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L-valley electron spin dynamics in GaAs

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Optical orientation experiments have been performed in GaAs epilayers with photoexcitation energies in the 3 eV region, yielding the photogeneration of spin-polarized electrons in the satellite *L* valley. We demonstrate that a significant fraction of the electron spin memory can be conserved when the electron is scattered from the *L* to the Γ valley following an energy relaxation of several hundreds of meV. Combining these high energy photoexcitation experiments with time-resolved photoluminescence spectroscopy of Γ-valley spin-polarized photogenerated electrons allows us to deduce a typical *L*-valley electron spin relaxation time of 200 fs, in agreement with theoretical calculations.

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Electron spin dynamics has been studied in great detail for about 50 years in semiconductors using optical orientation techniques.[1,2] However, all these experiments were performed with optical excitation energies close to the band gap (typically 1.5–2 eV in GaAs), yielding the photogeneration of spin-polarized electrons in the Γ valley. In addition to its fundamental aspect, the understanding of the electron spin dynamics in the upper valleys is crucial for devices based on electrical injection such as spin light-emitting diodes (LEDs)[3–5] and spin lasers[6] where electrons populate not only the Γ valley but also the satellite *L* and *X* valleys. The spin polarization dynamics of the *L* and *X* electrons will therefore make an important contribution to the overall spin injection efficiency in spin LEDs based on a ferromagnetic layer (FM) and a Schottky barrier and is also vital for the observation of the recently predicted spin Gunn effect, i.e., the spontaneous generation of a spin-polarized current.[7]

Despite their importance, experimental determination of the spin relaxation times in the *L* and *X* valleys, which have been predicted to be much shorter than in the Γ valley, is lacking.[5,8–10] The interplay between Γ and *L* electrons in GaAs has been studied in detail in experiment and theory in the context of the classic, spin-independent Gunn effect.[11–13] Apart from their different energies, Γ and *L* electrons experience a Dresselhaus intrinsic spin splitting of a very different amplitude, which is a key parameter for the spin polarization. The spin-orbit coupling parameters in the upper valleys, for $k_0 = L$ or $k_0 = X$, have been calculated recently by different groups.[14–16] Compared to the Γ valley of III-V semiconductors, larger *k*-dependent spin splittings in the surrounding of the *L* point were predicted.[15] As an important consequence, the Dyakonov-Perel spin relaxation mechanism in the *L* valleys is expected to be very efficient.

The few experimental investigations of the *L*-valley electron spin polarization were performed by photoemission spectroscopy in GaAs.[17,18] In these experiments the GaAs surface is treated with Cs and O to obtain a negative electron affinity. The spin polarization of electrons photoemitted from (110) GaAs following the excitation with circularly polarized light (∼3 eV) measured by means of a Mott polarimeter was 8% at low temperature. However, *L*-valley electron spin relaxation times are difficult to extract from these photoemission experiments[18] since (i) the kinetic energy of electrons was not measured simultaneously with their spin so that it is impossible to assign this polarization to *L* electrons only or to a mixture of *L* and Γ electrons, and (ii) depolarization can occur when the electrons photoemitted from GaAs pass through the Cs-O layer.

In order to access the spin polarization of *L*-valley electrons in an all optical experiment, we have performed optical orientation experiments with laser excitation energies in the range $h\nu = 2.8$–3.2 eV and detected the variation of the luminescence polarization at the fundamental gap transition ($E_g \sim 1.5$ eV) as a function of $h\nu$ [Fig. 1(a)]. These measurements allow us to precisely quantify the energy-dependent optical orientation of *L* electrons and the significant, remaining polarization of electrons that relaxed from the *L* to the bottom of the Γ valley. These experiments, combined with classical time-resolved optical orientation experiments performed with an excitation energy close to 1.5 eV, allowed us to measure a typical *L*-valley electron spin relaxation time $\tau_S^L = 200$ fs, in good agreement with theoretical predictions.

