Optical polarization of nuclei in semiconductors with magnetic impurities

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The behavior of the optical polarization of crystal-lattice nuclei is studied in silicon containing magnetic impurities in a broad range of concentrations. The degree of optical polarization of the nuclei and the nuclear spin-lattice relaxation time are found to grow very rapidly at high concentrations. At such concentrations, a small decrease in the temperature compared to the room temperature induces a sharp (10^8 times) increase of the resistivity of the crystals [N. T. Bagraev and L. S. Vlasenko, Sov. J. Tech. Phys. Lett. 7, 80 (1981)]. It is shown that the experimental results can be explained by taking into account localization of electrons in the regions of increased magnetic-impurity concentrations. Under such conditions a change occurs in the coupling energy and in the density of the wave function of the electron trapped by the impurity center. This results in an experimentally observed redistribution of the contributions from the dipole-dipole and contact interactions between the lattice nuclei and localized electrons. The observed increase in the degree of nuclear optical polarization is due to the absence of spin-lattice relaxation of the electrons in the conduction band. At low magnetic impurity densities the optical polarization processes are connected with the formation of (shallow donor + magnetic impurity) pair centers.

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Under optical-pumping conditions, when the photoexcited electrons have average spin projections $\langle S_z^e \rangle$ that differ from the equilibrium S_0, dynamic polarization of the lattice nuclei can arise in semiconductors.[1-6] A system of photoexcited electrons that are not at equilibrium in spin can be easily produced by irradiating the semiconductor with circularly polarized light in a longitudinal magnetic field. It was shown earlier[2] that hyperfine interaction between lattice nuclei and photoexcited electrons that are not at equilibrium in spin does not lead to dynamic polarization of the lattice nuclei. Nuclei become polarized only when they interact with nonequilibrium electrons captured by impurity centers and other crystal-lattice defects. A connection was established between the magnitude and direction of the nuclear magnetization that is produced by optical pumping and the impurity composition of the semiconducting materials.[5,6] The advancements made in obtaining appreciable optical polarization of nuclei are due to the study of the relative contributions made to the polarization by the dipole-dipole and contact components of the hyperfine interaction between the electrons captured by lattice defects and the magnetic moments of the nuclei.[5,6]

One of the most interesting and promising ways of obtaining large optical polarization of lattice nuclei is to use as the optical-pumping objects semiconducting materials that have high densities of impurities with unfilled *f* or *d* shells [rare-earth elements (REE) and a number of transition elements]; these have many properties that are similar to those of magnetic semiconductors.

The present paper is devoted to an investigation of the influence of magnetic ordering and of impurity complex formation on the processes of optical polarization of nuclear moments in silicon doped with rare-earth elements.

EXPERIMENTAL PROCEDURE

Silicon single crystals were doped with rare-earth elements (gadolinium and praseodynium) during their growth from the melt by the Czochralski method. The total rare-earth-element density in the crystals was determined by a neutron-activation analysis and ranged from 10^{13} to 10^{21} cm^{-3}. The density of the phosphorus donor atoms, which will be shown below to determine in most cases the electric properties of the rare-earth-doped silicon, was varied in the samples between 2×10^{13} and 10^{15} cm^{-3}.

The obtained rare-earth-doped single crystals were comprehensively investigated by IR microscopy, local x-ray spectral analysis, metallographic analysis, and electron microscopy. In addition, in the samples with large rare-earth-element density, we investigated the temperature dependence of the resistivity and the spectral dependences of the photoconductivity.

The procedure used for optical polarization of the nuclear moments was described in sufficient detail in earlier papers.[2,5] The samples were irradiated at 77 K by circularly polarized light in a longitudinal magnetic field whose value ranged from 0.1 to 300 Oe. The light source was a 1 kW incandescent lamp. The irradiation duration ranged from several minutes to several dozen hours. The nuclear spin-lattice relaxation times at all the magnetic fields used in the experiments was long enough to permit the transfer of the samples after illumination to the magnet of an NMR microwave spectrometer with crossed coils and to register the nuclear magnetization produced by the optical pumping, as revealed by the increase of the NMR signals, observed by the adiabatic fast passage method,[7] of the ^{29}Si nuclei.

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EXPERIMENTAL RESULTS

Figures 1(a) and 1(b) show the experimental dependence of the degree of optical polarization of the nuclear moments and of the time of nuclear spin—lattice relaxation on the total density of the gadolinium in silicon single crystals, having a phosphorus content $N(P) \approx 2 \cdot 10^{13}$ cm^{-3}, obtained by optical pumping of circularly polarized light in a magnetic field $H_0 = 7.5$ Oe. The direction of the nuclear polarization corresponds to contact interaction between the ^{29}Si nuclei and the localized electrons. In silicon samples with gadolinium density $N(Gd) < 10^{16}$ cm^{-3} the degree of optical polarization of the ^{29}Si nuclei and the time of nuclear spin-lattice relaxation T_1 are exactly the same as in the silicon doped only with phosphorus at $N(P) \approx 2 \cdot 10^{13}$ cm^{-3} (Ref. 5). In this case the optically oriented electrons photoexcited into the conduction band are captured by the phosphorus impurity centers, where they interact with the surrounding nuclei of the ^{29}Si lattice. Since phosphorus in silicon is a shallow hydrogenlike center, contact interaction predominates in the hyperfine interaction.[5] The polarization of the nuclei propagates next from the phosphorus centers over the entire volume of the sample via nuclear spin diffusion.

