	Experiment title: Origin of the ferromagnetism in wurtzite GaN doped Mn semiconductors	**Experiment number**: HE-1894
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Report:

The theoretical work of T. Dietl *et al*. [1] on Diluted Magnetic Semiconductor (DMS) has propelled wordwide rechearch on III-V wide band gap semiconductors and especially (Ga,Mn)N, due to the prediction of a Curie temperature (T_C) above room temperature. In particular, Dietl's calculations, based on the Zener model of ferromagnetism, predict that GaN doped with 5% Mn (Mn^{2+}) and $3.5x10^{20}$ holes per cm^3 should exhibit the highest Curie temperature Tc (~420K) compared to other semiconductors. However, those calculations are unrealistic since the highest hole concentration achieved in (Ga,Mn)N is of the order of 10^{18} holes per cm^3. Only very recently, more realistic models based on Monte Carlo calculations or using an effective Heisenberg Hamiltonian and that take into account disorder effects, predict a T_C for the (Ga,Mn)N in the order of ~40-50K for 7 at.% Mn (e.g. ref. [2]). Independently of the models, all calculations agree that the magnetic ground state of (Ga,Mn)N is ferromagnetic with a Mn magnetic moment of 3-4μ_B/atom.

Many groups have actually succeed in the growth of (Ga,Mn)N thin films either by molecular beam epitaxy, sputtering, pulsed laser deposition or metal-organic vapor phase epitaxy. Nevertheless, many discrepancies can be found in the literature regarding their magnetic properties. Nearly all type of magnetism can be found, varying from antiferromagnetism to paramagnetism and of course ferromagnetism. In the case of ferromagnetism, the T_C is spread out over an extremely wide range, from 2K up to 940K. Most of the works which show the existence of ferromagnetism are mainly based on spontaneous magnetization measurements based on superconducting quantum interference device (SQUID). However, some results have suggested the presence of parasitic secondary phases that are ferromagnetic and may produce the observed ferromagnetism. In the case of (Ga,Mn)N films, those

parasitic phases are mainly cubic clusters of $GaMn_3N$ and/or Mn_4N, as identified from high angle X-ray diffraction (XRD).

Only an element specific technique, sensitive to magnetism, and able to probe the local symmetry and the surrounding environment, will allow to go further in the understanding of the origin of the magnetism in (Ga,Mn)N DMS and to clarify what is its intrinsic magnetic ground state.

We have grown using plasma-assisted molecular beam epitaxy, high structural quality wurtzite (Ga,Mn)N thin layers. In particular, the growth conditions (temperature and III/V flux ratio) were carefully optimised in order to control the two-dimensional growth mode and to prevent the appearance of secondary phases (e.g $GaMn_3N$ and/or Mn_4N clusters) inside the wurtzite structure.

Firstly, in order to ensure the high structural quality of our samples, beyond the XRD experiments performed in our lab, we have performed X-ray Linear Dichroism (XLD) measurements at the Mn K-edge and at the Ga K-edge on wurtzite epitaxial $Ga_{1-x}Mn_xN$ thin films (with x=0.04%, 0.4%, 4%, 6.3%) and on a reference sample of wurtzite GaN single crystal. In Fig. 1, we have plotted the XLD signal recorded at the Mn K-edge and Ga K-edge for a $Ga_{0.937}Mn_{0.063}N$ thin film. The XLD was recorded using a quarter wave plate which allows to flip the linear polarization of the incident beam from horizontal to vertical at each energy point. The sample was measured at the 10° grazing incidence, in such a way that the horizontal linear polarization is parallel to the (a,b)-plane and the vertical polarization nearly perpendicular to the c-axis. The total fluorescence yield was collected via 8 photodiodes forming a large detection solid angle and mounted in backscattering geometry. We have observed that the intensity and shape of the XLD signal at the Ga K-edge recorded for both samples (pure GaN and (Ga,Mn)N) were identical within less than 0.01% accuracy. These results show us directly that the incorporation of Mn for concentrations up to 6.3% does not destroy the wurtzite structure/symmetry of the crystal. Moreover, we observe a strong XLD signal at the Mn K-edge, which resembles strongly to the XLD signal recorded at the Ga K-edge. Using the FDMNES code [3], and by assuming a $Ga_{0.9375}Mn_{0.0625}N$ crystal with lattice parameters as the bulk GaN, we have obtained a very good agreement regarding the shape and amplitude of the XLD spectra at both the Mn and Ga K-edge in comparison to the experiment. Moreover, the theoretically calculated XLD spectra, nicely reproduce the ratio of the XLD intensity of Ga:Mn which is equal to approximately ~1.8:1.0. Furthermore, for other possible Mn sites occupation, *e.g.* N substituted or interstitial sites, no agreement was found with the experimental spectra. The presence of metallic Mn clusters, $GaMn_3N$ and/or Mn_4N phases would be manifested in both the XANES and the XLD spectra. It is important to mention that we have observed the same Mn K-edge XLD signal (edge part) in shape and in amplitude (within 3%) for all (Ga,Mn)N samples with a Mn concentration ranging from 6.3% down to 0.04%, where the presence of secondary phases is unlikely. ***The XLD experiments show that the Mn atoms are Ga substituted and do not reveal the presence of any secondary phases or metallic clusters.***

