Ultrafast spin dynamics in magnetic wide-bandgap semiconductors

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Received 29 September 2013, revised 20 February 2014, accepted 20 February 2014
Published online 2 April 2014

Keywords diluted magnetic semiconductors, spintronics, ultrafast spin dynamics, wide-bandgap semiconductors

Magnetic wide-bandgap semiconductors based on ZnO and GaN are promising for spintronics applications and interesting for studying the interaction of charge carriers with magnetic ions. We use time-resolved Faraday rotation spectroscopy to investigate the ultrafast spin dynamics in Zn₁₋ₓMnₓO and Ga₁₋ₓMnₓN. The mean field electron–magnetic ion exchange constant is determined by measuring the transient effective g-factor (g') for these materials. The relevant scattering processes are revealed by analyzing the ensemble spin dephasing time $T_2$.

1 Introduction
Spintronic devices based on diluted magnetic semiconductors (DMS) have received a lot of attention recently [1]. Exploiting the exchange interaction between magnetic dopants and charge carriers is a promising approach to control carrier spins due to the giant Zeeman splitting effect [2]. The wide-bandgap semiconductors ZnO and GaN doped with magnetic ions are interesting candidates for fabricating such devices [3], because room temperature ferromagnetism has been reported in these materials [4, 5]. However, the origin of this effect is still under debate [6]. Time-resolved optical experiments employing ultrafast laser pulses have shown to be a powerful tool for revealing physical processes in semiconductors. In particular, time-resolved Faraday rotation (TRFR) spectroscopy has recently been used to unveil the ultrafast spin dynamics in bulk semiconductors and semiconductor nanostructures [7–10].

2 Ultrafast spin dynamics in wide-bandgap semiconductors

2.1 Ultrafast spin dynamics in GaN, ZnO, and Zn₁₋ₓCo₂O Soon after the surprising observation of ultralong electron spin dephasing times in bulk n-doped GaAs exceeding 100 ns [11], the ultrafast spin dynamics in the wide-bandgap semiconductor GaN was studied. Dephasing times reaching 20 ns at cryogenic temperatures have been measured [12]. Electron spin coherence at room temperature has been detected [12]. In 2005, time-resolved experiments on the ultrafast spin dynamics in ZnO yielded spin dephasing times of 190 ps at room temperature [13]. Only recently, the ultrafast spin dynamics in a magnetically doped wide-bandgap semiconductor has been investigated for the first time. Using TRFR spectroscopy Zn₁₋ₓCo₂O sol–gel thin films have been studied [14]. The mean-field electron-Co²⁺ exchange energy in Zn₁₋ₓCo₂O $N_{ex} = +0.25 ± 0.02$ eV has been determined. The ensemble spin dephasing time $T_2$ increased with rising temperature, allowing spin precession to be observed even at room temperature. This anomalous temperature dependence of $T_2$ has also been found in magnetically undoped ZnO with a record $T_2$ in the range of nanoseconds. This effect has been attributed to hole trapping at grain surfaces in the sol–gel thin films. It showed the importance of charge-separated states to control the electron spin dynamics [14].

2.2 Ultrafast spin dynamics in Zn₁₋ₓMnₓO In the following, we present the ultrafast electron spin dynamics in chemically prepared Zn₁₋ₓMnₓO sol–gel films, measured...
via TRFR spectroscopy in the ultraviolet. ZnO films are prepared by modification of a sol–gel synthesis method reported previously [14]. To fabricate Zn$_{1-x}$Mn$_x$O films, a fraction of the Zn(OAc)$_2$ was replaced by a stoichiometric amount of Mn(OAc)$_2$. The Mn$^{2+}$ ion in ZnO has a completely filled 3$d$ shell and, correspondingly, carries no magnetic moment. If Zn is replaced by Mn, the valence charge 2$+$ is not changed, leading to Mn$^{2+}$ ions on Zn$^{2+}$ lattice sites [15]. The obtained sol was spin-coated onto 500 $\mu$m thick c-plane oriented sapphire substrates layer by layer and annealed for 1.5 h at 280 $^\circ$C to form the final sol–gel film. Finally, it was baked at 550 $^\circ$C for 3h. We use TRFR spectroscopy to directly probe the electron spin dynamics in Zn$_{1-x}$Mn$_x$O. In this ultrafast pump-probe technique, ultraviolet laser pulses pump and probe spin-polarized carriers [14]. To ensure maximum excitation efficiency, we tune the laser wavelength in resonance with the $^3$D$^0$X exciton transition at 368.4 nm.

