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Element specific magnetic properties of Gd:GaN: very small polarization of Ga and paramagnetism of Gd

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Abstract

Element specific x-ray magnetic dichroism measurements have been carried out at the Ga K- and Ga and Gd L_3-edges of the dilute magnetic semiconductor (DMS) Gd:GaN grown by molecular beam epitaxy. This DMS material has previously been reported to exhibit room temperature magnetic order accompanied by colossal effective magnetic moments. We detect only a very small magnetic polarization of the order of at most $10^{-5}\mu_B$/Ga atom in Gd:GaN which cannot account for the colossal effective magnetic moments. Further, the element specific magnetic properties at the Gd sites do not reveal any ferromagnetic-like signatures but rather behave paramagnetic. Thus, the ferromagnetism in Gd:GaN is caused by polarization of the N site or by extrinsic mechanisms such as magnetic polarization of defects or residual oxygen in these samples.

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The search for ferromagnetism in dilute magnetic semiconductors (DMS) at room temperature is motivated by potential spintronic applications where the spin degree of freedom is used to augment performance. However, the origin of the long range magnetic order in DMS materials is still controversial. Recently long range magnetic order above room temperature has been demonstrated for wurtzite Gd:GaN [1] even for a dopant concentration as low as 10^{16}atoms/cm^3 grown by molecular beam epitaxy (MBE) [2]. The long range magnetic order is accompanied by a huge effective magnetic moment per Gd atom in the ultradilute limit if it is calculated from superconducting quantum interference device (SQUID) magnetometry data, an effect which is even more pronounced in Gd-ion-implanted GaN [3]. The materials for eventual phase segregation are limited to GdN ($T_N = 56$ K), and Gd ($T_C = 293$ K) which makes them unlikely candidates to explain magnetic order above 300 K. The occurrence of magnetic order in wurtzite Gd:GaN was phenomenologically explained by large "spheres of influence" surrounding the Gd dopant atoms inside which the GaN matrix is magnetically polarized [2]. The polarization inside this "sphere of influence" was assumed to be constant and fitting a coalescence model to the SQUID data yields a small polarization of $1.1 \cdot 10^{-3}\mu_B$/atom and a large radius of these spheres of about 28 nm [2]. The additional polarization for overlapping spheres was marginal [2]. For a more thorough understanding of the magnetic properties of Gd:GaN it is useful to verify the predicted magnetic polarization of the GaN host and its origin. Previous magneto-photoluminescence (PL) measurements have demonstrated a clear polarization of the donor-bound exciton (D^0, X) emission at low temperatures [4]. The donor responsible for the (D^0, X) transition in the PL spectra is oxygen which is found in all the Gd:GaN samples with a concentration around 10^{18}/cm^3.

Here we will focus on element specific x-ray magnetic dichroism measurements at the Ga K-edge of previously well-characterized Gd:GaN films [5]. We can demonstrate by x-ray magnetic circular dichroism (XMCD) that the Ga sites in Gd:GaN show a very small magnetic polarization of the order of at most $10^{-5}\mu_B$ which cannot fully account for the unusual magnetic properties of the DMS material as measured by SQUID. Furthermore, additional XMCD measurements at the Gd L_3-edge substantiate that ferromagnetic-like properties of the Gd dopant are absent as previously indicated [5].

Gd:GaN films grown by ammonia-assisted MBE on SiC(0001) have been characterized in detail using in situ reflection high energy electron diffraction (RHEED), x-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS), and magneto-PL measurements [2, 4].

They exhibit long range magnetic order at and above room temperature together with colossal effective magnetic moments as measured by integral SQUID magnetometry [2]. We have chosen to study the potential magnetic polarization of the GaN host in the concentration range above 10^{19} Gd/cm^3, where—according to the coalescence model—the entire GaN matrix should be filled with magnetically polarized "spheres of influence" [2], i. e., the polarization per Ga atom is expected to be maximized. X-ray linear dichroism (XLD) studies demonstrate that Gd predominantly occupies Ga substitutional sites [5]. On the other hand, the element specific hysteresis at the Gd-L_3-edge significantly deviates from the integral magnetic properties as measured by SQUID [5]. The x-ray absorption near edge spectra (XANES) at the Ga L_3-edges in the soft x-ray regime were recorded using electron yield at beamline 4.0.2 at the Advanced Light Source (ALS), whereas for the Ga K-edge and the Gd L_3-edge we used hard x-rays from the ID12 beamline at the European Synchrotron Radiation Facility (ESRF) detecting the total fluorescence yield which is bulk sensitive. For all dichroism measurements both the helicity of the x-ray beam and the magnetization were reversed to assure that the spectra are free from artifacts.

