We experimentally demonstrate ultralong spin lifetimes of electrons in the one-dimensional (1D) quantum limit of semiconductor nanowires. Optically probing single wires of different diameters reveals an increase in the spin relaxation time by orders of magnitude as the electrons become increasingly confined until only a single 1D subband is populated. We find the observed spin lifetimes of more than 200 ns to result from the robustness of 1D electrons against major spin relaxation mechanisms, highlighting the promising potential of these wires for long-range transport of coherent spin information.

Nanowires (NWs) present three key assets: their unique cylinder-like shape, an exceptional surface-to-volume ratio and a high level of control during the epitaxial crystal growth. These features have established NWs in a cornerstone role for an impressively diverse area of nanoscale concepts, ranging from custom-tailored light-matter interaction [1–3], energy harvesting and sensing [4, 5] to ballistic quantum transport [6]. By controlling the diameter at the nanoscale, NWs can for instance be tailored to a specific application by matching them with the length scale of a particular (quasi-) particle. Introducing radial spatial quantum confinement for electrons in semiconductor NWs, thus leaving only one direction of free motion, opens an experimental route to fascinating new phenomena such as Majorana-bound states [7], the unique Coulomb interactions in Tomonaga-Luttinger liquids [8] or long-range, coherent spin transport. Promising groundwork towards long-range spin transport has been demonstrated in wire-like, but yet diffusive systems [9–18]. While these studies highlight a correlation between the wire width and the spin relaxation, going beyond diffusive systems by pushing experiments into the one-dimensional (1D) quantum limit should give access to a new realm of spin coherence.

In this Letter, we present a series of GaAs NWs with different diameters to investigate how spin relaxation evolves in the transition from a continuous three-dimensional (3D) dispersion to the electronic 1D quantum limit, where only a single 1D subband is occupied. Our optical approach allows us to investigate single, free-standing NWs. In our NW system, spatially confining electrons to 1D is expected to completely remove the usually very efficient mechanism of Dyakonov-Perel spin relaxation [19]. Indeed, we experimentally observe extraordinarily long spin relaxation times of more than 200 ns for the thinnest NWs: an increase by a factor ≈ 500 for the transition from 3D to 1D. We qualitatively discuss which mechanism then causes this finite spin relaxation in the 1D NWs and conclude that a 1D quantum theory is needed to fully understand the origin of spin relaxation in 1D. In our experimental approach, the optical spin orientation, the finite spin relaxation time may be limited by the electron-hole exchange interaction.

The GaAs/Al0.36Ga0.64As core/shell NWs were synthesized in the wurtzite (WZ) phase with high phase purity [20] by molecular beam epitaxy using the Au-seeded vapour-liquid-solid growth technique on GaAs(111)B substrates. The NWs are nominally undoped and grow vertically on the substrate with the growth direction parallel to the WZ c || ⟨0001⟩-axis. By focusing the laser beam to a spot size of 1 μm, we were thus able to utilize confocal micro-photoluminescence (μ-PL) spectroscopy to address single upright standing wires and investigate their emission properties [21]. All PL spectra were obtained at 4.2 K under continuous-wave (cw) or pulsed (70–500 ps pulses at a repetition frequency of 1 MHz) excitation of a near-resonant (1.58 eV) laser diode. The emitted PL was imaged onto the entrance slit of a grating spectrometer and detected by a charge-coupled device. Time-resolved photoluminescence signals were acquired by a Hamamatsu streak camera system with a minimum time resolution of 50 ps.

We fabricated eight individual wafers in total, each resulting in a NW ensemble with a narrow distribution (±5 nm) around the average diameters: 20, 25, 40, 90, 110, 160, 235 and 490 nm. Figure 1 shows two exemplary scanning electron micrographs of such single free-standing GaAs NWs with the respective diameters of (a) 113 nm and (b) 22 nm. For all eight NW wafers the GaAs core was passivated by a 10 nm thick Al0.36Ga0.64As shell to suppress non-radiative recombination at the bare GaAs surface. A 5 nm thick GaAs cap prevents oxidation of the shell. The length of the NWs decreases from 6 to 1 μm as the diameter decreases. In the following, size indications refer to the diameter of the GaAs core as measured by scanning electron microscopy between two opposite corners of the hexagonal cross-section.

A general observation we make in our μ-PL studies on single wires is that upon decreasing the NW diame-
Below 50 nm, we observe a significant increase in the emission energy. To demonstrate this behaviour, we show a series of time-integrated p-PL spectra, obtained under cw excitation, for eight different single NWs, which are representative for the respective wafer, in Fig. 1c. The averaged emission energy of several single NWs of nominally identical diameter is further summarized in Fig. 1d for each of the eight different wafers. While no significant energy shift occurs for NW diameters in the range of 490 to 20 nm, a clear increase in the emission energy can be observed for d < 50 nm. For the larger NWs, we measure an average emission peak energy of 1.521 eV, which is consistent with earlier reports of the low-temperature PL emission energy in WZ GaAs NWs [20, 23]. Upon decreasing the diameter below 50 nm, the emission continuously shifts towards higher energies by a total amount of $\Delta E \approx 20$ meV. We attribute this spectral shift to the increasing spatial quantum confinement in the NW core. It marks the transition from a continuous, 3D dispersion to a quantized 1D system in our thinner NWs [22, 24]. We estimate the splitting between the 1D subbands and find that, under the optical excitation used in our experiments, only the first subband is occupied by electrons in NWs with diameters smaller than 35 nm, while the same condition is fulfilled for the holes at diameters $d < 90$ nm (see Supplemental Material [22]). As a consequence, in our experiment, photoexcited electrons in wires with $d < 35$ nm represent a 1D quantum system with only one populated subband. In the following, these wires will be denoted as 1D NWs. Covering the diameters from 490 to 20 nm thus allows us to study the evolution of the NW spin dynamics in the transition from a 3D dispersion to a true 1D system.

