Spin-dependent processes in one-dimensional disordered dangling-bond systems in semiconductors

N. T. Bagraev, A. I. Gusarov, and V. A. Mashkov

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad

(Submitted 9 July 1986)
Zh. Eksp. Teor. Fiz. **92**, 968–987 (March 1987)

A model of an amphoteric dislocation dangling bond in semiconductors is proposed based on the concept of coupling of electron-vibrational interactions and local multiplet spin correlations. This model is used to study the spin-dependent capture, transport, and recombination of carriers in one-dimensional systems of dislocation dangling bonds. Polaron tunneling factors, which are responsible for structural changes in the dangling bonds when their spin or charge states change, are shown to contribute substantially to the spin dependence of the probabilities for these charge-exchange reactions of dislocation dangling bonds. Basic equations describing the behavior of spin-dependent recombination in semiconductors containing defects with deep levels are derived. A study is made of the effect of the singlet and triplet recombination channels on the magnitude and sign of the spin-dependent recombination in semiconductors with dislocation dangling bonds. In each case, the effect of the spin-dependent recombination is shown to be determined by the nonequilibrium polarization of the dislocation dangling bonds which arises during spin-correlated transport of triplet centers polarized as a result of a selective filling of magnetic sublevels. The formation during optical pumping of polarization triplet centers, which participate in the polarization and magnetic ordering of chains of dislocation dangling bonds, is demonstrated through a study of the optical polarization of nuclear spins in plastically deformed silicon single crystals. It is found that the spin-dependent processes in this case depend on the extent to which the dislocation chain are filled with equilibrium electrons captured from shallow donors to singlet states at dislocation dangling bonds.

1. INTRODUCTION

Line defects in plastically deformed semiconductor single crystals have recently attracted increased interest because edge dislocations are a readily grasped model of disordered one-dimensional Fermi systems. The presence of unpaired electrons on dislocation chains can easily be detected by an ESR method.[1–4] Extensive studies of the energy spectrum of dislocations (or of dangling bonds) in semiconductors[2,5–7] by the ESR method, by the microwave-conductivity method, by the photoconductivity method, and by other methods have shown that the one-dimensional system of electrons of the dangling bonds of the cores of edge dislocations is in a Mott-Hubbard insulator state with narrow bands. The width of the bands in a Mott-Hubbard insulator is a consequence of the deformation disorder and polaron effects. It has been found through the optical polarization of nuclear spins[8,9] and by measurements of the microwave conductivity[5,6,10] that disorder in a system of dangling bonds influences the transport of current carriers along dislocation chains. The transport of electrons captured in triplet and singlet states is responsible for magnetic ordering processes in the system of dangling bonds[8] and itself depends on the ground state of the chain.

Studies of the optical polarization of nuclei and of spin-dependent recombination[11–14] have shown that all processes by which carriers are captured at a dangling bond with the accompanying formation of a triplet or a singlet, their transport, their recombination, and magnetic ordering in systems of dangling bonds are spin-dependent in low-dimensionality systems. In a study of the behavior of dangling bonds in a semiconductor, it is thus necessary to consider the following: 1) A dangling bond is a complex electron-vibrational system with several charge states and a multiplet spin correlation; 2) the electron-electron correlation at each dangling bond of the system are responsible for the formation of a Mott-Hubbard insulator with narrow bands; 3) the carrier mobility in the system of dangling bonds reflects the extent of deformational disorder and depends, by virtue of spin correlations on the type of magnetic ordering in the chain.

These positions serve as the starting point in the present paper, which is a study of the interrelation between electron-vibrational interactions and spin correlations in low-dimensionality systems. In §2 we construct a model of a dangling bond on the basis of this concept. Here the dangling bond is represented as an amphoteric defect whose electron wave functions reflect local correlations and the electron-vibrational interaction. This model applies if the spin relaxation time at a defect is longer than the time required for an electron to hop between defects. These results are used in §3 as a basis for studying spin-dependent reactions involving charge exchange of defects. Expressions are derived for the corresponding carrier-capture probabilities in semiconductors with an indirect band gap. An important point is that the spin dependence of the probabilities for electron transitions arises not as a result of the standard rule for combining angular momenta but as a result of the presence of polaron tunneling factors which depend on the total spin of the defect. In §4 the results of an analysis of spin-correlated transport and recombination of carriers are used to study the application of this theory in interpreting experiments on optical polarization of nuclei and spin-dependent recombination. The re-

0038-5646/87/030548-12$04.00

sults are compared with experimental data on spin-dependent recombination from Refs. 11 and 13. In this paper we report the first experimental detection of a temperature dependence of the optical polarization of nuclei during optical pumping with unpolarized light. This temperature dependence correlates well with corresponding data on the spin-dependent recombination. In a study of optical polarization of nuclei during step-by-step annealing, we studied the relative contributions made to spin-dependent processes by linear chains of dangling bonds and by point defects at the nuclei of edge dislocations. We have shown experimentally and theoretically that the extent to which dangling bonds are filled by equilibrium and nonequilibrium carriers strongly influences the extent of the optical polarization of nuclei. The experimental results found here can be described completely on the basis of this new concept of an interrelation between spin correlations and electron-vibrational interactions at structural defects in semiconductors.

2. MODEL OF A DANGLING BOND

2.1. Basis wave functions of a dangling bond

The pronounced localization of the electrons of dangling bonds[1–4] which stems from the deformational disorder allows us to describe the properties of the system by making use of data from the model of an isolated dangling bond.

We know that in a study of spin-triplet localized excitations, e.g., triplet molecular excitons,[15] it is necessary to consider two basis states of the electron at each center. The same comment applies to small-radius spin correlations, which determine the properties of the ground and excited two-electron states of an isolated bond. To describe a singlet correlation in a two-electron ground state it is sufficient to consider a single state of the orbital motion of the electron, with the wave function $\varphi_0(\mathbf{r})$ (a one-electron D state; see Fig. 1 in Ref. 13). In order to describe a triplet correlation it is necessary to consider two orbitals, $\varphi_0(\mathbf{r})$ and $\varphi_1(\mathbf{r})$ (the wave functions of the D and D^* states, respectively; Fig. 1). The exchange interaction gives the excited singlet state an energy higher than that of the lowest triplet state. The corresponding energy gap increases as the two basis states of the orbital motion (D and D^*) become closer together and as their Bohr radius decreases. It is apparently this case of approximately equal states φ_0 and φ_1 which prevails for the dangling bonds of the cores of edge dislocations in silicon, where, according to the data of Refs. 2 and 6, there is some excited state D^* near the D ground state (Fig. 1c). The difference between the energies of the D and D^* states for a dangling bond of an edge dislocation in silicon is on the order of[2,6] 0.03 eV. In pursuing the study of two-electron states we will accordingly consider only the singlet ground state and the lowest-lying triplet state.

2.2. Hamiltonian and adiabatic potentials of a dangling bond

We consider the model of a center with a multiplet electron-electron correlation of small radius, several charge states, and a direct order of levels[2,5,6] (Fig. 1b), but with a nonmonotonic dependence of the constant of the electron-vibrational interaction on the charge state[16] and on the total spin.[1)] Since D and D^* are nearly the same (Subsection 2.1 and Fig. 1b), we consider only the following charge states: a one-electron ($n = 1$) ground state A_0 ($A_0 = D$), one-electron excited state A_0^* ($A_0^* = D^*$), a two-electron ($n = 2$) singlet state A_S ($A_S = D + S$), a two-electron triplet state A_T ($A_T = D + T$), and a vacant A_+ state ($n = 0$)—a so-called hole center. Figure 1a is a diagram of the adiabatic potentials of these states versus the configurational coordinate Q. The state A_S corresponds to an absolute minimum of the energy of the system. The orbital motion of the electrons in states A_0 and A_0^* is described by the two orthogonal orbitals φ_0 and φ_1, as mentioned in Subsection 2.1. The Hamiltonian corresponding to the diagram in Fig. 1 is

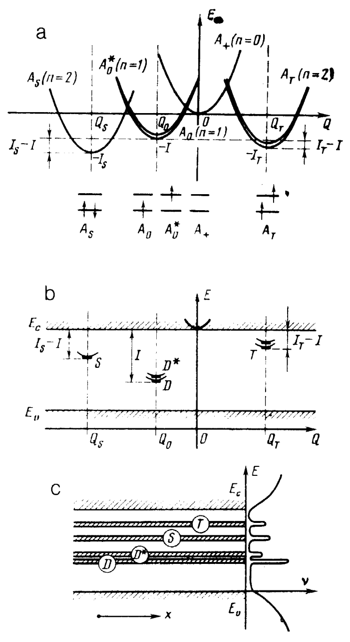

FIG. 1. Electronic states of a "dangling-bond" defect in silicon. a—Diagram of adiabatic potentials for states of a deep center with various values of the total charge and the total spin. Shown at the bottom is the order in which the electronic states at a site are filled; this order leads to electron-vibrational terms of the given type; b—equivalent one-electron diagram versus the configurational coordinate Q; c—narrow zones formed by various states of dislocation dangling bonds in the band gap of silicon versus the Cartesian coordinate x, along with the corresponding state diagram.[2]

$$H=\frac{P^2}{2M_0}+\frac{\varkappa}{2}Q^2+E_0n_0+E_1n_1+Un_{0\uparrow}n_{0\downarrow}+U_1(n_{0\uparrow}n_{1\downarrow}+n_{0\downarrow}n_{1\uparrow})$$

