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The study of structure, magnetism, electricity, and their correlations at martensitic transition for magnetostriction system $Cu_{1-x}Mn_xNMn_3$ ($0 \le x \le 0.5$)

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The antiperovskite functional compound $CuNMn_3$ exhibits magnetostriction below the non-collinear ferromagnetic (FM)-paramagnetic (PM) transition (accompanied by a martensitic transformation). After the substitution of Mn for Cu, martensitic transformation is decoupled from FM transition. Meanwhile, the tetragonality of the martensitic phase and the magnetostriction are weakened. The combined analysis indicates that the spin, charge, and lattice are closely coupled around martensitic transformation temperature (T_{MS}). The low-temperature martensitic phase is associated with a metastable magnetic state characterized by small magnetocrystalline anisotropy. Additionally, the depression of T_{MS} with introducing the Mn dopant is revelatory for the development of low-temperature negative thermal expansion material. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4725471]

I. INTRODUCTION

$CuNMn_3$, as an important antiperovskite manganese compound, has attracted more and more attention because of the interesting functional properties including magnetostriction and low temperature coefficient of resistivity (TCR).[1,2] Around the Curie temperature ($T_C = 143$ K), $CuNMn_3$ undergoes a first-order transition from high-temperature paramagnetic (PM) to low-temperature non-collinear ferromagnetic (FM) phase which is accompanied by a cubic-to-tetragonal martensitic transformation.[1] This kind of lattice instability results in close correlations among spin, lattice, and charge around magnetic transition.[3] By controlling this kind of correlation through doping, well optimized functional properties have been achieved. The substitution of Ge, Sn for Cu effectively broadened the volume change and achieved large negative thermal expansion (NTE).[4–6] The substitution of Ag for Cu, C for N, or Co for Mn could realize zero-TCR in appropriate doping level.[7,8] Obviously, the control and study of the correlations among various degrees of freedom is a key for the development of smart materials in the antiperovskite manganese compounds. In this work, we perform the substitution of Mn for Cu in $CuNMn_3$ considering the following two reasons: (1) The element at A site plays an important role in deciding the physical properties of the antiperovskite compounds $ANMn_3$;[9] (2) Mn is magnetic element which may introduce the direct magnetic interactions between the face-central-Mn and corner-Mn atoms and affects the original magnetic order. Based on the above reasons, the gradual substitution of Mn for Cu will definitely change the correlations of different degrees of freedom. Therefore, the systematical studies on the physical properties of $Cu_{1-x}Mn_xNMn_3$ may be helpful to explore not only the new kind of material but also the natural physical mechanism.

II. EXPERIMENTS

Polycrystalline samples $Cu_{1-x}Mn_xNMn_3$ ($0 \le x \le 0.5$) were prepared by direct solid-state reaction.[10] X-ray powder diffraction (XRD) was performed using a Philips X′pert PRO x-ray diffractometer with Cu Kα radiation at room temperature. To study the evolution of the structure characteristic, XRD patterns were also obtained for the samples with $x = 0.2$, 0.4, and 0.5 by Rigaku TTRIII x-ray diffractometer with Cu Kα radiation changing temperature to 15 K. The magnetic and resistivity measurements were performed on a quantum design superconducting quantum interference device (SQUID) magnetometer and physical property measurement system (PPMS), respectively.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the room-temperature powder XRD patterns of $Cu_{1-x}Mn_xNMn_3$. All the diffraction peaks could be indexed by the cubic antiperovskite structure (space group: *Pm*3*m*) and no detectable secondary phase exists. Figures 1(b)–1(d) show the temperature dependent XRD for $x = 0.2$, 0.4, and 0.5, respectively. The refined lattice constants are plotted as a function of temperature in the insets. As shown in Fig. 1(b), for $x = 0.2$, the peak (200) keeps a single component above 100 K, indicating that the cubic structure is maintained. Otherwise, the peak (200) splits into two parts below 100 K. The inset indicates that the lattice constant a is equal to b and both are much longer than lattice constant c. So, the structure of $Cu_{0.8}Mn_{0.2}NMn_3$ changes into tetragonal from cubic below 100 K. Similar to $CuNMn_3$, this deformation can be classified as a martensitic transformation.[1,2,9] Figure 1(c) shows that the peak (200) does not split into two parts until the temperature

