Effects of spin-selective trapping of polarized electrons by dislocation dangling bonds in semiconductors

V. L. Berdinskiĭ

Division of Institute of Chemical Physics, USSR Academy of Sciences

(Submitted 19 March 1986)
Zh. Eksp. Teor. Fiz. **91**, 2120–2131 (December 1986)

A theoretical investigation is reported of macroscopic manifestations of spin-selective trapping of conduction-band electrons by paramagnetic centers with spin $S = \frac{1}{2}$, such as dislocation dangling bonds (DDB) in semiconductors. It is assumed that the trapping is only from singlet exchange-coupled pairs consisting of DDB and conduction-band electrons. The spin density matrix method is used to obtain a system of nonlinear algebraic equations that describe the dependences of the stationary densities and polarizations of the electrons and DDB on the experimentally varied parameters. It is shown that even interaction with unpolarized electrons is capable of producing strong spin polarization of the DDB. It is established that spin-selective electron trapping can alter the photoconductivity of a semiconductor and influence the degree of circular polarization of its luminescence.

Recent research has shown that spin-dependent processes in which nonequilibrium carriers participate are observed in a great variety of semiconductors, such as amorphous and crystalline silicon with various paramagnetic defects and impurities, and also in organic semiconductors such as polyacetylene. These effects are usually manifested in experiment as a change of the electric conductivity or luminescence of samples acted upon by resonant rf fields. This permits the ESR signals of the paramagnetic centers to be recorded by using unconventional detection methods that are more sensitive than the usual magnetic-resonance methods.

The variety of semiconductor types and of the conditions for observing spin-dependent recombination (SDR) in them attests to the action of various mechanisms and calls for a separate theoretical analysis of the roles of various electrically active centers responsible for the SDR. For example, in a study of SDR in irradiated Si there were recorded nonequilibrium ESR signals of several types of radiation defects, and it was shown that the SDR processes are due to the presence, in the forbidden band, of triplet levels whose nonequilibrium populations result from spin-selective decay of charged states of the defects, while these triplet states were not selectively produced.[1] A different situation arises in plastically deformed Si containing unsaturated valency bonds in the dislocation cores, called dislocation dangling bonds (DDB), which are paramagnetic centers. ESR spectra were recorded by standard methods in the absence of nonequilibrium carriers, and reliably identified for DDB.[2]

Further study of SDR in Si containing DDB has shown that these ESR spectra agree quite closely, even in their details, with the spectrum of the sample photoconductivity variation caused by a resonant saturating microwave field.[3] This important experimental result cannot be explained by assuming direct spin-selective (singlet) recombination of electron-hole pairs[4,5] whose spin state, and hence recombination probability, can be altered by interaction with a resonant microwave field. (This model was proposed in Ref. 4 to explain the relatively large SDR effect and its weak dependence on the intensity of the constant magnetic field.) The similarity between the "SDR spectra" and ESR of DDB in plastically deformed Si indicates unequivocally that the microwave field acts not on the conduction electrons and not on the electron-hole pairs, but on the DDB spin systems, which in turn influence the sample photoconductivity. It was therefore proposed in Ref. 3 that the spin-selective stage in plastically deformed Si comprises trapping of a conduction-band electron by a DDB. The subsequent capture of a hole by a singlet charged DDB does not depend here on the spin variables, and if the holes undergo rapid spin relaxation in the valence band their capture does not polarize the DDB.

This spin selectivity of single DDB, which differs from the spin properties of the radiation defects investigated in Refs. 1 and 6, can be explained in the following manner. As a result of the breaking and redistribution of the covalent bonds with the neighboring atoms under plastic deformation, and of subsequent annealing of the crystal, the dislocations capture Si atoms that are bound to three rather than four neighboring atoms, and have on the valence shell seven *sp* electrons with total spin $S = \frac{1}{2}$. The character of the occupation of the electron shell permits these atom to accept from the conduction band only one additional electron, and to form only one singlet charged center. A triplet state of a single DDB with a localized additional electron lies apparently far above the bottom of the conduction band and is not realized. The physical cause of the attraction of the electron to the DDB may be an "exchange" interaction that acts during the electron-capture stage.

It is obvious from general considerations that any spin effect can be quite strongly manifested in those cases when polarized particles participate in the spin-dependent process. For many semiconductors, particularly Si, there exist effective optical methods of polarizing electrons that are thrown into the conduction band via interband absorption of circularly polarized light.[7,8] The use of spin-polarized electrons permits observation of new manifestations of spin-de-

0038-5646/86/121260-07$04.00

pendent effects and development of new methods for the study of dislocations.

Our purpose here is a theoretical investigation of effects due to spin-selective trapping of nonequilibrium carriers by paramagnetic DDB in the absence of rf fields. When processes with participation of polarized particles (e.g., conduction electrons) are considered, account must be taken of the influence of the spin-lattice relaxation and of the spin exchange, since they tend to equalize the polarizations of the participants of the exchange scattering.[9] Obviously, the experimental manifestations of such spin processes in semiconductors will always depend on the real ratio of the efficiencies of the spin-independent and spin-dependent channels for trapping and recombination of nonequilibrium carriers. Both channels must therefore be taken into account in the theory as fully as possible. It must be noted that the requirement of taking into account *ab initio* the different polarizations of the interacting electrons and of the DDB follows logically from the general theories of recombination of paramagnetic particles.[10]

