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# Spin-dependent electron dynamics and recombination in $GaAs_{1-x}N_x$ alloys at room temperature

*V. K. Kalevich*[1)], *A. Yu. Shiryaev, E. L. Ivchenko, A. Yu. Egorov, L. Lombez*, D. Lagarde*, X. Marie*, T. Amand**

*A. F. Ioffe Physico-Technical Institute, 194021 St. Petersburg, Russia*

**LNMO-INSA, 31077 Toulouse, France*

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We report on both experimental and theoretical study of conduction-electron spin polarization dynamics achieved by pulsed optical pumping at room temperature in $GaAs_{1-x}N_x$ alloys with a small nitrogen content ($x$ = 2.1, 2.7, 3.4%). It is found that the photoluminescence circular polarization determined by the mean spin of free electrons reaches 40–45% and this giant value persists within 2 ns. Simultaneously, the total free-electron spin decays rapidly with the characteristic time $\approx$ 150 ps. The results are explained by spin-dependent capture of free conduction electrons on deep paramagnetic centers resulting in dynamical polarization of bound electrons. We have developed a nonlinear theory of spin dynamics in the coupled system of spin-polarized free and localized carriers which describes the experimental dependencies, in particular, electron spin quantum beats observed in a transverse magnetic field.

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**1. Introduction.** Spintronics devices require generation of high electron spin polarization in non-resonant excitation conditions and its conservation that must be sufficient to store and manipulate spin information. We show here that these requirements can be achieved at room temperature in dilute nitride III-V semiconductor heterostructures under optical pumping. For this, we use spin-dependent capture of free electrons by deep paramagnetic centers present in semiconductor crystal. The spin-dependent capture results in dynamical polarization of bound electrons which, in its turn, acts as a spin filter increasing polarization of free electrons [1 – 4]. We demonstrate here, that, after a short optical pump pulse, the decay of both a difference of the free-electron spin-up and spin-down densities and their sum is controlled by the same fast spin relaxation in the conduction band. As a result, the spin polarization of free electrons is constant while their total spin decays fast when the time delay increases.

**2. Experimental results.** The samples under study are undoped 0.1-$\mu$m-thick $GaAs_{1-x}N_x$ ($x$ = 2.1, 2.7, 3.5%) layers grown by MBE on a (001) GaAs substrate [5]. We investigate electron spin properties by polarized time-resolved photoluminescence (PL). The samples are excited along the growth axis ($z$-axis) by circularly ($\sigma^+$) polarized 1.5 ps pulses generated by a mode-locked Ti-sapphire laser with a repetition rate of 80 MHz. The PL intensities co-polarized ($I^+$) and counter-polarized ($I^-$) with the excitation laser are recorded in the backward direction using a $S1$ photocathode Hamamatsu Streak Camera with an overall time-resolution of 8 ps. We measure the PL circular polarization degree $\rho = (I^+ - I^-)/(I^+ + I^-)$ proportional to free-electron spin polarization $P_e = (n_+ - n_-)/(n_+ + n_-)$ where $n_+$ and $n_-$ are the densities of spin-up and spin-down free electrons, and $n = n_+ + n_-$ is the free-electron total density. Simultaneously, we measure the free-electron (total) spin density $S_z = (n_+ - n_-)/2$, which for the bimolecular recombination process writes: $S_z \propto (I^+ - I^-)/\sqrt{I}$, where $I = I^+ + I^-$ is the total PL intensity.

Figure 1 shows the experimental kinetics $I(t)$ (solid line), $\rho(t)$ (points) and $S_z(t)$ (circles) measured in $GaAs_{0.979}N_{0.021}$ alloy at room temperature [6]. One can see that $I$ and $S_z$ first rise for $\sim$ 45 ps, which results from relaxation and thermalization of photogenerated carriers. During this time, $\rho$ varies slightly being close to 25%. Then the PL decays in two steps: the first one is fast and the second one is slower with the characteristic decay times of $\approx$ 15 and $\approx$ 70 ps, respectively. Simultaneously with the fast initial PL decay, the PL polarization monotonously rises up to $\approx$ 43% and afterwards keeps the value at least 2 ns as we estimated considering noise fluctuations. Such a long conservation of the high PL polarization is quite surprising since at room temperature spin relaxation time of free electrons in undoped bulk semiconductors of a zinc-bland structure is of the order of magnitude of 100 ps [7, 8], i.e. 10 times

