Optical absorption and photoeffect spectra of shallow acceptor impurities in semiconductors

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A numerical nonvariational method is proposed for the calculation of the wave functions and energies of bound states and of the wave functions of the continuous spectra of shallow acceptor impurities (SAI) in cubic semiconductors, with account taken of the terms linear in the parameter δ that determines the nonsphericity of the equal-energy surfaces of the holes. The oscillator strengths of the spectral lines, the spectrum of the cross section of the photoeffect from the SAI, and the deformation-potential constants are calculated for a number of levels. The singularities of the SAI optical absorption spectrum in Ge are obtained and compared with the absorption spectrum of hydrogenlike atoms. A sum rule is obtained for the shallow-impurity optical-absorption cross section. Numerical calculations are performed for impurities of group III in Ge.

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§1. INTRODUCTION

Although intensive research into the energy spectrum and other properties of shallow acceptor impurities (SAI) in cubic semiconductors has been going on for more than 25 years, interest in their study remains unabated. The reason is, first, that even in the effective-mass approximation the equations for the wave functions and eigenvalues of the energy of thee impurities comprise a complicated system of differential equations that cannot be solved analytically, while its numerical solutions must be obtained separately for each semiconductor. Second, with advances in the technology of obtaining ever purer semiconducting materials and with the development of new methods for their investigation (in particular, photoelectric spectroscopy), the SAI spectra are being constantly refined, and a new set of problems arises when it comes to interpreting these spectra, especially in highly excited states.

Following the formulation of the effective-mass equations for the SAI,[1-3] Schechter calculated the energies of the ground and first excited levels of SAI in Ge by a standard variational method.[4] He noted that the problem becomes noticeably simpler if the terms having cubic symmetry are neglected in the effectivemass Hamiltonian and only the spherically symmetrical term are retained. In this spherical approximation, the equations reduce to a system of two ordinary second-order differential equations for the radial functions.[5-6] A similar system was obtained earlier by Mendelson and James from a variational principle, using trial functions in a form corresponding to the spherical approximation.[7] Baldereschi and Lipari,[8,9] using the technique of irreducible spherical tensor operators, represented the effective-mass Hamiltonian H_0 for the SAI in a form most convenient for obtaining the spherical approximation and of the corrections for it. In the case when the valence band Γ_7 split-off by the spin-orbit interaction can be disregarded ($\Delta \gg |E|$),

$$H_0=\frac{\hbar^2\gamma_1}{2m_0}\{p^2-\mu(P^{(2)}\cdot J^{(2)})+\delta([P^{(2)}\times J^{(2)}]_4^{(4)}+[P^{(2)}\times J^{(2)}]_{-4}^{(4)} + \sqrt{14/5}[P^{(2)}\times J^{(2)}]_0^{(4)})\}. \qquad (1)$$

Here $\hbar p$ is the momentum operator, $P^{(2)}$ is an irreducible spherical tensor operator of second rank, made up in the usual manner of the components of the symmetrical tensor $p_ip_k-(1/3)p^2\delta_{ik}$; $J^{(2)}$ is analogously connected with the matrices J of the angular momentum with $J=3/2$. The parameters $\mu=2(2\gamma_2+3\gamma_3)/5\gamma_1$, $\delta=(\gamma_3-\gamma_2)/\gamma_1$, γ_i are the valence-band parameters introduced by Luttinger, and m_0 is the mass of the free electron. Tables of γ_1, μ, and δ in cubic semiconductors are given in Refs. 8 and 9.

The first two terms of the expression for H_0 have spherical symmetry, and the part proportional to δ has cubic symmetry. In practically all the cubic semiconductors (with the exception of silicon) the parameter $\delta \ll 1$ and perturbation theory based on smallness of the cubic-symmetry terms in H_0 (Ref. 9) is effective enough.

The variational method was used by now to calculate the energies of the ground and several excited levels for a large number of values of μ and δ, i.e., for almost all cubic semiconductors, and a number of optical transitions from the ground states of SAI in Ge and Si have been reliably identified.[8-12] There are, however, many problems whose solution calls not only for knowledge of the level energies, but also for knowledge of the corresponding wave functions with good accuracy. These include the calculation of the intensities of the spectral lines (which are needed, in particular, for a reliable interpretation of the spectra, especially for transitions between excited levels), the calculation of the deformation-potential constants (for discrete levels) as well as of the Zeeman-effect parameters, the SAI polarizabilities in the ground and excited states, and the calculation of the transition probabilities between SAI bound states with participation of phonons.[13] It is known that if the relative inaccuracy of the variationally determined eigenfunctions is of the order Δ (it depends on the choice of the trial functions), then the inaccuracy of the obtained energy eigenvalues is $\sim\Delta^2$. The variational method yields thus accurate enough values of the terms, but the accuracy of the wave functions is lower (and is quite indeterminate). We develop therefore in this paper, for the solution of some of the problems

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listed above, a numerical but nonvariational method of calculating the SAI energies and wave functions, with account taken of the terms linear in $\delta \ll 1$ in the equations for the radial functions (see §2 below). The accuracy of the results is limited only by the discarded higher powers of δ, and can therefore be estimated beforehand.

The method developed allows us also to solve a number of problems connected with the continuous spectrum of the SAI (these problems had heretofore not been solved at all). These include the calculation of the cross section of the photoeffect from an impurity center, the cross sections of the non-Born scattering from an ionized impurity, and others.

The direct cause for undertaking this work was a contradiction that arose in the determination of the transition oscillator strengths and of the photoeffect cross sections from the known optical absorption spectra of group-III impurities in Ge.[14] These quantities were needed for the solution of the following problem. It is known (see, e.g., the review of Kogan and Lifshitz[15]) that at photon energies $h\nu$ lower than the impurity ionization energy ε_i, a photoconductivity is observed connected with photothermal ionization of the impurity, i.e., with its optical excitation and subsequent thermal ionization on account of phonon absorption. The probability I of thermal ionization of an impurity center in the excited state (the alternate process is the return to the ground state) is of interest not only for photoelectric spectroscopy, but also for the physics of cascaded carrier capture by an attracting impurity. The values of I for various states of an impurity center can be obtained by comparing the photoconductivity and optical-absorption spectra of this impurity,[10] namely, it is necessary to find the ratio of the area under the line in the photoconductivity spectrum to the magnitude of the photoresponse at $h\nu = \varepsilon_i$, and then find the analogous ration in the optical absorption spectrum, and divide the first ratio by the second. By comparing in this manner the photoconductivity spectra of ultrapure p-Ge with the SAI optical-absorption spectra obtained in Ref. 14, Sidorov[17] obtained values of I larger than 1, thus casting doubts either on the correctness of the values of the oscillator strengths of the optical transitions and of the photoionization cross sections determined from the spectra,[14] or else on the photoconductivity mechanism at $h\nu = \varepsilon_i$. To resolve this contradiction if was necessary to calculate the oscillator strengths of the principal lines in the spectra of the SAI in Ge and the photoionization cross section on the red edge of the photoeffect. This is due in the present paper (§§5, 6).