$$+U_2\sum_\sigma n_{0\sigma}n_{1\sigma}-Q(F_0(n_0+n_1)+F_1n_{0\uparrow}n_{0\downarrow}+F_2n_0n_1),$$

$$n_0=n_{0\uparrow}+n_{0\downarrow},\quad n_1=n_{1\uparrow}+n_{1\downarrow}, \tag{1}$$

where P and Q are the canonical momentum and coordinate of the center, M_0 and $\varkappa$ are its mass and strength constant, and E_0, E_1 and $n_{0\sigma}$, $n_{1\sigma}$ are the one-electron energies and operators representing the filling of the center by electrons with spins $\sigma = \uparrow,\downarrow$, corresponding to the orbitals φ_0, φ_1. The electron-electron interaction and the constant of the electron-vibrational interaction at a center depend on the spin state: U, the Hubbard repulsion in the states φ_0, and U_1 and U_2, the interaction of the electrons in the states φ_0 and φ_1, which corresponds to the projections of the total spin of the triplet A_T, $M = 0$, ± 1. In this model, the quantity $U_1 - U_2$ is an analog of the longitudinal-transverse spin splitting of triplet states which results from the interaction with the crystal field. The quantities F_1 and F_2 are admixtures to the ordinary constant of the electron-vibrational interaction, F_0, in the singlet and triplet states. By diagonalizing (1) with respect to the charge and spin states of the defect under consideration, which is a readily interpreted model for a dangling bond, we find explicit expressions for the adiabatic potentials for various values of $n = n_0 + n_1 = 0, 1, 2$ (see Fig. 1a, where the origin for the energy scale is at the bottom of the conduction band):

$$E_\alpha(Q)=\Big\{\frac{\varkappa}{2}Q^2,\ n=0;\ -I+\frac{\varkappa}{2}(Q-Q_0)^2,\quad n=1;\ -I_S+\frac{\varkappa}{2}(Q-Q_S)^2,\quad n=2,\ S=0;\ -I_M+\frac{\varkappa}{2}(Q-Q_T)^2,\ n=2,\ S=1,\ M=0,\ \pm1\Big\}, \tag{2}$$

where

$$\begin{gathered} Q_0=F_0/\varkappa,\ Q_S=F_S/\varkappa,\ Q_T=F_T/\varkappa,\ F_S=2F_0+F_1,\\ F_T=2F_0+F_2,\ I=-E_0+F_0^2/2\varkappa,\ I^*=-E_1+F_0^2/2\varkappa,\\ I_S=-(2E_0+U)+F_S^2/2\varkappa,\ I_M=-(E_0+E_1+U_M)+F_T^2/2\varkappa,\\ U_M=\{U_1,\ M=0;\ U_2,\ M=\pm1\}, \end{gathered} \tag{3}$$

and M is the spin projection of the triplet. The adiabatic potential of the A_0^* state is found by replacing I by I^*. According to (2), therefore, the essence of a multiplet correlation is that when an electron is added to a singly filled dangling bond the energy of this electron depends on the relative orientation of the spins of the two electrons. A characteristic of a dangling bond is that the strength F_S and F_T differ in sign (Fig. 1a); as a result, there is a decrease in the probability for the triplet-singlet transition (the T-S transition; Subsection 3.3). The direct order of levels of a dangling bond is described by the inequalities

$$I_S>I_0>I_{\pm1}>I>I^*>0, \tag{4}$$

where indicate stability of two-electron configurations.[1)]

2.3. Wave functions of a deep center; background and correlated electrons

To calculate the probabilities for various quantum transitions involving a dangling bond, we need to supplement relations (1)–(3) with explicit expressions for the one-electron wave functions incorporating two-electron correlations at a site [see (2)]. If we are interested in one-electron transitions of an electron captured at a dangling bond (a correlated electron), the transition energy and wave functions of this electron are determined by the total spin of the two-electron system, despite the fact that the state of the "main" electron of a dangling bond (the background electron) remains unchanged.[2)] Accordingly, we supplement the notation introduced above for the two-electron states, A_S and A_T, with S and T, respectively the singlet and triplet one-electron states of a correlated electron at two-electron centers A_S and A_T (Fig. 1, b and c). As we will see below, at nonzero temperatures the S and T centers are mobile elementary electron-vibrational excitations in a system of dangling bonds and are responsible for the electrooptic and magnetooptic activity of plastically deformed semiconductors.

According to (2), the one-electron wave functions which we need for electrons at a given dangling bond, and which depend on the total spin and excitation multiplicity N of the local mode, are $(N = 0,1,2,\ldots)$

$$\varphi_\lambda(r,\ \xi)=\varphi_\alpha(\mathbf{r},\ \sigma,\ \xi)\Phi_N(Q-Q_\alpha),\qquad \lambda=(\alpha,\ N),\quad r=(\mathbf{r},\ \sigma,\ Q). \tag{5}$$

The electron functions, which depend on the variables of either the background electron (D or D^*) or the correlated electron (S or T), are given by

$$\varphi_\alpha=\Big\{\begin{pmatrix}\varphi_0(\mathbf{r})\\ \varphi_1(\mathbf{r})\end{pmatrix}u_{\sigma'}(\sigma),\quad \alpha=\Big(\begin{pmatrix}D\\ D^*\end{pmatrix},\ \sigma'=\uparrow,\downarrow\Big);\ \varphi_0(\mathbf{r})\chi_S(\sigma,\xi),\ \alpha=S;\quad \varphi_1(\mathbf{r})\chi_M(\sigma,\xi),\ \alpha=(T,M=0,\pm1)\Big\}, \tag{6}$$

where u_σ is the spinor of the background electron. The spin functions of a correlated electron are

$$\left.\begin{matrix}\chi_S\\ \chi_0\end{matrix}\right\}=\frac{1}{2^{1/2}}\left(\xi u_\downarrow(\sigma)\mp(1-\xi)u_\uparrow(\sigma)\right),\qquad \begin{matrix}\chi_{+1}=\xi u_\uparrow(\sigma)\\ \chi_{-1}=(1-\xi)u_\downarrow(\sigma)\end{matrix} \tag{7}$$

and incorporate the local electron-electron correlation. They depend on the random parameter $\xi = \xi^2$, which characterizes the ground state of the given dangling bond. The values $\xi = 0, 1$ correspond to states of the background electron with spin projection $\sigma' = \downarrow,\uparrow$. A local mode (5) is described by the function Φ_N of the Nth excited state of an oscillator which is centered at the point Q_α, whose position depends on the electron configuration of the dangling bond. In general, the one-electron second-quantized operator

$$\Psi(r,t,\xi)=\sum_\lambda b_\lambda\varphi_\lambda(r,\xi)e^{-iE_\lambda t/\hbar},\qquad \{b_\lambda,b_{\lambda'}^+\}=\delta_{\lambda\lambda'} \tag{8}$$

also depends on the polarization parameter ξ of the background electron. Here

$$\begin{gathered} E_\lambda=E_\alpha+\hbar\omega_0(N+{}^1/_2),\\ E_\alpha=\{-I,\alpha=(D,\sigma'=\uparrow,\downarrow);\ -(I_S-I),\ \alpha=S;\ -(I_M-I),\ \alpha=(T,M=0\pm1)\}, \end{gathered} \tag{9}$$

where $\omega_0 = (\varkappa/M_0)^{1/2}$ is the frequency of the local mode. The radius of the electron-electron correlation and the localization radius, which are determined by both the pronounced disorder along the dislocation chain and polaron effects,[18] are comparable in magnitude. Consequently, the energy of the level corresponding to a correlated electron depends on the spin state of the background electron at the site, despite the fact that in the case of a neutral dislocation these energies lie respectively above and below the Fermi level.

To outline the region of applicability of this concept of correlated and background electrons, we note that the spin-lattice relaxation time of the background electrons is substantially longer than the average time for thermal hops of a correlated electron in a system of dangling bonds.[5] As a result, we can say that the spin correlations in two-electron centers cannot be averaged in a regime of pronounced localization. The spin state at a site is not averaged by the motion of the electrons, so that the mean-field approximation is not applicable.

3. CAPTURE OF CARRIERS TO A DANGLING BOND

3.1. Role of dangling bonds in excitation and recombination; classification of transitions

The kinetics of photostimulated electronic processes in plastically deformed semiconductors is determined primarily by the electron states on dislocation chains of dangling bonds.[2] A specific feature of such states is that (for example) the capture of a polarized photoelectron from the conduction band to the core of a neutral dislocation, accompanied by the formation of an S or T center, is not recombination in its pure form, since the hole captured at a dislocation may settle in another place, spending a certain amount of time below the Fermi level. The S and T centers are always above the Fermi level, i.e., are excitations of the electron system, and are therefore always nonequilibrium centers. The recombination process thus depends strongly on the particular features of the transport of carriers of the opposite sign in dislocation cores.

Let us examine some possible one- and two-electron transitions (adiabatic and nonadiabatic) in the scheme of terms in Fig. 1. The role played by dangling bonds in the excitation and recombination in a semiconductor is determined by the values of the corresponding transition probabilities, which will be calculated in the following subsections. Below we give the thresholds for photostimulated reactions and the energy transfer for spontaneous indirect transitions involving thermalized carriers. For dislocation dangling bonds in silicon, the following are some typical numerical values: $I = 0.77$ eV, $I - I^* = 0.03$ eV, $I_S = 1.20$ eV, $I_T = 0.97$ eV, $I_S - I = 0.43$ eV, $I_T - I = 0.2$ eV, and $E_g = 1.19$ eV (at $T = 77$ K). We denote by Ω the frequency of the pump light.

