Nonequilibrium electron polarization and maser effect in spin-dependent recombination through exchange-coupled pairs

V. S. L'vov and O. V. Tretyak

Institute of Automation and Electrometry, Siberian Branch, Academy of Sciences of the USSR

(Submitted 13 October 1983)
Zh. Eksp. Teor. Fiz. **87**, 234–240 (July 1984)

The exchange interaction between the members of a pair is taken into account in an analysis of spin-dependent recombination. The recombination rate is derived as a function of the strength of the static magnetic field and that of the resonant alternating magnetic field. The exchange interaction raises the typical value of the weakest influential magnetic field. A qualitatively new effect is predicted: a differential and integral polarization of electrons in recombination-coupled states. Several consequences of the polarization are discussed. Specifically, it may be possible to use a semiconductor with this recombination mechanism as an active medium to amplify electromagnetic oscillations and to produce differential and integral polarization of nuclei.

Nonequilibrium electron-hole pairs in various types of disordered silicon (amorphous silicon, polycrystalline silicon, and silicon plastically deformed in a certain way, with a dislocation density exceeding 10^7 cm^{-2}) recombine through coupled states (paired states) in the band gap. According to this model, the electron and hole are captured from the allowed bands to centers which are geometrically close to each other; the recombination terminates in the transfer of an electron between the centers (the members of the pair). In the substances which we just listed the transfer of an electron between levels is spin-dependent, as was shown convincingly in Refs. 1–3. We have previously[4] used this model to calculate the rate of the spin-dependent recombination as a function of the strength of the magnetic field for the case in which the spin Hamiltonian of the pair has only the Zeeman energy of the interaction of the external field with unpaired electrons at centers.

Denoting by r_0 the large radius of the wave function of a member of a pair, and denoting by r the distance between the members, we can assert that the probability for a transition between centers is proportional to[5] $\exp(-2r/r_0)$ and becomes significant when the distance between the members of a pair is small. Under these conditions, the exchange interaction between unpaired electrons may prove important. The nature of the centers which form bound states has not been unambiguously determined, they may be two centers which lie close together simply by chance, or they may be a pair of states which arise in close geometric proximity for some fundamental reason. Some typical examples of the latter case are donor-acceptor pairs and the states associated with dislocations, one being a broken bond and the other a defect associated with a compression or extension region near a dislocation which has captured an electron. Analysis of experimental results on the spin-dependent recombination in amorphous silicon[5,6] and in plastically deformed silicon[3,4] shows that several possible pairs probably exist in these substances, although in several cases (e.g., in a certain temperature interval or when the microwave resonant field is modulated in a certain frequency interval) a situation may arise in which only certain bound states will completely control the recombination of nonequilibrium carriers. For simplicity we will therefore be discussing the effects in semiconductors which contain only one type of paired states (including several types would not exchange the physical picture fundamentally, but the calculations would have to include taking certain averages over the different pairs). It is clear from general considerations that incorporating the exchange interaction in a pair should change the absolute rate of the spin-dependent recombination and should give rise to several new effects. In the present paper we describe some of these new effects: nonequilibrium differential and integral polarization of electrons at recombination centers and an amplification of resonant rf radiation (a maser effect).

§ 1. BASIC EQUATIONS

As in Ref. 4, we start with an equation of motion for the density matrix of the pairs, $\rho_{\alpha\beta}$:

$$d\rho/dt = -i[\mathscr{H}, \rho] + \hat{R}\rho, \tag{1}$$

where $\hat{R}$ describes stochastic processes (the thermal dissociation of pairs, at the rate W_D; singlet recombination, at the rate W_s; nonequilibrium pair production, at the rate G; and the spin relaxation of pairs, with a scale time T_s). An explicit expression for $\hat{R}\rho$ is given in Ref. 4. In the Hamiltonian $\mathscr{H}$ we incorporate the interaction of the magnetic moments of the electrons of the pairs with the constant field $\mathbf{H}_0$, which is directed along the z axis, and with the alternating field $\mathbf{h}$, which is perpendicular to the static field and which has a circular polarization ($h_x = h\cos\omega t$, $h_y = -h\sin\omega t$, $h_\pm = h_x \pm ih_y$). This Hamiltonian also incorporates the exchange interaction in the pair, $\mathscr{H}_{\mathrm{ex}}$:

