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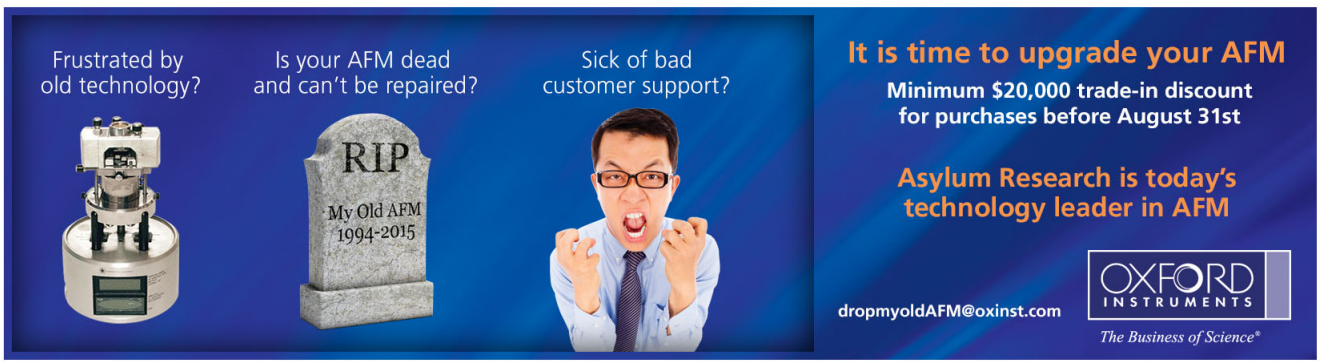

Continuously tunable temperature coefficient of resistivity in antiperovskite $AgN_{1-x}C_xMn_3$ ($0 \le x \le 0.15$)

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The antiperovskite intermetallic compounds $AgN_{1-x}C_xMn_3$ ($0 \le x \le 0.15$) have been synthesized. As x increases, the temperature coefficient of resistivity (TCR) above room temperature decreases monotonically and finally changes the sign from positive to negative above $x = 0.1$. Meanwhile, the temperature range is gradually broadened. For $x = 0.07$, TCR is ~3.1 ppm/K between 280 K and 375 K. Both the resistivity and its slope are insensitive to the external magnetic field, indicating an insignificant contribution from magnetic scattering or short-range magnetic ordering to the observed low-TCR. As manifested by the Hall effect, the charge carrier density in the paramagnetic state for $x = 0.15$ is reduced by an order of magnitude in comparison with that for $x = 0$. The reduction of carrier density and the enhancive disorders when x increases was proposed to be responsible for the decrease in TCR and its sign switch. © *2014 AIP Publishing LLC*.
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I. INTRODUCTION

The electrical resistivity of different materials varies over more than 32 orders of magnitude.[1] Upon heating, resistivity is known to increase in metals, while it decreases in semiconductors or insulators. The precise control of the resistivity value and its temperature dependence is of particular interest both fundamentally and practically. Low temperature coefficient of resistivity (TCR) refers to the phenomenon that resistivity is less temperature dependent in an adequate temperature range, which has been only found in a very limited number of materials so far.[1–4] Materials with a low-TCR play an important role in electronic equipment, such as normal resistors (e.g., wire resistor, wire-wound resistor, and film resistors) in high precision electronic apparatus, thermoelectric devices, and various functional sensors.[5–7] Otherwise, the present commercial low-TCR materials still take on many intrinsic problems (e.g., the environmental pollution and high cost), and extensive work has been done to develop new kinds of low-TCR materials.[8]

The manganese nitrides ordered in the antiperovskite structure with the general formula $ANMn_3$ (A represents for some main group elements, or some 3*d* or 4*d* transition metal elements) provide a new platform for exploring the low TCR effect. $CuNMn_3$ is the first antiperovskite compound in which the low TCR was discovered with the value of 46 ppm/K above T_C (~150 K).[3] Subsequently, low TCR was found in the paramagnetic (PM) state of $NiNMn_3$ and $AgNMn_3$ as well.[9,10] Improved TCR with wider temperature span and reduced magnitude was achieved in chemically doped $ANMn_3$.[8,10–13] However, the underlying physics is still ambiguous for the low-TCR in those materials. A few mechanisms were proposed, such as strong magnetic scattering,[14] short-range ordering,[11] and the balance between opposing changes in carrier density and mobility.[9,15] However, solid experimental results that support those proposed mechanisms are still lacking. Here, we report that partial substitution of C for N in $AgNMn_3$ can effectively convert the TCR value from positive to negative and expand the working temperature range. Moreover, the field dependence of resistivity and TCR indicates that the low TCR is not associated with the magnetism. Instead, the decreasing carrier density as revealed by Hall effect measurement, together with the increasing disorder, was thought to account for the reduced TCR as x increases.

