Near-zero-moment ferromagnetism in the semiconductor SmN

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(Received 16 October 2008; published 6 November 2008)

The magnetic behavior of SmN has been investigated in stoichiometric polycrystalline films. All samples show ferromagnetic order with Curie temperature (T_C) of 27 ± 3 K, evidenced by the occurrence of hysteresis below T_C. The ferromagnetic state is characterized by a very small moment and a large coercive field, exceeding even the maximum applied field of 6 T below about 15 K. The residual magnetization at 2 K, measured after cooling in the maximum field, is $0.035\mu_B$ per Sm. Such a remarkably small moment results from a near cancellation of the spin and orbital contributions for Sm^{+3} in SmN. Coupling to an applied field is therefore weak, explaining the huge coercive field. The susceptibility in the paramagnetic phase shows temperature-independent Van Vleck and Curie-Weiss contributions. The Van Vleck contribution is in quantitative agreement with the field-induced admixture of the $J=\frac{7}{2}$ excited state and the $\frac{5}{2}$ ground state. The Curie-Weiss contribution returns a Curie temperature that agrees with the onset of ferromagnetic hysteresis, and a conventional paramagnetic moment with an effective moment of $0.4\mu_B$ per Sm ion, in agreement with expectations for the crystal-field modified effective moment on the Sm^{+3} ions.

DOI: 10.1103/PhysRevB.78.174406 PACS number(s): 75.50.Pp, 75.30.Cr, 74.70.Ad

I. INTRODUCTION

The rare-earth nitrides (RN) (R=rare-earth atom) have gained attention recently as simple (NaCl) structures for which the influence of strong correlations on the electronic band structures can be treated with some confidence.[1] In parallel with theoretical advances, there has developed an experimental interest in the growth and passivation of thin films.[2,3] This interplay of theory and experiment has revealed a number of interesting properties of both fundamental and technological importance. First the ambient-temperature paramagnetic phase has a narrow indirect gap that varies systematically across the series. Second in the ferromagnetic state (which may be the ground state for them all), they are predicted to have spin-polarized carriers, opening the potential to doped spintronic structures. Early data on these compounds were plagued by a lack of stoichiometric reproducibility and a rapid degradation of the RN under atmosphere.[4,5] The magnetic properties in particular are very sensitive to nitrogen vacancies and oxygen impurities, which are difficult to control in these materials. Even the exchange interactions between the rare-earth $4f$ spins are not well understood although a number of theoretical models have been proposed.[6] The exchange is usually described to operate within two competitive channels of superexchange via the nitrogen atom. The nearest-neighbor (nn) interaction is configured at 90° and is believed to be ferromagnetic. It strongly depends on the carrier concentration and becomes dominant when Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect interactions take place via the polarization of conduction electrons. The next-nearest-neighbor (nnn) interaction is configured at 180°, is antiferromagnetic, and in principle is dominant for nonmetals. Note that the existence of a ferromagnetic order in semiconducting rare-earth nitrides implies that a ferromagnetic interaction dominates even in the absence of free carriers.[6]

The most thoroughly studied of these compounds is GdN, which has a half-filled $4f$ shell with the maximum $\frac{7}{2}$ net spin and zero net orbital angular momentum. It is ferromagnetic below 70 K, with a saturation moment of $7\mu_B$ and is an indirect-gap semiconductor with an optical gap of 1.3 eV in the paramagnetic phase, reduced to 0.9 eV below the Curie temperature.[7] For the lighter rare earths, Hund's rules specify that L is antiparallel to S in the ground state. Within that scenario SmN is of special interest; Sm^{+3}, with two electrons below half filling, has $S=\frac{5}{2}$, $L=5$, and a net magnetic moment given by $M \approx (L_z+2S_z)\mu_B \ll \mu_B$. There is thus the potential for Sm compounds to condense into a ferromagnetic phase in which the spins are ferromagnetically ordered but with their spin moment nearly canceled by an opposing orbital moment. Moments substantially smaller than the free-ion moment of $0.71\mu_B$ are not unknown in ferromagnetic Sm compounds[8–13] but its occurrence in a semiconductor has to our knowledge not been reported previously. Such a material offers special advantages for spintronics: (i) it can inject spin-polarized electrons into a conventional semiconductor without the deleterious effects of a fringe magnetic field,[14] and (ii) in principle it can form field-free, fully spin-polarized electronically active structures.