I. Dipole excitation of a background electron:

$$A_0+\gamma\to A_0^*;\ \hbar\Omega=\Delta E=I-I^*.$$

II. Photoionization of a one-electron center and the inverse reaction—the capture of an electron to the center—

$$A_0+\gamma\to A_++e,\ \Delta E=I+N\hbar\omega_0,\ \hbar\Omega\geqslant I;$$

$$A_++e\to A_0+(ph),\ \Delta E=-I+N\hbar\omega_0.$$

III. Photoionization of two-electron centers and the inverse capture of an electron to a dangling bond, accompanied by the formation of an S or T center ($A_- = A_S$ or $A_- = I_S$ or I_T):

$$A_-+\gamma\to A_0+e,\ \Delta E=I_--I+N\hbar\omega_0,\ \hbar\Omega\geqslant I_--I;$$

$$A_0+e\to A_-+(ph),\ \Delta E=I-I_-+N\hbar\omega_0.$$

IV. (The double photoionization of two-electron centers A_S and A_T is unimportant because of the low concentrations of these centers.) The inverse capture of two electrons to a dangling bond, accompanied by the formation of S and T centers:

$$A_++2e\to A_-+(ph),\ \Delta E=-I_-+N\hbar\omega_0.$$

V. Photoionization of a hole center and the inverse capture of a hole to a one-electron center:

$$A_++\gamma\to A_0+h,\ \Delta E=E_g-I+N\hbar\omega_0,\ \hbar\Omega\geqslant E_g-I = 0.42\text{ eV};$$

$$A_0+h\to A_++(ph),\ \Delta E=-(E_g-I)+N\hbar\omega_0.$$

VI. Photoionization of a hole from a one-electron center, accompanied by the formation of an S or T center, and the inverse capture of a hole to a two-electron center:

$$A^{\bullet}_0+\gamma\to A_-+h,\quad \Delta E=E_g+I-I_-+N\hbar\omega_0,$$

$$\hbar\Omega\geqslant\{0.76\text{ eV for } A_S \text{ and } 0.99\text{ eV for } A_T\};$$

$$A_-+h\to A_0+(ph),\quad \Delta E=-(E_g+I-I_-)+N\hbar\omega_0.$$

VII. Double photoionization of a hole center and the inverse capture of two holes to a two-electron center:

$$A_-+2h\to A_++(ph);\ \Delta E=-2E_g+I_-+N\hbar\omega_0$$

$$= -(1.18\text{ eV for } A_S \text{ and } 1.41\text{ eV for } A_T) + N\hbar\omega_0.$$

VIII. A T-S transition;

$$A_T\to A_S+(ph),\ \Delta E=-(I_S-I_T)+N\hbar\omega_0=-0.23\text{ eV}+N\hbar\omega_0.$$

IX. In a two-center system, there is a possibility of a neutralization of positively and negatively charged centers as a result of a transfer of charge between centers:

$$A_-+A_+'\to A_0+A_0'+(ph),\ \Delta E=I_--2I+N\hbar\omega_0.$$

The radiationless recombination of electrons and holes in semiconductors involving multiply charged deep centers, which produce donor and acceptor levels in the band gap, occurs in three steps: 1) the capture of a conduction electron to an acceptor level of a center; 2) the capture of a hole from the valence band to a donor level of the center; 3) the recombination of current carriers, in the course of which the excess energy is transferred to the lattice. In a plastically deformed semiconductor, a neutral dangling bond exhibits donor and acceptor properties simultaneously,[2,6] so that recombination involving dangling bonds goes by the following pathway:

$$\begin{aligned}&(\text{III})\ A_0+e\to A_-+(ph),\ A_-=(A_S\text{ or }A_T),\\&(\text{V})\ A_0+h\to A_++(ph),\\&(\text{IX})\ A_-+A_+'\to A_0+A_0'+(ph).\end{aligned}\tag{10}$$

the final step of the recombination is a neutralization reaction with an exchange of charge between centers (IX); this reaction occurs primarily between nearest neighbors. Accordingly, this final step is separated from the first two steps, III and V, by a transport of holes and of correlated electrons along the dislocation in opposite directions.

3.2. Probability for the formation of *S* and *T* centers

The particular features of a calculation of the probabilities of one-electron transitions accompanied by tunneling of a deep center between different equilibrium positions were discussed in Refs. 17 and 19. In this subsection we use the reactions which give rise to T and S centers as examples in order to find explicit expressions for the general relations given in Ref. 19. We consider the second of the inverse capture reactions (III), in which a center tunnels from the ground state to the Nth excited state of a local mode:

$$A_0+e\to A_T+(ph),\quad \Delta E = -0.2\text{ eV} + N\hbar\omega_0.\tag{11}$$

It is assumed that the conduction electron which is captured is thermalized ($E_k \approx k_B T$) and that the center is rigid in the sense of Ref. 19: $\hbar\omega_0 \gg \hbar\omega_{ph} \approx k_B T$. This scheme (Fig. 1a), which incorporates the rigidity of the electron wave functions,[19] predicts that the probability for transition (11) will be small, on the order of the tunneling probability. Consequently, this capture of an electron accompanied by a change in the position of the center in the lattice (Fig. 1a) goes quite slowly, and all of the photoexcited carriers have time to thermalize.

Making use of the explicit expressions for the one-electron wave functions [see (5)–(7)], we can write the probability for the capture of a thermalized conduction electron to an isolated dangling bond, accompanied by the formation of a T center, as follows:

$$\begin{aligned} W_{MN}(\sigma,\xi) &= \frac{2\pi}{\hbar}\sum_q\sum_k f_{\mathbf{k}\sigma}|V_{fi}|^2[(\mathcal{N}_q+1)\Delta(E_{\mathbf{k}}+I_M-I-N\hbar\omega_0-\hbar\omega_q) \\ &\quad +\mathcal{N}_q\Delta(E_k+I_M-I-N\hbar\omega_0+\hbar\omega_q)], \\ |V_{fi}|^2 &= V^{-1}|C_q|^2\eta_M K_N(Q_T-Q_0)\,b_{\mathbf{k}}(\mathbf{q}), \end{aligned} \tag{12}$$

where $M=0,\ \pm 1$; V is the normalization volume;

$$K_N(Q_T-Q_0)=\left|\int dQ\,\Phi_N^*(Q-Q_T)\,\Phi_0(Q-Q_0)\right|^2 \tag{13}$$

is the tunneling factor for the transition of a center between states of shifted oscillators (Fig. 1)[17,19]; and the factor

$$\eta_M(\sigma,\xi)=\left|\sum_{\sigma_1}\chi_M^*(\sigma_1,\xi)\,u_\sigma(\sigma_1)\right|^2 \tag{14}$$

determines the spin selection rules in the capture processes. The values $\xi=0, 1$ correspond to the spin projections of the background electron of the dangling bond, $\sigma'=\downarrow,\uparrow$ or $\xi=\frac{1}{2}(1+\sigma')$. Using (7) for the spin wave functions of the triplet, we find the explicit expression

$$\begin{aligned} \eta_M = \{&{}^1/_2(\xi\delta_{\sigma\downarrow}+(1-\xi)\delta_{\sigma\uparrow}),\ M=0;\ \xi\delta_{\sigma\uparrow}, \\ &M=+1;\ (1-\xi)\delta_{\sigma\downarrow},\ M=-1\}, \end{aligned} \tag{15}$$

where

$$b_{\mathbf{k}}(\mathbf{q})=|\langle\varphi_1(\mathbf{r}-\mathbf{Q}_T)|e^{-i\mathbf{q}\mathbf{r}}|\psi_{\mathbf{k}}\rangle|^2 \tag{16}$$

is the Fourier overlap of the wave function of the deep center and the Bloch function of the conduction electron; $f_{\mathbf{k}\sigma}$ and $E_{\mathbf{k}}$ are the occupation numbers and energy of the thermalized conduction electrons; σ is the spin projection; $\psi_{\mathbf{k}}$ are the corresponding Bloch functions; the quasimomentum $\mathbf{k}$ varies within the first Brillouin zone; $\hbar\omega_q$, $\mathcal{N}_q$ and C_q are the energies and occupation numbers of three-dimensional phonons and the matrix element of the electron-phonon interaction; and the function

$$\Delta(\omega)=(\Gamma/2\pi\hbar)(\omega^2+\Gamma^2/4)^{-1}, \tag{17}$$

where $\hbar\omega=E_{\mathbf{k}}+I_M-I-N\hbar\omega_0\pm\hbar\omega_q$ [see (12)]; describes energy conservation in the process by which an electron is captured to a dangling bond, and Γ is the probability for intrawell relaxation of a local mode due to an interaction with three-dimensional phonons.