We performed time- and polarization-resolved experiments, in which a single free-standing NW is excited with a circularly polarized $\sigma_+$ laser pulse propagating parallel to the axis of the NW [21]. In the WZ crystal phase optical orientation thus creates an ensemble of e-h pairs which is homogeneously spin-polarized along the propagation direction of light [25]. Upon recombination, these e-h pairs will emit partially polarized luminescence. Resolving the emission into left ($I_-$) and right ($I_+$) circularly polarized components directly links the experiment to the relaxation of the optically injected spin polarization. The spin relaxation time $\tau_s$ can then be extracted from fitting the degree of polarization $P_\text{C} = (I_+ - I_-) / (I_+ + I_-)$ to a single exponential decay function, or by separately fitting the difference $(I_+ - I_-)$ and sum $(I_+ + I_-)$ signals (see Supplemental Material [22]). With this optical orientation experiment, we have recently determined an effective g-factor in WZ GaAs NWs of $|g^*| = 0.28$ [21], which can be unambiguously attributed to conduction electrons, since the effective g-factor of heavy holes in this configuration is zero [26, 27]. Along with the usual assumption of rapid hole spin relaxation, this renders our experiment sensitive to the spin relaxation processes of the conduction electrons [28–30].

We estimate the e-h pair density $n$ under pulsed excitation. In the 3D NWs we find $n_{3D} = 8 \times 10^{16}$ cm$^{-3}$, whereas $n_{1D} \approx 1 \times 10^8$ cm$^{-1}$ in the 1D NWs [22]. Such carrier densities characterize an e-h system above the metal-insulator (or Mott-) transition—the notion of an exciton is therefore no longer applicable [31–33]. Our experiment thus probes the dynamics of free and unbound e-h pairs rather than that of excitons.

In Fig. 2, we present two exemplary sets of decay traces, as obtained directly from the streak camera images. The curves show the temporal evolution of the polarized emission in a spectrally integrated narrow (5 meV) window centered at the peak of the PL emission. Figure 2a shows the temporal decay of the circularly polarized emission of a 3D NW with a diameter of $\approx 110$ nm on the scale of a few ns. We observe a large splitting between the $I_+$ and $I_-$ component, which decreases as a function of time until the two curves merge at $\approx 2.5$ ns. This time scale provides a rough measure of the spin relaxation. From our data analysis [22] we determine a spin relaxation time of 1.0 ns and a photocarrier lifetime.
Opposed to this 3D case, we find the time scale on which spin relaxation occurs to be very different for the thin NWs. This is demonstrated for a 1D NW (d = 25 nm), as shown in Fig. 2b. In this case, the splitting between the $I_+ \text{ and } I_-$ curves decays over hundreds of ns with a photocarrier lifetime of 87 ns (see Supplemental Material [22]). At $t > 250 \text{ ns}$, the two curves do not yet appear to be in equilibrium, but their difference vanishes below the noise level. For the NW shown in Fig. 2b, we determine a spin relaxation time of $\tau_s = 98 \text{ ns}$. This strong increase of the spin relaxation time from 1 ns in a wide 3D to 98 ns in a narrow 1D NW already suggests the occurrence of a strong suppression of the dominant spin relaxation mechanism.

To map the evolution of spin relaxation in the transition from 3D to 1D, we have measured and determined the spin relaxation time for the full diameter range from 490 to 20 nm. The statistically averaged spin relaxation times of several (3-8) single NWs from each of the eight different wafers are summarized and displayed in Fig. 3.

For the largest NWs of our study (d = 490 nm) we find relaxation times of $\tau_s = 0.4 \text{ ns}$. Note that a model for fully diffusive carrier motion [34] predicts substantially shorter spin relaxation times of only a few picoseconds for these wire diameters, as we discuss in the Supplemental Material [22]. The inconsistency between our experiment and the model strongly suggests that, even in our NWs with the largest diameters, all prerequisites of the diffusive model are not fulfilled. A plausible reason may be that the carrier motion is not fully diffusive along the radial direction, which would be in line with elastic mean free paths of electrons observed in other III-V NWs [6, 35, 36] and the fact that our NWs are undoped and of high crystalline phase purity.

By reducing the NW diameter in the experiment, we progressively confine the free carrier motion to a movement along the NW axis—a process that gradually induces a fundamental transition in the dimensionality of the electronic band structure. In the range from 235 to 90 nm we find only a weak increase of the spin relaxation time as the diameter decreases. Interestingly, entering the regime where the transition from 3D to 1D gets clearly visible in Fig. 1c,d correlates with a 35-fold increase of the spin relaxation time between NW diameters 90 to 40 nm. When we then reduce the diameter beyond the 1D limit (d < 35 nm), the increase becomes very steep, culminating in the observation of the spin relaxation time $\tau_s = 202 \text{ ns}$ in the thinnest NWs investigated in our study: an increase by a factor of five hundred compared to the 3D NWs.