§2. METHOD OF CALCULATING THE BOUND STATE WAVE FUNCTIONS AND ENERGIES

At $\delta = 9$, the effective-mass Hamiltonian of SAI in cubic semiconductors [see (1)] is spherically symmetrical. Therefore the total angular momentum is $F = L + J$ where L is the orbital angular momentum and is conserved. The wave functions of a hole in the Coulomb field of an impurity can be represented in the form[6,7]

$$\Psi_{LFF_z}(r)=R_L(r)\,|LJFF_z\rangle+R_{L+2}(r)\,|L+2,\ JFF_z\rangle, \tag{2}$$

where $|LJFF_z\rangle$ are known function in the L–S coupling scheme, and F and F_z are the quantum numbers of the total angular momentum and of its projection. Given $F \geqslant 3/2$, the orbital quantum number L (an integer) is equal either to $F - 3/2$ or to $F - 1/2$, depending on the parity of the state. At $F = \frac{1}{2}$ Eq. (2) contains only one term with $L = 2$ (even state) or $L = 1$ (odd). If the energy is measured in units of $R_a = m_0 e^4/2\hbar^2 \varkappa^2 \gamma_1$, where $\varkappa$ is the dielectric constant, and the distances are measured in units of $a = \hbar^2 \varkappa \gamma_1 / m_0 e^2$, then the equations for the radial functions take at $F \geqslant 3/2$ the form[5,6,8,9,18] $(V = -2r)$

$$\begin{gathered}
\left\{\left(1+\frac{1-\beta^2}{1+\beta^2}\mu\right)\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{L(L+1)}{r^2}\right]-V+E\right\}R_L\cdot\\
-\frac{2\beta\mu}{1+\beta^2}\left[\frac{d^2}{dr^2}+\frac{2L+5}{r}\frac{d}{dr}+\frac{(L+1)(L+3)}{r^2}\right]R_{L+2}=0,\\
-\frac{2\beta\mu}{1+\beta^2}\left[\frac{d^2}{dr^2}-\frac{2L+1}{r}\frac{d}{dr}+\frac{L(L+2)}{r^2}\right]R_L\\
+\left\{\left(1-\frac{1-\beta^2}{1+\beta^2}\mu\right)\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{(L+2)(L+3)}{r^2}\right]-V+E\right\}R_{L+2}=0,\\
\beta=3^{L-F+1}[(F+{}^3/_2)/(F-{}^1/_2)]^{1/2}.
\end{gathered} \tag{3}$$

At $F = \frac{1}{2}(L = 0$ or $1)$

$$\left\{(1+\mu)\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{L(L+1)}{r^2}\right]-V+E\right\}R_L(r)=0. \tag{3a}$$

Allowance for the cubic-symmetry term in (1) in first order in δ has no effect whatever on the energies of the states with $F < 5/2$, but leads to a splitting of the levels with $F > 5/2°$ In this approximation the wave functions that transform in accord with definite double valued representations Γ_6, Γ_7, or Γ_8 of the T_d group must be sought in the form[9]

$$\Psi_{F\Gamma n}(r)=R_{LF\Gamma}(r)\,\Phi(LF\Gamma n)+R_{L+2,\,F\Gamma}(r)\,\Phi(L+2,\ F\Gamma n), \tag{4}$$

where Γ is one of the indicated representations, the index n labels the functions belonging to one representation, and

$$\Phi(LF\Gamma n)=\sum_{F_z}c(F\Gamma nF_z)\,|LJFF_z\rangle. \tag{4a}$$

The matrix of the coefficients $c(F\Gamma nF_z)$ can be easily found for each F and Γ.

When account is taken of the terms linear in δ, the equations for the radial functions differ from (3).[9] The corrections to the differential operators acting on R_L and R_{L+2} are conveniently represented in matrix form

$$-3\sqrt{30}(2F+1)\,\delta\lambda_{F\Gamma}\begin{Bmatrix}4 & F & F\\ 2 & L_1 & L_2\\ 2 & {}^3/_2 & {}^3/_2\end{Bmatrix}(L_1\|P^{(2)}\|L_2). \tag{5}$$

Here L_1 and L_2 take the values L and $L + 2$, the curly brackets contain a $9j$-symbol, $(L_1 \| P^{(2)} \| L^2)$ is a reduced matrix element, and $\lambda_{F\Gamma}$ is an eigenvalue of the system of equations for the determination of$^{1)}$ $c(F\Gamma nF_z)$.

The method used by us to solve Eqs. (3) for the radial functions (with the correctness linear in δ taken into account) consists of finding the fundamental solutions of these equations in the form of power series, and finiding a linear combination of these solutions that behaves correctly as $r \to \infty$. A similar procedure was used in Ref. 7 to solve the system of equations obtained for the radial functions from the variational principle.

In general form, the idea of selecting a linear combination of the fundamental solutions was set forth also by Gel'mont and D'yakonov.[6]

We seek the first fundamental solution in the form

$$f_L(r)=\sum_{n=0}^{\infty}a_nr^n,\quad f_{L+2}(r)=\sum_{n=0}^{\infty}b_nr^n. \tag{6}$$

Substitution of (6) in (3) leads to the following recurrence relations for the coefficients (for simplicity, we leave out here the terms proportional to δ):

$$\begin{gathered}\left(1+\frac{1-\beta^2}{1+\beta^2}\mu\right)(n-L)(n+L+1)a_n+2a_{n-1}+Ea_{n-2}\\ -\frac{2\beta\mu}{1+\beta^2}(n+L+1)(n+L+3)b_n=0,\\ -\frac{2\beta\mu}{1+\beta^2}(n-L)(n-L-2)a_n+\left(1-\frac{1-\beta^2}{1+\beta^2}\mu\right)(n-L-2)\\ \times(n+L+3)b_n+2b_{n-1}+Eb_{n-2}=0.\end{gathered} \tag{7}$$

It is seen that at $n<L+2$ we have $a_n=b_n=0$, while a_{L+2} and b_{L+2} are connected by the equation

$$b_{L+2}=\frac{1+\beta^2+\mu(1-\beta^2)}{\beta\mu(2L+5)}a_{L+2}. \tag{8}$$

The series in (6) thus begin with $n=L+2$. We put for the sake of argument $a_{L+2}=1$.

We seek the second fundamental solution in the form

$$g_L(r)=\sum_{n=0}^{\infty}c_nr^n+kf_L(r)\ln r,\quad g_{L+2}(r)=\sum_{n=0}^{\infty}d_nr^n+kf_{L+2}(r)\ln r, \tag{9}$$

where k is a constant. The recurrence relations for c_n and d_n are of the form

$$\begin{gathered}\left(1+\frac{1-\beta^2}{1+\beta^2}\mu\right)(n-L)(n+L+1)c_n+2c_{n-1}+Ec_{n-2}-\frac{2\beta\mu}{1+\beta^2}(n+L+1)\\ \times(n+L+3)d_n=-\left(1+\frac{1-\beta^2}{1+\beta^2}\mu\right)(2n+1)ka_n+\frac{2\beta\mu}{1+\beta^2}2(n+L+2)kb_n,\\ -\frac{2\beta\mu}{1+\beta^2}(n-L)(n-L-2)c_n+\left(1-\frac{1-\beta^2}{1+\beta^2}\mu\right)(n-L-2)(n+L+3)d_n\\ +2d_{n-1}+Ed_{n-2}=\frac{2\beta\mu}{1+\beta^2}2(n-L-1)ka_n-\left(1-\frac{1-\beta^2}{1+\beta^2}\mu\right)(2n+1)kb_n.\end{gathered} \tag{10}$$

It follows therefore that $c_n=d_n=0$ at $n<L$. Putting $n=L$ in (10), we find that $d_L=0$. At $n=L+1$ we find that d_{L+1} and c_L are connected by the relation

$$d_{L+1}=-\frac{\beta\mu}{(1+\beta^2)(1-\mu^2)^2(L+1)(L+2)}c_L. \tag{11}$$

From Eqs. (10) with $n=L+2$, taking (8) and (11) into account, we obtain the connection between c_L and $ka_{L+2}=k$. Assuming for the sake of argument $c_L=1$ (we recall that $d_L=0$), we obtain an expression for the coefficient k:

$$k=\frac{2\beta^2\mu^2}{(1+\beta^2)^2(1-\mu^2)^2(L+1)(L+2)}. \tag{12}$$

Both solutions, (6) and (9), are finite as $r\to0$. We need also a third fundamental solution of (3), which diverges as $r\to0$:

$$\begin{gathered}h_L(r)=\sum_{n=-L-1}^{\infty}m_nr^n+g_L\ln r-kf_L(\ln r)^2/2,\\ h_{L+2}(r)=\sum_{n=-L-1}^{\infty}p_nr^n+g_{L+2}\ln r-kf_{L+2}(\ln r)^2/2.\end{gathered} \tag{13}$$

An analysis of the recurrence relations (which we shall not write down) shows that the lowest power of n is $-L-1$, a fact already accounted for in (13).

