Lattice contraction and magnetic and electronic transport properties of Mn 3 Zn 1 − x Ge x N

Ying Sun, Cong Wang, Yongchun Wen, Kaigui Zhu, and Jingtai Zhao

---

Articles you may be interested in

Magnetic structure and lattice contraction in Mn3NiN
J. Appl. Phys. **114**, 123902 (2013); 10.1063/1.4822023

Influence of carbon content on the lattice variation, magnetic and electronic transport properties in Mn 3 SnC x
Appl. Phys. Lett. **96**, 041903 (2010); 10.1063/1.3295695

The effect of Ni doping on the magnetic and transport properties in Pr 0.5 Ca 0.5 Mn 1 − x Ni x O 3 manganites
J. Appl. Phys. **106**, 013913 (2009); 10.1063/1.3168422

Strain, luminescence, and electrical properties of Zn 1 − x Mn x S nanocrystalline films prepared on silicon wafers
J. Appl. Phys. **104**, 013532 (2008); 10.1063/1.2955270

Dependence on cation distribution of particle size, lattice parameter, and magnetic properties in nanosize Mn–Zn ferrite
J. Appl. Phys. **91**, 2211 (2002); 10.1063/1.1432474

Lattice contraction and magnetic and electronic transport properties of Mn₃Zn₁₋ₓGeₓN

Ying Sun, Cong Wang,[a)] Yongchun Wen, and Kaigui Zhu
Center for Condensed Matter and Materials Physics, School of Science, Beijing University of Aeronautics and Astronautics, Beijing 100083, People's Republic of China

Jingtai Zhao
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China

The lattice and electronic and magnetic transport properties of the antiperovskite structure $Mn_3Zn_{1-x}Ge_xN$ compounds were investigated. For Mn_3ZnN, there is a magnetic transition from antiferromagnetic to paramagnetic near 185 K. Correspondingly, the resistivity shows an abrupt drop, but any sudden change of lattice parameters is not found. However, it is interesting that the partial substitution of Ge for Zn induces a lattice contraction near the magnetic transition temperature, where a drop of the resistivity remain, and the transition temperature point increases and the temperature range is broadened with increasing doped Ge contents. The thermodynamics properties were also investigated. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2822813]

Antiperovskite manganese compounds Mn_3XN (X=Ga, Zn, Cu, Ge, and Sn), in which the nonmetal atom N is at the body-centered position, are well known for a couple of years.[1] These compounds show a wide variety of interesting physical phenomena such as superconductivity, giant magnetoresistivity, and a nearly zero temperature coefficient of resistivity.[2–5] Therefore, these compounds with antiperovskite structure have attracted great attentions.

There exists a magnetic phase transition in Mn_3XN compounds at certain temperature, sometimes accompanied by a large discontinuous lattice contraction with increasing temperature. As the lattice volume shows a sharp change, it is unsuitable for actual applications. Very recently, Takenaka and Takagi reported that the discontinuous lattice contraction induced by the magnetic transition was modified into continuous contraction by introducing the element Ge into X position in the antiperovskite manganese nitrides.[6,7] So the study on $Mn_3XN(C)$ regains interest for the abnormal thermal expansion and the correlated electronic and magnetic transport properties.

In Mn_3XN, there is a very stable basic chemical unit, the Mn_6N octahedron, whereas the other metal X, located at the corners of the cube, is less bound to the N.[8] This fact allows the introduction of various metals on the site of X. Since a small substitution on X can affect the magnetic transition, and then change the thermal expansion properties, it is very hopeful to find the suitable negative or near zero thermal expansion in different temperature ranges for practical applications.

In this paper, the thermal expansion properties of $Mn_3Zn(Ge)N$ compounds were studied by variable temperature x-ray diffraction measurements. As there is a close correlation among lattice, spin, and charge in this kind of materials,[9] other physical properties were also investigated.

Polycrystalline samples $Mn_3Zn_{1-x}Ge_xN$ (x=0, 0.1, 0.3, and 0.5) were prepared by solid-state reaction using the powders of Mn_2N, Zn, and Ge as the starting materials. Stoichiometric amounts of the starting materials were mixed and pressed into pellets. The pellets were wrapped in a Ta foil and then sealed in a vacuumized quartz tube. The quartz tube was sintered in a box furnace at 780 °C for 80 h, and then cooled down to room temperature.