For d < 35 nm, in the 1D limit of our NWs, we are confronted with an interesting situation: the most common reason for spin relaxation in III-V semiconductors, the Dyakonov-Perel (DP) mechanism, which is based on a momentum-dependent spin splitting in the presence of spin-orbit coupling (SOC) [19, 30, 37], does not contribute to the experimentally observed spin relaxation for the smallest NW diameters. Indeed, due to the symmetry of the WZ crystal, the spin splitting in the conduction band is intrinsically zero for electrons moving along the NW [0001]-axis [38–40]. By now spatially confining the carriers solely to a motion along this direction for small NW diameters, we completely eliminate DP spin relaxation in the transition to the 1D NW regime. Interestingly, this argument also holds for any 1D NW in the zincblende phase growing along the cubic [111] direction.
Now, even in the absence of the DP mechanism, we observe a steeply increasing, yet finite, spin relaxation time. The resulting question which spin relaxation mechanism may dominate in 1D NWs has scarcely been addressed, making it worthwhile to discuss possible candidates in the following.

A prominent one is the Elliott-Yafet (EY) mechanism [41, 42], based on the admixture of spin eigenstates in the presence of SOC. A semiclassical description of the EY process in the transition from 3D to 1D predicts a dramatic decrease in the spin relaxation time as the diameter of a NW decreases [43]. This prediction is in striking contradiction to our experiment where we instead observe a clear increase in $\tau_s$ as the NW diameter crosses the 1D limit. Furthermore, a contribution of EY-related mechanisms involving scattering between 1D subbands is excluded in the 1D limit of our NWs, because only a single subband is occupied at low temperatures, preventing scattering between successive subbands. While a fully quantum-mechanical description may deliver new hints, a dominant contribution of EY to the electron spin relaxation in our experiment thus seems unlikely.

In the few other examples of systems showing comparably long electron spin relaxation times ($\tau_s \geq 100\,\text{ns}$), electrons are bound to quantum dots, or impurities, i.e. 0D localized carriers [44–47]. Here, the hyperfine (HF) interaction between carrier spins and fluctuating nuclear spins was found to limit the spin relaxation time. Unlike localized states, however, the wave function of carriers in 1D is delocalized which effectively averages the fluctuating HF fields of many nuclei. The spin relaxation due to HF interaction is therefore much weaker in 1D as compared to 0D [48, 49] and is not relevant in our experiment.

A more realistic mechanism of spin relaxation may arise from the fact that our optical approach simultaneously creates an equal number of electrons and holes in the system. The exchange coupling $\Delta_{\text{exc}}$ between electron and hole spins can then result in efficient electron spin relaxation as long as hole spin relaxation is very fast. This mechanism, introduced by Bir, Aronov and Pikus (BAP) [50], critically depends on the mean distance between electrons and holes, i.e. the exciton Bohr radius $a_B$. Although our experiment rather probes the dynamics of free e-h pairs instead of excitons, the exciton Bohr radius is still a natural unit of length in the system. The spin relaxation time scales as $\tau_s \propto a_B^{-6}$ (see Supplemental Material [22]). Since $a_B$ is predicted to decrease with the diameter of the NWs [51–53], this proportionality in principle may induce the experimentally observed steep increase in the spin relaxation time for our 1D NWs. In this case the dominating spin relaxation mechanism would directly result from the spin injection scheme, i.e. optical orientation, suggesting that the spin relaxation time of these 1D NWs may be even longer than 200 ns. Note, however, that a precise treatment of the 1D quantum system is necessary to conclude on BAP being the limiting relaxation mechanism in our experiment, since the exchange coupling $\Delta_{\text{exc}}$ also depends on $a_B$.

In conclusion, we have successfully fabricated NWs which experimentally show a clear 1D character, i.e. only a single subband is occupied under photoexcitation. Entering this 1D NW regime is accompanied by the observation of spin relaxation times which are extraordinarily long for GaAs: $\tau_s$ exceeds 200 ns, more than a factor of 500 longer than in our NWs with a 3D dispersion. We attribute this observation to the suppression of the DP mechanism in III-V 1D NWs, a mechanism which is known to be highly efficient in most semiconductor structures. For our experiment, we conclude that the very weak, yet finite spin relaxation is most likely driven by electron-hole exchange and would thus be a mere consequence of the optical spin injection scheme. In III-V semiconductor structures, electron spin relaxation times of this order have so far only been observed for localized, 0D electrons [44–47]. In contrast to these 0D systems, the electrons in our NWs are free to move along the 1D channel, making these wires ideal systems for the transport of coherent spin information, e.g. to interconnect spintronic devices on chip or allow coherent spin manipulation. Our study also shows that a quantum mechanical theory of spin relaxation in 1D will be essential to harness these advantageous aspects of 1D NWs.

