Relation between exciton splittings, magnetic circular dichroism, and magnetization in wurtzite (Ga,Fe)N

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The question of the correlation between magnetization, band splittings, and magnetic circular dichroism (MCD) in the fundamental gap region of dilute magnetic semiconductors is examined experimentally and theoretically taking the case of wurtzite Ga₁₋ₓFeₓN as an example. Magnetization and polarization-resolved reflectivity measurements have been performed down to 2 K and up to 7 T for x = 0.2%. Optical transitions originating from all three free excitons A, B, and C, specific to the wurtzite structure, have been observed and their evolution with the magnetic field determined. It is demonstrated that the magnitude of the exciton splittings evaluated from reflectivity-MCD data can be overestimated by more than a factor of 2, as compared to the values obtained by describing the polarization-resolved reflectivity spectra with appropriate dielectric functions. A series of model calculations shows that the quantitative inaccuracy of MCD originates from a substantial influence of the magnetization-dependent exchange interactions not only on the spin splittings of excitons but also upon their linewidth and oscillator strength. At the same time, a method is proposed that allows to evaluate the field and temperature dependencies of the magnetization from MCD spectra. The accurate values of the excitonic splittings and of the magnetization reported here substantiate the magnitudes of the apparent sp – d exchange integrals in (Ga,Fe)N previously determined.

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I. INTRODUCTION

Excitonic magneto-optical phenomena in the fundamental gap region of dilute magnetic semiconductors (DMSs) are a prime source of information on the sp – d exchange splitting of electronic states, spin dynamics, also in reduced dimensionality systems, such as nanowires and quantum dots. One of the widely studied magneto-spectroscopy effects is the magnetic circular dichroism (MCD) arising from the difference between optical absorption or reflectivity for left and right-circular polarized light. In many DMSs, MCD depends linearly on the exchange-induced splitting of free exciton states, which, in turn, is proportional to the magnetization of localized spins. To these systems belong zinc-blende DMSs, such as (Cd,Mn)Te, whose description can be reliably determined from either the splitting of free exciton transitions or, equally well, from the magnitude of the MCD.

In the case of wurtzite DMSs like (Ga,Fe)N or (Zn,Co)O, the description of the magneto-optical phenomena associated with free excitons is, however, more intricate. Here, due to the effect of the trigonal crystal field and anisotropic spin-orbit coupling, the top of the valence band splits into three subbands. As a result, three free exciton transitions emerge in the spectral region near the band gap, and they are labeled as A, B and C. They are close in energy and often not well resolved in the optical spectrum. Moreover, at a given circular polarization, the magnetization-induced shift of exciton B is opposite to the ones of excitons A and C. It has been suggested that this may even lead to the mutual cancellation of the magneto-optical effects associated with the excitons A and B. Furthermore, the electron-hole exchange interaction leads to a mixing between A and B excitonic states, resulting in an anticrossing that affects the magnetization-induced shifts of the excitonic states. These factors can make that the relation between the magnitudes of MCD, exciton splitting, and magnetization is not longer linear in wurtzite DMSs.

In this work we report on magneto-reflectivity and magnetization measurements carried out on paramagnetic (Ga,Fe)N layers, whose high crystalline quality has been demonstrated by a range of structural characterization methods. We aim at clarifying, in the case of wurtzite DMSs with low carrier densities and randomly distributed magnetic ions, the relation between the magnitudes of (i) free exciton splittings, (ii) MCD obtained from magneto-reflectivity, and (iii) magnetization. From near band gap reflectivity data we determine the MCD spectra as well as the exciton splittings by fitting the magneto-reflectivity spectra with an appropriate dielectric function. An excellent proportionality is found between the field dependence of the magnetization and the
shift of the exciton $A$ line in $\sigma^-$ polarization. In contrast, the degree of proportionality between the magnitudes of MCD and of the magnetization depends on the choice of the method for the determination of the MCD magnitude from the MCD spectra. We indicate a method assuring the highest degree of proportionality. Furthermore, we show that despite the opposite signs of the exchange splittings, the contributions of the excitons $A$ and $B$ to the MCD do not cancel out. We explain this fact presenting a series of MCD simulations demonstrating that the MCD signal depends not only on the magnitude of the exchange-induced exciton splittings but also on changes of the exciton linewidth and oscillator strength with the magnetic field. It is expected that our conclusions apply to a wide class of wurtzite DMSs, e. g., nitrides, oxides, and selenides, like (Ga,Mn)N, (Zn,Co)O, and (Cd,Mn)Se. Our results substantiate also the magnitudes of the apparent $sp - d$ exchange integrals determined previously for (Ga,Fe)N.$^7$

