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Ultrafast optical orientation and coherent Larmor precession of electron and hole spins in bulk germanium

C. Hautmann,[1,2,*] B. Surrer,[1,†] and M. Betz[2]

[1]*Physik-Department E11, Technische Universität München, DE-85748 Garching, Germany*

[2]*Experimentelle Physik 2, Technische Universität Dortmund, DE-44227 Dortmund, Germany*

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Circularly polarized light is demonstrated to inject partially spin-polarized electrons and holes in bulk germanium via both direct and indirect optical transitions. While the degree of spin polarization is markedly reduced when compared to prototypical III-V semiconductors, coherent spin precessions in an external magnetic field are well resolved in ultrafast magneto-optics. At cryogenic temperatures, hole (electron) spins exhibit remarkably long coherence times of $\sim$100 ps ($\sim$1 ns).

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The idea of exploiting the spin degree of freedom for information processing initialized huge efforts to explore mechanisms of spin injection and to investigate spin dynamics in semiconductors. In particular, optical orientation based on the selection rules for interband transitions is an efficient tool for photon-to-spin conversion.[1] It has been established in the prototypical material GaAs and is now widely available in III-V and II-VI semiconductors and their nanostructures.[2,3] In marked contrast, little is known about optical orientation in the elementary semiconductors silicon and germanium (Ge), while long spin-coherence times are predicted for both materials.[4–6] Recently, it has been predicted that the optical emission of spin-polarized charge carriers is partially polarized for phonon-assisted transitions in silicon.[7] For direct optical transitions in Ge, Rioux *et al.* simulate a degree of spin polarization up to $\sim 50\%$ ($\sim 80\%$) for electrons (holes)[8] and suggest that hole spins might dominate the spin-dependent optical response because electrons are scattered to the L side valleys. However, in III-V materials of comparable spin-orbit coupling, it is commonly argued that hole spins relax on subpicosecond time scales.[9,10] A recent study by Loren *et al.*[11] on spin-dependent carrier scattering after excitation of Ge across its direct band gap indeed shows signatures of both spin-polarized holes and electrons. These room-temperature experiments reveal that side-valley scattering as well as hole spin relaxation occur within <200 fs. Despite this progress, no magneto-optical analysis of spin dynamics and coherence in any indirect band gap or group-IV semiconductors has been reported to date.

In this paper, we demonstrate that the indirect band gap of Ge neither inhibits optical orientation nor spin detection via time-resolved magneto-optics. We find that circularly polarized light initializes long-lived carrier spins, which coherently precess in an external magnetic field. Different signal strengths, effective g factors, as well as coherence times permit us to differentiate spin coherence of electrons and holes. This paper is organized as follows: We start by discussing potential origins of spin-dependent optical responses in an indirect semiconductor since such mechanisms are much less evident compared to direct band-gap materials. We move on to describe the sample and the ultrafast magneto-optical setup. In the main part of this paper, results on hole and electron spin coherence in bulk Ge are presented for a wide range of temperatures and excitation densities. Most importantly, we extract extraordinarily long coherence times for both species. Finally, we compare excitations via indirect and direct optical transitions and demonstrate similar degrees of electron spin polarization for both cases.

Theoretical aspects of spin-dependent optical responses in an indirect semiconductor are largely unclear. After photoexcitation of bulk Ge via indirect optical transitions, holes remain in the Γ valley, while electrons reside in the L valleys of the conduction band. Most of this paper utilizes probe photon energies, which are resonant only to indirect optical transitions in Ge. Due to the energetic proximity of Γ and L valleys in the conduction band ($\Delta_{\Gamma L} = 0.17$ eV at low temperatures[12]), such energies intrinsically are not far from being resonant with direct optical transitions. As a result, two plausible mechanisms for optical spin readout exist. (i) Any hole spin population in the Γ valley probably induces Faraday rotation (FR) for these probe photon energies because they are only slightly detuned to the direct band gap [cf. corresponding results in GaAs (Ref. 13)] and thereby might reveal hole spin dynamics. (ii) If optical orientation across indirect optical transitions is possible, then, conversely, any spin population in the L valley will affect such optical transitions via Pauli blocking. Therefore, it is reasonable to expect a circular dichroism and/or FR for such indirect transitions, which reflect electron spin dynamics in the L valleys. Our results indicate that both of these mechanisms for spin-dependent optical responses indeed exist, although the latter is two orders of magnitude weaker than the former.