We thank M. Gmitra for helpful discussions and gratefully acknowledge financial support by the German Research Foundation (DFG) via SFB 689, 1277 and project 336985961. PEFJ and JF also acknowledge the financial support of the Alexander von Humboldt Foundation and Capes (grant No. 99999.000420/2016-06).
SUPPLEMENTAL MATERIAL

Supplemental Material 1 | Optically excited carrier density

An important parameter to characterize our nanowire (NW) system is the density of optically excited electron-hole (e-h) pairs. We first determine the carrier density \( n_{3D} \) in our three-dimensional (3D) NWs from the absorbed number of photons

\[
n_{3D} = \frac{\bar{P}}{h\nu} f_{\text{rep}}^{-1} \alpha(h\nu). \tag{1}
\]

Here \( \bar{P} = 1.4 \text{ W/cm}^2 \) is the time-averaged output power density \( \bar{P} \) of the excitation laser, \( h\nu = 1.58 \text{ eV} \) is the energy of the laser photons and \( f_{\text{rep}} = 1 \text{ MHz} \) is the repetition frequency of the laser pulse. To calculate \( n_{3D} \) we further use the value of the absorption coefficient of bulk GaAs \( \alpha(h\nu) = 14.8 \times 10^3 \text{ cm}^{-1} \) at the excitation energy 1.58 eV [54]. Evaluating Eq. (1) under the conditions indicated above results in an optically excited e-h pair density of \( n_{3D} = 8 \times 10^{16} \text{ cm}^{-3} \) in our larger wires (\( d = 490–90 \text{ nm} \)).

Calculating the carrier density for the one-dimensional (1D) wires is less straightforward. The photonic nature of the 1D NWs strongly affects the absorption and emission of light, i.e. in this regime of very thin NWs both processes sensitively depend on the NW diameter [1]. A simple conversion of the carrier density from 3D to 1D based on the absorption coefficient of bulk therefore largely overestimates the actual 1D carrier density. In order to still get a rough estimate of the 1D carrier density, we assume that the probabilities of absorbing and emitting a photon are affected to the same extent in our thinner NWs. The assumption is reasonable, because the excitation is near-resonant, i.e. the absorbed and emitted photons approximately have the same wavelength. In our time-resolved photoluminescence (TRPL) experiment, the reduced emission probability can be measured and is most noticable for NW diameters in the range \( d = 20–90 \text{ nm} \). Here, it produces a large increase in the photocarrier lifetime from an averaged recombination time of \( \tau_{\text{rep}} = 1.7 \text{ ns} \) for diameters \( d = 110–490 \text{ nm} \) to \( \tau_{\text{pl}} \approx 75 \text{ ns} \) at \( d = 20–25 \text{ nm} \). With the above assumption, we estimate that the absorption probability of a photon in the 1D NWs is rescaled by the factor \( \frac{1.7 \text{ ns}}{75 \text{ ns}} \approx \frac{1}{50} \). This allows us to reformulate Eq. (1) into

\[
n_{1D} = \frac{\bar{P}}{h\nu} A f_{\text{rep}}^{-1} \alpha'(h\nu), \tag{2}
\]

where \( \alpha'(h\nu) = \frac{1}{50} \alpha(h\nu) \) for \( h\nu = 1.58 \text{ eV} \), \( \bar{P} = 267.0 \text{ W/cm}^2 \) and \( A = \frac{3\sqrt{3}}{2} d^2 \) is the cross-sectional area of the hexagonal NW. Under the above approximation we therefore find a 1D carrier density \( n_{1D} \approx 1 \times 10^6 \text{ cm}^{-1} \) in the NWs with diameters 20–25 nm.

Equation (2) takes into account the change in absorption due to the photonic effects of the NWs. Although we believe that this is the dominant effect, we would like to note that it does not account for changes in the absorption coefficient that are related to an alteration of the electronic density of states.

Supplemental Material 2 | Luminescence properties of 1D wires

In support of the \( \mu \)-PL results shown in the main body of the manuscript, we further investigated the one-dimensional character of our NWs by analyzing the diameter and power density dependence of their luminescence. To avoid PL signal from the substrate and to ensure that the observed luminescence originates exclusively from the NWs, we remove the free-standing wires from the GaAs growth substrate and disperse them onto non-luminescent Si/SiO\(_2\) substrates. Due to small differences in the thermal expansion between GaAs and Si, at low temperatures the substrate strains the deposited NWs and thus slightly lowers the overall band gap as compared to the unstrained, free-standing wires [55].

In Figure 4a-c we show the low-temperature luminescence from three NWs with diameters decreasing from 110 to 25 nm. Under the low-power continuous wave (cw) excitation used to create carrier densities far below the Mott transition, the luminescence is dominated by excitonic transitions [56, 57]. Hence, the main emission peak observed in Fig. 4a-c is attributed to the free-exciton recombination in our wires, its smooth line shape reflecting the distribution of free carriers with a full width at half maximum of \( (1.7 \pm 0.2) \text{ meV} \) that varies only slightly as the diameter decreases. Importantly, when the NW diameter crosses the 1D limit, the free-exciton emission retains its overall line shape, as is expected for a delocalized 1D wave function [57, 58].
FIG. 4. (a)-(c) Low-temperature luminescence profiles of three NWs with different diameters. The low-power cw excitation reveals a second peak emerging at the low-energy side of the free exciton emission. (d) Carrier density dependence of the luminescence from a 1D NW. Under low-power cw excitation, the 1D carrier density is $n_0 \approx 4 \times 10^4$ cm$^{-1}$. Driving the optically excited carrier densities beyond the Mott transition significantly broadens the emission spectra.