It is known that for excited SAI states, especially states with $L>0$, the effective-mass approximation is valid with high accuracy. In this case (the ground state will be calculated below) the sought radial functions must be sought in the form of a linear superposition of the solutions (6) and (9), which do not diverge at $r=0$:

$$R_L(r)=C(g_L+Mf_L),\quad R_{L+2}(r)=C(g_{L+2}+Mf_{L+2}). \tag{14}$$

Here C is the normalization constant, and M is a coefficient whose value, just as the eigenvalue of the energy E of the state, must be found from the conditions for the correct behavior of the radial functions at infinity.

To analyze the asymptotic behavior of the radial functions it is convenient to change over from Eqs. (3) for R_L and R_{L+2} to equations for the functions

$$F_h(r)=(1+\beta_h^2)^{-1/2}r(R_L+\beta_hR_{L+2}),\ F_l(r)=(1+\beta_l^2)^{-1/2}r(R_L+\beta_lR_{L+2}), \tag{15}$$

where

$$\beta_{h,l}=\frac{u-v\pm[(u-v)^2+4w^2]^{1/2}}{2w};\quad w=\frac{2\beta\mu}{1+\beta^2}+\Delta_{L,L+2},$$

$$u=1+\frac{1-\beta^2}{1+\beta^2}\mu+\Delta_{L,L},\quad v=1-\frac{1-\beta^2}{1+\beta^2}\mu+\Delta_{L+2,L+2},$$

$$\Delta_{L,L}=-3\sqrt{10}(2F+1)\delta\lambda_{F\Gamma}\begin{Bmatrix}4 & F & F\\ 2 & L & L\\ 2 & 3/2 & 3/2\end{Bmatrix}\left[\frac{L(2L+1)(2L+2)}{(2L-1)(2L+3)}\right]^{1/2},$$

$$\Delta_{L,L+2}=\Delta_{L+2,L}=-3\sqrt{30}(2F+1)\delta\lambda_{F\Gamma}\begin{Bmatrix}4 & F & F\\ 2 & L & L+2\\ 2 & 3/2 & 3/2\end{Bmatrix}\left[\frac{(L+1)(L+2)}{2L+3}\right]^{1/2}.$$

The equations for $F_h(r)$ and $F_l(r)$ are of the form.

$$\begin{gathered}\left\{(u-\beta_hw)\frac{d^2}{dr^2}+E-V\right\}F_h+\frac{1}{\beta_h-\beta_l}\left(\frac{1+\beta_l^2}{1+\beta_h^2}\right)^{1/2}[2\beta_h(u-v)+(2L+1)\beta_h^2w\\ +(2L+5)w]\frac{1}{r}\frac{dF_l}{dr}+\frac{1}{\beta_h-\beta_l}[L(L+1)\beta_lu-(2L^2+6L+3)w\\ -(L+2)(L+3)\beta_hv]\frac{F_h}{r^2}-\frac{1}{\beta_h-\beta_l}\left(\frac{1+\beta_l^2}{1+\beta_h^2}\right)^{1/2}\{\beta_h[L(L+1)u-(L+2)(L+3)v\\ +2(u-v)]+\beta_h^2(L^2+4L+1)w-(L^2+2L-2)w\}\frac{F_l}{r^2}=0.\end{gathered} \tag{16}$$

The second equation is obtained from this one by interchanging F_h and F_l as well as β_h and β_l. We note that at $F=3/2$, and in the spherical approximation also at $F>3/2$, we have $\Delta_{L_1,L_2}=0$, $\beta_h=\beta^{-1}$, $\beta_l=-\beta$, and expressions (15) and equations (16) become much simpler.

An asymptotic expansion of the solutions (16) as $r\to\infty$ can be easily obtained by usual methods (see, e.g., Ref. 19). We write down only the first terms of the corresponding series in r^{-1}:

$$F_h\cong A_h^+r^{-\alpha_h}e^{\lambda_hr}+A_h^-r^{\alpha_h}e^{-\lambda_hr},\quad F_l\approx A_l^+r^{-\alpha_l}e^{\lambda_lr}+A_l^-r^{\alpha_l}e^{-\lambda_lr}. \tag{17}$$

In this expansion, $A^{\pm}_{h,l}$ are coefficients,

$$\lambda_{h,l}=[-E/(u-\beta_{h,l}w)]^{1/2}, \tag{17a}$$

$$\alpha_{h,l}=\left(\frac{u-\beta_{h,l}w}{|E|}\right)^{1/2}\frac{2-2(u-\beta_{h,l}w)+\Delta_{L,L}+\Delta_{L+2,L+2}}{2(uv-w^2)-(u-\beta_{h,l}w)^{1/2}(2+\Delta_{L,L}+\Delta_{L+2,L+2})}. \tag{17b}$$

In the case of excited states of the discrete spectrum ($E<0$) the constant M in (14) and the energy eigenvalue E should be chosen such that $A_h^+=A_l^+=0$, i.e., that the wave functions behave properly as $r \to \infty$. Thus, in contrast to the solutions of the usual Schrödinger equation, which (at arbitrary energy E) contains one exponential that increases as $r \to \infty$, in the SAI problem the solutions of the equations for the radial functions contain, generally speaking, two increasing exponentials: a rapidly increasing "heavy-hole" $\exp(\lambda_h r)$ and a relatively slower "light-hole" $\exp(\lambda\ r)$. The condition that the wave function decrease at infinity leads correspondingly to a determination not only of the discrete values of the energy, but also of the discrete values of the coefficient M.

We denote by $A_{fh}^\pm$, $A_{fl}^\pm$, and $A_{gh}^\pm$, $A_{gl}^\pm$ the coefficients in the asymptotic expansions of the functions F_{fh}, F_{fl} and F_{gh}, F_{gl}, determined with the aid of (15) from the fundamental solutions (6) and (9) of Eqs. (3), According to (14),

$$A_h^\pm(E)=A_{gh}^\pm(E)+MA_{fh}^\pm(E),\quad A_l^\pm(E)=A_{gl}^\pm(E)+MA_{fl}^\pm(E). \tag{18}$$

If the energy E is close to a certain eigenvalue E_0, and the coefficient M is close to the corresponding correct value M_0, then in the linear approximation in $\delta E = E - E_0$ and $\delta M = M - M_0$ we have the coefficient

$$A_h^+(E)=\left[\left(\frac{dA_{gh}^+}{dE}\right)_{E_0}+M_0\left(\frac{dA_{fh}^+}{dE}\right)_{E_0}\right]\delta E+A_{fh}^+(E_0)\delta M. \tag{19}$$

A similar equation holds for $A_l^+(E)$.

Assume that at a given E (generally speaking not coinciding with any eigenvalue E_0) the coefficient M in (14) is chosen such that $A_h^+=0$. We designate this value of M by $M(E)$. However, at $M=M(E)$, generally speaking, $A_l^+\neq 0$. The latter goes through zero and reverses sign only when the energy coincides with the eigenvalue E_0, and $M=M(E_0)=M_0$.

We describe now the procedure for numerically calculating the wave functions and energies of the discrete excited levels. Using the fact that at $r<1$ the series in (6) and (9) converge rapidly, it is necessary, after specfiying a certain value of E, to use these series to calculate f_L, f_{L+2} and g_L, g_{L+2}, as well as their first derivatives at a certain small but finite $r=r_0<1$. To attain the necessary accuracy it suffices to calculate only the first few terms of each of the series (6) and (9). It is next necessary to find with the aid of (15) the value of the functions F_{fh}, F_{fl}, F_{gh}, and F_{gl} and their first derivatives at $r=r_0$. Their linear combination [see (14)] with a certain value of M is the initial value in the numerical computer solution of Eqs. (16) at $r>r_0$. At each given energy E the value of $M(E)$ can be easily found, since it is precisely at $M=M(E)$ that the asymptotic form $F_h(r)$ reverses sign.

