Selective optical pumping and quasiresonance intervalley scattering of electrons by neutral donors in many-valley semiconductors

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Selective optical pumping of electrons by pulses of linearly polarized light is used to make direct measurements of the intervalley scattering probability at liquid-helium temperatures in silicon crystals containing various concentrations of donor phosphorus. It is concluded that the intervalley scattering of electrons is due to the interaction with phosphorus neutral donors, and the scattering cross section at $T = 4.2$ K is determined to be $\sigma = (0.4 \pm 0.1) \cdot 10^{-12}$ cm^2. The intervalley scattering by neutral donors is calculated theoretically using the zero-radius-potential model generalized to the case of many-valley semiconductors. A formula is obtained which relates the intervalley scattering cross section to the valley-orbital splitting of the level of the D^- center. The results of the theoretical calculation are in good agreement with the experimental data.

In many-valley semiconductors of the silicon and germanium type, the indirect optical transitions which occur under illumination by linearly polarized light are accompanied by the nonuniform generation of electrons into the valleys of the conduction band, because the probability of these transitions to an individual valley in general depends on the relative orientation of the axis of the valley and the polarization vector e of the incident light.[1–4] The most efficient intervalley scattering mechanism is the interaction between electrons and intervalley phonons, which have energies of hundreds of degrees. The characteristic time for this interaction is 10^{-12} sec.[5] At low temperature ($kT \ll \hbar\omega_f$) the intervalley scattering by phonons is suppressed, and an appreciable difference arises in the populations of the valleys. This selective optical pumping by linearly polarized light was first observed[6] in silicon and germanium crystals by the microwave cyclotron resonance technique, which, because of the anisotropy of the effective masses of the electrons, is capable of detecting the electrons in the different valleys separately.

In the present paper the selective pumping effect during pulsed optical excitation is used to study the mechanisms of intervalley scattering of current carriers in pure crystals at low temperatures. We make the first detailed study of the mechanism of intervalley quasiresonance scattering by neutral donors and show that this scattering is due to the presence of a shallow level for an additional electron at the neutral donor, which on trapping an electron forms a D^- center.[7] We calculate the intervalley scattering probability in the zero-radius-potential approximation and find that the valley-orbital splitting of the level of the D^- center is uniquely determined. The results of the theoretical calculation are in good agreement with the experimental data.

In Sec. 1 we discuss the experimental technique, and in Sec. 2 we present a phenomenological model and the main experimental results obtained on silicon crystals. It is shown that under the conditions of the experiment the intervalley scattering is dominated by scattering on shallow donors consisting of phosphorus in a neutral state. Section 3 gives a theoretical calculation of the probabilities of quasiresonance intravalley and intervalley scattering by neutral donors in many-valley semiconductors. In Sec. 4 we compare the theoretical and experimental results.

1. EXPERIMENTAL TECHNIQUES

Figure 1 shows a simplified block diagram of the apparatus used to study the kinetics of electron recombination at low temperature under conditions of cyclotron resonance and pulsed optical excitation of the free carriers by linearly polarized light. The photoexcited carriers were detected by the microwave cyclotron resonance technique[8] with the aid of a homodyne spectrometer for the 8-mm range, which, depending on the magnetic field strength, could discriminate the signal proportional to the electron density in one valley or another. The sample was placed in a plunger-shorten section of rectangular waveguide in front of an aperture in the wider wall, through which light was admitted for optical excitation.

After the spectrometer detector the pulses were amplified and sent to a recording system which fixed both the time dependence of the electron density in one of the valleys and the electron density in different valleys after a variable delay following the excitation pulse.

In the present study the experimental objects were silicon crystals. It has been shown[9] that the largest anisotropy in the distribution of electrons over the valleys of the conduction band in silicon arises under linearly polarized optical excitation in the region of the indirect absorption edge (processes involving the creation of a TO phonon), which corresponds to an exciting photon energy of $h\nu = 1.26$ eV. The lack of suitable lasers in this region of the spectrum necessitated the use of a laser converter[10] based on an InP/InGaAsP/InP double heterostructure,[1)] excited by a standard LGI-505 pulsed nitrogen laser, which emits 8-nsec pulses of light at $\lambda = 337$ nm with a repetition rate of 1200 Hz. In addition to the elements shown in Fig. 1, the experimental apparatus had a device for monitoring the intensity of the laser radiation and an optical converter.

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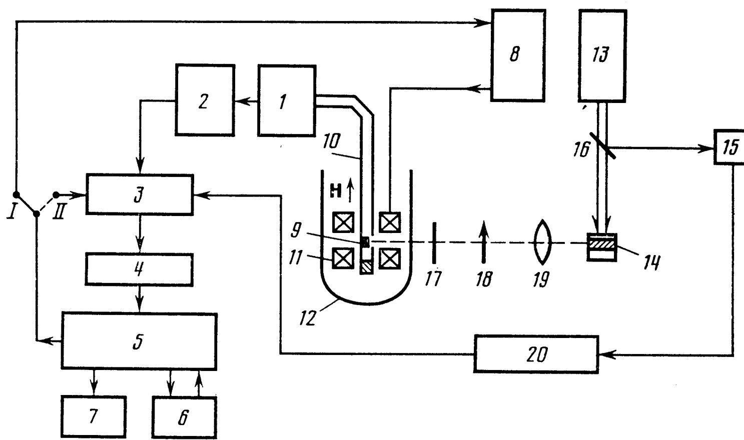

FIG. 1. Simplified block diagram of the apparatus: 1) homodyne spectrometer for the 8-mm range, 2) pulse amplifier, 3) stroboscopic converter, 4) F-30 voltmeter, 5) input-output device, 6) DZ–28 microcomputer, 7) plotter, 8) solenoid power supply, 9) sample, 10) waveguide, 11) coil of superconducting solenoid, 12) optical helium cryostat, 13) pulsed nitrogen laser, 14) laser converter, 15) trigger-pulse shaper, 16) glass plate, 17) half-wave plate, 18) infrared polarizer, 19) condensing lens, 20) delay line for trigger pulse; version I is a magnetic-field sweep, version II is a time sweep.