The investigated sample has been grown by molecular beam epitaxy on nominally undoped (001) GaAs substrates. It consist of a 1 μm beryllium doped GaAs epilayer with $p_0 = 10^{18}$ cm^{-3}. We present in this Rapid Communication the experimental results obtained at 10 K. The excitation source is a mode-locked frequency doubled Ti:Sa laser with a 1.5 ps pulse width and a repetition frequency of 80 MHz. The laser beam propagating perpendicular to the sample surface is focused onto the sample to a 100 μm diameter spot with an average power $P_{exc} = 15$ mW and its helicity is modulated σ^+/σ^- with a photoelastic modulator at a frequency of 50 kHz; in addition to an increased measurement accuracy, this avoids the buildup of the dynamic nuclear polarization.[19] For the polarized photoluminescence excitation (PLE) experiments, the time-integrated photoluminescence (PL) intensity is dispersed by a spectrometer and detected by a silicon photodiode with a double-modulation lock-in technique. For near band-gap excitations, the time-resolved PL measurements are performed with a S20 photocathode streak camera with an overall time resolution of 8 ps.[20] The Ti:Sa excitation laser is circularly polarized σ^+ and the resulting PL circular polarization P_c is calculated as $P_c = (I^+ - I^-)/(I^+ + I^-)$. Here, I^+ and I^- are the PL intensity components copolarized and counterpolarized to the σ^+ excitation laser.

Figure 1(b) presents the time-integrated PL spectrum for an excitation energy $E_{exc} = 2.987$ eV. The PL peak position (∼1.494 eV) is consistent with the band-gap shrinkage induced

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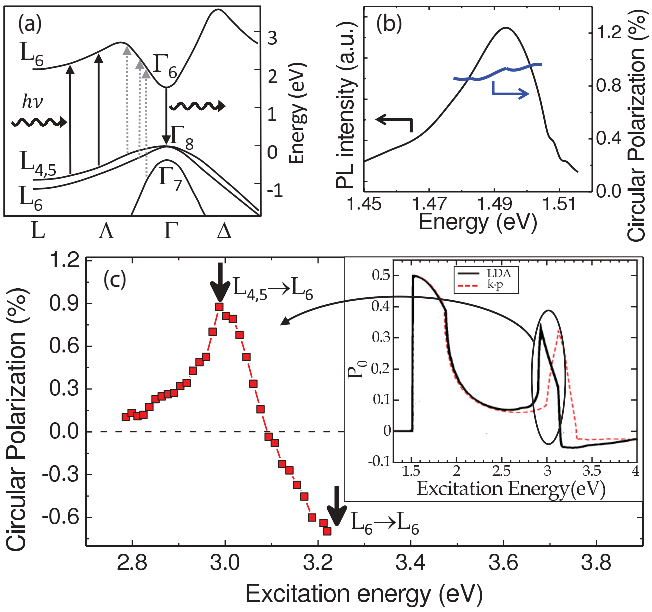

FIG. 1. (Color online) (a) Schematics of the GaAs band structure; the arrows present the optical excitation and detection energies used in (b) and (c). (b) Time-integrated photoluminescence spectrum and the corresponding circular polarization following a σ^+-polarized laser excitation at an energy $E_{exc} = 2.987$ eV. (c) PL circular polarization as a function of the excitation energy. The vertical arrows indicate the energy position of L-valley transitions. Inset: Dependence of the calculated photogenerated electron spin polarization after Ref. 21.

