# Origin and Control of Ferromagnetism in Magnetically Doped Semiconductors: the Case of (Ga,Fe)N

**A. Bonanni, A. Navarro-Quezada, T. Li, M. Wegscheider, B. Faina,**
**R. Lechner, and G. Bauer**
**Institut für Halbleiter- und Festkörperphysik, Universität Linz – Austria**

**Z. Matey, and V. Holý**
**Dept. of Condensed Matter, Charles University, Prague – Czech Republic**

**W. Pacuski, M. Sawicki, and T. Dietl**
**Institute of Physics, Polish Academy of Sciences, Warsaw – Poland**

The control over the incorporation of magnetic ions into a semiconducting host is fundamental for the functionality of magnetically doped semiconductors. Our magneto-optical data on diluted samples corroborate recent suggestions that the strong *p-d* hybridization specific to nitrides and oxides leads to a significant renormalization of the valence band exchange splitting. Furthermore, through a structural analysis at the nanoscale, we give experimental evidence that the aggregation of Fe ions in (Ga,Fe)N and consequently the magnetic response of the material are affected by the growth rate and doping with acceptors or donors.

## Introduction

The comprehensive search for materials exhibiting spintronic functionalities has resulted in the discovery of a number of magnetically doped and nominally undoped wide-band gap semiconductors and oxides exhibiting ferromagnetic features persisting up to high temperatures. The nature of this puzzling robust ferromagnetism has become one of the most controversial topics in nowadays materials science and condensed matter physics [1]. In order to shed new light on the origin of high-$T_C$ ferromagnetism, we have undertaken studies of (Ga,Fe)N [2] – [5] grown by metalorganic vapor phase epitaxy (MOVPE), either undoped or co-doped with Si or Mg, combining magnetic (SQUID and electron paramagnetic resonance), magnetooptical, and x-ray absorption near-edge spectroscopy (XANES) investigations with a comprehensive structural and chemical characterization (secondary ion mass spectroscopy – SIMS, transmission electron microscopy – TEM, electron diffraction spectroscopy - EDS, synchrotron x-ray diffraction – XRD), that provides information on the Fe distribution at the nanoscale.

Here, we first discuss our quantitative study of the exchange coupling between the spins S = 5/2 localized on the Fe ions and the effective mass electrons. Our results point to an anomalous *p-d* exchange splitting of the valence band [4], that we explain in terms of a renormalization of extended states occurring if the impurities perturb strongly the crystal potential [6]. We then show that the Fe ions are distributed in the nitride matrix in a way giving rise either to a diluted random alloy [2] – [5] or to ferromagnetic nanocrystals that aggregate by precipitation [2], [3], [5] or by spinodal decomposition into regions more or less rich in the magnetic component [3], [5]. Our latest results demonstrate that this aggregation can be controlled by growth conditions and co-doping with either acceptors or donors.

## Strong Coupling Effects in (Ga,Fe)N

In II-VI oxides and III-V nitrides, a small bond length and, thus, strong *p-d* hybridization, should result in a large value of $N_0|\beta|$, and this prediction is supported by photoemission experiments [7]. Surprisingly, however, abnormally small exciton splittings in (Zn,Co)O [8] and (Zn,Mn)O [9] have been observed. Prompted by these observations, a theory has been put forward [6], which shows that the strong *p-d* coupling makes the apparent exchange energy $N_0\beta^{(app)}$ describing the valence band splitting small and of opposite sign than expected. In order to test the above model, magnetization and magnetoreflectivity in the free exciton region of (Ga,Fe)N epilayers have been studied [4], as reported in Fig. 1(a, b). Since in GaN – in contrast to ZnO – the actual ordering of valence subbands is settled, the sign of $N_0\beta^{(app)}$ can be unambiguously determined from polarization-resolved magnetooptical spectra. Furthermore, unlike Mn, Fe in GaN is an isoelectronic impurity with the simple $d^5$ configuration [2], [10], allowing a straightforward interpretation of the data.