Samples with dimensions of $2.5\times2.6\times1.4$ mm were prepared from single crystals of dislocation-free silicon with resistivities $\rho = 250$ and 10^4 $\Omega\cdot$cm, grown by float zoning in vacuum. The samples were oriented with the aid of an x-ray diffractometer. The large faces through which the volume excitation of the samples was carried out were polished. The n-type silicon sample with $\rho = 250$ $\Omega\cdot$cm contained $2.5\cdot10^{13}$ atoms/cm^3 of phosphorus and $5\cdot10^{12}$ atoms/cm^3 of boron. The concentrations of these shallow donors and acceptors in the crystals with $\rho = 10^4$ $\Omega\cdot$cm were $2\cdot10^{12}$ and $2.5\cdot10^{12}$ cm^{-3}. Some of the samples of high-resistivity silicon were subjected to γ radiation from a Co^{60} source, producing A centers (oxygen + vacancy) and E centers (phosphorus + vacancy), which are stable at room temperature.[11] The radiation dose was $2.5\cdot10^{17}$ cm^{-2}. Comparison of the luminescence intensities of the bound many-exciton complexes at the phosphorus donors[12] in the irradiated and unirradiated crystals showed that as a result of the formation of E centers, the concentration of shallow phosphorus donors in the irradiated crystals decreased by around an order of magnitude.

2. KINETICS OF RELAXATION TO AN EQUILIBRIUM DISTRIBUTION OF ELECTRONS OVER THE VALLEYS OF THE CONDUCTION BAND OF SILICON

Suppose that a silicon crystal is subjected to a short pulse of linearly polarized light, generating electrons and holes near the extrema of the corresponding bands. Along each of the fourfold symmetry axes C_4 of silicon there are two valleys that are indistinguishable by both the optical and cyclotron-resonance methods. We shall therefore treat each pair of equivalent valleys along each C_4 axis as a single valley, introducing for these pairs of valleys the notation X, Y, Z and taking n_x, n_y and n_z to mean the total density of electrons in these pairs. The intervalley scattering probability γ will then mean the probability of scattering an electron into an individual pair of equivalent valleys, e.g., scattering from the X valleys into the Y valleys.

Under the conditions of the experiment the duration of the exciting pulse, $\tau_p \approx 10^{-8}$ sec, is considerably shorter than the characteristic times γ^{-1} and w^{-1}, where w is the electron recombination probability. Therefore, by the end of the excitation pulse ($t = 0$) the density of electrons in valleys X, Y, and Z (Fig. 2) is governed by the rate g of electron–hole pair generation and the anisotropy of the photoabsorption in a single valley. For example, for excitation by light having polarization $\mathbf{e}_1$, which is parallel to the [010] axis, we have at $t = 0$

$$n_x(\mathbf{e}_1)|_{t=0}=n_z(\mathbf{e}_1)|_{t=0}=n_0^{\perp}=g\tau_p k_{\perp}/k, n_y(\mathbf{e})|_{t=0}=n_0^{\parallel}=g\tau_p k_{\parallel}/k. \quad (1)$$

If the incident light has polarization $\mathbf{e}_2 \parallel [100]$, we have analogously

$$n_x(\mathbf{e}_2)|_{t=0}=n_0^{\parallel}=g\tau_p k_{\parallel}/k,$$
$$n_y(\mathbf{e}_2)|_{t=0}=n_z(\mathbf{e}_2)|_{t=0}=n_0^{\perp}=g\tau_p k_{\perp}/k. \quad (2)$$

Here $k_{\parallel}$ and $k_{\perp}$ are the photoabsorption coefficients for a pair of equivalent valleys for light polarized parallel and perpendicular to the valley axis, $n^{\parallel}$ and $n^{\perp}$ are the corresponding electron densities in the valleys, and $k = 2k_{\perp} + k_{\parallel}$ is the total photoabsorption coefficient of the crystal.

The time dependence of the electron density in the valleys for $t > 0$ is described by the system of homogeneous lin-

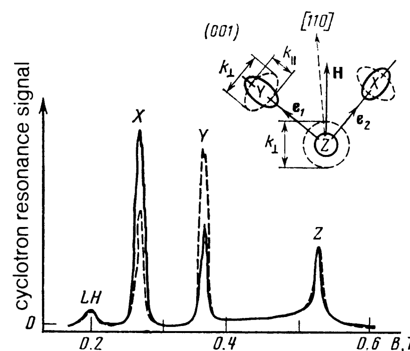

FIG. 2. Cyclotron absorption spectra at $T = 1.6$ K for light holes (LH) and electrons in valleys X, Y, and Z of a silicon crystal with $\rho = 10^4$ $\Omega\cdot$cm under excitation by pulses of linearly polarized light with $h\nu = 1.26$ eV and a delay time $\tau_d = 0$, for the experimental geometry shown in the inset; the solid curve is for polarization $\mathbf{e}_1$, the dashed curve for polarization $\mathbf{e}_2$. In the inset the solid lines are the projections of the effective-mass ellipsoids, the dashed lines are the projections of he coefficient of indirect absorption of linearly polarized light in an individual valley on the (001) plane; **H** indicates the direction of the magnetic field.

ear differential equations

$$\dot{n}_x = -(2\gamma+w)n_x+\gamma(n_y+n_z),$$
$$\dot{n}_y = \gamma(n_x+n_z)-(2\gamma+w)n_y, \qquad (3)$$
$$\dot{n}_z = \gamma(n_x+n_y)-(2\gamma+w)n_z.$$