FUNDAMENTAL EQUATIONS

To describe the macroscopic manifestations of effects of spin-selective trapping of polarized electrons by single paramagnetic DDB in semiconductors such as Si, it is necessary to consider the following sequence of events that are schematically represented in Fig. 1. Circularly polarized light produces in the conduction band spin-polarized electrons that move with constant velocity w near DDB and form exchange-coupled "DDB + conduction electron" pairs. The nature and causes of formation of paired electron-hole or electron-DDB states are discussed in detail in Refs. 3 and 5. In plastically deformed semiconductors, for example, the cause of formation of intermediate paired states may be a preliminary trapping of an electron in a shallow potential well due to a deformation potential near a dislocation, at distances on the order of the delocalization radius of the unpaired electron of the DDB.[3] In the present paper we take the physical criterion for formation of electron-DDB pairs to be the condition $J = 0$, where J is the integral of the exchange interaction of the unpaired DDB electron and a conduction-band electron in a certain region of space around the DDB. These exchange-coupled pairs either decay with the electron returning to the conduction band (the characteristic lifetime of such pairs is τ_p), or are transformed at a rate w_s, only from singlet pairs, into singlet charged centers by trapping an electron by the DDB. At the present status of the theoretical and experimental research, it would be premature to consider situations with different lifetimes of the singlet and triplet exchange-coupled pairs. The lifetime of a singlet charged DDB is determined by time of transfer of one of the electron to the valence band, i.e., by the time τ_h of hole trapping. The spin-independent hole trapping results in formation of the initial unpolarized DDB that is capable of again trapping conduction-band electrons.

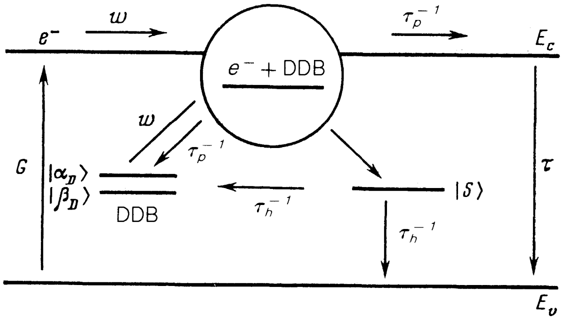

FIG. 1. Schematic representation of processes accompanying spin-selective capture of electrons (e^-) from exchange-coupled pairs ($e^- + \mathrm{DDB}$).

Since principal attention is paid in the present paper to processes that depend on the spin states of the conduction electrons and of the DDB, it is convenient to describe all the changes of the experimentally observable quantities with the aid of spin density matrices $\hat{\rho}^e$ and $\hat{\rho}^D$ normalized to the densities N_e and N_D of the electrons and of the DDB, i.e.,

$$\mathrm{Sp}\,\hat{\rho}^{e,D}=N_{e,D}=N_{e,D}^{\alpha}+N_{e,D}^{\beta}, \tag{1}$$

where $N_{\alpha,\beta}$ are the populations of the corresponding spin states $|\alpha\rangle$ and $|\beta\rangle$. Here N_e and N_D are not constants and depend on the processes that take place in the exchange-coupled pairs and described by a spin density $\hat{\rho}^t$, and in the "DDB + trapped electron" states, to which a density matrix $\hat{\rho}^s$ corresponds. In the spin Hamiltonians $\hat{\mathscr{H}}_e$ and $\hat{\mathscr{H}}_D$ of the electrons and of the DDB we shall take into account only isotropic Zeeman interactions with the constant magnetic field H_0 directed along the z axis of the coordinate frame:

$$\hat{\mathscr{H}}_{e,D}=g_{e,D}\beta\hat{S}_z^{e,D}H_0, \tag{2}$$

where $g_{e,D}$ are the isotropic g factors of the electron and DDB, $\hat{S}_z^{e,D}$ are their spin operators, and β is the Bohr magneton. If interband absorption of circularly polarized light produces in the conduction band electrons with predominant spin orientation parallel or antiparallel to the field $\mathbf{H}_0$, it follows from the symmetry of the problem that in the absence of coherent microwave fields the transverse components of the magnetization vectors are zero. This means that $\hat{\rho}^e$ and $\hat{\rho}^D$ written each in its own basis $|\alpha\rangle$ and $|\beta\rangle$ are diagonal, and

$$[\hat{\mathscr{H}}_e, \hat{\rho}^e]=[\hat{\mathscr{H}}_D, \hat{\rho}^D]=0. \tag{3}$$

Therefore the only terms remaining in the $\hat{\rho}^e$ and $\hat{\rho}^D$ evolution equations are those that describe phenomenologically the stochastic processes. For $\hat{\rho}^e$, for example, we have

$$d\hat{\rho}^e/dt=\hat{G}-\tau^{-1}\hat{\rho}^e-(\hat{\rho}^e-\hat{\rho}_0{}^e)T_{1e}{}^{-1}-w\hat{\rho}^eN_D+\tau_p{}^{-1}Sp_D\hat{\rho}^p. \tag{4}$$

The first term in the right-hand side describes here the production of spin-oriented electrons in the conduction band (G is a diagonal matrix whose components describe the rates of appearance of electrons with corresponding spin orientation). The second term describes the spin-independent linear recombination of the carriers with characteristic time τ, and the third the spin-lattice relaxation of the electrons (T_{1e} is the relaxation time). The remaining terms describe the changes of the number and states of the electrons as a result of formation and decay of pairs ($\mathrm{Sp}_D\hat{\rho}^p$ means that a partial spur is taken over the DDB spin variables).