Upon decreasing the diameter of our wires from $d = 110$ nm beyond the 1D limit to $d = 25$ nm, the low-power cw excitation first reveals a shoulder emerging in the spectrum at the low-energy side of the free exciton emission, which further develops into a clearly distinguishable second peak at $d = 25$ nm (cf. Fig. 4a-c). We suppose that this lower energy peak originates from the three-particle trion complex—single excitons bound to residual charge carriers—also observed in two-dimensional structures [59, 60]. Simultaneously, in Fig. 4b and c, we observe an increasing energy separation between the peaks such that, at $d = 25$ nm, the two peaks are clearly distinguishable and separated by a peak-to-peak distance of $3$ meV. This relative shift is expected to result from the differences in the dielectric screening predicted for excitons and trions in semiconductor NWs [61].

In Fig. 4d we additionally show the power density dependence of the luminescence from the 1D NW with $d = 25$ nm. To estimate the optically excited 1D carrier density $n_0$ under continuous excitation, we modify Eq. (2) by replacing the inverse laser repetition frequency $f_{\text{rep}}^{-1}$ with the photocarrier lifetime [56] $\tau_{\text{pl}} = 9.7$ ns of these 1D wires lying on Si/SiO$_2$ substrates. Again rescaling the absorption probability $\alpha'(h\nu) = 0.18 \alpha(h\nu)$ renders the 1D carrier density $n_0 \approx 4 \times 10^4$ cm$^{-1}$ created under the low-power cw excitation density of $\bar{P} = 104$ W/cm$^2$. Now, as demonstrated in Fig. 4d, increasing the laser power by up to two orders of magnitude brings the optically excited carriers into a regime above the Mott transition, which broadens the emission peaks [57]. Both luminescence signals overlap until the two peaks are no longer distinguishable at high carrier densities. This effect, purely related to carrier-carrier interactions, and not, e.g., to the emission from defect-bound, localized states, results in the apparent broadening of the linewidth observed in Fig. 1c in the main body of our manuscript.

This deeper analysis of the luminescence properties of our thinnest NWs further confirms their one-dimensional character, as evidenced by the smooth PL lineshape of the free-exciton emission [57, 58] and the increased exciton-trion energy splitting predicted by theory [61].

Supplemental Material 3 | One-dimensional subband formation
FIG. 5. One-dimensional band structure in a NW. (a) shows the diameter-dependence of the five lowest possible energy states as estimated from a circular potential well model for the electrons (red shaded lines), as well as for the heavy holes (blue-shaded lines). The insets show a magnified view of the region of interest. The kinetic energy of the photoexcited carriers is distributed along the direction of free motion. Their parabolic dispersion is plotted in a simple two band scheme in (b) together with the respective Fermi levels (dashed horizontal lines). Red and blue colors are again associated with conduction and valence bands. The electrons or holes in the NW have reached the 1D limit when the splitting between the two lowest subbands $\Delta_{e,h}$ is larger than the respective Fermi level $E_{F,e,h}$. The diameter dependence of $\Delta_{e,h}$ is shown in (c), where the Fermi levels are depicted as dashed horizontal lines. The two crossing points reflect the 1D limit for electrons (red) and holes (blue).

In this letter, we refer to a NW as being in the electronic 1D limit, when only the lowest 1D subband is occupied by the photoexcited carriers. After photoexcitation the carriers relax to the minimum of the conduction or valence band. The 1D limit is therefore reached when the thermalized energy distribution of electrons or holes is smaller than the splitting $\Delta$ between the two lowest 1D subbands. When we increase the spatial confinement by shrinking the NW diameter in our experiment, the energetic separation between two successive subbands increases. We estimate the effect of the spatial confinement on the subband energies in our NWs from a circular potential well model with hard wall boundaries

$$E_{n,l} = \frac{\hbar^2 \zeta_{n,l}^2}{2 m_\perp (d/2)^2},$$  

(3)

where $E_{n,l}$ are the energy eigenvalues that represent the 1D subbands, $\zeta_{n,l}$ denotes the n-th zero of the Bessel function of the first kind $J_l(\rho)$ and $m_\perp$ is the effective mass along the direction of confinement, i.e. perpendicular to the NW axis [62]. In Fig. 5a we plot the five lowest possible energy states for electrons (red shaded lines) and holes (blue shaded lines) as a function of the NW diameter. To calculate these subband energies, we have used the effective masses given in Ref. [63]: $m_{\perp,e} = 0.075 m_0$ and $m_{\perp,h} = 0.12 m_0$. The results of Ref. [63] agree well with a recent experimental study on the electronic properties of wurtzite GaAs NWs [27]. The hard wall boundary condition typically overestimates the actual subband energies, but it provides a good measure of the splitting between two successive subbands.

Starting from the lowest possible energy, the optically excited carriers fill all available states from $k = 0$ to the Fermi wave vector $k_F$. At the low temperatures of our experiment ($T=4$ K), the highest occupied energy state is then given by the quasi-Fermi level in the conduction or valence band

$$E_F = \frac{\hbar^2 k_F^2}{2 m_\parallel},$$  

(4)

where $k_F = n_{1D} \pi / 2$ relates the carrier density $n_{1D}$ to the Fermi wave vector $k_F$ in one dimension [64]. In Eq. (4), the energy of the electrons and holes is determined by their effective mass $m_\parallel$ along the direction of free motion. We use
m_{\perp,e} = 0.060m_0$ and $m_{\parallel,h} = 0.75m_0$ from Ref. [63] to find that $E_F^e = 16.5\text{meV}$ for the electrons, whereas it is only $E_F^h = 1.3\text{meV}$ for the holes. In Fig. 5b we show the corresponding parabolic dispersion along the positive $k_{\parallel}$-direction in a simplified two-band model. The horizontal dashed lines indicate the position of the Fermi levels relative to the minimum of the bands and the vertical dashed line marks the Fermi wave vector $k_F$.