by the high p doping.[22] For this photoexcitation energy, Fig. 1(a) shows that four types of optical transitions are allowed. Three of them (dotted lines) will photogenerate electrons in the conduction band (CB) near the Γ point through, respectively, the heavy-hole band $\rightarrow$ CB ($\Gamma_8 \rightarrow \Gamma_6$), light-hole band $\rightarrow$ CB ($\Gamma_8 \rightarrow \Gamma_6$), and the spin-orbit split-off band $\rightarrow$ CB ($\Gamma_7 \rightarrow \Gamma_6$). In the effective mass approximation, this yields the photogeneration of electrons with a kinetic energy of 1310, 830, and 800 meV, respectively. In addition to these three optical transitions leading to the photogeneration of Γ_6 electrons, a strong absorption occurs due to the allowed $L_{4,5} \rightarrow L_6$ transitions in the vicinity of the L valley. Note that the CB L-valley minimum lies 296 meV above the Γ one. As depicted in Fig. 1(a), there is a large region in k space where the L_6 conduction and $L_{4,5}$ valence bands are parallel; this feature, together with the fact that the corresponding masses are larger than the ones in Γ, make these L-valley transitions dominant in this spectral region.[23] For an excitation energy ~200 meV larger, the absorption peak associated to the $L_{4,5} \rightarrow L_6$ transitions vanishes and is replaced by a second peak with a similar amplitude corresponding to the $L_6 \rightarrow L_6$ transitions.

Figure 1(c) displays the PL circular polarization detected at the fundamental gap ($E_{det} = 1.494$ eV) as a function of the excitation energy. The vertical arrows indicate the absorption peaks associated to the $L_{4,5} \rightarrow L_6$ and $L_6 \rightarrow L_6$ transitions, respectively.[23] Remarkably, we observe a significant polarization though the photogenerated spin-polarized electrons have experienced a very large energy loss before radiative recombination at the bottom of the Γ_6 valley. Let us remind that the PL circular polarization P_c detected at the fundamental gap tracks directly the electron spin polarization P_s, $P_s = 2P_c$, according to the well-known optical selection rules and the fact that the hole spin relaxation time is of the order of 1 ps or less.[2] For $E_{exc} = 2.987$ eV, we observe a peak in the PL circular polarization $P_c \sim 0.9\%$. This peak coincides unambiguously with the absorption peak corresponding to the $L_{4,5} \rightarrow L_6$ transition;[23] its position is also similar to the one observed in photoemission experiments.[17] This demonstrates that the electrons photogenerated in the L valley preserve a fraction of the initial spin polarization after the scattering in the Γ valley and subsequent radiative recombination.

The detected electron spin polarization depends both on (i) the maximum photogenerated spin polarization P_0 linked to the optical selection rules imposed by the symmetry of the carrier wave functions and (ii) the ratio between the electron spin relaxation time and electron lifetime. The inset in Fig. 1(c) displays the photogenerated electron spin polarization P_0 as a function of the optical excitation energy deduced from pseudopotential band structure calculations based on the local density approximation (LDA) or 30 band $\mathbf{k} \cdot \mathbf{p}$ calculations.[21] We observe a good qualitative agreement between the excitation energy dependence in the 3 eV region of the measured PL circular polarization and the calculated maximum spin polarization despite the great complexity inherent in the calculation of high energy electron wave functions. The energy of the measured circular polarization peak (2.987 eV) is closer to the one calculated with LDA (2.90 eV) than with the $\mathbf{k} \cdot \mathbf{p}$ method (3.15 eV).

When the excitation energy increases further we observe in Fig. 1(c) that the measured circular polarization decreases and becomes negative in the 3.2 eV excitation energy region. This is in full agreement with the expected reversed spin polarization when the transition $L_6 \rightarrow L_6$ is excited; indeed, the spin-orbit splitting energy between the $L_{4,5}$ and L_6 bands is ~220 meV.[24] Note that Nastos *et al.* calculated a photogenerated spin polarization in this region $P_0 \sim -5\%$ [inset in Fig. 1(c)].[21] The reversal of the spin polarization sign for the two types of L-valley transitions can be explained qualitatively as follows. If we consider the excitation of states in a single L valley by a σ^+-polarized light propagating along the valley axis (e.g., [111]), the photogenerated electron spin polarization would be 100% for transitions from $L_{4,5}$ to L_6 with a corresponding wave function $|(X - iY)\downarrow\rangle/\sqrt{2}$ and $|S\downarrow\rangle$, and -100% for transitions from L_6 to L_6 with a corresponding wave function $|(X - iY)\uparrow\rangle/\sqrt{2}$ and $|S\uparrow\rangle$.[17,25] Taking into account the eight different L-valley orientations [Fig. 2(b)], the respective joint densities of states for each transitions and a light propagation along the [001] direction (as in the experiments presented here) yields the calculated value P_0 ~30% for a resonant excitation of the $L_{4,5} \rightarrow L_6$ transition and $P_0 \sim -5\%$ for the $L_6 \rightarrow L_6$ one [inset in Fig. 1(c)].

