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Metastable magnetism and memory effects in dilute magnetic semiconductors

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Abstract
Detailed magnetic measurements on the dilute magnetic semiconductors (DMS) Cr:InN and Gd:GaN are carried out. These two materials have previously been reported to exhibit room temperature magnetic order. We show that the existence of magnetic hysteresis cannot be taken as proof for conventional ferromagnetism. Instead, we find an unparalleled metastable magnetic behavior together with memory effects in both materials, suggesting that for most DMS metastability plays a crucial role in accounting for the magnetic order even at elevated temperatures up to 400 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The search for ferromagnetism in dilute magnetic semiconductors (DMS) at room temperature is motivated by potential spintronics devices where the spin degree of freedom is used in a semiconductor-based device to augment its performance. For some DMS materials, such as p-type Mn:GaAs, ferromagnetic order is restricted to temperatures below 200 K [1]. To date, room temperature magnetic order is mostly claimed in n-type or highly resistive (non-p-type) DMS such as Mn:GaN [2] and Co:ZnO [3]. These claims are primarily based on hysteresis measurements using a superconducting quantum interference device (SQUID) magnetometer and the findings of different groups are sometimes contradictory and remain controversial. For example, in Mn:GaN intrinsic ferromagnetism was recently identified by combined SQUID and x-ray absorption measurements but only at very low temperatures [4]. Also from a theoretical viewpoint the origin of the long range magnetic order, especially in n-type DMS materials, is still unclear. Most models proposed are phenomenological, e.g. [3, 5]. The concept of spinodal decomposition leading to dopant-rich and dopant-deficient regions with different electric and magnetic properties was recently used to explain the observed magnetic behavior [6]; however, without offering a mechanism for the dopant-rich regions to interact. Indeed, clustering in a precipitate-free Mn:Ge DMS leads to superparamagnetism [7]. Thus, the existence of intrinsic ferromagnetism in most DMSs at room temperature is still under debate. Nevertheless, a more rigorous understanding would be useful for both practical applications and a fundamental understanding of long range interactions in magnetically doped semiconductor materials.

Here we will focus on two different, previously well-characterized DMS materials. Long range magnetic order at and above room temperature has been demonstrated in Gd:GaN with colossal effective magnetic moments [5] and in Cr:InN with moderate magnetic moments [9]. The potential materials for eventual phase segregation are limited to CrN ($T_N = 273$ K), Cr ($T_N = 313$ K), GdN ($T_C \sim 60$ K), and Gd ($T_C = 293$ K) which makes them unlikely candidates to explain magnetic order well-above room temperature, unless one assumes that an altered crystallographic structure leads to a shift in the magnetic order temperature. In the case of CrN, which shows a slight orthorhombic distortion at the Néel temperature [10], such an assumption is reasonable; however a shift of more than 100 K seems to be unlikely. Both DMS are based on a nitride III–V semiconductor but they are distinct in many other respects: The band gap (about 0.7–0.9 eV for Cr:InN versus 3.6 eV for Gd:GaN), the carrier concentration (1.5×10^{20} cm^{-3} for Cr:InN and highly resistive for Gd:GaN), and the dopant concentration (a few % Cr in

InN versus only 10^{16} cm^{-3} Gd in GaN) are very different and the magnetic dopants belong to the 3d and 4f series, respectively. Thus they span a broad variety of non-p-type DMS materials. Here we will show that Gd:GaN exhibits comparable metastable properties like Cr:InN. Furthermore in both materials this metastability is accompanied by a magnetic memory effect which is different from spin glass behavior. Thus, our SQUID measurements exhibit experimental features not consistent with conventional ferromagnetism.

2. Experimental details

The samples under investigation are Cr:InN grown by plasma-assisted molecular beam epitaxy (MBE) on Al_2O_3(0001) substrates and Gd:GaN films grown by ammonia-assisted MBE on 6H-SiC(0001). All samples have been characterized in great detail using *in situ* reflection high energy electron diffraction (RHEED), Rutherford backscattering (RBS), x-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS), Hall and photoluminescence (PL) measurements, and SQUID magnetometry. Findings for Gd:GaN [5, 11] and Cr:InN [9, 12, 13] have been reported elsewhere. More recently we have demonstrated for Gd:GaN by means of x-ray linear dichroism, that the Gd predominantly occupies Ga substitutional sites [8]. 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 [8]. It was also shown that Cr:InN exhibits metastable magnetic properties which are inconsistent with common ferromagnetism [14].