Assume that we vary E in certain steps, choosing $M=M(E)$ each time, an let us track the sign of the asymptotic form $F_l(r)$. When E goes through a certain value E_0, the sign of $F_l(r)$ is reversed. This value $E=E_0$ is in fact the sought energy eigenvalue, and the functions F_h and F_l obtained thereby (meaning also R_L and R_{L+2}) are then the sought radial functions.

At energies E close to the sought eigenvalue E_0 we can obtain the values of $M(E)$ for any E, knowing only $M(E)$ for two values of E, viz., $M_1=M(E_1)$ and $M_2=M(E_2)$. Indeed, from (19) it follows that

$$M(E)=\frac{M_2E_1-M_1E_2+E(M_1-M_2)}{E_1-E_2}. \tag{20}$$

The use of this relation simplifies the calculations greatly.

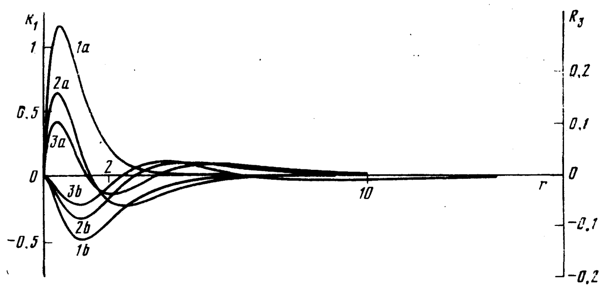

FIG. 1. Radial functions R_1 and R_3 of the first three states of type $P_{3/2}$ (Γ_8^-) of SAI in Ge. The states are numberd in order of increasing energy: a) R_1, b) R_3. The radius r is in units of a = 108.5 Å.

By varying the energy in certain steps, we obtain successively its eigenvalues and the corresponding radial functions for each value of F, Γ, and parity.

The general form of the radial functions R_L and R_{L+2} can be established also without a numerical calculation. It follows from (6), (9), and (14) that near $r=0$ we have $R_L \sim r_L$ and $R_{L+2} \sim r_{L+2}$. Therefore in the S states $R_0(0)\neq 0$ and R_2 has a node at zero. At $L>0$ each radial function has a node at zero. It follows from (11) that near $r=0$ the functions R_L and R_{L+2} are always of opposite sign.[2] Since the asymptotic form of the correct (decreasing at infinity) radial functions are determined by the exponential $\exp(-\lambda_l r)$, and the function $F_l(r)$, according to (15), enters in R_L and R_{L+2} with opposute signs, the radial functions approach zero from opposite sides as $r \to \infty$ i.e., they always are of opposite sign at large r. At each given combination of the quantum number F and the parity, the radial functions of the state with the lowest energy have sites only at $r=0$ (see above). With increasing number of the state of given symmetry, the number of nodes of the radial functions increases in succession. Since R_L and R_{L+2} must have opposite signs as $r \to \infty$, the number of nodes of R_L and R_{L+2} increases simultaneously.

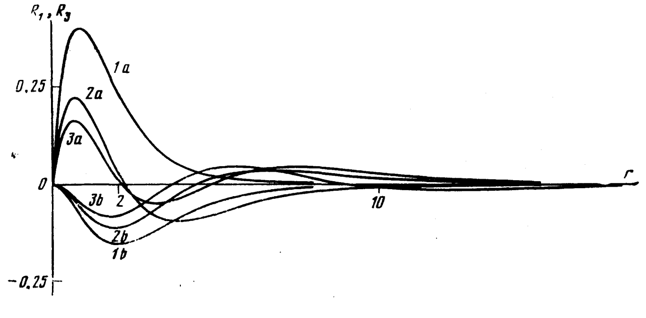

FIG. 2. Radial functions R_1 and R_3 of the first three states of type $P_{5/2}$ (Γ_7^-) of SAI in Ge. The remaining notation is the same as in Fig. 1.

The method described was used in calculations for SAI in Ge($\gamma_1=13.35$, $\mu=0.766$, $\delta=0.108$). The obtained radial functions of several of the excited states are shown in Figs. 1–3, and the corresponding level energies are given in Table I. We note that in all cases the obtained energies are lower than those of the same levels calculated in the same approximation by the δ-variational method[9] (the states $3P_{3/2}(\Gamma_8^-)$ and $3P_{5/2}(\Gamma_7^-)$ were calculated for the first time ever).

It is known that the accuracy of the effective-mass approximation decreases near that crystal cell in which the impurity center is located. This inaccuracy is especially substantial for the ground state and causes its energy to deviate from the value obtained in the effective-mass approximation. This correction to the level energy can be called the central-cell correction (CCC). Although the central cell influences noticeably the energy of the ground level, the behavior of the wave function in this region has little effect on its normalization and all the more on the dipole-moment matrix elements calculated by us (see below), since their integrands contain an additional power of the radius r. For our purposes it suffices to obtain the wave function outside the central cell, where the effective-mass approximation is valid, but it is necessary to specify the experimental values of the energy $E(1\Gamma_8^+)$ of the ground level, i, e, to take the CCC into account (a similar calculation for donors in Si was performed in Ref. 21). This not only leads to a more accurate form of the ground-state wave function, but also allows us to track the variation of the different properties in an SAI sequence in one and the same semiconductor.

Allowance for the cubic-symmetry terms in H_0 would lead to corrections of the order of $\delta^2|E(1\Gamma_8^+)|$ to $E(1\Gamma_8^+)$. The CCC are usually larger, therefore allowance for the CCC within the framework of the spherical approximation is justified.

So long as we are seeking solutions outside the region $r\approx 0$, it is necessary to include in the sought linear combination of the fundamental solutions also the solution (13), which behaves for the ground state ($L=0$) like r^{-1} as $r\to 0$;

$$R_0=C(g_0+Mf_0+Nh_0),\quad R_2=C(g_2+Mf_2+Nh_2). \tag{21}$$

The coefficients M and N are determined from two conditions that the functions decrease at infinity: $A_h^+=A_l^+$ $=0$ (the value of the energy E, on the other hand, is taken from experiment). The procedure of determining M and N is similar to the procedure described above for finding M and E of the excited states, but is much simpler, since the dependence of the sought solution on M and N is explicit and linear (in contrast to the dependence on E). In particular, a formula similar to (20), with E replaced by N, is valid for all N (and not only near the "eigenvalue" N_0).

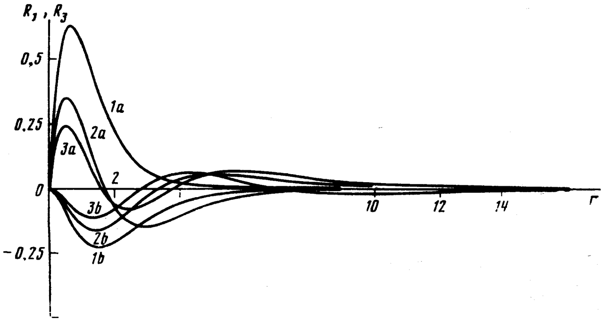

FIG. 3. The radial functions R_1 and R_3 of the first three states of type $P_{5/2}(\Gamma_8^-)$ of SAI in Ge. The remaining notation is the same as in Fig. 1.

TABLE I. Energies of excited states (in units of $R_a=m_0e_4/2\hbar^2\varkappa^2\gamma_1=4.35$ meV) and oscillator strengths of optical transitions (in units of 10^{-3}) from the ground state $1\Gamma_8^+$ and from the excited state $2\Gamma_8^+$ for shallow acceptor impurities in Ge.