Finally let us emphasize that for excitation energies of less than 2.8 eV (i.e., smaller than the L-valley absorption), we measure in Fig. 1(c) a circular polarization close to zero. The calculations predict in this energy region a maximum photogenerated spin polarization $P_0 \sim 10\%$. Thus our results indicate that the total contribution of the spin-polarized hot electrons photogenerated in the Γ_6 conduction band [dotted arrows in Fig. 1(a)] to the PL circular polarization detected

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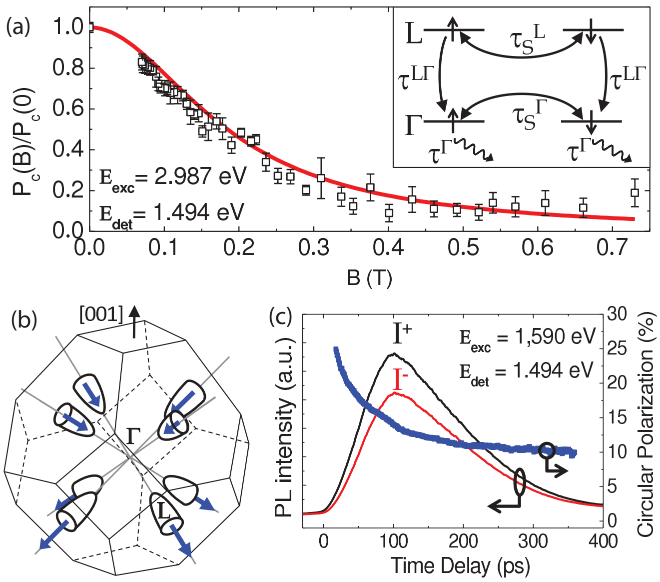

FIG. 2. (Color online) (a) Hanle curve: Variation of the PL circular polarization as a function of the transverse magnetic field B. The full line is a Lorentzian curve with $T_S = 140$ ps (see text). Inset: Schematic representation of the two-level model including the spin relaxation times in both L and Γ valleys (see text). (b) Sketch of the Brillouin zone of GaAs displaying the eight L valleys. The blue arrows represent the photogenerated spins in L valleys. (c) Time evolution of the PL circular components I^+ and I^- and the corresponding circular polarization P_c for a near band-gap excitation.

at the bottom of the Γ_6 band is very weak in this excitation energy range. The spin relaxation time for these high energy electrons in the Γ_6 CB is very short as a result of the large electron k wave-vector values and the cubic k form of the Γ-valley Dresselhaus spin-orbit coupling in bulk GaAs.[2,10] As a consequence, the detected $P_c \sim 0.9\%$ measured for an excitation energy of 2.987 eV can undoubtedly be assigned to the spin-polarized electrons photogenerated in the L valley. This is confirmed by the fact that the contribution of the L-valley transitions to the absorption in this energy range is much larger than the Γ-valley ones.[21,23] For the sake of simplicity we will neglect in the following the small contribution of these photogenerated Γ_6 hot electrons.

