

Pressure effects on the stability of magnetic structure of $\text{Mn}_3\text{Zn}_{1-x}\text{Ge}_x\text{N}$ ($x=0, 0.1$)

X. B. Kong,¹ Y. Sun,² L. X. Yang,¹ Y. Yu,¹ C. Q. Jin,¹ C. Wang,² and R. C. Yu^{1,a)}

¹Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100190, People's Republic of China

²Center for Condensed Matter and Materials Physics, School of Science, Beijing University of Aeronautics and Astronautics, Beijing 100191, People's Republic of China

(Received 30 July 2009; accepted 2 October 2009; published online 1 December 2009)

This paper reports that the pressure effects on the electronic transport properties of Mn_3ZnN and $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ were measured under pressures up to 2.4 GPa. Cooling and warming cycles of the temperature-dependent magnetization curves of Mn_3ZnN show a hysteresis phenomenon near the transition, implying a first order transition. The cracks which appear in the vicinity of magnetic transition at ambient pressure for Mn_3ZnN and at applied pressures not more than 0.3 GPa for $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ are restrained under higher pressures. The paramagnetic-antiferromagnetic transition temperature T_N decreases almost linearly at the rate of 1.9 and 51 K/GPa for Mn_3ZnN and $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ respectively, which is explained by the model of T_N discussed by Fruchart and the Labbé–Jardin tight-binding approximation model. © 2009 American Institute of Physics. [doi:10.1063/1.3257258]

I. INTRODUCTION

Metallic Mn_3XM compounds (X=divalent metal ion such as Ga, Zn, Cu, Ge, and Sn; M=N, C) have an antiperovskite-type cubic crystal structure, in which the metalloid M atom is at the body-centered position, Mn atoms are located on the face-centered positions and X atoms on the cubic corners. So we can get a rather extended family by putting different metal elements on the site of X. The magnetic structure of these compounds is paramagnetic at high temperatures and ferromagnetic or antiferromagnetic at low temperatures.^{1–15} In many cases, such as in Mn_3CuN , Mn_3GaC and Mn_3GaN , the magnetic transition is accompanied by a discontinuous lattice expansion, which is also called magnetovolume effect (MVE).^{2,3} The negative volume expansion in these compounds is due to the mismatch of the magnetic structure and crystal structure near the antiferromagnetic transition. By partially substituting the metallic atoms in these compounds by some other metal atoms, for example, the Ge element, it is possible to get zero thermal expansion materials which can be used in high-precision optical applications. Other physical properties such as magnetostriction, nearly zero temperature coefficient of resistivity in Mn_3CuN (Refs. 2 and 4) and giant magnetoresistance in Mn_3GaC (Ref. 5) were also studied.

The properties of Mn_3ZnN have been studied for a long time. All the researches reported that this material changes from a paramagnetic state to a triangular Γ^{5g} antiferromagnetic state with decreasing temperature while the symmetry remains cubic.^{6–9} Simultaneously, an abrupt lattice expansion generally occurs round the magnetic transition, which could lead to an appearance of microcracks in some cases.⁷ Partial substitution of Zn by Ge is in favor of increasing the mag-

netic transition temperature and is also quite efficient for broadening the temperature range of lattice expansion.³ However, the recent works done by Sun *et al.*⁸ pointed out that no abrupt lattice expansion was observed in Mn_3ZnN , whereas the $\text{Mn}_3\text{Zn}_{1-x}\text{Ge}_x\text{N}$ ($x=0.1, 0.3, 0.5$) samples acted similarly as the previous reports.

As a tunable thermodynamic parameter, the external pressure plays an important role in material sciences. It can affect not only the crystal structure but also the magnetic structure, charge ordering, and orbital ordering. In this letter, we report the pressure effects on the stability of magnetic structure of Mn_3ZnN and $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$.

II. EXPERIMENTS

The samples were prepared by solid-state reaction method. Powders of Mn_2N , Zn, and Ge were mixed stoichiometrically and pressed into a pellet, which was then wrapped with in a tantalum foil and sealed in a vacuumed quartz tube. The tube was sintered in a box furnace at 780 °C for 80h and then cooled down to room temperature naturally.

The measurements of temperature-dependent resistance curves $R(T)$ under hydrostatic pressures up to 2.4 GPa were carried out by using the four-probe technique in a piston-cylinder pressure cell, which is similar to the one used in Ref. 10, with a 1: 1 mixture of silicon oil and coal oil as pressure transmitting medium. The pressures were loaded at room temperature at intervals of 0.3 GPa until the highest 2.4 GPa.

Cooling and warming cycles of the temperature-dependent magnetization curves of Mn_3ZnN were measured at 300 G by magnetic property measurement system (60 K < T < 300 K) with the same rate of cooling and warming temperature.

^{a)}Author to whom correspondence should be addressed. Electronic mail: rcyu@aphy.iphy.ac.cn.