The conditions $E_{\mathbf{k}}, \hbar\omega_q \ll I, I_M, \hbar\omega_0$ allow us to take the function (17) through the sign indicating the summation over the Brillouin zone in (12); the calculation of the probability W_{MN} then reduces to a calculation of the volume-independent sum:

$$(2\pi/\hbar V)\sum_{\mathbf{k},\mathbf{q}}|C_q|^2(2\mathcal{N}_q+1)f_{\mathbf{k}\sigma}b_{\mathbf{k}}(\mathbf{q}). \tag{18}$$

Noting that (1) the important values of $\mathbf{q}$ are concentrated near the center of the Brillouin zone and the values of $\mathbf{k}$ are concentrated near the bottoms of six valleys in the conduction band of silicon, (2) the wave functions of the deep center, φ_0 and φ_1, are orthogonal to the wave functions of the band extrema, and (3) in calculating Fourier overlap (16) we need to use a **kp** perturbation theory and a two-band model with indirect transitions in silicon, we can rewrite sum (18) as

$$\frac{64\pi^2}{3\hbar^2}\frac{n_\sigma}{k_0^8a_1^5}\frac{m_\parallel\langle E\rangle}{\mu E_g}\left(1+\frac{\hbar^2k_0^2}{\mu E_g}\right)^{-1}\int\frac{d^3q}{(2\pi)^3}|C_q|^2(2\mathcal{N}_q+1). \tag{19}$$

Here $n\sigma=\rho_\sigma n_e$ is the density of conduction electrons with spin projection σ [the spin density matrix is $\rho_\sigma=(1/2)(1+p\sigma)$, where p is the spin polarization of the electrons], k_0 is the quasimomentum of the center of the valley, a_1 is the localization radius of the orbital φ_1 (in the isotropic approximation), $\mu=(m_c^{-1}+m_h^{-1})^{-1}$ is the reduced mass of the carriers, m_c and m_h are the effective masses of the electrons and holes in silicon, averaged over directions and over the various branches of the spectrum, $m_\parallel$ is the longitudinal effective mass of an electron at the bottom of a valley, E_g is the width of the indirect band gap, and $\langle E\rangle$ is the average kinetic energy of a conduction electron. The integral over the Brillouin zone in (19), which we denote by Λ, depends on the temperature T, the type of phonons involved in reaction (11), and the nature of the electron-phonon interaction. In the pertinent region, $v_sp_0<k_BT<\hbar\Omega_0$ (v_s is the longitudinal sound velocity, p_0 is the boundary quasimomentum of the Brillouin zone, and Ω_0 is the frequency of an optical phonon), this integral can be conveniently written in the following forms for the cases of deformation-acoustic scattering (DA), deformation-optical scattering (DO), polar-optical scattering (PO), and scattering by piezophonons (PA):

$$\Lambda=\frac{p_0}{\pi^2}\left\{\frac{\Xi^2k_BTp_0^2}{6\hbar^2c_L}\ \mathrm{DA};\quad \frac{\mathscr{E}^2\Omega_0p_0^2}{12\hbar\bar{c}}\ \mathrm{DO};\quad \frac{e^2k_BT}{\varepsilon\hbar^2}\mathscr{P}^2\ \mathrm{PA};\quad \frac{\pi e^2\Omega_0}{\varepsilon\hbar}\ \mathrm{PO}\right\}. \tag{20}$$

Here we are using the following notation:

$$\begin{aligned} &c_L={}^1/_5(3c_{11}+2c_{12}+4c_{44}), \\ &c_T={}^1/_5(c_{11}-c_{12}+3c_{44}),\quad \bar{c}={}^1/_3c_L+{}^2/_3c_T \end{aligned} \tag{21}$$

are elastic constants;

$$\Xi^2=a^2+\frac{c_L}{c_T}\left(b^2+\frac{1}{2}d^2\right),\quad \mathscr{E}^2=\frac{3d_0\bar{c}}{2\mathcal{N}\Omega_0^2c_0^2} \tag{22}$$

are strain-energy constants; and

$$\mathscr{P}^2=\frac{h_{14}^2}{35}\left(\frac{12}{c_L}+\frac{16}{c_T}\right), \tag{23}$$

is the longitudinal piezoelectric modulus of the electromechanical coupling. The quantities a, b, d, and d_0 are strain energies which were introduced in Ref. 20; $\mathcal{N}$ is the atomic number density; c_0 is the lattice constant; h_{14} is the piezoelectric stress tensor; $\varepsilon 0$ is that static dielectric constant; and $\varepsilon = (\varepsilon_\infty^{-1} - \varepsilon_0^{-1})^{-1}$ is the dielectric constant which appears in the Fröhlich coupling constant.

We thus have the following expression for the probability for the capture of a thermalized electron to an isolated dangling bond, accompanied by the formation of a T center:

$$W_{MN}(\sigma, \xi) = \rho_\sigma \eta_M(\sigma, \xi) K_N(Q_T - Q_0) w_T, \tag{24}$$

$$w_T = \frac{64\pi^2}{3\hbar} \frac{n_e \Lambda}{k_0^8 a_1^5} \frac{m_\parallel \langle E\rangle}{\mu E_g} \left(1 + \frac{\hbar^2 k_0^2}{\mu E_g}\right)^{-1} \Delta(I_M - I - N\hbar\omega_0). \tag{25}$$

A similar expression for the probability W_{SN}, for the formation of an S center, can be found by replacing $Q_T, I_M, \eta_M, \varphi_1$, by $Q_S, I_S, \eta_S, \varphi_0$, where

$$\eta_S(\sigma, \xi) = \left| \sum_{\sigma_1} \chi_S^*(\sigma_1, \xi) u_\sigma(\sigma_1) \right|^2 = \eta_0(\sigma, \xi). \tag{26}$$

As a result we find

$$W_{SN}(\sigma, \xi) = \rho_\sigma \eta_S(\sigma, \xi) K_N(Q_S - Q_0) w_S, \tag{27}$$

where W_S differs from (25) again by the replacement of a_1 by a_0, the localization radius of orbital φ_0. An important point is that if the dangling bonds have a random rigidity, i.e., if the frequency ω_0 of a local mode at the bond is distributed over a certain frequency interval with a normalized distribution function $P(\omega_0)$, then the density of final states, $\Delta(\Delta I - N\hbar\omega_0)$, which appears in w_T and w_S, is replaced by $P(\Delta I / N\hbar)$, provided that the width of the P distribution is larger than the probability for intrawell relaxation in (17).

It can be seen from relations (24) and (27) that the capture of a thermalized electron to an isolated dangling bond is spin-dependent not only because of the spin factor (η_M, η_S) but also because of the difference in the values of the tunneling factor K_N for the S and T centers. As a rule, different magnetic sublevels of a triplet center are filled selectively: either sublevels with projections $M \parallel \pm 1$ or sublevels with $M = 0$ are filled preferentially. As a result, polarized T centers form in the course of optical pumping in a magnetic field which corresponds to anticrossing of sublevels.[21] Selective filling may result from a dependence of the constant of the electron-vibrational interaction on the magnetic projection M and an associated relative shift of the adiabatic terms with projections $M = \pm 1$ and $M = 0$ along the coordinate, which may not coincide with the coordinate for the charge-exchange reaction, Q.

3.3. *T-S* transition

A T cener at a dangling bond may spontaneously convert into an S center. This transition, which mixes states with different total spins, results from the spin-orbit interaction of an electron at the center, which may be modulated by phonons. The constant of the spin-orbit interaction is of the form $(\lambda_0 + \lambda_1 \nabla \mathbf{u})$, where the second term is the strain energy of the spin-phonon interaction.[22] In the nonresonant situation in which we are interested here, quantum transitions involving T and S centers occur only if significant inhomogeneous broadening of the vibrational terms [$\Delta(\omega)$ or $P(\omega_0)$ in (25)] takes place. The probability for a T-S transition W_{MS} due to the spin-orbit interaction of an electron at an isolated dangling bond can be found by writing an expression correspond to (12). After appropriate calculations (see Subsection 3.2 and the Appendix) we find

$$W_{MS} = K_N(Q_S - Q_T) w_{MS}, \tag{28}$$

$$w_{MS} = \frac{\pi}{2} A_M \left(\lambda_0^2 + \frac{\lambda_1^2 k_B T p_0^3}{6\pi^2 c_L} \right) \Delta(I_S - I_T - N\hbar\omega_0), \tag{29}$$

where

$$A_M(\xi) = \{ |\langle \varphi_0 | l_z | \varphi_1 \rangle|^2,\ M=0;$$
$$\xi |\langle \varphi_0 | l_+ | \varphi_1 \rangle|^2,\ M=+1;\quad (1-\xi) |\langle \varphi_0 | l_- | \varphi_1 \rangle|^2,\ M=-1\}, \tag{30}$$

and $l_z, l_\pm$ are components of the operator representing the orbital angular momentum. If, following Ref. 23, we approximate the wave functions of the dangling bond, φ_0 and φ_1, as p orbitals which are preferentially oriented perpendicular to the chain, then a simple estimate of the matrix elements (30) is

$$A_M(\xi) = y\{0,\ M=0;\ \xi,\ M=+1;\ (1-\xi),\ M=-1\},\ y \leqslant 0.1. \tag{31}$$

The values of y decrease with increasing contribution of the s orbitals to φ_0 and φ_1.

The probability of a T-S transition for electrons captured to a dangling bond is usually much smaller than the probabilities for capture to the S and T states of a correlated electron (W_{SN} and W_{MN}) and much smaller than the probabilities for hopping between sites of the chain (more on this below). The reason for this situation is the large difference in the values of K_N (Fig. 1). As a result, there is a spin correlation at a dislocation dangling bond and in a dislocation chain.