X-ray diffraction patterns at room temperature were obtained from a Rigaku D/MAX 2200PC diffractometer using Cu $K\alpha$ radiation. A software named POWDER X (Ref. 10) was used for indexing and lattice parameter calculations. For the measurements of coefficient of thermal expansion, variable temperature x-ray diffraction from 80 to 523 K was done on a X'Pert PRO multipurpose diffractometer. dc magnetization was measured at 50 Oe by superconducting quantum interference device (50 K≤T≤ room temperature) for Mn_3ZnN and $Mn_3Zn_{0.9}Ge_{0.1}N$. Electrical resistivity measurements (5 K≤T≤ room temperature) were accomplished using standard four-probe technique. Heat capacity analysis was conducted using PPMS for Mn_3ZnN in the temperature range from 50 to 300 K and TAQ200 DSC for other $Mn_3Zn_{1-x}Ge_xN$ samples from 150 to 550 K, respectively.

As clearly seen in Fig. 1(a), with increasing T, the magnetic phase transition from antiferromagnetic (AFM) to paramagnetic (PM) takes place at around 185 K in Mn_3ZnN. Simultaneously, there exists a corresponding large abrupt change for the resistivity starting from 179 K and ending at 167 K with decreasing temperature. As to the temperature dependence of cubic lattice parameter (a), a normal thermal expansion behavior over the entire temperature range is obtained, as shown in Fig. 1(b). The a-T curve is nearly linear and the linear thermal expansion coefficient β is estimated to be 9.2×10^{-6} K^{-1}. This phenomenon is quite different from the results in Refs. 6 and 11, in which an abrupt change of the lattice parameter was always observed near the magnetic transition temperature. We repeated the measurement and the same result was always remained. For further testifying the result, we carried out a calorimetric measurement. As shown in Fig. 1(b) large anomaly of heat capacity is observed in Mn_3ZnN, which is corresponding to the AFM-PM transition,

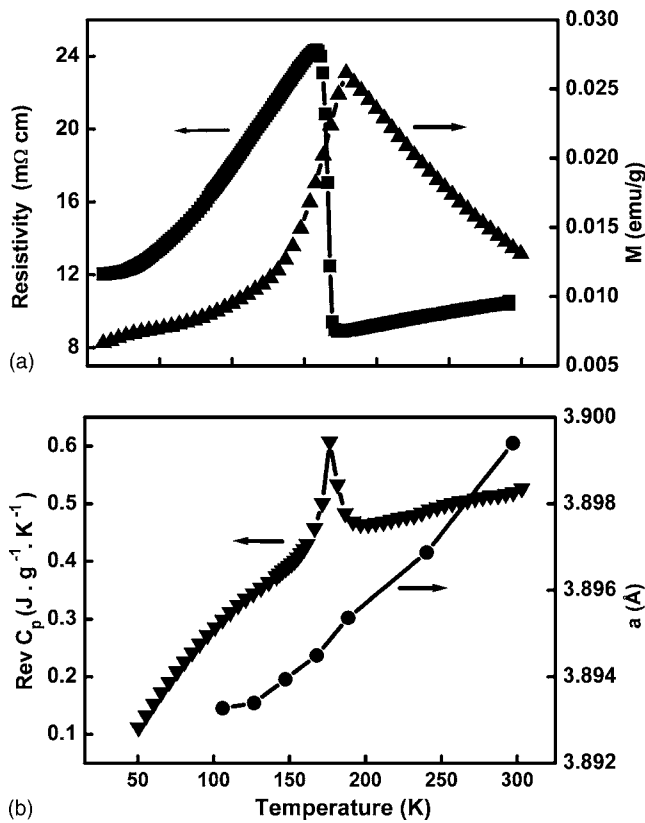a)Author to whom correspondence should be addressed. Electronic mail: congwang@buaa.edu.cn.

FIG. 1. (a) Temperature dependence of the magnetization (▲ symbol) and the resistivity (■ symbol) for Mn$_3$ZnN. (b) Temperature dependence of the lattice parameters (● symbol) and heat capacity curve (▼ symbol) for Mn$_3$ZnN.