It should be noted that at $N(Gd) < 10^{16}$ cm^{-3} and $N(P) \approx 2 \cdot 10^{13}$ cm^{-3} the rare-earth impurity has practically no effect on the electric characteristics of the samples. In addition, in the density region 10^{13} cm^3 $< N(Gd) < 10^{16}$ cm^{-3} at $N(P) \approx 2 \cdot 10^{13}$ cm^{-3}, only the intrinsic photoconductivity of the silicon is observed in the samples, and there is no impurity photoconductivity.[8,9] The reason is that the level energy of a rare-earth element in the forbidden band is determined by the exchange interaction of the electron in the conduction band with the f-electrons of the impurity.[8] The exchange-interaction energy, for centers with screened f or d shells, exceeds the Coulomb energy. The exchange-interaction energy operator is defined as

$$\mathcal{H} = a(\mathbf{SL})\delta(\mathbf{r}-\mathbf{R});$$

here a is the constant of the exchange interaction of an electron in the conduction band with the f electrons of the rare-earth impurity, $\mathbf{S}$ and $\mathbf{r}$ are the spin and radius-vector of the electron in the conduction band, and $\mathbf{L}$ and $\mathbf{R}$ are the spin and radius vectors of the rare-earth impurity. The cross section for the capture of an electron from the conduction band by a rare-earth impurity is extremely small, and it is this which causes the absence of electrical activity of the rare-earth element in silicon.[8] We note that certain elements with screened unfilled d shell, such as Ti, Zr, and Hf, also have a weak electric activity in silicon.[10]

The capture of an electron from the conduction band on an exchange level of a rare-earth element is possible only with participation of a shallow donor impurity, such as phosphorus, when the electron is first captured by the donor level and next goes over to the rare-earth element. The formation of paired centers (phosphorus +rare-earth element) with increasing rare-earth density to above 10^{16} cm^{-3} [at $N(P) \approx 2 \cdot 10^{13}$ cm^{-3}] is the cause of the onset of impurity conductivity in the investigated samples.[8,9] With increasing phosphorus density, the impurity photoconductivity due to the exchange levels appears at lower rare-earth-element (REE) density, since the distance between the phosphorus and rare-earth atoms decreases with increasing $N(P)$, and the probability of formation of paired centers increases.

It will be shown in detail below that the observed smooth growth of the degree of optical polarization P_n of the nuclei and of the time T_1 at gadolinium densities 10^{16} cm^{-3} $< N(Gd) < 3 \cdot 10^{18}$ cm^{-3} (see Fig. 1), which appears in synchronism with the onset of impurity conductivity,[8] is due to the increase in the probability of formation of paired P + REE centers with increasing REE density.

When the REE density increases above $3 \cdot 10^{18}$ cm^{-3}, the impurity photoconductivity vanishes.[8,10] At the same time, as seen from Fig. 1, a giant jump takes place in the optical polarization and in the time of the spin-lattice relaxation of the nuclei in silicon doped with gadolinium.

To explain the observed effects in silicon containing magnetic impurities, comprehensive investigations were made of the optical polarization of the lattice nuclei, of the electric characteristics, of the structure and impurity composition of the samples. It will be shown below that the observed anomalies in the optical polarization of the nuclei and in other properties of silicon that contains magnetic impurities are due to the formation, at very high densities, of large inclusions of a second phase in which magnetic-ordering takes place.

1. Optical polarization of silicon lattice nuclei, induced by paired (shallow donor + REE) centers

We consider the hyperfine interaction between a lattice nucleus located at a distance r from a neutral donor atom, and an electron captured by this donor atom. The Hamiltonian of the hyperfine interaction can be written in the form

$$\mathcal{H}_{hf} = \gamma_e \gamma_n \hbar^2 \mathbf{I} \left\{ \frac{1}{r^3} \left[\mathbf{S} - \frac{3\mathbf{r}(\mathbf{Sr})}{r^2} \right] - \frac{8\pi}{3} \mathbf{S} |\Psi(r)|^2 \right\}, \quad (1)$$

where $\mathbf{r}$ is the radius-vector joining the nucleus having a spin $\mathbf{I}$ and an electron having a spin $\mathbf{S}$, γ_e and γ_n are

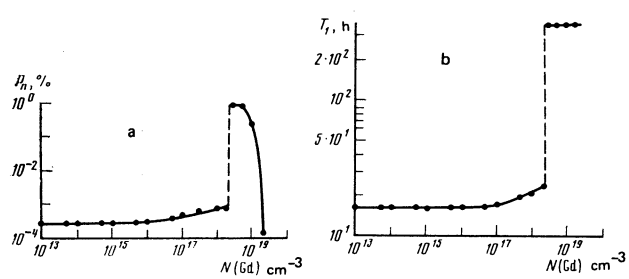

FIG. 1. Plots of P_n (a) and of T_1 (b) against the total gadolinium density N(Gd) in silicon samples containing phosphorus with $N(P) \approx 2 \cdot 10^{13}$ cm^{-3} and optically pumped by circularly polarized light in a magnetic field $H_0 = 7.5$ Oe.

the gyromagnetic ratios of the electron and nucleus, respectively, and $\hbar = h/2\pi$ is Planck's constant.

The expression in the square brackets is the dipole-dipole interaction between an electron captured by donor center and a lattice nucleus. At small r this expression is negligibly small compared with the second term, which represents the contact interaction due to the nonzero density of the wave function of the donor electron $|\Psi(r)|^2$ at the location of the lattice nucleus.[5] At large distances from the donor center, the dipole-dipole interaction begins to exceed the contact interaction. Such a spatial distribution of the dipole-dipole and contact interactions influences strongly the processes of optical polarization of the lattice nuclei.[5]

The interaction (1) can cause various transitions between the magnetic sublevels of the electron + nucleus system. The following expressions can be obtained for the probabilities of these relaxation transitions[5]:

$$w_{1c} = \frac{16}{9}\pi^2\gamma_e^2\gamma_n^2\hbar^2\frac{n_d}{N_d}\frac{\tau_c}{1+(\omega_e-\omega_n)^2\tau_c^2}|\Psi(r)|^4 \qquad (2)$$

is the probability of the nuclear spin flip in contact interaction with the electron spin (flip-flop transitions, i.e., transitions with the relative flipping of the electron and nuclear spins in opposite directions), n_d/N_d is the degree of filling of the donor centers with electrons, $\omega_e = \gamma_e H_0$, $\omega_n = \gamma_n H_0$ are the Larmor frequencies of the electron and nucleus, respectively, and τ_c is the time of correlation of the impurity-electron hyperfine field on the lattice nuclei. In semiconductors doped with shallow donors, the modulation of the magnetic field of the electron at the lattice nuclei at $T = 77$ K is effected by thermal jumps between the donor levels in the conduction band. $\tau_c = 1/w_d$, where w_d is the probability of the thermal ejection of an electron from a donor level into the conduction band per unit time. At lower temperatures, and also in the case of deeper impurity levels, other mechanisms can contribute to the modulation of the hyperfine field at the lattice nuclei, such as hopping conduction, capture of holes from the valence band, and others.

