)$ .

In the calculations we used  $\epsilon_i = 2.5$  meV. The dependence  $\alpha^-(T)$  was found by investigating strongly compensated Si:B samples with concentrations  $N_A$  close to those in the sample under consideration ( $\alpha^- \propto 1/T^{0.5}$  if  $E \approx 0.25$  V/cm at  $T > 2^\circ\text{K}$ ; at  $T < 2^\circ\text{K}$ ,  $\alpha^- = \text{const}$ ). The ratio  $\Phi/\alpha^-$  was deduced from the hole density at  $T = 4.2^\circ\text{K}$  for several Si:B samples with  $N_A < 5 \times 10^{14} \text{ cm}^{-3}$  and compensations exceeding 10% ( $\Phi/\alpha^- \approx 6 \times 10^6 \text{ cm}^{-3}$ ).

In the determination of  $\Phi^*$  it seemed desirable to find the role of the short-wavelength part of the phonon radiation, governing the value of  $\Phi$ . It is clear from Fig. 6a that a reduction in  $\Phi$  (curve 2) lowers  $T_1$  and  $T_2$  [saturation of the dependence  $p(T)$  does not occur at all down to  $T = 1.4^\circ\text{K}$ ]. An increase in  $\Phi$  (curve 3 in Fig. 6a) increases  $T_1$  and  $T_2$ . It follows from these results that in the absence of additional submillimeter radiation the annihilation of the  $A^+(D^-)$  centers is dominated by high-energy photons and  $\Phi^* = \beta\Phi$ , where  $\beta$  is a dimensionless coefficient.

The proportionality of  $\Phi$  and  $\Phi^*$  is indicated also by a good agreement between the values of  $\mu$  in region III (Fig. 6b) obtained for different rates of excitation of holes from neutral acceptors. Clearly, in this range the value of  $\mu$  is governed primarily by the scattering on charged centers. If we assume that the various scattering mechanisms are additive ( $1/\mu = 1/\mu_i + 1/\mu_n + 1/\mu_{ac}$ ), we find that subtraction of the contributions of the scattering by acoustic lattice vibrations  $\mu_{ac}$  and neutral centers  $\mu_n$  gives the dependence on  $T$  of the mobility  $\mu_i$  governed by the scattering on charged impurities (dashed curves in Fig. 6b). We can see that the values of  $\mu_i$  converge at  $T = 1.4^\circ\text{K}$ ; the dependences  $\mu_i(T)$  are analogous to  $p(T)$  and they have the same inflections characterized by the temperatures  $T_1$  and  $T_2$ . This is to be expected, because  $\mu_i$  and  $p$  depend in the same way on the ionized acceptor concentration. In the absence of coupling between  $\Phi$  and  $\Phi^*$ , the values of  $N_{A^+}$  and  $N_{A^-}$  and, consequently, the values of  $\mu_i$  for illuminations corresponding to curves 2 and 3 should have differed by a factor of 10 [see Eq. (4)].

We shall now estimate the value of  $\beta$ . The expression governing the ratio of the hole densities in ranges I and III,

$$p_I/p_{III} = N_A \alpha_{III}^- N_{A^+} / N_D \alpha_I^- N_A,$$

can be used to determine the maximum value of the ratio  $N_{A^+}/N_A$  for several samples provided we know  $N_A/N_D$ ,  $\alpha_{III}^-/\alpha_I^-$ , and  $p_I/p_{III}$ . We then have

$$N_{A^+}/N_A \approx 0.05. \quad (9)$$

If  $\Phi^* = \beta\Phi$ , Eq. (4') with the aid of Eq. (9) transforms to

$$N_{A^+}/N_A = (\alpha_0/\beta\alpha^-)^{1/2} \approx 0.05. \quad (10)$$

Using the values for  $\alpha_0$  ( $\alpha_0 \approx 10^{-7}$  cm<sup>3</sup>/sec<sup>[12,141]</sup>) and  $\alpha^-$  ( $\alpha^- \approx 1 \times 10^{-5} - 5 \times 10^{-5}$  cm<sup>3</sup>/sec<sup>[261]</sup>), we find that Eq. (10) is satisfied well for  $\beta \approx 1$ . Moreover, if  $\beta \approx 1$  ( $\Phi^* = \Phi$ ), the temperature  $T_2$  given by Eq. (6) agrees with the experimental value. In fact, the interaction between high-energy photons ( $h\nu > 45$  meV in the case of Si:B) with the  $A^+$  centers may destroy the latter by at least two processes: either by the direct detachment of the excess carrier or by the detachment of one of the original carriers. The photodetachment cross sections of the latter process is clearly close to the photoionization cross section of a neutral acceptor. Therefore, the value of  $\beta$  may be of the order of unity.

