Optical polarization of lattice nuclei in plastically deformed silicon

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The processes of optical polarization of lattice nuclei are investigated in plastically deformed n- and p-type silicon. It is shown with the aid of nuclear magnetic resonance that an appreciable polarization of the lattice nuclei is produced when the plastically deformed silicon crystals are optically pumped with unpolarized light. This depolarization is due to formation of centers with spin $S > \frac{1}{2}$ on the dislocation chains when the photoexcited electrons recombine. The investigations have determined the role played by broken nuclear bonds of the edge dislocations and of centers induced by the deformation potential. It is shown that the optical polarization of the lattice nuclei depends on the degree of filling of the edge dislocations, as well as on the transport processes along the dislocation chains.

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1. INTRODUCTION

Recent investigations of optical polarization of nuclei (OPN) in silicon[1–4] have established the important role of lattice defects as centers of polarization and magnetic relaxation of ^{29}Si nuclei. DPN processes were studied in silicon containing various defects, such as impurity atoms with deep and shallow levels in the forbidden band,[1,2] and radiation and thermal defects.[3,4] In certain charge states these defects are paramagnetic and their spin state can change when the crystal is illuminated. Spin polarization of ^{29}Si lattice nuceli is due to the presence of time-modulated hyperfine interaction between the electron spins of the paramagnetic centers whose polarization, when iluminated in a magnetic field, is different from the equilibrium Boltzmann polarization, and of their nearest lattice nuclei. The polarization of the nuclei propagates from the centers over the entire crystal volume via nuclear spin diffusion.[5] The nuclear polarization produced by illuminating crystals in a magnetic field is recorded and measured by the usual nuclear magnetic resonance technique by amplifying the NMR signals of the ^{29}Si.

The deviation of the spin polarization of the paramagnetic impurity centers from the Boltzmann value is the result of capture of electrons that are nonequilibrium in spin and are excited into the conduction band by circularly polarized or unpolarized light with a photon energy corresponding to the width of the forbidden band.[1,2] In a number of cases DPN was observed in silicon following impurity absorption of light.[6] The polarization of paramagnetic centers can be changed also via exchange scattering of oriented conduction electrons by the centers.[7] We note that the direct interaction of ^{29}Si nuclei with optically oriented conduction electrons is quite small and does not lead to noticeable polarization and relaxation of the nuclei.[8] The dynamic polarization of the lattice nuclei and their relaxation time are determined entirely by electrons localized on the crystal defects.

The use of circularly polarized light produces in silicon containing impurity centers much large degrees of polarization of the ^{29}Si nuclei than illumination by unpolarized light, inasmuch as circularly polarized light leads to a larger deviation of the spin polarization of the photoexcited electrons, and hence of the paramagnetic centers from their Boltzmann values.[9]

It was observed, however, in silicon containing radiation effects that the degree of DPN does not depend on the polarization of the pumping light, and hence on the spin polarization of the photoexcited electrons.[3] The polarization of the ^{29}Si nuclei in such silicon crystals is due to the presence of structure defects which are in excited triplet states and have a nonequilibrium population of the magnetic sublevels under illumination.

The influence of the properties of the defects on OPN processes and on the magnetic relaxation of ^{29}Si nuclei is the basis of the use of the OPN and NMR methods for the investigation of doped silicon single crystals, for the study of the properties of point defects, and for the investigation of the decay of solid solutions of impurities in silicon.[10,11]

It is of interest to investigate with the aid of OPN silicon single crystals containing edge dislocations having on their cores, as in point defects, unpaired broken-bond electrons that act as donor or acceptor, depending on the position of the Fermi level.[12,13]

The recent interest in the study of plastically deformed silicon is due to the fact that the dislocations constitute an illustrative model of a one-dimensional Fermi system. The presence of unpaired electrons on linear dislocation chains can be easily observed by the EPR method.[14,15] It has been established that a one-dimensional system of electrons of dislocation-core broken bonds is in a state of a Mott-Hubbard dielectric with a gap 0.25 eV and with band widths E_1, $E_2 \approx 0.06$ eV, located at the center of the silicon band gap.[13] The band wisths of a Mott-Hubbard dielectric is governed by the exchange interaction of the electrons of neighboring broken bonds (E_1 $E_2 \approx 0.06$ eV, coresponding to a distance $r = 5$ Å between the broken bonds). At a temperature $T > 50$ K the broken-bond electrons are in a paramagnetic state, and at $T \lesssim 45$–50 K they go over into an antiferromagnetic state.[16]

Besides the levels connected with the presence of broken bonds on the dislocation cores, strains can produce in

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the forbidden band of silicon an entire system of levels connected with the Coulomb and deformation potentials.[13] Other features of plastically deformed silicon are the presence of microwave conductivity along the dislocation chains[13] and of a spin-dependent carrier recombination.[17]

We have investigated OPN processes in plastically deformed silicon single crystals and studied the OPN peculiarities connected with the peculiarities of dislocations as linear defects, with carrier recombination, and with carrier motion along the dislocations.

2. MECHANISM OF OPTICAL POLARIZATION OF NUCLEI IN SEMICONDUCTORS

We consider briefly the OPN mechanisms in semiconductors containing various defects, and the main regularities that manifest themselves in OPN and NMR experiments.

The magnitude and direction of nuclear polarization relative to the external magnetic field in which the crystal is illuminated are determined by the deviation of the degree of polarization P_e of the paramagnetic centers from its equilibrium value P_{e0}, by the relative contribution made to the hyperfine interaction by the contact and dipole-dipole interactions, as well as by the mechanisms whereby this interaction is modulated.