Recorded TRFR transients exhibit a delta-shaped artifact at zero pump-probe delay and a slowly varying background (data not shown), which are both subtracted before data analysis. Figure 1 shows TRFR signals of an undoped ZnO sol–gel film recorded at a temperature of $T = 10$ K and an external transverse magnetic field of $B = 1.4$ T, along with traces collected from Zn$_{1-x}$Mn$_x$O films at various Mn$^{2+}$ concentrations. Fitting the TRFR signal of undoped ZnO yields an effective $g$-factor of $g^* = 1.98$, which agrees well with $g^*$ of electrons for epitaxial and sol–gel ZnO thin films [13, 14]. In contrast, effective $g$-factors of hole spins in ZnO have been determined to be 0.5 and 1.2 in epitaxial layers and commercial ZnO bulk substrates [15, 16]. The observed Zn$_{1-x}$Mn$_x$O signals are biexponentially damped oscillations:

$$\theta_E(t) = A_1 e^{-(t/T_{12})} \cos(\omega_{12} t - \varphi_1) + A_2 e^{-(t/T_{22})} \cos(\omega_{12} t - \varphi_2),$$

where $\theta_E$ is the Faraday rotation angle, $A_1$ and $A_2$ are the amplitudes of the two precession components, $\omega_{1}$ and $\omega_2$ are the Larmor precession frequencies, $t$ is the time delay between pump and probe pulses, $T_{12}$ and $T_{22}$ are the ensemble spin dephasing times, and $\varphi_1$ and $\varphi_2$ are the phase shifts of both components.

From $\omega_1$, we can determine the effective $g$-factor ($g^*$) according to

$$g^* = \frac{h\omega_1}{\mu_B B_x}.$$  

2.3 Electron–Mn$^{2+}$ magnetic exchange coupling

We first concentrate on the fast decaying component of the oscillation, which only lasts for the first tens of ps. This signal is attributed to spins of electrons that interact with magnetic dopant ions. Measurements of samples of different Mn$^{2+}$ concentrations allow us to determine the sign and magnitude of the mean field exchange energy $N_0\alpha$ between electrons and Mn$^{2+}$ ions. A rising concentration of Mn$^{2+}$ ions (up to $x = 0.0014$) increases the precession frequency by over 30%, which scales linearly with effective $g$-factor. Within the mean-field and virtual-crystal approximations, $g^*$ for a conduction-band electron in a DMS may be described using

$$g^* = g_{\text{int}} - \frac{xN_0\alpha\langle S_y \rangle}{\mu_B B_x}.$$  

The mean field Mn$^{2+}$-electron exchange parameter $N_0\alpha$ can be extracted from the slope of the $g^*(x)$ dependence, as presented in Fig. 2. The first term in Eq. (3), $g_{\text{int}}$, is the intrinsic electron $g$-value in the absence of magnetic dopants. From our undoped ZnO sol–gel film, $g_{\text{int}} = +1.98$ was determined. The second term describes the contribution to $g^*$ induced by electron–Mn$^{2+}$ magnetic exchange coupling. $\langle S_y \rangle$ is the expectation value of the Mn$^{2+}$ spin perpendicular to the $c$-axis of ZnO, i.e., along the external magnetic field ($B_x$). By convention, $\langle S_y \rangle$ is defined as a negative number.
Depending on the magnetic ion concentration.

As mentioned before, the first, fast decaying component with a time constant of a few tens of ps and effective g-value above 1.98 is attributed to electrons interacting with magnetic dopant ions. The second, slow component varies between 100 and 200 ps and exhibits an effective g-value around 2. It either originates from electrons not interacting with magnetic ions or from the Mn$^{2+}$ ions themselves. To resolve this question we have performed TRFR measurements as a function of temperature (Fig. 4).

The slow spin dephasing time stays constant in the temperature range $T = 10$–$110$ K, which strongly suggests that this part of the TRFR signal is due to precessing Mn$^{2+}$ ions and not electrons. For electrons, a change of $T_2^*$ with temperature would have been expected. Furthermore, the absolute value for the measured spin dephasing time in the range of 100–200 ps is in good agreement with previous measurements on Zn$_{1-x}$Mn$_x$O (sol–gel films and nanocrystals) and Zn$_{1-x}$Co$_x$O sol–gel films for comparison, depending on the magnetic ion concentration.