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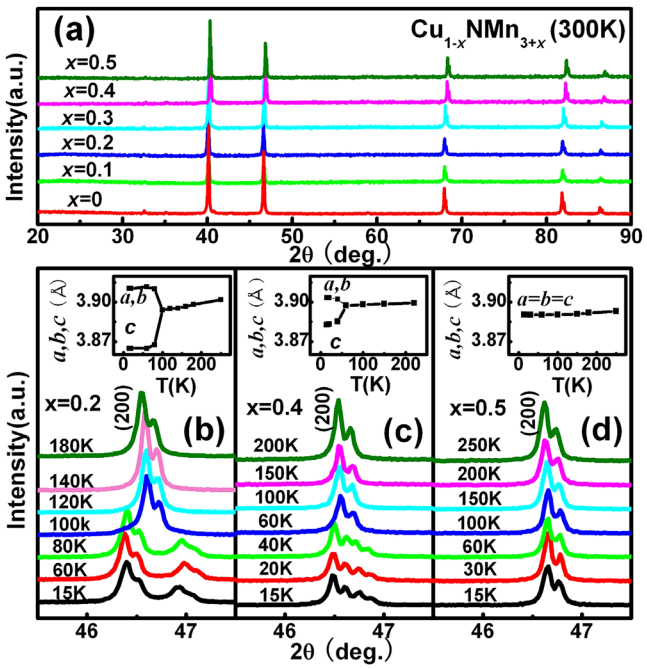

FIG. 1. (a) The XRD patterns of $Cu_{1-x}Mn_xNMn_3$ ($0 \le x \le 0.5$) at room temperature. (b) Temperature dependence of the (200) peak for $x = 0.2$. Inset: the refined lattice parameters between 15 K and 250 K. (c) Temperature dependence of the (200) peak for $x = 0.4$. Inset: the refined lattice parameters between 15 K and 220 K. (d) Temperature dependence of the (200) peak for $x = 0.5$. Inset: the refined lattice parameters between 15 K and 250 K.

is decreased to 60 K for $x = 0.4$. As shown in Fig. 1(d), the (200) peak is single in the whole temperature range for $x = 0.5$, which indicates the disappearance of the martensitic transformation. All in all, T_{MS} decreases gradually with increasing x and the martensitic transformation disappears when x is above 0.5. Meanwhile, the calculated discontinuous jump of lattice constant a, b, and c for $x = 0$, 0.2, and 0.4 (estimated as $\Delta a/a$, $\Delta b/b$ and $\Delta c/c$, respectively) decreases with increasing x, indicating that the substitution of Mn for Cu weakens the martensitic transformation and the tetragonality of the martensitic phase. As we know, the martensitic transformation is one kind of displacive phase transition which originates from the tilting of octahedra in many perovskite compounds.[11,12] For antiperovskite compounds, the pair distribution function analysis indicates that the tetragonal distortion in $GeNMn_3$ originates from the tilting of Mn_6N octahedron, but the martensitic transformation in $CuNMn_3$ is not due to the tilting of Mn_6N octahedron.[13,14] Therefore, the physical origin of martensitic transformation in $Cu_{1-x}Mn_xNMn_3$ still needs the further study, which will be helpful for the understanding of the correlation among the physical properties around martensitic transformation in this system.

As reported,[1,3] $CuNMn_3$ exhibits a large magnetostriction under 90 kOe and the rearrangement of martensite variants under external fields is considered as the deciding factor. In CuN_xMn_3, the martensitic transformation also appears and the smaller magnetostriction can be ascribed to the smaller value of $1\text{-}c/a$.[3] Similarly, the existence of martensitic transformation well indicates magnetostriction property of $Cu_{1-x}Mn_xNMn_3$. The calculated value of $1\text{-}c/a$ for $x = 0.20$, 0.40, and 0.50 decreases with the increase of x, indicating the magnetostriction decreases with increasing the Mn-doping level. When $x \ge 0.5$, the magnetostriction vanishes owing to the disappearance of the martensitic transformation. Additionally, the structural analysis shows Mn dopant can obviously depress T_{MS}, which is only 60 K when x is up to 0.4. Considering Sn and Ge elements can effectively broaden the discontinuous lattice expansion, it may be promising to find the low-temperature NTE material by introducing the Sn/Ge dopant in the Cu site of $Cu_{1-x}Mn_xNMn_3$.