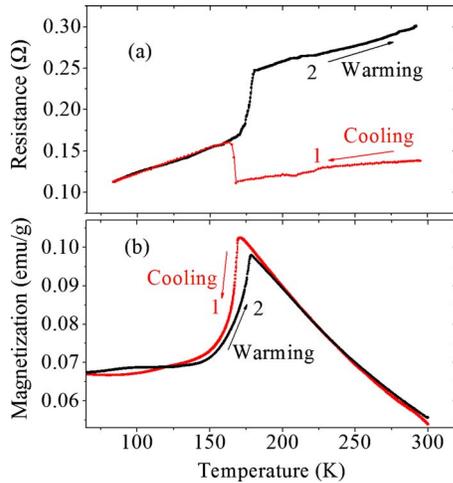


FIG. 1. (Color online) (a) The temperature-dependent resistance curve $R(T)$ at ambient pressure. (b) The cooling and warming cycles of temperature-dependent magnetization curves of Mn_3ZnN measured at 300 G.

III. RESULTS AND DISCUSSION

The structure of our samples Mn_3ZnN and $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ were examined by x-ray diffraction and it is confirmed that they both possess a cubic structure. For Mn_3ZnN , as shown in Fig. 1(a), the warming cycle of the temperature-dependent resistance curve $R(T)$ measured at ambient pressure shows an abrupt increase at the magnetic transition, indicating an occurrence of cracks accompanied with the transition. Such a phenomenon was also observed by other groups,⁷ where the cracks were induced by the magnetic ordering in the vicinity of the magnetic transition. There are two different reports about the lattice parameter change at the transition, one is abrupt expansion and contraction^{3,6,7} and the other is continuous.⁸ The result shown in Fig. 1(a) suggests that it is the former case for our sample. It is reported that Mn_3CuN undergoes a first order transition at $T_C = 143$ K from the high temperature paramagnetic state to the low temperature ferromagnetic state with Γ^{4g} spin structure, but the volume is conservative.^{1-3,11} The sample $\text{Mn}_3\text{Cu}_{1-x}\text{Ge}_x\text{N}$, however, has a cubic structure and shows MVE during the magnetic transition from a paramagnetic state to an antiferromagnetic state with Γ^{5g} antiferromagnetic spin structure.^{3,11} In Ref. 11, Iikubo *et al.* concluded that both a cubic crystal structure and a Γ^{5g} antiferromagnetic spin structure are two key ingredients for the large MVE in $\text{Mn}_3\text{Cu}_{1-x}\text{Ge}_x\text{N}$. Since Mn_3ZnN and $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ both have the above two determinative factors, it is understandable that they should have MVE associated with the magnetic transition, just as that observed in our experiments.

The magnetization curves of Mn_3ZnN measured at 300 G are shown in Fig. 1(b), in which the cooling and warming cycles are obtained by changing the temperature at the same rate. An antiferromagnetic transition is clearly observed in both the two cycles. However, the transition temperature T_N transfers from 170 K in the cooling cycle to 178 K in the warming cycle. Such hysteresis phenomenon is also shown in Fig. 1(a) where T_N shifts from 163 K in the cooling cycle to 171 K in the warming cycle. In both the two cases, ΔT

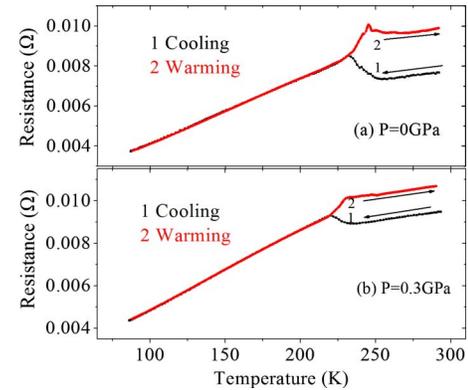


FIG. 2. (Color online) Cooling and warming cycles of resistance curves $R(T)$ of $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ measured at ambient pressure and under 0.3 GPa, respectively.

$= 8$ K, this result is similar to the thermal hysteresis of $\Delta T = 7.5$ K detected between cooling and warming cycles of heat capacity C_p ,⁶ and implies a first order transition, this fact was assured by other groups as well.⁷

As shown in Fig. 2, the warming cycles of the temperature-dependent resistance curves $R(T)$ for $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ measured at ambient pressure and at 0.3 GPa both show an increase near the magnetic transition, which means that the cracks accompanied with the magnetic transition in Mn_3ZnN also occur in $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$. Furthermore, the appearance of cracks is not suppressed at applied pressures within 0.3 GPa. Here we should point out that among the compounds in the series of Mn_3XN , the MVE is largest in the Mn_3ZnN ,^{3,7} so very small pressure can prevent the sample from further appearing cracks, just observed in our experiments. So the cracks of Mn_3ZnN are restricted immediately under pressure but still appear within 0.3 GPa in $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$.