[1)]e-mail: kalevich@solid.ioffe.ru

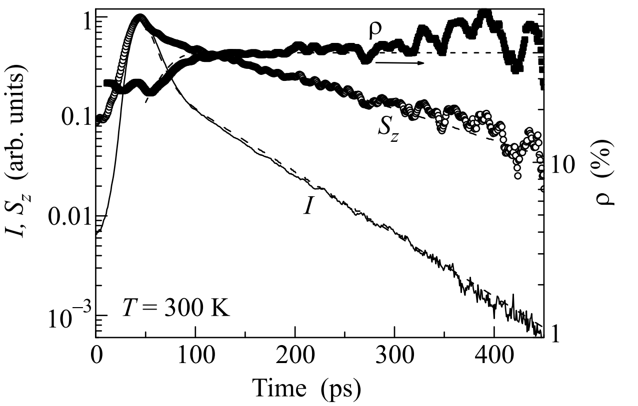


Fig.1. Time-resolved PL intensity (solid line), circular polarization (points) and total free-electron spin (circles) measured in $GaAs_{0.979}N_{0.021}$ alloy at room temperature. The laser excitation energy is $h\nu_{exc} = 1.39$ eV which corresponds to the photogeneration of carriers below GaAs barrier. The pump average power is $W = 130$ mW. Detection energy corresponds to the dominant conduction band – heavy-hole recombination [5]. Dashed curves are calculated in framework of the applied model (see text)

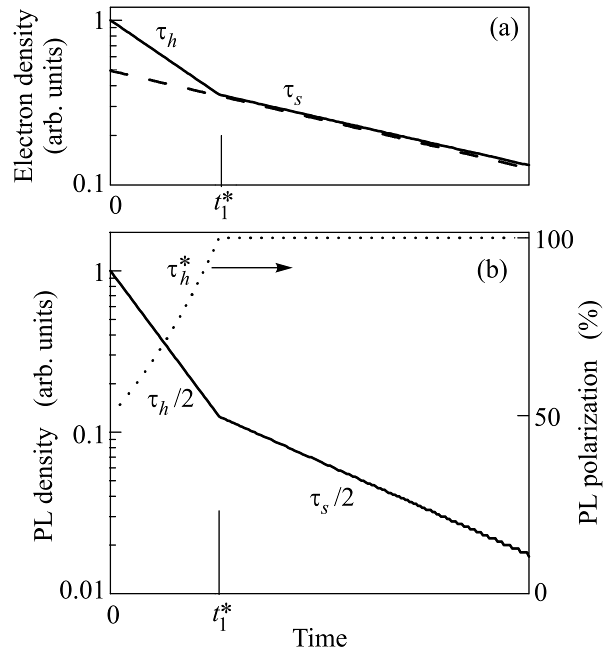


Fig.2. Time evolution of (a) the total (solid line) and difference (dashed) electron densities and (b) the PL intensity (solid) and circular polarization (dotted), in schematic representation

shorter than we observed. However, the total electron spin $S_z$ decays fast with a single characteristic time of about 150 ps.

**3. Theoretical model and discussion.** Let us give first a qualitative explanation of the effects observed. Figure 2 describes schematically two successive regimes of the spin-dependent electron dynamics responsible for the formation of high electron spin polarization and its persistence under the circularly polarized interband pulsed photoexitation. We assume that (i) the density $n_0$ of photoinjected electrons exceeds the concentration $N_c$ of deep centers containing at equilibrium one electron per center, (ii) the deep center can only capture a photogenerated electron from the conduction band with a spin antiparallel to the spin of the already present electron, forming a singlet two-electron bound state [1], (iii) the interband electron-hole recombination contributes negligibly to the balance regulating the electron and hole densities and (iv) photoinjected holes are unpolarized because of their fast spin relaxation [7].