It follows from Eq. (9) that in the case of unipolar excitation of free carriers the influence of the  $A^+$  centers on the recombination and scattering processes may be manifested only by samples with compensations below 5%.<sup>4)</sup> An increase in the electric field (a reduction in  $\alpha^-$ ) increases the permissible range of compensations.

The experimental values of  $\epsilon_i$ ,  $\Phi/\alpha^-$ , and  $N_D/N_A$  were used in a calculation of the dependences  $p(T)$  for three values of  $\Phi$ :  $\Phi_1 = \Phi$ ,  $\Phi_2 = \Phi/10$ ,  $\Phi_3 = 10\Phi$  on the assumption that  $\Phi^* = \Phi$ .

Since the conditions of validity of the simple relationships (3) and (4) for the sample under consideration are satisfied in our experiments strictly only in narrow temperature intervals, we used the general system (1). In Fig. 5a the calculated curves are superimposed on the corresponding experimental dependences and they agree well with the latter.

A change in the electric field alters the carrier energy and, consequently, the coefficient of the capture of a hole by an attractive center  $\alpha^-$ . In the sample under discussion the temperature  $T = 4.2$  °K corresponds to range I (see Fig. 5a), where the concentration of the recombination centers is equal to the concentration of the compensating impurity ( $N_i = N_D$ ), so that the dependence  $p(E)$  in fields  $E < 100$  V/cm is entirely due to the dependence  $\alpha^-(E)$ :  $p \propto 1/\alpha^-$  in accordance with Eq. (2). At lower temperatures when  $N_{A^+} \gg N_D$  (ranges II and III), the field  $E$  not only alters  $\alpha^-$  but also the number of the recombination centers  $N_i \approx N_{A^+}$ . In weak fields ( $E < E_1$ , curve 4 in Fig. 5b), when the carrier energy is low and there are no breakdown effects in the  $A^+$  centers, we have  $p \propto 1/\sqrt{\alpha^-}$  [see Eq. (3)], because an increase in  $E$  increases the concentration of the recombination centers:  $N_i = N_{A^+} \propto 1/\sqrt{\alpha^-}$ , in accordance with Eq. (3). It is this increase in the number of the  $A^+$  centers with rise in  $E$  that is responsible for the increase of the inflection temperature  $T_1$  (see Fig. 5a).<sup>[13]</sup>

A further increase in the electric field ( $E > E_1$ ) makes the hole energy comparable with the binding energy of the  $A^+$  centers and we can then expect the annihilation of these centers by impact processes. Therefore, in fields  $E > E_1$  the hole density  $p$  should rise steeply with  $E$  because in these fields both  $\alpha^-$  and  $N_i = N_{A^+}$  decrease simultaneously. An increase in  $E$  in the range  $E > E_2$  reduces  $N_{A^+}$  to a value below  $N_D$  ( $N_i = N_D = \text{const}$ ) and the dependence  $p(E)$  corresponds again, as in range I, to the dependence  $\alpha^-(E)$  with  $N_i = \text{const}$  (Fig. 5b). The assumption that for  $E > E_2$  we have  $N_{A^+} < N_D$  is confirmed by the absence of an exponential region in the dependence  $p(T)$  in fields  $E > E_2$  (curve 5 in Fig. 5a). It is clear from Fig. 5a that an increase in the electric field increases not only  $T_1$  but also  $T_2$ . In fact, in electric fields exceeding  $E_1$  the annihilation of the  $A^+$  centers is no longer due to the background radiation  $\Phi^*$  but due to impact processes (the value of  $E^*$ ), which are enhanced by an increase in  $E$  and, consequently, may begin to predominate over the thermal release at higher temperatures [ $\Phi^*$  in Eq. (4) should be replaced with  $\Phi^* + E^*$ ]. In the range  $E > E_2$  the value of  $E^*$  is so high that  $N_{A^+}$  does not exceed  $N_D$  at any temperature and the exponential dependence  $p(T)$  is not observed at all (curve 5 in Fig. 5a).

It follows from Eq. (7) that the value of  $\delta p/p$  is governed by  $\xi_0$ . At  $T = 1.4$  °K, we have  $T^* < \Phi^*$  and  $\xi_0 = \Phi^* + E^*$ . An increase in the electric field above  $E_1$  causes  $\xi_0$  to rise and, consequently, reduces  $\delta p/p$ . In fact, in fields  $E > E_1$  the value of  $\delta p/p$  falls strongly (Fig. 5b). The influence of the electric field is manifested also by the rise of  $T_2$  in the dependence of  $\delta p/p$  on  $T$  (Fig. 3b) and in the dependence  $p(T)$ .