3.4. Probability for the capture of a hole to a dangling bond

Let us examine the reaction in which thermalized holes are captured to a dangling bond (reaction V):

$$A_0 + h \to A_+ + (ph), \quad \Delta E = I - E_g + N\hbar\omega_0. \tag{32}$$

This process corresponds to the tunneling of a center from $Q \approx Q_0$ to $Q \approx 0$ (Fig. 1) and the excitation of a local mode. Like reaction (II), it is fast in comparison with (III) and consists of a quantum transition of a background electron with spin polarization ξ to a free state $(-\mathbf{k}, j, -j_z)$ near the top of the valence band, where $(\mathbf{k}, j, j_z)$ are the quantum numbers of the hole. Taking into account the explicit expression for the one-electron wave functions [see (5) and (6)], we can describe the probability for reaction (32) by an expression similar to (12), in which the factor which specifies the spin selection rule [$\xi = \frac{1}{2}(1 + \sigma')$] in hole-capture processes takes the following form (see the Appendix):

$$\eta(J, J_z, \xi) = \{ {}^1/{}_2 \delta_{\downarrow\sigma'} (n_x^2 + n_y^2),$$
$$J = J_z = {}^3/{}_2;\quad {}^1/{}_6 [\delta_{\uparrow\sigma'} (n_x^2 + n_y^2) + 4\delta_{\downarrow\sigma'} n_z^2],$$
$$J = {}^3/{}_2,\quad J_z = {}^1/{}_2;\quad {}^1/{}_3 [\delta_{\uparrow\sigma'} (n_x^2 + n_y^2) + \delta_{\downarrow\sigma'} n_z^2],\quad J = J_z = {}^1/{}_2\}, \tag{33}$$

where $\mathbf{n}$ is a unit vector of oriented orbital φ_0 (Ref. 23). An expression for the spin factor in the case $J_z < 0$ can be found from (33) by replacing ↑ by ↓, and vice versa. After calculations similar to those in Subsection 3.2, we find the following expression for the probability for reaction (32):

$$W_N(J, J_z, \xi)=\rho_{JJ_z}\eta(J, J_z, \xi)K_N(Q_0)w_J, \tag{34}$$

$$w_J=\frac{64\pi^2}{\hbar}p_J\Lambda a_0{}^3\frac{m_J{}^h\langle E_J\rangle}{\mu E_g}\Delta(E_g-I-N\hbar\omega_0), \tag{35}$$

where

$$\rho_{JJ_z}=\frac{1}{2J+1}\left[1+\frac{1}{J}p^h(J)J_z\right] \tag{36}$$

is the spin density matrix of the holes, and p_J, m_J^h and $\langle E_J\rangle$ are the concentration, effective mass, and average energy of a hole with an angular momentum J. The notation is otherwise the same as in (24) and (25). The spin dependence of the probability for the capture of a hole to a dangling bond is therefore determined by the relative orientation of the (vector) external magnetic field, which determines the quantization axis for the angular momentum of the hole in the valence band, and the direction **n** of the orbital φ_0.

We discussed some possible processes by which carriers might be captured to dislocation dangling bonds above, and we showed that the spin dependence of the corresponding probabilities is a result of an interrelation between the electron-vibrational interaction and local spin correlations at defects. A complete understanding of the nature of the spin-dependent effects (spin-dependent recombination and optical polarization of nuclei) which result from the presence of dislocation dangling bonds, however, will require analyzing the spin-correlated transport of carriers along one-dimensional dislocation chains. Such processes may turn out to dominate in several cases in experiments on spin-dependent effects.

4. SPIN-DEPENDENT EFFECTS OF THE TRANSPORT AND RECOMBINATION OF CURRENT CARRIERS IN ONE-DIMENSIONAL SYSTEMS OF DISLOCATION DANGLING BONDS IN SEMICONDUCTORS

4.1. Spin-correlated transport along dislocation chains in semiconductors

The concept of a small-radius spin correlation which was presented above is also part of the basis for calculating the probabilities for the transport of T and S centers and holes (A_+) along dislocation chains. An electron and a hole move by virtue of thermally stimulated hops along exclusively those sites in the chain which agree in terms of spin and energy with the initial state of the T centers, S centers, and hole centers which are formed during optical pumping. Taking into account the small occupation number of the dislocation dangling bonds, f, along with the electron-phonon and electron-electron interactions, we find the following relations for the probabilities for the spin-correlated transport of T and S centers and of holes (see Ref. 24 and Subsection 3.2):

$$\begin{aligned}W_{ij}=w_{ij}\{&{}^1/_4(\xi_i\xi_j+(1-\xi_i)(1-\xi_j))K_N(Q_0-Q_S),\ S;\\ &\xi_i\xi_jK_N(Q_0-Q_T),\ T,\ M=1;\\ &(1-\xi_i)(1-\xi_j)K_N(Q_0-Q_T),\ T,\ M=-1;\ {}^1/_4(\xi_i\xi_j\\ &+(1-\xi_i)(1-\xi_j))K_N(Q_0-Q_T),\ T,\ M=0;\ K_N(Q_0),\ A_+\},\end{aligned} \tag{37}$$

where w_{ij} is a spin-independent factor which is determined by the deformation disorder and by DA phonons,[24] and i and j are the indices of the sites in the chain. The value of the spin variable of a background electron averaged over sites, $P_D = \langle\xi_i\rangle$, depends on the time because of magnetization processes in the course of the spin-correlated transport of a T center with a projection $M=\pm 1$ along chains of finite length. The time average of this quantity is

$$P_D=P_0+(P_b-P_0)[1-\exp(-t_{\text{eff}}/\tau_2)], \tag{38}$$

where P_0 is the initial Boltzmann spin polarization of the background electrons, P_b is the nonequilibrium polarization of the background electrons which arises during the magnetization in the course of the spin-correlated transport, τ_2 is the spin-spin relaxation time of the background electrons of the dislocation dangling bonds,[25] and t_{eff} is the total effective time spent by a polarized T center ($M=\pm 1$) near a given site, with allowance for self-crossing in a random walk in a one-dimensional system.[24] The time t_{eff} increases with decreasing length of the chain; this length is limited by points of an intersection with adjacent edge dislocations. Magnetization effects do not occur during the motion of S and T centers with $M=0$, so that their mobility is substantially lowered. Consequently, the motion of T centers with $M=\pm 1$ is usually limited not by the length of the chain but by the distance between the relatively immobile S and T centers with $M=0$.

4.2. Spin-dependent recombination in semiconductors with dislocation dangling bonds

This study of the interrelation between the electron-vibrational interaction and spin correlations in semiconductors with dislocation dangling bonds has shown that the capture and transport of carriers in such systems are spin-dependent processes. It can be concluded from this result that the overall recombination process—which underlies experiments on spin-dependent recombination and optical polarization of nuclei in semiconductors with dislocation dangling bonds—is a spin-dependent process. In this subsection of the paper we will find the basic relations for interpreting the results on spin-dependent recombination found from the change in the conductivity of a semiconductor crystal when the ESR of the background electrons of dislocation dangling bonds are saturated.[13]

The behavior of conduction electrons which are not in equilibrium in terms of spin in a semiconductor can be described by the kinetic equation

$$\begin{gathered}\dot{n}_\sigma(t)=G_\sigma-\frac{\sigma}{2\tau_s}\left(n_\uparrow-n_\downarrow+\frac{\Delta}{2}n_{-\sigma}\right)-\frac{n_\sigma}{\tau},\\ \sigma=\uparrow,\downarrow\quad(\sigma=\pm1),\end{gathered} \tag{39}$$

where $\Delta=\gamma_e\hbar H_0/k_BT$, γ_e is the gyromagnetic ratio of the electron, τ and τ_s are respectively the lifetime and spin-lattice relaxation time of an electron in the conduction band, $G\sigma$ is a function describing the generation of electrons in the conduction band during optical pumping, and

$$R_{n\sigma}=n_\sigma/\tau=R_{n\sigma}{}^S+R_{n\sigma}{}^T+R_{n\sigma}{}^+, \tag{40}$$

$R^S_{n\sigma}$, $R^T_{n\sigma}$, and $R^+_{n\sigma}$ determine the rates of the generation of S and T centers and of holes on dislocation chains as a result of the capture of conduction electrons and of holes in the valence band. On the basis of the analysis above of spin-dependent capture to dislocation dangling bonds in semiconductors, we can easily derive the following expression for $R^S_{n\sigma}$, $R^T_{n\sigma}$, and $R^+_{n\sigma}$:

$$
\begin{aligned}
&R_{n\sigma}{}^{S}={}^{1}/_{4}(1-pP_{D})C_{S}K_{S}(f)(n_{\sigma}N_{0}-n_{1S}N_{S}),\ A_{0}+e\leftrightarrow A_{S};\\
&R_{n\sigma}{}^{T}={}^{1}/_{4}(3+pP_{D})C_{T}K_{T}(f)g_{M}(n_{\sigma}N_{0}-n_{1TM}N_{TM}),\\
&M=0,\ \pm1,\quad A_{0}+e\leftrightarrow A_{TM};\\
&R_{n\sigma}{}^{+}=C_{+}K_{+}(n_{\sigma}N_{+}-n_{1}N_{0}),\ A_{+}+e\leftrightarrow A_{0},
\end{aligned}
\tag{41}
$$