Figure 1(a) shows XANES spectra at the Ga K-edge for $2 \cdot 10^{19}/\mathrm{cm}^3$ Gd in GaN recorded at 7 K with the x-ray beam at normal incidence and 15° grazing incidence. A comparison of the XANES spectra for both geometries shows clear differences in the fine structure. In the case of grazing incidence the x-ray E-vector has a finite component parallel to the c-axis whereas under normal incidence it remains within the a-plane. The difference in the XANES spectra is therefore indicative of the presence of a substantial XLD effect as measured for the wurtzite crystallographic structure of GaN [5, 6]. Figure 1(b) shows the respective XMCD spectra which were recorded at 7 K in an external field of ± 6 T for grazing and normal incidence. Note that all Figures show the spectra corresponding to the positive field direction. The XMCD at the Ga K-edge is a measure of only the $4p$ orbital contribution to the total magnetic moment. We can detect an XMCD signal of the order of 0.013% at the Ga K-edge for 15° grazing and normal incidence exhibiting relatively similar spectral features. Comparable spectral features have been recorded at the Ga K-edge of 2.7% Mn-doped GaN samples [7]; however, the size of the signal was about 0.1%, and the measurement temperature of 7 K is close to the respective Curie-temperature of that sample [6, 7]. Therefore, we have to conclude that the magnetic polarization of the Ga sites is much weaker compared to Mn-doped GaN.

Since the XMCD signal in Fig. 1(b) is very small we want to discuss it in more detail. First we want to point out that the circular polarization transfer rate of the x-ray beam which is monochromatized by a Si(111) double crystal monochromator is about 98%. A small linear polarization component at 45° (P_2 Stokes-Poincaré parameter) is also generated by the monochromator at this energy and is of the order of 3%. By reversing the phase of the helical undulator, not only the circular polarization of the monochromatic x-ray beam is altered (helicity is reversed) but also there is a significant change of P_2 [8]. Since the c-axis of the sample is never aligned perfectly parallel to the vertical component of the light when looking into the light source, this situation leads to a contamination of the experimental spectra with a linear dichroism signal. However, this residual XLD signal does not reverse with the magnetic field and thus can be analyzed separately. This residual XLD signal is shown in Fig. 1(b) as well. Note, that the data were reduced by a factor of 20. Since the residual XLD clearly dominates over the XMCD signal it makes the detection of such a small XMCD signal very challenging. Second we try to estimate the expected size of the XMCD signal at the Ga K-edge, which is a measure of the orbital fraction of the magnetic moment at the Ga $4p$ states. From the SQUID measurements a overall magnetic polarization of $1.1 \cdot 10^{-3}\mu_B$ has been inferred inside the "spheres of influence" [2]. The XMCD results can be compared to recent experimental data recorded at the Ga K-edge of (InGaMn)As [9]. Here a Ga $4p$ orbital moment of $8(4) \cdot 10^{-5}\mu_B$ has been correlated with a maximum XMCD intensity of 0.05%. In turn this means that from the size of the XMCD in Fig. 1(b) one can roughly estimate a magnetic moment of the order of at most $10^{-5}\mu_B$ as upper bound, since the integral of the XMCD in our case is close to zero, whereas in Ref. [9] the spectral shape indicates only one positive feature, i. e., a larger integral for the same amplitude. This is between one and two orders of magnitude smaller than what is expected from the SQUID measurements. Nevertheless, our measurements are consistent with an extremely small orbital magnetic polarization of at most $10^{-5}\mu_B$/Ga. To be consistent with an expected magnetic polarization of $1.1 \cdot 10^{-3}\mu_B$ the normalized XMCD signal should be between one and two orders of magnitude larger, depending on the fraction (1 to 10%) of the orbital contribution to the overall magnetic polarization.

Figure 2 shows XANES and XMCD asymmetry measurements for an uncapped Gd:GaN at the Ga L_3-edge at 100 K which detects the total magnetization but only probes the surface of the sample (total electron yield in the soft x-ray regime, about 2 to 3 nm probing depth).