The temperature dependence of $\langle S_y \rangle$ is obtained from the Brillouin function.

A fit of the available data at a temperature of $T = 10$ K and an external magnetic field of $B = 1.4$ T, yields a value of $N_{0g\alpha} = +0.089 \pm 0.019$ eV. The sign of $N_{0g\alpha}$ is determined unambiguously from the observation that $g^*$ increases rather than decreases with Mn$^{2+}$ doping (see Eq. 3).

The obtained value for $N_{0g\alpha}$ is surprisingly low when compared to theoretical predictions for this material [17]. In principle, it is conceivable that in the Zn$_{1-x}$Mn$_x$O sol–gel film Mn$^{2+}$ ions are not entirely incorporated into the ZnO host lattice. As a consequence, the Mn$^{2+}$ concentration in Zn$_{1-x}$Mn$_x$O might be overestimated and our determined value for $N_{0g\alpha}$ might represent a lower bound. We therefore performed additional measurements on Zn$_{1-x}$Mn$_x$O nanocrystals, where the Mn$^{2+}$ concentration has been determined by inductively coupled plasma-atomic emission spectroscopy. The nanocrystals with diameters 4–5 nm were incorporated in a dodecylamine (DDA) matrix and spin-coated on a sapphire substrate. As evident in Fig. 2, the TRFR measurements yielded $N_{0g\alpha} = 0.082 \pm 0.008$ eV, which is in good agreement with the value obtained with the Zn$_{1-x}$Mn$_x$O sol–gel films.

$N_{0g\alpha}$ may also be determined with a temperature dependent measurement (Fig. 3). For the Zn$_{1-x}$Mn$_x$O sol–gel film with $x = 0.0014$ $N_{0g\alpha} = 0.090 \pm 0.016$ eV was determined, which is in good agreement with the values obtained by changing the magnetic ion concentration.

These relatively low values for $N_{0g\alpha}$ in Zn$_{1-x}$Mn$_x$O might be explained by localization of holes at the Mn$^{2+}$ ions [18, 19, 20], i.e., we measure an apparent value for $N_{0g\alpha}$ with TRFR.

2.4 Ultrafast spin dephasing in Zn$_{1-x}$Mn$_x$O As mentioned before, the first, fast decaying component with a shift of the band gap with temperature.

![Figure 2](image1.png)

**Figure 2** Effective electron g-factors $g^*$ in Zn$_{1-x}$Mn$_x$O (sol–gel films and nanocrystals) and Zn$_{1-x}$Co$_x$O sol–gel films for comparison, depending on the magnetic ion concentration.

![Figure 3](image2.png)

**Figure 3** Temperature dependence of the effective g-factor $g^*$ in a Zn$_{1-x}$Mn$_x$O sol–gel film with $x = 0.0014$, measured at a temperature of $T = 10$ K and various photon energies due to the shift of the band gap with temperature.

![Figure 4](image3.png)

**Figure 4** Temperature dependence of the slow spin dephasing time in a Zn$_{1-x}$Mn$_x$O sol–gel film with $x = 0.0014$, measured at a temperature of $T = 10$ K and various photon energies due to the shift of the band gap with temperature.
measurements in (Zn, Cd, Mn) Se [21, 22] and GaMnAs quantum wells [23].

2.5 Ultrafast spin dynamics in wurtzite GaN and Ga$_{1-x}$Mn$_x$N We use TRFR spectroscopy to directly probe the transient electron spin dynamics in wurtzite GaN and Ga$_{1-x}$Mn$_x$N. Wurtzite n-type GaN of 1 μm thickness is grown by plasma assisted molecular beam epitaxy (PAMBE) on a 500 μm thick c-cut sapphire substrate [24]. The electron density, as well as the density of Si and O impurities, are determined by elastic recoil detection (ERD) and room temperature Hall measurements and amount to $n_e = n_D \approx 1 \times 10^{17}$ cm$^{-3}$. At this carrier concentration the longest electronic spin dephasing times have been reported in GaN [12]. Two Ga$_{1-x}$Mn$_x$N layers of 1.2–1.3 μm thickness are also prepared by PAMBE. Their manganese concentration is determined by ERD to be $x_{\text{Mn}} = 0.0134$ (sample 1) and 0.005 (sample 2) [25]. 98% of all dopant ions are in the Mn$^{3+}$ or “Mn$^{2+}$ + hole” state. This fraction was determined by comparing the Mn ion concentration measured by ERD and electron spin resonance, which detects only Mn$^{2+}$ ions [25]. The high impedance prohibits unambiguous Hall measurements on this type of samples.