After solving the balance equation (3) under the two different conditions (1) and (2), we find that the quantity

$$A=(n^{\perp}-n^{\parallel})/(2n^{\perp}+n^{\parallel}), \qquad (4)$$

which has the meaning of the anisotropy of the distribution of electrons over valleys, depends on time according to the simple exponential law

$$A(t)=A_0\exp(-3\gamma t), \qquad (5)$$

where $A_0 = (k_\perp - k_\parallel)/k$. Therefore, by measuring the function $A(t)$ one can directly determine the value of the electron intervalley scattering probability γ. From Ref. 4 one can find that $k_\parallel/k_\perp = 0.5$ in silicon in the region of indirect transitions involving *TO* phonons; hence $A_0 = 0.2$, and so one expects rather large values of the initial anisotropy of the distribution of electrons over valleys. We note that the total electron density in the valleys, $n_x + n_y + n_z = 2n^\perp + n^\parallel$, does not depend on the polarization of the excitation, and its relaxation is governed solely by the recombination probability w. The possibility of direct detection of the time dependences $n^\parallel(t)$ and $n^\perp(t)$ enables one to determine both w and γ. Our experiments focused on determining γ. The functional dependence (5) necessary for this was found according to (4) by measuring $n^\parallel$ and $n^\perp$ from the cyclotron resonance spectra obtained at a certain time $t = \tau_d$ which was fixed with respect to the excitation pulse. This method of measuring $n^\parallel$ and $n^\perp$ is less sensitive to the synchronous rf noise that arises in the operation of the nitrogen laser than is the direct measurement of the time dependences $n^\parallel(t)$ and $n^\perp(t)$ at fixed values of the magnetic field corresponding to resonance of the electrons in the X and Y valleys. The time $t = \tau_d$ was distinguished by strobing the cyclotron resonance signals with a 4-nsec strobe at a fixed delay with respect to the laser pulses; here the magnetic field was scanned in the region of the cyclotron resonance of the electrons in the X and Y valleys. The spectra at $T = 1.6$ K for various values of τ_d in an unirradiated sample of the $\rho = 10^4\ \Omega\cdot$cm silicon during excitation of the carriers by linearly polarized light with energy $h\nu = 1.26$ eV are shown in Fig. 3. It is seen that when the direction of the polarization vector is changed from $\mathbf{e}_1$ to $\mathbf{e}_2$, the ratio of the electron densities in the X and Y valleys changes to the reciprocal, whereas the values of $A(\tau_d)$ for these valleys are practically the same. Because of the exponential dependence of $A(t)$, the time $\tau_d = 0$ can be chosen arbitrarily; in our experiments it corresponds to the maximum of the cyclotron resonance signal, which occurs 20–25 nsec after the beginning of the excitation pulse.

Figure 4 shows the averaged values of A as a function of the delay time τ_d at $T = 1.6$ and 4.2 K for a sample with $\rho = 10^4\ \Omega\cdot$cm, for two values of the photon energy of the excitation ($h\nu = 1.26$ and 1.35 eV). It is seen that the experimental points correspond to a dependence of the form (5).

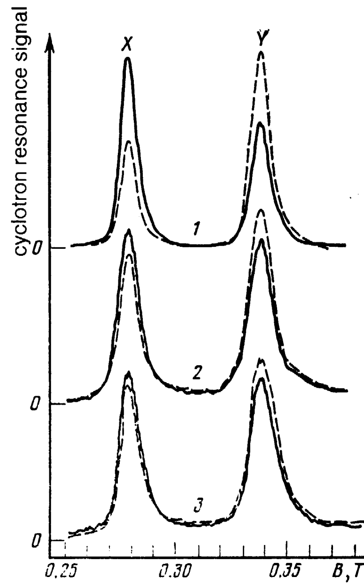

FIG. 3. Cyclotron resonance spectra of electrons in the X and Y valleys in an unirradiated crystal with $\rho = 10^4\ \Omega\cdot$cm for excitation by pulses of linearly polarized light with $h\nu = 1{,}26$ eV and polarization vectors $\mathbf{e}_1$ (solid curve) and $\mathbf{e}_2$ (dashed curve) at $T = 1.6$ K for various value of the delay time τ_d (in nsec): 1) 0, 2) 110, 3) 200.

We note that for excitation with a photon energy $h\nu = 1.35$ eV the initial kinetic energy of the photoexcited electrons is $\gtrsim 100$ meV, considerably higher than the energy of allowed intervalley phonons.[5] The emission of such phonons by electrons while they are thermalizing, which is completed by the time $\tau_d = 0$, leads to a decrease of A_0 by a factor of almost 3.5 in comparison with the case of excitation by photons with $h\nu = 1.26$ eV.

Since the measurements of $A(\tau_d)$ were made for thermalized electrons, the slopes of the interpolated straight lines for the two values of $h\nu$ are practically identical ($\gamma^{-1} = 0.4$–$0.5\ \mu$sec).

Figure 5 shows curves of $A(\tau_d)$, i.e., the anisotropy of the distribution of electrons over valleys as a function of the delay time, obtained in various silicon samples at $T = 1.6$ K for $h\nu = 1.26$ eV. We see that in the sample with $\rho = 10^4\ \Omega\cdot$cm, the intervalley scattering probability decreases sub-

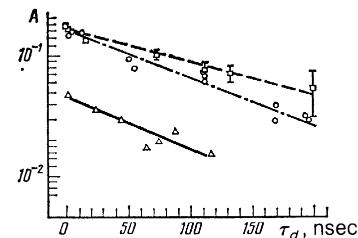

FIG. 4. Anisotropy of the distribution of electrons over valleys, $A = (n_\perp - n_\parallel)/(2n_\perp + n_\parallel)$ versus the delay time for a silicon sample with $\rho = 10^4\ \Omega\cdot$cm for various values of the temperature and exciting photon energy $h\nu$: □) $T = 1.6$ K; ○) $T = 4.2$ K, $h\nu = 1.26$ eV; △) $T = 1.6$ K, $h\nu = 1.35$ eV. The slopes of the approximately straight lines correspond to the following values of γ^{-1}: 0.5 μsec for the dashed line, 0.3 μsec for the dot-and-dash line, and 0.4 μsec for the solid line.