For this measurement the magnetization direction was reversed by an external magnetic field of ± 0.5 T at every energy point. Furthermore these spectra are the result of appropriately averaging data obtained with opposite circular polarization. The XMCD asymmetry does not show any dichroic signature within the noise level of the experiment. The absence of any XMCD signal at the L_3-edge and L_2-edge (not shown) indicates that the magnetic polarization of the Ga sites cannot be dominated by the spin moment but is merely of the order which is inferred by the hard x-ray measurements. Consequently, our detailed XMCD measurements in the soft and hard x-ray regime can only provide experimental evidence for a tiny magnetic polarization located at the Ga sites of Gd:GaN samples in a regime where the entire GaN matrix is expected to be magnetically polarized, i. e., where the polarization should be largest.

We further refined our previous studies [5] at the Gd L_3-edge of Gd:GaN by recording XMCD spectra at 15 K and 295 K and the element specific hysteresis at 15 K with high field resolution in the range of ± 0.6 T. The experimental results are shown in Fig. 3(a) and (b), respectively both recorded under 15° grazing incidence. Figure 3(a) reveals a sizable XMCD signal at 15 K but none at 295 K although the SQUID measurements show magnetic hysteresis well above 300 K [2] for such samples. Further, the low-field dependence of the previously recorded XMCD signal at the Gd L_3-edge was measured at 15 K as shown in Fig. 3(b). No significant remanence, coercivity or curvature of the $M(H)$ curve is observed even if the field resolution is further increased (not shown). Thus, we find no experimental evidence for ferromagnetic-like behavior of the Gd dopant down to 15 K which could account for the SQUID data but it rather suggests paramagnetic behavior.

We want to discuss the implications of our experimental results. The integral magnetic properties measured by SQUID infer ferromagnetic-like behavior with huge effective moments whereas magnetic studies with element specificity at the Ga and Gd edges point towards paramagnetic behavior of the dopant and only a tiny magnetic polarization on the Ga sites which is about one order of magnitude lower than what is inferred from the SQUID measurements. Therefore, the microscopic origin of the magnetic properties has to be located elsewhere. Previous magneto PL studies [4] were already able to demonstrate the large effect of Gd doping on the band structure of GaN. However, these studies were restricted to low temperatures and thus they cannot be correlated directly to the remarkable magnetic properties at 300 K and above. It would be interesting to systematically study,

e. g., the influence of oxygen co-doping on the integral magnetic properties of Gd:GaN. The absence of ferromagnetic-like signatures at the Gd dopant already indicates that Gd itself cannot directly account for the integral magnetic properties but rather activates magnetism, e. g., via creating lattice distortions or nitrogen interstitials as inferred before by annealing experiments [10]. Recent theoretical calculations highlight the importance of Ga vacancies to account for the magnetic properties of Gd:GaN [11]. Doping of GaN with rare earth elements of comparable size to Gd atoms but with smaller or even null magnetic moment could provide further insight even using integral magnetometry.

In summary, our experiments rule out significant magnetic polarization as measured at the Ga K- and L_3-edges of Gd:GaN for the Gd dopant regime where the largest effects are expected. Only a very small orbital magnetic polarization of the order of at most $10^{-5}\mu_B$ can be inferred from the hard x-ray measurements, which is too small to account for the colossal effective magnetic moment. Further, no ferromagnetic-like signatures such as remanence, coercivity or magnetic hysteresis can be found at the Gd L_3-edge. Therefore, the exceptional magnetic properties of Gd:GaN as measured by integral SQUID magnetometry cannot be assigned to the Ga or the Gd sites as probed by element specific synchrotron measurements.