FIG. 2. Temperature dependence of the lattice parameters for Mn$_3$Zn$_{1-x}$Ge$_x$N by XRD.

and the peak shape is similar with λ type, a characteristic shape of the second-order phase transition.[12] As we all know, discontinuous volume change usually does not take place in a second-order phase transition. Thus, the result of heat capacity measurement verifies the right measurement of the lattice parameter from another point.

As reported early, magnetically induced changes in the volume of Mn$_3$XN usually occur near the magnetic ordering temperature.[13] So the magnetic property is relevant to the lattice effect. In addition, the electric transport property of Mn$_3$XN is also highly correlated with the variation of lattice parameter.[11] However, our results are absolutely different from that. It is readily noticed that the discontinuity in the lattice parameter does not occur while magnetic transition and the sudden change of resistivity take place for Mn$_3$ZnN. This phenomenon reveals that magnetic transition and the sudden change of resistivity are only essential but not enough for abnormal change in lattice. In other words, the AFM-PM transition is not the only cause of the abrupt change of lattice parameters near the magnetic temperature.

We try to dope some Ge into Mn$_3$ZnN, with substitution on Zn position and forming Mn$_3$Zn$_{1-x}$Ge$_x$N (x=0.1, 0.3, and 0.5). Surprisingly, the lattice parameters show a sudden and pronounced decrease near 202 K (when x=0.1) with increasing temperature, i.e., Ge doping produces a transition from normal lattice expansion to lattice contraction at a certain temperature range in the antiperovskite Mn$_3$ZnN materials. As shown in Fig. 2, with a further increase of Ge concentration, the transition temperature is correspondingly increased and the narrow temperature range of lattice contraction is broad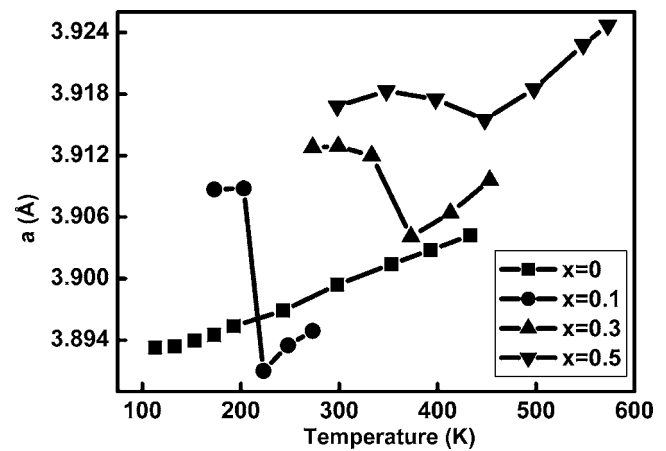ened by ΔT=100 K when x=0.5. The thermal expansion coefficients are β=-2.28×10^{-4} K^{-1} (202 K$<T<$222 K), -3.10×10^{-5} K^{-1} (299 K$<T<$373 K), and -7.15×10^{-6} K^{-1} (348 K$<T<$448 K) for x=0.1, x=0.3, and x=0.5, respectively. The absolute values of β are smaller compared with the results reported by Takenaka and Takagi, in which they measured $\Delta L/L$ using only a strain gauge.[6]

In order to understand the cause of Ge-doped effect, we further investigated the magnetic and electronic transport and thermodynamics properties of Mn$_3$Zn$_{1-x}$Ge$_x$N. In Fig. 3(a), we display the magnetization curve of pure Mn$_3$ZnN and Mn$_3$Zn$_{0.9}$Ge$_{0.1}$N. It is found that the AFM-PM transition peak of Mn$_3$Zn$_{0.9}$Ge$_{0.1}$N is not so sharp as Mn$_3$ZnN and the magnetic transition temperature is drastically enhanced by Ge doping. The magnetization curves of other Mn$_3$Zn$_{1-x}$Ge$_x$N samples are also obtained. The transition peak becomes broader with increasing Ge contents and the
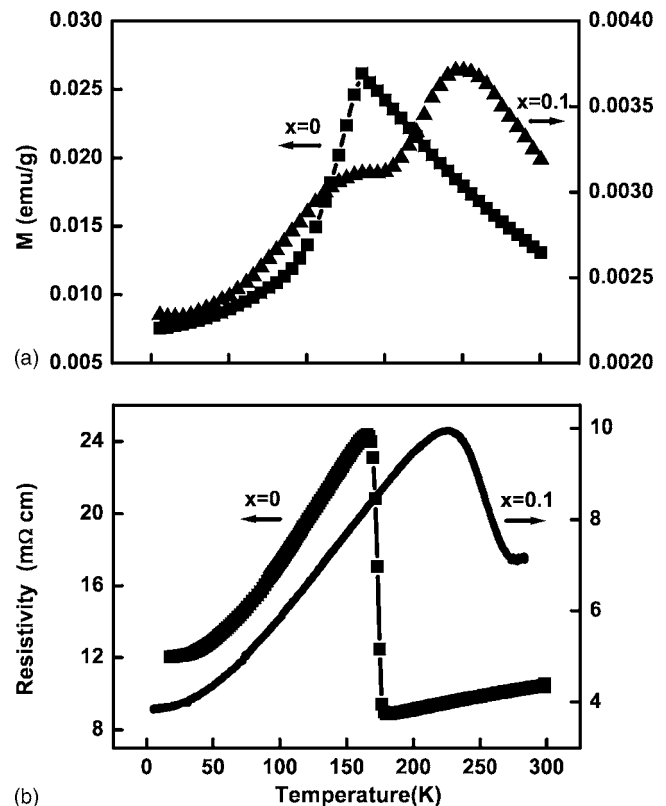