$$\begin{gathered}\mathscr{H} = \mathscr{H}_{ex} + \mathscr{H}_0, \quad \mathscr{H}_{ex} = -{}^1/_4 J\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2, \quad \mathbf{S} = {}^1/_2\boldsymbol{\sigma}, \\ \mathscr{H}_0 = -{}^1/_2(\gamma_1\boldsymbol{\sigma}_1 + \gamma_2\boldsymbol{\sigma}_2)(\mathbf{h} + H_0), \quad \gamma_1 \neq \gamma_2.\end{gathered} \tag{2}$$

As in Ref. 4, we write the initial equations in the "spin representation":

$$N_{\alpha\beta} = \mathrm{Sp}\,(\rho\sigma_1{}^\alpha\sigma_2{}^\beta), \tag{3}$$

where σ_1^α and σ_2^β are Pauli matrices which act on the spin

0038-5646/84/070136-04$04.00

states of the first and second members of a pair. The indices α and β run over the four values 0 ($\sigma^0 = 1$), z, and $\pm$ ($\sigma^\pm = \sigma^x \pm i\sigma^y$). In these terms the original system of equations (1), (2), becomes

$$
\begin{gathered}
dN_{00}/dt=G-W_D-R,\quad R={}^1/_4W_s(N_{00}-N_{zz}-\operatorname{Re}N_{+-}),\\
dN_{zz}/dt=-N_{zz}/\tilde{T}+R+\operatorname{Im}[h_+(\gamma_1N_{-z}+\gamma_2N_{z-})],\\
\frac{dN_{0z}}{dt}=-\frac{N_{0z}}{T^*}+\frac{W_sN_{z0}}{4}+\frac{iJ}{4}(N_{+-}-N_{-+})+i\gamma_2(h_-N_{0+}-h_+N_{0-}),\\
\frac{dN_{z0}}{dt}=\frac{-N_{z0}}{T^*}+\frac{W_sN_{0z}}{4}-\frac{iJ}{4}(N_{+-}-N_{-+})+i\gamma_1(h_-N_{+0}+h_+N_{-0}),\\
\frac{dN_{+-}}{dt}=-i\omega_{12}N_{+-}-\frac{N_{+-}}{T^*}+\frac{W_sN_{-+}}{4}+2R+iJ(N_{0z}-N_{z0})\\
+i\gamma_1h_+N_{z-}-i\gamma_2h_-N_{+z},\quad \omega_{12}=\omega_1-\omega_2,\quad \omega_1=\gamma_1H_0,\quad \omega_2=\gamma_2H_0,\\
\frac{dN_{+z}}{dt}=-i\omega_1N_{+z}-\frac{N_{+z}}{T^*}+\frac{W_sN_{z+}}{4}+\frac{iJ}{2}(N_{+0}-N_{0+})\\
+ih_-\gamma_2N_{++}-ih_+\gamma_2N_{+-}+i\gamma_1h_+N_{zz},\\
\frac{dN_{z+}}{dt}=-i\omega_2N_{z+}-\frac{N_{z+}}{T^*}+\frac{W_sN_{+z}}{4}-\frac{iJ}{2}(N_{+0}-N_{0+})\\
+ih_-\gamma_1N_{++}-ih_+\gamma_1N_{-+}+i\gamma_2h_+N_{zz},\\
\frac{dN_{+0}}{dt}=-\frac{N_{+0}}{T^*}+\frac{W_sN_{0+}}{4}-i\omega_1N_{+0}-\frac{iJ}{2}(N_{z+}-N_{+z})+ih_+\gamma_1N_{z0},\\
\frac{dN_{0+}}{dt}=-\left(i\omega_2+\frac{1}{T^*}\right)N_{0+}+\frac{W_sN_{+0}}{4}+\frac{iJ}{2}(N_{z+}-N_{+z})+ih_+\gamma_2N_{0z},\\
1/T^*=1/\tilde{T}+{}^1/_4W_s,\quad 1/\tilde{T}=1/T_s+W_D.
\end{gathered}
\tag{4}
$$