Acknowledgments

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Figures

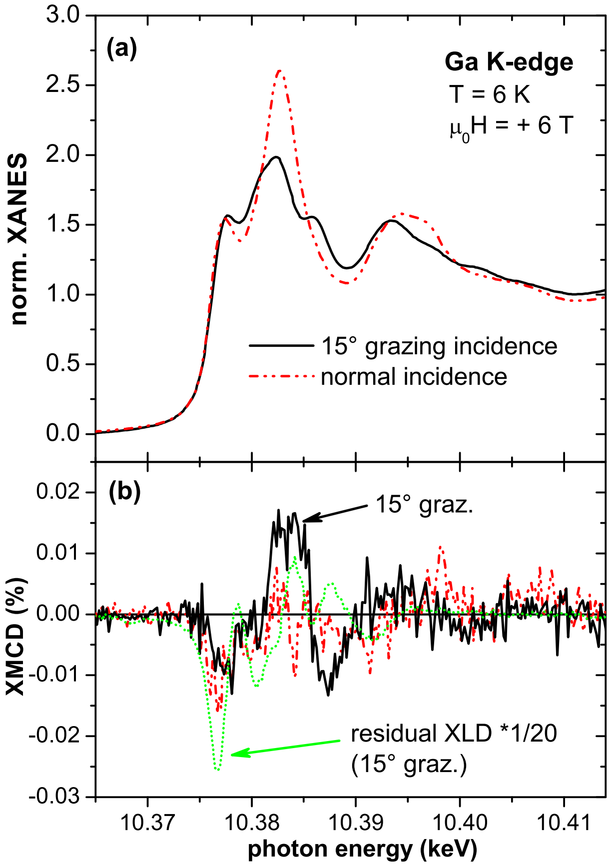

FIG. 1: (a) Normalized XANES spectra at the Ga K-edge of Gd:GaN recorded at 7 K for 15° grazing incidence (full black line) and normal incidence (dash-dotted red line) of the x-rays. (b) Respective normalized XMCD signal at 7 K and an external field of ±6 T for grazing and normal incidence. The residual x-ray linear dichroism (XLD) for grazing incidence is shown reduced by a factor of 20 (dotted green line).

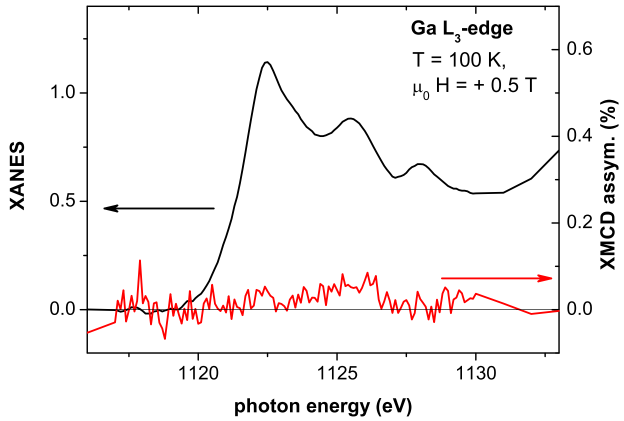

FIG. 2: XANES and XMCD spectra at the Ga L_3-edge of Gd:GaN recorded at 100 K and under 30° grazing incidence.

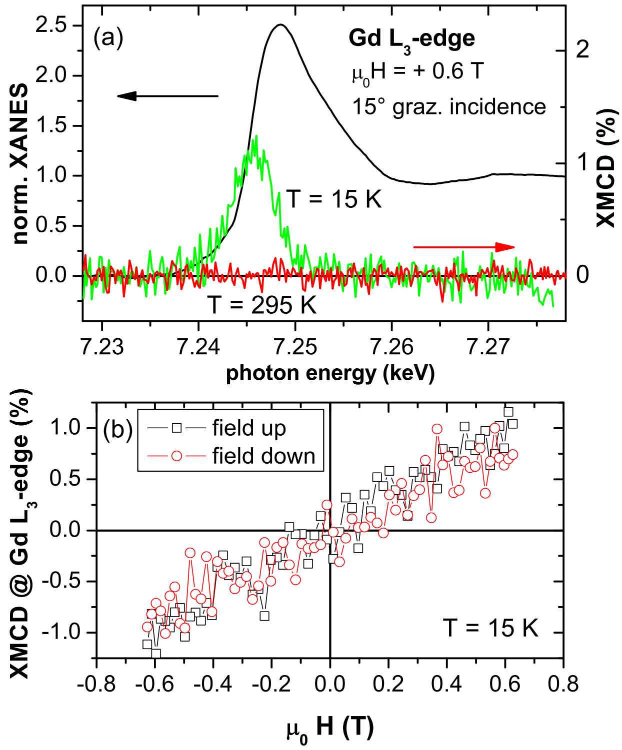

FIG. 3: (a) XANES and XMCD spectra at the Gd L_3-edge of Gd:GaN recorded under 15° grazing incidence of the light revealing an XMCD signature at 15 K but none at 295 K. (b) The element specific hysteresis recorded at 15 K at the Gd L_3-edge for sweeping the external magnetic field with high field resolution in both directions. No opening of the $M(H)$ curve is visible.