The first regime starts when all the centers acquire the second electron, the fast electron capture is blocked and the further capture is controlled by the photohole nonradiative recombination with the bound electrons described by the hole lifetime $\tau_h = (R_h N_c)^{-1}$, where $R_h$ is a constant. Thus, the electron and hole densities decay as $n = (n_0 - N_c)\exp(-t/\tau_h)$, $p = n_0 \exp(-t/\tau_h)$ (solid line in Fig.2a). For the PL intensity one has $I \propto \exp(-2t/\tau_h)$. This regime ends at the moment $t_1^*$ when the spin minority photoelectrons disappear from the conduction band: $n_-(t_1^*) \approx 0$. This time can be estimated by $t_1^* \approx \tau_h \ln(1/|P_i|)$, where $P_i$ is the initial degree of electron spin polarization [9]. Within the time $t_1^*$ the minority density exponentially decreases to zero while the density of the majority electrons tends to a finite value $n_0|P_i|$ which results in a monotonously increasing free-electron spin polarization up to $\approx 100\%$, see the dotted curve in Fig.2b.

The second regime is characterized by the almost unoccupied minority spin conduction subband and the spin-polarized bound electrons. The kinetics is governed by the free-electron spin relaxation time $\tau_s$: the recombination rate for the free electrons and holes is given by $n_+(t)/\tau_s$. This can be understood taking into account the following balance of rates in the second regime. The decrease of the electron majority density due to the spin-flip processes is determined by the rate $n_+(t)/2\tau_s$. The reverse-spin electrons are immediately captured by deep centers which next capture unpolarized holes to generate unpolarized paramagnetic centers. The majority free electrons are captured at the generated paramagnetic centers with the rate $n_+(t)/2\tau_s$. This leads to the total decay rate $n_+(t)/\tau_s$ for free photoelectrons, so that $n(t) \approx n_+(t_1^*)\exp(-t/\tau_s)$, $I(t) \propto \propto \exp(-2t/\tau_s)$ while their spin polarization keeps on at the level $\approx 100\%$. The densities of one-electron (paramagnetic) and two-electron (nonmagnetic) centers,

$N_1$ and $N_2$ ($N_2 \equiv N_c - N_1$), respectively, are constant. Particularly, $N_2 \approx (R_h\tau_s)^{-1}$ because the hole lifetime equals $\tau_s$. The second regime ends at the moment $t_1^* + t_2^*$ when the decreasing free-electron density becomes smaller than $N_2$ and the further kinetics is determined by the hole recombination processes. The time $t_2^*$ is approximately given by $\tau_s \ln(n_0|P_i|R_h\tau_s)$ which can remarkably exceed $\tau_s$. It is worth to stress that in contrast to $t_1^*$ the time $t_2^*$ is a function of the pump intensity and can be varied in a wide range.

In contrast to the two-stage decrease of the free-electron density $n(t)$ with two characteristic times $\tau_h$ and $\tau_s$ (solid line in Fig.2a), the spin-dependent difference $n_+(t) - n_-(t)$ decays with a single characteristic time $\tau_s$ (dashed line in Fig.2a). Therefore, the total spin $S_z = (n_+ - n_-)/2$ of free electrons is controlled by the short time, $\tau_s$, of their spin relaxation: $S_z(t) = S_z(0)\exp(-t/\tau_s)$.

The experimental data in Fig.1 are obtained at the pump average power of $W = 130$ mW. At this power, as our estimations show (see below), the ratio $n_0/N_c \sim 10$. In addition, the PL exponential decay at long delay also indicates bimolecular mechanism of recombination. This means that $n \approx p$ and $n > N_2$ up to 425 ps. Thus, the suggested model can be applied for description of the experiment. Since $n \approx p$, the GaAsN layer under study represents an intrinsic semiconductor where the lifetimes of photogenerated electrons and holes coincide, $\tau_e \approx \tau_h$. At the first stage, the PL decay time-constant, $\tau_1$, is equal to $\tau_h/2 = (15.0 \pm 0.5)$ ps, therefore, $\tau_e \approx \tau_h = (30 \pm 1)$ ps. At the second stage, where $\tau_e \approx \tau_s$, the PL decay constant equals $\tau_2 = \tau_s/2 = (72 \pm 2)$ ps, which yields $\tau_e \approx \tau_h = (144 \pm 4)$ ps.