To characterize the magnetically undoped n-type GaN sample, we first carry out photoluminescence (PL) and transmission measurements at a temperature of $T = 10$ K. Figure 5a depicts the PL spectrum, excited near-resonance at a photon energy of 3.550 eV. We observe a broad asymmetric emission centered at 3.490 eV at the well-known energy around 3.47 eV compared to the free excitons FX$_A$, FX$_B$, and FX$_C$ [27, 28]. TRFR measurements (i)–(ix) are performed at photon energies indicated by the vertical dotted lines in the PL and transmission spectra (Fig. 5a and b). The narrow spectral width of the laser pulses of 0.15 nm (full width at half maximum) ensures a high energy resolution in this experiment. In the TRFR data the delta-shaped artifact at zero pump-probe delay and a slowly varying background (data not shown) are both subtracted before data analysis. Damped oscillatory signals ranging for nanoseconds are clearly visible (see inset of Fig. 5b).

The decay of the TRFR signal (i) recorded at a photon energy of $E = 3.488$ eV is bi-exponential, i.e., it exhibits a fast and a slow dephasing component, $\omega_{\text{L1}}$ and $\omega_{\text{L2}}$ are extracted from the TRFR signals via the Fast Fourier Transform (FFT). For n-type GaN we obtain $g^* = 1.953 \pm 0.005$, where $\omega_{\text{L1}} = \omega_{\text{L2}}$. This value is in good agreement with previous works and a clear signature of electrons [12, 29, 31]. In contrast, the effective $g$-factor $g^*$ of holes in GaN was found to be $g = 2.17$ and 2.27 in orthogonal directions [30]. Oscillatory TRFR signals at photon energies of 3.488 eV (i) and 3.483 eV (ii) are attributed to spin precession of electrons at the energy of the free exciton (FX). The decay of spin polarization is bi-exponential. The first component decays with $T_{2,\text{fast}} = 30–50$ ps. It is due to the fast initial exciton recombination after pulsed optical excitation and associated with the decrease of the number of spin-polarized electrons [31, 32]. Indeed, carrier and spin dynamics in GaN are intimately linked in the first tens of picoseconds, as has already been shown for ZnO quantum dots [33]. The dephasing time of the second, long-lived component varies between $T_{2,\text{slow}} = 2.0–2.5$ ns. This TRFR signal is attributed to free doping-related electrons. Their spin relaxation is governed by the Dyakonov–Perel mechanism (DP) and in good agreement with earlier measurements on n-doped GaN (2.8 ns at $B = 2$ T in Ref. [12]).
At a photon energy of 3.478 eV (curve (iii)), a prominent change in spin precession occurs. A striking phase shift of 180° is observed in the TRFR oscillation at a time delay $t_D = 50$ ps. Trace (iv) still exhibits the short-lived precession component, but with a very low amplitude. At even lower photon energies 3.468–3.439 eV (v)–(ix), only a single exponential decay is present. The amplitude of the first oscillation in (i), (ii), and (iii) has a positive sign, indicated by vertical black arrows in Fig. 5c. For Faraday signals (iv)–(ix) it has a negative sign. We measure the Faraday rotation signal in curves (iv)–(ix) at the energies of the donor bound exciton D0X, as indicated by dashed vertical lines in the photoluminescence spectrum (Fig. 5a). Binding energies of the neutral donor bound exciton of 6–7 meV [26] and the positive donor bound exciton of 11.2 meV [34] in GaN suggest their presence at a low temperature of $T = 10$ K. Interestingly, the observation of delocalized and localized electrons at high and low photon energies is also directly evident when analyzing the spin dephasing times $T_2$ in Fig. 6.

There are clearly two regions with almost constant $T_2$ over a wide energy range, if photon energies are resonant either with free excitons or donor bound excitons. At the FX energy, they amount to 2 ns, while at the D0X energy, they become twice as large (up to 4 ns). To gain insight into the spin dephasing mechanism, we investigate the temperature dependence of the spin dephasing time $T_2$ (Fig. 7).