The $\hat{\rho}^D$ evolution equation is

$$d\hat{\rho}^D/dt=-(\hat{\rho}^D-\hat{\rho}_0{}^D)T_{1D}{}^{-1}-w\hat{\rho}^DN_e+\tau_p{}^{-1}Sp_e\hat{\rho}^p+\tau_p{}^{-1}\,\mathrm{Sp}_e\,\hat{\rho}^s. \tag{5}$$

The first term in the right-hand side describes here the DDB spin-lattice relaxation with characteristic time T_{1D}, the second describes the change of the number of free DDB as a result of formation of exchange-coupled pairs with conduction-band electrons, and the third and fourth describe the appearance of free DDB as a result of pair dissociation and hole trapping by singlet charged DDB. The last two processes are phenomenologically described as taking the partial spurs, in the spin variables, of the density matrices $\hat{\rho}^p$ and $\hat{\rho}^s=|S\rangle N_s\langle S|$ ($|S\rangle=2^{-1/2}|\alpha_e\beta_D-\beta_e\alpha_D\rangle$ is the vector of the spin singlet state). The use of the form (5) for the equation presupposes that magnetic interactions between single DDB in the sample can be neglected.

The simplest equation is that for the evolution of the density matrix $\hat{\rho}^s$ of charged singlet formations, viz. DDB with trapped electron:

$$d\hat{\rho}^s/dt=w_s\hat{P}_s\hat{\rho}^p\hat{P}_s-\tau_h^{-1}\hat{\rho}^s, \tag{6}$$

where the first term describes the formation of these states out of singlet pairs ($\hat{P}_s=|S\rangle\langle S|$ is the operator of projection on the singlet spin subspace), and the second describes the decay of these states as a result of hole capture.

According to (5) and (6), the states of the conduction electrons and of the DDB depend on various processes that occur in the exchange-coupled DDB + conduction-band electron pairs. To take explicitly into account the influence of the polarizations of the electrons and the DDB, the $\hat{\rho}^p$ evolution equation must be supplemented by a term that describes production of pairs made up of noninteracting DDB and conduction-band electrons, obviously, this term must be proportional to the direct product of the density matrices $\hat{\rho}^e$ and $\hat{\rho}^D$. If we neglect magnetic relaxation in exchange-coupled pairs, the change of $\hat{\rho}^p$ is described by the equation

$$\begin{aligned} d\hat{\rho}^p/dt &= -i\hbar^{-1}[\hat{\mathscr{H}}_p,\hat{\rho}^p]-\tau_p{}^{-1}\hat{\rho}^p \\ &-(w_s/2)(\hat{P}_s\hat{\rho}^p+\hat{\rho}^p\hat{P}_s)+w\hat{\rho}^e\otimes\hat{\rho}^D. \end{aligned} \tag{7}$$

Besides the $\hat{\rho}^p$ evolution specified by the Hamiltonian $\hat{\mathscr{H}}_p$, account is taken here of the decays of the pairs that exist during the time τ_p, the vanishing of the pairs as a result of the spin-selective trapping of the electrons by the DDB (phenomenologically described by the anticommutator of the operators $\hat{\rho}_s$ and $\hat{\rho}^p$, Refs. 5, 10, and 11), and production of pairs consisting of free DDB and conduction-band electrons. Equation (7) makes it possible to describe also other possible physical situations, for example direct spin-selective trapping of a conduction-band electron by a deep center with spin $S=\frac{1}{2}$. Owing the closure condition $\hat{P}_s+\hat{P}_t=1$ (P_t is the projection operator in triplet states) many equations that describe different variants of spin-selective trappings reduce to Eq. (7) with other values of the kinetic coefficients.

We take into account in the spin Hamiltonian $\hat{\mathscr{H}}_p$ only the isotropic interactions between the pair partners and the external field $\mathbf{H}_0$, and their exchange interaction with one another:

$$\hat{\mathscr{H}}_p=\hat{\mathscr{H}}_e+\hat{\mathscr{H}}_D-J\hat{\mathbf{S}}_e\hat{\mathbf{S}}_D, \tag{8}$$

where J has the meaning of the mean value in the DDB vicinity. Note that the g factor of the electron in an exchange-coupled pair, i.e., near a dislocation, can differ from the g factor of a conduction-band electron situated in an unstrained crystal volume. Spin Hamiltonians of type (8) were investigated in detail, e.g., in the theory of high-resolution NMR; its eigenvalues and eigenvectors $|\psi_i\rangle$ are[12]

$$\begin{gathered} E_1=(g_e+g_D)\beta H_0/2-J/4,\quad |\psi_1\rangle=|\alpha_e\alpha_D\rangle, \\ E_2=J/2-C,\quad |\psi_2\rangle=|\alpha_e\beta_D\rangle\cos\theta-|\beta_e\alpha_D\rangle\sin\theta, \\ E_3=J/2+C,\quad |\psi_3\rangle=|\alpha_e\beta_D\rangle\sin\theta+|\beta_e\alpha_D\rangle\cos\theta, \\ E_4=-(g_e+g_D)\beta H_0/2-J/4,\quad |\psi_4\rangle=|\beta_e\beta_D\rangle, \\ \cos 2\theta=\Delta g\beta H_0/2C,\quad \sin 2\theta=-J/2C, \\ C=[J^2+(\Delta g\beta H_0)^2]^{1/2}/2,\quad \Delta g=g_D-g_e. \end{gathered} \tag{9}$$

The system of matrix equations (4)–(7) has a particular integral, since

$$\mathrm{Sp}\,(d\hat{\rho}^D/dt)+\mathrm{Sp}\,(d\hat{\rho}^p/dt)+\mathrm{Sp}\,(d\hat{\rho}^s/dt)=0.$$

Consequently

$$N_D+\mathrm{Sp}\,\hat{\rho}^p+N_s=N_{\mathrm{DDB}}, \tag{10}$$

where N_s is the density of the singlet "DDB with trapped electron" states, and N_{DDB} is the density of the DDB introduced into the crystal. This simple but important relation indicates that the number N_D of the DDB interacting with the conduction-band electrons does not remain constant but depends on the density of the photoexcited carriers (electrons), and differs in the general case from the density N_{DDB} of the DDB produced in the crystal in the course of the deformation and the subsequent annealing.