The PL polarization is not sensitive to free-electron spin relaxation, and, therefore, it cannot be used for measuring the time $\tau_s$. However, the total free-electron spin $S_z$ decays exponentially with the time constant $\tau_s$. The time was found from the experimental dependency $S_z(t)$ shown in Fig.1 to be $\tau_s = (150 \pm 15)$ ps. Within the experimental error, this value is two times longer than $\tau_2 = (72 \pm 2)$ ps which coincides completely with the model predicting $\tau_s = 2\tau_2$. Thus, the measurement of slow PL decay time at spin-dependent recombination allows us to find the free-electron spin relaxation time. Note, that the method is more precise as compared to the measurement of the total spin decay where the ratio of $(I^+ - I^-)/\sqrt{I}$ is found.

The suggested model is based on the dynamical polarization of deep centers, which causes a decrease in the recombination rate of the majority spin electrons at the second regime. If the deep-center polarization is destroyed then the free-electron recombination rate increases up to the one at the fast regime. The disappearance of the slow range and the PL decay with the single short time $\tau_1 \sim 16$ ps are observed under the change of the exciting light polarization from the circular ($\sigma^+$) to linear ($\pi$) (Fig.3a). Switching on the perpendicular

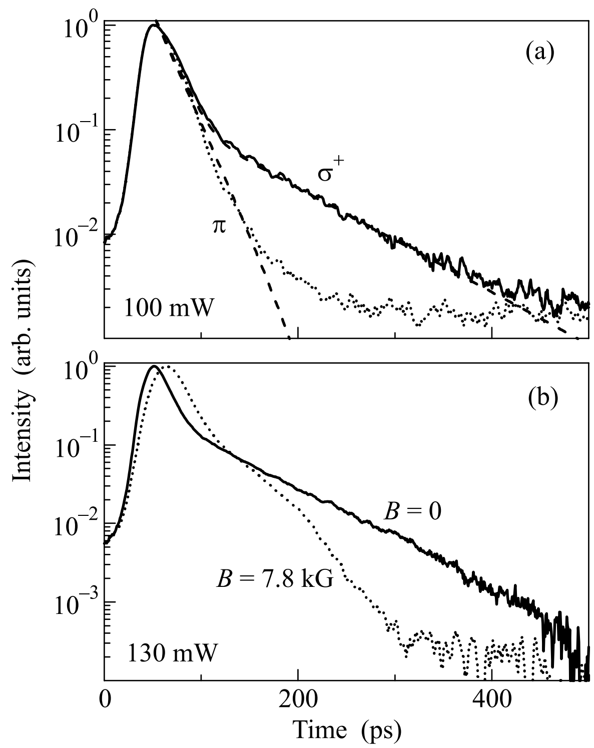


Fig.3. PL decay in $GaAs_{0.979}N_{0.021}$ alloy under $\sigma^+$- and $\pi$-polarized excitation (a) and under $\sigma^+$ excitation in the absence and presence of a transverse magnetic field (b). Solid and dotted curves are experimental transients, dashed curves are the result of calculation. $W$(mW): 100 (a), 130 (b)

magnetic field of 7.8 kG under $\sigma^+$-pumping leads to the same effect (Fig.3b). It again evidences the relevance of the suggested model.