II. SAMPLES AND EXPERIMENT

The studied 0.24 $\mu$m thick (Ga,Fe)N layers are grown by metal-organic vapor phase epitaxy (MOVPE) on a 1 $\mu$m thick GaN buffer deposited on a [0001] sapphire substrate, which results in single crystal layers with the $c$-axis perpendicular to the film plane.$^7$ According to previous electron paramagnetic resonance (EPR) studies,$^7$ and as confirmed by the observation of photoluminescence (not shown) corresponding to intracenter $^4T_1(G) \rightarrow ^6A_1(S)$ transitions at 1.3 eV,$^7$ the iron in the studied samples is present predominantly as Ga-substitutional Fe$^{3+}$ ions in the high spin $S = 5/2$ configuration. The Fe concentration resulting from magnetometry measurements, estimated as a difference between the magnetization values$^7$ measured at 1.8 and 5 K, is $x = 0.2 \%$.

Reflectivity measurements are performed at pumped helium temperatures ($T \approx 2$ K), in a magnetic field $B$ up to 7 T applied in the Faraday configuration (magnetic field parallel to the direction of the light propagation) and with the light propagation along the $c$ axis of the film. The sample is illuminated by unpolarized white light at normal incidence. The signal is detected by a Peltier cooled CCD camera coupled to a grating monochromator (2400 grooves/mm). A set of a quarter wave plate and a linear polarizer inserted in the signal path enables the detection of the signal at both circular polarizations $\sigma^+$ and $\sigma^-$.

Magnetization measurements are carried out in a superconducting quantum interference device (SQUID) as a function of a magnetic field up to 7 T applied perpendicularly and in parallel with respect to the sample growth axis at temperatures from 2 to 300 K, according to the procedure outlined recently.$^7$

High-resolution transmission electron microscopy (HRTEM) measurements performed on cross-sectional specimens of the samples prepared by a standard mechan-ical polishing followed by Ar+ ion milling at 4 kV, did not reveal iron-rich precipitations in the studied films, consistent with the absence of a ferromagnetic component in the magnetization data.

III. RESULTS OF MAGNETIZATION MEASUREMENTS

In Fig. 1 the magnetization in the magnetic field perpendicular and parallel to the sample growth axis is reported. No magnetic anisotropy is observed and the data are well described by a paramagnetic isotropic Brillouin function for $S = 5/2$,

$$M(T, H) = g\mu_B x N_0 S B_T^S (T, H),$$

confirming that the uncoupled Fe$^{3+}$ ions determine the magnetic properties in the studied samples. Here, $g = 2.0$, $N_0$ is the cation concentration, and the Fe concentration is $x = 0.2 \%$ for the data presented in Fig. 1.

IV. REFLECTIVITY SPECTRA AND THE DETERMINATION OF EXCHANGE INTEGRALS

In Fig. 2(a) a typical reflectivity spectrum of the studied samples in the near bandgap spectral region at zero magnetic field is presented. The presence of all three $A$, $B$ and $C$ excitonic transitions, as indicated in the plot, confirms the high crystal quality of the studied layers. A giant polarization-dependent shift of the excitonic transitions is observed in the magnetic field, as shown in Figs. 2(b) and 2(c). The $A$ and $B$ excitons shift in opposite directions and are spectrally well resolved at $\sigma^-$ polarization (Fig. 2(b)), while they gradually merge with the increase of the magnetic field in $\sigma^+$ polarization (Fig. 2(c)).
Since the magnitudes of the excitonic shifts and linewidths are comparable, in order to determine accurately the magnitude of the exciton splittings in the magnetic field we describe the entire experimental reflectivity spectra by appropriate response functions. The model takes into account the refractive index of each layer and the multiple reflections of the light in the three layer structure. First, the reflectivity coefficients are calculated for each interface between adjacent layers as,

