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Ferromagnetic and paramagnetic magnetization of implanted GaN:Ho,Tb,Sm,Tm films

M. Maryško,[1,a)] J. Hejtmánek,[1] V. Laguta,[1] Z. Sofer,[2] D. Sedmidubský,[2] P. Šimek,[2] M. Veselý,[2] M. Mikulics,[3,8] C. Buchal,[3] A. Macková,[4,5] P. Malínský,[4,5] and R. A. Wilhelm[6,7]
[1]Institute of Physics of ASCR v.v.i., Cukrovarnická 10, 162 00 Prague 6, Czech Republic
[2]Department of Inorganic Chemistry, Institute of Chemical Technology, 166 28 Prague 6, Czech Republic
[3]Peter Grünberg Institut, PGI-9, Forschung Centrum, Jülich D-52425, Germany
[4]Nuclear Physics Institute of the ASCR v.v.i., 250 68 Řež, Czech Republic
[5]Department of Physics, Faculty of Science, J.E.Purkinje University, České mládeže, 400 96 Ústí nad Labem, Czech Republic
[6]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Dresden, Germany
[7]Technische Universität Dresden, 01062 Dresden, Germany
[8]JARA, Fundamentals of Future Information Technology, D52425 Jülich, Germany

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The SQUID magnetic measurements were performed on the GaN films prepared by metal-organic vapour phase epitaxy and implanted by Tb^{3+}, Tm^{3+}, Sm^{3+}, and Ho^{3+} ions. The sapphire substrate was checked by the electron paramagnetic resonance method which showed a content of Cr^{3+} and Fe^{3+} impurities. The samples $5 \times 5\,mm^2$ were positioned in the classical straws and within an estimated accuracy of 10^{-6}emu, no ferromagnetic moment was detected in the temperature region of 2–300 K. The paramagnetic magnetization was studied for parallel and perpendicular orientation. In the case of GaN:Tb sample, at $T = 2$ K, a pronounced anisotropy with the easy axis perpendicular to the film was observed which can be explained by the lowest quasi-doublet state of the non-Kramers Tb^{3+} ion. The Weiss temperature deduced from the susceptibility data using the Curie-Weiss (C-W) law was found to depend substantially on the magnetic field.
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In recent years, a great attention was devoted for searching the room temperature ferromagnetic (FM) ordering in dilute magnetic semiconductor (DMS) GaN layers doped by transition metals and rare earths (RE). The FM state at $T = 300$ K was reported for GaN:Gd,[1,2] Dy,[3] Tb,[4] and only recently Sm[5] films. The origin of the FM state in these films has not yet been explained. For GaN:RE, in contrast to GaN:Mn films, the calculations of the electronic structure do not predict the FM moment at $T = 300$ K.[6] It seems, however, that especially in the case of the implanted films, the FM state is essentially influenced by the presence of defects.[7] In many cases, there is a question about the presence of the FM state since it is not easy to detect a very small moment of the GaN:RE layer superimposed on the large diamagnetic (DM) contribution of the sapphire substrate. The problem of the measurements of such films has been recently analyzed in a great detail in the papers.[8–10] Starting from these works and following our earlier contributions,[2,3] we performed the study of the FM and paramagnetic (PM) magnetization of the implanted GaN:Ho, Sm, Tb, Tm layers. To our knowledge, the magnetic properties of these films with exception of GaN:Tb[11] and GaN:Sm[5] have not yet been studied and in most cases the measurements were not performed in the low temperature region. In our case, the magnetic moment measurements were supplemented by the electron paramagnetic resonance (EPR) study of the sapphire substrate with the aim to obtain information on PM impurities in the sapphire and GaN/sapphire films.

GaN layers with a thickness of about 3 μm were grown by low pressure metal-organic vapour phase epitaxy (MOVPE) on c-plane sapphire substrates with thickness of 0.45 mm. These GaN layers were implanted with Tb^+, Tm^+, Sm^+, Ho^+ ions using an energy of 200 and 400 keV and some samples subsequently annealed at 900 °C for 15 min. The details of preparation of the GaN:RE films and their description including the disorder densities N_D/N for GaN:Tb,Sm layers were reported in the work.[12] The as-prepared layers used in experiments (Table I) are characterized by a implantation energy and fluency and by a total amount N of the implanted RE atoms N per unit of area determined from the Rutherford backscattering (RBS) and the concentration profile obtained by secondary ion mass spectrometry (SIMS).