The expressions for the probabilities of the electron-nuclear transitions due to the dipole-dipole interaction (w_{1d}, w_2, w_3) were also obtained earlier.[5,6] In contrast to (2), these probabilities decrease like $1/r^6$ with increasing r.

Using the probabilities of the transitions induced by the alternating magnetic field due to the action of the electron spin S on the nuclear spin I, we can set up kinetic equations for the populations of the n^+ and n^- states having nuclear spin projections $+1/2$ and $-1/2$. These equations lead to the following expression for the stationary value of the degree of polarization of the lattice nuclei[5,6]:

$$P_n = -\xi f P_e \frac{H_0^2}{H_0^2+3H_L^2}, \qquad (3)$$

where P_e is the degree of polarization of the photoexcited electrons captured by the donor centers. In the case of optical pumping of silicon by circularly polarized light, P_e is given by

$$P_e = 0{,}125\frac{\tau_{se}}{\tau_{se}+\tau}\frac{\tau_{sd}}{\tau_{sd}+\tau_d}. \qquad (4)$$

Here τ_{se} is the spin-lattice relaxation time of the electrons in the conduction band, τ is the lifetime of the electrons in the conduction band, τ_{sd} and τ_d are respectively the time of the spin-lattice relaxation and the lifetime of the electrons at the impurity center, f is the nuclear-polarization leakage factor,

$$\xi = \frac{w_3-w_{1c}-w_{1d}}{w_3+2w_2+w_{1c}+w_{1d}}, \qquad (5)$$

ξ shows the relative contribution made to the polarization of the lattice nuclei by the dipole-dipole and contact interactions; this contribution varies with the distance r. Depending on the relative contributions of these interactions, ξ can take on different values and be positive as well as negative, and the nuclear polarization can have different directions.

The hyperfine interaction of the lattice nuclei with electrons localized on impurity centers decreases with increasing r, and at a definite distance $r = \delta$ the probability of nuclear spin flip as a result of this interaction, $1/T_1(r)$, becomes equal to the probability of the nuclear spin flip upon interaction with the neighboring lattice nucleus, D/a_0^2:

$$1/T_1(r)|_{r=\delta} = D/a_0^2.$$

Here $T_1(r)$ is the local nuclear-relaxation time, $1/T_1(r) = 2w_{1c}$ for contact interaction $1/T_1(r) = 2(w_{1d}+w_2+w_3)$ in the case when dipole-dipole interaction predominates, D is the nuclear-spin diffusion coefficient ($D = 2.4\cdot10^{-14}$ cm^2/sec for the ^{29}Si nuclei in silicon), and a_0 is the average distance between the magnetic isotopes of the lattice nuclei ($a_0 = 6.5$ Å for ^{29}Si nuclei in silicon). The spin-spin interaction between the ^{29}Si nuclei in a silicon lattice is responsible for the diffusion of the nuclear spin,[11] and consequently for the spreading of the nuclear polarization from the donor centers over the entire volume of the crystal.

Thus, in the course of the optical polarization, a sphere, of radius δ, made up of lattice nuclei surrounding the impurity centers, is first magnetized via hyperfine interaction within a short time. The magnetization then spreads over the entire crystal via nuclear spin diffusion. The distance δ defined above is the nuclear-spin diffusion radius.[11,12] Thus, the value of ξ in Eq. (3) must be taken at $r = \delta$. The magnitude and direction of the nuclear polarization that spreads by diffusion of the nuclear spin over the entire crystal will correspond to that hyperfine-interaction component which predominates at the distance $r = \delta$.

The foregoing analysis of relaxation with allowance for nuclear-spin diffusion is made complicated in a number of cases if the relaxation rate of the impurity centers is low (rapid diffusion in the presence of a diffusion barrier[13]). In this case the diffusion is brought up to a distance β, which is determined from the relation $H_e(\beta) = H_L$, Ref. 5, where H_L is the local field of the lattice nuclei ($H_L = 0.176$ Oe for ^{29}Si in

silicon), H_e is the d.c. component of the fluctuating field of the electrons[13] on the lattice nuclei; this component can be easily obtained from expression (1) for both dipole-dipole and contact interactions.

Thus, in all cases the direct relaxation is confined to a region of radius $\rho = \sup\{\delta_c, \delta_d, \beta_c, \beta_d\}$, (Ref. 11), where δ_c and δ_d are the diffusion radii for the contact and dipole-dipole interactions, respectively, and β_c and β_d are the diffusion barriers for the contact and dipole-dipole interactions.

If the polarization of the nuclei is due to shallow hydrogen-like impurity centers, a simplified expression for the density of the wave function of the electron at the lattice nuclei is used in the calculations, namely

$$|\Psi(r)|^2 = \frac{\eta}{\pi b^3}\exp\left(-\frac{2r}{b}\right); \tag{6}$$

$\eta = 186$ for silicon, and for phosphorus in silicon $b = 17$ Å is the Bohr radius of the electron localized on the phosphorus atom. If the impurity center is more complicated then, as will be shown below, to find the values of the electron wave function it is necessary to solve the Schrödinger equation in each specific case.

The degree of optical polarization of the nuclei, which is determined by (3), depends thus on the characteristics of the impurity centers that participate in the polarization and on the optical-pumping conditions: the values of the magnetic field H_0 and the degrees of filling of the donor centers by the electrons n_d/N_d, which can be easily varied by changing the intensity of the light.