In order to find the 1D limit for the carriers in our NWs we calculate the diameter-dependent splitting $\Delta_{e,h}$ between the two lowest subbands for the electrons (e) and holes (h). The result is plotted in Fig. 5c. The horizontal dashed lines again denote the position of the Fermi levels, whereas their intersection with the $\Delta_{e,h}$-curve (full lines) determines the diameter below which only one single subband is occupied. Due to the highly anisotropic effective mass of the heavy holes, the 1D limit is reached already at larger diameters in the valence band. For $d < 90\text{nm}$ only the lowest subband is populated by the holes in the valence band, while the same condition is fulfilled at diameters $d < 35\text{nm}$ for the conduction electrons.

**Supplemental Material 4 | Optical orientation and the spin relaxation time**

In order to investigate the dynamical properties of spins in our NWs, we utilize the method of time-resolved optical orientation [65]. As described in the article’s main body, a circularly polarized ($\sigma_+\text{)} laser pulse propagating parallel to the axis of the NW creates a non-equilibrium spin polarization among the photoexcited electrons. The dynamical change in the population of spin-up ($N_+$) and spin-down ($N_-$) oriented electrons is given by the rate equations

\begin{align}
\frac{dN_+}{dt} &= -\frac{N_+}{\tau_{pl}} - \frac{N_+}{2\tau_s} + \frac{N_-}{2\tau_s} \\
\frac{dN_-}{dt} &= -\frac{N_-}{\tau_{pl}} - \frac{N_-}{2\tau_s} + \frac{N_+}{2\tau_s}
\end{align}

where $\tau_{pl}$ and $\tau_s$ are the photocarrier lifetime and the electron spin relaxation time [65]. By separately analyzing the time-resolved NW emission of the right $I_+(t)$ and left $I_-(t)$ circularly polarized components, we obtain direct experimental access to the individual decay traces $N_+(t)$ and $N_-(t)$.

The most direct, and also most commonly applied way to obtain the spin relaxation time $\tau_s$ from the experimental curves, is by fitting the degree of spin polarization $P_s(t) = (N_+(t) - N_-(t)) / (N_+(t) + N_-(t))$ to the single exponentially decaying solution

\begin{equation}
P_s(t) = S_0 \exp(-t/\tau_s),
\end{equation}

where $S_0 = (N_+^0 - N_-^0)/(N_+^0 + N_-^0)$ is the initial degree of spin polarization at $t = 0$. Another approach to obtain the spin relaxation time $\tau_s$ from the experimental $N_+(t)$ and $N_-(t)$ curves is to separately fit the difference and sum signal to the single exponential solutions

\begin{align}
N_+(t) - N_-(t) &= (N_+^0 - N_-^0) \exp(-t/\tau) \\
N_+(t) + N_-(t) &= (N_+^0 + N_-^0) \exp(-t/\tau_{pl})
\end{align}

where we have introduced the decay constant $1/\tau = 1/\tau_{pl} + 1/\tau_s$ in Eq. (8). We can see from Eqs. (7) to (9) that the dynamical changes in the experiment are entirely determined by the spin relaxation time $\tau_s$ and the photocarrier lifetime $\tau_{pl}$. Although the two approaches (Eq. (7), or Eqs. (8) and (9)) to determine the spin relaxation time are mathematically fully equivalent, we will show that the quality of the fit can differ in the case of a realistic data set.

In order to evaluate which of the above described approaches to extract $\tau_s$ allows for the most accurate results, we have performed a numerical simulation of the system dynamics. The procedure is as follows: we first calculate a realistic set of decay curves with specific input parameters and then fit these curves to see how accurately the individual fits reproduce the input parameters. We stress the importance of the term realistic, as it refers to adding a small level of random noise (signal-to-noise ratio $S/N \approx 100$) to the calculated curves. The results are plotted in Fig. 6. The left, middle and right column respectively show the dynamics of the experimentally obtained curves $N_+(t)$ and $N_-(t)$, the calculated spin polarization $P_s(t)$ and the difference signal $(N_+(t) - N_-(t))$ for two limiting cases. The initial degree of spin polarization $S_0$ was set to 0.7 for all calculations. For the first case (cf. Fig. 6a-c), which we would like to discuss, we set $\tau_s = 1.0$ and $\tau_{pl} = 5.0$. This represents a system in which the spin relaxation occurs much faster than the carrier recombination.

In Fig. 6a, we observe a time-dependent decrease of the difference between $N_+(t)$ and $N_-(t)$ until the two curves merge at $t \approx 3$. Note that, while the difference has apparently vanished at $t \approx 3$, the total signal intensity has not. This originates from the fact that the photocarrier lifetime is larger than the spin relaxation time. We fit the decay of
the spin polarization $P_s(t)$ according to Eq. (7) as well as the difference signal $(N_+(t) - N_-(t))$ by Eq. (8) and find, in both cases, that the fit reproduces the input parameter $\tau_s = 1.0$ with very high accuracy.