Excited states	$-E$	Oscillator strengths for transitions from $1\Gamma_8^+$.			Designation of transition		Oscillator strengths for transitions from $2\Gamma_8^+$.
		B	Al	Ga	from [14]	from [20]	
$1P_{3/2}(\Gamma_8^-)$	0,979	2.5	2,1	1,9	G	G	-51
$1P_{5/2}(\Gamma_8^-)$	0,638	120	120	120	D	D	12
$1P_{5/2}(\Gamma_7^-)$	0,475	46	43.2	42,5			
		}54	}51	}50	C	C	73
$2P_{3/2}(\Gamma_8^-)$	0.443	7.6	7.4	7.1			
$2P_{5/2}(\Gamma_8^-)$	0,324	8.4	9,2	9,0	B	B	150
$3P_{3/2}(\Gamma_8^-)$	0.253	2,1	2.0	2.0	–	A_4	26
$2P_{5/2}(\Gamma_7^-)$	0.246	6,7	6,9	6.7	A''	A_3	30
$3P_{5/2}(\Gamma_8^-)$	0.203	4.2	4.1	4.3	A'	A_2	3.2
$3P_{5/2}(\Gamma_7^-)$	0,156	3,3	3,2	3.2	–	I_8	3.2
$1P_{1/2}(\Gamma_6^-)$	0,142	4.6	3,9	3,9	–	I_7	120

Figure 4 shows the radial functions R_0 and R_2 at $r>0.1$ for the ground states $1\Gamma_8^+$ of B, Al, and Ga impurities in Ge (the energies of the ground levels were taken from Ref. 10).

Once the wave functions are known, it is easy to find for each level the deformation potentials that describe the change of the spectrum due to uniaxial strains. The expression for the splitting of the SAI level Γ_8, as is well known,[22] differs from the expression for the splitting of the edge of the valence band only in that the deformation potentials are different: b' replaces b and d' replaces d. A simple analysis shows that in the approximation employed by us we have for all levels of the type $S_{3/2}(\Gamma_8^+)$

$$\frac{b'}{b}=\frac{d'}{d}=\int_0^\infty dr\,r^2\left(R_0^2-\frac{3}{5}R_2^2\right). \tag{22}$$

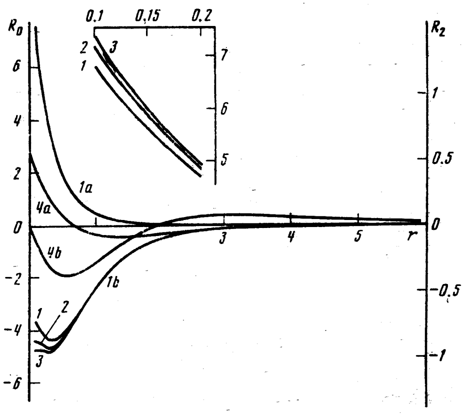

FIG. 4. Radial functions R_0 and R_2 of the ground state $1S_{3/2}(\Gamma_8^+)$ of group-III impurities in Ge and of the excited state $1S_{3/2}(\Gamma_8^+)$. 1) B, 2) Al, 3) Ga, 4) state $2S_{3/2}(\Gamma_8^+)$: a) R_0, b) R_2. Inset—initial sections of R_0 of ground levels. The radius r is in units of 108.5 Å.

For the ground levels of B, Al, and Ga in Ge, the ratios (22) are equal respectively to 0.551, 0.548, and 0.546, i.e., they decrease slightly with increasing depth of the ground level. For the $2S_{3/2}(\Gamma_8^+)$ state we have $b'/b = d'/d = 0.645$.

The ratios b'/b and d'/d for the ground level of SAI in Ge were found earlier 23 using Schechter's variational functions[4] $b'/b = 0.56$ and $d'/d = 0.61$. The authors of Ref. 23 note, however, that it was difficult to assess the calculation accuracy since the accuracies of the employed variational functions were unknown.

The constants b' and d' for the ground level of SAI in Ge were measured in Ref. 24 and found to be $b' = -1.4$ eV and $d' = -2.5$ eV. Using the experimental values of the band constants in Ge ($b = -2.21 \pm 0.13$ eV and $d = -4.4 \pm 0.3$ eV, Ref. 25) and the ratios obtained by us, we obtain for the ground levels of the SAI in Ge the values $b' = -1.22 \pm 0.07$ eV and $d' = -2.42 \pm 0.17$ eV. It is seen that the value of d' is close to the experimental one, while b' is somewhat less in absolute magnitude.

For the $P_{3/2}(\Gamma_8^-)$ levels we have $b'/b = d'/d = -1/3$, and for $P_{5/2}(\Gamma_8^-)$

$$\frac{b'}{b} = 4\frac{d'}{d} = \frac{4}{5}\int_0^\infty dr\, r^2\left(-R_1^2 + \frac{11}{14}R_3^2\right). \tag{23}$$

Calculation using the real functions determined by us yields for $1P_{5/2}(\Gamma_8^-)$ the ratio $b'/b = -0.185$.

The constant b' for the $2P_{3/2}(\Gamma_8^-)$ level of the SAI in Ge was measured by Gershenzon, Gol'tsman, and Kagana[26]: $b' = 0.45 \pm 0.05$ eV. This agrees with the calculated $b' = -b/5 = 0.44 \pm 0.03$ eV.

We note that a small uniaxial strain does not shift the Γ_7 levels.

§3. CONTINUUM STATES

We normalize the functions of the continuous spectrum, as usual, to $\delta(E - E')$. Then

$$\int_0^\infty dr[F_h^*(E',r)F_h(E,r) + F_l^*(E',r)F_l(E,r)] = \delta(E-E'). \tag{24}$$

The normalization of the continuous-spectrum functions is determined by their asymptotic behavior. From an analysis of Eqs. (16) it follows that as $r \to \infty$

$$\begin{aligned} F_h &\approx A_h(E)\sin[k_h r + \alpha_h \ln 2k_h r + \delta_h(E)],\\ F_l &\approx A_l(E)\sin[k_l r + \alpha_l \ln 2k_l r + \delta_l(E)], \end{aligned} \tag{25}$$

where $k_{h,l}$ are given by Eq. (17a) for $\lambda_{h,l}$, in which $-E$ must be replaced by E; $\delta_{h,l}$ are the phase shifts.

For any value $E > 0$ we can find two linearly independent solutions (6) and (9) for R_L and R_{L+2}, which are regular at zero. According to (15), they correspond to two solutions of Eqs. (16): F_{hf}, F_{lf} and F_{hg}, F_{lg}. Their asymptotic form is given by (25) with the corresponding aplitudes (A_{hf}, A_{lf} and A_{hg}, A_{lg}) and phase shifts (δ_{hf}, δ_{lf} and δ_{hg}, δ_{lg}) of the sinusoids. These solutions, generally speaking are not orthogonal to one another. We obtain now their orthogonal linear combinations (the index i takes two values):

$$F_{hi} = C_i(F_{hg} + M_i F_{hf}), \quad F_{li} = C_i(F_{lg} + M_i F_{lf}). \tag{26}$$

The orthonormalization condition (24) takes the form ($E > 0$)

$$\begin{aligned} &C_i(E)C_j(E)\pi E^{1/2}\{[A_{hg}^2 + M_iM_jA_{hf}^2 + A_{hg}A_{hf}(M_i+M_j)\cos(\delta_{hg}\\ &-\delta_{hf})](u-\beta_h w)^{1/2} + [A_{lg}^2 + M_iM_jA_{lf}^2 + A_{lg}A_{lf}(M_i+M_j)\\ &\times\cos(\delta_{lg}-\delta_{lf})](u-\beta_l w)^{1/2}\} = \delta_{ij}. \end{aligned} \tag{27}$$