The spin-lattice relaxation time of the nuclei, with allowance for the nuclear spin diffusion, is obtained from the relation[11]

$$\frac{1}{T_1} = 4\pi\int_\rho^\infty \frac{1}{T_1(r)} r^2 dr, \tag{7}$$

T_1, just as P_n, depends on the characteristics of the impurity centers and on the pumping conditions.

We consider now the influence of the formation of paired phosphorus + REE centers at REE densities $> 10^{16}$ cm^{-3} influences the degree of optical polarization P_n and the time T_1.

The degree of filling of the donor centers by electrons in a semiconductor upon illumination is defined as[14]

$$\frac{n_d}{N_d} = \left[1 + \frac{1}{2}\exp\left(\frac{E_d - E_F^*}{kT}\right)\right]^{-1}, \tag{8}$$

where E_d is the energy of the donor level in the forbidden band ($E_d = -0.044$ eV for phosphorus in silicon), and E_F^* is the Fermi quasilevel.

The stationary density of the electrons in the conduction band is

$$n_e = N_c \exp(E_F^*/kT),$$

where N_c is the state density in the conduction band ($N_c = 3.6 \cdot 10^{18}$ cm^{-3} for silicon at $T = 77$ K). For the stationary hole density in n-type silicon we have

$$p = N_c \exp(E_F^*/kT) - N_d.$$

As shown in photoconductivity experiments, in Si: ⟨P + Gd⟩ (Refs. 8 and 9), with increasing REE density, the probability of formation of paired (shallow donor + REE) centers increases. In this case the REE participates in the recombination process, the electron is first captured from the conduction electrons by a shallow donor center, after which it goes over to the REE, where it recombines with the hole. In the presence of the REE, the stationary hole density is changed

$$p = N_c \exp(E_F^*/kT) - N_d - N_f;$$

where N_f is the REE density that takes part in the recombination process, so that in the stationary case we have the following equation for the recombination of electrons in silicon containing paired (phosphorus + REE) centers:

$$I - n_d w_p p - N_f w_f p = 0, \tag{9}$$

where I is the number of electrons excited by the light into the conduction band per unit time, and w_p and w_f are the probabilities of recombination via the shallow donor and the REE, respectively. From the solution of Eq. (9) we obtain the following expression for n_d/N_d:

$$\frac{n_d}{N_d} = \frac{1}{2}\{-(y+j) + [(y+j)^2 + 4j]^{1/2}\}, \tag{10}$$
$$j = 2I/N_d N_c w_p \exp(E_d/kT),$$

where y is connected with the probability of production of paired (P + REE) centers by the relation

$$W = \frac{w_p}{w_f} y = \left[1 - \exp\left(-\frac{4}{3}\pi r_{cr}^3 N_0\right)\right], \tag{11}$$

where W is the probability of production of paired (P + REE) centers, N_0 is the density of the REE in the sample, and r_{cr} is the dimension of the region surrounding the shallow donor center, within which the REE take part in the process of recombination of an electron captured by a shallow donor center. The REE located outside a sphere of radius r_{cr} take no part in the recombination. The dimensions r_{cr} are determined in experiments on the photoconductivity in silicon doped with the REE.[8,9]

The value of n_d/N_d decreases with increasing y, inasmuch as an ever-increasing number of REE atoms are in the immediate vicinity of the donor and participate in the electron recombination process. At larger values of N_0, the electron is in practice not located on the phosphorus atom, and is directed captured by the REE center. In this case, one might think that the degree of optical polarization of the nuclei should be decreased by the increasing density N_0, so that n_d/N_d decreases [see (3)]. It must be recognized here, however, that such a "local" compensation of the donor centers by the REE atoms leads also to a certain decrease of the electron lifetime τ, and correspondingly to an increase of the degree of polarization P_e of the

photoexcited electrons [see (4)]. In this case $I\tau = n_e$ and

$$\frac{1}{\tau} = \frac{2I(1-n_d/N_d)}{N_c \exp(E_d/kT)\, n_d/N_d}. \qquad (12)$$

Thus, on the one hand, the formation of paired (phosphorus + REE) centers leads to a decrease of P_n on account of the decrease of n_d/N_d, and on the other hand a decrease is observed in the electron lifetime, which leads to an increase of P_n because of the increase of P_e. In other words, there exists an optimal REE density in the course of production of paired centers, at which a maximum degree of polarization of the lattice nuclei is reached. As for the spin-lattice relaxation time T_1 of the nuclei [see (7)], it always increases with decreasing n_d/N_d, inasmuch as the density of the parametric donor centers is decreased thereby. Since the increase of the REE density leads to a decrease of n_d/N_d, it follows that T_1 increases with increasing N(Gd). A calculation in accordance with (7) permits a description of the smooth section of the curve in Fig. 1(b).

The calculated dependences of P_n on y are shown in Fig. 2. The same figure shows the experimental results on optical polarization of ^{29}Si nuclei when silicon doped with phosphorus having $N(P) \approx 2 \cdot 10^{13}$ cm^{-3} and gadolinium with varying density is eliminated by circularly polarized light in a magnetic field $H_0 = 7.5$ Oe.

With increasing density of the phosphorus atoms, the probability of production of paired centers begins to increase at lower REE densities, i.e., a smooth increase of P_n should take place at low densities of the REE in the silicon. Calculation and the experimental data on the optical polarization of nuclei in silicon doped with gadolinium and containing phosphorus at a density $2 \cdot 10^{14}$ cm^{-3} are also shown in Fig. 2 (curve 5). Analogously, with increasing phosphorus density T_1 increases at lower values of N(Gd), as was in fact observed in experiment.

