J Mater Sci (2010) 45:2770–2774
DOI 10.1007/s10853-010-4265-2

Magnetic and transport properties of $Mn_{3+x}Ga_{1-x}N$ compounds

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Received: 24 June 2009 / Accepted: 26 January 2010 / Published online: 9 February 2010
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Abstract $Mn_{3+x}Ga_{1-x}N$ compounds with $x = 0.0$ and 0.1 were prepared by re-sintering $Mn_2N_{0.86}$, Ga bulk and Mn powders. These compounds are deduced to be the N-deficiency ones. In Mn_3GaN, a step-like magnetic transition, from frustrated antiferromagnetism to paramagnetism with increasing temperature, occurs at 370 K, while the same magnetic transition of $Mn_{3.1}Ga_{0.9}N$ is far above 380 K. The enhanced magnetization of Mn_3GaN at low temperatures is ascribed to the fast lowering of antiferromagnetism. The electrical resistivity of Mn_3GaN exhibits a typically metallic conducting behavior with a positive magnetoresistance of 4–7%.

Introduction

Ternary and complex transition-metal nitrides/carbides exhibit unique combinations of interesting and potentially useful magnetic, electrical, and other properties. In particular, much interest has been focused on the investigation of anti-perovskite nitrides as Mn_3CuN [1], Mn_3ZnN [2], $Mn_3(Cu_{1-x}Ge_x)N$ [3], or anti-perovskite carbides $Mn_{3+x}Sn_{1-x}C$ and $Mn_3Zn_xSn_{1-x}C$ [4], etc. Among these compounds, much attention has been paid to Mn_3GaN_δ ($0 < \delta \leq 1$) compounds. Samson et al. [5] reported the preparation of Mn_3GaN via the solid-state reaction of Mn and GaN with lattice parameter $a = 0.3898$ nm. Bouchaud et al. [6] found a large first-order transition from antiferromagnetic to ferromagnetic ordering at 298 K in Mn_3GaN, along with abrupt jumps in the temperature dependences of the magnetostriction and the resistivity. Besides, they also determined the lattice parameters as a function of atomic percentage of nitrogen. Fruchart et al. [7] found that Mn_3GaN exhibits a magnetic transition at 298 K, below which it shows antiferromagnetic ordering with a triangular antiferromagnetic configuration (Γ^{5g}). According to García et al. [8–10], a magnetic transition, from triangular antiferromagnetic to paramagnetic ordering, occurs at 278.5 K in Mn_3GaN. They also report the entropy and enthalpy changes (i.e., ΔS and ΔH), as well as the electronic specific heat γ, around the transition temperature. Moreover, a systematic analysis of the electronic band structure, for compounds of Mn_3XN- and Mn_3MC-type, has shown that a broad conduction band overlaps with a narrow one, which results from strong hybridization between the p states of the metalloid and d states of manganese [11]. Navarro et al. [12] investigated magnetic properties of $Mn_{4-x}Ga_xN$ solid solution, and found the coexistence of spin-glass-like and ferrimagnetic phases at low temperatures for $0.7 < x < 1$. Akoi et al. [13] report the preparation of a $Mn_{3.07}Ga_{0.93}N$ single crystal with Curie and Néel temperatures of 107 and 270 K, respectively. Recently, we have studied the structural, magnetic, and transport properties of $Mn_{3.1}Sn_{0.9}$ and $Mn_{3.1}Sn_{0.9}N$ [14, 15]. Glassy ferromagnetism was observed in the Ni_3Sn-type compound $Mn_{3.1}Sn_{0.9}$ [14]. The cubic anti-perovskite compound $Mn_{3.1}Sn_{0.9}N$ was prepared via nitrogenation of the hexagonal compound $Mn_{3.1}Sn_{0.9}$ [15]. For $Mn_{3.1}Sn_{0.9}N$, parasitic ferromagnetism was found to

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exist in the temperature range of 5–370 K, including a spin-reorientation at about 280 K [15].