The degree of the OPN produced in a crystal by optical pumping is described by the expression

$$\frac{dp_n(t)}{dt}=-\frac{p_n(t)-P_{n0}}{T_1}-\xi\frac{P_e-P_{e0}}{T_{1e}}, \tag{1}$$

where P_{n0} is the equilibrium Boltzmann polarization of the lattice nuclei, ξ is a factor that determines the contribution made to the nuclear polarization by electron-nucleus transitions of various types in contact and dipole-dipole interactions of the lattice nuclei with paramagnetic centers that are nonequilibrium in spin, T_{1e} is the time of nuclear spin-lattice relaxation and determines the processes that polarize the lattice nuclei, T_1 is the total time of the nuclear relaxation $(T_1=(1/T_{1e}+1/T_1')^{-1})$ due both to the polarization-centers (T_{1e}) and to extraneous paramagnetic impurities (T'_1) that lead to leakage of the nuclear polarization.[2]

The time T_{1e} is determined by the distance between the paramagnetic centers, the polarization between which propagates via nuclear spin diffusion. At optical polarization, the OPN is initially produced inside a sphere of radius ρ around each center, as a result of hyperfine interaction with the paramagnetic centers that are in a nonequilibrium spin state, and becomes established after a time T_1 in the entire volume of the crystal. (The value of ρ for different impurity centers in silicon is of the order of 10–50 Å, Ref. 2). It is important to note that the magnitude and sign of the nuclear polarization in the entire volume of the crystal, due to the nuclear spin diffusion, are determined by the magnitude and sign of the polarization of the nuclei at a distance $r=\rho$ from the paramagnetic center, determined in turn primarily by which of the hyperfine-interaction components predominates at the distance ρ; this is accounted for in Eq. (1) by the factor ξ (Ref. 2):

$$\xi=\frac{w_3-w_{1c}-w_{1d}}{w_{1c}+w_{1d}+2w_2+w_3}, \tag{2}$$

where

$$w_{1c}=C_1(n_d/N_d)(1+\omega_e^2\tau_c^2)^{-1}|\psi(r)|^4$$

is the probability, per unit time, of nuclear spin flip with simultaneous electron spin flip in the opposite direction, induced by the fluctuating contact interaction between the nuclear spin I and the electron spin S of the paramagnetic center;

$$w_{1d}=C_2(n_d/N_d)(1+\omega_e^2\tau_c^2)^{-1}r^{-6}$$

is the probability of flips of the nuclear and electron spins in opposite directions (flip-flop transitions) in dipole-dipole hyperfine interaction;

$$w_2=C_3(n_d/N_d)(1+\omega_n^2\tau_c^2)^{-1}r^{-6}$$

is the probability of nuclear spin flip without electron spin flip in dipole-dipole interaction;

$$w_3=C_4(n_d/N_d)(1+\omega_e^2\tau_c^2)^{-1}r^{-6}$$

is the probability of nuclear and electron spin flips in the same direction (flip-flip transitions) in dipole-dipole interaction; the coefficients C_1, C_2, C_3, and C_4 were calculated in Ref. 2; τ_c is the correlation time of the fluctuating hyperfine interaction and is determined, for centers that produce shallow levels in the forbidden band, by the probability, per unit time, of thermal excitation of the electron from the level into the conduction band, w_T, i.e., $\tau_c=1/w_T$. For centers with deep levels, τ_c coincides with the spin-relaxation time τ_s of the paramagnetic centers; $|\psi(r)|^2$ is the density of the wve function of the localized electron, and for shallow hydrogen-like centers

$$|\psi(r)|^2=(\eta/\pi b^3)\exp(-2r/b),$$

where η is the degree of localization of the wave function of the conduction electrons at the lattice sites ($\eta=186$ for silicon[18]), b is the Bohr radius of the localized electron, $\omega_e=\gamma_e H_0, \omega_n=\gamma_n H_0$ are the Larmor frequencies of the electron and the nucleus in the magnetic field H_0; γ_e and γ_n are the gyromagnetic ratios of the electron and the nucleus, n_d/N_d is the degree of filling of the donor centers by electrons, and N_d is the density of these centers.

Thus, ξ is a function of the distance r from the paramagnetic center, and in Eq. (1) it is necessary to use ξ at $r=\rho$.

If the contact interaction predominates in the hyperfine interaction, a situation typical of shallow hydrogenlike donor centers, then ξ is negative, as can be seen from (2). In the case when the dipole-dipole interaction predominates, as is typicak of deep impurity centers in which the impurity-electron wave function is localized near the center, ξ is positive.[2] The dipole-dipole and contact interactions lead therefore to oppositely directed nuclear polarization by optical pumping.

In strong magnetic fields, when $\omega_e\tau_c\gg 1$, we have $\xi\to 1$, inasmuch as under these conditions the predominant probability is w_2, which corresponds to nuclear-spin transitions that are not accompanied by electron spin flip and do not lead to polarization of the nuclei. In this case the OPN decreases and eventually vanishes with increasing H_0.

In the same magnetic fields, an increase is observed in the time of the nuclear spin-lattice relaxation T_1, defined for

the entire volume of the crystal by[5]

$$\frac{1}{T_1}=4\pi N_d\int_\rho^\infty \frac{r^2}{T_1(r)}dr, \quad (3)$$

where $1/T_1(r) = 2(w_{1c} + w_{1d} + 2w_2 + w_3$ is the rate of the-local relaxation of the lattice nuclei located at a distance r from the paramagnetic center, D is the coefficient of nuclear spin diffusion ($D = 2.4\times 10\text{–}14\ \text{cm}^2/\text{sec}$ for silicon[5]).

From the dependence of T_1 on H_0 we can determine the correlation time τ_c by measuring the magnetic field H_0 at which the growth of T_1 begins:

$$\tau_c=1/\gamma_e H_0'. \quad (4)$$

In the case of shallow hydrogenlike centers, knowing $\tau_c = 1/w_T$ we can determine the ionization energy of this center.

In OPN experiments one measures the degree of polarization $P_n(t)$ of the lattice nuclei of the entire volume of the crystal as a function of the illumination time t. It can be seen from (1) that this dependence is exponential with a time constant T_1. From this dependence one determines the time T_1 of the spin lattice relaxation of the nuclei and the stationary degree P_n of the OPN; an expression for the latter is obtained from (1) at $dp_n(t)/dt = 0$

$$P_n=P_{n0}-\xi f(P_e-P_{e0}), \quad (5)$$

where $f = T_1/T_{1e}$ is the nuclear-polarization leakage factor.

Thus, the lattice nuclear polarization produced in a crystal by optical pumping is determined to a considerable degree by the deviation of the degree of polarization P_e of the paramagnetic centers from its equilibrium value P_{e0}, in accord with the results of Ref. 19:

$$P_e-P_{e0}=(P_e^i-P_{e0}^i)\frac{\tau_s}{\tau_s+\tau}\frac{\tau_{sd}}{\tau_{sd}+\tau_d}, \quad (6)$$

where P_e^i is the maximum polarization of the photoexcited electrons in the conduction band, and P_{e0}^i is its equilibrium value. The factor $\tau_s/(\tau_s + \tau)$ describes the decrease of the electronpolarization due to their spin relaxation (τ_s) over the lifetime in the conduction band (τ), and $\tau_{sd}/(\tau_{sd} + \tau_d)$ takes into account the decrease of the polarization of the localized electrons due to their spin relaxation τ_{sd}) during their sojourn on the center (τ_d).