There is of course a certain leeway in the choice of the values of M_i for each given energy. We can put, for example, $M_1 = -M_2 = M$. Then

$$M^2 = \frac{A_{hg}^2(u-\beta_h w)^{1/2} + A_{lg}^2(u-\beta_l w)^{1/2}}{A_{hf}^2(u-\beta_h w)^{1/2} + A_{lf}^2(u-\beta_l w)^{1/2}}, \tag{28}$$

$$\begin{aligned} C_{1,2} = {} &(2\pi)^{-1/2}E^{-1/4}\{A_{hg}[A_{hg} \pm MA_{hf}\cos(\delta_{hg}-\delta_{hf})](u\\ &-\beta_h w)^{1/2} + A_{lg}[A_{lg} \pm MA_{lf}\cos(\delta_{lg}-\delta_{lf})](u-\beta_l w)^{1/2}\}^{-1/2}. \end{aligned} \tag{29}$$

Thus, for each value $E > 0$ there are two linearly independent solutions of the system (16), given by expressions (26), (28), and (29), and accordingly two orthonormalized solutions for R_L and R_{L+1}. In the numerical calculation it is necessary first to use formulas (16)–(12) to obtain the solutions f_L, f_{L+2} and g_L, g_{L+2} and their first derivatives at $r_0 \ll 1$. With the aid of (15) we calculate the corresponding functions F_h and f_l at $r = 0$, which are then used as the initial conditions in the numerical computer solution of (16) in the region $r > r_0$. With the aid of the obtained amplitudes and phase shifts of the asymptotic sinusoids we get from (26) and (27) the parameters of the orthonormalized solutions of the system (3).

Just as in the problem of the hydrogen atom, the solution of the equations for the wave functions at $E = 0$ calls for a separate analysis, since the asymptotic form (25) is valid only at $\sqrt{E}r \gg 1$. We make the following substitutions.

$$x = (8r)^{1/2}, \quad F_{h,l} = x^{1/2}U_{h,l}. \tag{30}$$

By substituting (30) in (16) we obtain the equations for U_h and U_l. At $E = 0$ we have

$$\begin{aligned} &\left[(u-\beta_h w)\frac{d^2}{dx^2} + 1\right]U_h + \frac{2}{\beta_h-\beta_l}[2\beta_h(u-v) + (2L+1)\beta_h^2 w\\ &+(2L+5)w]\frac{1}{x}\frac{dU_l}{dx} - \left\{\frac{3}{4}(u-\beta_h w) - \frac{2}{\beta_h-\beta_l}[L(L+1)u\beta_l\right.\\ &\left.-(2L^2+6L+3)w - (L+2)(L+3)\beta_h v]\right\}\frac{U_h}{x^2} - \frac{1}{\beta_h-\beta_l}\{2\beta_h[2L(L+1)u\\ &-2v(L+2)(L+3) + 3(u-v)] + \beta_h^2 w(4L^2+14L+3) - w(4L^2+10L-3)\}\frac{U_l}{x^2} = 0. \end{aligned} \tag{31}$$

The second equation is obtained from the above by interchanging U_h and U_l, as well as β_h and β_l. The asymptotic form of the solutions (31) is

$$U_{h,l} \approx B_{h,l}\sin[(u-\beta_{h,l}w)^{-1/2}x + \Delta_{h,l} - \alpha_{h,l}(\ln\alpha_{h,l} - 1)]. \tag{32}$$

The asymptotic form of the solutions of (16) at $k_l r \gg 1$ [see (25)] and the asymptotic forms of the corresponding solutions (31) at $r \gg 1$ [see (32)] are interconnected. As $E \to 0$ we have

$$A_{h,l} = 2E^{-1/4}B_{h,l}, \quad \Delta_{hg} - \Delta_{hf} = \delta_{hg} - \delta_{hf}, \quad \Delta_{lg} - \Delta_{lf} = \delta_{lg} - \delta_{lf}. \tag{32a}$$

To calculate the wave functions at $E = 0$ it is necessary to use formulas (6)–(12), (15), and (30) to obtain the functions U_{hf}, U_{lf}, U_{hg}, and U_{lg} and their derivatives at $r = r_0 \ll 1$, and to solve Eqs. (31) numerically with a computer at $r > r_0$. The obtained functions, amplitudes, and phase shifts of the asymptotic sinusoids are used [with the aid of (28), (29), and (32)] to construct two orthonormalized solutions of the system at $E=0$.

§4. SUM RULE FOR THE OPTICAL ABSORPTION CROSS SECTION OF A SHALLOW IMPURITY

If the known conditions for the applicability of the effective-mass approximation are satisfied, the motion of the conduction electron or hole not only in a static field but also in a high-frequency field is determined by the smooth (macroscopic) part of this field. This makes it possible to express the probability (per unit time) the transition of a carrier in a shallow impurity from one stationary state to another, under the influence of the radiation, in terms of the matrix elements of the dipole moment on the smooth effective-mass functions. An elementary calculation shows that the cross section for impurity absorption, neglecting the line broadening, is

$$\sigma(\omega)=\frac{4\pi^2e^2\omega}{c\varkappa^{1/2}}\sum_{m,n}w_m|(\mathbf{er})_{mn}|^2\{\delta(E_n-E_m-\hbar\omega)-\delta(E_n-E_m+\hbar\omega)\}. \quad (33)$$

Here ω is the cyclic frequency of the radiation, $\mathbf{e}$ is the unit vector of the radiation polarization, the subscripts m and n number the quantum states of the impurity center, and w_m is the probability of the stay of the impurity center in the state m.

Let us integrate (33) with respect to the photon energy. Since $\sigma(\omega)$ becomes negligible already at energies that exceed the ionization energy ε_i of the shallow impurity by only a few times (and $\varepsilon_i \ll E_g$), the upper limit of the integral can be set equal to infinity. After the usual transformations[27] we obtain

$$\int_0^\infty d\hbar\omega\,\sigma(\omega)=\frac{2\pi^2e^2}{\hbar c\varkappa^{1/2}}\langle[\mathbf{er}[\hat{H},\mathbf{er}]]\rangle. \quad (34)$$

The angle brackets denote here averaging over states with probabilities w_m.

The effective-mass Hamiltonian $\hat{H}=\hat{H}_0+V$, where $V(\mathbf{r})$ is the potential-energy operator and $\hat{H}_0(\mathbf{p})$ is in the absence of a magnetic field a quadratic form of the components of the momentum operator $\hbar\mathbf{p}$. Since the dipole-moment operator commutes with $V(\mathbf{r})$ and with the spin operators, expression (34) reduces to

$$\int_0^\infty d\hbar\omega\,\sigma(\omega)=\frac{4\pi^2e^2}{\hbar c\varkappa^{1/2}}\langle H_0(\mathbf{e})\rangle, \quad (35)$$

where $H_0(\mathbf{e})$ is the operator $\hat{H}_0$, in which $\mathbf{p}$ was replaced by $\mathbf{e}$.

In cubic semiconductors a substitutional impurity has the symmetry T_d, therefore the optical-absorption cross section in the absence of external fields should be isotropic and independent of the polarization $\mathbf{e}$. This means that only the spherically symmetrical part of $H_0(\mathbf{e})$ contributes in fact to the sum rule (35).

If the shallow impurity is an acceptor, then H_0 is in the general case a 6×6 matrix (see, e.g., Ref. 22). A simple calculation yields

$$\int_0^\infty d\hbar\omega\,\sigma(\omega)=\frac{2\pi^2\hbar e^2\gamma_1}{m_0c\varkappa^{1/2}}=1.09\cdot10^{-16}\,\frac{\gamma_1}{\varkappa^{1/2}}\,\mathrm{eV}\cdot\mathrm{cm}^{-2}. \quad (36)$$

The sum rule is thus determined by only one parameter γ_1 of the valence band. The remaining ones (γ_2, γ_3, and Δ) influence only the distribution of the absorption over the spectrum.