In this measurement, photon energies of the laser were tuned between 3.483 eV at $T = 10$ K and 3.415 eV at $T = 300$ K to account for the gradual shift of the optical bandgap at elevated temperatures. Two regimes of spin dephasing exist with different functional dependencies around $T = 50$ K. This value coincides with the Fermi temperature $T_F = \left(\frac{\hbar^2}{2m_e} n_e \right)^{1/3}$ of 45 K for this system, with $m_{\text{eff}}$ being the effective electron mass in GaN of 0.2$m_0$ and $n_e = 1 \times 10^{17}$ cm$^{-3}$ being the electron density of the sample. At temperatures $T < T_F$, electron spin dynamics is governed by the Dyakonov–Perel mechanism due to ionized impurity scattering in the degenerate regime [35, 36].

Our measured data (Fig. 7) are in good agreement with the expected $T_2 \sim T^0$ dependence [35]. Below $T_F = 45$ K, our data indicate a $T_2 \sim T^{0.29}$ temperature dependence at photon energies of the bound exciton D0X and an almost temperature independent behavior $T_2 \sim T^{0.07}$ at energies of the free exciton FX. For temperatures $T > T_F$, the spin dephasing time $T_2$ decreases with a $T^{-2}$ proportionality (Fig. 7). Other works have reported a $T_2 \sim T^{-1.3}$ proportionality for $T > 25$ K in GaN [12] and $T_2 \sim T^{-2.5}$ for $T > 30$ K in GaAs [11] under similar experimental conditions, which is in fair agreement with our data. At these higher temperatures $T > T_F$, the temperature dependence changes for ionized impurity scattering and additional scattering mechanisms, such as longitudinal optical photon scattering gain importance [35], leading in total to the observed $T^{-2}$ proportionality.

We now turn to magnetically doped GaN. Ga$_{1-x}$Mn$_x$N sample 1 with a manganese concentration of $x_{\text{Mn}} = 0.0134$ shows weak photoluminescence at photon energies of the bound exciton D0X, while sample 2 with $x_{\text{Mn}} = 0.005$ does not exhibit any detectable photoluminescence. The onset of transmission is virtually unchanged compared to magnetically undoped GaN, revealing only a slight redshift of 3 meV (data not shown). Both spectra are dominated by donor-bound exciton related absorption.

Damped oscillatory Faraday rotation transients are observed in both Ga$_{1-x}$Mn$_x$N samples 1 and 2 (Fig. 8a). Interestingly, the oscillation frequency strongly changes with time delay. To extract the instant frequency and hence the effective g-factor, a wavelet analysis is used [37]. For sample 1 we find a steep drop of the effective g factor in the first tens of picoseconds before it stays constant at $g^* \approx 1.97$ (Fig. 8b). Due to the random distribution of magnetic ions in...
the crystal, electrons exist in different magnetic surroundings and possess different effective $g$-factors $g^*$ [14]. Directly after zero pump probe delay the oscillation period of the TRFR signal is the smallest, indicative of an effective $g$-factor $g^* = 2.8$ at $T = 8$ K. These electrons reside in volumes of highest Mn$^{3+}$ (or “Mn$^{2+}$–hole”) concentration and dephase the fastest ($T_{2,\text{fast}}$). Electron spins surrounded by a lower Mn$^{3+}$ concentration are identified by their lower $g^*$ and slower dephasing. After 50 ps, all electron spins in the vicinity of Mn$^{3+}$ ions have dephased. What remains is a signal with a constant effective $g$-factor $g^* \approx 1.97$. To clarify its origin, we investigate the spin dephasing time $T_{2,\text{slow}}$ depending on photon energy (at $T = 10$ K) and on temperature. In Ga$_{1-x}$Mn$_x$N TRFR oscillations are only present in a narrow spectral range between $E = 3.460$ and 3.485 eV, which is in contrast to magnetically undoped GaN. The absence of the FX-related TRFR signals in Ga$_{1-x}$Mn$_x$N is most probably attributed to a manganese-related blueshift of the free exciton energies ($\geq 40$ meV) to a spectral region, not accessible by our laser system [38]. For Ga$_{1-x}$Mn$_x$N the photon energies, where oscillations are observed, lie in the vicinity of the neutral bound exciton D$^0X$ (Fig. 9a). $T_{2,\text{slow}}$ remains almost constant at 100 ps, only rising to 500 ps as the excitation is tuned to lower energies, where the TRFR signal eventually vanishes. The smaller value of $T_{2,\text{slow}}$ of several hundreds of picoseconds in Ga$_{1-x}$Mn$_x$N, compared to nanoseconds in magnetically undoped GaN, is most probably the consequence of increased impurity related scattering in the magnetically doped system.