Here R is the rate at which current carriers recombine through paired states, N_{00} is the number of pairs, $N_{z0} = p_1N_{00}$, and $N_{0z} = p_2N_{00}$, where p_1 and p_2 are the polarizations of the first and second numbers of a pair. Here $p_+ = (p_1 + p_2)/2$ is a measure of the integral polarization of the pair, while $p_- = (p_1 - p_2)/2$ is a measure of the differential polarization of the pair.

§ 2. SPIN-DEPENDENT RECOMBINATION AND DIFFERENTIAL POLARIZATION OF EXCHANGE-COUPLED PAIRS IN A STATIC MAGNETIC FIELD

We begin with the simple case in which there is no alternating magnetic field. In this case the number of equations in system (4) reduces to six. Specifically, we are left with equations for N_{00}, N_{zz}, N_{0z}, N_{z0}, and $N_{+-} = N_{-+}^*$. Solving them in the steady state, we find an expression for the recombination rate as a function of the magnetic field:

$$
\begin{gathered}
R=G[4(W_s+W_D)/W_s-3/(1+W_DT_s)-2W_D\tilde{T}f_0(H^2)]^{-1},\\
f_0(H^2)=\omega_{12}{}^2/(\omega_{12}{}^2+\Delta_0{}^2),\quad \Delta_0{}^2=(J^2+\tau_0{}^{-2})\tau_0\tilde{T}^{-1},\\
\tau_0{}^{-1}=\tilde{T}^{-1}+{}^1/_2W_s.
\end{gathered}
\tag{5}
$$

If there is no exchange interaction in the pairs (if $J = 0$) this expression becomes Eq. (1.14) of Ref. 4. The only effect of incorporating exchange is to increase the typical value (H^*) of the magnetic field at which this field becomes important:

$$
\gamma_{12}H^*=\Delta_0,\quad \gamma_{12}=\gamma_1-\gamma_2. \tag{6}
$$

We recall that the static field H increases the recombination rate by mixing S–T_0 states of the pairs with the frequency ω_{12}, equal to the difference between precession frequencies. It thus seems natural that the exchange interaction, which lifts the energy degeneracy of the singlet and triplet states, hinders S–T_0 transitions and correspondingly reduces the effect of a magnetic field. It can be seen from (5) that the magnitude of the exchange splitting competes with the scale "width" of the state, τ_0^{-1}.

A qualitatively new effect arises when the exchange interaction is taken into account in the theory of spin-dependent recombination through paired states: a differential polarization of the pairs. Let us examine this effect. From the solution of Eq. (4) we find

$$
p_-=p_1=-p_2=\frac{-J\tau_0\omega_{12}W_s}{(4+W_s\tilde{T})\omega_{12}{}^2+(4+3W_s\tilde{T})\Delta_0{}^2}. \tag{7}
$$

This polarization arises under the simultaneous effects of the magnetic field (if $\omega_{12}\neq 0$) and the exchange interaction (if $J\neq 0$). This polarization is related in a fundamental way to the occurrence of a singlet recombination in the pairs, which shifts the singlet-triplet equilibrium. The sign of the polarization p_- is determined by the direction of the magnetic field (i.e., by the sign of H_0), by the relation between γ_1 and γ_2, and by the sign of the exchange integral J. In weak fields $H < H^*$, with $\omega_{12} < \Delta_0$, the polarization p_- is proportional to H and may be much larger than its thermodynamic-equilibrium value $\mu H/T$. In strong fields $H > H^*$, in which S–T_0 transitions are near saturation, the differential polarization falls off as $1/H$. The maximum polarization reached at any field is