The content of PM impurities in the sapphire substrate was detected using the EPR measurement at X band and $T = 77$ K. The spectrum with the magnetic field perpendicular to the plane (Fig. 1) shows two lines at 1.9 and 2.2 kOe originating from the Cr^{3+} ions. The positions of these lines correspond to the expected resonances and the simulation of the lineshape for the isotope ^{53}Cr ($I = 3/2$) agrees with experiment and a rough estimate of concentration of Cr impurity is a few tens of ppm. Some smaller lines without satellites are most probably from Fe^{3+}. The presence Cr^{3+} and Fe^{3+} ions is in accord with the EPR experiment on the sapphire/GaN

[a)]Author to whom correspondence should be addressed. Electronic mail: marysko@fzu.cz.

TABLE I. List of the layers, total amount of the RE atoms N, Curie constant from experiment, effective Bohr magnetons from the $\chi(T)$, and free ion theoretical value.

Layer, energy, impl.fluence	$N \times 10^{-15}$ atoms cm^{-2}	$C \parallel / C\perp$ (emu K Oe^{-1} cm^{-2})	$\mu_{eff} \parallel / \mu_{eff} \perp \mu_B$	$\mu_{efftheor.}\ \mu_B$
GaN:Ho, 200 keV, 1×10^{16} atoms cm^{-2}	7.6	$4.4 \times 10^{-8}/4.5 \times 10^{-8}$	3.4/3.4	10.6
GaN:Sm, 400 keV, 5×10^{15} atoms cm^{-2}	6.17	…	…	0.84
GaN:Tb, 400 keV, 1×10^{15} atoms cm^{-2}	1.79	2.32×10^{-8}/-	7.7/-	9.72
GaN:Tb, 400 keV, 5×10^{15} atoms cm^{-2}	6.67	$6.39 \times 10^{-8}/13.6 \times 10^{-8}$	6.8/9.9	9.72
GaN:Tm, 200 keV, 1×10^{16} atoms cm^{-2}	11.3	$4.48 \times 10^{-8}/5.04 \times 10^{-8}$	4.37/4.4	7.57

reported by Bonanni *et al.*[8] A similar spectrum with the Cr and Fe lines was observed for a GaN/sapphire film. The $m(H)$ curve at $T = 2$ K and $m(T)$ dependence for $H = 10$ kOe for the GaN/sapphire sample are shown in the insets (a) and (b) of Fig. 1, respectively.

The magnetic measurements were carried out using a Reciprocating Sample Option (RSO) of the SQUID option of the SQUID magnetometer MPMS XL (Quantum Design). The samples with dimensions about 5×5 mm^2 were positioned in classical drink straws for parallel and perpendicular orientation of the magnetic field with respect to the plane of the film. Most experiments, especially all room temperature measurements were made in parallel configuration. At $T = 300$ K, the magnetic moment corresponding to the GaN:RE layer is obtained after subtracting the DM contribution of the sapphire substrate evaluated between the fields 10 and 25 kOe. The accuracy of the measurement is influenced by two factors. The first is an FM impurity content in the GaN/sapphire sample, which depends on the quality of the pure GaN and sapphire. The second factor is connected with the procedure of the measurement, where an apparent FM moment can be detected due to a deformation of the straw around the sample, disturbing a cylindrical symmetry, e.g., Ref. 9. (The material of the straw contains FM impurities with the saturation magnetization of the order 10^{-4} emu/g corresponding to Fe content several ppm). In our experiments, the influence of the second factor was minimized by careful positioning of the sample in the straw and repeating the measurement with different straws. As a result, the hysteresis curves shown in Fig. 2 reflect from the greater part only the possible intrinsic FM moment and the moment due to FM impurities in GaN/sapphire film. The first curve on the top of Fig. 2 with saturation moment smaller than 5×10^{-7} emu corresponds to the pure GaN/sapphire sample. The essential fact is that all the hysteresis curves of the GaN:RE layers exhibit a large dispersion of the measured points and the saturated moment smaller than 1×10^{-6} emu. This value can be taken as the accuracy of the measurement. Within this accuracy 10^{-6} emu in the measured moment and 0.25 emu/cm^3 in the magnetization (taking the depth range of RE ions about 150 nm), we may state that at room temperature and in the parallel configuration the GaN:Ho, Sm, Tb, Tm films do not exhibit a spontaneous FM moment. Also the low temperature measurements (see below) and the measurements on the annealed samples show the absence of the FM ordering in the whole temperature region of 2–300 K. We cannot, however, exclude the presence of a FM contribution with the saturation moment on the level of FM impurities, i.e., below 10^{-6} emu.

