Electric-field ionization of optically excited donor atoms

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The photofield ionization of impurity centers in semiconductors, which is analogous to the ionization of optically excited atoms in a gas or in an atomic beam by an electric field, is investigated. The ionization rate of excited nonhydrogenlike shallow donor atoms in many-valley semiconductors is calculated as a function of the strength of the applied electric field, using an asymptotic method. The photoconductivity-spectrum line intensity arising from photofield ionization of impurities is estimated. It is shown that the previously observed "flareup" of extrinsic-photoconductivity lines in phosphorus-doped silicon on increasing the strength of the applied electric field can be attributed to photofield ionization of the donor atoms.

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1. INTRODUCTION

If an atom is in a static uniform electric field, an atomic electron may be able to tunnel through the Coulomb barrier and escape from the atom. The ionization of atoms by a static electric field is a well-known phenomenon in atomic spectroscopy (see Refs. 1 and 2 and the recent reviews, Refs. 3 and 4). This phenomenon manifests itself, in particular, in the disappearance of spectrum lines associated with radiative transitions from some excited state to lower-lying states, and in the appearance of a photocurrent upon optical excitation of atoms in a strong electric field.[2-4]

Ionization of impurity centers in semiconductors by an electric field should result in the appearance of extrinsic photoconductivity with a line spectrum at photon energies $h\nu$ below the impurity-ionization energy E_i even at low temperatures $T \ll (E_i - h\nu)/k_B$ at which the thermal ionization of excited impurity centers is insignificant. In analogy with the term "photothermal ionization" for the process in which an impurity center is first excited optically and is then ionized by the thermal motions of the crystal (see the review article, Ref. 5), we may use the term "photofield ionization" (PFI) to refer to the two-stage extrinsic-photoconductivity mechanism described above.

Some of the optically excited impurity centers undergo radiative transitions to deeper levels from which the ionization rate in the applied electric field is negligible, and therefore do not contribute to the photoconductivity. Other excited impurity atoms, however, are ionized by the field. Let us denote the field-ionization rate of a given level by W_{fi} and the intraimpurity relaxation rate by τ_{ph}^{-1}. The intensity of a line in the PFI spectrum is determined by the ionization probability I of the impurity center:

$$I_{fi}=W_{fi}/(W_{fi}+\tau_{ph}^{-1}). \quad (1)$$

When impurity centers are optically excited from the ground state, the strongest lines correspond to transitions to comparatively deep excited levels. Fields exceeding the threshold field for low-temperature impurity breakdown might be needed to appreciably ionize these levels. However, we shall show that the field-ionization probability in silicon doped with shallow donors is considerable even in fields with strengths in the range 100–800 V/cm (depending on the level), which are much weaker than the breakdown field.

Lanczos[6] has already made detailed quasiclassical-approximation calculations of the ionization rates of hydrogenlike atoms in an electric field. The development of the theory up to the mid 1950s is reflected in the monograph by Bethe and Salpeter.[2] A review of recent studies will be found in Ref. 4 (also see Ref. 7). All these calculations relate to hydrogenlike atoms and are not directly applicable either to donors in semiconductors in which the effective mass is anisotropic (as in Ge and Si) or to acceptors, because of their complicated structure associated with the degeneracy of the edge of the valence band and the presence of light and heavy holes.

Below we shall calculate the field-ionization rate for excited shallow donors in a semiconductor in which the electron effective mass is anisotropic.[1)] It is easy to understand how the mass anisotropy affects the ionization. In excited states (especially in odd ones to which transitions from the ground state give rise to intense lines) the central-cell corrections which mix states of different conduction-band valleys are unimportant; the excited states are degenerate and each state of the level can be associated with a definite valley. Because of the mass anisotropy, a wave function associated with a given valley will fall off differently in different directions: it will decrease most slowly in the plane perpendicular to the longitudinal axis of its valley, i.e., in the directions of the transverse effective mass $m_\perp < m_\parallel$. It is to be expected that the state will be ionized most rapidly if the field lies in that plane, and that it will be ionized least rapidly if the field is parallel to the axis of the valley. In silicon, for example, if $\mathbf{F} \parallel [100]$ ($\mathbf{F}$ is the electric field vector) the ionization rate for states belonging to the [100] and $[\bar{1}00]$ valleys should be lower than the ionization rate for excited states of the same level that belong to the other four valleys.