Figure 3 shows the dependence of P_n on the pump-light intensity in silicon with $N(P) \approx 2 \cdot 10^{13}$ cm^{-3} and with varying gadolinium density. It is seen that at a low REE density the dependence of P_n on I_L is subject to saturation (curve 1), which characterizes the saturation of the filling of the phosphorus donor centers by

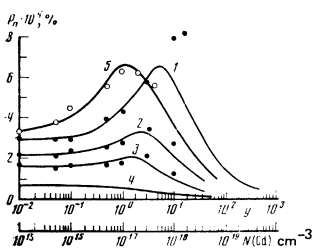

FIG. 2. Plots of P_n against the total gadolinium density N(Gd) at $H_0 = 1$—300 Oe: ● (1–4)—at a phosphorus density $N(P) \approx 2 \times 10^{13}$ cm^{-3}, 1) $I_L = I_{max}$; 2) $I_L = 0.5I_{max}$; 3) $I_L = 0.3I_{max}$; 4) $0.1I_{max}$; ○(5)—at $N(P) \approx 2 \cdot 10^{14}$ cm^{-3}, $I_{max} = 3 \cdot 10^{18}$ cm$^{-3} \cdot$ sec^{-1}. Solid curve—calculated plots of P_n vs y.

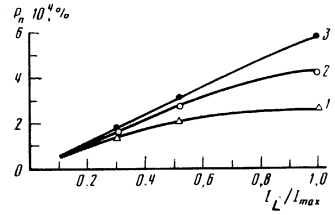

FIG. 3. Dependence of P_n on the pump-light intensity I_L/I_{max} in silicon doped with gadolinium and phosphorus with $N(P) \approx 2 \times 10^{13}$ cm^{-3} at $H_0 = 20$–300 Oe: Δ—N(Gd) = 10^{15} cm^{-3}, ○—10^{17} cm^{-3}, ●—$3 \cdot 10^{17}$ cm^{-3}, 1, 2, 3—calculated plots of P_n vs I_L/I_{max}: 1) $y = 10^{-2}$, 2) $y = 1$, 3) $y = 3.16$.

electrons. The REE impurity does not take part in the electron recombination in this case. At large gadolinium densities, the dependence of P_n on the pump light intensity I_L is practically linear, i.e., the phosphorus atoms in these samples are much less filled and the electrons, which recombine via the phosphorus atoms, stay on the center for a short time and are immediately captured by the REE centers that are located alongside.

The calculations have thus shown that the smooth growth of P_n and T_1 shown in Figs. 1(a) and 1(b) at a density N(Gd) > 10^{16} cm^{-3} is due to the contribution made to the polarization and relaxation of the nuclei by the (shallow donor + REE) pair centers produced under these conditions. The paired centers may turn out to be more effective in the polarization of the lattice nuclei than shallow donor centers, so that the use of paired centers as a source of lattice-nuclei polarization is one of the ways of attaining an appreciable nuclear polarization in semiconductors. On the other hand, optical polarization of the nuclei can be used to investigate phenomena that accompany transitions between impurities in semiconductors.

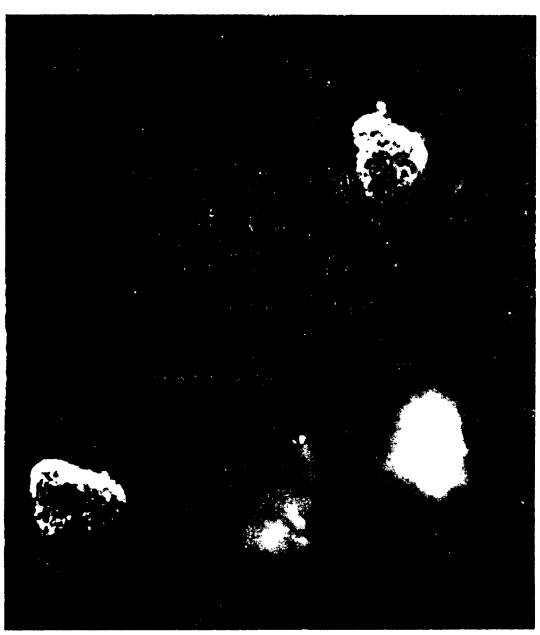

FIG. 4. Group of second-phase inclusions on mechanically polished silicon doped with gadolinium at N(Gd) > 3×10^{18} cm^{-3}.

2. Optical polarization of lattice nuclei in Si:REE containing large inclusions of the second phase

In silicon single crystals with a high gadolinium density [$> 3 \cdot 10^{18}$ cm^{-3}, this is precisely the density at which a giant anomaly is observed in the optical polarization of the nuclei, see Figs. 1(a) and 1(b)], large inclusions of the second phase were observed and were exhaustively investigated by the procedure described above. The first to observe and study second-phase inclusions containing an appreciable density of rare-earth impurities were Dranchuk *et al.*[15]

Figure 4 shows the results of investigations of inclusions of the second phase in gadolinium-doped silicon [$N(\mathrm{Gd}) > 3 \cdot 10^{18}$ cm^{-3}], performed with the aid of a raster electron microscope. The inclusions of the second phase can take different forms: triangles, as shown in Fig. 4, oriented along the principal crystallographic directions of the ⟨111⟩ plane, "boats," "comets," etc.

It should be noted that the formation of large inclusions of the second phase in silicon containing other REE or transition-element impurities takes place at concentrations that differ from $3 \cdot 10^{18}$ cm^{-3}. Thus, in Si:Pr the inclusions are produced at $N(\mathrm{P}) \approx 5 \cdot 10^{19}$ cm^{-3}, while at Si:Ti they are produced at $N(\mathrm{Ti}) \approx 10^{21}$ cm^{-3}. The reason is the difference between the solubility limits of the impurities in the silicon. In the samples investigated by us, which were doped with gadolinium, the density of the large inclusions N_1 ranged from 10^7 to $5 \cdot 10^9$ cm^{-3}, and their dimensions were $2R \approx 10$ μm. The density of the gadolinium impurity inside the inclusion differed by several orders of magnitude (10^{17}–10^{18} cm^{-3} outside the inclusions, whereas the density of the gadolinium inside the inclusions, according to local x-ray spectral analysis data, ranged in the samples from 10^{20} to $5 \cdot 10^{20}$ cm^{-3}).