\[ r_{i;i+1}^\pm = \frac{\sqrt{\epsilon_i^\pm} - \sqrt{\epsilon_{i+1}^\pm}}{\sqrt{\epsilon_i^\pm} + \sqrt{\epsilon_{i+1}^\pm}}, \]

where \( \epsilon_i^\pm \) is the energy dependent, complex dielectric function of the \( i \)-th layer in \( \sigma^+ \) and \( \sigma^- \) polarization, respectively. The \( \epsilon_i^\pm \) and \( \epsilon_i^\mp \) are determined for the (Ga,Fe)N layer and GaN buffer respectively taking into account the A, B and C free exciton transitions, the excited states of the excitons, and the continuum of unbound states within each layer. The energy positions, linewidths, and theoretical data is evident in the whole near-bandgap spectral region. The energy positions, linewidths, and experimental results are shown together with the experimental results in Figs. 2(b) and 2(c). A good match of the experimental data and \( \pm \) (b) and \( \pm \) (c) polarizations. The optical transitions corresponding to the excitons, A, B and C are indicated. In panel (d) the experimental (points) and theoretical (lines) MCD spectra are given, as determined from the reflectivity spectra shown in panels (b) and (c).

![FIG. 2: (color online) Experimental (points) and fitted (solid lines) reflectivity spectra at \( B = 0 \) T (a) and at 1 T for \( \sigma^- \) (b) and \( \sigma^+ \) (c) polarizations. The optical transitions corresponding to the excitons, A, B and C are indicated. In panel (d) the experimental (points) and theoretical (lines) MCD spectra are given, as determined from the reflectivity spectra shown in panels (b) and (c).](image-url)
the influence of the antiferromagnetic $p - d$ exchange on the band states in a nonperturbative way. The strong coupling effects are particularly relevant in the case of nitrides and oxides, where – owing to the short bond length – the $p - d$ hybridization is large. This approach demonstrates that if the potential brought about by the transition metal impurity is deep enough to bind a hole with an antiparallel spin, the corresponding extended states are pushed out of the magnetic impurity, as they must be orthogonal to the bound state. In particular, the theory anticipates a sign reversal of the $s - d$ exchange energy is reduced in comparison to the $p - d$ exchange energies for the conduction and valence band.

In zinc-blende DMSs with degenerate valence bands at $k = 0$ and, thus, with a single free exciton state, the splitting is proportional to the magnetization. Furthermore, the total area under the MCD curve and the MCD intensity at a chosen wavelength are proportional to the excitonic splitting. By contrast, in wurtzite DMSs, three spectrally close excitonic transitions contribute to the reflectivity spectra near the band gap. In the case of (Ga,Fe)N, only exciton A in $\sigma^-$ polarization, whose energy decreases with the magnetic field, does not interact with other states. In this case, as shown in Fig. 3, the redshift of exciton A in $\sigma^-$ polarization and the magnetization show the same dependence on the magnetic field.

V. MCD VS. MAGNETIZATION

In zinc-blende DMSs with degenerate valence bands at $k = 0$ and, thus, with a single free exciton state, the splitting is proportional to the magnetization. Furthermore, the total area under the MCD curve and the MCD intensity at a chosen wavelength are proportional to the excitonic splitting. By contrast, in wurtzite DMSs, three spectrally close excitonic transitions contribute to the reflectivity spectra near the band gap. In the case of (Ga,Fe)N, only exciton A in $\sigma^-$ polarization, whose energy decreases with the magnetic field, does not interact with other states. In this case, as shown in Fig. 3, the redshift of exciton A in $\sigma^-$ polarization and the magnetization show the same dependence on the magnetic field.

