find that $\mathbf{k}\cdot\mathbf{r} \ll 1$ for the filled states in the conduction band. Making allowance for this point, we can obviously write the one-particle spectrum of the conduction electron in a wide-gap magnetic semiconductor with $l^2 \ll 1$ in the form

$$\mathscr{E} = \frac{\hbar^2k^2}{2m} - \frac{2}{N}[a\mathbf{k}\mathbf{I}_1 + I_0]\sum_{j=1}^{N}\left(\mathbf{s}_0\mathbf{S}_j + \frac{z}{4}\right), \qquad (23)$$

where I_0 and $\mathbf{I}_1$ are the coefficients of the expansion of I of Eq. (18) in terms of $a\mathbf{k}$. For real ferromagnetic semiconductors the total energy of the exchange interaction of a carrier with the d (f) electrons represents a few tenths and may even approach 1 eV. This is probably proved most directly by the published experiments,[17,18] so that a typical value of the quantity $a\mathbf{k}\cdot\mathbf{I}_1$ should represent a few hundreds of degrees, which—for nondegenerate semiconductors—is considerably greater than the kinetic energy of the conduction electrons and, therefore, this term should have a strong influence on the behavior of the other terms. For example, it is clear that allowance for this term cardinally alters the nature of certain transport effects in these materials.

[1)] In principle, this influence can be allowed for in the appropriate one-particle Hartree-Fock equation using the perturbation theory, which in this case should work well because usually the localized-electron spectrum depends weakly on the degree of magnetic ordering of a crystal.

[2)] It should be noted that this term differs slightly from that considered by Eremin and Khaliullin [9] although it is of the same order of magnitude; Eremin and Khaliullin consider (in our notation) terms of the $\mathcal{L}\alpha = \mathcal{L}\langle 0, j\,|\,V(\mathbf{r}, \mathbf{r}')\,|\,j, 0\rangle$ type [compare with Eqs. (8) and (11)], which cannot appear in our treatment because we have assumed right from the beginning that $\mathcal{L} \approx 0$.

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Thermal ionization of impurities in strong electric fields

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It is shown that the well-known Poole–Frenkel formula, describing the dependence of the thermal ionization coefficient β on the electric field $\mathscr{E}$ in a semiconductor, should be modified. In addition to the exponential dependence of β on $\mathscr{E}$, which appears because of the reduction in the ionization energy of an impurity in the applied field, allowance should be made for the electric-field dependence of the preexponential factor, associated with the change in the rate of diffusion of electrons over highly excited impurity states in the presence of the field. The Pitaevskiĭ method is used to obtain an expression for the coefficient of thermal ionization from a Coulomb impurity center in an electric field in the specific case when the ionization is due to the interaction of electrons with acoustic phonons.

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1. The probability of thermal ionization of an impurity center in strong electric fields is known to rise exponentially with the field intensity. This is known as the Poole–Frenkel effect, named in this way because Poole was the first to observe an exponential increase in the conducitvity of an insulator in the prebreakdown state[1] and Frenkel explained this effect theoretically.[2]

The Frenkel idea was that the application of an elec-

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tric field $\mathcal{E}$ lowers the ionization potential of an impurity center by an amount $E_{\mathcal{E}}$, equal to

$$E_{\mathcal{E}}=2(e^3Z\mathcal{E}/\varkappa)^{1/2}, \tag{1}$$

because of distortion of the potential well of the impurity. In this expression, $\varkappa$ is the permittivity and eZ is the charge of the center. The reduction in the ionization potential increases the probability of thermal ionization of an impurity in an electric field $\beta(\mathcal{E})$ in accordance with the law

$$\beta(\mathcal{E})=\beta\exp(E_{\mathcal{E}}/kT), \tag{2}$$

where β is the probability of ionization in the absence of an electric field, T is the temperature of the investigated crystal, and k is the Boltzmann constant. The formula (2) does indeed apply if the thermal ionization takes place from the ground state directly to an allowed band. However, recombination-ionization processes involving impurities in semiconductors are of cascade nature.