In this work, the successful preparation of $Mn_{3+x}Ga_{1-x}N$ compounds with $x = 0$, 0.1, by solid-state reaction of $Mn_2N_{0.86}$, Ga bulk and Mn powder, is reported. The magnetic and transport properties of $Mn_{3+x}Ga_{1-x}N$ have been investigated and are discussed in detail.

Experimental details

The details of the preparation of $Mn_2N_{0.86}$ compound have been reported elsewhere [16]. The X-ray diffraction (XRD) pattern shows that the single-phase compound $Mn_2N_{0.86}$ has been prepared successfully [16]. Powders of Mn and $Mn_2N_{0.86}$ were mixed in appropriate proportion and pressed into pellets, which were placed horizontally into Al_2O_3 crucibles. Pieces of bulk Ga were located on top of the pellets. All this was sealed in an evacuated silica tube and sintered at 773 K for 3 days, and subsequently at 1,100 K for 4 days. After cooling, the obtained material was pulverized, mixed, pressed into pellets, and sintered again at 1,100 K for 7 days, in order to homogenize the samples perfectly.

XRD analysis of the powder samples was carried out using Cu $K\alpha$ radiation in a Rigaku D/max-γA rotating-target diffractometer equipped with a graphite crystal monochromator. The magnetic properties were investigated in a superconducting quantum-interference device (SQUID, Quantum Design). In the magnetic measurements, the compound was cooled in zero field from 295 to 5 K and a dc magnetic field was applied at 5 K. Then the compound was heated while measuring the magnetization at the constant field. A rectangular parallelepiped with dimensions of $1 \times 1 \times 8$ mm^3 cut from the sample was used for the measurement of transport properties. The temperature dependence of the electrical resistivity was measured by a standard four-probe method.

Results and discussion

Figure 1 shows the XRD patterns of as-prepared $Mn_{3+x}Ga_{1-x}N$ compounds. Obviously, a cubic anti-perovskite structure, i.e., Mn_3GaN or $Mn_3GaN_{0.5}$, can be indexed, in addition to a minor impurity phase MnO. According to the (311) reflection, the lattice parameters of the $Mn_{3+x}Ga_{1-x}N$ compounds with $x = 0$ and 0.1 are 0.38957 and 0.38846 nm, respectively. On the basis of the lattice parameters, as shown in Table 1 reported in Ref. [6], we find the nitrogen content of the compounds with $x = 0$ and 0.1 to approximately be 0.83 and 0.68, respectively. This means that both compounds are nitrogen deficient, which is basically

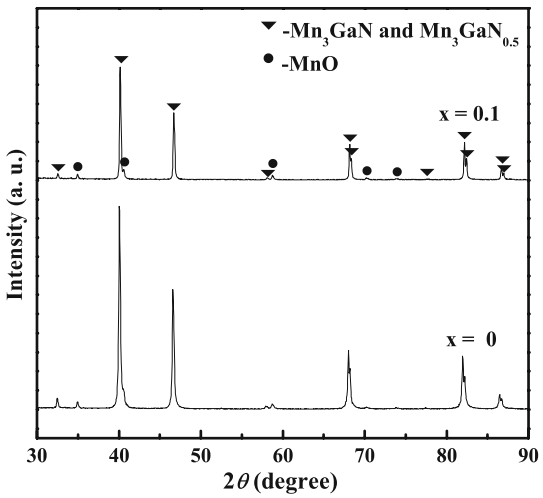

Fig. 1 X-ray diffraction patterns of $Mn_{3+x}Ga_{1-x}N$ ($x = 0$, 0.1) compounds

Table 1 Lattice parameters, a, and magnetic transition temperature, T_{t_1} and T_{t_2}, of Mn_3GaN_{1-x} compounds from different references

x	a (nm)	T_{t_1} (K)	T_{t_2} (K)
0	0.3898[a]	–[a]	–[a]
	0.3903[b]	298[b]	–[b]
	0.38886[c]	107[c]	270[c]
0.10	0.3902[b]	326[b]	–[b]
0.18	0.3897[b]	422[b]	–[b]
0.20	0.3895[b]	451[b]	–[b]
0.34	0.3883[b]	514[b]	–[b]
0.46	0.3871[b]	534[b]	–[b]