Figure 2 displays the temperature dependent magnetization $M(T)$ of $Cu_{1-x}Mn_xNMn_3$ at 100 Oe under zero-field-cooled (ZFC) and field-cooled (FC) modes. $CuNMn_3$ is characterized by a single, first-order phase transition at Curie temperature T_C (143 K).[2,9] As it can be seen from Fig. 2(a), the result is basically consistent with the reported value. However, Figures 2(b)–2(e) show that $Cu_{1-x}Mn_xNMn_3$ ($x = 0.1$, 0.2, 0.3, and 0.4) present two magnetic transitions: The lower one coincides with the martensitic transformation, indicating the magnetostructural correlation and the higher one corresponds to a FM-PM transition, whose temperature is defined as T_C. Obviously, T_{MS} decreases with the increase of x but T_C increases with increasing x. As a result, the FM region becomes broader with increasing x. As shown in Fig. 2(f), for $x = 0.5$, T_C is up to 488 K and the M_{ZFC} curve begins to drop at 5 K which means that martensitic transformation will happen at lower temperature. Generally, antiperovskite manganese compounds were considered to be itinerant magnetism in great variety and the magnetism mainly originates from the Mn atoms.[15,16] In $CuNMn_3$, the Mn_6N octahedron exhibits a three-dimensional geometrical frustration of magnetic interaction. The long-range magnetic order is stabilized under the action including the nearest-neighbor Mn-Mn antiferromagnetic (AFM) interaction and next-nearest-neighbor Mn-N-Mn FM interaction.[17] After the substitution of Mn for Cu, the Mn atoms at the corner would interact with the nearest Mn atoms at the face center, affecting the original magnetic order. The study of magnetic structure for Mn_4N showed that Mn atom at the corner assuredly had an important contribution to the magnetic exchange interaction.[18,19] So, the evolution of T_C in $Cu_{1-x}Mn_xNMn_3$ could be attributed to the gradual enhancement of Mn-Mn direct exchange interaction.

Another obvious character is that there exists a large bifurcation between M_{ZFC} and M_{FC} curves below T_{MS} for $x = 0.1$, 0.2, 0.3, and 0.4. In order to make clear the ground state, the sample with $x = 0.20$ is selected for the further investigations. First, the sample was cooled down at 50 K from 300 K under two different processes: (1) ZFC and (2) FC with $H = 10$ Oe, then the magnetization was recorded as a function of time (t) under (1) 10 Oe and (2) 0 Oe, respectively. As shown in Fig. 3(a), the t-dependent magnetization $M(t)$ curves are plotted for $x = 0.2$ at 50 K. Obviously, the magnetic moment increases with increasing the measured time, which shows the typical characteristic of the relaxation phenomenon. It indicates that the magnetic ground state of this system is far away from the equilibrium state and should be a magnetic metastable state.[20,21] Generally, the appearance of magnetic metastable state is closely correlated with the magnetic frustration or magnetic disorder which maybe

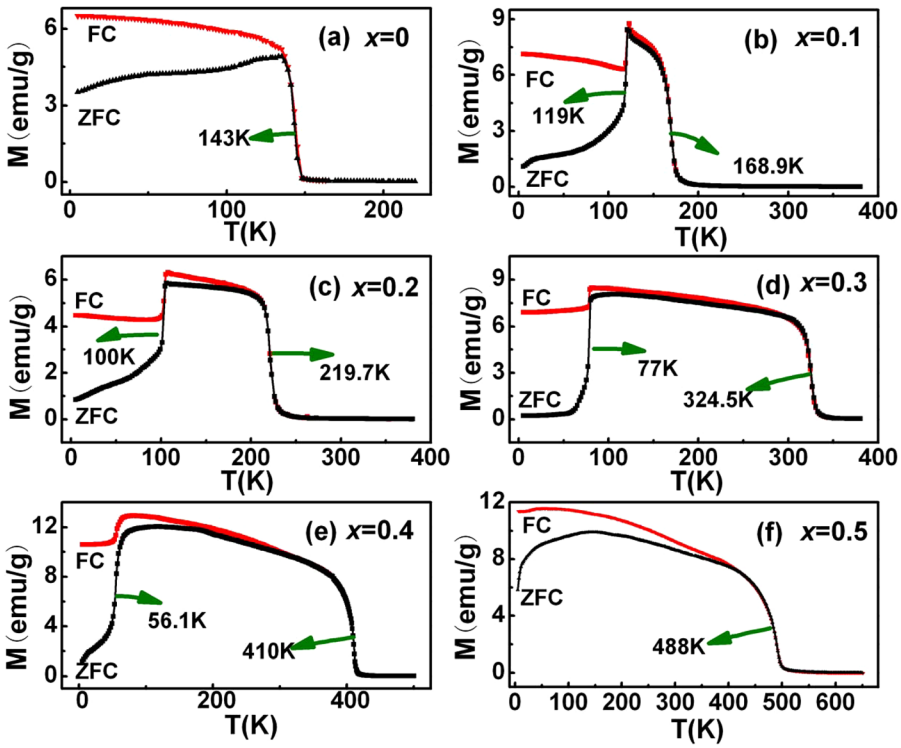

FIG. 2. The temperature dependence of magnetization $M(T)$ for (a) $x=0$, (b) $x=0.1$, (c) $x=0.2$, (d) $x=0.3$, (e) $x=0.4$, and (f) $x=0.5$ under ZFC and FC processes at H = 100 Oe.