Early magnetic measurements suggested that SmN was antiferromagnetic below 20 K (Refs. 4 and 5) but this was not confirmed by neutron diffraction,[15] suggesting that it might indeed be ferromagnetic but with near cancellation between the spin and orbital moments. More recently we reported clear ferromagnetism in GdN (Refs. 3 and 7) and DyN (Ref. 16) but somewhat weaker ferromagnetic evidence

in SmN.[16] The resistivities of the films show them all to be semiconductors with the expected anomaly at T_C signaling a narrowed gap in the ferromagnetic state. In the present work we report magnetic experiments performed on thicker SmN films, seeking to resolve the uncertainties concerning the magnetic state of this unusual material, and a clear picture of near-zero moment ferromagnetism emerges.

II. EXPERIMENTAL DETAILS

SmN films were grown in a vacuum chamber pumped to a base pressure in the 10^{-9} mbar range. Sm metal was evaporated in the presence of an atmosphere of pure N_2 gas at a pressure of 10^{-4} mbar; the growth conditions, the structure, and the stoichiometry have been reported previously.[3,7] For the present measurements, the films were deposited on Si substrates covered by their natural oxide. X-ray diffraction exhibits the Bragg peaks of only the rock salt cubic structure and establishes the films as untextured polycrystalline with an average crystal grain size of 10 nm. The lattice parameter (5.07 Å) is consistent with the previous data for the rare-earth nitride series, confirming that samarium is trivalent. All *ex situ* measurements are performed on films protected by a cap layer of nanocrystalline GaN. Conductivity and x-ray spectroscopies on the films have established them to be semiconductors in both the ambient-temperature state and to 4 K in the magnetically ordered low-temperature state.[16]

Three films of differing thicknesses (300–400 nm) were used for magnetic measurements reported here. These magnetic properties were investigated with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) working up to a maximum applied field of 6 T. All experiments were performed with the magnetic field applied parallel to the film plane. The films were prepared in parallel on both thick (400 μm) and thin (100 μm) Si substrates in order to apply more reliable corrections for substrate signals, which are of the same order of magnitude as the SmN signal. Si is diamagnetic and the susceptibility is supposed to be temperature independent. The susceptibility measured on the uncovered Si substrates is in agreement with the theoretical susceptibility $\chi(\mathrm{Si})=-3.4\times10^{-6}$ at room temperature within a 5% error. This Si signal is characterized well enough to permit a trouble-free correction in the data shown below.

The magnetic signal from the capping layer is somewhat more problematic. GaN is weakly paramagnetic mainly because self-doping is provided by N vacancies, for which we collected reference data from a measurement on a Si substrate covered with a GaN layer of the same thickness. In a phenomenological approach, we have fit the temperature variation in the magnetization using a theoretical calculation by Sonder and Schweinler,[17] predicting a modified Curie law for the susceptibility of interacting donor centers in doped semiconductors: $\chi=\frac{C}{T^{(1-\alpha)}}$. In this model the parameter α is proportional to the donor concentration n_d. We find $C=4.05\times10^{-3}$ and $\alpha=0.86$ but uncertainty about the donor concentration prevents further analysis. We note that this approach has been used to explain the susceptibility of a zinc-blende GaN thin film.[18] The authors derive $\alpha\simeq0.8$ for which they estimate $n_d=2\times10^{17}$ cm^{-3}, in agreement with the experimental value attributed to nitrogen vacancies.