In general, however, due to the anticrossings between excitonic states occurring when their exchange-induced shifts increase (see Fig. 3), the excitons exchange splittings cease to be proportional to the magnetization. A question then arises on the nature of the relation between MCD and magnetization in such a case.

We define the experimental reflectivity-MCD as

\[ MCD = \frac{I^+ - I^-}{I^+ + I^-} \]

where $I^+$ and $I^-$ denote the $\sigma^+$ and $\sigma^-$ polarized components of the reflectivity signal. The experimental MCD and theoretical MCD ($MCD_{\text{fit}}$) values defined in this way are shown for (Ga,Fe)N at 1 T as a function of the photon energy in Fig. 2(d). As seen, the MCD spectrum exhibits a wide pronounced maximum ($MCD_{\text{max}}$) in the spectral region of excitons A and B, centered around 3495 meV. The $MCD_{\text{max}}$ is accompanied by two minima ($MCD_{\text{min}L}$ and $MCD_{\text{min}R}$) on its sides, as marked in Fig. 2(d). The MCD signal is weak outside this region, indicating that the A and B excitons provide the main contribution to the magnitude of near band-gap MCD in (Ga,Fe)N.

The shape of the MCD spectrum shown in Fig. 2(d), although resulting from the contributions of three excitons, is actually similar to the typical spectra of zinc-blende DMSs. It is interesting to analyse which characteristics of the MCD spectrum in (Ga,Fe)N would assure the highest degree of agreement with magnetization. We consider three quantities: 1) the total area under the MCD curve ($MCD_{\text{area}}$); 2) the maximum of the MCD intensity, $MCD_{\text{max}}$; 3) the sum of the absolute values of the MCD extrema, $MCD_{\text{extrema}} = |MCD_{\text{min}L}| + MCD_{\text{max}} + |MCD_{\text{min}R}|$. These quantities normalized to their values at 7 T are plotted, together with the magnetization.

FIG. 3: (color online) Energy positions (a), linewidths (b), and the oscillator strength (c) of the A, B and C excitons for both circular polarizations (points), as obtained by fitting the reflectivity spectra shown in Fig. 2. The solid lines in (b) and (c) are guides to the eye (a), whereas in (a) they represent the theory with two fitting parameters, the apparent $s - d$ and $p - d$ exchange energies for the conduction and valence band, respectively.

FIG. 4: (color online) Integrated area under the MCD curve $MCD_{\text{area}}$ (solid line), amplitude of the main MCD peak $MCD_{\text{max}}$ (dashed line), the sum of the absolute values of the MCD extrema $MCD_{\text{extrema}}$ (dotted line) plotted together with the exciton A shift in polarization $\sigma^-$ (circles) and magnetization (squares), all normalized by their values at 7 T.
in Fig. [2] As seen, all quantities as a function of the magnetic field have a Brillouin-like shape and exhibit saturation in high magnetic fields. An excellent agreement is observed between the values of MCDarea and the magnetization. This is not the case, however, of the MCDmax, which deviates significantly from the magnetization. We have checked that for the studied layers, in contrast to zinc-blende DMSs, there is no specific photon energy for which the MCD intensity is proportional to the magnetization. The agreement between the MCD magnitude and the magnetization can be, however, restored after adding to MCDmax the magnitudes of the side extrema |MCDminL| and |MCDminR|.

It can be expected that the magneto-optical methods of magnetization determination will break down when the exciton linewidth becomes larger than either the splitting of the excitonic states or of the energy difference between particular excitons. In order to determine the range of exciton linewidths assuring an agreement between MCD and magnetization, we calculate the MCD spectra varying the linewidths of the excitons A, B and C by a factor from 1/2 to 2 with respect to their original value at 1 T. When the excitonic linewidths increase, the contributions of the excitons A and B are no longer resolved in the reflectivity spectrum. At the same time, as seen in Fig. [3] a less intense and broadened MCD spectrum is expected. It is clearly visible, however, that the MCD signals originating from excitons A and B do not cancel out, as suggested previously, but rather add. Actually, despite the opposite splittings, a difference in the energy of excitons A and B makes that they contribute with the same sign to the MCD signal.