The SQUID measurements were carried out using three different SQUID magnetometers (Quantum Design MPMS XL) and great care was taken to rule out artifacts from the SQUID measurements themselves and the sample mounting. The maximum external magnetic field was 5 and 7 T, respectively, and the measurement temperature ranged from 2 to 400 K. The measurement of the remanent magnetization is performed under nominally zero field, however, the superconducting coil of the magnetometer can have residual fields of ∼0.5–1.5 mT after applying high fields to saturate the sample. However, no artificial increase of the remanence can occur, since the residual field is parallel to the previously applied external field and, therefore, the diamagnetic contribution of the substrate can only cause an apparent reduction of the remanence. The investigation with respect to the spin-glass behavior was carried out in accordance with earlier investigations of CoFe nanodots [15]: the samples are demagnetized and cooled in zero field (zero field cooling, ZFC) with or without a waiting time of 3 h at a certain temperature. Subsequently, the magnetization is measured in a small external field of typically 10 mT while heating (field heated magnetization, FHM). Such stop-time experiments are expected to show a memory effect at the stop temperature if this is below the characteristic glass temperature of the system. The standard magnetic measurements like hysteresis loops as well as field cooled (FC) versus zero field cooled (ZFC) magnetization curves are published elsewhere for Gd:GaN [5] and Cr:InN [9].

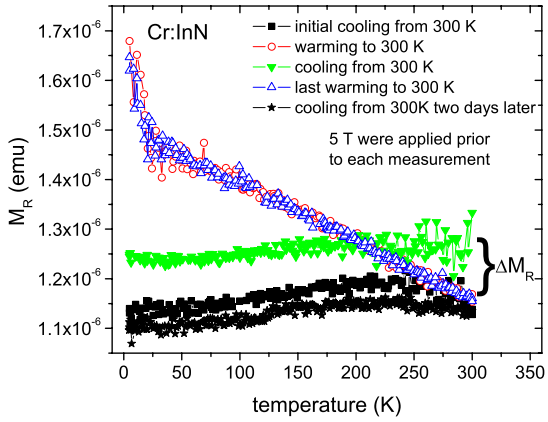

Figure 1. History dependence of the ΔM_R-effect. The remanence is measured as a function of temperature while cooling and warming after a field of 5 T has been applied. the ΔM_R-effect is absent for the initial cycle and after two days (and removal from the SQUID). It can only be observed if the sample has been exposed to low temperatures and high magnetic fields. In all cases the remanence is virtually constant while cooling down.

We have already reported the so-called ΔM_R-effect for Cr.InN samples [14]. To study the ΔM_R-effect the sample is first cooled down to 5 K. At this temperature, a field of 5 T is applied to magnetically saturate the sample. Then, the field is set to zero again followed by the measurement of the remanence while warming up the sample to an elevated temperature, e.g., 300 K. In the next step, the sample is saturated at 300 K in a field of 5 T again, the field is switched off and the remanence is now measured while cooling the sample down to 5 K. During such a cycle two atypical observations can be made: (i) the remanence does not increase with decreasing temperature but stays constant or even decreases slightly. (ii) The remanence after applying the external field is increased compared to the last value measured at the end of the warm-up. It has already been shown that for Cr:InN the ΔM_R-effect is restricted to temperatures above 200 K and persists up to 400 K, the highest attainable temperature for the SQUID magnetometer. Furthermore the ΔM_R-effect saturates at magnetic fields around 1–2 T [14].