$$
\max p_-=\frac{-JW_s\tilde{T}}{[(J^2+\tau_0{}^{-2})(W_s\tilde{T}+4)(2W_s\tilde{T}+4)(3W_s\tilde{T}+4)]^{1/2}} \tag{8}
$$

with the constraint

$$
W_s\tilde{T}=4T_sW_s[T_sW_s+4W_DT_s+4]^{-1}\leqslant 4. \tag{9}
$$

If the spin relaxation and the dissociation are slow in comparison with the singlet recombination ($W_s \gg W_D$, $W_s \gg T_s^{-1}$), then we have $W_s\tilde{T} = 4$ and

$$
\max p_-\approx -0{,}1J(J^2+\tau_0{}^{-2})^{1/2}\approx -0{,}1(J^2+{}^1/_4W_s{}^2)^{-1/2}. \tag{10}
$$

It follows that the maximum differential polarization can reach 10% in the case $J \gg W_s$. The spin relaxation proper, described by the time T_s, and the spin relaxation caused by dissociation obviously act only to reduce the values of p_-. This reduction, however, is very slight. With $W_s = W_D$ and $W_s \gg T_s^{-1}$, for example, we have

$$\max p_- \approx -0{,}06 J (J^2 + {}^1/{}_4 W_s^2)^{-1/2}. \qquad (11)$$

The same result is found with $W_s = T_s^{-1}$ and $W_s \gg W_D$.

§ 3. NONEQUILIBRIUM INTEGRAL POLARIZATION IN STATIC AND ALTERNATING RESONANT FIELDS

The nonequilibrium integral polarization of electrons in exchange-coupled pairs which has been predicted may, under certain conditions, also lead to an integral polarization in the system of spins. This situation can be arranged by somehow disrupting the polarization of the spins of one of the members of the pairs. If the microwave resonances at the frequencies ω_1 and ω_2 for the members of a pair differ by an amount greater than the widths of these resonances (the case of saturation of the static magnetic field, with $\omega_{12}\tilde{T} \gg 1$; see Ref. 4), then an integral polarization can be produced in the system by disrupting the polarization of the spins of one of the members by means of its resonant alternating field h. This assertion can be demonstrated by solving the complete system of equations (4) ($h \neq 0$) in the steady state near a resonance of one of the members of a pair (the first, say). After the lengthy calculations, we find the following solution for the recombination rate at resonance for an arbitrary field:

$$R = \frac{G}{W_D}\left[\frac{4}{W_s} + \frac{1}{W_D} + 3\tilde{T} + B^2 \tilde{T} f(H^2)\right]^{-1}, \qquad (12)$$

where

$$B^2(H^2) = 2 + 4\frac{\gamma_1\gamma_2 h^2 T^* \tilde{T}}{4 + J^2 T^{*2} + 4\gamma_1 \tilde{T} T^* h^2},$$

$$B^2(0) = 2, \qquad B^2(\infty) = 3,$$

$$f(H^2) = \omega_{12}^2[\omega_{12}^2 + \Delta^2]^{-1}, \qquad \Delta^2 = (J^2\tau + 1/\tilde{T} + {}^1/{}_4 W_s),$$

$$\tau^2(h^2) = \frac{2T^*}{16A^2 - (T^* W_s)^2}$$

$$\left[2(4 - W_s T^*) + \frac{\gamma_1^2 h^2 T^{*2}}{4 + J^2 T^{*2}}(16\gamma_1 - 2(2 - W_s T^*)\gamma_2)\right],$$