In pure silicon crystals $\tau_s \ll \tau$, and this leads to a considerable decrease of $P_e - P_{e0}$ and consequently of the degree P_n of the nuclear polarization. The difference $P_e - P_{e0}$, and accordingly also P_n, can be greatly increased by shortening τ via introduction of compensating impurities with deep levels into the semiconductor crystal. The compensation, however, decreases the degree of filling of the centers by electrons, n_d/N_d, and decreases ξ, which leads in turn to a decrease of P_n. That is to say, at a low degree of compensation P_n is small because of the small P_e, and in the overcompensation region P_n decreases because of the decrease of ξ. There exists thus an optimal compensating-impurity density at which maximum values of P_n are reached.[2]

A nonequilibrium polarization of paramagnetic centers in a crystal can be produced by illumination with circularly polarized as well as unpolarized light. If the latter is used, equal numbers of electrons with spin projections $+\frac{1}{2}$ and $-\frac{1}{2}$ are excited into the conduction band, so that the spin polarization P_e^i of the electrons excited by unpolarized light is zero, but differs from the Boltzmann value. A stronger polarization of the conduction electrons, considerably higher than the equilibrium value, is obtained by interband absorption of circularly polarized light. The density ratio of the electrons with spin projections $+\frac{1}{2}$ and $-\frac{1}{2}$ is determined by the corresponding selection rules for the right- and left-polarized light.[20] The use of circularly polarized light leads then to a much higher polarization of the lattice nuclei than in the case of unpolarized light (the maximum polarization in silicon is $P_{e\,\max}^i \approx 25\%$).

As noted in the Introduction, another mechanism of paramagnetic-center polarization, independent of the spin polarization of the electrons in the conduction band, was observed in silicon. This mechanism is a characteristic of paramagnetic centers with spin $S > \frac{1}{2}$ and, in particular, of triplet centers with $S = 1$. The nonequilibrium population of the magnetic sublevels of the triplet centers with $m_s = \pm 1$ and $m_s = 0$, produced by capture of photoexcited electrons, is due to the difference between probabilities of electron capture into states with $m_s = \pm 1$ and $m_s = 0$ and to the selective transition of the center from an excited triplet to a ground singlet state.[21,22]

The maximum nuclear polarization P_n is reached in a magnetic field $H_0 \approx H_D$ corresponding to the region of the anticrossing of the magnetic sublevels of the triplet center. The field H_D is numerically equal to the constant D (expressed in magnetic-field units) that describes the splitting of the magnetic sublevels of the triplet center in a zero magnetic field. In this case

$$P_n=\mathscr{P}_1\frac{\tau_{sT}}{\tau_{sT}+\tau_T}, \quad (7)$$

where $\mathscr{P}_1$ is the maximum degree of polarization of the triplet center at $H_0 \approx H_D$, τ_{sT} is the time of spin relaxation of the triplet center, and τ_T is its lifetime. At $H_0 > H_D$ or $H_0 < H_D$ one observes a decrease of P_n. In strong magnetic fields, $H_0 \gg H_D$, the expression for P_n takes the same form as (5) and (6) with $P_e = 0$.

A similar behavior of the OPN, independent of the pump-light polarization, is observed as a rule in silicon containing structure defects whose broken bonds can be in metastable excited triplet states upon capture of photoexcited electrons. As noted above, edge dislocations in plastically deformed silicon single crystals constitute chains of broken bonds, which can be in excited triplet states upon capture of photoexcited electrons. The possibility of formation of triplet centers on triplet chains was reported in Refs. 23 and 24.

Besides the possible manifestation, in OPN, of triplet centers due to dislocations, one can expect a contribution to the nuclear polarization from the dislocation-chain segments that can become magnetically ordered by exchange interaction via the captured electrons.[16] In this case the mechanism that produces the OPN can be the interaction of the lattice nuclei with ferrons that are nonequilibrium in spin.[19]

3. EXPERIMENTAL PROCEDURE

The investigations were carried out with silicon single crystals of n-type with phosphorus density $N(P) \approx 10^{15}$ cm^{-3} and of p-type with boron density $N(B) \approx 10^{13}$ cm^{-3}, grown by crucibleless zone melting.

The plastic deformation of the crystals and their investigation by the methods of EPR, microwave conductivity, spin-dependent recombination, and other were carried out by Yu. A. Osip'yan, V. A. Grazhulis, V. V. Kveder, and coworkers at the Institute of Solid State Physics of the USSR Academy of Sciences and were subsequently supplied for the OPN investigations.

The crystals were deformed, using the procedure described in Ref. 12, by uniaxial compression at $T = 700$ °C at a constant load 14 kgf/mm^2 in an argon atmosphere. After the deformation the samples were cooled by a procedure such that most point defects were annealed.[12] The characteristics of the investigated samples of the plastically deformed silicon are listed in Table I.

The relative elongation of the sample after deformation is designated $\varepsilon = \Delta l / l$. The degree of filling of the dislocations by electrons (f_n) or by holes (f_p) is defined as the ratio of the density of thephosphorous or boron impurity atoms to the density N_D of the broken bonds. The number of paramagnetic broken bonds in a dislocation chain limited by the captured carriers is $m_s 1/f_{n,p}$.

The OPN experiments were performed by a procedure described in Refs. 1, 2, and 8. The samples were illuminated at $T = 77$ K by light from a 1-kW incandescent lamp. The optical pumping was with both circularly polarized and unpolarized light. The values of the degree of the OPN were determined by measuring the amplitudes of the NMR signals of the ^{29}Si nuclei with a microwave NMR spectrometer with crossed coils. The direction of the nuclear magnetization produced by optical pumping relative to the external magnetic field was determined from the sign of the NMR signal.

In the experiments we measured the dependence of the degree of the OPN on the time of the optical pumping of the crystal in a magnetic field H_0 at a definite light intensity I_l. From this dependence, which is exponential, we determined the limiting degree of polarization P_n of the ^{29}Si nuclei, their spin-lattice relaxation time T_1. We studied the dependences of P_n and T_1 on the magnetic field H_0 in which the samples were illuminated and on the pump-light intensity I_l.