We have also measured the dependence of the circular polarization on a transverse magnetic field (Voigt configuration) when the spin-polarized electrons are photogenerated in the L valley. Figure 2(a) presents the corresponding Hanle curve for $E_{\text{exc}} = 2.987$ eV and a detection energy $E_{\text{det}} = 1.494$ eV. The observed depolarization induced by the magnetic field is another proof that the measured circular polarization of luminescence is the result of the optical orientation of electron spins. Because of the fast $L \rightarrow \Gamma$ scattering time, the Hanle curve can be well described by a simple Lorentzian function which takes into account only the electron spin relaxation time τ_S^Γ and the electron lifetime τ^Γ in the Γ valley, $P(B)/P(0) = [1 + (\Omega \cdot T_S)^2]^{-1}$, where $\Omega = g\mu_B B/\hbar$, $g = -0.44$ is the Γ electron g factor, and μ_B the Bohr magneton. The Γ electron spin lifetime T_S writes simply $(T_S)^{-1} = (\tau_S^\Gamma)^{-1} + (\tau^\Gamma)^{-1}$. The full line in Fig. 2(a) is the result of a fit with $T_S = 140$ ps, in satisfactory agreement with the direct measurement by time-resolved photoluminescence spectroscopy presented below.

In order to extract quantitative information about the electron spin dynamics in the L valley from the measured polarization of the luminescence displayed in Fig. 1(c), we have explicitly developed the directional optical selection rules in the L valley which are different from the very well-known ones for the Γ valley.[26]

In contrast to the well-known optical selection rules yielding the photogeneration of spin-polarized electrons in the Γ_6 valley, the calculated photogenerated spin polarization in the L valley requires to consider the eight different $\langle 111 \rangle$ valleys whose orientation are different from the [001] σ^+-polarized light propagation axis [see Fig. 2(b)]. For the $L_{4,5} \rightarrow L_6$ optical transition, it can be shown that the corresponding spin polarization in the L valley is $P_0^L = 50\%$, considering a quantization axis along [001];[26] this value is consistent with $P_0 \sim 30\%$ calculated by Nastos *et al.* [inset in Fig. 1(c)] for an optical excitation energy resonant with $L_{4,5} \rightarrow L_6$ but which also includes a weak contribution of the hot photogenerated electrons in the Γ_6 valley characterized by a smaller spin polarization.[21] The maximum circular polarization of the luminescence detected at the fundamental gap ($\Gamma_8 \rightarrow \Gamma_6$) is thus $P_0^L/2 = 25\%$ (the factor 2 is due to the transitions involving both heavy holes and light holes[19]). We emphasize that this "loss" of spin polarization arises from symmetry considerations and not from any spin relaxation mechanisms which have been so far neglected. We have independently measured the spin relaxation time of the electrons in the Γ valley by recording the time- and polarization-resolved photoluminescence spectrum following a direct photogeneration of Γ electrons. Figure 2(c) presents the time evolution of the luminescence copolarized I^+ and counterpolarized I^- to the σ^+ excitation laser; the excitation energy is $E_{\text{exc}} = 1.590$ eV, yielding the photogeneration of spin-polarized electrons in the Γ_6 conduction band only. The measured initial circular polarization of luminescence is $\sim$25%, in very good agreement with the optical selection rules in bulk GaAs.[19] From these kinetics we measure $\tau_S^\Gamma \sim 200$ ps and $\tau^\Gamma \sim 105$ ps. These values are consistent with previous measurements performed in p-doped GaAs epilayers with similar doping values, where it was demonstrated that the spin relaxation of thermalized electrons in the Γ valley is due to the Bir-Aronov-Pikus mechanism.[16,19,27–30]