$$\tau(0) = 4T^*(4 + T^* W_s)^{-1}, \qquad \tau(\infty) = T^*(4 + W_s T^*)/16,$$

$$A^2 = 1 + 4\gamma_1^2 h^2 T^{*2}[4 + J^2 T^{*2}]^{-1}.$$

In the absence of an exchange interaction, the expression for the recombination rate in (12) is the same as the corresponding expression for R in Ref. 4. The exchange interaction shifts the maximum of the $R(H)$ dependence upward and weakens the h dependence of R, so that a given value of $\Delta R / R$ is reached at a higher value of h^2. An important distinguishing feature of the case at hand is the appearance of an integral polarization, as predicted. Instead of (7) we find the following expressions for p_1 and p_2 at $h = 0$:

$$p_1 = \frac{2JT^*(4 - W_s T^*)B^2 F(H)}{16A^2 - T^{*2} W_s^2},$$

$$p_2 = \frac{-2JT^*(4A^2 - W_s T^*)B^2 F(H^2)}{16A^2 - T^{*2} W_s^2} \qquad (13)$$

where

$$F(H^2) = W_s \omega_{12}[\Delta^2(4 + 3W_s\tilde{T}) + \omega_{12}^2(4 + (3 - B^2)\tilde{T} W_s]^{-1}. \qquad (14)$$

The integral polarization is correspondingly written

$$p_+ = 8JT^*(1 - A^2)F(H)[16A^2 - T^{*2}W_s^2]^{-1}. \qquad (15)$$

The maximum integral polarization, $\max p_+$, is reached at saturation of the spin resonance, i.e., at $h \gg h^*$, and at the optimum magnetic field H^*:

$$\max p_+ = -3JT^* W_s [8\Delta(\infty)(4 + 3W_s\tilde{T})^{1/2}]^{-1},$$

$$4\gamma_1^2 \tilde{T} T^* |h^*|^2 = 4 + J^2 T^{*2}, \qquad \omega_{12}^* = \Delta(\infty)[4 + 3W_s\tilde{T}]^{1/2}/2. \qquad (16)$$

As the exchange interaction becomes stronger, the integral polarization $\max p_+$ increases, and at

$$4\tilde{T}^2 J^2 > (4 + W_s\tilde{T})^2$$

it reaches its maximum possible value p_+^*:

$$\max p_+ \leqslant p_+^* = -{}^3/{}_2 W_s \tilde{T}[2(4 + 3W_s\tilde{T})(2 + 3W_s\tilde{T})]^{-1/2} \leqslant 0{,}43. \qquad (17)$$

This estimate is slightly too low (by a factor of about two) because we have ignored the overlap of the resonances at the optimum value $H = H^*$.

CONCLUSION

The nonequilibrium polarization of electrons in exchange-coupled pairs which we have predicted should have several important consequences. First, there is the possibility of obtaining a population inversion at Zeeman sublevels of one member of the pair. At the resonant frequency corresponding to the energy of the Zeeman splitting of the given member we will observe an emission, while at the resonant frequency of the second member we will observe an anomalously strong absorption. A semiconductor in which this recombination mechanism is operating can therefore serve, under certain conditions, as an active medium for amplifying electromagnetic oscillations at a fixed frequency, which can be tuned with the help of a magnetic field. To see this point, we consider the following simple expression for the imaginary part of the transverse rf susceptibility $\chi_\perp''$ at resonance (at $\omega = \omega_1$) which follows from the equation for N_{+0}:

$$\chi_\perp'' = 4\gamma_1 T^* p_1 N_{00}[4 + J^2 T^{*2}]^{-1}. \qquad (18)$$

We first note that $\chi_\perp''$ (per center) is anomalously large because the polarization p_1 may be much greater than its thermodynamic-equilibrium value. Another important point is that $\chi_\perp''$ is proportional to N_{00}, i.e., to the deviation of the system from equilibirum (the illumination of the sample). The most important feature is that $\chi_\perp''$ can go negative (at $p_i < 0$, where $i = 1, 2$), and we should correspondingly observe an amplification, rather than an absorption, of the resonant radiation. A substantial body of experimental evidence has now been accumulated on electron spin resonances in semiconductors with paramagnetic centers. We know, for example, that illuminating the surface of a silicon sample will cause the ESR signal to increase by several orders of magnitude[8]; the signal representing photoinduced ESR in amorphous silicon depends in a complicated way on the illumination level[9]; and, finally, an amplification of incident microwave power has been detected[10] for the first time at a photoinduced spin resonance in paramagnetic centers at a silicon surface. We see that all of these experimental effects can be described by our theory for the events which occur in semiconductors with a spin-dependent recombination through exchange-coupled pairs. It is a simple matter to offer at least a qualitative explanation for these effects at this stage of development of the theory.