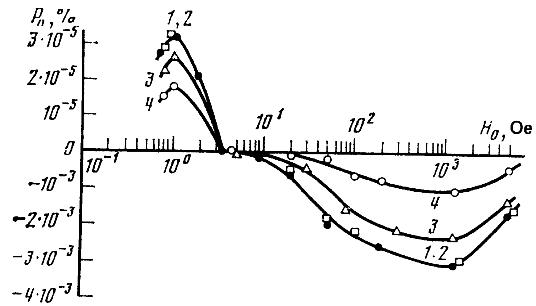

FIG. 1. Dependence of the degree P_n of the OPN on the magnetic field H_0 in plastically deformed silicon illuminated by polarized light, at different degrees of deformation ε, and will phosphorus content $N(\mathrm{P}) \approx 10^{15}$ cm^{-3}: 1—$\varepsilon = 5.1\%$, 2—4.0%, 3—2.0%, 4—1.5%.

4. EXPERIMENTAL RESULTS AND DISCUSSION

No optical polarization of the ^{29}Si nuclei was observed in p-silicon prior to the introduction of the dislocations. In n-type silicon, weak polarization of ^{29}Si ($P_n \approx 10^{-4} - 10^{-5}\%$) was observed when illuminated with circularly polarized light in magnetic fields $H_0 \approx 1$–300 Oe. Optical pumping with unpolarized light in stronger magnetic fields enhanced the polarization of the nuclei, $P_n / P_{n0} \approx -2$. Investigations have shown that the OPN in these crystals is due to the interaction between the ^{29}Si nuclei and the electrons captured by phosphorus centers.[2,8]

After the plastic deformation, an appreciable polarization of the ^{29}Si nuclei was observed in all silicon samples, both n- and p-type, when illuminated by unpolarized light in a wide range of magnetic fields H_0. The enhancement P_n / P_{n0} of the nuclear polarization reached $\approx 3 \times 10^3$. Plots of the degree P_n of the OPN vs H_0 for plastically deformed n-silicon with phosphorus content $N(\mathrm{P}) \approx 10^{15}$ cm^{-3} and of p-silicon with boron density $N(\mathrm{B}) \approx 10^{13}$ cm^{-3}, illuminated by unpolarized light, are shown in Figs. 1 and 2.The negative values of P_n on Figs. 1 and 2 correspond to a direction of P_n opposite to the direction of the equilibrium nuclear polarization P_{n0}. It can be seen from Figs. 1 and 2 that the maximum absolute value of the polarization of ^{29}Si is reached, for all optically pumped samples, in a magnetic field $H_0 \approx 1200$ Oe. With decreasing H_0, a decrease of P_n is observed and at $H_0 < 5$ Oe the ^{29}Si nuclei reveal a weak polarization of opposite sign (the P_n ordinates are shown in Figs. 1 and 2 in enlarged scale). We note that despite the small values of P_n at

TABLE I.

Sample №	Type of conductivity	N, cm^{-3}	ε, %	Δ, 10^r cm^{-2}	Density of broken bonds, N_D, 10^{16} cm^{-3}	f_n, f_p	m_s
1	n	10^{15}	5.1	10—12	5.2	0.019	52
2	n	10^{15}	4.0	7	3	0.033	30
3	n	10^{15}	2.0	3—4	1.5	0.066	15
4	n	10^{15}	1.5	2.5	1.1	0.C9	11
5	p	10^{13}	4.3	7—9	3.5	0.0003	3500
6	p	10^{13}	3.5	4—6	2.4	0.0004	2400
7	p	10^{13}	1.5	2.5	1.1	0.0009	1100

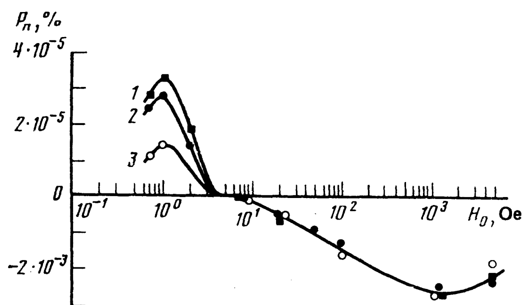

FIG. 2. Dependence of the degree P_n of the OPN on H_0 in plastically deformed p-silicon illuminated by unpolarized light: 1—$\varepsilon = 4.3\%$, 2—3.5%, 3—1.5%.

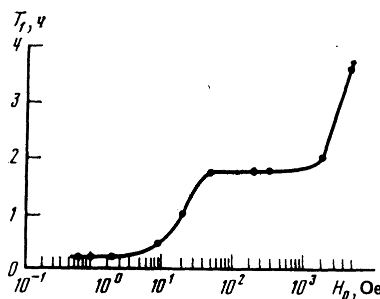

FIG. 3. Dependence of the spin-lattice relaxation time T_1 of the ^{29}Si nuclei on H_0 under optical irradiation in plastically deformed n-silicon with $N(\mathrm{P}) \approx 10^{15}$ cm^{-3} and $\varepsilon = 5.1\%$.

$H_0 \approx 1$ Oe, the enhancement of the nuclear polarization over its equilibrium value, in the same magnetic field, is quite large. The ratio $P_n/P_{n0} \approx 3000$ and is close to the maximum theoretical enhancement of the nuclear polarization in the case when the polarization of the electrons localized on the centers is determined by the deviation of the spin polarization of the photoexcited electrons in the conduction band from the equilibrium polarization. In fact, if it is assumed that $P_e^i = P_e = 0$ when the crystal is illuminated with unpolarized light, i.e., there is no electron relaxation in the conduction bands and on the center, and there is no leakage of the nuclear polarization, $f = 1$, it can be readily obtained from (5) that

$$P_n/P_{n0} = 1 + \xi P_{e0}/P_{n0} = 1 + \xi \gamma_e/\gamma_n. \tag{8}$$

In silicon, $\gamma_e/\gamma_n = 3310$. The maximum theoretical value for ξ in the case of dipole-dipole interaction is $+0.385$ (Ref. 1), and for contact interaction $\xi = -1$. We thus obtain from (8) $P_n/P_{n0} = -3310$ for contact interaction and $P_n/P_{n0} = +1275$ for dipole-dipole interaction. The experimental values of P_n/P_{n0} obtained in various samples of plastically deformed silicon optically pumped by unpolarized light are equal to $+300$ at $H_0 = 1$ Oe and -3000 at $H_0 = 1200$ Oe.

If the OPN in plastically deformed silicon were determined only by spin polarization of the electrons excited by light into the conduction band, it would be natural to expect a much larger nuclear polarization in illumination by circularly polarized than by polarized light, i.e., under these conditions the OPN would be close to the theoretical value ~25%.