Thus, because of the anisotropy of the effective mass, states belonging to different valleys should have different ionization rates, and the entire effect must depend on the direction of the field in the crystal. The

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angular dependence of the field-ionization rate should be especially steep in a uniaxial deformed multivalley semiconductor, in which all the optical transitions take place either in a single valley or in two valleys having the same orientation.

Photofield ionization is not the only possible mechanism for the "flare-up" of the extrinsic-photoconductivity line spectrum observed in a number of semiconductors when the electric field strength is increased. This effect has been attributed[9-12] to photoimpact ionization (the ionization of an optically excited atom by a hot current carrier) and has also been interpreted[13] as a manifestation of conductivity due to hopping between excited levels of impurity centers.

The purpose of the present work is to call attention to the possibility of PFI of impurities in semiconductors and to obtain an expression for the field-ionization rate that could be used to estimate the contribution from this phenomenon to the observed extrinsic photoconductivity with a line spectrum.

2. ASYMPTOTIC BEHAVIOR OF THE DONOR WAVE FUNCTION IN THE ABSENCE OF A FIELD

To solve the problem of the ionization of an atom by an electric field in the lowest approximation of the asymptotic method (see, e.g., Refs. 1 and 7) we must know the behavior at large distances of the wave function for an electron in a state with the given energy E in the absence of the uniform electric field $\mathbf{F}$. In this case the wave function satisfies the effective-mass equation:

$$\left\{-\frac{\hbar^2}{2m_\perp}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)-\frac{\hbar^2}{2m_\parallel}\frac{\partial^2}{\partial z^2}-\frac{e^2}{\varkappa r}-E\right\}\Psi(\mathbf{r})=0. \tag{2}$$

Here $m_\perp$ and $m_\parallel$ are the transverse and longitudinal effective masses, and $\varkappa$ is the dielectric constant of the crystal. We shall express lengths in units of $a_\perp=\hbar^2\varkappa/m_\perp e^2$, and energy in units of $E_\perp=\hbar^2/m_\perp a_\perp^2$ and shall write $n^*=(2|E|)^{-1/2}$ and $\gamma=m_\perp/m_\parallel$. In addition, we shall perform a scale transformation on the coordinate z, i.e., we shall transform to the coordinates

$$X=x/a_\perp,\quad Y=y/a_\perp,\quad Z=z/\gamma^{1/2}a_\perp,\quad R=(X^2+Y^2+Z^2)^{1/2},$$
$$\cos\vartheta=Z/R,\quad \operatorname{tg}\varphi=Y/X.$$

Then Eq. (2) takes the form

$$\left[\Delta_R+\frac{2q(\vartheta)}{R}-\frac{1}{n^{*2}}\right]\Psi(\mathbf{R})=0, \tag{2a}$$

$$q(\vartheta)=[1-(1-\gamma)\cos^2\vartheta]^{-1/2}. \tag{3}$$

In the absence of an external field, the system has a symmetry axis parallel to Z. Hence the wave function can be taken in the form

$$\Psi(R,\vartheta,\varphi)=(2\pi)^{-1/2}e^{iM\varphi}\psi(R,\vartheta). \tag{4}$$

We shall seek the function $\psi(R,\vartheta)$ for $R\gg 1$ in the form $R^{-1}e^{iS(R,\vartheta)}$. We introduce the notation

$$p(R,\vartheta)=i\left(\frac{1}{n^{*2}}-\frac{2q(\vartheta)}{R}\right)^{1/2} \tag{5}$$

and write

$$\frac{\partial S_0(R,\vartheta)}{\partial R}=p(R,\vartheta). \tag{6}$$

We express the unknown function $S(R,\vartheta)$ in the form

$$S(R,\vartheta)=S_0(R,\vartheta)+{}^1/_2 i\ln p+S_1(R,\vartheta) \tag{7}$$

and show that at large distances R from the Coulomb center the function $S_1(R,\vartheta)$ decreases with increasing R, and may be dropped in the first approximation as compared with the other terms in Eq. (7). On the left-hand side of the equation