The experimental setup relies on the widely used concept of time-resolved Faraday rotation in the Voigt geometry. The light source is a 250-kHz optical parametric amplifier (OPA) delivering $\sim$ 60-fs pulses tunable between 1200 and 1600 nm. The Ge sample is kept in a cryostat between 3 and 100 K and can be exposed to in-plane magnetic fields of up to 700 mT generated by an electromagnet. Circularly polarized excitation pulses are focused onto a spot of $r \sim 70$ μm on the sample. Faraday rotation of the linearly polarized (degenerate) probe pulses is detected with a polarization bridge taking advantage of lock-in detection referenced to a 1.5-kHz modulation of the excitation. The sample is an optical grade, [111]-oriented, and 1.5-mm thick wafer of Ge (Techspec, Edmund Optics). This thickness is related to the weak absorption of Ge when excited solely across its indirect band gap. Room-temperature resistivity and Hall mobility reveal $\rho = (20.3 \pm 1.0)\ \Omega$cm and a residual n-type conductivity $[n = (6 \pm 2) \times 10^{13}\ \text{cm}^{-3}]$.

Throughout most of this paper, we focus on detecting FR transients after excitation via the indirect band gap. To this end, the OPA is tuned to a central wavelength of ~ 1500 nm so that the photon energies $\hbar\omega = 0.82$ eV (FWHM 0.04 eV) are between the indirect ($E_G = 0.72$ eV) and the direct band gap ($E_{\Gamma 1} = 0.89$ eV) of Ge at low temperatures (cf. excitation spectrum and Gaussian fit to it in Fig. 1(b) and schematic excitation conditions in Fig. 1(a)). Note that the absorption coefficient of Ge (Refs. 14 and 15) varies by three orders of magnitude when comparing the two extreme tails of the laser pulse and, therefore, only a minimal fraction of carriers is excited via direct transitions. FR data for a lattice temperature of $T = 8$ K, an external magnetic field of $B = 700$ mT, and

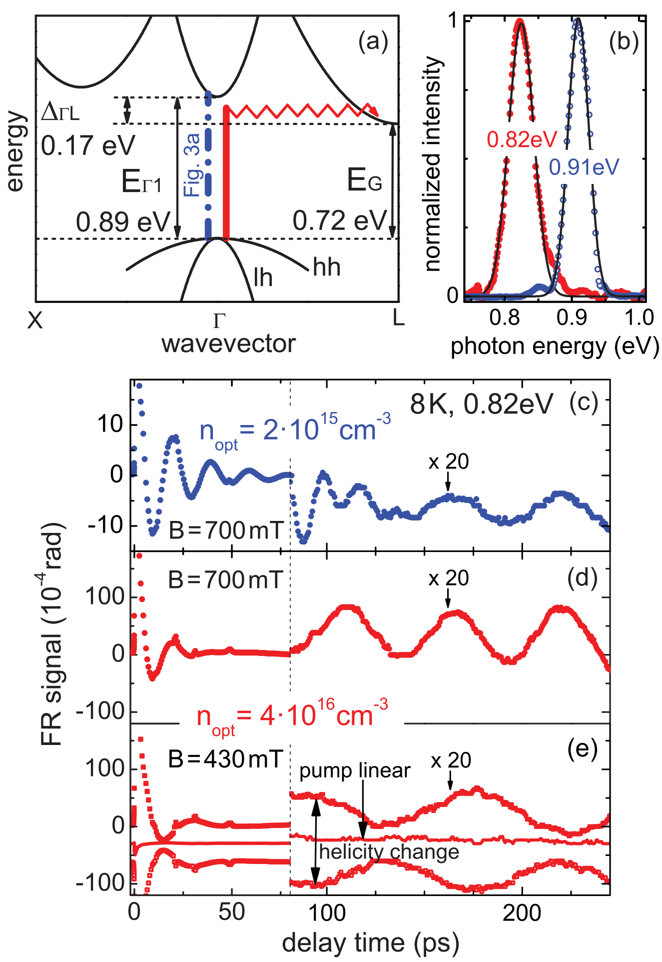

FIG. 1. (Color online) (a) Simplified band structure of Ge indicating the excitation conditions for excitation predominantly across the indirect band gap (central photon energy 0.82 eV) as well as across the direct band gap (central photon energy 0.91 eV). (b) Spectral shape of the laser pulses, solid lines: Gaussian fits to the data. (c)–(e) FR signals at $T = 8$ K and excitation across the indirect band gap with circularly polarized light. (c) Transient for $B = 700$ mT with $n_{\text{opt}} = 2 \times 10^{15}\ \text{cm}^{-3}$. (d), (e) Transients with $n_{\text{opt}} = 4 \times 10^{16}\ \text{cm}^{-3}$ for $B = 700$ and 430 mT together with transients for changed pump helicity and linear pump [in (e), the transients are shifted vertically for clarity].