The temperature dependence of $T_2$ depicted in Fig. 9b is investigated both at low ($E = 3.468$ eV) and high ($E = 3.478$ eV) energies of the D$^0X$ region. The general dependence on temperature is similar to magnetically...
undoped GaN (Fig. 7). $T_2^*$ increases with temperature up to a maximum before it decreases again. For Ga$_{1-x}$Mn$_x$N the maximum occurs at $T = 75$ K, which is slightly higher than for magnetically undoped GaN. The origin of this behavior is presently unclear, but might be explained by an increased number of impurity centers, i.e., the Mn$^{3+}$ ions, in Ga$_{1-x}$Mn$_x$N [39]. The measured relations of $T_2^* \sim T^{0.35}$ ($E = 3.468$ eV) and $T_2^* \sim T^{0.38}$ ($E = 3.478$ eV) in Ga$_{1-x}$Mn$_x$N at low temperature underline the assignment to the neutral bound exciton D$^0$X, due to their resemblance of the $T_2^* \sim T^{0.29}$ dependence observed in magnetically undoped GaN.

At higher temperatures we also find roughly a $T^{-2}$ dependence, which is the same as for magnetically undoped GaN and indicative of the Dyakonov–Perel spin relaxation mechanism. At this temperature range, bound excitons cease to exist and dissociate to free excitons.

In contrast, Fig. 9c shows the temperature dependence of the fast component $T_{2,\text{fast}}$, which is associated with electrons interacting with magnetic ions. $T_{2,\text{fast}}$ is observed at photon energies $E = 3.468$ eV $- E = 3.435$ eV and is monotonically increasing with rising temperature.

We now turn to the effective g-factor $g^*$ and the strength of the magnetic ion-electron exchange coupling, which we determine by a temperature dependent measurement of $T_{2,\text{fast}}$ (Fig. 10).

Only the first oscillation period of the TRFR transient is used to determine $g^*$, because of the already mentioned steep g-factor decrease with time delay (Fig. 8b). From the extracted frequency $\omega_{\text{L},1}$ we obtain the effective g-factor $g^*$ via Eq. (2). Figure 10 shows the temperature dependence of $g^*$ for the two different Mn concentrations (sample 1 with $x = 0.0134$ and sample 2 with $x = 0.005$) and magnetically undoped n-GaN for comparison. For sample 1 at $T = 8$ K and $E = 3.473$ eV, we obtain $g^* = 2.80 \pm 0.05$. With increasing temperature $g^*$ monotonically decreases and approaches the electron $g$ factor in undoped GaN of $\approx 1.96$ at $T = 100$ K. Sample 2 shows the same behavior, but smaller values of $g^*$ at lower temperatures due to the lower Mn concentration. This behavior is due to exchange coupling between the Mn$^{3+}$ ions and electrons. It is quantified by the mean field electron–Mn$^{3+}$ exchange energy $\alpha_{\text{eff}}$. For a conduction band electron in a DMS, $g^*$ may be described using

$$g^* = \frac{1}{\mu_B B_\text{s}} \frac{x_{\text{eff}}N_\lambda \alpha (S_z)}{S_z}.$$  

Equation (4) differs from Eq. (3) only by $x_{\text{eff}}$, which is the effective Mn$^{3+}$ concentration, reflecting a possible antiferromagnetic coupling among Mn$^{3+}$ ions at doping levels above 1% [40, 41]. In sample 1 we assume an effective concentration of $x_{\text{eff}} = 0.0114$ due to partial antiferromagnetic coupling of the Mn$^{3+}$ ions (this correction is necessary at $x > 0.01$).

The extracted effective g-factors $g^*$ have slightly different values when measured at various photon energies for both Ga$_{1-x}$Mn$_x$N samples (Fig. 10). As a result, $\alpha_{\text{eff}}$ changes, too. This fact might indicate a slightly increased magnetic coupling at photon energies of the bound excitons. However, the deviation of $\alpha_{\text{eff}}$ is small compared to the error induced by the uncertainty of Mn concentration, temperature, and determination of the Larmor frequency. A global fit of the data for both Ga$_{1-x}$Mn$_x$N samples yields $\alpha_{\text{eff}} = 14 \pm 5$ meV.