$$\left(2p+i\frac{\partial\ln p}{\partial R}\right)\frac{\partial S_1}{\partial R}+\left(\frac{\partial S_1}{\partial R}\right)^2-i\frac{\partial^2 S_1}{\partial R^2}=\frac{1}{R^2}\exp\left\{-i\left(S_0+\frac{1}{2}i\ln p+S_1\right)\right\}$$
$$\times\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)-\frac{M^2}{\sin^2\vartheta}\right]\exp\left\{i\left(S_0+\frac{1}{2}i\ln p+S_1\right)\right\}$$
$$+p^{1/4}\frac{\partial^2}{\partial R^2}p^{-1/4} \tag{8}$$

for S_1, only the first term is important, while on the right-hand side we may retain only $S_0(R,\vartheta)$ in the arguments of the exponentials. The last term may be simply dropped since it is proportional to R^{-3} when $R\gg 2n^{*2}(\vartheta)$, while the first term is proportional to R^{-2}.

It follows from Eqs. (6) and (7) that when $R\gg 2n^{*2}q(\vartheta)$ we have

$$\exp\left\{i\left[S_0(R,\vartheta)+\frac{1}{2}i\ln p\right]\right\}=\exp\{iS_0(\vartheta)\}\left(\frac{R}{n^*}\right)^{n^*q(\vartheta)}\exp\left(-\frac{R}{n^*}\right), \tag{9}$$

where $\exp\{iS_0(\vartheta)\}$ is a function of the angle ϑ which, in view of the fact that $q(\vartheta)$ is even, has the same symmetry properties as the complete function $\psi(R,\vartheta)$, and which can be determined only by numerical calculation of the donor state under consideration. We shall require only the value of this function in the direction of the external field, and we shall assume it to be known.

Now we substitute (9) into (8) on the right and retain only terms of the highest degree in R:

$$\frac{\partial S_1}{\partial R}=\frac{1}{2pR^2}\exp\{-iS_0(\vartheta)\}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)-\frac{M^2}{\sin^2\vartheta}\right]\exp\{iS_0(\vartheta)\}. \tag{10}$$

When the operator for the squared angular momentum acts on a function the symmetry of the function remains unchanged. Hence the expression on the right in (10) remains finite even at points at which $\exp\{iS_0(\vartheta)\}$ vanishes because of symmetry, and $\partial S_1/\partial R\sim R^{-2}$. Hence it follows that $S_1\sim R^{-1}$ when R is large, i.e., as R tends to infinity, S_1 tends to zero [whereas $S_0(R,\vartheta)+(1/2)i\ln p$ does not].

We write

$$\exp\{iS_0(\vartheta)\}=k\Theta(\vartheta)$$

and choose the coefficient k so that the maximum value of $\Theta(\vartheta)$ will be of the order of unity. Passing to the limit $\gamma\to 1$ is equivalent to going over to the case of a hydrogenlike atom, so we require the following behavior of the function $\Theta(\vartheta)$:

$$\lim_{\gamma\to 1}\Theta(\vartheta)(2\pi)^{-1/2}e^{iM\varphi}=Y_{LM}(\vartheta,\varphi). \tag{11}$$

As $\gamma\to 1$, $n^*=(2|E|)^{-1/2}\to n$, where n is the principal quantum number, so when condition (11) is satisfied (see Ref. 1) we have

$$\lim_{\gamma\to 1}k=2^n n^{-2}[\Gamma(n+L_0+1)\Gamma(n-L_0)]^{-1/2}. \tag{11a}$$

This condition obviously does not determine k unambiguously when $\gamma\neq 1$. We shall take k equal to the right-hand side of (11a) with n replaced by n^*. With this sub-

stitution we may suppose that the maximum value of $\Theta(\vartheta)$ will be ~1 when $n^* \sim 1$.

Thus, when $r = R/q(\vartheta) \gg 2n^{*2}$ the wave function for an electron bound to a donor impurity will be given by

$$\Psi(R,\vartheta,\varphi) \approx 2^{n^*} \frac{1}{n^{*2}} [\Gamma(n^*+L_0+1)\Gamma(n^*-L_0)]^{-1/2} \times \left(\frac{R}{n^*}\right)^{n^* q(\vartheta)-1} \exp\left(-\frac{R}{n^*}\right) \Theta(\vartheta)(2\pi)^{-1/2} \exp(iM\varphi). \quad (12)$$

It should be recalled that $R = rq(\vartheta)$, and that the exponential part of the asymptotic formula, $\exp(-R/n^*)$, must therefore also depend on the angle ϑ (this exponential was obtained earlier[14]).