As a counterexample, we also calculate the decay traces for a system in which spin relaxation occurs on a much longer timescale than the recombination process of the carriers. We therefore set $\tau_s = 5.0$ and $\tau_{pl} = 1.0$ and show the results in Fig. 6d-f. Again the difference between $N_+(t)$ and $N_-(t)$ in Fig. 6d vanishes at $t \approx 3$, but in contrast to the first case, the total signal amplitude also decreases to zero. In this case, we find that fitting the spin polarization degree $P_s(t)$ shows a much lower accuracy and the fit consequently overestimates the spin relaxation time by $\tau_s = 6.4$. Instead, fitting the difference signal $(N_+(t) - N_-(t))$ provides a much higher accuracy and reproduces the input parameter accurately as $\tau_s = 5.0$. For the values listed above, the statistical fit error of $\tau_s$ is smaller than the specified number of valid digits.

By calculating a realistic set of decay traces we obtain important insight into the different approaches to fitting the TRPL data. We find that fitting $P_s(t)$, as well as $(N_+(t) - N_-(t))$, both describe the numerical data with very high accuracy, as long as the process of spin relaxation is faster than the carrier recombination. In the reverse case, i.e. if $\tau_s > \tau_{pl}$, our numerical tests suggest that fitting the difference signal $(N_+(t) - N_-(t))$ provides a much better accuracy.

We next apply both fit methods to two complementary sets of experimental data. Unless specified otherwise, the statistical error of the fit is smaller than the number of valid digits. In Fig. 7a, we show the experimental decay curves $I_+(t)$ and $I_-(t)$ as recorded from a NW with a diameter $d = 90 \text{ nm}$. While the two curves merge at $t \approx 4 \text{ ns}$, the total signal amplitude is still large compared to the background noise. From a separate measurement we determine the photocarrier lifetime $\tau_{pl} = 6.7 \text{ ns}$. In Fig. 7b, fitting the spin polarization $P_s(t)$ results in $\tau_s = 1.1 \text{ ns}$. At the same time, we also determine $\tau_s = 1.1 \text{ ns}$ from the $(I_+(t) - I_-(t))$-fit by using $\tau_{pl}$ as an input parameter. The experimental decay traces of Fig. 7a-c therefore confirm the results of the numerical simulations: for $\tau_{pl} > \tau_s$ both fitting procedures give the same results for the spin relaxation time. This condition applies for all NWs with diameters in the range from 490 to 90 nm and we use the $P_s(t)$-fit to determine the spin relaxation times $\tau_s$ that are plotted in Fig. 4 of the

![Simulation](image)
The spin relaxation in many III-V semiconductor structures is dominated by the Dyakonov-Perel (DP) mechanism [19, 30, 37]. In our recent theoretical analysis, we have investigated the role of this mechanism in the 3D diffusive regime of wurtzite NWs and found that for NW diameters \(d \geq L_{so}/2\), where \(L_{so}\) denotes the spin precession length, the DP spin relaxation time \(\tau_{s}^{DP}\) becomes comparable to the corresponding bulk value \(\tau_{s}^{DP,\text{bulk}} = L_{so}^{2}/(8\pi^{2}D_{e})\) [34]. Here, \(D_{e} = \hbar k_{F}l_{e}/(3m_{e})\) denotes the 3D diffusion constant, \(k_{F} = (3\pi^{2}n_{3D})^{1/3}\) the Fermi wave vector and \(l_{e}\) the mean free path. We use the optically excited carrier density in the 3D wires, \(n_{3D} = 8 \times 10^{16}\) cm\(^{-3}\), and the DP spin relaxation time \(\tau_{s}\) regime of wurtzite NWs and found that for NW diameters \([19, 30, 37]\). In our recent theoretical analysis, we have investigated the role of this mechanism in the 3D diffusive regime of wurtzite NWs and found that for NW diameters \(d \geq L_{so}/2\), where \(L_{so}\) denotes the spin precession length, the DP spin relaxation time \(\tau_{s}^{DP}\) becomes comparable to the corresponding bulk value \(\tau_{s}^{DP,\text{bulk}} = L_{so}^{2}/(8\pi^{2}D_{e})\) [34]. Here, \(D_{e} = \hbar k_{F}l_{e}/(3m_{e})\) denotes the 3D diffusion constant, \(k_{F} = (3\pi^{2}n_{3D})^{1/3}\) the Fermi wave vector and \(l_{e}\) the mean free path. We use the optically excited carrier density in the 3D wires, \(n_{3D} = 8 \times 10^{16}\) cm\(^{-3}\), and the DP spin relaxation time \(\tau_{s}\) regime of wurtzite NWs and found that for NW diameters \([19, 30, 37]\). In our recent theoretical analysis, we have investigated the role of this mechanism in the 3D diffusive regime of wurtzite NWs and found that for NW diameters \(d \geq L_{so}/2\), where \(L_{so}\) denotes the spin precession length, the DP spin relaxation time \(\tau_{s}^{DP}\) becomes comparable to the corresponding bulk value \(\tau_{s}^{DP,\text{bulk}} = L_{so}^{2}/(8\pi^{2}D_{e})\) [34]. Here, \(D_{e} = \hbar k_{F}l_{e}/(3m_{e})\) denotes the 3D diffusion constant, \(k_{F} = (3\pi^{2}n_{3D})^{1/3}\) the Fermi wave vector and \(l_{e}\) the mean free path. We use the optically excited carrier density in the 3D wires, \(n_{3D} = 8 \times 10^{16}\) cm\(^{-3}\), and