In order to quantify the degree of agreement between MCD and magnetization, we define a correlation coefficient \( \rho \) as \( \rho = 1 - \int_0^1 \sqrt{(y-z)^2} \, dy \int_0^1 z, \) where \( y \) and \( z \) are the magnitudes of MCD and magnetization, normalized by their values at 7 T. The coefficient \( \rho \) corresponds to the ratio of the two areas shown in the inset to Fig. [3] and attains a value of 1 for a perfect agreement between normalized MCD and magnetization.

The values of \( \rho \) are plotted in Fig. [4] as a function of the relative broadening \( W = \Gamma_A/(E_B - E_A) \), where \( \Gamma_i \) and \( E_i \) are the linewidth and energy of the \( i \)-th exciton in the absence of a magnetic field. According to the results displayed in Fig. [4] for \( W < 5 \) (the case of narrow exciton lines) the magnitudes of integrated MCD (MCDarea) and the sum of the MCD extrema MCDextrema agree reasonably well (\( \rho > 0.9 \)) with the magnetization. However, with increasing excitonic broadening \( \Gamma_A \) the degree of correlation \( \rho \) diminishes. For \( W > 5 \), \( \rho \) calculated for the sum of the MCD extrema drops rapidly, showing that MCDextrema is no longer proportional to the magnetization. The influence of the exciton broadening on \( \rho \) is less pronounced in the case of MCDarea. Since in a typical case \( E_B - E_A \approx 10 \) meV, even if \( \Gamma_A \) is as large as 50 meV, MCDarea still describes correctly the normalized magnitude of the magnetization.

VI. EFFECTS OF EXCITON SPLITTING, LINEWIDTH, AND OSCILLATOR STRENGTH ON MCD

It is well established that the \( sp-d \) exchange interaction affects not only the energy of excitons but also their linewidth and oscillator strength. It is often assumed, however, that only the excitonic splitting, \( \Gamma \), the difference in energy of the transitions observed for \( \sigma^+ \) and \( \sigma^- \) polarizations, contributes to MCD or to the Faraday rotation. It was shown, however, that in (Cd,Mn)Te a greater contribution to the Faraday rota-
MCD (see Fig. 7) indicates that the determination of the excitonic splitting when neglecting the contributions related to excitonic linewidth and oscillator strength would lead to the values overestimated by a factor of at least two. Since it is practically impossible to distinguish experimentally between different contributions to MCD, it is rather unrealistic to determine excitonic splittings basing solely on the MCD signal. This means that in order to evaluate the excitonic splittings and thus the exchange energies meaningfully, a fitting of reflectivity or absorption spectra at various polarizations, as performed in the present work, is necessary.

VII. CONCLUSIONS

Magneto-reflectivity and magnetization data obtained for (Ga,Fe)N layers, supplemented by relevant theoretical calculations, reemphasize that a quantitative information on free exciton splittings requires a full description of the polarization-resolved reflectivity or absorption spectra as a function of magnetic field. This is particularly important in wurtzite DMSs, in which the near-band-gap spectrum consists of three closely lying free exciton lines. The fit of the magneto-reflectivity data has led to the determination of the apparent exchange energies for (Ga,Fe)N, $N_0\alpha^{(app)} = -0.05 \pm 0.1$ eV and $N_0\beta^{(app)} = +0.5 \pm 0.2$ eV, in agreement with previously reported values. At the same time, MCD data cannot serve to determine the exciton splittings because of the significant contributions to the MCD magnitude coming from magnetization dependent excitonic linewidth and oscillator strength. However, according to our results, MCD provides quantitative information on the magnitude of the magnetization. The best agreement between normalized MCD and magnetization is obtained when the magnitude of MCD is determined by integrating the MCD signal over frequency, pointing to the existence of a sum rule. The conclusions of the present work are expected to be valid also in the case of other wurtzite DMSs, e. g. nitrides, oxides, and selenides.

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