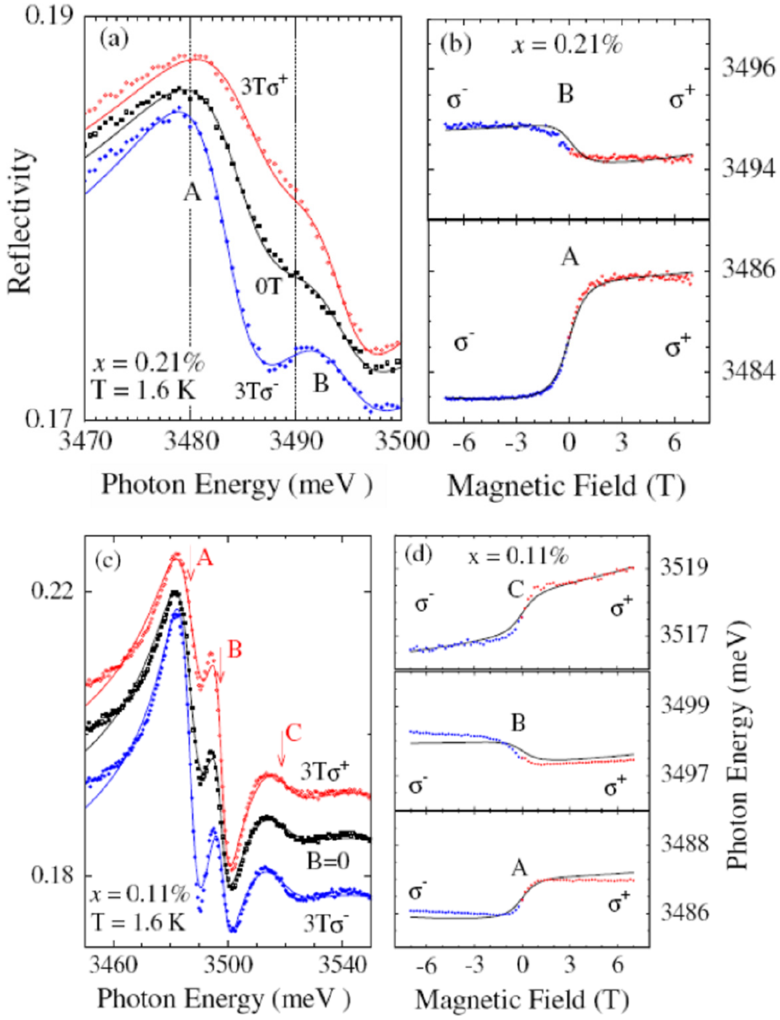

Fig. 1: Reflectivity of (Ga,Fe)N in Faraday configuration at 1.6 K for x = 0.21% (a) and 0.11% (c) where particularly well-resolved excitons A, B, and C are visible in $\sigma^-$ polarization. Panels (a), (c) show experimental data (symbols) and their fitting with the polariton model (solid lines). Symbols in (b), (d) present exciton energies obtained from such a fitting at various magnetic fields; solid lines are the expectation of the exciton model for the exciton.

The fitting procedure, whose results are presented in Fig. 1 (b), (d) yielded $N_0\beta^{(app)}$ = +0.5 ± 0.2 eV and $N_0\alpha^{(app)}$ = +0.1 ± 0.2 eV. We note that this evaluation of $N_0\alpha^{(app)}$ includes, within the experimental error, the values of $N_0\alpha^{(app)}$ = 0.25 ± 0.06 eV found in early studies of Mn-based II-VI DMSs [11]. We have no reason to question here the applicability of the standard description of the conduction band in (Ga,Fe)N. For the expected *d* level arrangement, both the ferromagnetic sign and the small magnitude of the apparent *p-d* exchange energy are surprising. Indeed, in GaN the Fe $d^5/d^6$ acceptor-like level resides less than 3 eV above the top of the valence band [10].