3. Metastable magnetic properties and memory effects

Figure 1 shows the results of the same type of measurement-protocol which was used before to demonstrate the metastable magnetic properties of Cr:InN and the existence of the so-called ΔM_R-effect [14]. In addition to the previous experiment, figure 1 includes the initial cooling curve, i.e. the sample was put in the SQUID and saturated in 5 T without recording any hysteresis loop at 5 K, as was done before. The remanence measured while cooling stays almost constant with temperature with a weak and broad maximum resembling a blocking-like behavior (full squares). Subsequently a standard ΔM_R-cycle is performed (open circles and full triangles). It is obvious, that after the warm-up the remanence at 300 K equals the value at the beginning of the first cool down. In other

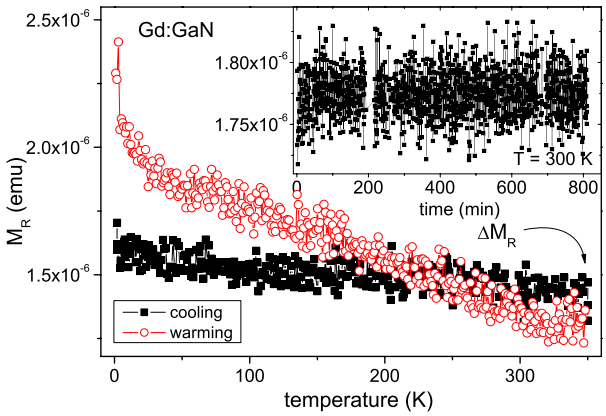

Figure 2. ΔM_R-effect at 350 K in GaN doped with 2×10^{19} cm^{-3} Gd atoms resulting from a saturating field of 3 T. The inset shows that the increased remanence is stable up to at least 800 min at 300 K.

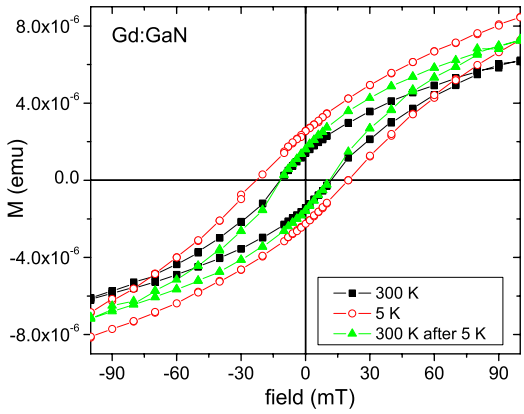

Figure 3. Magnetic hysteresis between ±5 T of GaN doped with 2×10^{19} cm^{-3} Gd atoms recorded subsequently at 300, 5 and 300 K again. The second hysteresis at 300 K exhibits clearly increased magnetization values whereas the coercive field remains unchanged (data only shown between ±100 mT).

words, the ΔM_R-effect is initially not present. On the contrary, during the second cooling all measured remanence values are systematically higher than initially and one can clearly see the ΔM_R-effect. On the other hand, the second warm-up leads to the same remanence as the first one. Note that all the data were taken during one single sequence without opening the SQUID, removing the sample or any kind of re-centering etc. Furthermore, exactly the same result could be found in another SQUID machine. We also took out the sample for about two days and re-measured the initial cool-down sequence after saturating the sample in 5 T (full stars); apart from a small off-set (presumably due to the slightly altered centering of the sample), we could reproduce the first measurement. Afterward, the well-known ΔM_R-cycles can be taken again. These measurements suggest that the ΔM_R-effect is only present after the sample has been at low temperatures (5 K) and high fields (5 T). In other words, the sample 'memorizes' that is has been at low temperatures and high fields and changes its magnetic behavior at 300 K depending on the sample history.

Comparable observations can be made in Gd:GaN samples. Figure 2 shows the ΔM_R-effect at 350 K and 3 T for a Gd:GaN sample with a Gd concentration of about 2×10^{19} cm^{-3}. The field dependence of ΔM_R at 300 K was also studied as the saturation occurs at a slightly lower field of about 1 T (not shown). The remanence is also metastable, i.e., it stays nearly constant during cooling and can be re-established at a lower temperature by applying a magnetic field. For this sample, we also show the time stability of the remanence after the ΔM_R-effect has been observed at 300 K. For these measurements the sample was exposed to 3 T at 300 K and then the magnetization was measured at nominally zero external magnetic field. The inset in figure 2 reveals that the remanence stays constant for at least 800 min. Although the remanence is increased after applying 3 T at 300 K, it stays constant on a timescale of a least 10 h after the field is switched off. Thus, a potential characteristic temperature for the magnetic system must be much higher than 300 K. For Cr:InN the time stability of the remanence has been corroborated up to 400 K but only for 2 h [14].