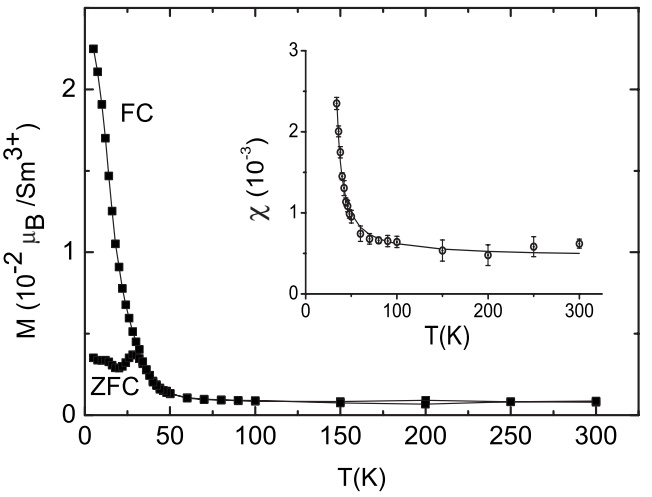

FIG. 1. Temperature dependence of the magnetization of SmN after cooling without (ZFC) and with (FC) an applied field of 0.5 T (sample I). The inset shows the result of the fit of the FC susceptibility ($\chi=M/H$) in a Van Vleck approach.

However, the susceptibility of GaN is very sensitive to N vacancy concentration.[18] There is some variation in the susceptibility of the GaN capping layers associated with minor differences in stoichiometry resulting from the ion-assisted deposition process. Nevertheless we are able to subtract the capping layer signal to reasonable accuracy, so the evidence of the remarkable magnetic behavior of SmN is not strongly affected by this uncertainty. Below we present the data both uncorrected and after correction for the substrate/capping layer signals.

III. RESULTS

Figure 1 shows the temperature variation in the magnetization of sample I in an applied field of 0.5 T, after cooling in zero field [zero field cooled (ZFC)] or in 0.5 T [field cooled (FC)]. The curves are superimposed down to 30 K, below which a sharp increase in the FC curve denotes ferromagnetic order with a spontaneous magnetic moment. The same behavior has been confirmed in an applied field as low as 5 mT. In the ZFC curve the increase in the magnetization below 20 K is assigned to the GaN cap layer. The transition temperature estimated from the maximum of the ZFC curve is found at $T_C=30\pm2$ K. The other two films gave Curie temperatures of 24 ± 2 and 26 ± 2 K. We have not been able to relate these small differences to the films' compositions or structures so we quote $T_C=27\pm3$ K. Note in this regard that it is known that N vacancies lower the Curie temperature in GdN.[19] Our films are close to stoichiometric but absolute measurements of the composition have an accuracy of about 5%. It is notable that earlier heat capacity[20] and magnetization[21] measurements suggested Curie temperatures in the 15–20 K range; they were likely performed on N deficient samples.

A. Ferromagnetic state

Above T_C the magnetization M is linear in field B with a paramagnetic susceptibility that includes both Curie-Weiss