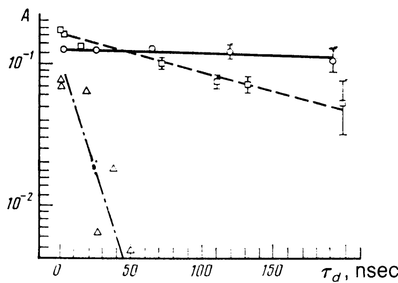

FIG. 5. Plot of $A(\tau_d)$ at $T = 1.6$ K for an exciting photon energy $h\nu = 1.26$ eV for various sample of silicon: △) $\rho = 250\ \Omega\cdot$cm; □) $10^4\ \Omega\cdot$cm; ○) $10^4\ \Omega\cdot$cm (γ-irradiated). The slopes of the approximately straight lines correspond to the following values of γ^{-1}: 0.04 μsec for the dot-and-dash line, 0.5 μsec for the dashed line, and 5 μsec for the solid line.

stantially as a result of γ irradiation: before irradiation $\gamma^{-1} = 0.5\ \mu$sec, while after irradiation it was an order of magnitude higher.

It should be noted that the phenomenological calculation given above has been carried out for conditions such that the electrons are not heated by the microwave field. At the same time, the presence of the hard-to-eliminate noise from the nitrogen laser made it impossible to measure γ at microwave powers low enough to avoid heating the electrons. The presence of heating is indicated by the broadening of the electron cyclotron resonance peaks as the level of microwave power supplied to the sample was increased. By determining the parameter $\omega\tau$ (Ref. 8) from the half-width of the cyclotron resonance peak in the X or Y valley and comparing it with the value $(\omega\tau)_0$ obtained in the absence of heating for $\tau_d = 0$ and at a low microwave power level, one can estimate the value of the temperature T_e of the electron system in accordance with Ref. 13. These values are given in Table I. For the sample with $\rho = 10^4\ \Omega\cdot$cm, we see that, prior to irradiation, the difference between T_e and the lattice temperature at $T = 4.2$ K is negligible. We therefore used these data in the quantitative comparison of the theoretical calculation with experiment.

Since all the investigated silicon samples were obtained by float zoning, it can be assumed that the concentration of uncontrolled impurities was approximately the same in all of them. Therefore, the near proportionality obtained in the experiment between the intervalley scattering probability and the concentration of phosphorus donors in the samples with $\rho = 250$ and $10^4\ \Omega\cdot$cm indicates that the phosphorus donors play a fundamental role in the intervalley scattering. This also follows from the increase of the intervalley scattering time after γ irradiation of the sample, As a result of irradiation, the density of deep centers in the sample only increased, on account of the formation of E and A centers, whereas the concentration of phosphorus donors decreased by an order of magnitude, as is shown by our comparison of the luminescence spectra of many-exciton complexes bound to the phosphorus atoms.

Under the experimental conditions practically all the phosphorus donors were found in the neutral state. In fact, for photoexcitation, by virtue of the large value of the cross section for the trapping of electrons by ionized donors and holes by ionized acceptors[14] and the low probability of donor-acceptor recombination,[15] neutralization of the charged centers occurs. On the other hand, we shall show that the density ΔN of donors which have trapped an additional electron (D^- centers) is also negligible under the experimental conditions. The change of ΔN with increasing delay time τ_d is given by the formula

$$\Delta N = (\alpha n_0 N/w)[1 - \exp(-w\tau_d)], \tag{6}$$

where n_0 is the density of photoelectrons at the time $\tau_d = 0$ (according to our estimates, $n_0 \sim 10^{12}$ cm^{-3}), α is a coefficient describing the trapping of the additional electron by a neutral donor, and N is the density of shallow (neutral) donors. According to Ref. 16, $\alpha = 10^{-7}$ cm^3 sec^{-1}. On the other hand, the lifetime of the nonequilibrium electrons in the unirradiated samples, according to our data, is 0.3–0.4 μsec. We then find from (6) that $\Delta N/N \leqslant 0.02$ for $\tau_d \leqslant 0.2$ μsec. Consequently, the experimentally measured value of γ is due to the scattering of photoelectrons by neutral phosphorus donors. It should be noted that the value of γ determined with the aid of (5) is the probability of intervalley scattering of an electron into a pair of equivalent valleys. For our subsequent comparison with the theory of intervalley scattering, it is convenient to use the value of the cross section to describe scattering into a single valley; it is given by

$$\sigma = \gamma/2N\langle v\rangle, \tag{7}$$

where $\langle v\rangle = (8kT/\pi m_d)^{1/2}$ is the average thermal velocity of an electron, and $m_d = (m_\perp^2 m_\parallel)^{1/3}$ is the density-of states effective mass.

Using the experimental values of γ obtained under conditions such that there was no heating by the microwave field, we find $\sigma(4.2\text{ K}) = (0.4 \pm 0.1)\cdot 10^{-12}$ cm^2.

Intervalley scattering is accompanied by a change in the electron momentum by a quantity of order a^{-1} (where a is the lattice constant) and is due to the short-range part of the impurity potential, which has a range $\sim a$. The value obtained for the cross section is several orders of magnitude larger than the simple geometrical estimate $\sigma \approx \pi a^2$.

TABLE I.

Sample (ρ, $\Omega\cdot$cm)	Lattice temperature, K	$\omega\tau$	$(\omega\tau)_0$	Range of electron temperatures, K
10^4	4,2	60	70	4–5
10^4	1,6	60	200	9–12
10^4 γ Radiation	1,6	65	220	9–12
250	1,6	55	100	4–6

In the next section we show that the large value of the experimental cross section is due to the resonance character of electron scattering by a neutral donor under conditions such that the electron energy is close to the binding energy of a localized electron (the binding energy of the D^- center).