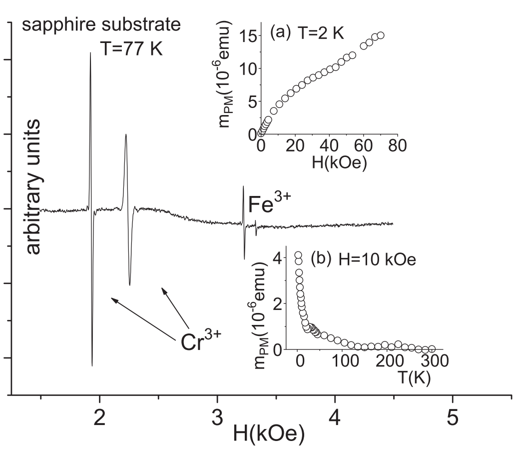

FIG. 1. EPR spectrum of Al_2O_3 substrate at $T = 77$ K and frequency $f = 9311$ MHz with the magnetic field perpendicular to the plane, in the inset (a) GaN/sapphire sample—the magnetic moment vs magnetic field dependence at $T = 2$ K, inset (b) GaN/sapphire substrate—the magnetic moment vs temperature under an applied field 10 kOe.

It is useful to compare this result, especially that for sample GaN:Tb 5×10^{15} atoms cm^{-2} (4.4×10^{20} atoms Tb in cm^3) and chemical index Tb_x ($x \approx 0.01$) with those reported for GaN:Tb.[4,11] In the first work,[11] the GaN:$Tb_{x=0.014}$ layers were prepared by the molecular beam epitaxy (MBE) method and only the PM behaviour was observed between 5 and 300 K. Contradictory to our results, in the second work, the GaN:Tb films prepared by dual energy ion implantation with the concentration of Tb atoms 5×10^{20}/cm^3 were found to be in a FM state at $T = 300$ K with the saturated moment of

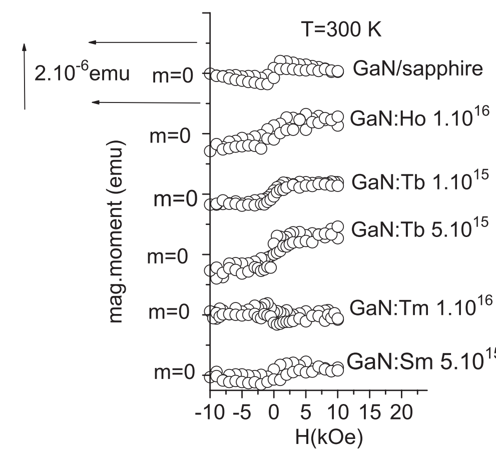

FIG. 2. Hysteresis curves at $T = 300$ K measured on the sample 5×5 mm^2, corrected for a diamagnetic contribution of the substrate.

1×10^{-5} emu (sample $6 \times 6\,\text{mm}^2$). At this place, it is important to remind the experimental finding that the FM state is to a great extent connected with defects as are Ga and N vacancies.[7] The content of defects in the MBE films is about an order of the magnitude below that for the implanted layers, which gives a reliable explanation for the absence of the FM state in GaN:Tb films.[11] Comparing our result $m_{FM} = 0$ with the work[4] suggests that the content of defects in our films can be smaller than that for the films prepared by dual energy implantation. The dual method yields a more homogeneous distribution of Tb ions but the number of defects could be increased by a repeated implantation process. This conjecture is supported by the negligible (GaN:Tb 5×10^{15})[12] and large[4] effects of annealing on the N_D/N and XRD data, respectively.