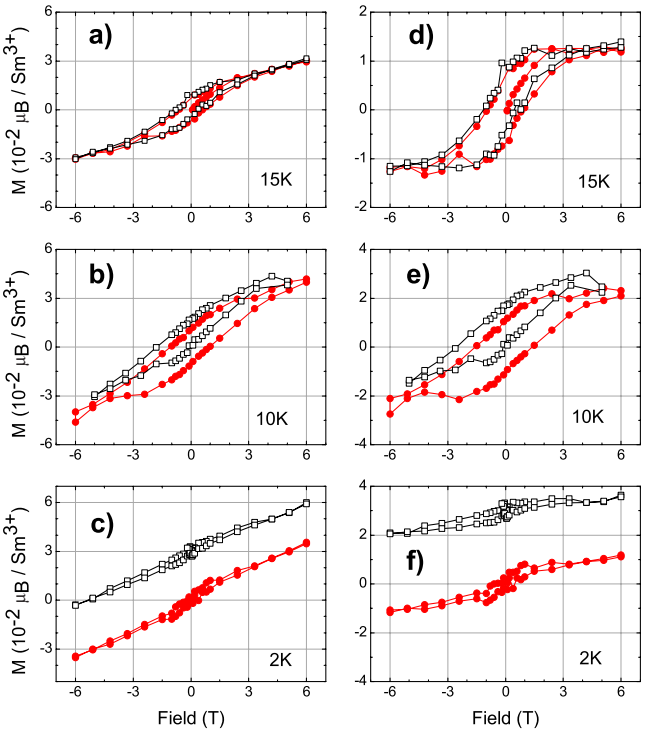

FIG. 2. (Color online) Magnetization loops of SmN (sample II) after cooling the film in zero-field (red full circles) and after cooling under 6 T (open black squares). Left: correction for the Si substrate only at (a) 15, (b) 10, and (c) 2 K. Right: additional correction for the paramagnetic signal of the GaN cap layer according to the curve shown in Fig. 3 at (d) 15, (e) 10, and (f) 2 K.

and temperature-independent Van Vleck contributions, as will be discussed in the following section. At T_C $M(B)$ becomes nonlinear, and a hysteresis loop develops. The evolution of the loop as the temperature is lowered is shown in Fig. 2. Here the left side [Figs. 2(a)–2(c)] represents the loops uncorrected for GaN while in the right side [Figs. 2(d)–2(f)] the correction is included. We first focus on the loops measured after cooling the films in zero field (red full dots). At 15 K [Fig. 2(a)] the saturation is achieved at 3 T. Beyond the irreversibility point, the magnetization is linear in field due to the paramagnetic contribution of GaN. After correction for GaN the loop exhibits a coercive field of 0.9 T [Fig. 2(d)]. At 10 K [Fig. 2(b)] the reversible part at high field is missing; the closing field lies above the 6 T maximum available. This behavior is exactly as expected when the maximum applied field is insufficient to achieve the reversal of the moments so that only minor loops are measured, signaling a magnetocrystalline anisotropy that grows at lower temperature.[22] At 5 K the loop shows only a very small opening and at 2 K [Fig. 2(c)] the hysteresis has completely disappeared so that only the GaN paramagnetic contribution is seen in the ZFC data. Clearly the magnetic field necessary to even initiate the reversal of ferromagnetic domains is higher than 6 T at these temperatures, and the magnetization process is dominated by the reversible paramagnetic contribution. Hysteretic behavior can nonetheless be confirmed at these temperatures by cooling in the presence of the maximum field of 6 T to prepare the film in a magnetized state. Thus Fig. 2 compares the hysteresis patterns obtained at 15, 10, and 2 K after zero-field cooling (red full dots) and after cooling in 6 T (black open squares). The loops are superimposed at 15 K [Figs. 2(a) and 2(d)] but at the lower temperatures the patterns are shifted from one another [Figs. 2(b) and 2(e) and Figs. 2(c) and 2(f)]. Exactly the same behavior is observed when cooling the system under −6 T although with the shifts found in the opposite sense. The results confirm that the coercive and saturation fields are larger than 6 T at these temperatures.