Our result agrees well with values of $\alpha_{\text{eff}}$ determined by electron paramagnetic resonance for GaN:Mn$^{3+}$ ($\alpha_{\text{eff}} = 0 \pm 100$ meV) [38] and GaN:Mn$^{2+}$ ($\alpha_{\text{eff}} = \pm 14$ meV) for Mn$^{2+}$ ions [42]. The determined value for $\alpha_{\text{eff}}$ in

![Figure 10](https://www.pss-b.com/feature_article.png)

**Figure 10** Temperature dependence of the effective g-factor $g^*$ in Ga$_{1-x}$Mn$_x$N sample 1 ($x_{\text{Mn}} = 0.0134$, dots) sample 2 ($x_{\text{Mn}} = 0.005$, squares), and sample 3 ($x_{\text{Mn}} = 0$, triangles) extracted from the fast dephasing component. Room temperature values for all samples are represented by the blue crossed square. For $x_{\text{Mn}} = 0.0134$ and $x_{\text{Mn}} = 0.005$, slightly different $g^*$ are observed for two excitation energies (blue closed symbols: $E_{\text{ex}} = 3.473$ eV; red open symbols: $E_{\text{ex}} = 3.478$ eV). Solid lines are calculated from Eq. (3) and correspond to values of $N_\lambda \alpha = +13.3$ meV and $N_\lambda \alpha = +15.5$ meV. (b) Temperature dependence of the effective g-factor $g^*$ in Ga$_{1-x}$Mn$_x$N sample 1 ($x_{\text{Mn}} = 0.0134$) extracted from the slow dephasing component for two photon energies (blue dots: $E_{\text{ex}} = 3.473$ eV; red squares: $E_{\text{ex}} = 3.478$ eV) and the magnetically undoped sample 3 (open stars). Lines are linear fits to the respective data sets. Error bars are depicted only for the first data points for clarity.
Ga\textsubscript{1-\textit{x}}\textit{Mn\textsubscript{x}}N is an order of magnitude smaller than in wurtzite II–VI DMSs. Interestingly, a similarly small value of \(N_{\text{fi}} = -20 \pm 6 \text{meV}\) was found for the III–V DMS (Ga\textsubscript{Mn}As) at low Mn concentrations \(x \leq 0.0013\) [43]. In GaMnAs the small value of \(N_{\text{fi}}\) was explained by a reduction of the s-d coupling, being a system with strongly bound holes [19]. However, we cannot distinguish between the Mn\textsuperscript{3+} and “Mn\textsuperscript{2+} + h” configuration in our measurements in Ga\textsubscript{1-\textit{x}}\textit{Mn\textsubscript{x}}N.

Figure 10b shows the effective g-factor \(g^*\) of the slow dephasing component depending on temperature, measured at the same photon energies as in Fig. 10a. With changing temperature, it remains virtually unchanged with an effective g-factor ranging around \(g^* = 1.96\). This value is identical to the g-factor of electrons in undoped GaN and corroborates our assignment of the long-lived spin precession to electrons not interacting with Mn ions.

3 Concluding remarks and outlook In conclusion, we have presented the ultrafast spin dynamics in wide-bandgap magnetic semiconductors. Time-resolved Faraday rotation spectroscopy was used to measure the transient effective g-factor \(g^*\) and ensemble spin dephasing time \(T_2^g\) in Zn\textsubscript{1-\textit{x}}\textit{Mn\textsubscript{x}}O sol–gel thin films and Ga\textsubscript{1-\textit{x}}\textit{Mn\textsubscript{x}}N grown with molecular beam epitaxy. In that way, the mean field electron–ion exchange energies \(N_{\text{fi}}\) could be determined and the types of observed carriers identified. This information is important for the design of spintronic devices based on these materials. Nanostructured systems fabricated via cost-effective techniques suited for mass production, such as gel synthesis, will be in the focus of future research.

Acknowledgements We thank Nils Janßen, Tim Thomay, Manfred Beyer, Alfred Leitenstorfer, Ulrich Rüdiger, Andrea Navarro Quezada, Alberta Bonanni, Andrey Bakin, Andreas Waag, and Klaus Köhler for their support in an early stage of this study. The authors acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG) through priority program SPP 1285 and from the U.S. National Science Foundation (CHE 0628252-CRC).

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