FIG. 3. Temperature dependence of (a) the magnetization and (b) the resistivity for Mn$_3$Zn$_{1-x}$Ge$_x$N.
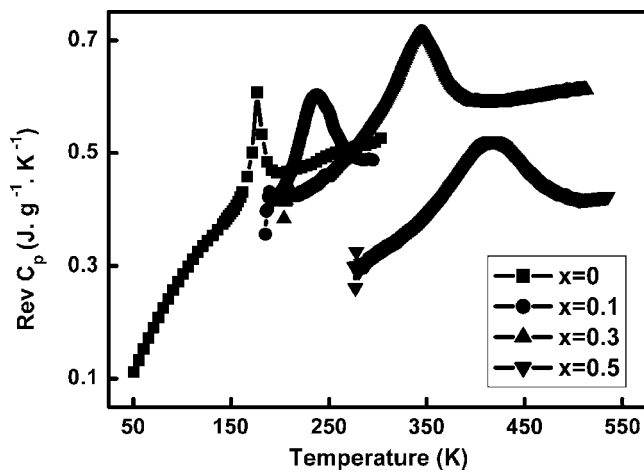
FIG. 4. Variation of the heat capacity with temperature for $Mn_3Zn_{1-x}Ge_xN$.

magnetic transition points are 351 and 435 K for $x=0.3$ and $x=0.5$, respectively.

The temperature dependence of the resistivity is shown in Fig. 3(b). For $Mn_3Zn_{0.9}Ge_{0.1}N$, the resistivity increases from 270 to 227 K with $d\rho/dT=-0.07$, of which the absolute value is rather lower compared with $(d\rho/dT)_{Mn_3ZnN}$ $=-2.38$ in the transition temperature range of 167 K$<T$ <179 K. Then the resistivity decreases with decreasing temperature such as pure Mn_3ZnN. Similar behavior is found in the temperature-dependent resistivity data of other $Mn_3Zn_{1-x}Ge_xN$ ($0.1<x\leqslant0.5$) samples, but enhanced transition temperature and widened temperature range are observed as a gradual increase of Ge concentration. The $d\rho/dT$ rates are -0.007 and -0.003 in the transition temperature range for $Mn_3Zn_{0.7}Ge_{0.3}N$ and $Mn_3Zn_{0.5}Ge_{0.5}N$, respectively.

In addition, we represent the heat capacity curves of $Mn_3Zn_{1-x}Ge_xN$ in Fig. 4. As expected from the results above, the peak shape of the heat capacity curves is noticeably changed after Ge introduced. With increasing Ge contents, the peak becomes broader. This reveals a qualitative change of the magnetic and structure transition behaviors of the solid solution.

From the above results, we could conclude that Ge doping does not only induces the large lattice contraction evoluted from normal lattice expansion but also retards the transition with increasing Ge contents. This stimulates our interest in the attempt of substituting Zn atoms by other elements. In Mn_3XN, narrow bands are formed near the Fermi level by the strong hybridation between N 2p and Mn 3d orbitals. The occupation of these narrow bands is sensitively changed according to the number of the valence electrons on X. Most previous papers thought that the number of valence electrons on X is a dominant factor for the structural and magnetic properties.[14,15] So we have tried to dope Sn element of which the valence electrons are as much as Ge element. However, It did not exhibit the broadened phenomenon of phase transition region, but the transition temperature was enhanced. Therefore, the broadening effect is mostly connected with the nature of Ge element.