We shall be interested henceforth only in stationary solutions of Eqs. (4)–(7), since this case corresponds to many interesting experimental situations. Here we note only that it is precisely this circumstance which allowed us to discuss the choice of the initial conditions for Eqs. (4)–(7). Adding and subtracting the individual equations of the system (4)–(7), it is easy to obtain for the case $d\hat{\rho}/dt=0$ a system of algebraic equation for the four physically observable quantities, N_e, $\Delta N_e=N_e^\beta-N_e^\alpha$, N_D and $\Delta N_D=N_D^\beta-N_D^\alpha$, expressed in terms of the elements of the density matrix $\hat{\rho}^p$ written in the proper basis of the Hamiltonian (8):

$$G-\tau^{-1}N_e-wN_eN_D+\tau_p{}^{-1}(Sp\hat{\rho}^p)=0, \tag{11a}$$

$$PG-\Delta N_e(T_{1e}{}^{-1}+\tau^{-1})-\Delta N_DT_{1D}{}^{-1}=0, \tag{11b}$$

$$-wN_eN_D+\tau_p{}^{-1}(Sp\hat{\rho}^p)+\tau_p{}^{-1}N_s=0, \tag{11c}$$

$$\begin{aligned} &\Delta N_DT_{1D}{}^{-1}+w(N_e{}^\alpha N_D{}^\beta-N_e{}^\beta N_D{}^\alpha)- \\ &-\tau_p{}^{-1}[(\rho_{22}^p-\rho_{33}^p)\cos 2\theta+(\rho_{32}^p+\rho_{23}^p)\sin 2\theta]=0. \end{aligned} \tag{11d}$$

Here $G=G_{\alpha\alpha}+G_{\beta\beta}$ is the intensity of the electron excitation into the conduction band and is proportional to the intensity of the absorbed light; $P=(G_{\beta\beta}-G_{\alpha\alpha})/G$ is the initial polarization of these electrons and depends both on the polarization of the light and on the properties of the crystal. Equation (11b) was derived with the equality (11d) taken into account. For the system (11) to be closed, it is necessary to express with the aid of Eqs. (7) the elements of the density matrix $\hat{\rho}^p$ in terms of the observable quantities and to substitute them in Eqs. (11). Since capture of an electron from the "triplet" states of the exchange coupled pairs $|\psi_1\rangle$ and $|\psi_4\rangle$ with formation of singlet pairs is impossible, and since $\langle S|\psi_1\rangle = \langle S|\psi_4\rangle = 0$, we easily obtain the stationary values cf ρ^p_{11} and ρ^p_{44}:

$$\rho^p_{11} = w\tau_p\langle\psi_1|\hat{\rho}^e\otimes\hat{\rho}^D|\psi_1\rangle = w\tau_p N_e{}^\alpha N_D{}^\alpha,$$
$$\rho^p_{44} = w\tau_p\langle\psi_4|\hat{\rho}^e\otimes\hat{\rho}^D|\psi_4\rangle = w\tau_p N_e{}^\beta N_D{}^\beta.$$

Owing to the structure of the recombination terms $\hat{P}_s\hat{\rho}^p + \hat{\rho}^p\hat{P}_s$ in Eqs. (7), the stationary values of ρ^p_{22} and ρ^p_{33} depend on the sum $\rho^p_{23} + \rho^p_{32}$ and accordingly on the values of $\langle\psi_2|\hat{\rho}^e\otimes\hat{\rho}^D|\psi_2\rangle$ and $\langle\psi_3|\hat{\rho}^e\otimes\hat{\rho}^D|\psi_3\rangle$. In turn, ρ^p_{23} and ρ^p_{32} depend on the sum $\rho^p_{22} + \rho^p_{33}$. These relations allow us to use in lieu of (7) a system of two linear equations for the quantities $\rho^p_{22} + \rho^p_{33}$ and $\rho^p_{23} + \rho^p_{32}$ of interest to us. Obviously, it is much easier to solve this system of two equations than a system of four algebraic equations for the individual elements of the density matrix $\hat{\rho}^p$. Finding these equations, we easily obtain an expression for the last combination $\rho^p_{22} - \rho^p_{33}$ of interest to us at this stage, a combination that depends, as all others, on the quantities $N^\alpha_e N^\beta_D - N^\beta_e N^\alpha_D$ and $N^\alpha_e N^\beta_D + N^\beta_e N^\alpha_D$.

At low temperatures the spin-lattice relaxation times of paramagnetic centers, including DDB, are quite long in semiconductors, so that it is permissible, at least in the present paper, to put $T_{1D} = \infty$. This assumption simplifies greatly the equations obtained when the rather cumbersome expressions from the system (11) for the desired combinations of elements of $\hat{\rho}^p$ are substituted in (11). For example, Eq. (11d) takes the form

$$a(N_e{}^\alpha N_D{}^\beta - N_e{}^\beta N_D{}^\alpha) + b(N_e{}^\alpha N_D{}^\beta + N_e{}^\beta N_D{}^\alpha) = 0, \tag{12}$$

where

$$\begin{aligned} a = {} & (w_s\tau_p/2)(1+w_s\tau_p/2)(1+w_s\tau_p+\omega^2\tau_p{}^2) \\ & +\omega^2\tau_p{}^2[1+w_s\tau_p/2+(w_s\tau_p/2)^2]\sin^2 2\theta, \\ b = {} & \omega^2\tau_p{}^2(w_s\tau_p/2)\sin 2\theta\cos 2\theta, \quad \omega=\omega_{23}=(E_2-E_3)/\hbar. \end{aligned} \tag{13}$$