The existence of anomalously large capture cross sections of attractive centers in semiconductors makes it necessary to assume that the main capture transitions are those of carriers to highly excited levels of a center.[3] It has been shown[4,5] that the capture process can be described as the continuous dropping of electrons or holes along the energy scale from positive to negative values of the energy.

Since thermal ionization is the converse of capture, it is natural to assume that thermal excitation from an attractive center again does not occur directly from the ground state to an allowed band but as a result of an upward rise along the excited states. In this case the application of an electric field not only lowers the ionization energy but also alters the rate of diffusion over the highly excited states of an impurity center. This alters the preexponential factor in the formula (2), which now becomes a function of the electric field and depends not only on the potential of the attractive center but also on the mechanism of the electron–lattice interaction.

The present paper is concerned with the theory of thermal ionization from a Coulomb impurity center as a result of the interaction of electrons and holes with acoustic phonons. The thermal ionization coefficient in an external field is described by

$$\beta(\mathcal{E})=(1+0.98E_{\mathcal{E}}/kT)^{-1}\beta\exp(E_{\mathcal{E}}/kT). \tag{3}$$

An experimental check of whether Eq. (2) or Eq. (3) is valid provides a direct answer to the question of whether thermal excitation occurs directly from the ground state to an allowed band (with the corresponding capture from the band directly by the ground state) or by a cascade process.

2. The probability of thermal liberation of an electron from an isolated Coulomb center will be calculated by the Pitaevskiĭ method[6] used earlier[4,5] to find the capture cross sections.

In an electric field $\mathcal{E}$ the bound states exist only in the range of negative values of the total energy E satisfying $|E|>E_{\mathcal{E}}$. The value of $E_{\mathcal{E}}$ is given by Eq. (1) and is the absolute total energy of an electron $E=\epsilon-e^2Z\varkappa^{-1}r^{-1}-e\vec{\mathcal{E}}\cdot\mathbf{r}$ (ϵ is the kinetic energy of an electron) at an extremum ($\partial E/\partial\mathbf{r}=0$, see Fig. 1). The thermal generation coefficient β is equal to the flux from a single isolated center, which exists in the range of bound states in a steady-state regime on condition that the population of the ground state is unity. Then, the electron distribution function $f(E)$ satisfies the condition

$$f(-E_i)={}^1/_2; \tag{4}$$

here, allowance has been made for the double spin degeneracy of the ground state, and the binding energy of an electron in this state is denoted by E_i.

In the range of highly excited bound states, which can be treated quasiclassically, the distribution function satisfies the equation

$$B(E,\mathcal{E})(f+kT\partial f/\partial E)=-\beta(\mathcal{E}), \tag{5}$$

where the "dynamic friction" coefficient B in the presence of an electric field is given by

$$B(E,\mathcal{E})=\int\varepsilon\tau_\varepsilon^{-1}\rho(\varepsilon)\delta\left(E-\varepsilon+\frac{e^2Z}{\varkappa r}+e\mathcal{E}r\right)d\varepsilon\,d^3r. \tag{6}$$

Here, $\rho(\epsilon)=8\sqrt{2}\pi(2\pi\hbar)^{-3}m^{3/2}\epsilon^{1/2}$ is the density of the energy states, $\tau_\epsilon(\epsilon)$ is the time constant of the energy relaxation due to the interaction of electrons of kinetic energy ϵ with acoustic phonons:

$$\tau_\varepsilon(\varepsilon)=l_0(m/2\varepsilon)^{1/2}, \tag{7}$$

where m is the effective mass and, in the case of scattering by acoustic phonons, the quantity l_0 is related to the mean free path l by $l_0=l(kT/2ms^2)$; s is the velocity of sound. The equation (5) describes the diffusion of electrons in the total-energy space. Equation (6) allows for the change in the shape of the potential well in an electric field.