3. CALCULATION OF THE PROBABILITY OF INTERVALLEY RESONANCE SCATTERING BY SHALLOW NEUTRAL DONORS

Intervalley scattering of electrons by shallow neutral donors is governed by the short-range part $V_0(\mathbf{r})$ of the impurity potential; this part is due to the different chemical natures of the impurity centers and lattice atoms. It should be noted that besides $V_0(\mathbf{r})$, the effective range of which is of the order of the lattice constant, the potential of a neutral donor has a second, smoother part $V_1(\mathbf{r})$, with a depth of the order of the Bohr energy E_B of a shallow donor and an effective range of the order of the Bohr radius $a_B = \hbar/(m_d E_B)^{1/2}$. It is the potential $V_1(\mathbf{r})$, which stems from the polarization interaction between a neutral donor and an additional electron, that leads to the formation of a D^- center with binding energy E_0. The energy E_0 is usually about 0.05 to 0.1 times the Bohr energy of a hydrogen-like impurity. The condition $E_0 \ll E_B$ allows one to use the zero-radius-potential method[17] for the wave function of the D^- centers and for describing the scattering of free electrons of low energy (at a temperature $T \sim E_0$ by neutral donors.

In generalizing the zero-radius-potential model to many-valley semiconductors such as silicon and germanium, one must note that each level of the D^{-1} center is degenerate, with a degeneracy equal to the number of equivalent valleys, if the effect of only the smooth part $V_1(\mathbf{r})$ of the impurity potential is taken into account. The presence of a short-range part $V_0(\mathbf{r})$ leads to a partial lifting of the degeneracy of the levels and to their orbital-valley splitting, in complete analogy with what happens to the levels of the ground state of a shallow Coulomb center.[18] In silicon, which has six equivalent energy minima lying along the fourfold symmetry axes (the [100] directions), the sixfold degenerate level of the D^- center should be split into a singlet (E_s), a triplet (E_t) and a doublet (E_d).[19,20] The following discussion will be for the example of silicon. In the calculations it is assumed that the entire multiplet of split levels lies in the band gap, and the matrix elements of the scattering amplitude are related to the corresponding binding energies E_s, E_t, and E_d.

The wave function of a free electron in valley l (l runs over the values X, $-X$, Y, $-Y$, Z, $-Z$) is of the form[18]

$$\psi_{l\mathbf{k}}(r) = V_0^{-1/2} \exp(i\mathbf{kr}) \exp(i\mathbf{k}_{0l}\mathbf{r}) U_{\mathbf{k}_{0l}}(\mathbf{r}), \tag{8}$$

where V_0 is the normalization volume, $\mathbf{k}_{0l}$ and $U_{\mathbf{k}_{0l}}(\mathbf{r})$ are the wave vector and Bloch amplitude corresponding to the bottom of valley l. The energy spectrum in the valleys is anisotropic:

$$\mathscr{E}_{l\mathbf{k}} = \frac{\hbar^2}{2m_\perp} k_{\perp l}^2 + \frac{\hbar^2}{2m_\parallel} k_{\parallel l}^2, \tag{9}$$

where $k_{\perp l}$ and $k_{\parallel l}$ are the components of the wave vector $\mathbf{k}$ perpendicular and parallel to the axis of valley l, and $m_\perp$ and $m_\parallel$ are the corresponding effective masses (in silicon $m_\perp = 0.19 m_0$, $m_\parallel = 0.98 m_0$).

Let us first consider the form of the wave function of an electron localized at a center. It is convenient to seek this wave function in the form of a series in the free-state wave functions[12]:

$$\psi(\mathbf{r}, E) = \sum_{l\mathbf{k}} C_{l\mathbf{k}}(E) \psi_{l\mathbf{k}}(\mathbf{r}). \tag{10}$$

After substituting (10) into the Schrödinger equation, we obtain the following system of equations for the coefficients $C_{l\mathbf{k}}(E)$, which in essence represent the wave function of a localized electron in momentum space:

$$(\mathscr{E}_{l'\mathbf{k}'} + E) C_{l'\mathbf{k}'}(E) + \frac{1}{V_0} \sum_{l''\mathbf{k}''} \langle \psi_{l'\mathbf{k}'} | V(\mathbf{r}) | \psi_{l''\mathbf{k}''} \rangle C_{l''\mathbf{k}''}(E) = 0. \tag{11}$$

Here E is the binding energy of an electron at a neutral center.

In the context of the zero-radius-potential model, for wave vectors $\mathbf{k}$ satisfying $k a_B \ll 1$ (the comparison must be made using the smooth part of the potential), the matrix elements of the potential are independent of $\mathbf{k}$, and

$$\langle \psi_{l'\mathbf{k}'} | V(\mathbf{r}) | \psi_{l''\mathbf{k}''} \rangle = V_{l'l''}. \tag{12}$$

It is easily shown by using the symmetry properties that all the matrix elements $V_{l'l''}$ are expressed in terms of three constants which characterize, respectively, the intravalley scattering, $V_i = V_{ll}$, the g-type intervalley scattering between two identically oriented equivalent valleys, $V_g = V_{l,-l}$, and the f-type intervalley scattering between any mutually perpendicular valleys, $V_f = V_{l,l'}$ ($l' \neq l$ and $l' \neq -l$). Keeping this fact in mind and introducing the quantity $\varphi_l(E) = \Sigma_{\mathbf{k}} C_{l\mathbf{k}}(E)$, we can convert system (11) to a system of homogeneous algebraic equations for the quantities $\varphi_l(E)$. In silicon this system is sixth order. Setting the determinant of this system equal to zero, we get an equation for the binding energies of a localized electron:

$$[V_i + V_g - a^{-1}(E)]^3 [V_i - V_g - 2V_f - a^{-1}(E)]^2 \times [V_i - V_g + 4V_f - a^{-1}(E)] = 0, \tag{13}$$

$$a(E) = \frac{1}{V_0} \sum_{\mathbf{k}} \frac{1}{(\mathscr{E}_{\mathbf{k}} + E)}. \tag{14}$$

It follows from (13) that there are three roots, corresponding to three levels: a singlet E_s, a triplet E_t, and a doublet E_d.

The relation we shall need between the constants V_i, V_g, and V_f and the energies E_s, E_t, and E_d can be found from (13):

$$\begin{aligned} V_i &= {}^1/_6[3a^{-1}(E_t) + 2a^{-1}(E_d) + a^{-1}(E_s)], \\ V_g &= {}^1/_6[3a^{-1}(E_t) - 2a^{-1}(E_d) - a^{-1}(E_s)], \\ V_f &= {}^1/_6[a^{-1}(E_s) - a^{-1}(E_d)], \end{aligned} \tag{15}$$

where $a(E_s)$, $a(E_t)$, and $a(E_d)$ are given by formula (14) with E equal to E_s, E_t, and E_d, respectively.