3. IONIZATION RATE IN AN ELECTRIC FIELD

We shall consider only the case in which the direction of the external electric field F is parallel to the plane perpendicular to the rotation axis of the effective-mass ellipsoid; this field direction corresponds to the maximum ionization rate. We shall express the field strength F in the atomic units $m_1^2 e^5/\hbar^4 \varkappa^3$. We shall assume that F is so small that there is a wide range of distances R from the Coulomb center in which the inequalities $2n^{*2} \ll R \ll (2n^{*2}F)^{-1}$ are satisfied. This will be possible if $F \ll F_c = (16n^{*4})^{-1}$, where F_c is the critical field strength for classical ionization. We shall use parabolic coordinates with the polar axis in the direction of the field F, which we take to be the direction of the X axis. Let Φ be the azimuthal angle for rotation about the field direction. Then

$$X = (\xi-\eta)/2, \quad Y = (\xi\eta)^{1/2}\cos\Phi, \quad Z = (\xi\eta)^{1/2}\sin\Phi, \quad R = (\xi+\eta)/2. \quad (13)$$

The equation for the function

$$\chi(\xi,\eta,\Phi) = (\xi\eta)^{1/2}\Psi$$

in a uniform electric field superimposed on a Coulomb field has the form

$$\left\{\xi\frac{\partial^2}{\partial\xi^2} - \frac{\xi}{4n^{*2}} + \frac{F\xi^2}{4} + \frac{1}{4\xi}\left(1+\frac{\partial^2}{\partial\Phi^2}\right) + \eta\frac{\partial^2}{\partial\eta^2} - \frac{\eta}{4n^{*2}} - \frac{F\eta^2}{4} + \frac{1}{4\eta}\left(1+\frac{\partial^2}{\partial\Phi^2}\right) + \left[1 - \frac{4\xi\eta}{(\xi+\eta)^2}(1-\gamma)\sin^2\Phi\right]^{-1/2}\right\}\chi = 0. \quad (14)$$

With the field direction as we have chosen it, the electrons tunnel out of the impurity center in the positive X direction. It is known[1] from the solution of the problem for $\gamma = 1$ that the tunneling rate is determined by the asymptotic behavior of Ψ for $\xi \gg \eta$, i.e., by its behavior in a small solid angle about the field direction. With the variables in this region, the last term on the left in (14) differs little from unity, and the variables may be approximately separated. In this approximation the wave function Ψ is a superposition of the functions

$$\chi_1(\xi)\chi_2(\eta)(2\pi\xi\eta)^{-1/2}e^{iM'\Phi}$$

with different M' values; here χ_1 and χ_2 are solutions of the equations

$$\left(\frac{d^2}{d\xi^2} - \frac{1}{4n^{*2}} + \frac{F\xi}{4} - \frac{M'^2-1}{4\xi^2} + \frac{\beta_1}{\xi}\right)\chi_1(\xi) = 0, \quad (15a)$$

$$\left(\frac{d^2}{d\eta^2} - \frac{1}{4n^{*2}} - \frac{M'^2-1}{4\eta^2} + \frac{\beta_2}{\eta}\right)\chi_2(\eta) = 0. \quad (15b)$$

Here β_1 and β_2 are separation parameters, so $\beta_1+\beta_2 = 1$. The field term has been omitted from the equation for $\chi_2(\eta)$ since $n^{*2}F\eta \ll 1$.

The solution of (15b) that is bounded and matches the function (12) in the region $\xi \gg \eta$ (see below) is

$$\chi_2(\eta) \sim \eta^{(|M'|+1)/2}\exp(-\eta/2n^*) \quad (16)$$

and is valid when

$$\beta_2 = (|M'|+1)/2n^*. \quad (16a)$$

Then

$$\beta_1 = 1-\beta_2 = 1-(|M'|+1)/2n^*. \quad (16b)$$

To solve Eq. (15a) we use the comparison-equation method,[7,15] as is usual in quasiclassical problems. Calculation shows that the asymptotic behavior of the wave function beyond the Coulomb barrier, i.e., when $\xi \gg 1/n^{*2}F$, is given by