Experiments have shown, however, that in silicon single crystals optically pumped with circularly polarized light and plastically deformed in magnetic fields $H_0 > 5$ Oe the degree P_n of the polarization of the ^{29}Si nuclei remained the same as when illuminated with unpolarized light. At $H_0 < 5$ Oe a weak contribution to the polarization of the nuclei from circularly polarized light was observed. This contribution will be discussed below and is due to point donors produced by deformation and not connected with the phosphorus, since it was observed both in n- and p-type silicon (see Figs. 6 and 7 below). There is no connection between OPN processes produced in crystals illuminated by circularly polarized and by unpolarized light in magnetic fields $H_0 < 5$ Oe; they are due to different mechanism of polarization of the lattice nuclei.

In all the plastically deformed silicon samples we measured the dependences of the ^{29}Si spin-lattice relaxation time on the external magnetic field H_0. The dependence for one of the samples is shown in Fig. 3, and the plots for the remaining samples are similar. It can be seen from Fig. 3 that the plot of T_1 vs H_0 has two rising sections at $H_0 \approx 10$ Oe and $H_0 \approx 2$ kOe, pointing to the presence of two different mechanisms of the spin-lattice relaxation. The decrease of the degree P_n of the OPN and the reversal of its sign at $H_0 < 20$ Oe (see Figs. 1 and 2) is also evidence of two different causes of the polarization of the ^{29}Si nuclei when illuminated with unpolarized light, which manifest themselves in "weak" ($H_0 < 5$ Oe) and "strong" ($H_0 > 5$ Oe) magntic fields. This fact confirms in addition that P_n has different dependences on the pump light intensities I_l in magnetic fields $H_0 \approx 5$ Oe and $H_0 \approx 1$ Oe. These dependences for $H_0 \approx 5$ kOe are shown in Fig. 4. It can be seen from this figure that P_n is independent of I_l when the light intensity varies in a wide range from $I_{\max}$ to $0.1\, I_{\max}$. In a weak magnetic field $H_0 \approx 1$ Oe it was

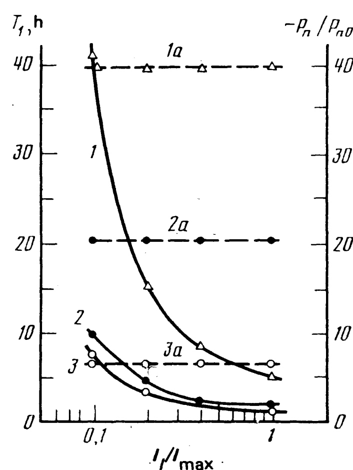

FIG. 4. Dependence of the time of nuclear spin-lattice relaxation T_1 (1,2,3) and of the enhancement of the degree of the OPN, P_n/P_{n0} ($1a,2a,3a$), on the OPN on the pump-light intensity Il: 1, $1a$—p-Si with boron density 10^{13} cm^{-3} and $\varepsilon = 5.1\%$; 2, $2a$—n-Si with $N(\mathrm{P}) \approx 10^{15}$ cm^{-3} and $\varepsilon = 4.0\%$; 3, $3a$—n-Si with $\varepsilon = 1.5\%$; $H_0 = 5.0$ kOe.

impossible to obtain such a dependence because of the low degree of polarization of the ^{29}Si nuclei and accordingly because of the weak NMR signals. It can be stated, however, that at $H_0 \approx 1$ Oe the value of P_n decreases with decreasing I_l, since the polarization of ^{29}Si was no longer observed when I_l was decreased by one-half.

The experimental results show that in plastically deformed silicon crystals there are observed at least three different processes of optical polarization of the ^{29}Si nuclei; these processes are connected with the crystal-structure defects produced by plastic deformation. Two of them are independent of the polarization of the pump light and of the spin polarization of the photoexcited electrons. The onset of strong nuclear polarization when the crystals are illuminated with unpolarized light, the independence of the degree of the OPN of the polarization of the pump light, and the presence of a maximum in the plot of the degree of OPN vs the magnetic field (Figs. 1 and 2, $H_0 > 5$ Oe) are typical of nuclear-polarization processes due to the presence in the crystals of defects that are in excited metastable triplet states when illuminated.[3,21]

This suggests that the OPN in plastically deformed silicon at $H_0 > 5$ Oe is due to polarization centers that are in excited triplet states when illuminated. These centers can be produced in optical excitation as a result of an electron from the conduction band on a broken dislocation bond containing on unpaired electron, into an excited state in which the electron spins are parallel. Such a center will have a spin $S = 1$. The density of the triplet centers increases with increasing light intensity, and this shortens the nuclear spin-lattice relaxation time T_1 (see Fig. 4).

From the experimental results shown in Figs. 1 and 2 we can estimate the constant D that characterizes the level splitting of the triplet centers connected with the dislocation chain in a zero magnetic field. Since the minimum values of P_n are reached at $H_0 \approx H_D \approx 1200$ kOe, it follows that $|D| = 225 \times 10^{-3}$ cm^{-1}.

The triplet centers produced upon capture of electrons from the conduction band by broken dislocation-core bonds differ from the pointlike triplet centers in that they can move along the dislocation chains. The dislocation-chain segments that are in contact with the triplet centers are then polarized. Dipole-dipole interaction of polarized dislocation chains with surrounding ^{29}Si nuclei leads to the appearance of OPN at $H_0 < 5$ Oe in unpolarized light.

Modulation of the hyperfine interaction between the ^{29}Si nuclei and the paramagnetic centers should be produced in the cases considered by two different mechanisms: 1) the interaction of the ^{29}Si nuclei with the triplet centers is modulated by the motion of the triplet centers along the dislocation chains, with a correlation time τ_{c1}; 2) the interaction of the ^{29}Si nuclei with polarized segments of dislocation chains is modulated by spin relaxation of the broken-bond electrons with a time τ_{c2}. The times τ_{c1} and τ_{c2} are generally speaking different: τ_{c1} is determined by the hopping time of the electron captured by the dislocation between neighboring broken bonds. This time can be determined from the value of the magnetic field, $H_0 \approx 2$ kOe, at which an increase of the spin-lattice relaxation time T_1 of the ^{29}Si nuclei is observed (see Fig. 3). For τ_{c1} we obtain $\tau_{c1} \approx (\gamma_e H_0)^{-1} \approx 3 \times 10^{-11}$ sec ($\gamma_e = 1.75 \times 10^7$ rad·Oe^{-1}·sec^{-}).