The temperature dependence of resistance curves $R(T)$ measured under different pressures at intervals of 0.3 GPa until 2.4 GPa are presented in Figs. 3(a) and 3(b) for Mn_3ZnN and $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$, respectively. For Mn_3ZnN , it is obvious that no more cracks appear after applying pressures since the increases of resistances near the magnetic transition disappeared. The paramagnetic-antiferromagnetic transition temperature T_N decreases abruptly from 171 to 157 K at the beginning of loading pressure, and then reduces slowly to lower temperature at the rate of about 1.9 K/GPa with further increasing pressures, this phenomenon is shown clearly in Fig. 4. While in $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$, the cracks are suppressed under pressures beyond 0.3 GPa. On the other hand, T_N decreases almost linearly at a rate of 51 K/GPa, also shown in Fig. 4. The behaviors of T_N versus pressure for both the two samples suggest that pressure favors the paramagnetic state but suppresses the antiferromagnetic state. It is reasonable because the lattice expansion is repressed under pressures.

The pressure effect on T_N can be understood according to the theoretical discussion of T_t for Mn_3XN given by Fruchart,^{1,12} in which the valence electrons of X play a dominating role in the variation of the magnetic order-disorder, and the magnetic order-disorder transition temperature T_t is well proportional to the electron density ζ ,

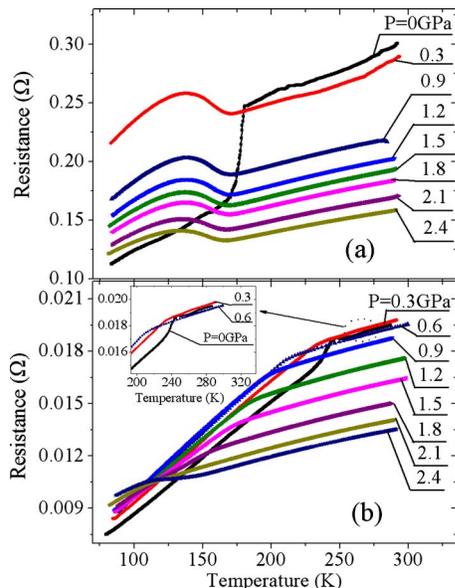


FIG. 3. (Color online) [(a) and (b)], the temperature-dependent resistance curves $R(T)$ of Mn_3ZnN and $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ measured under pressures at intervals of 0.3 GPa up to 2.4 GPa, respectively.

$$\zeta = K \times n_v (1 + \Delta r_a / r_a),$$

where n_v is the number of valence electrons of X, r_a its atomic radius, and Δr_a the difference of radii between X in the perovskite structure which can be approximately equal to $a/2$ calculated from the unit cell parameter of Mn_3XN and the element X. Since the value of Δr_a decreases with increasing pressures while the other factors keep unchanged, we can easily get the conclusion that T_N decreases with increasing pressure, just as that observed in our experiments. Since n_v of Ge is two times of Zn, it is reasonable that T_N of $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ decreases more quickly under pressures than that of Mn_3ZnN .

In addition to the fact that T_N rises abruptly with the increase in the content of Ge dopant in $\text{Mn}_3\text{Zn}_{1-x}\text{Ge}_x\text{N}$ ($x = 0, 0.1, 0.3, 0.5$),⁸ the very different behavior between T_N of $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ and Mn_3ZnN under pressures validates the conclusion that the properties of the structure and magnetic transition of Mn_3XN are mainly dominated by the types of element on the X site.

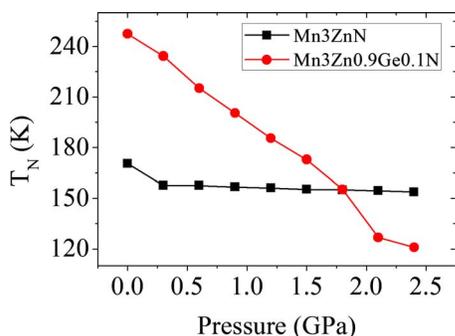


FIG. 4. (Color online) The paramagnetic-antiferromagnetic transition temperature T_N vs pressure P , showing the change in T_N at an approximate rate of -1.9 K/GPa for Mn_3ZnN and -51 K/GPa for $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$, respectively.