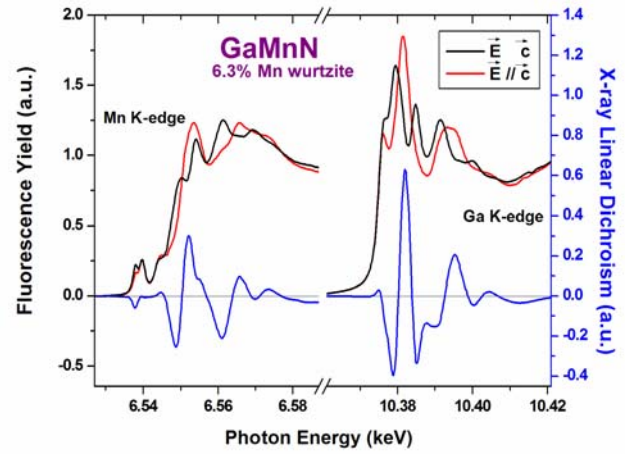

Fig.1 : *X-ray Linear Dichroism spectra recorded at the Mn K-edge and Ga K-edge for a $Ga_{0.937}Mn_{0.063}N$ at 300 K.*

Secondly, for the same serie of wurtzite epitaxial $Ga_{1-x}Mn_xN$ thin films (with x=0.04%, 0.4%, 4%, 6.3%), we have performed X-ray Magnetic Circular Dichroism (XMCD) experiments at the K-edge of Mn. In Fig. 2 we show the XMCD signal of the sample with the maximum concentration in Mn (6.3%). We notice a very intense XMCD signal (1.6% with respect to the edge jump), mainly at the first peak of the XANES spectrum. Since the XMCD signal at the K-edge is proportional to the orbital

polarization of the absorbing atom, our result clearly shows that the Mn atoms in (Ga,Mn)N carry an orbital magnetic moment. The observation of a sizeable orbital moment by XMCD is a strong argument in favor of the Mn^{3+} valence state. Indeed, in the case of Mn^{2+} where the 3*d* and 4*p* orbital moments are nearly zero, the XMCD signal is usually one order of magnitude smaller.

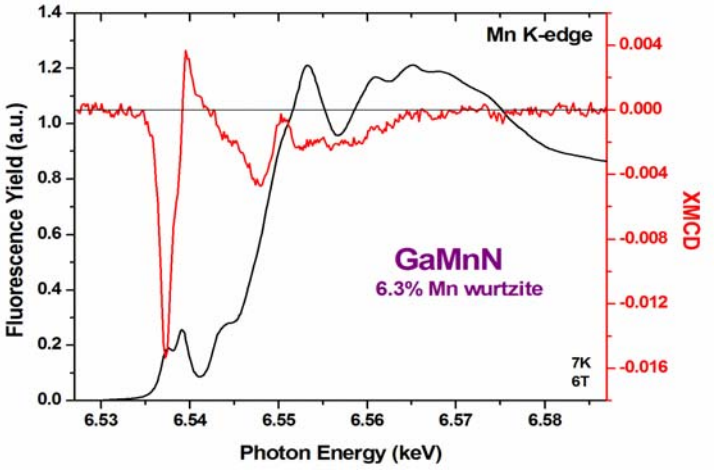

Fig.2 : *X-ray Magnetic Circular Dichroism signal recorded at the Mn K-edge at 7K and under an external magnetic field of 6 Tesla for a* $Ga_{0.937}Mn_{0.063}N$ *sample.*