Equation (12) enables us to determine the conditions under which $N^\alpha_e N^\beta_D - N^\beta_e N^\alpha_D = 0$ i.e., the spin temperatures T_S of the conduction electrons and the DDB, or their respective polarizations $P_e = (N^\beta_e - N^\alpha_D)/N_e$ and $P_D = (N^\beta_D - N^\alpha_D)/N_D$, become equal. It can be seen that $P_D = P_e$ if $b = 0$, i.e., the following occur: (i) there is no spin-selective electron trapping ($w_s = 0$); (ii) there is no exchange interaction between the conduction-band electrons and the DDB ($\sin 2\theta \sim J = 0$); (iii) the unlikely condition that the g factors of the DDB and the conduction electrons are equal, $\cos 2\theta \sim \Delta g = 0$, is met. "Turning on" either the exchange interaction or the spin-dependent electron trapping at $J = 0$ equalizes the spin temperatures of the conduction-band electrons and the DDB. At $w_s = 0$, Eqs. (11) are transformed into the equations of the spin-exchange theory, which predicts equalization of the polarization of spin systems coupled by exchange interaction.[9,13] It follows from (12) that even in the absence of exchange interaction, i.e., at $J = 0$, spin-selective electron trapping by DDB suffices to equalize the polarizations of the conduction-band electrons and the DDB.

Joint action of spin exchange and spin-selective trapping, however, leads to a substantial difference between the polarizations of the conduction-band electrons and the DDB, and at $T_{1D} = \infty$ and $Ne \neq 0$ it follows from (12) that

$$P_D = (aP_e - b)(a - bP_e)^{-1}. \tag{14}$$

If the conduction-band electrons are not polarized, i.e., $P_s = 0$ but $J \neq 0$, the electron spins of the DDB are polarized only as a result of spin-selective trapping electron by exchange-coupled pairs, and

$$P_D = -b/a. \tag{15}$$

This polarization results from the action of the spin selection rule that governs the electron capture from exchange-coupled pairs, and from the spin dynamics of these pairs, (which leads to the difference between the probabilities of observing a pair in an $|S\rangle$ state when it is produced from the $|\alpha_e\rangle|\beta_D\rangle$ — and $|\beta_e\rangle|\alpha_D\rangle$ states of the partners). This result agrees with one of the conclusions of Ref. 14, in which are described various spin effects produced when unpolarized electrons are trapped by paramagnetic centers with spin $S > \frac{1}{2}$. In Eqs. (14) and (15), the DDB polarization P_D does not depend on the density of the conduction-band electrons, and in the stationary case these equations are valid as $N_e \to 0$, but the value of Ne determines the time required to reach the stationary regime.

The interaction of the spin systems of the conduction-band electrons and the DDB in semiconductors, and the ensuing interrelation of their spin polarization, indicates that in the general case the rate of the spin-selective capture and of the spin-dependent recombination cannot be described by the expression $1 - P_e P_D$,[15] where P_e and P_D are assumed to be independent. At $P_D = P_e$ the rate of the SDR can be proportional to $1 - P_e{}^2$, where P_e differs from the equilibrium value and is determined by the initial polarization of the electrons and by the times of their spin—lattice relaxation and recombination. Particular attention must be paid to the case when the spin polarization of the DDB is determined both by spin-exchange processes and by spin-selective trapping of nonequilibrium carriers, and is described by Eq. (14). To obtain the answer we must express $N^\alpha_e N^\beta_D \pm N^\beta_e N^\alpha_D$ in terms of P_e and P_D and, next, using (14), find explicit expressions for the ρ^p elements and substitute them in (11a). After a number of prolonged and laborious transformations, this equation reduces to

$$G - \tau^{-1}N_e - {}^1/_4 w w_s \tau_{\text{п}} N_D N_e (1 - P_e{}^2) F = 0, \tag{16}$$

where $F = F(\omega^2\tau^2_p,\ w_s\tau_p,\ \sin 2\theta,\ \cos 2\theta,\ P_e)$ is a certain function of several variables, whose explicit form is too large to be cited here. For the most important and physically realistic case $w_s\tau_p \ll 1$ it turns out that $F \approx 1$. At $J=0$, i.e., $\sin 2\theta = 0$ and $\cos 2\theta = 1$, we have

$$F=(1+\omega^2\tau_p{}^2+w_s\tau_p/2)\,[\,(1+w_s\tau_p)\,(1+w_s\tau_p/2)\,(1+\omega^2\tau_p{}^2)\,]^{-1}.$$

If $w_s\tau_p \gg 1$, we get $F \approx (w_s\tau_p)^{-1}$ and the corresponding term that describes spin-selective trapping in (16) becomes equal to $wN_DN_e \times (1-P_e^2)/4$. An interesting property of (16) at $w_s\tau_p \ll 1$ is that the rate of the spin-selective trapping is proportional to $1-P_e^2$ even if $P_D \neq P_e$, but is described by Eq. (14).