It follows from Eq. (7) that as a result of increase in  $C^*$  the dependence  $\delta p/p \propto C^*$  should cease to be obeyed when  $C^*$  becomes comparable with  $\xi_0$ . At high temperatures the value of  $\xi_0$  is large and  $\delta p/p \propto C^*$  (Fig. 4a). When the temperature is lowered,  $\xi_0$  decreases exponentially and the dependence of  $\delta p/p$  on  $C^*$  changes from linear to sublinear, and at  $T = 1.4$  °K and for high values of  $C^*$  it is close to  $\sqrt{C^*}$ . An increase in the electric field above  $E = E_1$  increases  $\xi_0$  and restores the proportionality between  $\delta p/p$  and  $C^*$  (Fig. 4b).

Since  $\xi_0$  may become less than  $C^*$  when  $C^*$  is large and temperature is low, the main factor which is responsible for the annihilation of the  $A^+$  centers is then unmodulated submillimeter radiation ( $\xi = \xi_0 + C^* \approx C^*$ ), and the value of  $T_2$  should rise, as observed experimentally (curves denoted by 4 in Fig. 6).

These results show that, as in the case of intrinsic excitation of carriers,<sup>[14]</sup> the recombination and scattering processes and the submillimeter photoconductivity under impurity excitation conditions in weakly compensated samples can, under certain conditions, be entirely due to the formation of  $D^-$  and  $A^+$  centers in semiconductors.