To describe the experimental results quantitatively, we use the set of equations [4] for the rates of the free- and bound-electron total spins, respectively, $\mathbf{S}$ and $\mathbf{S}_c$, transformed to the form:

$$\frac{dn}{dt} + \frac{R_e}{2}\,(nN_1 - 4\mathbf{S}\mathbf{S}_c) = G\,,$$
$$\frac{dp}{dt} + R_h(N_c - N_1)p = G\,,$$
$$p = N_c - N_1 + n\,,$$
$$\frac{d\mathbf{S}}{dt} + \frac{R_e}{2}\,(\mathbf{S}N_1 - \mathbf{S_c}n) + \frac{\mathbf{S}}{\tau_s} + \mathbf{S}\times\boldsymbol{\omega} = \frac{P_i}{2}\,G\mathbf{o}_z\,,$$
$$\frac{d\mathbf{S_c}}{dt} + \frac{R_e}{2}\,(\mathbf{S_c}n - \mathbf{S}N_1) + \frac{\mathbf{S_c}}{\tau_{sc}} + \mathbf{S_c}\times\boldsymbol{\Omega} = 0\,.$$

Here $G = G_+ + G_-$, $G_\pm$ are the photogeneration rates of electrons with the spin $\pm 1/2$, $P_i = (G_+ - G_-)/G$, $\tau_{sc}$ is spin relaxation time of bound electrons, $\mathbf{o}_z$ the unit vector directed along the growth axis $z$ coinciding with the exciting beam, $\boldsymbol{\omega}, \boldsymbol{\Omega}$ are the Larmor frequencies defined by $\hbar\boldsymbol{\omega} = g\mu_B\mathbf{B}$, $\hbar\boldsymbol{\Omega} = g_c\mu_B\mathbf{B}$, $g$ and $g_c$ are the $g$-factors of free and bound electrons, $\mathbf{B}$ is the magnetic field. Note that $N_1 = N_+ + N_-$ , $S_{c,z} = (N_+ - N_-)/2$, where $N_\pm$ are the densities of spin-up and spin-down paramagnetic centers, and we assume $\mathbf{B} \perp z$. The sign of experimentally observed positive PL polarization in Fig. 1 corresponds to the recombination of conduction electrons with heavy holes [5]. For the recombination, $\rho = P'P_e = 2P'S_z/n$ [7], where $P'$ is a depolarization factor.

Our model considers kinetics when the PL decay starts. We assume that the decay begins at the time delay $\Delta t = 55$ ps which is used as a fitting parameter. Calculated dependencies of the PL intensity $I(t)$, degree of circular polarization $\rho(t)$ and spin $S_z(t)$ shown by dashed curves in Fig.1 and Fig.3a are obtained for the following parameters: $n_0/N_c = 10$ and 7.7 for Fig. 1 and Fig. 3a, respectively, $R_e/R_h = 4$, $\tau_s = 140$ ps, $\tau_{sc} = 1500$ ps, $P_i = 50$ and 0% at $\sigma^+$ and $\pi$ excitations. One can see, that the calculated curves fit well the experimental ones. Note that the average value of $\rho$ measured within the plateau in Fig.1 equals 43%. It is two times smaller than the value, 95%, calculated assuming recombination of conduction electrons with heavy holes. We attribute the difference in the $\rho$ value to admixture of the conduction electron–light-hole recombination having the opposite sign of $\rho$ [5]. A coincidence of the calculated (dashed) curve $\rho(t)$ with the experimental one in Fig.1 is obtained using the fitting coefficient of $P' = 0.452$.

The calculations (not presented here) show that the normalized relations $\rho(t)$ and $I(t)$ depend weakly on variation of the parameters $n_0/N_c$ and $R_e/R_h$. Specifically, they virtually coincide at $n_0/N_c > 20$ and $R_e/R_h > 6$. At the same time, we found that calculated for a continuous-wave (CW) excitation dependencies $I$ and $\rho$ on both the excitation intensity and transverse magnetic field (Hanle effect) are very sensitive to these parameters. Fitting of experimental curves found in Ref. [4] at CW excitation of the same $GaAs_{0.979}N_{0.021}$ sample allowed us to estimate the value of $N_c \sim 4 \cdot 10^{16}$ cm$^{-3}$. This provided in turn to find the relation of $n_0/N_c \sim 10$ and $R_e/R_h \sim 4$ at the average pulse pump power $W = 130$ mW.