II. EXPERIMENTS

Polycrystalline samples $AgN_{1-x}C_xMn_3$ ($x = 0$, 0.03, 0.05, 0.07, 0.1, and 0.15) were prepared by direct solid-state reaction. The powders of Ag (3N), Mn (4N), C (4N), and self-made Mn_2N were mixed in a desired ratio, pressed into pellets (the pressure is ~25 MPa), sealed in the evacuated tubes (the vacuum degree ~ 10^{-6} torr), and then sintered at 1023 K for three days. Then, the samples were slowly heated to 1073 K and lasted for five days. After the tubes were quenched to room temperature, the products were grounded carefully, pressed into pellets, sealed in the evacuated tubes, and annealed at 1073 K for eight days to obtain the homogeneous samples. X-ray powder diffraction (XRD) was carried out using a Philips X′pert PRO X-ray diffractometer with Cu Kα radiation at room temperature. The diffraction peaks can be indexed with the cubic antiperovskite structure (Space group: *Pm*3*m*), expect for a very small amount of MnO.[16] The resistivity, Hall effect, and specific heat measurements were performed on a physical property measurement system (PPMS, Quantum Design).

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III. RESULTS AND DISCUSSION

In Fig. 1, the temperature dependent resistivity ρ(T) normalized by the value at 230 K, i.e., ρ(T)/ρ(230 K), was plotted for $AgN_{1-x}C_xMn_3$ ($0 \le x \le 0.15$). For the parent compound $AgNMn_3$, it shows a metallic behavior below the antiferromagnetic (AFM) transition temperature ($T_N \sim 278$ K, basically consistent with previously reported[13]). Above T_N, the ρ(T) keeps increasing with a much smaller slope than that below T_N. Upon doping with C on N sites, T_N reduces gradually to 215 K for $x = 0.15$, in agreement with the result of magnetic susceptibility measurement.[16] Meanwhile, the overall slope of ρ(T) decreases as x increases. Interestingly, negative slope of ρ(T) is seen for $x \ge 0.1$. The continuous decrease of the resistivity slope allows for extremely low TCR through the definition, $\rho_0^{-1}(d\rho/dT)$, where ρ_0 is the resistivity at 273 K. As shown in the inset of Fig. 1, the TCR evolves with x in the same way as $d\rho/dT$ does. Especially, for $x = 0.07$, $d\rho/dT$ ($\sim 1.2 \times 10^{-9}\,\Omega$ cm/K) is reduced by an order of magnitude in comparison with that for $x = 0$ ($\sim 4.3 \times 10^{-8}\,\Omega$ cm/K), where the TCR value is only 3.1 ppm/K between 280 K and 375 K. This value is far less than that of commercially available low-TCR materials, such as Manganin (typically 10 ppm/K or less).[10] Taking into account the tendency that the $d\rho/dT$ switches sign somewhere between $x = 0.07$ and 0.1, the TCR can be further decreased at an optimized doping level x, i.e., $0.07 \le x \le 0.1$. This behavior resembles our previous work on $CuN_{1-x}C_xMn_3$ ($0 \le x \le 0.15$) and $CuNMn_{3-y}Co_y$ ($0 \le y \le 0.4$).[8] In those compounds, the TCR reduces gradually as the doping level (x or y) increases and extremely low TCR value is obtained near the critical doping levels where the $d\rho/dT$ changes sign.