[a] Ref. [5]

[b] Ref. [6]

[c] Ref. [13]

correspondent with the XRD data. Furthermore, Bouchaud et al. [13] have reported the lattice parameters of Mn_3GaN [6] (see Table 1) and Mn_3GaC [17] to be $a = 0.38980$ and 0.38960 ± 0.00005 nm, respectively, while others report $a = 0.38886(9)$ nm for a single crystal of $Mn_{3.07}Ga_{0.93}N$ [13]. As can be seen in Table 1, the lattice parameters of the $Mn_{3+x}Ga_{1-x}N$ compounds determined in the present work are in reasonable agreement with the literature results.

Temperature dependences of magnetization of Mn_3GaN are plotted in Fig. 2, measured in a dc field of 10 mT and 0.2 T, respectively. In the field of 10 mT, with decreasing temperature, the magnetization first displays unchangeable characteristic from 380 K. From 375 K, it decreases abruptly, and then at onset of about 310 K it becomes large increasingly, with the occurrence of a cusp at 117 K. At lower temperatures, especially below 35 K, the

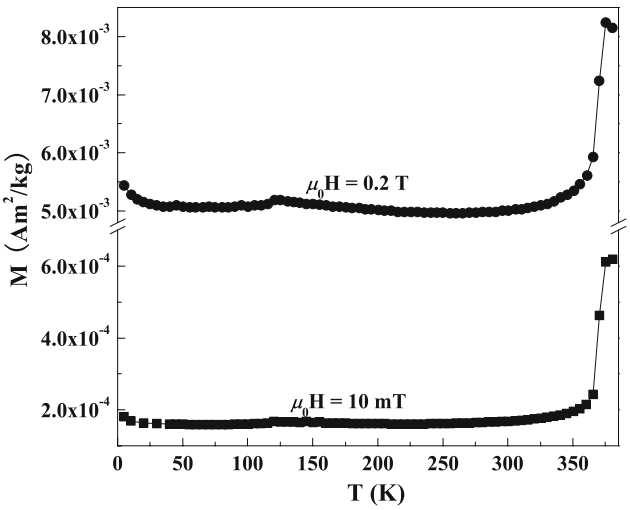

Fig. 2 Temperature dependences of the zero-field-cooled magnetization of Mn_3GaN in a dc magnetic field of 10 mT and 0.2 T, respectively

magnetization exhibits a fast increase again. The magnetization curve in the field of 0.2 T are almost the same as the one of 10 mT. It is particularly noted that the magnetization curves in different fields exhibit the same magnetization behavior. Figure 3 shows the magnetizations, as a function of temperatures, of $Mn_{3.1}Ga_{0.9}N$ compound in the filed of 10 mT and 0.2 T, respectively. Obviously, the curves display the similar behavior as that of Mn_3GaN compound, in addition to the shift of the abrupt jump toward the temperature beyond our measuring temperature range.

The iso-thermal magnetization curves and the hysteresis loop at 5 K of Mn_3GaN compound are shown in Figs. 4, 5,