It is natural to assume that an electron which arrives in the region of the continuous spectrum from the region of bound states is characterized by a negligible probability of returning back to the center because the phase volumes are not comparable. This means that in calculating the distribution function in the region of bound states we may assume that an absorbing wall is placed at the boundary $E=-E_{\mathcal{E}}$ separating finite from infinite ($E>-E_{\mathcal{E}}$) trajectories. Then, the boundary con-

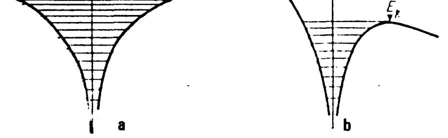

FIG. 1. Coulomb well: a) in the absence of an electric field $\mathcal{E}$; b) in the presence of an electric field $\mathcal{E}$ (the energies $E_{\mathcal{E}}$ are explained in text).

dition for Eq. (6) is

$$f(-E_{\mathscr{E}})=0. \tag{8}$$

The solution of Eq. (5) with the boundary condition (8) gives

$$f(E)=\frac{\beta(\mathscr{E})e^{-E/kT}}{kT}\int_{E}^{-E_{\mathscr{E}}}\frac{dE'}{B(E',\mathscr{E})}e^{E'/kT}. \tag{9}$$

In the range $|E|\gg kT$ the distribution function (9) reduces to the Boltzmann distribution

$$f(E)=\frac{\beta(\mathscr{E})e^{-E/kT}}{kT}\int_{-\infty}^{-E_{\mathscr{E}}}\frac{e^{E'/kT}}{B(E',\mathscr{E})}dE'. \tag{10}$$

This is a consequence of the fact that an exponentially small flux β does not perturb the thermodynamic-equilibrium distribution over deep states far from the absorbing wall. Normalization to the Boltzmann distribution should be such as to satisfy the condition (4). Therefore, the thermal ionization coefficient β is

$$\beta(\mathscr{E})=\frac{kT}{2}\exp\left(-\frac{E_i}{kT}\right)\Bigg/\int_{-\infty}^{-E_{\mathscr{E}}}\frac{\exp(E'/kT)}{B(E',\mathscr{E})}dE'. \tag{11}$$

Naturally, the energy state is largely discrete near the ground state and here Eq. (5) is inapplicable. However, if the energies $-kT$ and $-E_{\mathscr{E}}$ are in the quasicontinuous spectrum (the condition of quasicontinuity of the spectrum is discussed in detail in the review by Abakumov *et al.*[5]), the solution (9) reduces to the Boltzmann distribution even in the region where Eq. (5) is inapplicable. It is natural to assume that this Boltzmann distribution is retained also at lower energies in the region of discrete spectrum.

In the absence of an electric field ($E_{\mathscr{E}}=0$), the thermal ionization coefficient β is

$$\beta=\frac{kT}{2}\exp\left(-\frac{E_i}{kT}\right)\Bigg/\int_{-\infty}^{0}\frac{\exp(E'/kT)}{B(E')}dE'. \tag{12}$$

The coefficient $B(E)$ in Eq. (12) can be calculated using Eq. (6) bearing in mind that $\mathscr{E}=0$. We now have

$$B(E)=\frac{8}{3\pi}\frac{m}{|E|l_0}\left(\frac{e^2Z}{\varkappa\hbar}\right)^3. \tag{13}$$

Substituting Eq. (13) into Eq. (12) and integrating, we find that the ionization coefficient β in the absence of an electric field is

$$\beta=\frac{4}{3\pi}\left(\frac{e^2Z}{\varkappa\hbar}\right)^3\frac{m}{kTl_0}\exp\left(-\frac{E_i}{kT}\right). \tag{14}$$

As expected, Eq. (14) is identical with the expression for β which can be obtained by equating the recombination and thermal ionization fluxes under thermodynamic equilibrium conditions:

$$\beta=\frac{1}{g}\sigma\langle v\rangle N_c\exp\left(-\frac{E_i}{kT}\right); \tag{15}$$

here, g is the degree of degeneracy of the ground state of an impurity (in the present case, we have $g=2$) and the capture cross section σ is given by[4,5]

$$\sigma=\frac{4}{3}\pi\left(\frac{e^2Z}{\varkappa kT}\right)^3\frac{1}{l_0}, \tag{16}$$

where the average velocity is $\langle v\rangle=(8kT/\pi m)^{1/2}$ and the density of states in the conduction band is $N_c=2(mkT/2\pi\hbar^2)^{3/2}$. It should be noted that if the degrees of degeneracy of the ground state of an impurity center g and of a state in a band g_1 are not equal (this may be true of a deep impurity), then Eq. (14) acquires the factor g_1g^{-1}.