The time τ_{c2} should be determined by the spin-relaxation time τ_s of the unpaired electrons of the dislocation broken bonds. At $H'_0 \approx 5$ Oe (see Fig. 3 we obtain $\tau_{c2} = \tau_s \approx 10^{-8}$ sec. This time is shorter than the value $\tau_s \approx 1(^{-5}$–10^{-6} sec determined in Refs. 12 and 14. It must be recognized, however, that in Refs. 12 and 14 the time τ_s was determined by an EPR method in a strong magnetic field $H_0 \approx 3$ kOe, while our value τ_{c2} corresponds to $H_0 \approx 5$ Oe. As a rule, the spin-relaxation time increases with increasing magnetic field.[25]

Let us examine the OPN features connected with the presence of donor and acceptor impurities and with the filling of dislocation by carriers in plastically deformed silicon single crystals.

a. Influence of filling of dislocation chains by carriers on OPN processes in plastically deformed silicon

A dislocation chain containing broken bonds can have either donor or acceptor properties.[12,15] Therefore, owing to the presence in silicon of donor or acceptor impurities with shallow levels, the dislocation can capture respectively either electrons or holes. Figure 5 shows plots of the degree P_n of the OPN vs the degree of filling of dislocations by electrons f_n (by holes, f_p), obtained on the basis of the data of Figs. 1 and 2 for two values of the magnetic field, $H_0 = 1.2$ kOe and $H_0 = 1$ Oe.

Consider the behavior of the OPN at $H_0 \approx 1.2$ kOe, when the polarization of the ^{29}Si nuclei is due to their interaction with triplet centers produced upon capture of photoexcited electrons by broken bonds. If the degree of filling of the dislocation chains by holes or by electrons is small, i.e., when the Fermi level coincides with position of the lower band of a Mott-Hubbard dielectric ($E_v + 0.4$ eV),[13] then P_n is independent of $f_{n,p}$ at $H_0 = 1.2$ kOe (see cruve 1 of Fig. 5). With increasing filling of the dislocation chains by electrons, the Fermi level shifts "jumpwise" into the position of the "upper" band of the Mott-Hubbard dielectric ($E_c - 0.4$ eV),[13] and no change of P_n takes place. Further increase of f_n ($f_n \gg 0.04$) is accompanied by motion of the Fermi level towards the conduction band[13] and by a decrease of P_n (Fig. 5, curve 1). The decrease of P_n at $f_n > 0.04$ is due to the longer lifetime τ_T of the triplet center on the dislocation chain with

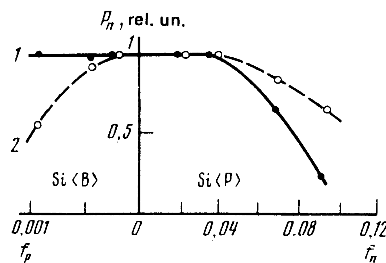

FIG. 5. Dependence of the degree P_n of the OPN on the degree f of filling of the dislocation chains by carriers: 1—at $H_0 = 1.2$ kOe, 2—at $H_0 = 1$ Oe.

increasing f_n (see Eq. (7)). It follows from (7) that at $\tau_T \ll \tau_{sT}$ the value of P_n is independent of τ_T. When τ_T becomes comparable with or larger than τ_{sT},P_n begins to decrease.

The lifetime τ_T of the triplet state can be defined by $1/\tau_T = w_S + w_R$, where w_S is the probability, per unit time, of the transition of the center from the triplet to the singlet state, and w_R is the probability, per unit time, of recombination with a hole. A radiative transition from an excited triplet state to a ground triplet state is forbidden, since $\Delta S = 1$ in this case. Therefore the excited triplet states are usually metastable with large lifetimes. It can therefore be assumed that $w_S \ll w_R$, i.e., the principal process that determines the triplet-center lifetime is recombination—capture of a hole by a dislocation chain.

The length of the dislocation chains in plastically deformed siliconis limited by the intersection points of dislocations located in the same glide plane. In the investigated silicon single crystals the dislocation chains contain on the average $\sim 10^3$ broken bonds. In n-silicon with $n(P) \approx 10^{15}$ cm^{-3} the donor electrons from the phosphorus atoms are captured by the dislocations. In this case the dislocation chain is broken up into sections in which the average number m_s of the broken chain is 10–50 (see Table I). A photoexcited electron captured into a triplet state by some section of a dislocation chain, bounded on both sides by electrons from phosphorus atoms, can stay on this section for a sufficiently long time and experience Coulomb repulsion from the boundary charges. The probability of hole capture by such a dislocation chain, w_R, is proportional to the length of the section, or to m_s, i.e., $w_R \propto \text{ms} \propto f_n^{-1}$. Thus, τ_T increases with increasing f_n. Consequently the increase of the filling of the dislocations by electrons leads to an increase of the lifetime of the triplet center that moves along the dislocation chain, and when this time exceeds the spin-relaxation time of the triplet center, $\tau_T > \tau_{sT}$, which takes place in the investigated samples at $f_n > 0.04$, a decrease is observed in the degree P_n of the OPN (Fig. 5, curve 1).

A somewhat different behavior of the degree of OPN is observed in optical pumping by polarized light in a magnetic field $H_0 = 1$ Oe. As noted above, under these conditions the OPN is due to the interaction of the ^{29}Si nuclei with dislocation-chain segments that acquire spin polarization on account of exchange interaction of the broken-bond electrons via the triplet center, which is ina nonequilibrium spin state and moves along the dislocation chain. In this case the degree of the OPN is decreased by capture of electrons from the donors and of holes from the acceptors, for in this case the length of the dislocation-chain segments responsible for the OPN decreases, and the number of broken bonds that do not participate in the polarization increases. The leakage of the nuclear polarization is then increased (see Eq. (5)). The decrease of P_n with increasing f_p in p-silicon at $H_0 = 1$ Oe takes place at smaller values of $f_{n,p}$ than in n-type silicon, since the presence of holes on the dislocation chains increases the recombination rate of the triplet centers, and this decreases strongly the lengths of the dislocation-chain segments responsible forthe OPN.

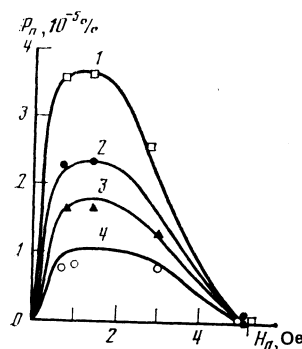

FIG. 6. Dependence of the degree P_n of the OPN on the magnetic field H_0 when plastically deformed n-silicon is illuminated with circularly polarized light: 1—$\varepsilon = 5.1\%$, 2—4.0%, 3—2.0%, 4—1.5%.

b. OPN due to point defects induced by a deformation potential

As already noted above, the influence of the polarization of the light on the OPN processes in plastically deformed n- and p-silicon manifested itself only for optical pumping in weak magnetic fields. The experimental dependences of P_n on H_0, obtained with illumination of plastically deformed n- and p-silicon samples by circularly polarized light, as shown in Figs. 6 and 7. It is important to note that despite the small values of P_n, the influence of the polarization of the pump light on the OPN processes could be separated from the background of the processes described above with sufficiently high accuracy. This was achieved by recording the difference between the degrees of the OPN for optical pumping of the samples with circularly polarized and unpolarized light of equal intensity.