where the capture constants $C_{(\ )}$ are unambiguously related to the probabilities for the capture of carriers to dislocation dangling bonds given in (24), (27), and (34): and $n_{1(\ )}$ are the densities of conduction electrons due to thermal generation from deep levels of various states of dislocation dangling bonds. This generation can be ignored over a broad temperature range. The product pP_D, of the spin polarizations of respectively conduction electrons and background electrons, arises as a result of the averaging over the spin disorder along the chains of dislocation dangling bonds, by analogy with (38): $p = -\frac{1}{4}\Delta\tau/(\tau+\tau_s)$. The quantity l is the extent to which the dislocation dangling bonds are filled by current carriers; and the functions $K_S(f)$ and $K_T(f)$ replace the constants K_S and K_T in (24) and (27), since field effects arise during the filling of dislocation chains by carriers during optical pumping.[5,14] These field effects reduce the tunneling factors in the capture probabilities [see (24), (27), and (34)]. Here we have $g=\Sigma_M g_M$, where g_M describes the selective nature of the capture resulting in the formation of T centers ($g_0 \neq g_1 = g_{-1}$). The degree of polarization of the background electrons, P_D, is proportional to the polarization (P_b of the triplet centers which are formed at dislocation dangling bonds [see (38)]. This polarization is given by[21] $P_b = P_m\tau_{ST}/(\tau_{ST}+\tau_T)$, where P_m is the maximum degree of polarization at the magnetic field value $H_0 = H_D$, which corresponds to a region of anticrossing of magnetic sublevels of a triplet center. The field H_D is numerically equal to the constant D (expressed in magnetic-field units) of the splitting of the magnetic sublevels of the T center in a zero magnetic field; τ_{ST} is the spin-lattice relaxation time of a T center which is diffusing along a chain; τ_T is the lifetime of a T center on a chain of dislocation dangling bonds, given by $\tau_T = \tau_{tr} + \tau^{T}_{\text{coll}}$; $\tau_{tr} = L^2_S/\mathscr{D}(H_1)$ is the diffusion time for a T center before recombination with a hole; L_S is the average distance between S centers on the chain [the concentration of the latter centers is higher than the concentration of T centers, by virtue of the relation $K_S(f) > K_T(f)g$ (Fig. 1); they limit the diffusion of T centers on dislocation dangling bonds]; and $\mathscr{D}(H_1)$ is the diffusion coefficient of a T center on chains of dislocation dangling bonds. It follows from (37) that $\mathscr{D}(H_1)$ is proportional to the average of bilinear combinations of the spin parameters[24] ξ_j, depends on the degree of magnetic order, and therefore depends on the conditions for the saturation of the ESR of the background electrons in the resonant field H_1. The time τ^{T}_{coll} is the time scale of the collapse of a T center with hole on a chain; under the given conditions (Fig. 1), this time is much shorter than τ^{S}_{coll}, the time scale for the collapse of a hole with an S center. Here we have $1/\tau^{T}_{\text{coll}} = K^{*}(f)Wf_T/f_S$, where W is the average probability for the hopping of an electron which has been captured at a dislocation dangling bond [see (37)], calculated with the help of the electron wave functions of a dislocation dangling bond. All the polaron effects accompanying these hops are incorporated in the tunneling factor K^{*} for the collapse process. The degrees to which the various charge states of the dislocation dangling bonds are filled (f_S, f_T, and f_+), like $K^{*}(f)$, $K_S(f\approx)$, and $K_T(f)$, are determined from the steady-state solution of the system of nonlinear kinetic equations for the populations of holes, triplet states, and singlet states. Here account is taken of the optical-pumping conditions, electrostatic and spin-dependent effects in the capture and transport of carriers along dislocation dangling bonds, and the concentrations of shallow donor and acceptor impurities.

We thus find the following expression for the lifetime of electrons in the conduction band:

$$
\begin{aligned}
1/\tau={}^{1}/_{4}[\,&(1-pP_{D})C_{S}K_{S}(f)\\
&+(3+pP_{D})C_{T}K_{T}(f)g]N_{0}+C_{+}K_{+}N_{+}.
\end{aligned}
\tag{42}
$$

This expression can easily be rewritten as

$$
\begin{gathered}
\frac{1}{\tau}=\frac{1}{\tau_0}+\frac{1}{\tau_+},\quad \frac{1}{\tau_0}=[1-pP_D\alpha(f)]\frac{1}{\tau_1},\\
\frac{1}{\tau_+}=C_+K_+N_+,\quad \frac{4}{\tau_1}=C_0K(f)N_0,\\
K(f)=K_S(f)+3K_T(f)g,\\
\Delta K(f)=K_S(f)-K_T(f)g,\quad \alpha(f)=\Delta K(f)/K(f).
\end{gathered}
\tag{43}
$$

If we ignore the hole photoconductivity, we can find the specific photoresistance detected in spin-dependent recombination from the steady-state solution of Eq. (40) and

$$
\rho=(e\mu n)^{-1}\approx(e\mu G\tau)^{-1},\qquad n=n_{\uparrow}+n_{\downarrow}=G\tau,
$$

where μ is the mobility of the conduction electrons. At ESR saturation of the background electrons, their polarization will vary, depending on the conditions under which the resonance is caused and the power of the microwave field:

$$
\delta P_D(H_1)=P_D(0)-P_D(H_1),
\tag{44}
$$

where $P_D(0)$ is the initial degree of polarization of the background electrons, and $P_D(H_1)$ is the polarization of the background electrons at ESR saturation. At complete saturation we have P_D. Using expressions (40)–(44), we find a basic relation for the relative magnitude of spin-dependent recombination:

$$
\delta\rho(H_1)/\rho_s=p\delta P_D(H_1)\alpha(f)\tau_+/(\tau_1+\tau_+),
\tag{45}
$$

where $\delta\rho(H_1)=\rho(H_1)-\rho(0)$, $\rho(0)$ is the initial photoresistance before ESR saturation, and $\rho_S=\rho(H_{1S})$ is the photoresistance at complete saturation of the ESR of the background electrons of the dislocation dangling bonds, where

$$
\rho(H_{1s})=(1/e\mu G)(1/\tau_1+1/\tau_+).
\tag{46}
$$

It follows from (45) that the magnitude and sign of the spin-dependent recombination depend on the degree of polarization of the background electrons of the dislocation dangling bonds, $P_D(0)$, which is proportional to the degree of polarization of a triplet center at a dislocation dangling bond, (38), because of spin-correlated transport, as we showed above. In turn, the sign of the polarization of a triplet center is determined by its structure and by the selective filling of magnetic sublevels with $M = 0, \pm 1$ (Ref. 21). Furthermore, spin-dependent recombination processes depend on the relative contributions to the recombination made by the

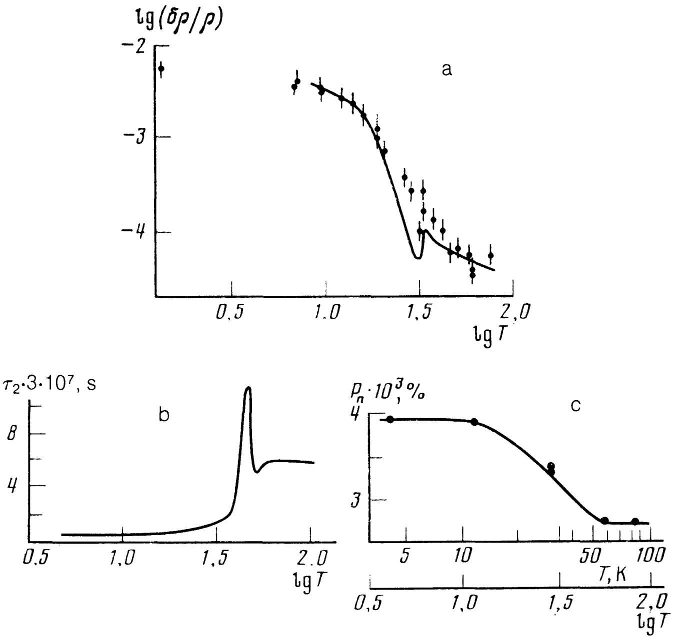

FIG. 2. Temperature dependence of (a) the extent of spin-dependent recombination, (b) τ_2, and (c) the degree of optical polarization of nuclei in plastically deformed silicon single crystals. The experimental data in parts a and b are from Refs. 5, 6, 13, 25, and 27; the experimental data in part c are from the present study. The solid curve in part a is the behavior of the spin-dependent recombination calculated from Eqs. (44)–(46) and (38) of the present paper; the solid curve in part c is the behavior of the optical polarization of nuclei calculated from Eqs. (47) and (38).

singlets and triplets formed on dislocation dangling bonds [depending on the sign of the quantity $\alpha(f)$]. If singlet recombination is predominant [$\alpha(g')>0$] we observe an increase in the specific photoresistance when the ESR of the background electrons of the dislocation dangling bonds saturates [see (45)]. In the opposite case [$\alpha(f)<0$], the triplet channel is predominant in the recombination, and we observe a decrease in ρ. However the sign of the spin-dependent recombination will ultimately be determined by the sign of P_b, as we mentioned above. Accordingly, we cannot work directly from the sign of the effect on the observed experimental spectra of the spin-dependent recombination to draw conclusions about whether singlet or triplet recombination is predominant. Drawing such conclusions requires additional studies of the dependence of the spin-dependent recombination on the strength of the external magnetic field, the temperature, and the intensity of the pump light.

For the model of a dislocation dangling bonds with the adiabatic potentials shown in Fig. 1 typically capture to the singlet state dominates, but the recombination of holes captured to the dislocation dangling bonds occurs more rapidly from triplet centers. However, we wish to emphasize again that both in the recombination of a hole with a triplet and in the recombination with a singlet the magnitude of the spin-dependent recombination is determined by the degree of polarization of the T center.