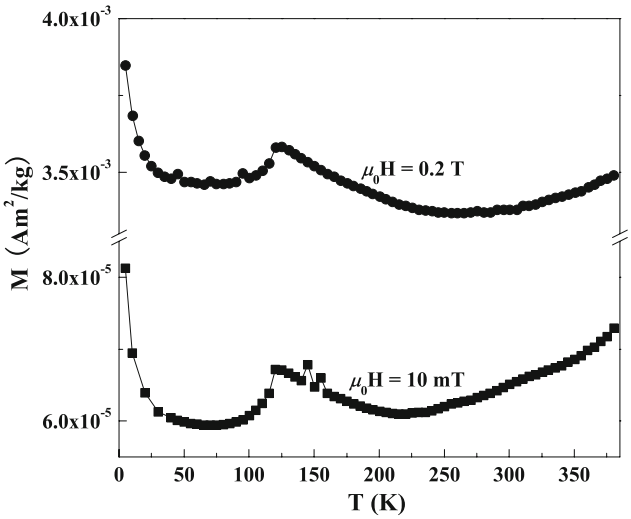

Fig. 3 Temperature dependences of the zero-field-cooled magnetization of $Mn_{3.1}Ga_{0.9}N$ in a dc magnetic field of 10 mT and 0.2 T, respectively

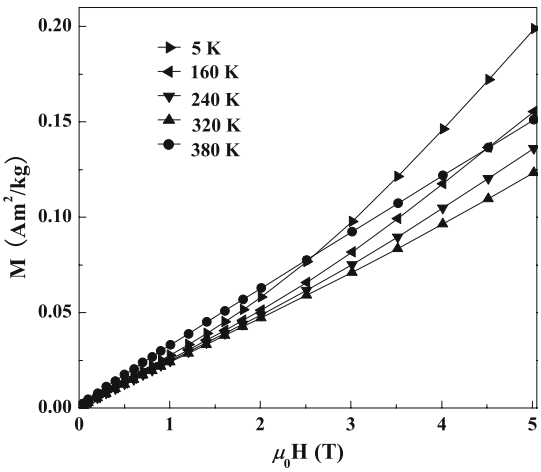

Fig. 4 Field dependences of magnetization at different temperatures for Mn_3GaN compound

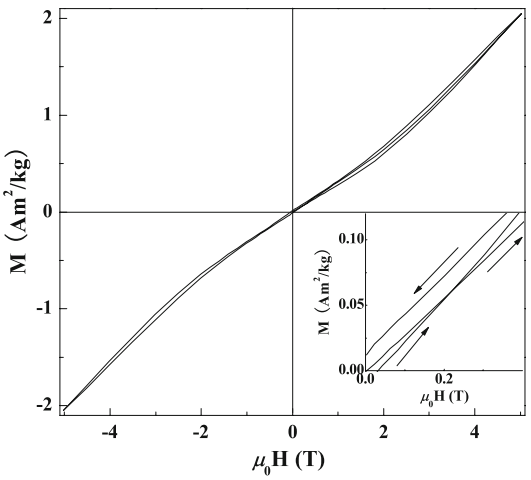

Fig. 5 Hysteresis loop, as well as the initial magnetization curve, for Mn_3GaN compound measured at 5 K. The inset shows the loop in a larger magnification for low field range

respectively. In Fig. 4, except for the magnetization curve at 380 K, all other curves display concave characteristics. Moreover, their curvature becomes continuously small as temperature increases. At 380 K, the iso-thermal magnetization gets almost linear with the largest magnetization below about 2.5 T. From Fig. 5, the shape of the hysteresis loop at 5 K in the first quadrant is concave, together with the almost linear dependence. The initial magnetization curve is outside of the loop with the coercivity of about 360 Oe.

In Mn_3GaN, Bouchaud et al. [6] reported an abrupt first-order magnetic transition from antiferromagnetic order above about 298 K to ferromagnetic order below this temperature. However, other authors [8, 9, 12, 13] have found a first-order transition from triangular antiferromagnetic to paramagnetic order at the temperature range