Figure 3 shows another remarkable consequence of the metastable magnetic properties of DMS systems. Here, a hysteresis loop between +5 and −5 T has been recorded at 300 K (squares) on the same Gd:GaN sample as shown in figure 2. Then the same hysteresis loop was recorded at 5 K (open circles). Both remanence and coercive field are clearly increased as is known from previous studies [5]. Then the hysteresis was re-measured at 300 K (triangles). Compared to the initial hysteresis at 300 K the remanence increased from 1.4×10^{-6} to 1.6×10^{-6} emu (not visible in the figure), i.e. by about 10%, which is of the same order as the ΔM_R-effect. Also all other $M(H)$-values are clearly increased compared to the first hysteresis measurement at 300 K. Obviously, the hysteresis at 300 K changes due to the preceding measurement at 5 K, although during both measurements the same field of 5 T was applied. Note, that the coercive field at 300 K remains unaffected. This behavior suggests that a fraction of the room temperature magnetic signal can only be magnetically activated at low temperatures by 5 T, or, in other words, Gd:GaN also remembers that it is has been at low temperatures and high magnetic fields.

Our measurements show, that the magnetic properties of Cr:InN and Gd:GaN are substantially different from conventional ferromagnets. We have already argued for Cr:InN that magnetic domain formation cannot be used to explain the ΔM_R-effect [14], therefore, the history dependence of this effect cannot be explained by such an assumption either. Since DMS materials are magnetically disordered systems, magnetic frustration could be taken into account; however, typical temperatures of frustrated systems are usually much lower, compared to the temperature regimes of the effects shown here. This is especially true for spin glasses. Nevertheless, we tried to find experimental evidence for spin glass behavior and performed stop-time experiments as summarized in figure 4. Two FHM measurements were recorded at 10 mT, one after ZFC and one after ZFC with a stop time of 3 h each at 150, 200 and 250 K for Gd:GaN and at 250 and 350 K for Cr:InN. Figure 4 shows the two 250 K cycles for Cr:InN (squares) and

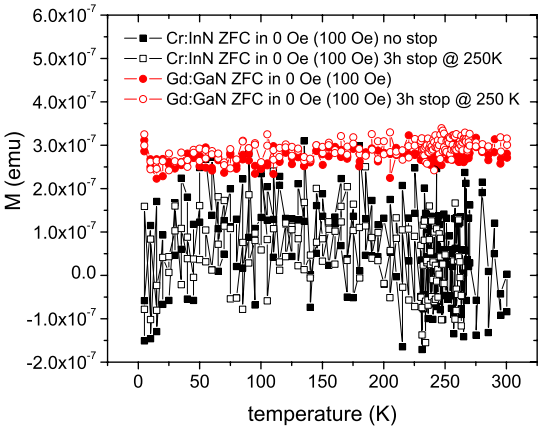

Figure 4. Stop-time experiments for Cr:InN and Gd:GaN. Even at 250 K and 3 h of waiting time, no effect is visible. All measurements were done at 10 mT and while warming the sample.

Gd:GaN (circles), respectively. The data were not corrected for the diamagnetic background of the substrate at 10 mT to illustrate that for Cr:InN the overall signal is much closer to the detection limit of the SQUID and thus the noise level is considerably increased. We were not able to detect any significant difference between the sequence with and without stop time for both compounds, which would be indicative of spin glass behavior [15]. However, such experiments should exhibit the strongest stop-time-effects at temperatures close to the characteristic temperature of the respective magnetic system [15], i.e. close to the temperatures where FC and ZFC curves merge, but for our samples it was shown that the FC and ZFC curves remain separate up to at least 400 K. This could indicate that the chosen waiting time of 3 h is too short for a sizable stop-time-effect. On the other hand, the ΔM_R-effect is observed between 200 and 400 K after a field has been applied for less than a minute [14]. Therefore, a stop-time-effect has to be present under the chosen experimental parameters in figure 4 if glass-like behavior accounts for the observed memory effect, which is obviously not the case.