A second important consequence is that an integral polarization can arise in a system of spins. To arrange this integral polarization it is sufficient to somehow disrupt the nonequilibrium polarization of the spins of one member of the pairs which arise. This can be done, as we have analyzed in detail, by imposing on the semiconductor an alternating field at resonance with one of the types of centers. It is also clear that if one of the centers of a pair exchanges carriers with an allowed band with an extremely short spin-relaxation time for free carriers, then a nonzero integral polarization of the pair, which is determined by the polarization of the second member, can arise even in the absence of a resonant microwave field.

Third, since silicon contains a substantial number (4%) of Si^{29} nuclei with spin 1/2, we can expect that the hyperfine interaction will give rise to a nuclear polarization, both differential and integral. The effect depends on whether the position of the Si^{29} nuclei near the members of a pair are equiprobable or correlated in some way. We do not know just how events will actually unfold but we can assert that in the former case there will be a differential polarization of the nuclei, while in the latter there will be an integral polarization. If an integral polarization of electrons by the mechanism discussed above can occur in a semiconductor, then this effect can also give rise to an integral nuclear polarization. It is pertinent to recall here that the experiments of Refs. 11 and 12 revealed a nonequilibrium nuclear polarization in disordered silicon (plastically deformed and polycrystalline), which as we know, also exhibits a spin-dependent recombination.

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

[2] V. V. Kveder, Yu. A. Osip'yan, and A. A. Shalynin, Zh. Eksp. Teor. Fiz. **83**, 699 (1982) [Sov. Phys. JETP **56**, 389 (1982)].

[3] L. S. Mima, V. I. Strikha, and O. V. Tretyak, Fiz. Tekh. Poluprovodn. **14**, 2242 (1980) [Sov. Phys. Semicond. **14**, 1328 (1980)].

[4] V. S. L'vov, L. S. Mima, and O. V. Tretyak, Zh. Eksp. Teor. Fiz. **83**, 1557 (1982) [Sov. Phys. JETP **56**, 897 (1982)].

[5] S. P. Depinna, B. C. Cavenett, I. G. Austin, and T. M. Searle, Solid State Commun. **41**, 263 (1982).

[6] R. A. Street, Phys. Rev. **B26**, 3589 (1982).

[7] R. A. Street, Phys. Rev. **B19**, 3027 (1979).

[8] S. N. Karyagin and V. V. Kurylev, 5-ĭ simpozium po élektronnym protsessam na poverkhnosti poluprovodnikov i na granitse razdela poluprovodnikdiělektrik (Fifth Symposium on Electronic Processes on Semiconductor Surfaces and at Semiconductor-Insulator Interfaces), Novosibirsk, 1974, p. 88.

[9] I. Solomon, in: Amorphous Semiconductors (ed. M. H. Brodsky), Springer, Topics in Applied Physics, Vol. 36, 1979, (Russ transl. Mir, 1982, p. 239).

[10] V. V. Kurylev and S. N. Karyagin, Phys. Status Solidi **a21k**, 239 (1974).

[11] N. T. Bagraev and L. S. Vlasenko, Zh. Eksp. Teor. Fiz. **83**, 2186 (1982) [Sov. Phys. JETP **56**, 1266 (1982)].

[12] L. S. Vlasenko, Izv. Akad. Nauk SSSR, Ser. Fiz. **46**, 469 (1982).

Translated by Dave Parsons