from 270 to 298 K. Moreover, Bouchaud et al. [6] also reported the magnetic transition temperatures as a function of the nitrogen content (see Table 1). Obviously, as nitrogen deficiency increases, the transition temperature becomes increasingly large. For the present Mn_3GaN, at about 370 K, a step-like jump indicates that the occurrence of magnetic transition. Combining this with Table 1, a rough estimate of nitrogen content gives its range from 0.82 to 0.90, which basically corresponds to the result from lattice parameter based on the XRD patterns. The cusp at 117 K on the temperature of magnetization of Mn_3GaN compound may be due to the Neél temperature (118 K) of MnO [18], which is present as an impurity, as shown in Fig. 1. This is coincident with the presence of a little MnO impurity reported by García et al. [8–10]. Furthermore, the magnetization of Mn_3GaN compound at low temperatures gets enhanced again. For single-crystalline $Mn_{3.07}Ga_{0.97}N$, an abrupt increase of the magnetization at lower temperatures is indicative of the occurrence of ferromagnetism [13]. According to the magnetic phase diagram (see Fig. 6) of $Mn_{4-x}Ga_xN$ [12], the enhancement of magnetization at low temperatures should be ascribed to the transition from AFM to FL, a phase in which spin-glass-like disorder coexists with ferrimagnetic order, supposed Ga content a little below 1.0. Nevertheless, the iso-thermal magnetization curve at 5 K, as shown in Fig. 4, seems to exhibit no any fundamentally difference from the ones at other temperatures, which is incompatible with the occurrence of ferro-/ferri-magnetism. The hysteresis loop at 5 K, as shown in Fig. 5, of the presently investigated Mn_3GaN compound, also exhibits the same behavior. Actually, at low temperatures, the phase diagram of $Mn_{4-x}Ga_xN$ [12] contains FL phase for $x = 0.7$–1.0. However, when

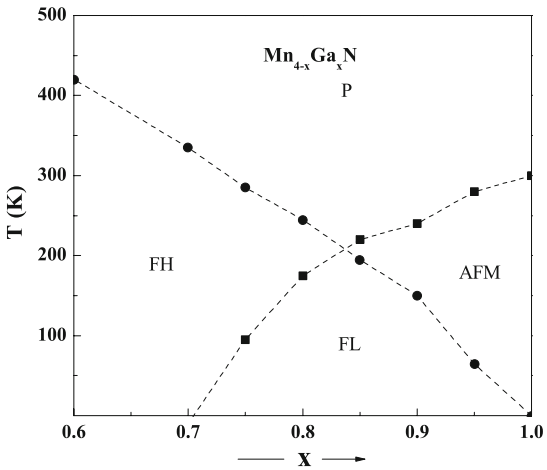

Fig. 6 Schematic phase diagram of the solid solution $Mn_{4-x}Ga_xN$ in the concentration range of $0.6 < x < 1.0$ cited from Ref. [12]. *FH* shows noncollinear ferromagnetic ordering, *FL* the co-existence of ferrimagnetic arrangement with some spin-glass-like disorder, *AFT* antiferromagnetic ordering, *P* paramagnetic disordering

$x = 1.0$, the report of Navarro et al. [12] reveal the purely linear curve of M vs. H down to 4.2 K, which indicates that the stoichiometric Mn_3GaN shows antiferromagnetism. On the other hand, FL phase for $Mn_{3.2}Ga_{0.8}N$ compound at 77.4 K represents a field-cooled asymmetric hysteresis loop of different magnetic behavior, as well as the initial iso-thermal curve crossing the loop from the fourth quadrant [10]. They ascribe this to spin-glass-like feature. Based on the analysis, our produced Mn_3GaN compound seems to present the frustrated antiferromagnetic characteristic, below about 360 K, including almost linear M–H dependence and the initial isothermal curve crossing the loops. Therefore, the increasing magnetization of Mn_3GaN compound at low temperatures should be ascribed to the fast reduction of the antiferromagnetism. From 360 K to about 375 K, a steeply step-like increase of magnetization indicates the occurrence of magnetic transition. As illustrated in the Fig. 4, the curvature of isothermal magnetization curve turns small with increasing temperature, together with the increment of magnetization. At 380 K, a linear magnetization, as a function of field, suggests the presence of paramagnetism or antiferromagnetism. According to the phase diagram of $Mn_{4-x}Ga_xN$ compounds shown in Fig. 6, combining similar results reported by many investigators [8, 9, 12, 13], we deduce that our prepared Mn_3GaN compound should exhibit paramagnetism above 375 K.