Jardin and Labbe have performed a band calculation of cubic perovskite compounds Mn_3XN by applying a simple tight-binding approximation to the d electrons of Mn atoms and p electrons of N atoms.[14] They pointed out that the Fermi energy E_F lies very close to the infinite singularities energy E_s in the electronic density of states. Attractively, the quality of the transition occurred in Mn_3XN is correlated

with the parameter $|E_F-E_s|$ which could depend on the exact chemical composition of a given compound. In addition, the sharp peak near the E_F may be broaden or smeared out with Ge doping, while the density of states near E_F must be modified with increasing Ge contents, then as a result the transition is retarded. All of that give us a clue for further understanding the Ge effect, although the origin needs to be confirmed by further exploration.

In conclusion, $Mn_3Zn_{1-x}Ge_xN$ ($x=0$, 0.1, 0.3, and 0.5) samples were prepared by solid-state reaction and their thermal expansion properties were studied by variable temperature x-ray diffraction. Pure Mn_3ZnN does not show any lattice contraction at the magnetic transition temperature. This provides an important clue to understand whether structural change triggers magnetic phase transition or vice versa. Interestingly, partial substitution of Zn by Ge induces the revival of lattice contraction and the lattice contraction behavior acts in accord with the magnetic transition from AFM to PM and changes with differrent Ge doping contents. Thus, we think that the combined action of the magnetic transition and Ge doping produces the abnormal lattice contraction. The thermal expansion coefficients β of $Mn_3Zn_{1-x}Ge_xN$ are -2.28×10^{-4} K^{-1} (202 K$<T<$222 K), -3.10×10^{-5} K^{-1} (299 K$<T<$373 K), and -7.15×10^{-6} K^{-1} (348 K$<T$ <448 K) for $x=0.1$, $x=0.3$, and $x=0.5$, respectively. The abrupt drop of resistivity occurred in the transition temperature is correspondingly broadened with increasing Ge concentration. Heat capacity C_p analysis indicates that the second-order transition occurred in Mn_3ZnN is changed by introduction of Ge since the peak is not so sharp as pure Mn_3ZnN. Further study is deserved for realizing the effect of Ge element and also for developing zero thermal expansion materials whose specific characteristics are attractive for aerospace, electronic, and high-precision optical applications.

[1]E. F. Bertaut, D. Fruchart, J. P. Bouchaud, and R. Fruchart, Solid State Commun. **6**, 251 (1968).

[2]R. Prozorov, A. Snezhko, T. He, and R. J. Cava, Phys. Rev. B **68**, 180502(R) (2003).

[3]A. F. Dong, G. C. Che, W. W. Huang, S. L. Jia, H. Chen, and Z. X. Zhao, Physica C **422**, 65 (2005).

[4]K. Kamishima, T. Goto, H. Nakagawa, N. Miura, M. Ohashi, N. Mori, T. Sasaki, and T. Kanomata, Phys. Rev. B **63**, 024426 (2000).

[5]E. O. Chi, S. Kim, and N. H. Hur, Solid State Commun. **120**, 307 (2001).

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

[7]K. Takenaka and H. Takagi, Mater. Trans. **47**, 471 (2006).

[8]J. García, J. Bartolomé, and D. González, J. Chem. Thermodyn. **15**, 465 (1983).

[9]W. S. Kim, E. O. Chi, J. C. Kim, H. S. Choi, and N. H. Hur, Solid State Commun. **119**, 507 (2001).

[10]C. Dong, J. Appl. Crystallogr. **32**, 838 (1999).

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

[12]Y. Yamamura, N. Nakajima, and T. Tsuji, Solid State Commun. **114**, 453 (2000).

[13]D. Fruchart, E. F. Bertaut, R. Madar, G. Lorthioir, R. Fruchart, T. Sasaki, and T. Kanomata, Solid State Commun. **9**, 1793 (1971).

[14]J. P. Jardin and J. Labbe, J. Solid State Chem. **46**, 275 (1983).

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