Let us also give form of the wave function of a localized

electron in coordinate space:

$$\psi_\nu(\mathbf{r})=\sum_l \alpha_{l\nu}\exp(i\mathbf{k}_{0l}\mathbf{r})U_{\mathbf{k}_{0l}}(\mathbf{r})\psi_l(\mathbf{r},E), \quad (16)$$

where

$$\psi_l(\mathbf{r},E)=\left(\frac{\varkappa_\perp^2\varkappa_\parallel}{2\pi}\right)^{1/2}\frac{\exp[-(\varkappa_\perp^2 r_{\perp l}^2+\varkappa_\parallel^2 r_{\parallel l}^2)^{1/2}]}{(\varkappa_\perp^2 r_{\perp l}^2+\varkappa_\parallel^2 r_{\parallel l})^{1/2}}, \quad (17)$$

$$\varkappa_\perp=(2m_\perp E)^{1/2}/\hbar, \quad \varkappa_\parallel=(2m_\parallel E)^{1/2}/\hbar,$$

$r_{\perp l}$ and $r_{\parallel l}$ are the components of the vector $\mathbf{r}$ perpendicular to and parallel to the axis of valley l. The subscript ν, which gives the number of the bound state, takes on six values: $\nu=1$ corresponds to the singlet state $E=E_s$, $\nu=2, 3, 4$ to the triplet $E=E_t$, and $\nu=5, 6$ to the doublet state $E=E_d$. The matrix of coefficients $\alpha_{\nu l}$ is given by the expression

$$\alpha_{\nu l}=\begin{Vmatrix} G^{-1/2} & G^{-1/2} & G^{-1/2} & G^{-1/2} & G^{-1/2} & G^{-1/2} \\ 2^{-1/2} & -2^{-1/2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 2^{-1/2} & -2^{-1/2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 2^{-1/2} & -2^{-1/2} \\ 2^{-1} & 2^{-1} & -2^{-1} & -2^{-1/2} & 0 & 0 \\ 2^{-1} & 2^{-1} & 0 & 0 & -2^{-1} & -2^{-1} \end{Vmatrix}. \quad (18)$$

Let us turn to the problem of finding the wave functions of an electron of the continuum in the presence of a neutral donor. This function is conveniently labeled by the symbols l_0 and $\mathbf{k}_0$, which give the number of the valley and the quasi-momentum of the wave indicent on the center. We shall again determine the wave function in the form of a series in the free-state wave functions (8):

$$\psi_{l_0\mathbf{k}_0}(\mathbf{r})=\sum_{l\mathbf{k}} C_{l\mathbf{k}}^{l_0\mathbf{k}_0}\psi_{l\mathbf{k}}(\mathbf{r}). \quad (19)$$

As is usual in scattering theory, we seek $C_{l\mathbf{k}}^{l_0\mathbf{k}_0}$ in the form

$$C_{l\mathbf{k}}^{l_0\mathbf{k}_0}=\delta_{l_0 l}\delta_{\mathbf{k}_0\mathbf{k}}-t(l\mathbf{k},l_0\mathbf{k}_0\mathscr{E}_{\mathbf{k}_0})/(\mathscr{E}_\mathbf{k}-\mathscr{E}_{\mathbf{k}_0}-i\gamma), \quad (20)$$

where $t(l\mathbf{k},l_0\mathbf{k}_0,\mathscr{E}_{\mathbf{k}_0})$ has the meaning of the amplitude for the elastic scattering of an electron with energy $\mathscr{E}_{\mathbf{k}_0}$ from state $l_0\mathbf{k}_0$ to state $l\mathbf{k}$. For the matrix elements of the scattering amplitude, we obtain from the Schrödinger equation the system of equations

$$t(l\mathbf{k},l_0\mathbf{k}_0,\mathscr{E}_{\mathbf{k}_0})=\frac{1}{V_0}\left[V_{ll_0}-\sum_{l'\mathbf{k}'}V_{ll'}\frac{t(l'\mathbf{k}',l_0\mathbf{k}_0,\mathscr{E}_{\mathbf{k}_0})}{\mathscr{E}_{\mathbf{k}'}-\mathscr{E}_{\mathbf{k}_0}-i\gamma}\right]. \quad (21)$$

Again introducing the auxiliary quantity

$$\varphi_{l'l_0}(\mathbf{k}_0)=\frac{1}{V_0}\sum_\mathbf{k}\frac{t(l\mathbf{k},l_0\mathbf{k}_0,\mathscr{E}_{\mathbf{k}_0})}{\mathscr{E}_\mathbf{k}-\mathscr{E}_{\mathbf{k}_0}-i\gamma}, \quad (22)$$

which is related to the scattering amplitude by the expression

$$t(l\mathbf{k},l_0\mathbf{k}_0,\mathscr{E}_{\mathbf{k}_0})=V_0^{-1}V_{ll_0}-\sum_{l'}V_{ll'}\varphi_{l'l_0}(\mathbf{k}_0), \quad (23)$$

we obtain a sixth-order system of algebraic equations for $\psi_{ll_0}(\mathbf{k}_0)$. After solving this system and using Eq. (23) and expressions (15), which give the matrix elements of the impurity potential in terms of the energies E_s, E_t, and E_d, we find the quantity that we are interested in, viz., $t(l\mathbf{k},l_0\mathbf{k}_0,\mathscr{E}_{\mathbf{k}_0})$.