It was established that the sign of P_n (Figs. 6 and 7) for optical pumping by circularly polarized light corresponds to contact interaction of the ^{29}Si nuclei with electrons captured by lattice defects, a situation typical for shallow donor centers.[2] It was thus shown that the OPN produced in optical pumping with circularly polarized light in plastically deformed silicon is due to shallow donor centers not connected with broken bonds of the dislocation chains that are in an equilibrium spin state, regardless of the polarization of the pumping light ($H_0 < 5$ Oe, Figs. 1 and 2).

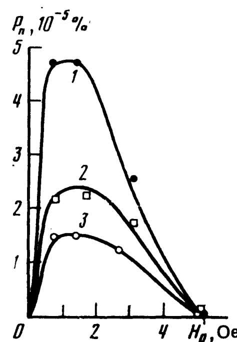

FIG. 7. Dependence of P_n on H_0 when plastically deformed p-silicon is illuminated with circularly polarized light: 1—$\varepsilon = 3.5\%$, 2—4.3%, 3—1.5%. Solid curves—calculated relations.

The narrow range of magnetic fields in which OPN is observed in optical pumping of circularly polarized light (see Figs. 6 and 7) corresponds to sufficiently large value of the correlation time of the electron field at the lattice nuclei surrounding the defect, $\tau_c = 3\times 10^{-8}$ sec (see (4)). With the aid of the obtained value of τ_c we can determine the level energy of the shallow donor center responsible for the OPN (Refs. 2, 6):

$$E_d=kT\ln\left[2(N_c\langle V\rangle\tau_c\sigma_{\rm capt})^{-1}\right], \qquad (9)$$

where N_c is the state density in the conduction band ($N_c = 3.6\times 10^{18}$ cm^{-3} at $T = 77$ K), $\langle V\rangle = 1.03\times 10^7$ cm/sec is the thermal energy of the electrons, $\sigma_{\rm capt}$ is the cross section for electron capture by a donor center (at $T = 77$ K and for shallow donor centers, the capture cross section varies little with E_d; for shallow donor centers in silicon at $T = 77$ K we have $\sigma_{\rm capt} = 2.6\times 10^{-12}$ cm^{-2}, Ref. 26). From the experimental plots in Figs. 6 and 7 we obtain with the aid of (9) the value $E_d = -0.08$ eV.

Thus, the OPN in optical pumping by circularly polarized light in plastically deformed silicon is produced in accord with the usual scheme [see (5) and (6)] as a result of hyperfine interaction of the lattice nuclei with spin-polarized electrons that produce levels E_c–0.08 eV in the forbidden band. These point defects are due to the initial donor and acceptor impurities (phosphorus and boron) and constitute secondary states of the electrons localized at the dislocation by the elastic-stress fields. That is to say, these point donor centers are induced by the deformation potential.[27,28] The difference inthe values of P_n, depending on Δ, both in n- and p-silicon (Figs. 6 and 7), is due to the different degrees of filling of the centers ($E_c - 0.08$ eV) by electrons, due to their compensation by the broken bonds of the edge-dislocation core.

Using relations (5) and (6) and taking into account the values of τ_c and the value of the local field $H_L = 0.176$ Oe of the lattice nuclei,[2] which leads to a decrease of the polarization in weak magnetic fields, we can calculate, for silicon containing point defects induced by the deformation potential, the dependences of P_n on H_0, of ξ on H_0 (see Figs. 6, 7, and 8), as well as of P_n on Δ (Fig. 9). The calculated dependences of P_n on H_0 (Figs. 6 and 7) and of P_n on Δ (Fig. 9) were normalized to the maximum values of P_n. In the calculation

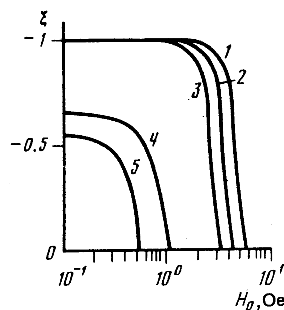

FIG. 8. Dependence of ξ on H_0, calculated for different values of n_d/N_d corresponding to different values of the dislocation density Δ: 1—$\Delta = 2.5\times 10^8$ cm^{-2}, 2—4×10^8, 3—8.5×10^8, 4—1.3×10^9, 5—2×10^9 cm^{-2}.

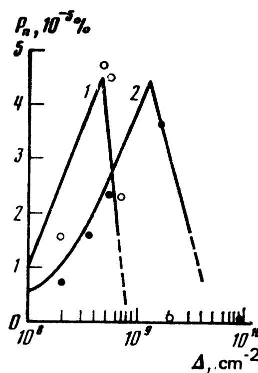

FIG. 9. Dependence of P_n on the dislocation density Δ in plastically deformed p-silicon (curve 1) and n-silicon (curve 2) illuminated by circularly polarized light in magnetic field $H_0 = 1$ Oe. Solid curves—theoretical relations. Points—experimental results for different investigated samples: ●—n-silicon ○—p-silicon.

of the curves in Figs. 6–9 we took into account also the different dependence of the electron lifetime τ in the conduction band for n- and p-silicon containing dislocations[29,30] ($\tau = 15/\Delta$ for n-silicon and $\tau = 10/\Delta$ for p-silicon).

The two pronounced maxima in the calculated and experimental plots of Fig. 9 (the number of samples used in these experiments was larger than in experiments on OPN with optical pumping by unpolarized light) show the conditions for optimal compensation of the donor centers induced by the deformation potential, by the acceptor centers of the broken bonds of the edge-dislocation nuclei, which are present in the crystal in the regime of a Mott-Hubbard dielectric.[13] At first P_n increases with increasing Δ, for in this case P_e increases (see (6)) on account of the decrease of τ ($\tau_s = 6\times 10^{-9}$ sec is the time of spin-lattice relaxation of the electrons in the conduction bands in weak magnetic fields). At large Δ, however, overcompensation leads, as noted above (see (2) and (5)), to a decrease of P_n because of the weak filling of the donor centers by electrons, a fact reflected by the decrease of ξ (see (2) and (5).[2] The optimum conditions for obtaining maximum polarization on account of centers induced by the deformation potential in plastically deformed n-silicon are reached at larger values of Δ than in p-silicon. The reason is the sharper decrease of τ when dislocations are introduced in p-silicon ($\tau = 10/\Delta$) compared with the data for n-silicon ($\tau = 15/\Delta$). The small value of P_n in optical pumping by circularly polarized light is due to the leakage of the nuclear polariation on account of the large concentration of the paramagnetic centers of the broken bonds of the edge-dislocation nuclei.