It is very common for antiperovskite manganese nitrides that low TCR occurs above the magnetic transitions (either T_N or T_C).[3,8,10–13] So it has been argued that the mechanism of the low TCR is related to the magnetic scattering (in other words, spin-dependent scattering).[10,14] Magnetic scattering is often known as the scattering of conduction carriers by the disordered spins near the magnetic transition.[17] In this sense, an external magnetic field can suppress the magnetic scattering, leading to negative magnetoresistance [$MR = (\rho_H - \rho_0)/\rho_0$].[17] Figure 2(a) shows a comparison of ρ(T) measured at zero magnetic field and at 50 kOe for $x = 0$ and 0.15. It is obvious that the magnetic field does not change the shape of ρ(T), particularly above T_N. Moreover, the ρ(T) at 50 kOe almost overlaps with that measured at zero magnetic field. That is to say, the TCR is barely changeable in a magnetic field as high as 50 kOe. Figures 2(b) and 2(c) display the MR measured up to 40 kOe at selected temperatures near T_N (i.e., 242.5 K, 274.5 K, and 300 K) for $x = 0$ and 0.15, respectively. The magnitude of MR is lower than 0.1% at 40 kOe at all the temperatures measured. Besides, the MR seems insensitive to the magnetic field and temperature. Therefore, the conduction mechanism, i.e., the low TCR for $AgN_{1-x}C_xMn_3$ is irrelevant to the magnetism. The tiny positive MR resembles the MR in simple metals.[17] For metals, the MR is associated with the cyclotron motion which can be significant when $\omega_c\tau \ge 1$, where ω_c and τ are the cyclotron frequency and the time between scattering events, respectively. Large MR could be expected when both ω_c and τ are large, which requires large magnetic field and low resistivity, respectively. The longer the relaxation time, the greater will be the influence of magnetic field on the resistivity. For polycrystalline copper, the positive MR reaches ~100% at 4.2 K under a magnetic field of 50 kOe.[18] The relatively small positive MR in current compounds may reflect the fact that their resistivity ($\sim 10^2\,\mu\Omega$·cm) is orders of magnitude larger than that in common metals ($\sim 10^{-2}$–$10^1\,\mu\Omega$·cm).[19]

Figure 3(a) shows the magnetic field dependent Hall resistivity ρ_{xy} for the parent compound $AgNMn_3$ at selected temperatures. At elevated temperatures, ρ_{xy} exhibits a linear temperature dependence, while at low temperatures (e.g., at 90 K), ρ_{xy} undergoes a sharp increase in low magnetic fields before becoming saturated at higher magnetic fields, which is ascribed to an anomalous Hall effect.[20] The glass-like ground state below 161 K may explain the anomalous Hall

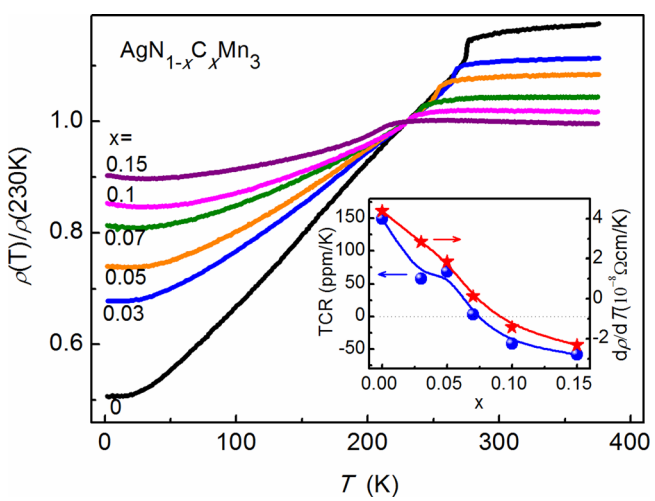

FIG. 1. Temperature dependent resistivity for $AgN_{1-x}C_xMn_3(0 \le x \le 0.15)$ normalized by the data at 230 K. Inset shows the TCR and the slope of resistivity ($d\rho/dT$) as a function of x.

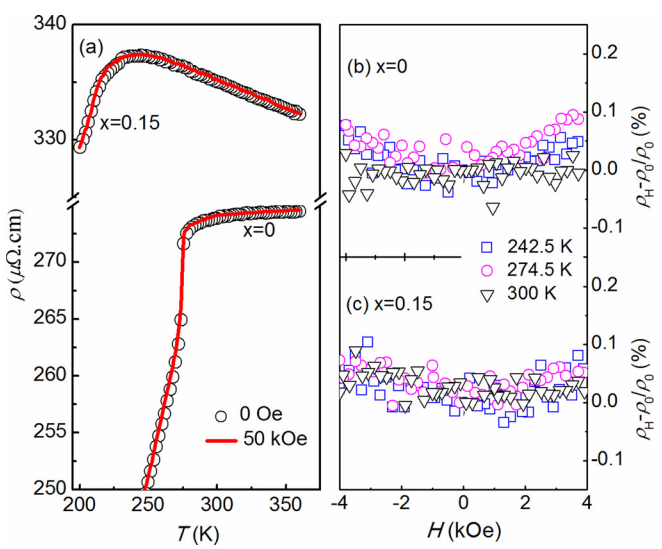

FIG. 2. The resistivity measured at both zero magnetic field and 50 kOe (a). The field dependent magnetoresistance in magnetic fields up to 40 kOe at selected temperatures for $x = 0.1$ (b) and $x = 0.15$ (c).