$$\Psi(\xi,\eta,\Phi) = \sum_{M'} A_{M'}[\xi P(\xi)]^{-1/2}\exp\left(i\frac{F^{1/2}}{3}\xi^{3/2}\right) \times \eta^{|M'|/2}\exp\left(-\frac{\eta}{2n^*}\right)\exp(iM'\Phi), \quad (17)$$

where $P(\xi) = (F\xi/4)^{1/2}$ and the coefficients $A_{M'}$ are determined by matching the wave function below the barrier in the region $n^* \ll \xi/n^* \ll 1/n^{*3}F$ with the asymptotic formula (12). In this ξ region the electric field F actually has a negligible effect on the form of the wave function, so that the latter can be approximated by (12). On the other hand, Eqs. (15) are also valid here.

In order to match the two functions we transform (12) to a coordinate system whose polar axis is in the direction of the field. We denote the polar and azimuthal angles of this system by θ and Φ. On rotating the initial coordinate system (whose polar axis is parallel to the rotation axis of the effective-mass ellipsoid) through an angle of $\pi/2$ about the Y axis, we obtain

$$\Theta(\vartheta)(2\pi)^{-1/2}e^{iM\varphi} = \sum_{M'}\sum_{L} a_L D^{(L)}_{M'M}\left(0,\frac{\pi}{2},0\right) Y_{LM'}(\theta,\Phi). \quad (18)$$

Here the a_L are the coefficients in the expansion of $\Theta(\vartheta)(2\pi)^{-1/2}e^{iM\varphi}$ in the spherical functions $Y_{LM}(\vartheta,\varphi)$ with different values of $L \geq |M|$, and $D^{(L)}_{M'M}$ is the rotation matrix[1]:

$$D^{(L)}_{M'M}\left(0,\frac{\pi}{2},0\right) = \left[\frac{(L+M')!(L-M')!}{(L+M)!(L-M)!}\right]^{1/2}\frac{1}{2^{M'}}P_{L-M'}^{(M'-M,M'+M)}(0), \quad (19)$$

where the $P_n^{(a,b)}(x)$ are Jacobi polynomials.

Let us substitute (18) into (12) and transform to the parabolic coordinates (13). Then we take account of the fact that near the direction of the field ($\vartheta \approx \pi/2, \theta \approx 0$) we have $q(\vartheta) \approx 1$, while for the spherical functions we have

$$Y_{LM'}(\theta,\Phi) \sim (\sin\theta)^{|M'|}, \quad \sin\theta \approx 2(\eta/\xi)^{1/2},$$

and the quantity R outside the exponential may be replaced by $\xi/2$. Then (12) takes the form

$$\Psi(\xi,\eta,\Phi) \approx \exp\left(-\frac{\xi+\eta}{2}\right)\sum_{M'} B_{M'}\left(\frac{\xi}{n^*}\right)^{n^*-1-|M'|/2}\eta^{|M'|/2}\exp(iM'\Phi), \quad (20)$$

$$B_{M'}=\frac{(-1)^{M'}2^{|M'|+1}}{(n^*)^{2+|M'|/2}[\Gamma(n^*+L_0+1)\Gamma(n^*-L_0)]^{1/2}}$$

$$\times\sum_L a_L i^L D^{(L)}_{M',M}\left(0,\frac{\pi}{2},0\right)\left[\frac{2L+1}{4\pi}\frac{(L-|M'|)!}{(L+|M'|)!}\right]^{1/2}\left(\frac{d^{|M'|}P_L(x)}{dx^{|M'|}}\right)_{x=1}. \quad (20a)$$

The asymptotic formula obtained by solving (15a) by the comparison-equation method has the same form as (20) in the matching region. We obtain the following expression for the coefficients $A_{M'}$ in (17) from the matching condition:

$$A_{M'}=B_{M'}\frac{1}{2(n^*)^{1/2}}e^{-i\pi/4}\left(\frac{4}{n^{*3}F}\right)^{n^*-(|M'|+1)/2}\exp\left(-\frac{1}{3n^{*3}F}\right). \quad (21)$$

Because of the factor $(n^{*3}F)^{|M'|/2}$, which is small when $M'\neq 0$, only the term with the smallest value of $|M'|$ should be retained in (17). As can be seen from (19), the sum over M' begins with $|M'|=1$ if M is even (or zero) and begins with $M'=0$ only if M is odd. Thus, when M is odd we may retain only the term with $M'=0$ in Eq. (21). In that case the sum over L reduces to $\Theta(\mathbf{F}/F)(2\pi)^{-1/2}$, where $\Theta(\mathbf{F}/F)$ is the value of $\Theta(\vartheta)$ in the direction of the field $\mathbf{F}$.