We can draw yet another important conclusion from our basic relation: Either the singlet component of the recombination process or the triplet component can be distinguished in spin-dependent-recombination effects, depending on the frequency of the microwave modulation of the field, ω_M. For example, if the relation $\omega_M<1/\tau^S_{\rm coll}$ holds ($\tau^S_{\rm coll}$ is the time of the collapse of a hole with a singlet on a chain: $A_+ + A_S \to A_0 + A_0$), we will detect the entire set of spin-dependent-recombination effects [$\alpha(f)>0$ for the model in Fig. 1]. If $1/\tau^T_{\rm coll}>\omega_M>1/\tau_{\rm coll}$, only the triplet component will participate in the recombination [$\alpha(f)<0$; see Fig. 1], so that there will be a change in the sign of the spin-dependent-recombination signal. However, here we should take into account the circumstance that the motion of a T center is still limited by the relatively immobile S centers, which influence the value of P_b, determining the value of τ_T [see (44), (38), and the relations following (41)]. Similar effects, involving a change in the sign of the spin-dependent recombination, depending on the conditions under which the resonance is crossed, have been detected experimentally.[12]

This analysis of spin-dependent recombination in semiconductors with dislocation dangling bonds can be illustrated conveniently in the example of the calculated temperature dependence in Fig. 2a. In the calculation from (45) we used the characteristics of the samples in Refs. 13 and 8, the temperature dependence of τ_{ST} from Ref. 26, and the dynamics of the transfer of polarization of a T center to background electrons of dislocation dangling bonds in the process of a spin-correlated transport as in (38). A characteristic feature of the dependence in Fig. 2a is the presence of an anomaly in the spin-dependent recombination at $T=50$ K. This anomaly stems from the behavior of τ_2 in this temperature interval (Fig. 2b). This anomaly has been detected in experiments on spin-dependent recombination in silicon containing linear chains of dislocation dangling bonds[11]; the results of those experiments are also shown in Fig. 2.

The sign of the spin-dependent recombination and the conditions under which it is observed indicate that the singularity combination channel dominates at[13] $\omega_M\tau^S_{\rm coll}<1$. The large value of the observed recombination effect, however, is determined by the nonequilibrium polarization of the dislocation dangling bonds which arises in the course of the transport of a polarized T center along dislocation chains.

Another important consequence of this new model for spin-dependent processes (44) and (45) is the prediction of nonlinearity in the dependence of the spin-dependent recombination on the intensity of the pump light, since the degree of polarization of a T center, P_b, is determined by the set of $\tau^T_{\rm coll}$ and τ_{tr}. The time $\tau^T_{\rm coll}$ decreases with increasing pump light intensity because of an increase in the probability for

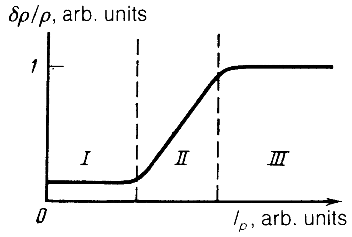

FIG. 3. Calculated extent of the spin-dependent recombination as a function of the intensity of the pump light, I_p, according to (44)–(46). In region I (low intensities) $\delta P_D \simeq P_0$ and $\tau_T \gg \tau_{ST}$, and the extent of the spin-dependent recombination does not depend on I_p; in region II $\delta P_D \sim P_b \sim \tau_{ST}/\tau_T \sim I_p$; in region III $\delta P_D \sim P_b \sim \tau_{ST}/\tau_{tr}$, and this quantity is independent of I_p since $\tau_{tr} = L_S^2/\mathscr{D}$ is an upper limit on τ_T.

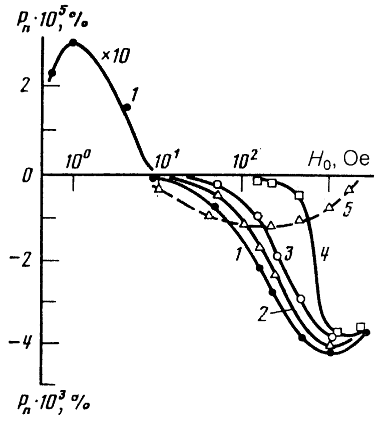

FIG. 4. Extent of the optical polarization of nuclei as a function of the magnetic field in silicon single crystals deformed plastically by uniaxial compression. $N(B) = 10^{13}$ cm^{-3}. 1–4—Sample deformed at 700 °C (degree of deformation $\varepsilon = 5.1\%$) and then annealed at $T_{\text{ann}} = 720$ °C; 1—annealing time $t_{\text{ann}} = 0$; 2—3 min; 3—11 min; 4—more than 1 h; 5—sample deformed at $T = 480$ °C.

the capture of a hole to segment L_S, while τ_{tr} remains essentially constant. In the case of weak pumping we would thus have $\tau_{\text{coll}}^T > \tau_{tr}$, so that $P_b \sim \tau_{ST}/\tau_T$ would be small and would depend on the intensity of the pump light (Fig. 3). In the case of strong pumping, τ_{coll}^T decreases until that it becomes smaller than τ_{tr}; the effect is to limit the growth of P_b and accordingly to lead to a saturation of the signal representing the spin-dependent recombination (Fig. 3). Nonlinearities in spin-dependent recombination similar to the calculated dependence in Fig. 3 have been observed in many experiments.[27]

4.6. Optical polarization of nuclear spins in semiconductors with dislocation dangling bonds

Studies of the optical polarization of nuclei in plastically deformed crystals of n-type and p-type silicon, with various phosphorus and boron concentrations, were carried out by the method described in detail in Refs. 8, 9, and 28. The samples were illuminated with unpolarized light from an incandescent lamp in various magnetic fields and at various temperatures. To measure the degree of optical polarization of the nuclei, P_n, we transferred the samples to the magnet of an NMR rf spectrometer, where we detected the magnetization of the ^{29}Si nuclei which rose in the course of the optical pumping. In all of the experiments, P_n was proportional to the amplitude of the NMR signals, while the direction of the nuclear magnetization with respect to the external magnetic field was determined from the phase of the NMR signal.[28] In the course of these experiments we measured the degree of optical polarization of the nuclei as a function of H_0 for various intensities of the pump light, curves corresponding to that shown in Fig. 4. The fact that illuminating the samples with circularly polarized light causes no changes in the optical polarization of the nuclei observed during optical pumping by unpolarized light indicates that the mechanism for the nuclear polarization involves a hyperfine interaction with spin-nonequilibrium T centers.[21] The T centers which arise at dislocation dangling bonds in the course of a selective capture to magnetic sublevels with $M = 0$, ± 1 interact with the surrounding nuclei of the silicon lattice, with the result that the latter become polarized in the strong magnetic field (Fig. 4):

$$P_n = \zeta P_b \approx \zeta P_m \tau_{ST}/(\tau_T + \tau_{ST}). \tag{47}$$

The results show that a contact interaction is dominant in the hyperfine interaction of the T center with surrounding ^{29}Si nuclei in silicon with dislocation dangling bonds. We thus have $\zeta = -1$ (Refs. 21 and 28). The polarization then propagates away from the ^{29}Si nuclei surrounding the dislocation dangling bonds to the entire volume of the sample through a nuclear spin diffusion, so that it becomes possible to detect the optical polarization of nuclei by an NMR method. The maximum degree of optical polarization of the nuclei corresponds to the value $H_0 = H_D$ as we mentioned above[21] (Fig. 4). It should be noted, however, that a contribution to the H_0 dependence of P_n can come from both the triplet centers which form at chains of dislocation dangling bonds and from triplet centers with large values of D which are localized at point defects in the lattice near the nuclei of edge dislocations. Furthermore, the shape of the experimental curve in Fig. 4 reflects a disorder in the system of dangling bonds. The extent of this disorder determines the range over which the constant D varies for the various dangling bonds of an edge dislocation. The contribution of T centers of various types at dislocation dangling bonds to the optical polarization of nuclei can be distinguished by carrying out successive annealings or by introducing dislocation dangling bonds at a low temperature (Fig. 4). In this case, linear chains of dislocation dangling bonds will form preferentially.

The T centers which form at point defects of the lattice in plastically deformed silicon crystals (cf. the region of large H_0) can apparently also contribute to the spin-dependent recombination.[12,14,29,30] In this case, however, we will observe a temperature dependence very different from that in Fig. 2a. Figure 2c shows the temperature dependence of the degree of optical polarization of nuclei; P_n decreases with increasing temperature because of a decrease in τ_{FT} [see (47)]. The good agreement between the experimental results and the calculated dependences, on the one hand, and the correlation in the behavior of the optical polarization P_n of the nuclei and the spin-dependent recombination $\delta p/p$, on the other (Fig. 2, a and c), suggest that a governing role is played by spin-nonequilibrium T centers in spin-dependent effects in one-dimensional systems of defects in semiconductors.

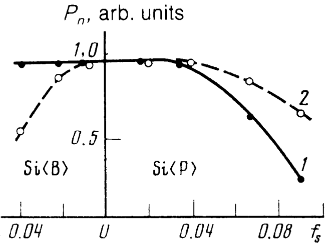

FIG. 5. Dependence of P_n in plastically deformed n-type and p-type silicon single crystals versus the extent of the filling of the dislocation dangling bonds in the singlet state. 1 — $H_0 = 1200$ Oe; 2 — $H_0 = 1$Oe.

As the concentration of shallow donors increases, the extent to which the dislocation dangling bonds are filled by singlets (l_S) increases. This effect correspondingly causes a decrease in P_n because of the increase in $\tau_T \sim \tau_{\text{coll}}^T$ (see the calculated results in Fig. 5). Also shown in Fig. 5 are experimental results on P_n, specifically, the results of measurements in plastically deformed silicon with various concentrations of shallow donors. The agreement between the values of P_n in the p-type material and in the lightly doped n-type material is seen to indicate a common value of L_S (τ_{tr}), because of the nonequilibrium S centers which arise during the optical pumping in crystals of both types, with an identical concentration of dislocation dangling bonds.