The temperature dependence of the PM susceptibility was measured between 2 and 300 K in the field-cooled regime mostly under an applied field of 10 kOe. Here, we limit ourself to the GaN:Tb films for which χ_{PM} ($\chi(T)$ corrected for the GaN/sapphire contribution) and related to number of Tb atoms are plotted in Fig. 3. First, we notice the coincidence of the results for samples 1×10^{15} and 5×10^{15} in parallel configuration, which verifies the proportionality of χ_{PM} to number N of Tb atoms. The susceptibility was interpreted using the C-W law $\chi = C/(T - \theta) + \chi_0$, where C is the Curie-constant and χ_0 is a susceptibility contribution independent on temperature formed primarily by the DM contribution of the substrate. The parameter θ represents the Weiss temperature, which is given by exchange interactions between PM centres. The positive and negative values of θ correspond to FM and antiferromagnetic (AFM) interactions, respectively. For the standard measurement (10 kOe), the values of θ evaluated from the $\chi(T)$ between 2 and 300 K were negative with the absolute value between 2 and 6 K. For the sample GaN:Tb 5×10^{15}, the parallel susceptibility vs T dependence was measured also for the fields $H = 5$ kOe, 2.5 kOe, and 700 Oe. With decreasing field, the evaluated value of θ decreased substantially as is shown in the inset of Fig. 3. This result suggests certain limitations with respect to the application of the C-W law. The C-W relation was derived using the first term in the series expansion of the Brillouin function under the assumption that $x = gJ\mu_B H/kT \ll 1$. For the Brillouin function with $J = 1/2$, we may express the magnetization as $m = m_s.\tanh(x)$ and illustrate this effect qualitatively. We take $g = 10.15$, $J = 1/2$ (see below), and zero interactions between the PM centres. The numerical approximation of m/H by the C-W law in the temperature region of 2–300 K then yields an apparent negative Weiss temperature θ depending on field. This value approaches zero in the limit of zero field (in the inset of Fig. 3). In real cases of finite interactions, the zero field limit determines the true Weiss temperature θ, which can have even an opposite sign that the apparent value of θ. In the case of the sample GaN:Tb 5×10^{15}, the quadratic extrapolation to $H = 0$ gets $\theta = -0.4$ K. In parallel configuration, g is not so large but the same effect leading to an increase of x can be achieved by admitting that the field H is increased by a positive molecular field, i.e., by assuming that some PM centres (Tb ions) exhibit a FM interaction. The pronounced field dependence of the apparent θ observed in parallel configuration therefore suggests the simultaneous occurrence of FM and AFM interacting Tb ions with an average value of θ corresponding to a weak AFM interaction predicted for the Ga vacancy induced FM state.[13] Let us remark that for DMS problems in determining θ and its interpretation have been already mentioned in the works.[14,15]

For GaN:Tb, Ho, Tm, the parallel and perpendicular magnetization curves at $T = 2$ K corrected for the GaN/sapphire contribution are plotted in Fig. 4. Using the number N of the RE atoms, we evaluated the magnetic moment per RE atom in Bohr magnetons. In GaN, the RE^{3+} ions substitute for Ga^{3+} ions. The $m(H)$ curves measured with increasing and decreasing field were practically identical, i.e., with differences of the moments of the order 10^{-7} emu, which verifies the conclusion about the absence of the FM moment up to $T = 2$ K. Comparing the $m(H)$ curves for the sample GaN:Tb 5×10^{15}, we observe a pronounced anisotropy with the easy axis perpendicular to the layer plane (c-axis). The

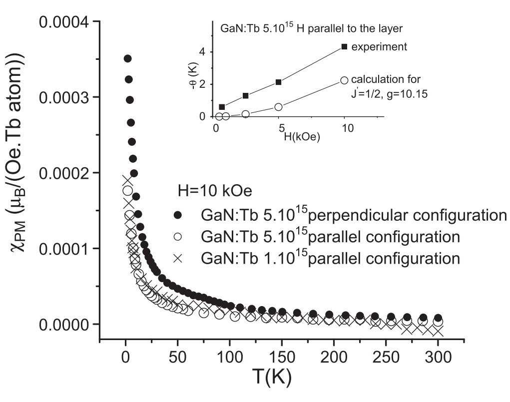

FIG. 3. The layers GaN:Tb, the PM susceptibility per Tb atom measured under an applied field of 10 kOe. In the inset, the evaluated values of the Weiss temperatures for different applied fields, by open circles the calculation for $J' = 1/2$, $g = 10.15$.