From the experimental results shown in Fig. 9 we can estimate (with the aid of (5) and (6)) the concentrations of the point centers induced by the deformation potential, viz., $N\approx 10^{12}$ cm^{-3} in all the samples of plastically deformed n- and p-silicon.

Our investigations of plastically deformed silicon have made it possible to establish the role played in OPN processes by broken bonds of the edge dislocations and centers, induced by the deformation potential. We have shown that the OPN due to the broken bond is the result of formation, in

the course of recombination, of photoexcited electron centers with $S > \frac{1}{2}$. It was shown that the OPN depends on the degree of filling of the broken bonds of the edge-dislocation nuclei, and also on the transport of the electrons and holes along the dislocation chains.

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[1]N. T. Bagraev and L. S. Vlasenko, Zh. Eksp. Teor. Fiz. **75**, 1743 (1978) [Sov. Phys. JETP **48**, 878 (1978)].
[2]N. T. Bagraev and L. S. Vlasenko, Fiz. Tverd. Tela (Leningrad) **21**, 120 (1979). [Sov. Phys. Solid State **21**, 70 (1979)].
[3]L. S. Vlasenko, Izv. AN SSSR, Ser. Fiz. **46**, 469 (1982).
[4]N. T. Bagraev, L. S. Vlasenko, M. P. Vlasenko, and V. M. Rozhkov, ibid. **46**, 476 (1982).
[5]R. G. Khutsishvili, Usp. Fiz. Nauk **87**, 211 (1965) [Sov. Phys. Usp. **8**, 743 (1966)].
[6]N. T. Bagraev and L. S. Vlasenko, Pis'ma Zh. Eksp. Teor. Fiz. **28**, 527 (1978) [JETP Lett. **28**, 488 (1978)].
[7]L. L. Buishvili, N. P. Giorgadze, and A. I. Ugulava, Fiz. Tverd. Tela (Leningrad) **16**, 3043 (1974) [Sov. Phys. Solid State **16**, 1966 (1974)].
[8]N. T. Bagraev, L. S. Vlasenko, and R. A. Zhitnikov, Zh. Eksp. Teor. Fiz. **71**, 952 (1976) [Sov. Phys. JETP **44**, 500 (1976)].
[9]N. T. Bagraev, L. S. Vlasenko, and R. A. Zhitnikov, Fiz. Tverd. Tela (Leningrad) **18**, 3054 (1976) [Sov. Phys. Solid State **18**, 1779 (1976)].
[10]N. T. Bagraev, E. P. Bochkarev, L. S. Vlasenko, V. P. Grishin, and Yu. A. Karpov, ibid. **21**, 515 (1979) [**21**, 305 (1979)].
[11]N. T. Bagraev, L. S. Vlasenko, and Yu. A. Karpov, J. Crystal Growth Lett. **50**, 764 (1980).
[12]V. A. Grazhulis, V. V. Kveder, and V. Yu. Mukhina, Phys. Stat. Sol. (a) **43**, 407 (1977).
[13]V. A. Grazhulis, V. V. Kveder, and V. Yu. Mukhina, ibid. **44**, 107 (1977).
[14]V. A. Grazhulis and Yu. A. Osip'yan, Zh. Eksp. Teor. Fiz. **58**, 1259 (1970); **60**, 1150 (1971) [Sov. Phys. JETP **31**, 677 (1970); **33**, 623 (1971)].
[15]U. Schmidt, E. Weber, H. Alexander, and W. Sander, Sol. St. Commun. **14**, 735 (1974).
[16]S. V. Broude, V. A. Grazhulis, V. V. Kveder, and Yu. A. Osip'yan, Zh. Eksp. Teor. Fiz. **66**, 1469 (1974) [Sov. Phys. JETP **34**, 721 (1974)].
[17]V. A. Grazhulis, V. V. Kveder, V. Yu. Mukhina, and Yu. A. Osip'yan, Pis'ma Zh. Eksp. Teor. Fiz. **24**, 164 (1976) [JETP Lett. **24**, 142 (1976)].
[18]R. G. Shulman and B. J. Wyluda, Phys. Rev. **103**, 1127 (1956).
[19]N. T. Bagraev, L. S. Vlasenko, and I. A. Merkulov, Zh. Eksp. Teor. Fiz. **81**, 2160 (1981) [Sov. Phys. JETP **81**, 1147 (1981)].
[20]J. Lampel, Proc. 9th Internat. Conf. on Semicond. Physics, Vol. II, Nauka, 1968, p. 1203.
[21]G. D. Watkins, Phys. Rev. **155**, 802 (1967).
[22]K. L. Brower, Phys. Rev. **B4**, 1968 (1971).
[23]D. Neubert, K. Hoffman, H. Techman, and R. Schleif, Sol. St. Electr. **21**, 1445 (1978).
[24]R. Haberkorn and W. Dietz, Sol. St. Commun. **35**, 505 (1980).
[25]N. T. Bagraev, L. S. Blasenko, and R. A. Zhitnikov, Fiz. Tekh. Poluprov. **10**, 2006 (1976) [Sov. Phys. Semicond. **10**, 1199 (1976)].
[26]N. T. Bagraev, L. S. Vlasenko, and R. A. Zhitnikov, Pis'ma Zh. Tekh. Fiz. **3**, 269 (1977) [Sov. Tech. Phys. Lett. **3**, 107 (1969)].
[27]V. Gold, A. Gold, and R. Thomson, Phys. Rev. Lett. **8**, 96 (1962).
[28]V. L. Bonch-Bruevich, Fiz. Tverd. Tela (Leningrad) **3**, 36 (1961) [Sov. Phys. Solid State **3**, 26 (1961)].
[29]H. F. Matare, Defect Electronics in Semiconductors, Wiley, 1971 (Russ transl. Mir, 1974, p. 119).
[30]H. Lemke, Phys. Stat. Sol. **12**, 125 (1965).

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