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- <sup>1</sup>The direct transitions from  $A^+$  to  $A^-$  centers<sup>[11]</sup> can be ignored for samples with  $N_A < 5 \times 10^{14} \text{ cm}^{-3}$ .
- <sup>2</sup>The formulas of the (3) and (5) type were first obtained in<sup>[13]</sup>.
- <sup>3</sup>This value of  $\epsilon_i$  represents the energy for the photodetachment of a hole from an isolated  $A^+$  center; it is clear from the experiments that in the  $N_A > 10^{15} \text{ cm}^{-3}$  range this energy rises with  $N_A$  (for example, <sup>[13]</sup> it may reach  $\epsilon_i \approx 5 \text{ meV}$  for Si. B).
- <sup>4</sup>In the ambipolar excitation case, <sup>[14]</sup> their influence is important for any value of the compensation.
- <sup>1</sup>N. S. Buchel'nikova, *Usp. Fiz. Nauk* **65**, 351 (1958).
- <sup>2</sup>Ya. M. Fogel', *Usp. Fiz. Nauk* **71**, 243 (1960) [*Sov. Phys.-Usp.* **3**, 390 (1960)].
- <sup>3</sup>D. R. Bates (ed.), *Atomic and Molecular Processes*, Academic Press, New York, 1962 (Russ. transl. Mir., M., 1964), Chap. 4.
- <sup>4</sup>J. B. Hasted, *Physics of Atomic Collisions*, Butterworths, London, 1964 (Russ. transl. Mir, M., 1965, p. 378).
- <sup>5</sup>M. A. Lampert, *Phys. Rev. Lett.* **1**, 450 (1958).
- <sup>6</sup>R. A. Brown and M. L. Burns, *Phys. Lett. A* **32**, 513 (1970).
- <sup>7</sup>H. Nishimura, *Phys. Rev.* **138**, A 815 (1965).
- <sup>8</sup>P. J. Dean, J. R. Haynes, and W. F. Flood, in: *Localized Excitation in Solids* (Proc. First Intern. Conf. on Localized Excitation in Solids, University of California, Irvine, 1967, ed. by R. F. Wallis), Plenum Press, New York, 1968, p. 276.
- <sup>9</sup>P. J. Dean, J. R. Haynes, and W. F. Flood, *Phys. Rev.* **161**, 711 (1967).
- <sup>10</sup>A. Honig and N. Lagnado, Proc. Tenth Intern. Conf. on Physics of Semiconductors, Cambridge, Mass., 1970, publ. by US Atomic Energy Commission, Washington, DC (1970), p. 809.
- <sup>11</sup>D. D. Thornton and A. Honig, *Phys. Rev. Lett.* **30**, 909 (1973).
- <sup>12</sup>E. M. Gershenson, Yu. P. Ladyzhinskiĭ, and A. P. Mel'nikov, *Pis'ma Zh. Eksp. Teor. Fiz.* **14**, 380 (1971) [*JETP Lett.* **14**, 256 (1971)].
- <sup>13</sup>É. É. Godik, Yu. A. Kuritsyn, and V. P. Sinis, *Pis'ma Zh. Eksp. Teor. Fiz.* **14**, 377 (1971) [*JETP Lett.* **14**, 254 (1971)].
- <sup>14</sup>E. M. Gershenson, Yu. P. Ladyzhinskiĭ, and A. P. Mel'nikov, *Fiz. Tekh. Poluprovodn.* **7**, 1100 (1973) [*Sov. Phys.-Semicond.* **7**, 746 (1973)].
- <sup>15</sup>A. P. Mel'nikov, *Fiz. Tekh. Poluprovodn.* **7**, 185 (1973) [*Sov. Phys.-Semicond.* **7**, 130 (1973)].
- <sup>16</sup>É. É. Godik, Yu. A. Kuritsyn, and V. P. Sinis, *Fiz. Tekh. Poluprovodn.* **8**, 2116 (1974) [*Sov. Phys.-Semicond.* **8**, 1373 (1975)].
- <sup>17</sup>T. Ohyama, K. Murase, and E. Otsuka, *J. Phys. Soc. Jpn.* **29**, 912 (1970).
- <sup>18</sup>V. F. Bannaya, E. M. Gershenson, Yu. A. Gurvich, Yu. P. Ladyzhinskiĭ, and T. G. Fuks, *Fiz. Tekh. Poluprovodn.* **7**, 1507 (1973) [*Sov. Phys.-Semicond.* **7**, 1009 (1974)].
- <sup>19</sup>E. M. Gershenson, G. N. Gol'tsman, and A. P. Mel'nikov, *Pis'ma Zh. Eksp. Teor. Fiz.* **14**, 281 (1971) [*JETP Lett.* **14**, 185 (1971)].
- <sup>20</sup>E. M. Gershenson, G. N. Gol'tsman, and N. G. Ptitsina, *Zh. Eksp. Teor. Fiz.* **64**, 587 (1973) [*Sov. Phys.-JETP* **37**, 299 (1973)].
- <sup>21</sup>E. M. Gershenson, Proc. Twelfth Intern. Conf. on Physics of Semiconductors, Stuttgart, 1974, publ. by Techner, Stuttgart (1974), p. 355.
- <sup>22</sup>É. É. Godik, Yu. A. Kuritsyn, and V. P. Sinis, *Fiz. Tekh. Poluprovodn.* **6**, 1662 (1972) [*Sov. Phys.-Semicond.* **6**, 1437 (1973)].
- <sup>23</sup>M. B. Golant, Z. T. Alekseenko, Z. S. Korotkova, L. A. Lunkina, A. A. Negirev, O. P. Petrova, T. B. Rebrova, and V. S. Savel'ev, *Prib. Tekh. Eksp. No. 3*, 231 (1969).
- <sup>24</sup>J. C. Hensel, *Phys. Lett.* **4**, 38 (1963).
- <sup>25</sup>L. E. Blagosklonskaya, E. M. Gershenson, Yu. P. Ladyzhinskiĭ, and A. P. Popova, *Fiz. Tverd. Tela (Leningrad)* **10**, 3010 (1968) [*Sov. Phys.-Solid State* **10**, 2374 (1969)].
- <sup>26</sup>V. L. Bonch-Bruevich and E. G. Landsberg, *Phys. Status Solidi* **29**, 9 (1968).

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## Dynamic Jahn-Teller effect for the $E$ -term with allowance for phonon dispersion

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It is shown that the dynamic Jahn-Teller effect for a non-Kramers doublet leads, in the presence of phonon dispersion of active  $E$  vibrations, to the possibility of appearance of local and pseudolocal electron-phonon states. Criteria for appearance of such states are found. The limits of applicability of the cluster model for impurity centers are discussed. Spectral effects of local and pseudolocal states in the optical and infrared absorption and in Raman scattering of light are considered.

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### 1. INTRODUCTION

The problem of electron-vibrational (vibronic) interaction in systems with electron degeneracy or quasi-degeneracy is extremely complicated, owing to the impossibility of separating, in the general case, the electronic and the nuclear motions. The manifestation of the vibronic interactions in such systems is customarily

called the Jahn-Teller effect (JTE). This effect has been the subject of many theoretical and experimental papers (see the books and reviews<sup>[1-6]</sup>). The greatest progress was attained in the solution of the so-called molecular vibronic problems, where the electrons, in the degenerate state, interact with a small number of vibrational degrees of freedom. This model is adequate for the description of phenomena connected with vi-