Here, by virtue of the symmetry properties and the short-range character of the impurity potential, all the matrix elements of the scattering amplitude, as one would expect, are independent of the scattering angle and of the direction of the incident electron and are expressed in terms of three quantities: $t_i(\mathbf{k}_0)$, $t_g(\mathbf{k}_0)$, and $t_f(\mathbf{k}_0)$. These quantities characterize the intravalley scattering amplitude, $t_i(\mathbf{k}_0)=t(l_0\mathbf{k},l_0\mathbf{k}_0,\mathscr{E}_{\mathbf{k}_0})$, the g-type intervalley scattering between two equivalent valleys along the same axis, $t_g(\mathbf{k}_0)=t(-l_0\mathbf{k}_0\mathbf{k}_0),\mathscr{E}_{\mathbf{k}_0})$, and the f-type intervalley scattering between two mutually perpendicular equivalent valleys, $t_f(\mathbf{k}_0)=t(l\mathbf{k},l_0\mathbf{k}_0,\mathscr{E}_{\mathbf{k}_0})$ ($l\neq l_0$ and $l\neq -l_0$). For the quantities $t_i(\mathbf{k}_0)$, $t_g(\mathbf{k}_0)$, and $t_f(\mathbf{k}_0)$ we have

$$t_i(\mathbf{k}_0)=c[3(E_t^{1/2}-i\mathscr{E}_{\mathbf{k}_0}^{1/2})^{-1}+2(E_d^{1/2}-i\mathscr{E}_{\mathbf{k}_0}^{1/2})^{-1}+(E_s^{1/2}-i\mathscr{E}_{\mathbf{k}_0}^{1/2})^{-1}], \quad (24)$$

$$t_g(\mathbf{k}_0)=c[3(E_t^{1/2}-i\mathscr{E}_{\mathbf{k}_0}^{1/2})^{-1}-2(E_d^{1/2}-i\mathscr{E}_{\mathbf{k}_0}^{1/2})^{-1}-(E_s^{1/2}-i\mathscr{E}_{\mathbf{k}_0}^{1/2})^{-1}], \quad (25)$$

$$t_f(\mathbf{k}_0)=c[(E_s^{1/2}-i\mathscr{E}_{\mathbf{k}_0}^{1/2})^{-1}-(E_d^{1/2}-i\mathscr{E}_{\mathbf{k}_0}^{1/2})^{-1}], \quad (26)$$

where

$$c=2^{1/2}\pi\hbar^3/6V_0(m_\perp^2 m_\parallel)^{1/2}. \quad (27)$$

We note that for a simple band with a minimum at the center of the Brillouin zone ($m_\perp=m_\parallel=m^*$, $E_s=E_t=E_d=E_0$), we have $t_g(\mathbf{k}_0)=t_f(\mathbf{k}_0)=0$, and $t_i(\mathbf{k}_0)$ goes over to the usual formula for the resonance scattering amplitude[17]:

$$t_i(\mathbf{k}_0)=2^{1/2}\pi\hbar^3/V_0 m^{*3/2}(E_0^{1/2}-i\mathscr{E}_{\mathbf{k}_0}^{1/2}). \quad (28)$$

Knowing the scattering amplitude, we can determine the relaxation time of electrons of energy $\mathscr{E}_{\mathbf{k}_0}$ localized in valley l_0 due to scattering by neutral impurities with a concentration N:

$$\tau_{ll_0}^{-1}(\mathscr{E}_{\mathbf{k}_0})=\frac{NV_0}{4}\sum_\mathbf{k}\frac{2\pi}{\hbar}|t(l\mathbf{k},l_0\mathbf{k}_0,\mathscr{E}_{\mathbf{k}_0})|^2 \times[1-\cos\sphericalangle\mathbf{k}\mathbf{k}_0]\delta(\mathscr{E}_\mathbf{k}-\mathscr{E}_{\mathbf{k}_0}). \quad (29)$$

The factor of 4 in the denominator of (29) allows for the fact that resonance scattering involves electrons whose spins are antiparallel to the spin of the electron localized at the neutral center.

Integrating (29) with allowance for the anisotropy of the electron energy spectrum, we obtain expressions for the three probabilities for the scattering of an electron of energy $\mathscr{E}_{\mathbf{k}_0}$ into a given valley, as a function of the incident electron energy [$1/\tau_i(\mathscr{E}_{\mathbf{k}_0})$ is the intravalley scattering probability, and $1/\tau_g(\mathscr{E}_{\mathbf{k}_0})$ and $1/\tau_f(\mathscr{E}_{\mathbf{k}_0})$ are the probabilities of g-type and f-type intervalley scattering]:

$$1/\tau_j=(1/\tau_0)\eta_j(\mathscr{E}_{\mathbf{k}_0}), \quad \tau_0=36(2E_s m_\perp^2 m_\parallel)^{1/2}/N\pi\hbar^2, \quad j=i,\ q,\ f, \quad (30)$$

where the coefficients $\eta_j(\mathscr{E}_{\mathbf{k}_0})$ determine the energy dependence of the corresponding quantities and are given by

$$\eta_t(\mathcal{E}_{\mathbf{k}_0}) = (E_s\mathcal{E}_{\mathbf{k}_0})^{1/2}\left\{\frac{9}{D_t}+\frac{4}{D_d}+\frac{1}{D_s}+\frac{12[\mathcal{E}_{\mathbf{k}_0}+(E_tE_d)^{1/2}]}{D_tD_d} + \frac{6[\mathcal{E}_{\mathbf{k}_0}+(E_tE_s)^{1/2}]}{D_tD_s}+\frac{4[\mathcal{E}_{\mathbf{k}_0}+(E_sE_d)^{1/2}]}{D_sD_d}\right\}$$

$$\eta_g(\mathcal{E}_{\mathbf{k}_0}) = (E_s\mathcal{E}_{\mathbf{k}_0}^{1/2})\left\{\frac{9}{D_t}+\frac{4}{D_d}+\frac{1}{D_s}-\frac{12[\mathcal{E}_{\mathbf{k}_0}+(E_tE_d)^{1/2}]}{D_tD_d} - \frac{6[\mathcal{E}_{\mathbf{k}_0}+(E_tE_s)^{1/2}]}{D_tD_s}+\frac{4[\mathcal{E}_{\mathbf{k}_0}+(E_sE_d)^{1/2}]}{D_sD_d}\right\}, \quad (31)$$