The T centers which form at chains of dislocation dangling bonds differ from those centers which form at point defects near the cores of edge dislocations in that they can diffuse along dislocation chains. As was shown above, segments of chains in contact with T centers become magnetically ordered (see also Ref. 26) and polarized [see (38)]. The dipole-dipole interaction of polarized chains of dislocation dangling bonds with surrounding ^{29}Si nuclei gives rise to optical polarization of nuclei at $H_0 < 5$ Oe (Ref. 8):

$$P_n \approx \zeta P_D f' \tag{48}$$

(see Fig. 4). In the case of dipole-dipole interaction we would have $\zeta > 0$ (Ref. 28). The factor f' describes the leakage of the optical polarization of nuclei due to the unpolarized segments of dislocation chains, on which there are no spin-nonequilibrium T centers; this factor is $f' \sim N_1/(N_1 + N_2) \sim L_S$, where N_1 is the concentration of polarized segments, and N_2 is the concentration of unpolarized segments. Here we have $f' \sim f_T$, where f_T is the degree to which the T centers are filled at the dislocation dangling bonds. Accordingly, as f_S increases in either n-type silicon or p-type silicon, the polarization P_n at $H_0 < 5$ Oe decreases, for two reasons: first, because of the decrease in P_b, described above [see (47) and (38)]; second, because of the decrease in the leakage factor for the optical polarization of the nuclei, f', due to the decrease in the concentration of polarized segments of dislocation chains. It can be seen from the curves in Fig. 5 that the latter mechanism for the decrease in the degree of optical polarization of nuclei is important in samples of both n-type and p-type material, in contrast with the behavior of the P_n which arises in the interaction of ^{29}Si nuclei directly with T centers (Fig. 5).

In summary, the spin-nonequilibrium triplet centers which form at chains of dislocation dangling bonds when the electron-vibrational interaction and spin correlations are interrelated participate in the polarization and in the magnetic ordering of the background electrons of dislocation dangling bonds and thereby determine the magnitude and sign of the spin-dependent recombination and the optical polarization of nuclei.

We wish to thank Yu. A. Osip'yan for suggesting the topics of this study and for support, V. I. Perel' for interest in this study and for a useful discussion of the results, and V. V. Kveder for furnishing the samples for the experiments and for many useful discussion of these results.

APPENDIX

In calculating W_{MS} in a system with a local correlation, we need to take account of the spin selection rules. For this purpose, in evaluating an expression like (12) we write the matrix elements incorporating the spin operators in the following form:

$$\langle\chi_S|\mathbf{S}|\chi_M\rangle\langle\varphi_0|\mathbf{l}|\varphi_1\rangle=\{-{}^1\!/_2\langle\varphi_0|l_z|\varphi_1\rangle,\ M=0;\tag{A.1}$$
$$ {}^1\!/_2\xi\langle\varphi_0|l_+|\varphi_1\rangle,\ M=+1;\quad -{}^1\!/_2(1-\xi)\langle\varphi_0|l_-|\varphi_1\rangle,\ M=-1\}.$$

Here we have used relations of the type ($S_\pm = S_x \pm iS_y$)

$$\langle\chi_S|S_z|\chi_{+1}'\rangle={}^1\!/_2(1-\xi)\xi',\ \langle\chi_S|S_z|\chi_{-1}'\rangle=-{}^1\!/_2\xi(1-\xi'),\tag{A.2}$$
$$\langle\chi_S|S_+|\chi_{\pm1}'\rangle=\begin{cases}0\\(1-\xi)(1-\xi')\end{cases}\qquad \langle\chi_S|S_-|\chi_{\pm1}'\rangle=\begin{cases}\xi\xi'\\0\end{cases}.$$

In a calculation of W_N, the electron part of the matrix element is

$$M_q(\mathbf{k},J,J_z|\xi)=\langle\psi_{v,-\mathbf{k}}|e^{-i\mathbf{qr}}|\varphi_0(\mathbf{r}-\mathbf{Q}_0)\rangle\Big\{\pm\frac{1}{\sqrt{2}}\begin{pmatrix}\delta_{\downarrow\sigma'}\\\delta_{\uparrow\sigma'}\end{pmatrix}n_\pm,$$
$$J={}^3\!/_2,\ J_z=\pm{}^3\!/_2;$$
$$\pm\frac{1}{\sqrt{6}}\left[\begin{pmatrix}\delta_{\uparrow\sigma'}\\\delta_{\downarrow\sigma'}\end{pmatrix}n_\pm\pm2\begin{pmatrix}\delta_{\downarrow\sigma'}\\\delta_{\uparrow\sigma'}\end{pmatrix}n_z\right],\quad J={}^3\!/_2,\quad J_z=\pm{}^1\!/_2;$$
$$\pm\frac{1}{\sqrt{3}}\left[\begin{pmatrix}\delta_{\uparrow\sigma'}\\\delta_{\downarrow\sigma'}\end{pmatrix}n_\pm\mp\begin{pmatrix}\delta_{\downarrow\sigma'}\\\delta_{\uparrow\sigma'}\end{pmatrix}n_z\right],\quad J={}^1\!/_2,\quad J_z=\pm{}^1\!/_2\Big\},\tag{A.3}$$

where $n_\pm = n_x \pm in_y$. Expressions (33)–(35) of the text proper then follow immediately.

[1)] The behavior of centers with levels in the opposite order, as a result of a nonmonotonic dependence of the constant of the electron-vibrational interaction on the charge state, was studied in Ref. 17.

[2)] For this reason, a background electron is not shown on the diagrams when the diagram technique is used to describe spin correlations in calculations of the probabilities of electronic transitions.

---

[1] V. A. Grazhulis and Yu. A. Osip'yan, Zh. Eksp. Teor. Fiz. **58**, 1259 (1970) [Sov. Phys. JETP **31**, 677 (1970)]; **60**, 1150 (1971) [**33**, 623 (1971)].

[2] Yu. A. Osip'yan, J. Phys. (Paris) **44**, C4-103 (1983).

[3] U. Schmidt, E. Weber, H. Alexander, and W. Sander, Solid State Commun. **14**, 735 (1974).

[4] E. R. Weber and H. Alexander, J. Phys. (Paris) **44**, C4-319 (1983).

[5] V. A. Grazhulis, V. V. Kveder, and V. Yu. Mukhina, Phys. Status Solidi **a43**, 407 (1977).

[6] V. A. Grazhulis, V. V. Kveder, V. Yu. Mukhina, Phys. Status Solidi, **a44**, 107 (1977).

[7] V. V. Kveder, Yu. A. Osip'yan, W. Schröter, and G. Zoth, Phys. Status Solidi **a72**, 701 (1982).

[8] N. T. Bagraev and L. S. Vlasenko, Zh. Eksp. Teor. Fiz. **81**, 2186 (1982) [Sov. Phys. JETP **56**, 1266 (1982)].

[9] N. T. Bagraev and L. S. Vlasenko, Fiz. Tverd, Tela (Leningrad) **24**, 3470 (1982) [Sov. Phys. Solid State **24**, 1974 (1982)].

[10] N. M. Zolotukhin, V. V. Kveder, and Yu. A. Osip'yan, Zh. Eksp. Teor. Fiz. **81**, 299 (1981) [Sov. Phys. JETP **54**, 160 (1981)].

[11] V. A. Grazhulis, V. V. Kveder, and B. Yu. Mukhina, Pis'ma Zh. Eksp. Teor. Fiz. **24**, 164 (1976) [JETP Lett. **24**, 142 (1976)].

[12] D. Neubert, K. Hoffman, H. Teichmann, and R. Schliff, Solid State Electron. **21**, 1445 (1978).

[13] V. V. Kveder, Yu. A. Osip'yan, and A. I. Shalynin, J. Phys. (Paris) **44**, C4-345 (1983).

[14] T. Figielski, J. Phys. (Paris) **40**, C6-95 (1979).

[15] A. S. Davydov, Teoriya tverdogo tela (Theory of Solids), Nauka, Moscow (1976).

[16] V. S. Vikhnin, I. M. Zaritskiĭ, A. A. Konchits, and B. K. Krulikovskiĭ, Fiz. Tverd. Tela (Leningrad) **17**, 3609 (1975) [Sov. Phys. Solid State **17**, 2348 (1975).

[17] N. T. Bagraev and V. A. Mashkov, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 211 (1984) [JETP Lett. **39**, 251 (1984)].

[18] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).

[19] N. T. Bagraev and V. A. Mashkov, Solid State Commun. **51**, 515 (1984).

[20] G. E. Pikus and G. L. Bir, Fiz. Tverd, Tela (Leningrad) **1**, 1643 (1959) [Sov. Phys. Solid State **1**, 1502 (1960)].

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

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

[23] V. A. Grazhulis, V. V. Kveder, Yu. A. Osip'yan *et al.*, Phys. Lett. **A66**, 398 (1978).

[24] N. T. Bagraev, A. I. Gusarov, and V. A. Mashkov, XI soveshchanie po teorii poluprovodnikov (Eleventh Conference on the Theory of Semiconductors), Uzhgorod, 1983, p. 35.

[25] V. A. Grazhulis, V. V. Kveder, and Yu. A. Osip'yan. Phys. Status Solidi **b103**, 519 (1981).

[26] N. T. Bagraev, L. S. Vlasenko, V. A. Mashkov, and V. A. Khramtsov, Fiz. Tverd, Tela (Leningrad) **28**, 634 (1986) [Sov. Phys. Solid State **28**, 358 (1986)].

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

[28] N. T. Bagraev and L. S. Vlasenko, Fiz. Tverd. Tela (Leningrad) **21**, 120 (1979) [Sov. Phys. Solid State **21**, 70 (1979)].

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

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

Translated by Dave Parsons