This state, $e_g\downarrow$, and the higher lying $t_2\downarrow$ level that can hybridize with the valence band states, remain unoccupied in intrinsic (Ga,Fe)N. At the same time, no donor-like $d^5/d^4$ state has been found within the GaN gap. This could be expected, as in the transition metal (TM) series a particularly large correlation energy *U* separates the $d^5$ and $d^6$ shells. Hence, the occupied Fe $t_2\uparrow$ levels reside within the valence band. According to the Schrieffer-Wolf theory, in such a case the *p-d* exchange coupling is antiferromagnetic: this was confirmed by magnetooptical studies of tellurides and selenides containing either Mn or Fe, including studies carried out in our labs, which lead systematically to $N_0\beta = -1.4 \pm 0.5$ eV [11].

However, it has been recently remarked [6] that for an appropriately strong TM potential like the one expected for oxides and nitrides, the magnetic ion can bind a hole – a trend which was already suggested by strong deviations from the virtual crystal approximation (VCA) in (Cd,Mn)S [12] and by results of the numerical diagonalization of a model Hamiltonian for diluted magnetic semiconductors (DMS) [13]. A summation of infinite series of relevant self-energy diagrams demonstrates that the spin splitting of extended states involved in the optical transitions remains proportional to the magnetization, but the apparent exchange energy becomes significantly renormalized [6]. For the expected coupling strength, the theory predicts $-1 < \beta^{(app)}/\beta < 0$, as observed for (Ga,Fe)N.

## Observation and Control of Fe Aggregation in (Ga,Fe)N

There is an increasing amount of evidence that owing to specific features of magnetic impurities in wide band-gap semiconductors and oxides, the epitaxial growth of these systems can result in the self-organized aggregation of magnetically robust nanocrystals embedded in the host paramagnetic matrix [1], [14], [15]. With no doubt this finding holds enormous potential for the fabrication of a range of multifunctional nanosystems relevant to spintronics, nanoelectronics, photonics, and plasmonics [14], [16].

A series of (Ga,Fe)N layers has been grown by MOVPE [5] and by combining TEM and synchrotron XRD with SQUID studies we have identified three distinct ways by which Fe incorporates into the GaN lattice: (i) substitutional $Fe^{3+}$ diluted ions accounting for the paramagnetic response [2]; (ii) Fe-rich (Ga,Fe)N wurtzite nanocrystals commensurate with and stabilized by the GaN host lattice and (iii) hexagonal $\varepsilon$-$Fe_3N$ precipitates, as summarized in Fig. 2. The formation of nanocrystals containing a large density of the magnetic constituent elucidates the origin of the ferromagnetic features persisting up to above room temperature.

Furthermore, we have found [5] that by increasing the growth rate we can reduce the presence of secondary phases and then hamper the spinodal decomposition. This influence of the growth rate on the nanocrystal formation indicates that the Fe aggregation occurs at the growth surface. Importantly, our TEM, synchrotron XRD, and SQUID data reveal that the aggregation of Fe cations can be diminished or even prevented by co-doping with either Si donors or Mg acceptors.

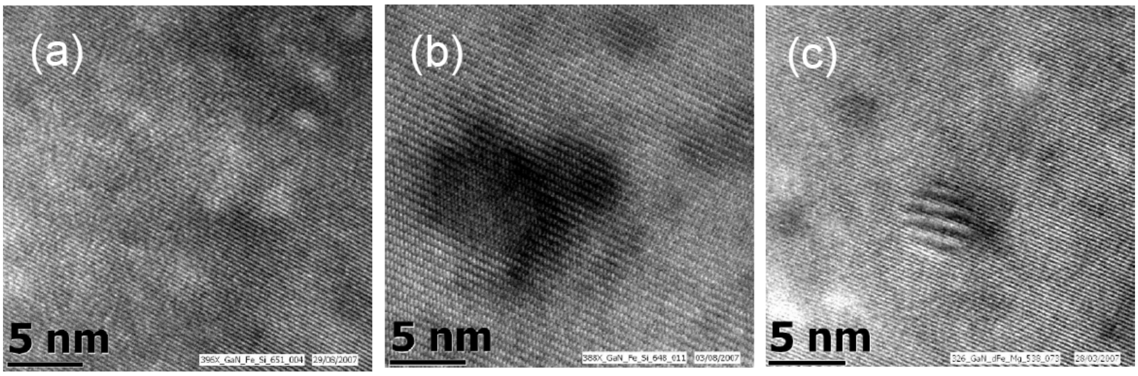

Fig. 2: High-resolution TEM images of (a) diluted GaN:Fe; (b) Fe-rich (Ga,Fe)N wurtzite regions coherent with the GaN matrix; (c) hexagonal $\varepsilon$-Fe$_3$N nanocrystal.