In the presence of an electric field the capture cross section σ and the thermal ionization coefficient β vary independently, and there is no direct relationship between them of the type given by Eq. (15). The change in the capture cross section σ is due to the deformation of the Coulomb well and due to the change in the distribution of free carriers in a field, depending on the mechanisms of elastic and inelastic carrier collisions. On the other hand, the thermal ionization coefficient β is in no way dependent on the free-carrier distribution.

We can calculate β given by Eq. (11) by finding the "dynamic friction" coefficient $B(E,\mathscr{E})$. Integration in Eq. (6) gives

$$B(E,\mathscr{E})=\frac{4m}{\pi l_0E_{\mathscr{E}}}\left(\frac{e^2Z}{\varkappa\hbar}\right)^3\chi\left(\frac{|E|}{E_{\mathscr{E}}}\right), \tag{17}$$

where

$$\chi(t)=t\int_{-1/t^2}^{1/t^2}dy\int_{0}^{x(y)}dx\{{}^1/_4x^2y+1-x\}^2,$$
$$x(y)=2y^{-1}[1-(1-y)^{1/2}]. \tag{18}$$

A simple analytic expression is obtained for the thermal ionization coefficient $\beta(\mathscr{E})$ if the field is sufficiently strong so that $E_{\mathscr{E}}\gg kT$. In this case, we can calculate $\beta(\mathscr{E})$ simply knowing the coefficient $B(E,\mathscr{E})$ corresponding to $E=-E_{\mathscr{E}}$. In fact, in this case the quantity $[B(E',\mathscr{E})]^{-1}$ in Eq. (11) can be taken outside the integral for the value $E'=-E_{\mathscr{E}}$ corresponding to the upper limit. It then follows from Eq. (18) that

$$\chi(1)={}^{16}/_3-{}^4/_5\sqrt{2}-4\ln(1+\sqrt{2})\approx0.68. \tag{19}$$

Consequently, the thermal ionization coefficient $\beta(\mathscr{E})$ is

$$\beta(\mathscr{E})=\frac{1.36m}{\pi l_0E_{\mathscr{E}}}\left(\frac{e^2Z}{\varkappa\hbar}\right)^3\exp\left[-\frac{E_i-E_{\mathscr{E}}}{kT}\right] \tag{20}$$

and it is related by Eq. (3) to the coefficient β in the absence of an electric field.

For an arbitrary value of the electric field $\mathscr{E}$, we find that the substitution of Eq. (17) into Eq. (11) gives

$$\beta(\mathscr{E})=\frac{4m}{3\pi l_0E_{\mathscr{E}}}\left(\frac{e^2Z}{\varkappa\hbar}\right)^3\frac{\exp[-(E_i-E_{\mathscr{E}})/kT]}{\psi(E_{\mathscr{E}}/kT)}, \tag{21}$$

where

$$\psi(\xi)=\frac{2}{3}\xi\int_{0}^{\infty}\frac{e^{-\xi t}dt}{\chi(1+t)}, \tag{22}$$

and the function $\chi(t)$ is given by Eq. (18).

Figure 2 shows a graph of the function $\psi(\xi)$ calculated

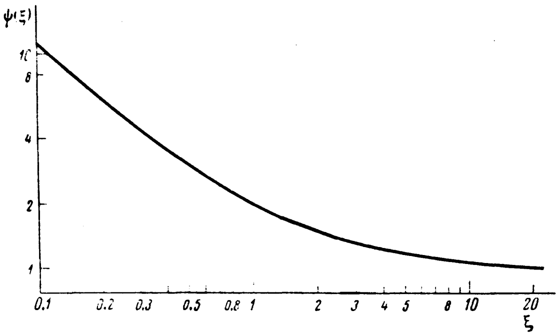

FIG. 2. Graph of the function $\psi(\xi)$ plotted on the basis of computer calculations ($\xi = E_{\mathscr{E}}/kT$).