According to the results of investigations of the magnetic susceptibility, magnetic-ordering processes are observed in silicon containing large inclusions of a second phase with large gadolinium density.[16] Measurements of the temperature dependences of the resistivity ρ in the investigated samples have revealed the presence of a giant growth of ρ at a negligible decrease of the temperature below room temperature.[17] This effect is due to localization of the electrons on the inclusions of the second phase, where the magnetic moments of the REE impurity are coupled by exchange interaction via the conduction electrons of via the electrons captured by shallow impurity centers.[17] Since the conduction-electron density in weakly doped silicon is low, no magnetic ordering is observed in the entire volume of the large second-phase inclusion. Some of the magnetic-impurity atoms (REE) (for example, the atoms surrounding the donor center of the phosphorus that is present inside the second-phase inclusion), for example, become magnetically ordered, and this produces in the second-phase inclusions local regions with magnetic orders; these are ferrons.[18] Ferrons can be free, produced by convectión electrons, as well as localized, in the production of which impurities take part.[18]

Thus, when the temperature is lower the conduction electrons becomes intensively localized on the second-phase regions and lead to formation of ferrons. This leads in turn to the experimentally observed giant increase of the resistivity[17] and to the anomalous increase of the degree of optical polarization of the nuclei [Figs. 1(a) and 1(b)].

In silicon doped with REE and containing shallow donor impurities, the nuclear-polarization centers are ferrons localized on the donor impurity centers.[1)] The degree of optical polarization of the nuclei can in this case be substantially larger than in the case of the interaction of lattice nuclei with donor electrons in the absence of a "magnetic shell," since the photoexcited spin-oriented electrons are instantly captured by the second-phase inclusion to form ferrons, and in this case there is no spin-lattice relaxation of the electrons in the conduction band [see (4)].

It should be noted that the nuclei can become polarized via interaction with ferrons localized on various lattice defects.[19]

The ferron energy E_f and the ferron wave function needed, as will be shown below, to calculate the optical polarization of the nuclei, were obtained by solving the Schrödinger equation for an electron captured by a shallow donor center, with account taken of its surrounding "magnetic shell" that consists of magnetic-impurity atoms coupled by exchange interaction via the impurity electron:

$$-\frac{\hbar^2}{2m}\Delta\Psi_f - \frac{e^2\Psi_f}{\varepsilon r} + \frac{a}{L}N\langle S\langle L\rangle\rangle\Psi_f = E\Psi_f. \tag{13}$$

We determine the average spin $\langle L\rangle$ of the magnetic impurity by assuming that it is connected with polarization of the impurity in the magnetic field of the donor electron:

$$\langle L\rangle = \left[L+\frac{1}{2}\right]\mathrm{cth}\left(\frac{(L+1/2)a}{LkT}|\Psi(r)|^2\langle S\rangle\right) - \frac{1}{2}\mathrm{cth}\left(\frac{a}{2kTL}|\Psi(r)|^2\langle S\rangle\right), \tag{14}$$

L is the spin of the magnetic impurity, S is the spin of the electron, and N is the density of the magnetic impurity that surrounds the donor center.

Figures 5 and 6 show the temperature dependence of the ferron energy and the density of the ferron wave

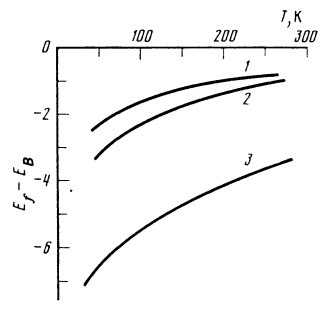

FIG. 5. Calculated dependence of the ferron energy E_f on the temperature for silicon containing a large REE density (E_B is the Coulomb energy for an electron localized on a shallow donor impurity, $E_d = -0.044$ eV for phosphorus in silicon). 1) $N = 10^{20}$ cm^{-3}, 2) $N = 2 \cdot 10^{20}$ cm^{-3}, 3) $N = 4 \cdot 10^{20}$ cm^{-3}.

function, both obtained by solving Eq. (13) for different values of the density of the magnetic impurity that participates in the formation of the ferron (the density of the REE inside the second phase regions is: $1-N\approx10^{20}$ cm^{-3}, $2-N\approx2\cdot10^{20}$ cm^{-3}, $3-N\approx4\cdot10^{20}$ cm^{-3}, corresponding to the gadolinium densities inside the second-phase inclusions in the samples used in the experiments on optical polarization of the nuclei).

The solution of the Schrödinger equation (13) yielded, together with the temperature dependence of E_f, also the temperature dependence of $|\Psi_f(r)|^2$. With decreasing temperature, $|\Psi_f(r)|^2$ behaves exactly in the same manner as when the magnetic impurity that participates in the formation of the ferron increases (see Fig. 6).

It is seen from Fig. 6 that when the ferron energy is increased, either by decreasing T or by increasing the magnetic-impurity density N, the wave function no longer propagates over large distances, as in the case of a shallow donor center in the absence of a magnetic shell. Thus, when E_f is increased the (phosphorus + magnetic shell) impurity center becomes non-hydrogenlike. This should lead to a redistribution of the contribution made to the optical polarization of the nuclei by the dipole-dipole and contact interactions [see Eqs. (3) and (5)]. At low temperatures or at high densities of the magnetic impurity that participates in the formation of ferrons, the predominant role in the hyperfine interaction is played by the dipole-dipole interaction of the ferrons with the surrounding semiconductor lattice nuclei, while at high temperatures and not-too-high densities, where the envelope of the ferron wave function is close to exponential (see Fig. 6), contact interaction predominates.