In addition a very small spontaneous moment is observed on the saturated loops; the temperature dependence of the magnetic moment down to 0 K is interesting to evaluate. At 15 K, $M_S=0.012\mu_B/\mathrm{Sm}$, compared to $0.008\mu_B/\mathrm{Sm}$ at remanence when the field is reduced to zero. The difference is due in part to single-domain crystallites relaxing to an easy-axis magnetization in the remanent state, leaving the moments distributed in a cone about the field direction. The easy axis in SmN is as yet unknown but if it lies along one of the high-symmetry directions ⟨100⟩, ⟨110⟩, or ⟨111⟩, the field-parallel component of the moment is reduced by about 15%, explaining about one half of the measured reduction from the saturation to the remanence. We conclude that the remnant moment provides a reasonable lower limit for the single-domain spontaneous magnetization. To refine the estimate we have performed experiments in which the material is prepared in the magnetized state by cooling in 6 T, followed by measurements of the magnetization in a small field of 20 mT. The resulting remnant magnetization drops to zero at the Curie temperature from a zero-temperature magnetization of $(0.030\pm0.006)\mu_B/\mathrm{Sm}$ averaged over the three films. Assuming that this value represents somewhat less than 85% of the spontaneous moment, we quote that moment as $(0.035\pm0.010)\mu_B/\mathrm{Sm}$ at the lowest temperature. Such a small moment explains the null result in the early neutron search for ferromagnetic order,[15] and is in agreement with the near cancellation of spin and orbital moments suggested by Larson *et al.*[1] The saturation field is large, rising above our 6 T maximum available field below 15 K. It is important in this regard to note that the ferromagnetic state, with its very small moment, couples relatively weakly with the magnetic field.

B. Paramagnetic state

Remarkably, the small moment found in the ferromagnetic phase is not carried across the transition; rather the paramagnetic behavior of SmN can be fully understood within the established description of Sm in the crystalline environment. We start by recalling that the ground-state configuration of the Sm^{3+} free ion is ${}^6H_{5/2}$ with $L=5$, $S=\frac{5}{2}$, and $J=\frac{5}{2}$. The Landé factor is $g_J=\frac{2}{7}$ and the magnetic moment is $\mu=0.71\mu_B$. The first-excited multiplet $J=\frac{7}{2}$ is not thermally populated but a paramagnetic moment will partly arise from an admixture of the multiplets induced by the applied magnetic field. As usually observed in trivalent Sm compounds, the reciprocal susceptibility is therefore not linear in temperature, preventing a Curie-Weiss-like analysis.

With the inclusion of the $J=\frac{7}{2}$ admixture in the $\frac{5}{2}$ ground state, the paramagnetic susceptibility of Sm^{3+} compounds is

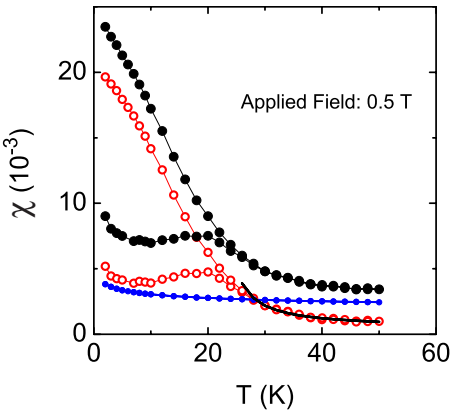

FIG. 3. (Color online) Susceptibility ($\chi=M/H$) versus temperature (sample II), before (full black circles) and after (open red circles) the correction for the GaN cap layer. The GaN signal used for the correction is shown in small blue dots. The full black line is the Van Vleck fit of the susceptibility to the fully corrected data, setting the multiplet separation $\Delta E=1500$ K.

reasonably well described by the Van Vleck approach, with[23]

$$\chi = \chi_0 + \frac{C}{T-\Theta_p}. \tag{1}$$

The second term is the conventional Curie-Weiss susceptibility involving the effective magnetic moment μ_{eff} for $J=\frac{5}{2}$, with $C=\mu_0 N\mu_{\text{eff}}^2/3k_B$, where N is the Sm ion density. The Van Vleck term χ_0 depends on the energy difference $\Delta E \simeq 1500$ K between the two lowest $J(\frac{5}{2},\frac{7}{2})$ multiplets:[8,23]