The sum rule (35) can be applied not only to shallow acceptors and donors, but also to absorption in the far infrared band of exciton and of exciton-impurity complexes. It can be used to monitor the measurements of the absolute values of impurity-absorption cross sections.

§5. INTENSITIES OF DISCRETE SPECTRUM LINES

We define now the oscillator strength of each line in the impurity spectrum as the fraction of this line in the total integral (36) of the absorption cross section:

$$f(a\to b)=\frac{2m_0}{\hbar^2\gamma_1}\frac{E_b-E_a}{g_a}\sum_{m=1}^{g_a}\sum_{n=1}^{g_b}|(\mathbf{er})_{mn}|^2. \quad (37)$$

Here a and b are the initial and final levels of the optical transition, E_a and E_b are the corresponding energies, and g_a and g_b are the degeneracy multiplicities of these levels. The summation is over all the states of the initial and final multiplets.

In the approximation in which the cubic-symmetry terms in H_0 are taken into account in the approximation linear in δ, the SAI wave functions take the form (4). Each level is characterized by the number of the representation Γ of the group T_d, and by the quantum number F (as well as by the parity). The matrix elements $\mathbf{er}$ on the functions (4) are expressed in terms of the matrix elements on the functions (2), and they can be expressed with the aid of the Wigner-Eckart theorem in terms of the irreducible matrix elements of the coordinate $(F\|x\|F')$. If the energy is measured in units of R_a and the lengths in units of a (§2), then the first coefficient of (37) vanishes. Expressions (37) take the form

$$f(\Gamma F\to\Gamma'F')=\frac{E_{\Gamma'F'}-E_{\Gamma F}}{g_{\Gamma F}}|(F\|x\|F')|^2\sum_{mm'F_zF_z'}(-1)^{F_z-F_z'}\begin{pmatrix}F & 1 & F'\\ -F_z & 0 & F_z\end{pmatrix}$$
$$\times\begin{pmatrix}F & 1 & F'\\ -F_z' & 0 & F_z'\end{pmatrix}c^*(\Gamma FmF_z)c(\Gamma FmF_z')c(\Gamma'F'm'F_z)c^*(\Gamma'F'm'F_z'). \quad (38)$$

In this equation

$$(F\|x\|F')=(-1)^{3/2+F'+L}[(2F+1)(2F'+1)]^{1/2}\left\{\begin{Bmatrix}L & F & 3/2\\ F' & L' & 1\end{Bmatrix}(L\|n\|L')\right.$$
$$\times\int_0^\infty dr\,r^3R_LR_{L'}+\begin{Bmatrix}L & F & 3/2\\ F' & L'+2 & 1\end{Bmatrix}(L\|n\|L'+2)\int_0^\infty dr\,r^3R_LR_{L'+2}$$
$$+\begin{Bmatrix}L+2 & F & 3/2\\ F' & L' & 1\end{Bmatrix}(L+2\|n\|L')\int_0^\infty dr\,r^3R_{L+2}R_{L'}$$
$$\left.+\begin{Bmatrix}L+2 & F & 3/2\\ F' & L'+2 & 1\end{Bmatrix}(L+2\|n\|L'+2)\int_0^\infty dr\,r^3R_{L+2}R_{L'+2}\right\},$$

$$(L\|n\|L-1)=-(L-1\|n\|L)=L^{1/2}, \quad (39)$$

and $3j$- and $6j$-symbols are used.

For transitions from even states with $F=3/2$ (in particular, from the ground level), expression (38) takes the simpler form

$$f(\Gamma_8^+, {}^3/_2 \to \Gamma'F') = {}^1/_4 (E_{\Gamma'F'} - E_{\Gamma_8 F}) \,|\, ({}^3/_2 \| x \| F') \,|^2 \times \sum_{m'F_z} \begin{pmatrix} F & 1 & F' \\ -F_z & 0 & F_z \end{pmatrix} |c(\Gamma'F'm'F_z)|^2, \tag{40}$$

and the second term in the curly brackets of (39) vanishes. The sum in (40) is equal to 1/3 at $F' \leqslant 3/2$, to 2/9 for transitions into the states $\Gamma_8^-(F=5/2)$, and to 1/9 for transitions into the states $\Gamma_7^-(F=5/2)$.

The oscillator strengths for all the noticeable transitions from the ground state $1\Gamma_8^+$ and from the excited state $2\Gamma_8^+$ in group-III impurities in Ge were obtained by using the radial functions calculated by the method described in §2. The results are given in Table I. It is seen that in agreement with all the experiments two intense lines dominate in the spectra of the SAI in Ge, namely D [transition $1\Gamma_8^+ - 1\Gamma_8^-(P_{5/2})$] and C [transitions into $1\Gamma_7^-(P_{5/2})$ and $2\Gamma_8^-(P_{3/2})$]. The oscillator strengths in them are weak, however. This distinguishes the SAI in Ge from the hydrogenlike atoms, in whose spectra the most intense line L_α accounts for 0.416 of the entire absorption in the discrete and in the continuous spectra. It is also of interest that the oscillator strengths in states of definite symmetry (e.g., $P_{3/2}$), vary nonmonontonically with the number of the state (see Table I).

No monontonic dependence of the oscillator strengths on the depth of the ground level of the SAI is observed; this can be seen also from the experimental data.[14] As for the absolute value of the "chemical effect," the intensities of the lines G and I_7 change greatly on going from one group-III impurity to another, but the lines themselves are weak. On the other hand, in the intense lines D, C, and B the chemical effect is small and does not exceed several percent. In particular, the fact that the ratio of the intensities of lines C and D in the spectrum of boron is larger than in the spectrum of aluminum can be seen in experiment.[14]

§6. SPECTRUM OF PHOTOEFFECT FROM SHALLOW ACCEPTOR IMPURITY

It follows from (33) and (39) that at $\delta \ll 1$ the cross section for the photoionization of the SAI from the ground state is equal to

$$\sigma(\omega) = \frac{4\pi^2 e^2}{3\hbar c \varkappa^{1/2}} a^2 \sum_{\Gamma' F_i'} W(\Gamma'F'i; \hbar\omega), \quad \hbar\omega > \varepsilon_i = |E(1\Gamma_8^+)|,$$

$$W(\Gamma'F'i; \hbar\omega) = \frac{\hbar\omega}{R_a} \alpha(\Gamma'F') \left\{ - \begin{Bmatrix} 0 & {}^3/_2 & {}^3/_2 \\ F' & 1 & 1 \end{Bmatrix} \int_0^\infty dr\, r^3 R_0 R_{1i}^{(\Gamma'F')} \right.$$

$$\left. + \sqrt{2} \begin{Bmatrix} 2 & {}^3/_2 & {}^3/_2 \\ F' & 1 & 1 \end{Bmatrix} \int_0^\infty dr\, r^3 R_2 R_{1i}^{(\Gamma'F')} - \sqrt{3} \begin{Bmatrix} 2 & {}^3/_2 & {}^3/_2 \\ F' & 3 & 1 \end{Bmatrix} \int_0^\infty dr\, r^3 R_2 R_{3i}^{(\Gamma'F')} \right\}^2. \tag{41}$$

Here $R0$ and $R2$ are the radial function of the initial state, $R_{1i}^{(F'\Gamma')}$ and $R_{3i}^{(F'\Gamma')}$ are the orthonormalized radial functions of the states of the continuous spectrum ($i=1$ and 2, see §3) with energy $E = \hbar\omega - |E(1\Gamma_8^+)|$; $\alpha(\frac{1}{2}, \Gamma_6) = \alpha(3/2, \Gamma_8) = 1$, $\alpha(5/2, \Gamma_8) = 2/3$, $\alpha(5/2, \Gamma_7) = 1/3$.