$$\eta_f(\mathcal{E}_{\mathbf{k}_0}) = (E_s\mathcal{E}_{\mathbf{k}_0})^{1/2}(E_s^{1/2}-E_d^{1/2})^2(D_sD_d)^{-1},$$

$$D_\alpha = \mathcal{E}_{\mathbf{k}_0}+E_\alpha, \quad \alpha = s,\ t,\ d.$$

The probability of interest to us, that of f-type intervalley scattering of an electron into a pair of equivalent valleys in the case of a nondegenerate electron distribution, is given by the expression

$$\gamma = \int \frac{4}{\tau_f(\mathcal{E}_{\mathbf{k}})} f(\mathcal{E}_{\mathbf{k}})\, d^3\mathbf{k} \left(\int f(\mathcal{E}_{\mathbf{k}})\, d^3\mathbf{k}\right)^{-1}, \quad (32)$$

where

$$f(\mathcal{E}_{\mathbf{k}}) = [n(2\pi\hbar^2)^{3/2}/4T^{3/2}(m_\perp^2 m_\parallel)^{1/2}]\exp(-\mathcal{E}_{\mathbf{k}}/T)$$

is the equilibrium electron distribution function, and n is the electron density in the pair of equivalent valleys. For the cross section σ, which determines the f-type scattering into one given valley and is related to γ by Eq. (7), we get

$$\sigma = \sigma_0 f(x,\ s), \quad \sigma_0 = \pi\hbar^2/18E_s m_d,$$

$$f(x,s) = \frac{s^2e^s}{x}\left[1-\frac{x}{2}-(1-x)^{1/2}\right] \times [\Gamma(0,s)-(1-x)e^{-xs}\Gamma(0,s(1-x))], \quad (33)$$

where $s = E_s/T$, $x = (E_s - E_d)/E_s$, T is the temperature in energy units, and $\Gamma(0,s)$ is the incomplete γ function.

4. DISCUSSION OF THE RESULTS

An estimate of the size of the splitting $\Delta = E_s - E_d$ for a phosphorus donor can be obtained using the value of the valley-orbital splitting of shallow Coulomb centers.[21–24] For phosphorus in silicon, the following values are given [21] for the binding energies of the multiplet levels: $\widetilde{E}_s = 44$ meV, $\widetilde{E}_t = 32$ meV, $\widetilde{E}_d = 30$ meV, and $\widetilde{\Delta} = \widetilde{E}_s - \widetilde{E}_d = 14$ meV.

For impurities of the same chemical nature, the short-range potential, which is responsible for the valley-orbital splitting of the levels, remains the same for both a neutral and ionized shallow donor. Therefore, assuming that the valley-orbital splitting of the D^- center is small, as it is in the case of Coulomb centers, and using pertubation theory, we find

$$\Delta = \widetilde{\Delta}|\psi(0)|^2/|\widetilde{\psi}(0)|^2, \quad (34)$$

where $|\widetilde{\psi}(0)|^2$ is the square of the modulus of the smooth envelope of the Coulomb wave function, and $|\psi(0)|^2$ is the corresponding quantity for the wave function of an additional electron at a neutral donor. Using the results of Ref. 18, in which a variational method was used to calculate the binding energy of a Coulomb center with allowance for the anisotropy of the energy spectrum, we have $|\widetilde{\psi}(0)|^2 = \alpha_1\alpha_2^2\pi a_0^3\epsilon_0^3$, where $a_0 = \hbar^2/m_0e^2$ is the Bohr radius, ε_0 is the dielectric constant, and α_1 and α_2 are variational parameters, which for silicon are given by $\alpha_1^2 = 0.216$ and $\alpha_2^2 = 0.0174$.

As usual, in the zero-radius-potential model the smooth envelope of $\psi(r,E)$ diverges for $r \to 0$. To estimate $|\psi(0)|^2$ it is natural to set r in (17) equal to the dimension of the neutral donor, i.e., $r_\perp = 2a_0\varepsilon_0/\alpha_2$, $r_\parallel = a_0\varepsilon_0/\alpha_1$, whereupon

$$|\psi(0)|^2 = \frac{\varkappa_\perp^2\varkappa_\parallel}{2\pi a_0^2\varepsilon_0^2}\,\frac{\alpha_1^2\alpha_2^2}{(2\varkappa_\perp^2\alpha_1^2+\varkappa_\parallel^2\alpha_2^2)}.$$

The energy of the ground level of the D^- center has been measured in a number of studies.[7,25–27] The results of those studies give values for E_s in the range 1.2–2.2 meV. For our calculations we have taken for E_s the value 1.8 meV found in Ref. 7. Then from (34) we have $\Delta = 1.46$ meV, i.e., the value of the valley-orbital splitting is of the order of the binding energy of a D^- center. For values of $x = (E_s - E_d)/E_s$ close to unity, one can obtain for the scattering cross section (33) the value $\sigma = 0.5\cdot 10^{-12}\ \text{cm}^2$ ($T = 4.2$ K). This value is in good agreement with the experimentally measured intervalley scattering cross section: $\sigma(4.2\ \text{K}) = (0.4 \pm 0.1)\cdot 10^{-12}\ \text{cm}^2$.

The large value of the cross section for intervalley scattering by a shallow neutral donor, substantially larger than the simple geometric estimate $\sigma \approx \pi a^2 = 9\cdot 10^{-15}\ \text{cm}^2$, is due to the resonance character of the electron scattering at low temperatures. If the energy of the incident electron is comparable to the binding energy of the ground state, then the process of resonance intervalley scattering can be thought of qualitatively as follows. An incident free electron belonging to a certain valley l is virtually trapped by a center, becoming distributed over the levels E_s, E_t and E_d, since the wave functions of each of the levels are superpositions of the states of all the valleys. While it is in the trapped state the electron is mixed over all the valleys by the short-range potential, and it can therefore emerge in another valley. A measure of the effect of the short-range potential $V_0(r)$ on a localized electron is the value of the valley-orbital splitting Δ. Therefore, the larger the valley-orbital splitting, the larger the intervalley scattering cross section.

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