a moderate density of optically induced carriers ($n_{\text{opt}} = 2 \times 10^{15}\ \text{cm}^{-3}$) are depicted in Fig. 1(c). n_{opt} refers to peak carrier densities taking into account the wavelength dependence of the absorption coefficient across the excitation spectrum.[14,15] Most strikingly, we observe two oscillatory signal components of different amplitude and frequency. In particular, the large-amplitude, high-frequency component decays on a time scale of ~ 50 ps, while oscillations of much smaller amplitude and lower frequency are seen to persist beyond 200 ps (note that the signal amplitude is rescaled by a factor of 20 for delay times $t_D > 80$ ps). Before we exploit the full parameter range of our experiment, we want to briefly demonstrate how FR transients qualitatively change with excitation intensity and magnetic field. For $n_{\text{opt}} = 4 \times 10^{16}\ \text{cm}^{-3}$ and $B = 700$ mT [cf. Fig. 1(d)], we find the high-frequency oscillation to be strongly damped. In marked contrast, the low-frequency oscillation still shows practically no damping beyond 200 ps. When the magnetic field is lowered to $B = 430$ mT [cf. panel 1(e)], the oscillation period is seen to increase as expected from a Larmor precession in an in-plane magnetic field. All these oscillatory FR signals reverse sign upon changing the helicity of the exciting laser pulse, while they are absent for the case of pumping with linearly polarized light [cf. sample traces in Fig. 1(e)]. From the data in Fig. 1, we can directly conclude that circularly polarized optical excitation of bulk Ge generates two different and rather long-lived species, which both exhibit coherent Larmor precession with significantly different frequencies $\omega_L = \frac{g^* \mu_B B}{\hbar}$ (g^* is the effective g factor). As will be corroborated by further data below, there is substantial evidence that the faster decaying part of the signal reveals hole spin coherence, whereas the long-lived part is related to electron spin coherence. By comparison of the initial amplitudes of the oscillatory FR signals for electrons and holes in Fig. 1, we find a ~ 100 times smaller signal amplitude per charge carrier for the electrons. This finding already indicates major differences in the optical orientation process and/or the spin detection compared to direct-gap semiconductors.

In the following, we subsequently analyze hole and electron spin coherence after excitation via the indirect band gap by choosing excitation conditions optimized to mainly observe one species. First, results for hole spin coherence at $T = 8$ K are investigated in more detail. Figure 2(a) shows FR signals without and with applied magnetic field for $n_{\text{opt}} = 8 \times 10^{14}\ \text{cm}^{-3}$. For the transient without magnetic field, the signal is plotted on a logarithmic scale to also show the peak of the FR signal at time overlap of excitation and probe pulses. This (polarization-dependent) peak signal is typically 10 to 20 times stronger than the initial amplitude of the hole spin signal and decays in < 500 fs. Among other effects, it might be related to two-photon absorption involving pump and probe photons. Such signals on subpicosecond time scales are not further analyzed here. Instead, we want to focus on coherent spin precessions on longer time scales. The hole spin signal without magnetic field can be modeled by a monoexponential decay depicted as a solid line. For $B = 700$ mT (430 mT), we clearly resolve damped oscillations with a decay time of 23 ps (29 ps). They allow us to infer an effective g factor of $|g^*| = 5.5 \pm 0.2$. Such a value is inconsistent with the expectation for electrons, taking into account the present

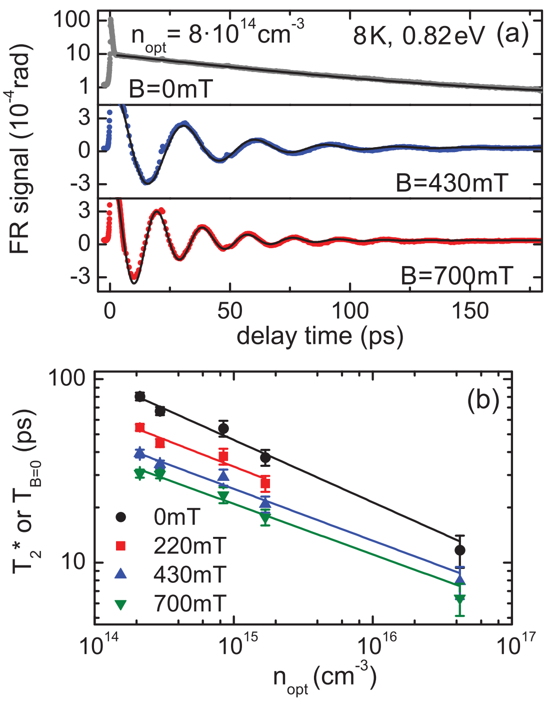

FIG. 2. (Color online) Hole spin coherence at $T = 8$ K and excitation across the indirect band gap (central photon energy 0.82 eV). (a) Transients with and without external magnetic field with $n_{opt} = 8 \times 10^{14}$ cm^{-3}. Solid lines are fits to the data. (b) Hole spin coherence times with (T_2^*) and without ($T_{B=0}$) external magnetic field for various B and n_{opt}. Solid lines are power-law fits to the data.