on a computer. Asymptotic values of the function $\psi(\xi)$ corresponding to small and large values of ξ are as follows:

$$\psi(\xi)=1/\xi, \quad \xi\to 0; \quad \psi(\xi)=0.98, \quad \xi\to\infty. \tag{23}$$

A computer calculation gives practically the same result as the simple interpolation formula for $\psi(\xi)$:

$$\psi(\xi)=0.98+1/\xi, \quad \xi=E_{\mathscr{E}}/kT. \tag{24}$$

Its limiting values are identical with those given by Eq. (23). Table I gives, by way of example, the values of $\psi(\xi)$ calculated on a computer or using Eq. (24) for a number of values of the parameter $\xi = E_{\mathscr{E}}/kT$.

Thus, the dependence $\beta(\mathscr{E})$ is described well by the formula (3). We recall that in deriving this formula we used Eq. (5), which is valid in the range of energies where electrons interact mainly with subthermal phonons, i.e., where the inequality $(|E|ms^2)^{1/2} \ll kT$ is obeyed. Consequently, there is an upper limit to the range of electric fields in which the formula (3) is valid:

$$E_{\mathscr{E}} \ll (kT)^2/ms^2. \tag{25}$$

We note also that the use of the quasiclassical approximation is permissible if the energies $E_{\mathscr{E}}$ and kT remain less than $0.25E_B$,[5] where E_B is the Bohr energy of a shallow impurity center. In the case of a singly charged center in silicon we have $E_B = 400$ °K with $ms^2 = 2.8$ °K for holes and $ms^2 = 1.8$ °K for electrons. By way of example, we shall mention also that in the case of silicon with $\varkappa = 12$ the energy $E_{\mathscr{E}}$ of a singly charged impurity is 2.5 °K in a field $\mathscr{E} = 1$ V/cm and 250 °K in a field $\mathscr{E} = 10^4$ V/cm.

3. The ratio of thermal ionization of traps can be determined directly by a number of methods.[7,8] These methods are based on a study of transient processes in p-i-n (p-type semiconductor–insulator–n-type semiconductor) structures. The current through a reverse-biased structure of this kind is governed by the rate of carrier liberation from traps in the i-type region. The liberated electrons and holes are driven practically instantaneously out of this region so that recombination does not take place. In this case the transient processes resulting from, for example, illumination of the i-type region or because of a change in the voltage applied to this region are governed entirely by the rate of carrier liberation from the traps. The dependence of rate of thermal liberation of the electric field is found by altering the reverse bias applied to a p-i-n structure. Extrapolation to zero field gives the rate of thermal ionization under thermodynamic equilibrium conditions. This method has been used to find the rate of thermal liberation of holes from a gold acceptor level in silicon[9,10] and of electrons from sulfur donor levels in silicon.[11]

TABLE I.

ξ	$\psi(\xi)$	
	computer calc.	from Eq. (24)
0.2	5.997	5.98
0.5	2.997	2.98
1.0	1.996	1.98
2.0	1.494	1.48
0.5	1.191	1.18
10	1.089	1.08

TABLE II.

Impurity*	E_t, meV	β^{exp}, sec^{-1}	β^{theor}, sec^{-1}
Au (T=200 K)	590	$2.0\cdot10^{-4}$	$2.5\cdot10^{-4}$
S (T=125 K)	275	$1.9\cdot10^{-2}$	$5.5\cdot10^{-2}$
S$^-$ (T=200 K)	530	$1.6\cdot10^{-2}$	$1.7\cdot10^{-2}$

*The temperature at which the theory and experiment are being compared is given in parentheses.

Unfortunately, these experiments have been carried out at such high temperatures and in such high electric fields which are either at the limit of validity of our theory or are even beyond this limit. In view of this it is not possible to carry out a detailed comparison of the theory and experiment. However, we can naturally expect the experimental values of the rate of thermal ionization at the lowest temperature to be quite close to the values of β calculated theoretically on the basis of Eq. (14). We calculated β using the ionization potentials E_t given by Sah *et al.*,[9-11] which are in good agreement with those generally accepted. The results of our comparison are presented in Table II.