Figure 3 shows the temperature-dependent magnetization curves recorded with SQUID together with the as-measured magnetization curve recorded by monitoring the Mn K-edge XMCD signal as a function of applied field at 7K. Under high magnetic fields the magnetization of Mn measured via XMCD seems to be saturated while the SQUID data exhibit a rather important slope. This discrepancy could be assigned to the contribution of paramagnetic defects in the sample and/or to errors in the substraction of the diamagnetic contribution of the substrate since, under high magnetic fields the diamagnetic signal becomes predominant with respect to the ferromagnetic one and the corrected SQUID signal is thus obtained with less accuracy. Under weak magnetic fields, the Mn magnetization measured with XMCD is nearly the same as the total magnetization recorded with SQUID. This low field part is a typical signature of a ferromagnetic system. From SQUID, we have determined that the Curie temperature of (Ga,Mn)N with a Mn concentration up to 6.3% is as low as 8K.

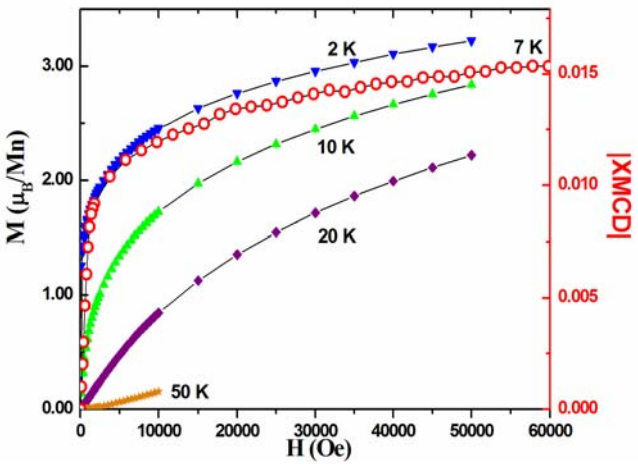

Fig. 3: *Temperature dependent magnetization curves measured by SQUID (full symbols, left scale) and XMCD magnetization curve measured at 7 K at the first peak at the Mn K-edge (open symbols, right scale) for a (Ga,Mn)N sample with 6.3% of Mn. The same magnetization curve was measured at different energy points in the XMCD spectrum.*

The XMCD spectra recorded at the Mn K-edge at 7K and at grazing incidence (the isotropic absorption spectra have been normalized to an edge jump of unity) for various Mn concentrations in (Ga,Mn)N are shown in Fig. 4. We can observe that the XMCD spectral shape is the same independently of the Mn concentration. However, the intensity of the XMCD signal is found to increase in amplitude as the concentration in Mn is decreased. However, we notice that in the case of highly diluted Mn atoms, the XMCD becomes much smaller and is also shifted to lower photon energy (the XAS spectra is hardly not changing as a function of the Mn concentration). This sample (0.04% in Mn) represents the case where the Mn atoms are isolated. In Fig. 5, the corresponding Mn magnetization curve measured at the maximum XMCD signal at the lowest temperature of 7K is shown. Clear different Mn magnetization behaviors are observed as a function of the Mn concentrations. For Mn

concentrations higher than 2%, the magnetization curve is typical of a ferromagnetic system. For a Mn concentrations between 2% and 0.5%, the magnetic behavior is paramagnetic but does not correspond to a Brillouin-type of paramagnetism expected for Mn^{+3} ions. Only for very highly diluted Mn atoms (0.04%), the Mn magnetization curve corresponds to a Brillouin type of paramagnetism where all the Mn ions are considered as isolated. Using XMCD experiments at the Mn K-edge, we were able to reveal different magnetic behavior of (Ga,Mn)N as a function of the Mn concentration.