We consider now the hyperfine interaction between a lattice nucleus located at a distance r from a ferron localized on a donor center, with an electron that participates in the formation of the ferron, as well as with the magnetic shell made up of the magnetic impurities. Let

$$\mathbf{J}=\sum_n \mathbf{j}_n+\mathbf{S}$$

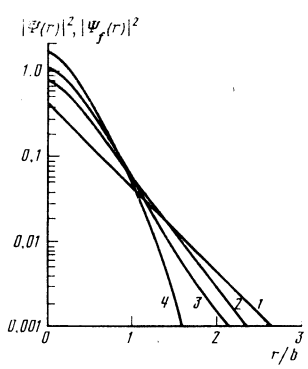

FIG. 6. Calculated dependence of the density of the ferron wave function $\psi_f(r)^2$, $T=77$ K, b—Bohr radius: 1) calculated dependence of the density of the wave function for a shallow donor center in the absence of REE: 2) $N\approx10^{20}$ cm^{-3}, 3) $N\approx2\times10^{20}$ cm^{-3}, 4) $N\approx4\cdot10^{20}$ cm^{-3}.

be the angular momentum of the ferron, $\mathbf{j}_n$ the angular momentum of the magnetic impurity, and $\mathbf{S}$ the angular momentum of the electron participating in the ferron formation,

$$\mathbf{j}_n=|j_n|\mathbf{J}/|J|, \quad \mathbf{S}=\mathbf{J}/2|J|,$$

where $|J|$ is the ferron spin.

The Hamiltonian of the interaction of the ferron with the lattice nucleus can be represented in the form

$$\mathcal{H}_{hf}=\gamma_j\gamma_n\hbar^2\mathbf{I}\sum_n\left[\frac{1}{r_n^3}\left(\mathbf{j}_n-\frac{3\mathbf{r}_n(j_n\mathbf{r}_n)}{r_n^2}\right)\right]$$
$$+\gamma_e\gamma_n\hbar^2\mathbf{I}\left\{\frac{1}{r^3}\left[\mathbf{S}-\frac{3\mathbf{r}(\mathbf{S}r)}{r^2}\right]-\frac{8\pi}{3}\mathbf{S}|\Psi_f(r)|^2\right\}. \quad (15)$$

Participating in the polarization of the lattice nuclei are optically spin-oriented electrons captured by donor centers, as well as the magnetic shell polarized by them. The magnetic shell always interacts with the lattice nuclei via dipole-dipole interaction, and the electron can interact with the lattice nuclei both via the dipole-dipole interaction and by contact interaction.

The analysis of the contribution made to the optical polarization of the nuclei by the dipole-dipole and contact interaction was subsequently carried out by us in analogy with (2)–(5). w_{1ef} differs from w_{1e} (2) in that the wave function in w_{1ef} is that of the ferron (Fig. 6), which can be non-hydrogenlike,

$$w_{1df}=w_{1d}|J|^2, \quad w_{2f}=w_2|J|^2, \quad w_{3f}=w_3|J|^2.$$

The value τ_{ef} of the correlation time of the ferron field on the lattice nuclei, which is used to calculate w_{1ef}, w_{1df}, w_{2f}, and w_{3f}, differs from $\tau_c=1/w_4$, which we used earlier to calculate the characteristic polarization of nuclei in phosphorus-doped silicon.

Upon production of ferrons, contributions to the modulation of the field at the lattice nuclei can be made not only by thermal hopping between the donor level and the conduction band, but also by other processes, such as exchange with spin flip. We have therefore used in the calculations the values $\tau_{ef}=4\cdot10^{-8}$ sec and $\tau_c=10^{-10}$ sec for phosphorus centers in silicon.

In analogy with the scheme described above, we calculated for various densities N (10^{20}, $2\cdot10^{20}$, $4\cdot10^{20}$ cm^{-3}) and various temperatures the dependences of $\rho=\sup\{\delta_{ef}, \delta_{df}, \beta_{ef}, \beta_{df}\}$ on the external magnetic field H_0 and on the intensity of the pumping light.

A plot of P_n against H_0 for various N is shown in Fig. 7. The time τ_{sf} of the spin-lattice relaxation of the ferron on the lattice nuclei, which was used in the calculations, was determined from the data of Ref. 20:

$$\frac{1}{\tau_{sf}}=\frac{2\omega_{cf}^2\tau_{cf}}{3(1+\omega_e^2\tau_{cf}^2)} \quad (16)$$

ω_{cf} is the frequency of the collision of the hyperfine of the nucleus of the lattice at the ferron: $\omega_{cf}^2=\gamma_e^2H_F^2$, H_F is the effective field of the lattice nuclei at the ferron,

$$\omega_{cf}^2=32\gamma_n^2\hbar^2\eta^2\gamma_e^2/|J|^2b^6.$$

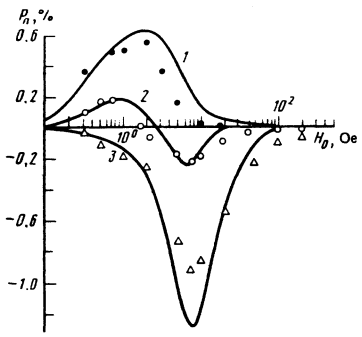

FIG. 7. Dependence of the degree of optical polarization P_n of ^{29}Si nuclei on H_0 in gadolinium-doped silicon, $N(P) \approx 2 \cdot 10^{31}$ cm^{-3}; ●—total gadolinium density $N(Gd) \approx 2 \cdot 10^{19}$ cm^{-3}; gadolinium density in the second phase inclusions $N \approx 4 \cdot 10^{20}$ cm^{-3}; ○—$N(Gd) \approx 10^{19}$ cm^{-3}, $N \approx 2 \cdot 10^{20}$ cm^{-3}; △—$N(Gd) \approx 5 \cdot 10^{18}$ cm^{-3}, $N \approx 10^{20}$ cm^{-3}. Solid curves—calculated plots ($\tau_f = 1.2 \cdot 10^{-4}$ sec) 1) $N = 4 \cdot 10^{20}$ cm^{-3}, 2) $N = 2 \cdot 10^{20}$ cm^{-3}, 3) $N = 10^{20}$ cm^{-3}.