4. Discussion

The underlying mechanism of the observed metastability and the magnetic memory effect does not fit into conventional schemes in a straightforward way and needs further investigation. Possible explanations may be found in the group of colossal magnetoresistance or even multiferroic materials, where orbital ordering plays a crucial role. One should consider that wurtzite GaN and InN are polar materials and piezoelectric. Along that line, it is noteworthy, that it was recently shown that cubic Gd:GaN does not show any long range magnetic ordering [16]. Based on our experiments we can rule out that the memory effect originates from a spin-glass-like behavior. Superparamagnetism can also be excluded, since the magnetic moments of the dopant atoms are too small (cf [8, 12]) to account for blocking at and above room temperature. For the case of Gd:GaN it is tempting to use the published effective magnetic moment of up to 4000 μ_B/Gd atom [5] to explain blocking at elevated temperatures; however, since this effective moment drops with increasing Gd concentration towards the Gd atomic value of 8 μ_B, such an assumption would suggest a decreasing blocking temperature with increasing doping, but the opposite behavior is experimentally observed: the characteristic temperature increases with increasing Gd doping. Another scenario which could account for the metastability and the memory effect of Gd:GaN samples is the fact, that different magnetic phases can exist in Gd:GaN samples [17]. Since the ΔM_R-effect exists around 30 K, it has to be related to the high temperature phase, which was taken as intrinsic ferromagnetism in the previous work [17]. The other phases lose their respective magnetic order below 100 K and cannot be considered for the magnetic behavior around 300 K.

As discussed elsewhere, the ΔM_R-effect could be understood by assuming phase segregated, magnetically uncompensated antiferromagnetic inclusions, which could go to a scissored state upon applying a magnetic field [14]. It has already been pointed out that this model cannot account for strong magnetic interactions between phase segregated regions. This could be overcome by assuming that the intrinsic magnetization direction of the antiferromagnetic compound is fixed by the crystallographic orientation of the material in the host lattice. Nevertheless, the memory effect cannot be accounted for by any of the above discussed models. The fact that a magnetic contribution can only be 'activated' at low temperature in a high magnetic field but not at room temperature in a high magnetic field, is in contradiction with all existing models of (ferro-)magnetism, where the material usually becomes magnetically softer with increasing temperature.

Since the magnetic order in DMS materials is claimed to be carrier mediated, the observed behavior shall be discussed in that respect as well. The InN films are highly n-type, however, the mobility of the electrons is low [9]. Note, that the series of necessary GaN and InN buffer layers makes it difficult to measure the carrier concentration and mobility of the Cr:InN layer separately. On the other hand the Gd:GaN samples are highly resistive, but they contain about 10^{18} oxygen atoms per cm^3 (revealed by SIMS) leading to the well-known neutral-donor-bond exciton PL [5, 11]. Thus it is reasonable to assume, that trapped carriers, most likely electrons, exist in both materials. Low temperatures could cause the carriers to be more confined or trapped, presumably close to some defects, i.e. also in the vicinity of the magnetic dopant. This could explain why they are magnetically polarizable only at low temperatures. We suggest studying comparable DMS materials with respect to metastable magnetic properties and at the same time illuminating the sample to generate photo-carriers. One can speculate that the ΔM_R-effect and the 'memory effect' vanish upon irradiation, which would be a strong indication for carrier mediated ferromagnetism in these samples. Note, that the initial remanence curve for Cr:InN as shown in figure 1 or the initial hysteresis at 300 K for Gd:GaN as shown in figure 3 were always recorded after the sample had been removed from the SQUID, i.e. exposed to ambient light. To test this hypothesis, the SQUID magnetometer would have

to be modified to illuminate the sample during measurement, which goes beyond the scope of the present paper; however, such experiments could be very useful in understanding the unusual magnetic behavior of such DMS materials in terms of carrier mediated long range magnetic order.

5. Conclusion

In summary, our experiments exclude a variety of known mechanisms to account for long range magnetic order in Cr:InN and Gd:GaN. Instead, these DMS materials exhibit a new kind of metastable magnetic behavior together with a 'memory effect' whose origin is still unclear. We can rule out common ferromagnetism, superparamagnetism or spin-glass-behavior as possible explanations for the observed effect by means of our SQUID measurements. Instead we suggest systematically investigating the role of potentially trapped carriers, e.g., by illuminating the sample during magnetometric studies. Magnetically polarized trapped carriers may account for the observed memory effect in a more straightforward way than common models for ferromagnetism can do. Nevertheless, the exceptional temperature and time stability of the magnetic properties are potentially useful and their origin needs further investigations.

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