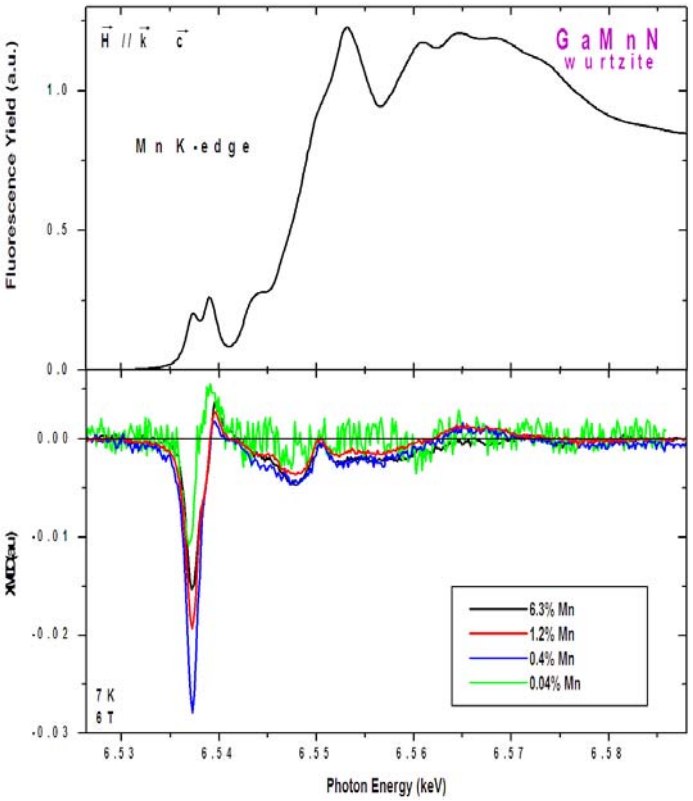

Fig. 4: *XAS and XMCD recorded at the Mn K-edge at 7K and under an exteranl magnetil field of 6 Tesla in $Ga_{1-x}Mn_xN$ thin films with different concentrations in Mn.*

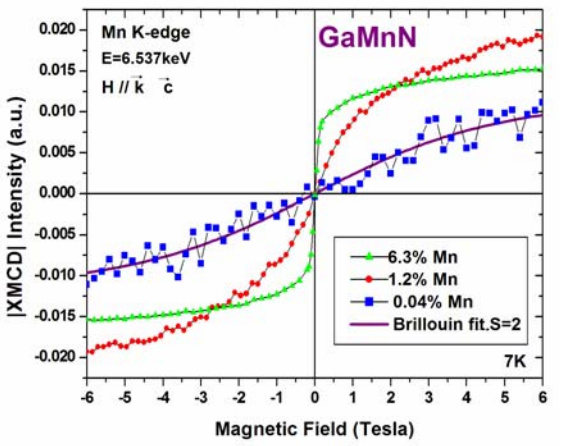

Fig. 5: *Mn magnetization curves measured at the maximum XMCD signal as a function of the external applied field at 7K in $Ga_{1-x}Mn_xN$ samples with different Mn concentration.*

Finally, by combining x-ray linear dichroism and x-ray magnetic circular dichroism experiments, we were able to demonstrate unambiguously that wurtzite (**Ga,Mn)N** for a Mn concentrations higher than 2% is ***intrinsically ferromagnetic*** [4] whereas different intrinsic paramagnetic behaviors are observed for a Mn concentration lower than 2% [5].

[1] T. Dietl et al., Science **287**, 1019 (2000).
[2] G. Bouzerar, T. Ziman, and J. Kudrnovsky, Europhys. Lett. **69**, 812 (2005).
[3] Y. Joly, Phys. Rev. B 63, 125120 (2001).
[4] E. Sarigiannidou, F. Wilhelm, E. Monroy, R.M. Galera, E. Bellet-Amalric, A. Rogalev, J. Goulon, J. Cibert, and H. Mariette, submitted to Phys. Rev. Lett. (2006)
[5] E. Sarigiannidou, F. Wilhelm, E. Monroy, R.M. Galera, E. Bellet-Amalric, A. Rogalev, J. Goulon, J. Cibert, and H. Mariette, under preparation.