originate from the competition between the AFM and FM component after the substitution of Mn for Cu. Representative hysteresis loops for $x=0.2$, measured at different temperatures after ZFC, are shown in Fig. 3(b), respectively. The $M(H)$ curve at 5 K shows a FM behavior and the coercive force (H_C) is about 598 Oe. However, around 150 K (between T_C and T_{MS}), the $M(H)$ curve displays soft FM behavior with $H_C=3$ Oe. As it is well known, H_C is closely connected with magnetocrystalline anisotropy and the pinning of domain wall.[22–24] As reported previously, though the magnetocrystalline anisotropy of stoichiometric $CuNMn_3$ and nitrogen-deficient $CuN_{1-x}Mn_3$ is small, it is still an essential qualification for magnetostriction.[1,3] Similarly, as magnetostriction compounds, the small magnetocrystalline anisotropy should be necessary for $Cu_{1-x}Mn_xNMn_3$($x=0.1$, 0.2, 0.3, and 0.4). Therefore, comparing with the H_C at

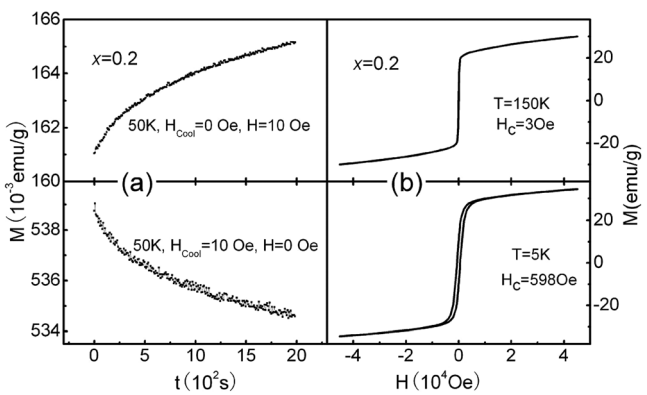

FIG. 3. (a) Time (t) dependence of magnetization (M) under (a) 10 Oe and (b) zero field at 50 K, which were cooled in ZFC and FC (10 Oe) modes, respectively. (b) Magnetic hysteresis loops at 5 K and 150 K for $Cu_{0.8}Mn_{0.2}NMn_3$.

150 K, the larger H_C at 5 K could be attributed to the presence of small magnetocrystalline anisotropy after the martensitic transformation, which may also be associated with the magnetic metastable state below T_{MS}.

The temperature dependent resistivity $\rho(T)$ of $Cu_{1-x}Mn_xNMn_3$ at 0 Oe and 50 kOe is shown in Fig. 4. As it can be seen from Figs. 4(a) and 4(b), the overall behavior of $\rho(T)$ for $x=0.1$ is very similar to that of $x=0$, in which the resistivity decreases first with decreasing the temperature, and then rises abruptly around T_{MS} to reach a maximum and decreases again with further decreasing the temperature. For $x=0.2$, the variation of resistivity shows a metallic behavior at high temperature, an anomalous increase around T_{MS} and a semiconductor-like transport property below T_{MS}. As shown in Figs. 4(d) and 4(e), both $x=0.3$ and $x=0.4$ show the metallic behavior covering the whole temperature range and a kink around T_{MS} (76.9 K for $x=0.3$ and 53.5 K for $x=0.4$). Based on the results of structure, magnetism, and electricity, the anomalous increase or kink around T_{MS} indicates the close correlation among lattice, spin, and charge for $Cu_{1-x}Mn_xNMn_3$. After the application of 50 kOe, a positive magnetoresistance occurs above T_{MS} for $x=0$ which is consistent with the previous report.[2] For $x=0.1$, 0.2, 0.3, and 0.4, the resistivity below T_{MS} is suppressed but the resistivity variation is not obvious above T_{MS} under 50 kOe. For $x=0.5$, no magnetoresistance occurs under 50 kOe in the whole temperature range. Additionally, the field dependence of resistivity at 20 K (below T_{MS}) and 150 K (between T_{MS} and T_C) for $x=0.1$, 0.2, 0.3, and 0.4 are displayed in the insets of Figs. 4(b)–4(e), respectively, exhibiting small negative magnetoresistance below T_{MS} and much smaller positive magnetoresistance above T_{MS}. According to the results of magnetic measurement, the magnetic ground state of $Cu_{1-x}Mn_xNMn_3$ ($x=0.1$, 0.2, 0.3, and 0.4) is a metastable