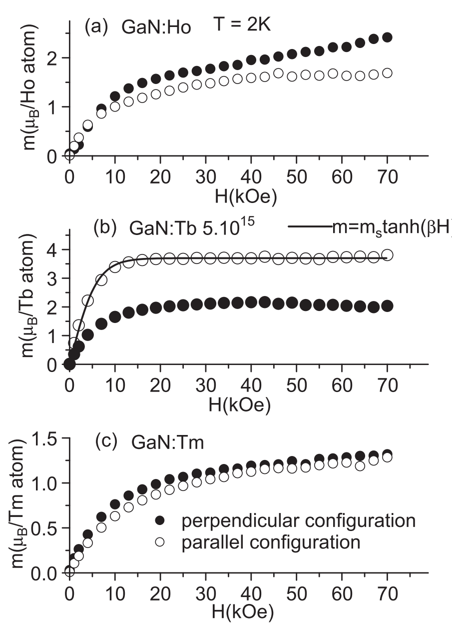

FIG. 4. The magnetic moment vs H curves at $T = 2$ K, the moment is expressed in Bohr magnetons per atom RE using the number N from Table I. (a) GaN:Ho, (b) GaN:Tb 5×10^{15}, and (c) GaN:Tm.

saturated moment along the easy axis amounts to $3.7\,\mu_B$, which is notable smaller than theoretical free ion value for Tb^{3+} $m_s = 9\,\mu_B$ ($g_J = 1.5$ and $J = 6$). Both these observations are caused by the crystal-field-splitting of RE levels. In our case, the anisotropy is expressed as the ratio $m\perp/m\parallel = 1.7$. (In the work,[11] the anisotropy at 5 K amounts to be 1.4.) The measured $m(H)$ curve along the easy axis can be well described by the Brillouin function for the quasi-doublet pseudospin $J' = 1/2$ in the form $m = m_s.\tanh(gJ'\mu_B H/kT)$ with $g = 10.15$ (Fig. 4).

The fact that the magnetization follows the Brillouin function for $J' = 1/2$ means that energy gap between two lowest singlets of non-Kramers Tb^{3+} ion in GaN is smaller than the Zeeman energy and these levels act as a doublet. This situation is analogical as mentioned by Knizek *et al.*[16] for the ion Tb^{3+} in cobaltites with the energy gap of $0.2\,cm^{-1}$. For the other our samples GaN:Ho (Fig. 4(a)) and GaN:Tm (Fig. 4(c)), the observed anisotropy is smaller. Also in these cases, the lowest energy singlets form quasi-doublets, but their energy gap exceeds that of Tb^{3+}.[17]

In summary, the SQUID measurements of the implanted GaN:Ho, Sm, Tb, and Tm films were performed between 2 and 300 K and the EPR method yielded information on the presence of Cr^{3+} and Fe^{3+} impurities in the sapphire substrate. In parallel configuration, within the accuracy 10^{-6} emu of the measured moment, we did not observe any FM ordering. This result which is in agreement with that for the MBE films[11] could be explained by a small defect content in our films. With exception of GaN:Sm (small signal), PM behaviour of Ho^{3+}, Tb^{3+}, and Tm^{3+} ions was observed. For GaN:Tb, the Weiss temperature evaluated using the C-W law was found to depend on the magnetic field which suggests the presence of both AFM and FM exchange interaction between the RE ions with an average value of θ corresponding to weak AFM interactions. At $T = 2$ K, for GaN:Tb, a pronounced anisotropy with the easy axis perpendicular to the film plane was observed. At this temperature, the magnetization curve points to the lowest quasi-doublet state of the non-Kramers Tb^{3+} ion.

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