Finally we have interpreted the experimental results of Fig. 1(c) in the framework of the following simple two-level rate equation system:

$$\begin{aligned} \frac{dn_{+(-)}^L}{t} &= \frac{n_{+(-)}^L - n_{-(+)}^L}{2\tau_S^L} - \frac{n_{+(-)}^L}{\tau^{L\Gamma}}, \\ \frac{dn_{+(-)}^\Gamma}{t} &= \frac{n_{+(-)}^\Gamma - n_{-(+)}^\Gamma}{2\tau_S^\Gamma} - \frac{n_{+(-)}^\Gamma}{\tau^\Gamma} + \frac{n_{+(-)}^L}{\tau^{L\Gamma}}, \end{aligned} \tag{1}$$

where $n_{+(-)}^L(n_{+(-)}^\Gamma)$ is the density of electrons with spins up and down in the L and Γ valley, respectively, and τ_S^L and τ_S^Γ the electron spin relaxation times in the L and Γ valley; $\tau^{L\Gamma}$ is the $L \rightarrow \Gamma$ relaxation time and τ^Γ the electron lifetime in Γ [inset in Fig. 2(a)]. The resolution of Eqs. (1) in steady state conditions leads to the calculated circular polarization of the photoluminescence detected on the fundamental gap following a photogeneration of electrons in the L valley:

$$P_c = \frac{P_0^L}{2} \frac{1}{\left(1 + \frac{\tau^\Gamma}{\tau_S^\Gamma}\right)\left(1 + \frac{\tau^{L\Gamma}}{\tau_S^L}\right)}. \quad (2)$$

For an excitation energy $E_{\rm exc} = 2.987$ eV yielding the photogeneration of L_6 electrons, Fig. 1(c) shows that the measured PL circular polarization is $P_c = 0.9\%$ and the calculated photogenerated electron spin polarization $P_0^L = 30\%$ [inset in Fig. 1(c)]. Assuming a $L \to \Gamma$ transfer time $\tau^{L\Gamma} = 2$ ps as measured by ultrafast spectroscopy,[31–33] we deduce from Eq. (2) that the electron spin relaxation time in the L valley is $\tau_S^L = 200$ fs. Following the same procedure we found a very similar spin relaxation time ($\sim$180 fs) in a second sample characterized by a smaller p doping (not shown). These measured values are in quite good agreement with recent calculations predicting a spin relaxation time $\tau_S^L \sim 100$ fs in GaAs at room temperature as a result of the strong spin-orbit splitting of conduction electrons in the L valley.[10] As expected, the L-valley spin lifetime in GaAs is much shorter than the L-valley electron spin relaxation time in centrosymmetric materials with a weaker spin-orbit interaction such as silicon or germanium.[34]

In conclusion, we have measured the electron spin relaxation time in the satellite L valley in GaAs with an all optical technique. Our measured L electron spin relaxation time ($\sim$200 fs) does indeed confirm the enhanced Dyakonov-Perel spin relaxation induced by the large Dresselhaus spin splitting. It can be expected that the enhanced electron-electron scattering in strongly n-doped GaAs should yield longer spin relaxation times,[35] which could allow the experimental demonstration of the spin Gunn effect. The optical generation of a significant L electron polarization is an important building stone for future spin laser and spin Gunn schemes operating at room temperature, both requiring only a very small initial polarization degree to initiate spin polarization amplification.[7]

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[1] G. Lampel, Phys. Rev. Lett. **20**, 491 (1968).

[2] M. Dyakonov, *Spin Physics in Semiconductors* (Springer, New York, 2008).

[3] B. T. Jonker, G. Kioseoglou, A. T. Hanbicki, C. H. Li, and P. E. Thompson, Nat. Phys. **3**, 542 (2007).

[4] R. Fiederling, M. Keim, G. Reuscher, W. Ossau, G. Schmidt, A. Waag, and L. Molenkamp, Nature (London) **402**, 787 (1999).

[5] R. Mallory *et al.*, Phys. Rev. B **73**, 115308 (2006).

[6] D. Basu, D. Saha, and P. Bhattacharya, Phys. Rev. Lett. **102**, 093904 (2009).