Since, quite generally, the binding energy of TM pairs depends on the valency of the open *d*-shells [17], there is a ground to suppose that the Fermi level engineering we evoke for (Ga,Fe)N:Si,Mg and others for (Zn,Cr)Te [18] can serve to control the magnetic ion aggregation in a number of semiconductors and oxides, providing a way to the self-organized fabrication of multi-component systems with tailored magnetic, magneto-optical, and magneto-transport properties at the nanoscale.

## Acknowledgements

This work has been supported by the Austrian Fonds zur Förderung der wissenschaftlichen Forschung - FWF (projects P17169, P20065 and N107-NAN)

## References

[1] A. Bonanni. Semicond. Sci. Technol., 22:R41, 2007.

[2] A. Bonanni, M. Kiecana, C. Simbrunner, T. Li, M. Sawicki, M. Wegscheider, M. Quast, H. Przybylinska, A. Navarro-Quezada, R. Jakiela, A. Wolos, W. Jantsch, and T. Dietl. Phys. Rev. B, 75:125210, 2007.

[3] M. Wegscheider, Tian Li, A. Navarro-Quezada, B. Faina, A. Bonanni, W. Pacuski, R. Jakie la, and T. Dietl. J. Phys: Condens. Matter, 20:454222, 2008.

[4] W. Pacuski, P. Kossacki, D. Ferrand, A. Golnik, J. Cibert, M. Wegscheider, A. Navarro-Quezada, A. Bonanni, M. Kiecana, M. Sawicki, and T. Dietl. Phys. Rev. Lett., 100:037204, 2008.

[5] A. Bonanni, A. Navarro-Quezada, T. Li, M. Wegscheider, Z. Matej, V. Holy, R.T. Lechner, G. Bauer, M. Kiecana, M. Sawicki, and T. Dietl. Phys. Rev. Lett., 101:135502, 2008.

[6] T. Dietl. Phys. Rev. B, 77:085208, 2008.

[7] T. Mizokawa, T. Nambu, A. Fujimori, T. Fukumura, and M. Kawasaki. Phys. Rev. B, 65:085209, 2005.

[8] W. Pacuski, D. Ferrand, J. Cibert, C. Deparis, J. A. Gaj, P. Kossacki, and C. Morhain. Phys. Rev. B, 73:035214, 2006.

[9] E. Przezdziecka, E. Kaminska, M. Kiecana, M. Sawicki, L. K lopotowski,W. Pacuski, and J. Kossut. Solid State Commun., 139:541, 2006.

[10] E. Malguth, A. Hoffmann, and M. R. Phillips. phys. stat. sol. (b), 245:455, 2008.

[11] P. Kacman. Semicond. Sci. Technol., 16:R25, 2001.

[12] C. Benoit à la Guillaume, D. Scalbert, and T. Dietl. Phys. Rev. B, 46:9853(R), 1992.

[13] R. Bouzerar, G. Bouzerar, and T. Zimai. Europhys. Lett., 78:67003, 2007.

[14] H. Katayama-Yoshida, K. Sato, T. Fukushima, M. Toyoda, H. Kizaki, V. A.Dinh, and P. H. Dederichs. phys.stat. sol. (a), 204:15, 2007.

[15] M. Jamet, A. Barski, T. Devillers, V. Poydenot1, R. Dujardin, P. Bayle-Guillmaud, J. Rotheman, E. Bellet-Amalric, A. Marty, J. Cibert, R. Mattana, and S. Tatarenko. Nature Mat., 5:653,2006.

[16] T. Dietl. J. Appl. Phys., 103:07D111, 2008.

[17] T. Dietl. Nature Mat., 5:673, 2006.

[18] S. Kuroda, N. Nishizawa, K. Takita, M. Mitome, Y. Bando, K. Osuch, and T. Dietl. Nature Mat., 6:440, 2007.