Figure 7 shows the experimental results on optical polarization of the nuclei in silicon-containing second-phase inclusions in which the gadolinium density was $N \approx 4 \cdot 10^{20}$ cm^{-3} for the first sample, $N \approx 2 \cdot 10^{20}$ cm^{-3} for the second sample, and $N \approx 4 \cdot 10^{20}$ cm^{-3} for the third. According to the experimental data, $\tau_f \approx 1.2 \cdot 10^{-4}$ sec.

It is seen that at a gadolinium density 10^{20} cm^{-3} inside the second phase, the polarization of the lattice nuclei is the result of contact interaction with the ferron. At $N \approx 2 \cdot 10^{20}$ cm^{-3} contributions to the polarization are made by both the contact and the dipole-dipole interaction, while at $N \approx 4 \cdot 10^{20}$ cm^{-3} the wave function is so localized on the donor center (see Fig. 6) that the contact interaction is completely suppressed and the contribution to the polarization of the lattice nuclei is made only by the dipole-dipole interaction. Therefore on Fig. 1(a), which shows the plot of P_n against the total gadolinium density, at $H_0 = 7.5$ Oe there is first a jump in the degree of polarization P_n, corresponding to the formation of inclusions of the second phase ($N \approx 10^{20}$ cm^{-3}), followed by a decrease of P_n, owing to the suppression of contact interaction, upon increase of the gadolinium density inside the second-phase inclusion; this increase accompanies the increase of the total density N_0.

By decreasing the lifetime τ_f of the electrons in the ferron it is possible to optimize the conditions for obtaining large values of P_n. Thus, optical polarization of the lattice nuclei in Si: ⟨P + Pr⟩, where $\tau_f \approx 10^{-5}$ sec ($N \approx 2 \cdot 10^{20}$ cm^{-3}), yielded a value $P_n \approx 1.5\%$ for dipole-dipole hyperfine interaction ($H_0 = 1$ Oe).

Since all the electrons are captured by the second-phase inclusion when ferrons are produced,[17] the phosphorus centers between the inclusions remain empty and do not contribute to the nuclear spin-lattice relaxation. In this case the centers of the optical polarization of the nuclei and of the nuclear spin-lattice relaxation are the second-phase inclusions themselves. The rate of nuclear spin-lattice relaxation is given by

$$1/T_1 = 4\pi N_1 DR. \qquad (17)$$

Since the density of the inclusions of the second phase is low ($N_1 \approx 5 \cdot 10^9$ cm^{-3} in the samples employed in the experiments), the distances between the nuclear-relaxation centers become tremendous, and this leads according to (17) to a giant jump in the time T_1 [see Fig. 1(b)].

It should be noted that within the second-phase inclusions, which are of considerable size, there is also diffusion of nuclear spin between the ferrons localized on the phosphorus centers (meaning diffusion within the relaxation center comprising the second-phase inclusion). The high REE density within the second-phase inclusion influences the nuclear-diffusion mechanism.[21]

If the conduction-electron density is high, then some of the electrons are not captured by the second-phase inclusion.[17] This leads automatically to the filling of the phosphorus centers outside the inclusions by electrons. Thus, an excess of the conduction electrons should eliminate the jump observed in Fig. 1(b) in the time T_1 of the nuclear spin relaxation. In this case T_1 is given by

$$1/T_1 = 4\pi N_1 DR + 1/T_{1P}, \qquad (18)$$

$1/T_{1P}$ is the rate of nuclear relaxation on account of the phosphorus centers outside the inclusions and is determined by (7). The calculated dependence of T_1 on the phosphorus density in silicon-containing second-phase inclusions with magnetic impurity is shown in Fig. 8. The same figure shows the results of experiments on the investigation of the nuclear spin-lattice relaxation in silicon containing phosphorus in various concentrations (the gadolinium density in the second-phase inclusions is the same for all samples, $N \approx 10^{20}$ cm^{-3}).

The appearance of filled phosphorus centers outside the second-phase inclusions at large density $N(P)$ leads to leakage of the nuclear polarization that appears in the crystal on account of diffusion of the nuclear spin between the inclusions. The nuclear polarization leakage coefficient is given in this case by

$$f = \frac{4\pi N_1 DR}{4\pi N_1 DR + 1/T_{1P}}. \qquad (19)$$

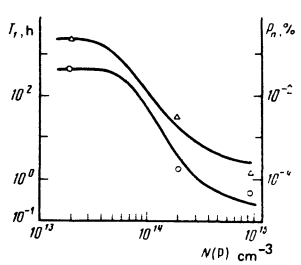

FIG. 8. Dependences of T_1 (○) and P_n (△) on the phosphorus density $N(P)$ in samples of silicon containing gadolinium ($N = 2 \cdot 10^{20}$ cm^{-3}) and illuminated by circularly polarized light in a magnetic field $H_0 = 8.5$ Oe. Solid curves—calculated relations.

The dependence of P_n on H_0 in silicon-containing second-phase inclusions with magnetic impurities, calculated with account taken of (19), is shown in Fig. 8. The same figure shows the experimental results for silicon containing second-phase inclusions with gadolinium.

Similar results were obtained by optical pumping with a large light flux ($I_{max} = 3 \cdot 10^{18}$ cm^{-3}/sec). In this case, [17] the second-phase inclusions can likewise not capture all the conduction electrons, and this has led to the experimentally observed decrease of P_n and T_1.

Thus, an appreciable polarization of the lattice nuclei can result from local magnetic ordering with formation of ferrons in semiconductors doped with magnetic impurities.

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[1)] In the course of measurements of the dependence of the time of nuclear spin lattice relaxation with allowance for diffusion of the nuclear spin within inclusions of the second phase on the pump-light intensity, we have observed in the experiment that the free ferrons, just as the conduction electrons,[2,3] make practically no contribution whatever to the nuclear relaxation and to the polarization of the nuclei.

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