spin-orbit coupling, but is in agreement to spin resonance data for light holes in bulk[16] and strained Ge.[17] This finding supports the interpretation of the dynamics in Fig. 2(a) as the decay of hole spin polarization. We note that we do not resolve Larmor precession of a second hole species.

Figure 2(b) depicts decay times of Faraday rotation transients for various magnetic fields and optically generated carrier densities. While decay times with and without magnetic field reflect the coherence of carrier spins in somewhat different ways, it is still instructive to compare them. As seen in Fig. 2(b), longer decay times are found without applied magnetic field when compared to data with applied magnetic field ($T_{B=0} > T_2^*$) and a further decrease of the coherence time T_2^* is seen with increasing B. This finding points to a mechanism where hole spin coherence is lost via momentum scattering, as reported for phonon- or impurity-mediated electron scattering described by Elliot and Yafet[18,19] as well as for electron-electron scattering in III-V materials.[20] Aside from the dependence on B, we observe the hole spin coherence to be strongly affected by elevated carrier densities n_{opt} reflected by a $\sim n_{opt}^{-0.3}$ dependence of the spin coherence times with and without magnetic field [power-law fits are included as solid lines in Fig. 2(b)]. We note that even the highest density n_{opt} used for the data in Fig. 2(b) is well below the Mott density in Ge and, thus, long-range carrier-carrier scattering apparently strongly influences the hole spin dynamics. Hole spin coherence is found to be even more robust when the OPA is tuned to 1550 nm, i.e., closer to the indirect band gap of Ge. The longest decay time within the analyzed parameter range is found to be $T_{B=0} \sim 150$ ps for $n_{opt} \sim 10^{14}$ cm^{-3} and somewhat lower temperatures (T = 3–6 K). Hole spin coherence is also analyzed for elevated temperatures of T = 60 K, where a strongly reduced coherence time of ∼10 ps is found (data not shown).

We now turn toward the analysis of FR for elevated excitation intensities where hole spins decay in <10 ps and the electron spin signal is dominant. A typical FR transient in a magnetic field of B = 700 mT at T = 8 K is shown in Fig. 3(b). The optically induced carrier density is $\sim 4 \times 10^{16}$ cm^{-3}. We note that the transients in Fig. 3 are extracted from the difference between the FR signals for $\sigma+$ and $\sigma-$ polarized excitation to remove a slowly varying background from the data. Upon closer inspection, we find a temporal beating in the transients of the coherent Larmor precession of the electron spins. A Fourier analysis reveals a dominant frequency corresponding to an effective g factor of $|g^*| = 1.83 \pm 0.01$ as well as two additional frequency components. The relative amplitudes of the additional frequency components are ∼20% of the main component while their frequencies are ∼ 80% and ∼50% of the dominant one. The surfaces of constant energy for electrons in Ge are ellipsoids resulting in different cyclotron masses for different angles of an external magnetic field with respect to their principal axes so that different frequency components can indeed be expected (see, e.g., Refs. 16 and 21). The effective g factor of $|g^*| = 1.83$ as extracted for the dominant frequency component is in line with electron spin resonance data as well as theoretical predictions for bulk Ge.[21,22]

The decay time of the electron spin signal is ∼0.5 ns at T = 8 K in a magnetic field of 700 mT. Lowering the magnetic field, we find coherence times exceeding 1 ns [a transient for B = 220 mT is shown in Fig. 3(c)] and observe those coherence times to remain practically constant for n_{opt} from