To derive the equation that describes the stationary value of N_D, i.e., the density of the DDB capable of interacting with the conduction-band electrons and of trapping them, Eq. (11c) must be modified somewhat. It follows from a comparison of (11a) with (16) that

$$-wN_eN_D+\tau_p{}^{-1}\mathrm{Sp}\hat{\rho}\hat{\rho}^p=-ww_s\tau_pN_eN_D(1-P_e{}^2)/4. \qquad (17)$$

Equations (10) and (17) allow us to rewrite (11c) in the form

$$\tau_h{}^{-1}(N_{\mathrm{DDB}}-N_D)-\tau_h{}^{-1}\mathrm{Sp}\,\hat{\rho}^p-ww_s\tau_pN_eN_D(1-P_e{}^2)/4=0. \qquad (18)$$

Using an equation in which $\mathrm{Sp}\hat{\rho}^p$ is expressed in terms of N_e and N_D in accordance with (17), we readily obtain the expression we need for N_D:

$$N_D=N_{\mathrm{DDB}}\{1+w\tau_pN_e[1+w_s\tau_p(1-P_e{}^2)/4]\}^{-1}. \qquad (19)$$

Equations (16), (11b), (19), and (14) make up the sought system of nonlinear equations needed to describe the stationary effects of spin-selective trapping of electrons by single DDB in semiconductors. The explicit final form of this system of equations is

$$G-\tau^{-1}N_e-{}^1/{}_4ww_s\tau_pN_eN_D(1-P_e{}^2)=0, \qquad (20a)$$

$$P_e=PGT_{1e}\tau/(T_{1e}+\tau)N_e, \qquad (20b)$$

$$N_D=N_{\mathrm{DDB}}\{1+w\tau_pN_e[1+w_s\tau_p(1-P_e{}^2)/4]\}^{-1}, \qquad (20c)$$

$$P_D=(a'P_e-b)(a'-bP_e)^{-1}, \qquad (20d)$$

where

$$a'=(w_s\tau_p/2)\,(1+\omega^2\tau_p{}^2)+\omega^2\tau_p{}^2\sin^2 2\theta.$$

Equation (20a) describes N_e, i.e., actually the photoconductivity of the sample, as a function of the rates of the spin-dependent and spin-independent recombination channels and of the polarization P_e of the electrons in the conduction band. Equation (20b) describes the influence of these processes on the spin polarization of the electrons. Equations (20c) and (20d) describe the dependences of N_D and P_D on the analogous parameters that characterize the conduction-band electrons.

INFLUENCE OF SPIN-DEPENDENT ELECTRON TRAPPING ON THE DDB ESR SIGNAL INTENSITY

If electrons are present in the conduction band, the intensity I of the DDB ESR signal is determined both by the number N_D of the "free" DDB and by their polarization $I \sim P_DN_D$. At low light intensities corresponding to the condition $w\tau_pN_e \ll 1$, the main contribution to the change of the DDB ESR signal intensity is made by the change of the polarization P_D which can, according to Eq. (20d), differ substantially from the equilibrium polarization $P_0 = g_D\beta H_0/kT$ (k is Boltzmann's constant and T is the sample temperature). Figure 2 shows the dependences of P_D and P_e at various values of the ratio b/a'. The most interesting feature of these dependences is that at $P_e = 0$ the DDB polarization differs from zero and is equal to

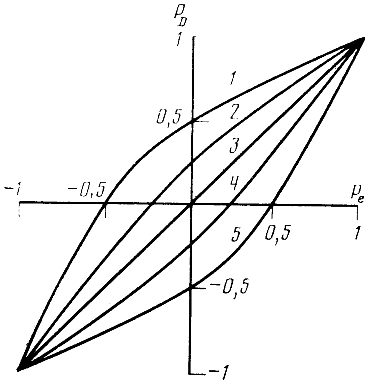

FIG. 2. Dependence of the stationary DDB polarization P_D on the electron polarization P_e in spin-selective trapping from exchange-coupled for different values of the ratio b/a': 1 — 0,5; 2 — 0,25; 3 — 0; 4 — 0,25; 5 — 0,5.

$$P_D=(J\tau_p)\,(\Delta g\beta H_0\tau_p)\,[\hbar^2+(\Delta g\beta H_0\tau_p)^2+2J^2(\tau_p/w_s)\,]^{-1}. \qquad (21)$$

This nonequilibrium polarization of the DDB sets in because of the competition between the influence of the spin exchange that depolarizes the DDB, on the one hand, and the DDB polarization of the DDB by selective trapping of electrons from exchange-coupled pairs, on the other. An important qualitative feature of the polarization P_D is its sign. Positive P_D correspond to coincidence of the DDB nonequilibrium magnetization vector with the equlibrium one, and negative to opposite directions of these magnetizations, i.e., to inverted population of the DDB Zeeman levels. By expressing the Hamiltonian $\hat{\mathscr{H}}_p$ in the form (8) we presuppose that the energies of the singlet states are lower than those of the triplet at $J<0$. It follows therefore from (21) that the nonequilibrium DDB polarization P_D will be positive at $\Delta g = g_D - g_e < 0$. If the g factor of the electron in the exchange-coupled pair is less than that of the DDB and $\Delta g > 0$, the nonequilibrium polarization of the DDB becomes negative, i.e., the magnetization of the polarized DDB is oriented counter to the field $\mathbf{H}_0$.