In fact, the decrease in T_N under pressures can also be understood with respect to the Labbé–Jardin tight-binding approximation model for Mn_3XN ,⁹ which consists of a large conduction band overlapping a narrow band resulted from the strong hybridization between N-2p orbital and Mn 3d_{eg} orbital, and the narrow band's structure is calculated with the tight-binding approximation. In detail, the Fermi energy E_F lies closely to the infinite singularity energy in the electronic density of states, the so-called E_S , which is sharp and degenerate in the cubic and paramagnetic state. The magnetic transition from the paramagnetic to the antiferromagnetic state is accompanied with the removal of that degeneracy.⁹ Moreover, the instability of the paramagnetic phase is caused by the negative variation of the free energy δF , which is composed of two parts: a large contribution δF_e to δF , which is negative and originated from the electrons inside the p-d_{eg} transferred from the degenerate E_S with higher energies to the new singularities with lower energies after the splitting of E_S ; another one is δF_0 , which is positive and contains all the other contributions in the model. It is assumed to stabilize the paramagnetic state and is temperature-independent.

Based on the above model, we can qualitatively understand the behaviors of T_N of both samples under pressure as follows: by applying pressures to the samples, energies of both the above states will be raised under pressure as well and the energies of the split singularities will be raised more remarkable than that of E_S . As a result, ΔE between E_S and the split singularities will be smaller under pressure than before and give rise to the decrease in the absolute value of δF_e . On the other hand, δF_0 will be larger than before, resulting from the rising of all the band energies under pressure. In conclusion, all the above factors will retard the negative change in δF and result in the decrease in T_N under pressure. Furthermore, due to the fact that Ge-doping in Mn_3ZnN greatly enhances T_N and widens the E_S singularity,⁸ the effect of applying pressure on δF of $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ will be more notable, which is verified in our experimental results that T_N of $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ decreases much more quickly than that of Mn_3ZnN under pressure.

IV. CONCLUSIONS

The stability of magnetic structure of Mn_3ZnN and $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ under hydrostatic pressures up to 2.4 GPa has been studied. We consider that the abrupt increases of the resistance at the magnetic transition in the warming cycle of Mn_3ZnN at ambient pressure and $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ within 0.3 GPa are caused by the appearance of cracks, which are restricted under higher pressures. The first order transition is clearly indicated by the temperature-dependent magnetization curves measured at 300G. The paramagnetic-antiferromagnetic transition temperature T_N of Mn_3ZnN and $\text{Mn}_3\text{Zn}_{0.9}\text{Ge}_{0.1}\text{N}$ decreases almost linearly at rates of 1.9 and 51 K/GPa under pressures up to 2.4 GPa, respectively. The decrease in T_N for both the two samples under pressures can be understood on basis of the model of T_t given by Fruchart and the Labbé–Jardin tight-binding approximation model.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 10774168 and 50621061) and the State Key Development Program for Basic Research of China (Grant Nos. 2005CB623602 and 2007CB925003).

¹D. Fruchart and E. F. Bertaut, *J. Phys. Soc. Jpn.* **44**, 781 (1978).

²K. Asano, K. Koyama, and K. Takenaka, *Appl. Phys. Lett.* **92**, 161909 (2008).

³K. Takenaka and H. Takagi, *Appl. Phys. Lett.* **87**, 261902 (2005).

⁴F. J. Rueckert, M. Steiger, B. K. Davis, T. Huynh, J. J. Neumeier, and M. S. Torikachvili, *Phys. Rev. B* **77**, 064403 (2008).

⁵K. Kamishima, T. Goto, H. Nakagawa, N. Miura, M. Ohashi, and N. Mori, *Phys. Rev. B* **63**, 024426 (2000).

⁶J. García, R. Navarro, J. Bartolomé, R. Burriel, D. González, and D.

Fruchart, *J. Magn. Magn. Mater.* **15–18**, 1155 (1980).

⁷W. S. Kim, E. O. Chi, J. C. Kim, N. H. Hur, K. W. Lee, and Y. N. Choi, *Phys. Rev. B* **68**, 172402 (2003).

⁸Y. Sun, C. Wang, Y. Wen, and K. Zhu, *Appl. Phys. Lett.* **91**, 231913 (2007).

⁹P. Jardin and J. Labbé, *J. Solid State Chem.* **46**, 275 (1983).

¹⁰S. L. Bud'ko, J. Guimpel, O. Nakamura, M. B. Maple, and I. K. Schuller, *Phys. Rev. B* **46**, 1257 (1992).

¹¹S. Iikubo, K. Kodama, K. Takenaka, H. Takagi, and S. Shamoto, *Phys. Rev. B* **77**, 020409(R) (2008).

¹²D. Fruchart, *Physica B & C* **86–88**, 423 (1977).

¹³E. F. Wasserman, in *Ferromagnetic Materials*, edited by K. H. J. Buschow and E. P. Wohlfarth (Elsevier, Amsterdam, 1990), Vol. 5, pp. 237–322.

¹⁴T. Kaneko, T. Kanomata, and K. Shirakawa, *J. Phys. Soc. Jpn.* **56**, 4047 (1987).

¹⁵J. H. Shim, S. K. Kwon, and B. I. Min, *Phys. Rev. B* **66**, 020406(R) (2002).