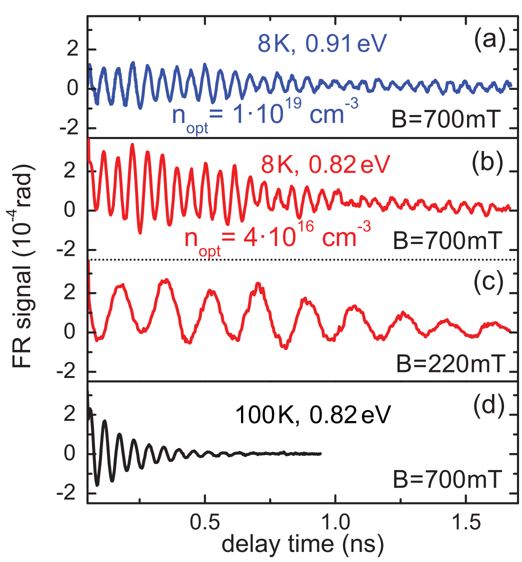

FIG. 3. (Color online) Results on electron spin coherence. (a) and (b) FR transients at T = 8 K comparing excitation across the direct band gap (central photon energy 0.91 eV) to excitation across the indirect band gap (central photon energy 0.82 eV) for B =700 mT. (c) Transient for B = 220 mT after excitation across the indirect band gap at T = 8 K. (d) Transient for B = 700 mT after excitation across the indirect band gap at T = 100 K.

2×10^{15} cm^{-3} to 4×10^{16} cm^{-3} (data not shown). In strong contrast to the temperature dependence of hole spin coherence, we find similar electron spin coherence times at $T = 60$ K (data not shown). Raising the temperature to $T = 100$ K shortens the coherence time to $\sim$150 ps at $B = 700$ mT [cf. Fig. 3(d)]. Taken together, electron spin coherence appears much more robust with respect to strong excitation conditions than observed for holes.

Finally, we compare excitation across the direct gap to the above results utilizing indirect transitions. For this purpose, excitation (and probe) pulses are tuned to a central wavelength of $\sim$1350 nm, corresponding to photon energies $\hbar\omega = 0.91$ eV (FWHM 0.04 eV) exceeding $E_{\Gamma 1} = 0.89$ eV so that absorption occurs predominantly via direct optical transitions (cf. excitation spectrum and Gaussian fit to it in Fig. 1(b) and schematic excitation conditions in Fig. 1(a)). Note that, in this case, Faraday rotation is detected with the extreme long-wavelength tail of the probe pulse around 1450 nm because all other wavelengths are absorbed in the optically thick sample. Naturally, excitation across the direct band gap leads to higher densities of photogenerated carriers when using similar irradiances. Figure 3(a) depicts a typical transient for $T = 8$ K, $B = 700$ mT, and a photogenerated carrier density of $n_{\text{opt}} \sim 1 \times 10^{19}$ cm^{-3}. Most strikingly, we observe Larmor precession of electrons similar to the trace in panel 3(b). The observation of long-lived Larmor precession at such high excitation densitites also confirms a very minor influence of impurities on the results presented here because $n_{\text{opt}} \sim 1 \times 10^{19}$ cm^{-3} is orders of magnitude larger than the residual defect density. The comparison of the signal strengths in panels 3(a) and 3(b) even reveals similar oscillation amplitudes. However, a quantitative comparison of signal amplitudes is difficult; while the number of electrons contributing to the signal is similar in both cases (note that the sample is optically thick for both excitation configurations and we use similar pulse powers), probing occurs at different photon energies in our degenerate configuration. We can, therefore, only conclude that the efficiency of optical orientation does not substantially differ between excitation via direct and indirect optical transitions.

It is very instructive to compare the magnitude of the magneto-optical response per photogenerated electron to the situation in III-V materials. For both excitation via the indirect as well as the direct band gap of Ge, we find the amplitude of the oscillatory FR response normalized to the number of electrons to be two to three orders of magnitude smaller than that for direct transitions in, e.g., GaSb.[23] Such weak FR signals might explain why no results on magneto-optics in Ge have been reported so far. However, a quantitative evaluation of the degree of spin polarization is not possible because our experiment is intrinsically sensitive to spin injection and detection at the same time.

In conclusion, we have demonstrated experimentally that optical orientation of electron and hole spins occurs in the indirect semiconductor Ge both via direct and indirect optical transitions. The degree of spin polarization is considerably smaller than for typical III-V materials, which is probably related to the multitude of phonon branches contributing to the absorption and/or side-valley scattering. Optical orientation and Larmor precession in an external magnetic field is then used to analyze electron and hole spin coherence. At low excitation intensities, hole spin coherence is preserved for 100 ps, i.e., orders of magnitude longer than in the prototypical material GaAs. The electron coherence time is of the order of 1 ns and is remarkably robust against elevated carrier densities.

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*christine.hautmann@ph.tum.de

†Present address: Institut für Experimentelle und Angewandte Physik, Universität Regensburg, 93053 Regensburg, Germany.

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