[7] Y. Qi, Z.-G. Yu, and M. E. Flatté, Phys. Rev. Lett. **96**, 026602 (2006).

[8] S. Saikin, M. Shen, and M.-C. Cheng, J. Phys.: Condens. Matter **18**, 1535 (2006).

[9] E. A. Barry, A. A. Kiselev, and K. W. Kim, Appl. Phys. Lett. **82**, 3686 (2003).

[10] H. Tong and M. W. Wu, Phys. Rev. B **85**, 075203 (2012).

[11] J. Gunn, Solid State Commun. **1**, 88 (1963).

[12] B. K. Ridley and T. B. Watkins, Proc. Phys. Soc. **78**, 293 (1961).

[13] D. Mirlin *et al.*, Solid State Commun. **37**, 757 (1981).

[14] J.-W. Luo, G. Bester, and A. Zunger, Phys. Rev. Lett. **102**, 056405 (2009).

[15] J.-M. Jancu, R. Scholz, G. C. LaRocca, E. A. de Andradae Silva, and P. Voisin, Phys. Rev. B **70**, 121306 (2004).

[16] M. Wu, J. Jiang, and M. Weng, Phys. Rep. **493**, 61 (2010).

[17] D. T. Pierce and F. Meier, Phys. Rev. B **13**, 5484 (1976).

[18] H.-J. Drouhin, C. Hermann, and G. Lampel, Phys. Rev. B **31**, 3872 (1985).

[19] F. Meier and B. Zakharchenya, *Optical Orientation* (North-Holland, Amsterdam, 1984).

[20] A. Balocchi, Q. H. Duong, P. Renucci, B. L. Liu, C. Fontaine, T. Amand, D. Lagarde, and X. Marie, Phys. Rev. Lett. **107**, 136604 (2011).

[21] F. Nastos, J. Rioux, M. Strimas-Mackey, B. S. Mendoza, and J. E. Sipe, Phys. Rev. B **76**, 205113 (2007).

[22] G. Borghs *et al.*, J. Appl. Phys. **66**, 4381 (1989).

[23] D. L. Greenaway, Phys. Rev. Lett. **9**, 97 (1962).

[24] D. J. Chadi, Phys. Rev. B **16**, 790 (1977).

[25] F. H. Pollak and M. Cardona, Phys. Rev. **172**, 816 (1968).

[26] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.87.041201 for the details of the method to determine the photogenerated initial electron spin polarization in GaAs L valleys.

[27] K. Zerrouati, F. Fabre, G. Bacquet, J. Bandet, J. Frandon, G. Lampel, and D. Paget, Phys. Rev. B **37**, 1334 (1988).

[28] D. Garbuzov, A. Ekimov, and V. Safarov, JETP Lett. **13**, 24 (1971).

[29] A. Aronov, G. Pikus, and A. Titkov, Sov. Phys. JETP **57**, 680 (1983).

[30] D. Rosen *et al.*, Appl. Phys. Lett. **39**, 935 (1981).

[31] J. Shah, B. Deveaud, T. C. Damen, W. T. Tsang, A. C. Gossard, and P. Lugli, Phys. Rev. Lett. **59**, 2222 (1987).

[32] C. J. Stanton and D. W. Bailey, Phys. Rev. B **45**, 8369 (1992).

[33] Note that the $\Gamma \to L$ transfer time is $\sim$100 fs, much shorter than the $L \to \Gamma$ one because of the smaller density of states in the valley linked to the very different effective electron masses, $m_\Gamma = 0.067 m_0$ and $m_L = 0.23 m_0$, with m_0 representing the free electron mass.

[34] F. Pezzoli *et al.*, Phys. Rev. Lett. **108**, 156603 (2012).

[35] W. J. H. Leyland, G. H. John, R. T. Harley, M. M. Glazov, E. L. Ivchenko, D. A. Ritchie, I. Farrer, A. J. Shields, and M. Henini, Phys. Rev. B **75**, 165309 (2007).