Measurements of the dependence of the thermal ionization coefficient of gold and sulfur impurities in fields of (1–14) × 10⁴ V/cm were also determined by Sah *et al.*[9-11] The experimental dependence was found to be much weaker than that predicted by the theory [Eq. (3)], which was naturally inapplicable in such fields because these fields corresponded to $E_{\mathscr{E}} \approx 1000$ °K. To the best of our knowledge, there have been no direct experimental determinations of the thermal ionization coefficient at low temperatures and weaker electric fields which would allow us to carry out a correct comparison with our theory.

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Influence of local anisotropy on the states and resonant properties of an optically oriented system of electron and nuclear spins of semiconductors

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A strong anisotropy has been observed in the optical orientation of the electron and nuclear spins in $Al_xGa_{1-x}As$ ($x \approx 0.25$) crystals at 77 K. Depending on the angle φ between the [110] crystallographic axis and the transverse magnetic field H_x (the light propagâtes in the z direction), different states of the spin system and transitions between them are observed. At small angles φ there is a range of fields in which two stable polarization states exist. The width and the position of the boundaries $H_{x1}{}^b$ and $H_{x2}{}^b$ of this range change abruptly (by several dozen oersteds) when φ changes by several degrees. The jumplike transitions from one stable state to another can be initiated by a change in the field H_x near H_{x1} or H_{x2}, by turning off the light for a short time, or by turning on an alternating field $H_{1y}^{\sim}$ at the nuclear magnetic resonance (NMR) frequency. With increasing φ, the width of the hysteresis region decreases, and at $\varphi \approx 3$–$5°$ undamped relaxation oscillations of the polarization set in, with a period from several to about 10 seconds. The period and the waveform of the oscillations depend on the angle and on the field H_x, and can vary under NMR conditions (at $\varphi = 45°$ (the [100] axis coincides with H_x) the behavior of the polarization is well described within the framework of the cooling of the nuclear spin system in the field of the electrons oriented by the light. Optical observation of NMR of As^{75} nuclei has made it possible to determine the role of the local anisotropy that arises in the semiconductor as a result of violation of the cubic symmetry when the Ga atoms of the initial GaAs crystal is replaced by Al. The angular dependences of the resonant frequencies include two branches that vary like $3\gamma H_x \cos\psi \cos\varphi$ and $3\gamma H_x \cos\psi \sin\varphi$, where ψ is the angle between the axes [111] and [110] and γ is the nuclear gyromagnetic ratios. These branches correspond to different positions of the substitutional Al atoms in the unit cell. Resonances have been observed at the subharmonics that correspond to multiquantum transitions. The probabilities of one-, two-, and three-quantum transitions ($\pm 3/2 \rightarrow \mp 3/2$) are compared. The role played by nuclear quadrupoles in the formation of the effective magnetic field that acts on the electron spins is discussed.

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1. INTRODUCTION

When circularly polarized light is absorbed in a semiconductor, the angular momentum of the light quanta can be transferred to the nuclear spin system. In an external magnetic field $H \gg H_L$, where H_L is the local field of the nuclei, it is possible to accumulate an appreciable nuclear polarization along that component of the field H which is parallel to the exciting-light beam.[1-4] This effect can be well described within the framework of the ordinary Overhauser effect. In weak magnetic fields, an appreciable lowering of the spin temperature of the nuclei by light is possible.[5-8] This leads to a number of characteristic singularities in the behavior of the optically oriented electrons. Thus, for example, in a weak magnetic field perpendicular to the light beam, the electron polarization can undergo strong changes.[7-9] This effect is due to the unique enhancement of the field by the hyperfine interaction. The electron spins are acted upon by the effective fields of the oriented nuclei, and this field can greatly exceed the external field. This situation is the converse of the standard situation in electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR), where the hyperfine fields at the electrons are much weaker than the external field.

The anisotropy of the hyperfine interaction should lead to anisotropy of the spin orientation of the electrons. Until recently there were no investigations of the anisotropy effects in optical orientation of spin in semiconductor. Our earlier paper[10] seems to be the first communication on this subject. As will be shown below,