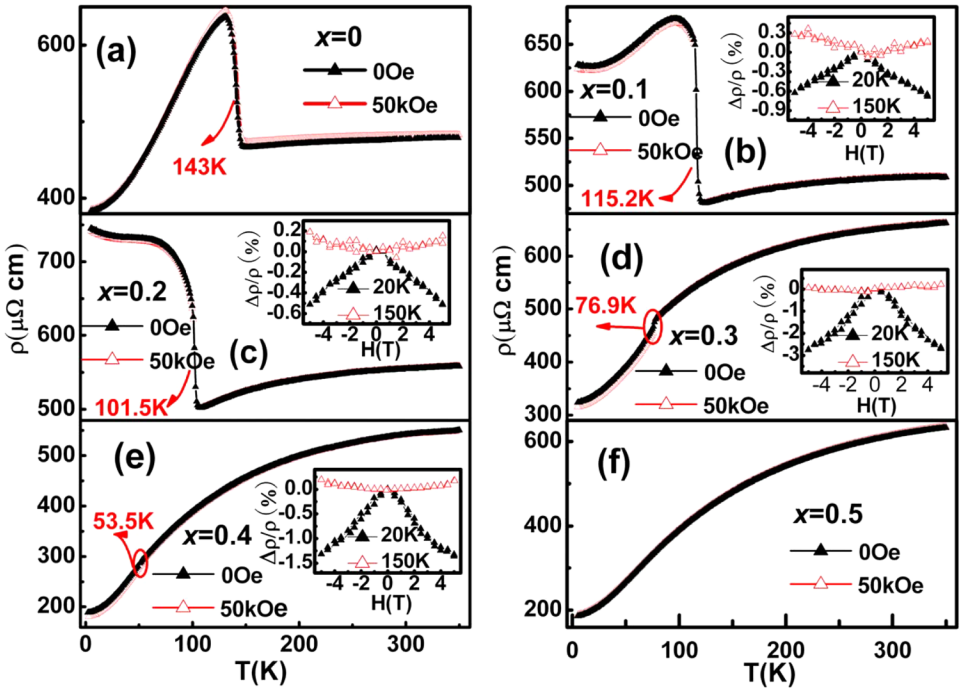

FIG. 4. (a) The temperature dependence of resistivity $\rho(T)$ for $x=0$ at 0 Oe and 50 kOe. (b) $\rho(T)$ for $x=0.1$ under 0 Oe and 50 kOe. Inset: The field dependence of resistivity at 20 K and 150 K for $x=0.1$. (c) $\rho(T)$ for $x=0.2$ under 0 Oe and 50 kOe. Inset: The field dependence of resistivity at 20 K and 150 K for $x=0.2$. (d) $\rho(T)$ for $x=0.3$ under 0 Oe and 50 kOe. Inset: The field dependence of resistivity at 20 K and 150 K for $x=0.3$. (e) $\rho(T)$ for $x=0.4$ under 0 Oe and 50 kOe. Inset: The field dependence of resistivity at 20 K and 150 K for $x=0.4$. (f) $\rho(T)$ for $x=0.5$ under 0 Oe and 50 kOe.

state below T_{MS} where the magnetic frustration or magnetic disorder may exist, which will result in the magnetic scattering. After the application of magnetic field, magnetic state becomes orderly, the magnetic scattering decreases, and the negative magnetoresistance occurs. However, at T = 150 K, $Cu_{1-x}Mn_xNMn_3$ ($x=0.1$, 0.2, 0.3, and 0.4) lie in stable FM state and the Lorentz force contribution plays an important role. Therefore, a smaller positive magnetoresistance is observed. So, the negative magnetoresistance also reflects the essence of a metastable state below T_{MS} for $x=0.1$, 0.2, 0.3, and 0.4.

In summary, we have studied the structural, magnetic, and electrical transport properties of $Cu_{1-x}Mn_xNMn_3$ and discussed the possible functional properties. After the introduction of Mn dopant atoms, martensitic transformation is decoupled from FM transition, FM phase occurs between T_C and T_{MS}, and the tetragonality of the martensitic phase and the magnetostriction are weakened. The spin, charge, and lattice are closely correlated around T_{MS}. The low-temperature martensitic phase is associated with a metastable magnetic state. Meanwhile, the depression of T_{MS} shows that it is promising to find the low-temperature NTE material by introducing the Sn/Ge dopant in the Cu site of $Cu_{1-x}Mn_xNMn_3$.

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