It follows from (21) that the nonequilibrium polarization P_D in weak magnetic fields H_0 is proportional at $(\Delta g\beta H_0\tau_p)^2 \ll \hbar^2$, $J^2\tau_p/w_s$ to the strength of the external magnetic field H_0. In strong magnetic fields $(\Delta g\beta H_0\tau_p)^2 \gg \hbar^2$, $J^2\tau_p/w_s$ the Larmor-precession frequency difference between the conduction electrons and the DDB in exchange-coupled pairs "intermixes" effectively the singlet and triplet states of the pairs, and this causes P_D to decrease in proportion to H_0^{-1}. At

$(\Delta g\beta H_0\tau_p)^2 = \hbar^2 + 2J^2\tau_p/w_s$ the polarization P_D reaches a maximum value

$$|P_D{}^m| = |J|\,\tau_p\{\hbar^2 + 2J^2\tau_p/w_s\}^{-1/2} \tag{22}$$

If the condition $J^2\tau_p/w_s \gg \hbar^2$ holds for the exchange-coupled pairs, we get $|P_D^m| = (w_s\tau_p/8)^{1/2}$. Consequently, for $w_s\tau_p > 8P_0^2$ and $\Delta g < 0$, a situation is possible in which the intensity of the DDB nonequilibrium ESR signal obtained by illuminating the sample will exceed the intensity of the equilibrium "darkness" signal even if $P_e = 0$. However, such an enhancement of the photo-ESR signal of a sample having a temperature T calls for the mean value of the exchange-interaction integral J in the exchange-coupled pairs to satisfy the condition

$$|J| < (|\Delta g|/g_D)kTw_s\tau_p. \tag{23}$$

Another possible mechanism whereby the light can influence the ESR signal of DDB involves a decrease of the density N_D of the "free" DDB because of formation of exchange-coupled pairs having an ESR spectrum of their own. (We disregard here the possible influence of the conduction-band electrons on the DDB magnetic-relaxation times.) If $w_s\tau_h \ll 1$, but a spin-independent recombination channel is effective, solution of Eqs. (20a) and (20c) yields

$$N_D/N_{\rm DDB} = 1 - w\tau_p\tau G\{1 + w\tau_p\tau[w_sN_{\rm DDB}(1-P_e^2)/4 + G]\}^{-1}. \tag{24}$$

This means that with increasing illumination intensity the ESR signal amplitude of polarized DDB should decrease monotonically.

INFLUENCE OF DDB ON CONDUCTION-BAND ELECTRONS

It is most convenient to begin the study of the influence of DDB on the macroscopic properties of conduction-band electrons by considering a relatively simple idealized situation, in which the spin-selective trapping of the electrons is the principal or even the only recombination channel for the nonequilibrium carriers. This is possible, strictly speaking, under the condition $\tau^{-1} \ll ww_s\tau_pN_D(1-P_e^2)$, but for the sake of the simplicity required for the initial treatment, we put here $\tau = \infty$. This approximation enables us to demonstrate the principal procedures for investigating the system (20), obtain exact solutions, and determine the characteristic physical "capabilities" of single spin-selective DDB. At $w_s\tau_h \ll 1$ we obtain from (20a) and (20b) the quadratic equation

$$\begin{gathered}(1-G/G_0)N_e^2 - G\tau_sN_e - (PGT_{1e})^2 = 0,\\ \tau_s^{-1} = ww_s\tau_pN_{\rm DDB}/4, \quad G_0 = w_sN_{\rm DDB}/4,\end{gathered} \tag{25}$$

whose solution

$$N_e = {}^1/_2G\tau_s(1-G/G_0)^{-1}\{1 + [1 + 4(1-G/G_0)(PT_{1e}/\tau_s)^2]^{1/2}\} \tag{26}$$

determines the stationary electron density N_e. This solution, together with Eq. (20b), makes it easy to determine the stationary spin polarization P_e of the electrons:

$$P_e = 2(PT_{1e}/\tau_s)(1-G/G_0)\{1 + [1 + 4(1-G/G_0)(PT_{1e}/\tau_s)^2]^{1/2}\}^{-1}. \tag{27}$$

We consider now the coefficient $k = P_e/P$, which characterizes the deviation of the stationary polarization of the electrons from their initial polarization $P \neq 0$ produced by interband absorption of circularly polarized light:

$$k = 2(T_{1e}/\tau_s)(1-G/G_0)\{1 + [1 + 4(1-G/G_0)(PT_{1e}/\tau_s)^2]^{1/2}\}^{-1}. \tag{28}$$

It follows from the definition (28) that at $P^2 < (1 - G/G_0 - \tau_s/T_{1e})$ and $G/G_0 \ll 1$ the stationary polarization P_e exceeds the initial one, i.e., $k > 1$. This ability of DDB to "enhance" the electron polarization is due to the fact that polarized DDB redirect to the conduction band, with unequal efficiencies, electrons having different spin orientations; by decreasing N_e, the increase P_e notwithstanding the depolarizing influence of the spin-lattice relaxation. If the characteristic time τ_s of the SDR due to the DDB is much shorter than T_{1e} and if $4(1 - G/G_0)(PT_{1e}/\tau_s)^2 \gg 1$, we have $N_e \approx GT_{1e}|P|$, i.e., the SDR rate is limited by the spin-lattice relaxation time of the electrons in the conduction band. According to (20b) and (14), the polarizations P_e of the electrons and P_D of the DDB reach maximum values $P_e = P_D = \pm 1$ and are independent of the initial electron polarization P.

Disregard of the spin-independent recombination channels, however, causes N_e to increase as $G \to G_0 = w_sN_{\rm DDB}/4$ without limit, and leads to $P_e \to 0$ because of the longer conduction-band average lifetime as $N_D \to 0$. Obviously, allowance for the additional recombination channels will eliminate these singularities.