$$\chi_0 = \frac{\mu_0 N\mu_B^2}{k_B}\frac{20}{7\Delta E}. \tag{2}$$

We have used Eq. (1) to fit the measured paramagnetic susceptibility curves above T_C, as shown in the inset of Fig. 1, for the magnetization curve obtained under 0.5 T. It can be seen that the free-ion Van Vleck term, with no adjustable parameters, provides an excellent fit to the temperature-independent tail at high temperatures. The diverging contribution below 100 K yields a Curie temperature $\theta_P=28\pm1$ K, in excellent agreement with the value of 30 ± 2 K where this film showed a cusp in the ZFC magnetization curve. Similar agreement has been found also with the other two films, as can be seen in Fig. 3 for sample II. A sense of the relative strength of the contributions to the susceptibility can be obtained by comparing the Van Vleck term $\chi_{\text{VV}}\sim\frac{60}{7\Delta E}=5.7\times10^{-3}$ obtained from Eq. (2) to the Curie-Weiss term $\chi_{\text{CW}}\sim\mu_B^{-2}\mu_{\text{eff}}^2/(T-\Theta_p)$. For example, with $\mu_{\text{eff}}=0.845\mu_B$, at 300 K $\chi_{\text{CW}}=2.6\times10^{-3}$ and at 100 K $\chi_{\text{CW}}=9.9\times10^{-3}$.

The effective magnetic moment derived from the Curie constant C for the three films is $\mu_{\text{eff}}=(0.45\pm0.1)\mu_B$ per Sm ion, somewhat smaller than the free-ion effective paramagnetic moment of $g_J[J(J+1)]^{1/2}\mu_B=0.845\mu_B$ although still larger than the value of $0.035\mu_B$ in the ferromagnetic phase. The paramagnetic moment is understood by noting that the $J=\frac{5}{2}$ level is decomposed by the cubic octahedral crystal field into a doublet Γ_7 and a quartet Γ_8. Specific heat data[20] quoted in Ref. 15 report that the Γ_7 sublevel is the ground state with a separation of 225 K to the Γ_8 sublevel for the bonding configuration of SmN. We can therefore assume that at 30 K only the ground doublet is significantly populated and calculate an approximate value for the low-temperature susceptibility. The Γ_7 Kramers doublet[24] can be described with the equivalent wave functions $|\pm\frac{1}{2}\rangle$ for a fictitious spin $S'=\frac{1}{2}$, for which we have calculated a Landé factor, g', of $\frac{10}{21}$. We obtain $\mu_{\text{eff}}(\Gamma_7)=[g'^2\mu_B^2S'(S'+1)]^{1/2}=0.41\mu_B$, in good agreement with the experimental effective moment. It is important to note that these results establish quite clearly that the entire Sm population in the films participates in the paramagnetic Curie-Weiss signal diverging at T_C, emphasizing that the full population also participates in the ferromagnetic order.

IV. CONCLUSION

The present work gives strong evidence for a ferromagnetic state in SmN. The magnetic moment in the ferromagnetic phase is an order of magnitude smaller than in the paramagnetic state, confirming a nearly zero-moment ferromagnet below 27 K. The magnetic behavior in the paramagnetic phase is in quantitative agreement with the expected moments of Sm, showing the effects of both the excited spin-orbit state and the constraints imposed by the crystal field. The reduced ferromagnetic moment is established quite clearly by the experiments but remains a theoretical challenge. The near-zero moment ferromagnetic state in a semiconductor has clear potential for various fundamental studies and devices involving control of spin, and charge degrees of freedom without the perturbing effects of a fringe magnetic field. For device applications it would clearly be interesting to investigate the prospect of raising the Curie temperature of this material, either by alloying or strain. However, there is also considerable possibility that specific high technology spintronic devices that run at 77 K (and even He temperature) will be used in the future.

ACKNOWLEDGMENTS

The MacDiarmid Institute is supported by the New Zealand Centre of Research Excellence Fund, and the research reported here is supported by a grant from the New Zealand New Economy Research Fund. C.M. is grateful to the staff of the School of Chemical and Physical Sciences for their hospitality, and acknowledges the financial support of the MacDiarmid Institute and of the Royal Society of New Zealand.

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