Knowing the wave function beyond the barrier [Eqs. (17) and (21)], we can calculate the current from an atom. The ionization rate of an atom initially in an odd state with odd M is given by the following equation (the parity of L_0 indicates the parity of the state):

$$W_{fi}(n,L_0,M)=\pi\gamma^{1/2}\xi P(\xi)\int_0^\infty d\eta|\Psi(\xi,\eta,\Phi)|^2 \quad (22)$$

$$=\left|\Theta\left(\frac{\mathbf{F}}{F}\right)\right|^2\frac{\gamma^{1/2}}{2n^{*4}\Gamma(n^*+L_0+1)\Gamma(n^*-L_0)}\left(\frac{4}{n^{*3}F}\right)^{2n^*-1}\exp\left(-\frac{2}{3n^{*3}F}\right).$$

The expression for $W_{fi}(n,L_0,0)$ differs from (22) by the substitution of the small factor $|(\partial\Theta/\partial\theta)_0|^2 n^{*4}F$ for $|\Theta(\mathbf{F}/F)|^2$.

It should be borne in mind that W_{fi} is given by Eq. (22) in effective atomic frequency units $m_\perp e^4/\varkappa^2\hbar^3$.

We have not taken the Stark effect into account. The linear Stark effect is not present in the effective mass approximation for nonhydrogenlike shallow impurity centers (a small linear effect arises because a substitution impurity is not a center of symmetry in the crystal,[16] but this effect is negligible in the case of odd states). Moreover, a quadratic change in the level energy $\sim F^2$ cannot substantially affect the magnitude of W_{fi} provided $F\ll F_c=(16n^{*4})^{-1}$.

4. COMPARISON WITH EXPERIMENT

Let $\delta U(h\nu)$ be the photoresponse of the semiconductor as a function of the photon energy. A characteristic of the height $\delta U(h\nu_n)$ of the line associated with the transition to the n-th level of the impurity center ($h\nu<E_i$) is the ratio of that height to the magnitude of the ordinary photoconductivity at its long-wavelength limit, i.e., to $\delta U(E_i)$. If we approximate the shape of the line by a Lorentz function, the area under the line in the photoconductivity spectrum will be $\pi\Gamma\delta U(h\nu_n)$, where Γ is the half width at half maximum. On the other hand, the area under the same line in the spectrum of the extrinsic optical absorption cross section $\sigma(h\nu)$ is

$$f_n\int_0^\infty dh\nu\sigma(h\nu),$$

where f_n is the oscillator strength of the optical transition and the integral is given by a well-known sum rule.[17] A current carrier produced by photofield ionization should be expected to make the same contribution to the photocurrent (i.e., to have the same mobility and lifetime) as a photocarrier excited right at the bottom of the band ($h\nu\approx E_i$). In that case

$$\frac{\pi\Gamma\delta U(h\nu_n)}{\delta U(E_i)}=I_n\frac{v_n}{v}\left[f_n\int_0^\infty dh\nu\sigma(h\nu)\right]\Big/\sigma(E_i). \quad (23)$$

Here I_n is the probability for field ionization of the n-th excited state as given by Eq. (1), v_n is the number of valleys that contribute to the photoionization for the given orientation of the electric field, and v is the total number of valleys.

The desired equation,

$$\frac{\delta U(h\nu_n)}{\delta U(E_i)}=I_n f_n\frac{v_n}{v}\frac{E_i}{\Gamma}\frac{\int_0^\infty dh\nu\sigma(h\nu)}{\pi E_i\sigma(E_i)}, \quad (24)$$

follows from Eq. (23). The last factor on the right in (24) is of order unity for all shallow impurities, and we also have $v_n/v\sim 1$. The oscillator strengths of the strongest lines in the optical absorption spectrum are of the order of one or several tenths of a unit. At the same time, $E_i/\Gamma\gtrsim 10^3$ in comparatively pure semiconductors. We may therefore expect the heights of the brightest PFI lines to be comparable with the height of the photoresponse at $h\nu=E_i$ even when $I_n\sim 10^{-2}$, i.e., when $W_{fi}\sim 10^{-2}\tau_{ph}^{-1}$.