The value $\tau_{sc} = 1500$ ps used in this paper is in agreement with the 600 ps estimate from below for $\tau_{sc}$ found in Ref. [4] from the analysis of the Hanle effect. It should, however, be mentioned that, in comparison to the continuous-wave measurements of Ref. [4], the time-resolved data are less sensitive to $\tau_{sc}$. Particularly, the "plateau" of the curve $\rho(t)$ lasts out up to 500 ps even for $\tau_{sc}$ decreased to 30 ps which clearly demonstrates dynamical character of the observed spin-dependent effects.

Fig.4 shows the beats in the $I^+$ (solid) and $I^-$ (dashed) PL components and in the polarization de-

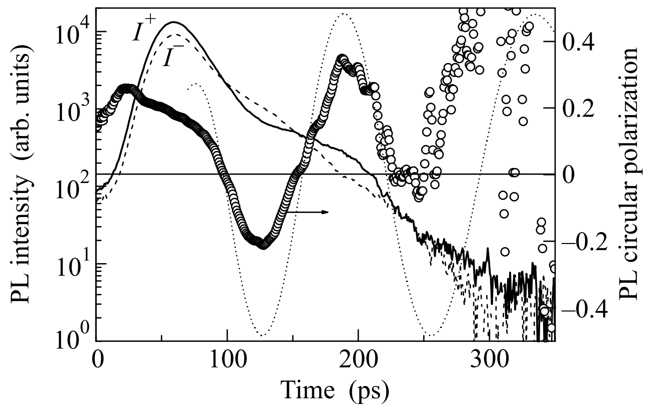


Fig.4. Room-temperature electron spin beats in the PL intensity $\sigma^+$ (solid) and $\sigma^-$ (dashed) components and the degree of PL circular polarization (circles). $W = 130$ mW. Dotted curve is the calculated one. $B = 7.8$ kG

gree $\rho$ (circles) recorded in $GaAs_{0.079}N_{0.021}$ alloy in the presence of the transverse magnetic field $B = 7.8$ kG. These beats result from the Larmor precession of electron spins. They have a complex shape since $g$-factors of free and bound electrons, $g$ and $g_c$, differ both in their value and sign. However, the exact values of $g$ and $g_c$ in $GaAs_{0.079}N_{0.021}$ are unknown. Since in our measurements [4] the sign of $g_c$ was found to be positive, we believe that the $g$-factor of bound electrons is close to the $g$-factor of electrons in vacuum, i.e., $g_c \approx 2$. As for $g$-factor of free electrons, a paper devoted to measuring $g$ in GaInAsN dilute nitrides is known only [10]. It was found in this paper that $g$ is negative. We used $g$-factor $g = -0.9$ in our calculations since at this value the calculated beat period fits the experimental one. It is seen in Fig.3b that the peak $I(t)$ is delayed by 14 ps in the magnetic field 7.8 kG as compared to the case of $B$=0. In accordance to this, we assume that, in the presence of magnetic field, $\Delta t = 69$ ps. Dotted line in Fig.4 shows the beats of $\rho$ calculated with $g = -0.9$, $g_c = 2$ and $\Delta t = 69$ ps. One can see that our model describes qualitatively the experimental beats for $t > 70$ ps.

We have also observed strong PL polarization and its stability at room temperature in an $n$-doped ($N_{\rm Si} \sim \sim 10^{17}$ cm$^{-3}$) GaAsN layer and in an undoped compressively strained quantum well InGaAsN/GaAs with small nitrogen content of the order of 1% [11]. This indicates the general character of the observed effects.

To conclude, we have measured the giant polarization ($\sim$ 45%) of free electrons and its persistence ($>$ 2 ns) in GaAsN alloys at room temperature. We have developed the nonlinear theory of spin dynamics in a coupled system of free and localized carriers controlled by spin-dependent recombination. The theory shows that the increase of both free and localized electron polarizations up to their limiting values is due to dynamical polarization of deep paramagnetic centers. When the latter is effective, the mean spin of free electrons is independent of their spin relaxation while the total free-electron spin decays in the conduction band with the short spin relaxation time of $\sim$ 100 ps. Also, electron spin quantum beats are observed in transverse magnetic field at room temperature and described theoretically.

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