We consider therefore now the influence of single DDB on electrons in a semiconductor in which the spin-independent mechanisms of linear electron-hole recombination are still in action. At low light intensities, when $w\tau_pN_e \ll 1$, we can neglect the change of the DDB density and put $N_D \approx N_{\rm DDB}$. At finite values of τ Eq. (20b), which describes the dependence of the electron spin polarization, takes the form

$$P_e = P_cG\tau/N_e, \tag{29}$$

where $P_c = PT_{1e}(T_{1e} + \tau)^{-1}$ is the stationary polarization of the electrons produced by light in a semiconductor in the absence of DDB and of spin-selective recombination mechanisms. The dependence of P_c on P, set by the polarization of the light, allows us here and below to regard P_c as an experimentally variable parameter; P_e is an observable quantity whose variation can be recorded by determining the degree of circular polarization of the luminescence.[7] The dependence of the density of the conduction-band electrons on P_c is described by an equation obtained after substituting (29) in (20a):

$$N_e^2(\tau^{-1} + \tau_s^{-1}) - GN_e - (P_cG\tau/\tau_s)^2 = 0, \tag{30}$$

and whose solution is

$$N_e = (N_{e0}/2)\{1 + [1 + 4P_c^2(\tau/\tau_s)(1 + \tau/\tau_s)]^{1/2}\}. \tag{31}$$

Here $N_{e0} = G\tau\tau_s(\tau + \tau_s)^{-1}$ is the stationary density of the electrons in a semiconductor exposed to unpolarized light, i.e., at $P_e = P_c = P = 0$. If the spin-selective trapping of electrons by DDB is the most effective recombination mechanism and if $\tau/\tau_s \gg 1$ and $P_c(\tau/\tau_s) \gg 1$, we have, as in the preceding case, $P_e = \pm 1$, but the electron density is now determined by the expression $N_e = G\tau |P_c|$. If, however, the spin-independent recombination channel is the most effective, i.e., $\tau < \tau_s$, we get

$$N_e \approx G\tau\{1+P_c^2\tau/\tau_s\} \tag{32}$$

and the photoconductivity of the semiconductor with DDB should therefore depend on the degree of circular polarization of the light.

In analogy with (28), we can define a polarization amplification factor $K = P_e/P_c$, which shows how introduction of DDB into the semiconductor will alter the electron polarization, and hence the luminescence polarization. From (29) and (31) we get

$$K=2(1+\tau/\tau_s)\{1+[1+4P_c^2(1+\tau/\tau_s)(\tau/\tau_s)]^{1/2}\}^{-1}. \tag{33}$$

It is easy to show that $K > 1$ for all $P_c^2 > 1$, i.e., spin-selective electron trapping by DDB will enhance the electron spin polarization regardless of the value of τ_s and of the density of the single DDB. Lowering the density N_D is equivalent to increasing τ_s; as $\tau_s \to \infty$ the value of K decreases to unity. Consequently, increasing the intensity of the absorbed light and of the electron density in the conduction band can decrease the degree of circular polarization of the luminescence of semiconductors with spin-selective DDB.

CONCLUSION

The macroscopic manifestations of spin effects described in the preceding sections can be features not only of semiconductors containing DDB, but also of semiconductors with deep centers of other type and capable of spin-selective trapping of electrons. Similar effects were observed in experiment, but some of the workers did not suggest a possible influence of spin-selective processes on the magnetic-resonance, electric, optical, and other properties of amorphous and plastically deformed crystalline semiconductors and semiconducting films. The relation we found between such properties of semiconductors with DDB is one of the results of the present study, in which a phenomenological description of the spin-selective trapping of electron was used. A detailed description of this process is one of the tasks of rigorous quantum-mechanical theory. The experimental manifestations of such spin effects should stimulate a search for new practical applications of such semiconductors.

The author is grateful to R. A. Vardanyan, L. S. Vlasenko, and V. V. Kveder for helpful discussions.

[1] L. S. Vlasenko, I. M. Zaritskiĭ, A. A. Konchits, and B. D. Shanina, Fiz. Tverd. Tela (Leningrad) **26**, 114 (1984) [Sov. Phys. Solid State **26**, 66 (1984)].

[2] V. Grazhulis and Yu. A. Osip'yan, Zh. Eksp. Teor. Fiz. **60**, 1150 (1971) [Sov. Phys. JETP **33**, 623 (1971)].

[3] V. V. Kveder, Yu. A. Osip'yan, and A. I. Shalynin, *ibid.* **83**, 699 (1982) [**56**, 389 (1982)].

[4] D. Kaplan, I. Solomon, and N. F. Mott, J. de Phys. **39**, 51 (1978).

[5] V. S. L'vov and O. V. Tretyak, Zh. Eksp. Teor. Fiz. **87**, 234 (1984) [Sov. Phys. JETP **60**, 136 (1984)].

[6] L. S. Vlasenko, Physica, **116B**, 281 (1983).

[7] M. I. D'yakonov and V. I. Perel', Zh. Eksp. Teor. Fiz. **60**, 1954 (1971) [Sov. Phys. JETP **33**, 1053 (1971)].

[8] *Optical Orientation*, F. Meier and B. Zakharchenya, eds. North-Holland, 1984.

[9] D. Pines, J. Bardeen, and Ch. Slichter, Phys. Rev. **106**, 489 (1957).

[10] A. L. Buchachenko, R. Z. Sagdeev, and K. M. Salikhov, Magnetic and Spin Effects in Chemical Reactions [in Russian]. Nauka, Novosibirsk, 1978.

[11] R. Habekorn, Mol. Phys. **32**, 1491 (1976).

[12] J. W. Emsley, J. Feeney, and L. M. Sutcliffe, *High-Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon, 1965, Chap. 8.

[13] K. I. Zamarek, Yu. N. Molin, and K. M. Salikhov, Spin Exchange [in Russian], Nauka, Novosibirsk, 1977.

[14] B. D. Shanina, Fiz. Tverd. Tela (Leningrad) **28**, 95 (1986) [Soviet Phys. Solid State **28**, 50 (1986)].

[15] I. Solomon, in: Amorphous Semiconductors, [Russ. transl.], Mir, 1982.

Translated by J. G. Adashko