Stradling *et al.*[13] observed the appearance of extrinsic photoconductivity with a line spectrum in the region $h\nu<E_i$ on applying a strong field under such conditions (low temperatures) that the photothermal ionization was negligible. They presented the spectra of three specimens: $n-Si:P$ ($N_D=10^{12}$ cm^{-3}, degree of compensation $K=0.3$, and $T=1.5$°K, $n-$Si : P ($N_D=3.7\times10^{15}$ cm^{-3}, $K=0.7$, and $T=1.5$°K, and $n-$CdTe ($N_D=0.9\times10^{14}$ cm^{-3}, $K=0.8$, and $T=4.2$°K). As the strength of the pulling field in Si : P increases, lines corresponding to transitions to deeper and deeper P levels successively "flare up" in the photoconductivity spectrum. In the specimen with the low P concentration the $4p_\pm$ and $3p_\pm$ lines become appreciable in a ~100-V/cm field, and the $2p_\pm$ line in a ~450-V/cm field. Stradling *et al.*[13] attribute the observed photoconductivity to hopping between excited levels of impurity centers. Below we shall explore the possibility of attributing the effects observed in the Si : P specimen with the low P concentration to PFI of the P atoms. It is difficult to compare the theory quantitatively with the experiment because there are no data in the literature on the intra-impurity relaxation times τ_{ph} for donors in Si, and because the orientation of the electric field with respect to the crystallographic axes (on which W_{fi} depends) was not stated in Ref. 13.

In Si we have $\varkappa=11.4$ and $m_\perp=0.190m_0$, and the atomic units of energy, frequency, and field strength introduced above have the values 39.78 meV, 6.06

$\times 10^{13}$ Hz, and 1.25×10^5 V/cm, respectively. According to Faulkner's calculations[18] the binding energies of the $4p_\pm$, $3p_\pm$, and $2p_\pm$ levels are 2.19, 3.12, and 6.4 meV, respectively. From the optical absorption spectra of Si : P presented in Ref. 19 we can estimate the oscillator strengths of the strongest transitions as $f(2p_\pm)\approx0.2$ and $f(3p_\pm)\approx0.02$, and the last factor on the right in Eq. (24) as ~0.35–0.4. From the spectrum given in Ref. 13 we can conclude that $\Gamma\approx0.07$ meV. The ionization energy of an impurity P atom is E_i = 45.54 meV. Using these data, we can write formula (24) for the $2p_\pm$ level in the form

$$\frac{\delta U(2p_\pm)}{\delta U(E_i)}=60I(2p_\pm)=60[1+(W_{fi}\tau_{ph})^{-1}]^{-1}. \qquad (25)$$

For donors in Si, as for donors in Ge, the differences between the level energies are such that the intraimpurity relaxation is determined by one-phonon transitions. In view of the fact that τ_{ph} for donors is determined by the largest effective mass,[20] i.e., by the longitudinal mass, and that $m_\parallel$ is smaller in Si than in Ge while the energy differences between levels are larger in Si than in Ge, we may expect that τ_{ph} will be no smaller for donors in Si than for donors in Ge, i.e., that it will be ~10^{-8}–10^{-9} sec.[20,21]