Therefore, our measurements reveal that, with temperatures increasing, the present Mn_3GaN compound experiences three phases: fast reduction of the antiferromagnetism → antiferromagnetism → paramagnetism, which is a little different from the phase diagram of $Mn_{4-x}Ga_xN$ at low temperatures [12]. At about 370 K, an antiferromagnetic to paramagnetic transition occurs, which basically corresponds to the aforementioned results [8, 9, 12, 13] and the phase diagram [12], but with a higher transition temperature. Based on the analysis above, we thought that the shift transition temperature should be ascribed the presence of nitrogen deficiency.

Results of electrical resistivity measurements over the temperature range of 5–380 K of the Mn_3GaN compound were plotted in Fig. 7. Besides metallic conductivity over the entire temperature range, the remnant resistivity of this compound is about 2.56 mΩ cm, which agrees with $CuNMn_3$ (2.2 mΩ cm) and Mn_3SnN (3.5 mΩ cm) compounds [1, 15]. As the temperature increases, the resistivity becomes increasingly large before about 300 K. After that, the resistivity gets smooth with temperature increasing. Moreover, the temperature dependence of the resistivity in an applied field of 5 T displays the same behavior as that in a zero field, together with the larger resistivity in the whole temperature range, which indicates a positive magnetoresistance (4–7%). As is known, $CuNMn_3$ also displays a positive magnetoresistance with a maximum of about 4%

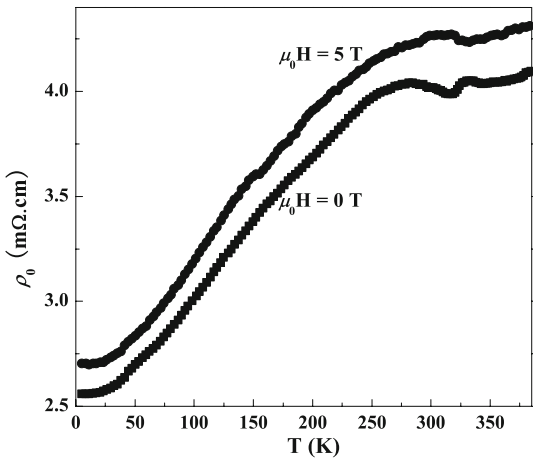

Fig. 7 Temperature dependences of the electrical resistivity for Mn_3GaN compound in a dc magnetic fields of 0 and 5 T, respectively

[1]. While magnetic measures reveal a step-like jump at about 370 K with temperature increasing, the transport measurements display a normal behavior in the corresponding temperature range. It seems that the change of magnetism has little effect on the transport property, as a result of too weak magnetism. In spite of a variety of others' results [6], our measurements show that no any obvious change of conductance occurs corresponding to the magnetic transitions for the present Mn_3GaN compound. We guess that it is the nitrogen deficiency that is responsible for the absence of conductance change at the magnetic transitions, despite no any direct evidence.

Conclusions

$Mn_{3+x}Ga_{1-x}N$ compounds were prepared via repeated sintering of $Mn_2N_{0.86}$ powder, bulk Ga metal, and Mn powder. By analysis of the lattice parameters, we deduce that nitrogen deficiency exists in these compounds. In Mn_3GaN, a steeply magnetization transition, from paramagnetism to frustrated antiferromagnetism with decreasing temperature, occurs at 370 K, while $Mn_{3.1}Ga_{0.9}N$ experiences the same transition at far above 380 K. The cusp at 117 K of Mn_3GaN arises from the occurrence of MnO impurity, whereas the increasing magnetization at low temperatures is due to the fast declination of antiferromagnetism. The temperature dependence of the resistivity of Mn_3GaN displays a typically metallic conducting behavior with a positive magnetoresistance of 4–7%.

Acknowledgements This work has been supported by the National Natural Science Foundation of China under Grant No. 50332020, that of Liaoning Province under Grant No. 20072056, and the Open Fund of Laboratory Centre of Shenyang Normal University under No. SYZX01.

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