To demonstrate that the opposite case (cf. Fig. 6d-f) also occurs in our NW series, we show the decay traces of an ultrathin NW with \(d = 20\) nm. Note that the initial large peak in Fig. 7a stems from the fast decay of the spectrally broad substrate signal and does not belong to the NW emission. In a certain regard, the evolution of \(I_{+}(t)\) and \(I_{-}(t)\) in Fig. 7d resembles the decay curves of Fig. 6d: the difference between \(I_{+}(t)\) and \(I_{-}(t)\), as well as the total signal intensity both apparently vanish at \(t \approx 250\) ns. This observation already suggests that \(\tau_{s} > \tau_{pl}\) and that the thinner NWs of our series therefore correspond to a rather peculiar system, in which the process of spin relaxation is slower than the carrier recombination process. From fitting the spin polarization \(P_{s}(t)\), we obtain \(\tau_{s} = (344.5 \pm 21.5)\) ns. Instead, the fit of the \((I_{+}(t) - I_{-}(t))\)-signal determines \(\tau_{s} = (215.7 \pm 10.1)\) ns again we have determined the photocarrier lifetime \(\tau_{pl} = (72.1 \pm 0.4)\) ns from a separate measurement and used as an input parameter for the \((I_{+}(t) - I_{-}(t))\)-fit. At this point, only the comparison to the results of the numerical simulation allows us to decide which of the two values reflects the real spin relaxation time of the system. We therefore fit all NWs with diameters in the range of 40 to 20 nm to the decay of the \((I_{+}(t) - I_{-}(t))\)-signal.

Supplemental Material 5 | The Dyakonov-Perel mechanism in 3D wires

The spin relaxation in many III-V semiconductor structures is dominated by the Dyakonov-Perel (DP) mechanism [19, 30, 37]. In our recent theoretical analysis, we have investigated the role of this mechanism in the 3D diffusive regime of wurtzite NWs and found that for NW diameters \(d \geq L_{so}/2\), where \(L_{so}\) denotes the spin precession length, the DP spin relaxation time \(\tau_{s}^{DP}\) becomes comparable to the corresponding bulk value \(\tau_{s}^{DP,\text{bulk}} = L_{so}^{2}/(8\pi^{2}D_{e})\) [34]. Here, \(D_{e} = \hbar k_{F}l_{e}/(3m_{e})\) denotes the 3D diffusion constant, \(k_{F} = (3\pi^{2}n_{3D})^{1/3}\) the Fermi wave vector and \(l_{e}\) the mean free path. We use the optically excited carrier density in the 3D wires, \(n_{3D} = 8 \times 10^{16}\) cm\(^{-3}\), and...
In their early work, Bir, Aronov and Pikus recognized that the exchange interaction between electrons and holes can readily lead to spin relaxation in optical orientation experiments [50, 66]. In 3D, the relaxation of electrons by free, non-degenerate holes is given by [66]

\[
\frac{1}{\tau_s} = \frac{2}{\tau_0} \frac{v_e}{v_B} |\Psi(0)|^2 \frac{(3\pi/64)\Delta_{exc}^2}{E_B},
\]

where \(h/\tau_0 = (3\pi/64)\Delta_{exc}^2/E_B\) defines a scattering time \(\tau_0\), that depends on the exchange parameter \(\Delta_{exc}\). \(E_B = h/(2m_ea_B^2)\) is the exciton binding energy, \(v_B = h/(m_ea_B)\) and \(a_B\) is the exciton radius. \(v_e\) is the electron velocity and \(|\Psi(0)|^2\) the Sommerfeld factor. We would like to note that, although as stated in the main text, our experiment rather probes the dynamics of free e-h pairs instead of excitons, the exciton Bohr radius is still a natural unit of length to describe the semiconductor system. From Eq. (10) we find the relation between the spin relaxation time and the exciton Bohr radius \(\tau_s \propto a_B^{-6}\) and the exchange parameter \(\tau_s \propto \Delta_{exc}^2\). For the wurtzite phase of GaAs, \(\Delta_{exc}\) and its dependence on \(a_B\) has not yet been investigated experimentally or theoretically.
See Supplemental Material at [URL will be inserted by publisher] for the calculation of the photoexcited carrier densities, further analysis of the 1D NW luminescence, the estimated 1D band dispersion, a detailed description of fitting the spin decay traces and an analytic expression of the Dyakonov-Perel and Bir-Aronov-Pikus mechanisms.

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Finland, and H. Weman, Nano Lett. 12, 6900 (2012).

N. Vainorius, S. Lehmann, A. Gustafsson, L. Samuelson, K. A. Dick, and M.-E. Pistol, Nano Lett. 16, 2774 (2016).

J. L. Birman, Phys. Rev. 114, 1490 (1959).

I. Broser and M. Rosenzweig, Phys. Rev. B 22, 2000 (1980).

M. De Luca, S. Rubini, M. Felici, A. Meaney, P. C. M. Christianen, F. Martelli, and A. Polimeni, Nano Lett. 17, 6540 (2017).

D. J. Hilton and C. L. Tang, Phys. Rev. Lett. 89, 146601 (2002).

T. Korn, Physics Reports 494, 415 (2010).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Finland, and H. Weman, Nano Lett. 12, 6900 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).

L. Ahtapodov, J. Todorovic, P. Olk, T. Mjäland, P. Slättnes, D. L. Dheeraj, A. T. J. van Helvoort, B.-O. Fimland, and H. Weman, Nano Lett. 12, 6090 (2012).