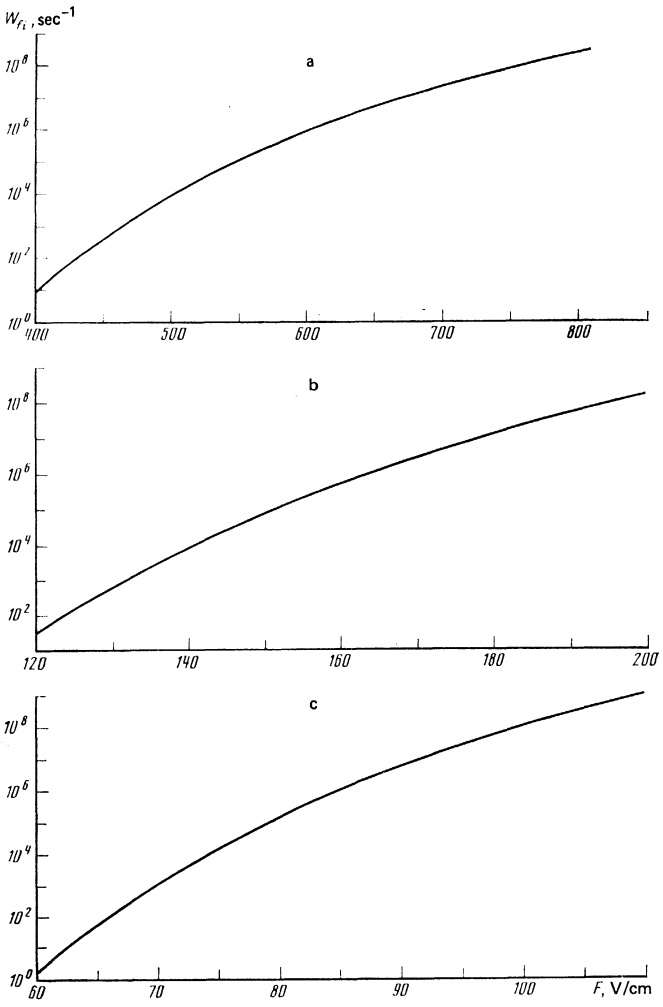

FIG. 1. Ionization rates of shallow donors in silicon vs the electric field strength for three states of $np_\pm$ type: a—$2p_\pm$, b—$3p_\pm$, c—$4p_\pm$. The ordinates are the ionization rates in sec^{-1} (logarithmic scale), and the abscissae are the electric field strengths in V/cm. The quantity $|\Theta(\mathbf{F}/F)|^2$ is set equal to unity.

Figure 1 shows field-strength dependences of the ionization rates from $np_\pm$ states of donors in Si as calculated with formula (22) under the assumption that the field is in the direction of a cubic axis. If we compare these dependences with the Si : P spectra given in Fig. 2 of Ref. 13 and take Eqs. (24) and (25) and the estimate of τ_{ph} into account, we must conclude that the extrinsic photoconductivity with a line spectrum reported in Ref. 13 for the Si specimen with the low donor concentration is due to PFI of donors.[2)]

Let us look qualitatively at the changes in the general form of the impurity PFI spectrum that take place when the electric field strength is increased. A field in which a line corresponding to an optical transition to a fairly deep level just begins to be appreciable may already be a very strong field from the point of view of shallower levels (see Fig. 1), giving rise to a very large Stark effect in these levels and resulting in the disappearance of the corresponding lines and their merging with the continuous spectrum (the latter takes place at a certain field strength $F_0\sim F_c$). When the field is so oriented as to maximize the ionization rate (when it is perpendicular to the valley axis), it not only shifts the $np_\pm$ lines, but also splits them. Even levels in valleys that do not contribute to the photocurrent are Stark shifted. In specimens that are not optically very thin, these levels yield dips (not peaks) in the photoconductivity spectrum, and these dips shift as the field strength changes and merge with the continuous spectrum in strong fields. Even when the Stark sublevels are not resolved, the Stark effect must manifest itself in a shall shift of all the $np_\pm$ lines toward the longer wavelengths, as compared with the lines of the optical absorption spectrum; this is due to the higher probability for ionization from the deeper Stark sublevels. This effect, which is known in atomic photoionization spectroscopy, is associated with the asymmetry of the wave functions of the Stark sublevels: the lowest level is so shifted as to facilitate ionization.[2]

It would be of interest to investigate the effect of an electric field on highly excited levels ($n^*\gg1$); even very weak fields might have a considerable effect on such levels. Photoelectric spectroscopy using transitions between excited levels (but not from the ground level) would apparently be the most suitable method for such studies.

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[1)] A recent paper[8] gives the results of numerical calculations of the ionization rates from their ground states of donors in Si and Ge as functions of the electric field strength; the anisotropy of the effective mass was not taken into account in the calculations.

[2)] At the same time, estimates show that the photoresponse associated with conductivity due to hopping between excited levels is quite negligible for two reasons: 1) the probability for jumps between impurities during the time τ_{ph} (even between excited levels of those impurities) under conditions in which the average distance between the impurities is two orders of magnitude greater than the radius of the excited state, is negligible; and 2) with this mechanism the lifetime of a photocarrier would be the intraimpurity relaxation time τ_{ph}, which in pure materials is shorter than the lifetime of band carriers.

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