To solve certain problems (for example, photoconductivity), we must know the probabilities of the generation of light and heavy holes, i.e., know the partial cross sections of the photoeffect with production of a light (σ_l) and heavy (σ_h) hole. An analysis based on the nonstationary perturbation theory leads to the following result:

$$\sigma_l(\omega) = \frac{4\pi^2 e^2}{3\hbar c \varkappa^{1/2}} a^2 \sum_{\Gamma'F'i} W(\Gamma'F'i; \hbar\omega) \left\{ 1 + \frac{v_h(E)}{v_l(E)} \left| \frac{A_{hi}^{(\Gamma'F')}(E)}{A_{li}^{(\Gamma'F')}(E)} \right|^2 \right\}^{-1} \tag{42}$$

$$\sigma_h = \sigma - \sigma_l.$$

Here v_h and v_l are the velocities of the heavy and light holes, $A_{hi}^{(\Gamma'F')}$ and $A_{li}^{(\Gamma'F')}$ are the amplitudes of the radial functions F_{hi} and F_{li} [see (25) and (26)].

TABLE II. Cross sections of the photoeffect from the ground state of a group-III impurity in Ge. Energy $E = \hbar\omega - \varepsilon_i$ in units of $R_a = 4.25$ meV, cross sections—in units of 10^{-14} cm^2. The partial cross sections σ_h and σ_l are given for the boron impurity.

E	Impurity			σ_h	σ_l	E	Impurity			σ_h	σ_l
	B	Al	Ga				B	Al	Ga		
0	1.40	1.35	1,34	–	–	0,4	1,04	1.02	1.01	0.44	0,60
0,05	1,25	1,23	1.21	0.80	0.45	1	0.77	0,76	0,75	0.19	0.58
0,1	1,48	1.44	1.35	1,02	0.46	2,5	0.55	0,55	0.55	0.14	0,41
0,2	1,20	1.17	1,16	0.45	0,75	5	0,37	0,37	0,37	0.036	0,33
0,3	1,14	1,12	1,09	0,47	0.67	10	0,207	0,208	0,209	0.032	0,175

The cross sections of the photoeffect of the SAI in Ge were calculated using wave functions obtained by the methods of §§ 2 and 3. The cross sections for a number of photon energies in three group-III impurities are given in Table II, and for the boron impurity also in Fig. 5. The accuracy of the results is limited by the approximation linear in δ used to calculate the wave functions. The expected error is therefore of the order of or less than ~10%.

The photoeffect cross section $\sigma(\varepsilon_i)$ near the red edge varies nonmonotonically, going through a minimum and a maximum. The formal cause is that the matrix element of the dipole moment of the transition in (41) is a sum of integrals with different signs. The decrease of $\sigma(\omega)$ past the maximum is relatively slow, so that the greater part of the total absorption (36) falls in the continuous spectrum. These features of the SAI photoeffect spectrum set it in strong contrast to the spectrum of the photoeffect of hydrogen atoms: in the latter $\sigma(\omega)$ decreases monotonically and much more rapidly with increasing photon energy (see Fig. 5).

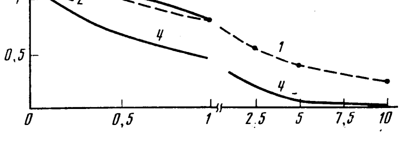

FIG. 5. Cross section of photoeffect of boron impurity in Ge: black circles connected by dashed curve 1—present calculation, curve 2—experiment[14]; curve 3—photoconductivity spectrum of Ge:Ga (Ref. 29) (see the text). Curve 4 photoionization cross section that would be possessed by a hydrogenlike impurity with the same ionization energy as the SAI in Ge, in a crystal with the same value of $\varkappa$. The energy $E = \hbar\omega - \varepsilon_i$ is in units of $R_a = 4.35$ meV.

The optical-absorption line spectra and the initial sections of the continuous spectra of group-III impurities in Ge were measured by Jones and Fisher.[14] Their measured cross sections $\sigma(\varepsilon_i)$ on the red edge of the photoeffect are 1.0, 1.9, and 0.87 (in units of 10^{-14} cm^2) for B, Al, and Ga, respectively. It is seen that our values of $\sigma(\varepsilon_i)$ differ significantly from the experimental ones and display furthermore a much smaller "chemical effect." The present calculation has shown that in the case of the SAI in Ge there are no reasons for the onset of so strong a "chemical effect" in $\sigma(\omega)$ as observed in Ref. 14.

The photoionization spectrum of the boron impurity, observed in Ref. 14, shows a monotonicity of $\sigma(\omega)$ of exactly the same type as in our calculation (Fig. 5).

Figure 5 shows also the spectrum of the impurity photoconductivity of SAI in Ge at $\hbar\omega > \varepsilon_i$. This spectrum was chosen (see Refs. 28–30) to have at $\hbar\omega > \varepsilon_i$ the same form as the photoeffect cross-section spectrum at sufficiently high crystal temperatures, strong electric fields, and low densities of the compensating impurity, when the effects of incomplete thermalization of the photocarriers are negligible. The experimental spectrum is matched to the theoretical one at $E = 1$.

The cross sections σ_h and σ_l near the red edge of the photoeffect are of the same order, while at higher photon energies, as expected, only light holes are generated in the main (see Table II).

As indicated in the Introduction, to determine the probabilities of the thermal ionization of the impurity centers over the spectrum of the impurity photoconductivity at values $\hbar\omega > \varepsilon_i$ it is necessary to know the ratio of the area under the lines in the spectrum of the optical-absorption cross section to the photoeffect cross section $\sigma(\varepsilon_i)$. According to the data of Tables I and II and formula (36), this ratio for the D line in the spectrum of the boron impurity in Ge is 0.32 meV. According to the spectra given in Ref. 14, this ratio is ~0.07 meV. The reasons for this strong discrepancy are not clear.

If we use the measured[17] spectra of the photoconductivity of Ge with B impurity ($N_A - N_D \sim 10^{11}$ cm^{-3}) and take the oscillator strengths and the cross sections $\sigma(\varepsilon_i)$ used above (rather than from Ref. 14), then the probabilities of thermal ionization at temperatures $T = 5$, 6, and 7 K, for the states into which the transitions from the ground state corresponds to the lines D and C, turn out to be respectively $I_D = 0.054$, 0.12, and 0.25 and $I_C = 0.17$, 0.36, and 0.55. It is seen that the obtained probabilities are less than 1, in contrast to the values obtained when the experimental data on absorption[14] are used (see the Introduction).

The parameters $\mu = 0.767$ and $\delta = 0.114$ of the valence band of GaAs are very close to the corresponding parameters of Ge. It follows therefore that the dimensionless energy levels and wave functions of the excited states of SAI in GaAs (energy unit R_a, length unit a) are very close to the corresponding values (calculated above, see Table I) in SAI in Ge, and it need be merely kept in mind that GaAs has $R_a = 11.3$ meV and $a = 50.8$ Å. The ground level of the SAI Zn in GaAs ($\varepsilon_i = 31$ meV $= 2.74 R_a$) is somewhat deeper than, say, the Ga level in Ge ($\varepsilon_i = 2.60 R_a$). Therefore the dimensionless wave functions of the ground state and the oscillator strengths of the optical transitions from the ground level should differ somewhat from the corresponding values calculated for grouping III impurities in Ge. The difference between the dimensionless ε_i, however, is so small that the main spectrum regularities obtained for the SAI in Ge should hold also in the case of the SAI in GaAs.

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[1] We note that an incorrect value of the correction to the coefficient of R_{L+2} for the case is given in Ref. 9 $F = 5/2$ and $\Gamma = \Gamma_8^v$: 34/115 should be changed to 34/175.

[2] Attention should be called to the fact that the functions R_{L+2} are given in Refs. 8 and 9 with incorrect sign.

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