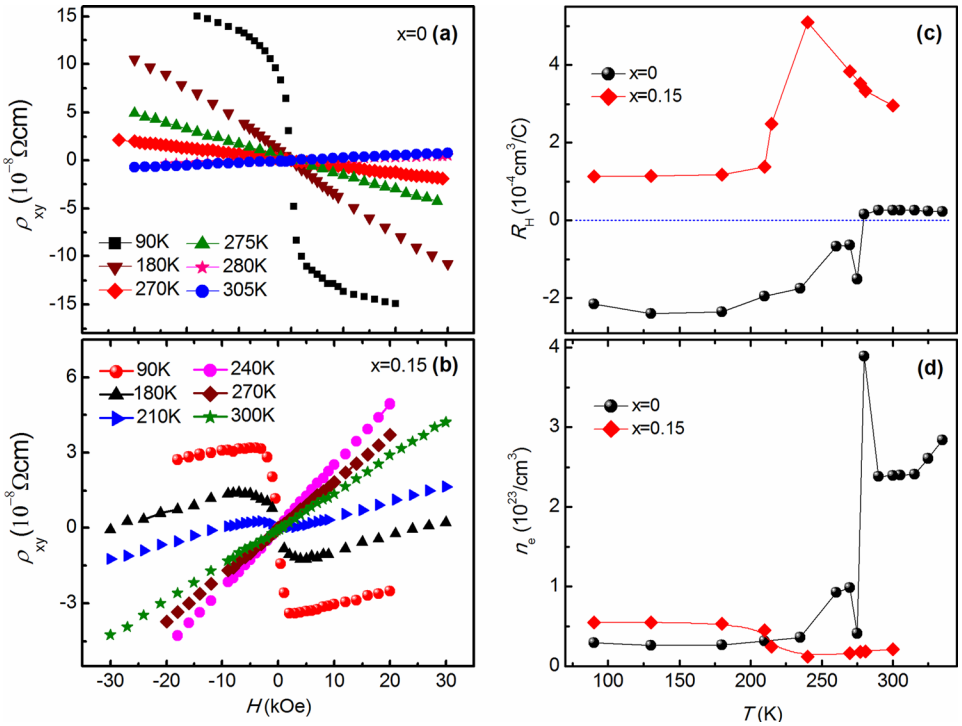

FIG. 3. Hall resistivity (ρ_{xy}) at various temperatures measured in the magnetic fields up to 30 kOe for $AgN_{1-x}C_xMn_3$ with $x=0$ (a) and 0.15 (b). The deduced temperature dependent Hall coefficient (R_H) and carrier density (n) for both $x=0$ and 0.15 are plotted in (c) and (d), respectively.

effect.[16] In addition, the slope of $d\rho_{xy}/dT$ at high magnetic fields switches from positive at high temperatures (e.g., 280 K and 305 K) to negative at low temperatures. As shown in Fig. 3(b), anomalous Hall effect is also observed for $x=0.15$, e.g., at 90 K, 180 K, and 210 K. Unlike the parent compound, the $d\rho_{xy}/dT$ for $x=0.15$ is always positive in the entire temperature region under investigation. The Hall coefficient (R_H) obtained from high field $d\rho_{xy}/dT$ is plotted in Fig. 3(c) as a function of temperature for both $x=0$ and 0.15 compounds. For $x=0$, the R_H is always positive, indicating that the conduction carriers are hole-like. As for $x=0.15$, the R_H changes its sign from negative below T_N to positive above T_N. This indicates that the dominant carriers change from electron-type to hole-type when crossing T_N from below. Usually, the carrier density n can be calculated by taking the relation $n=1/|eR_H|$ in single band model, where e is the elementary electric charge. Therefore, we can roughly estimate the n value by this formula. As shown in Fig. 3(d), the n value for $x=0.15$ is slightly larger than that for $x=0$ below 200 K. For $x=0$, the n value is increased by one order of magnitude in the PM state in comparison with the AFM state. On the contrary, the n value for $x=0.15$ shows a clear reduction at T_N upon heating. Consequently, 15% substitution of N sites with C causes a reduction of carrier density by an order of magnitude at room temperature. The abrupt changes of the Hall effect at T_N indicate a sudden reconstruction of the electronic structure, i.e., the density of states (DOS) near the Fermi level, E_F.

Figure 4 shows the specific heat as a function of temperature for $x=0$ and 0.15. The AFM transition is evidenced by a peak in the $C(T)$ curve at 211 K for $x=0$ and 277 K for $x=0.15$, basically in line with the resistivity data shown in Fig. 1. As shown in the inset of Fig. 4, the low-temperature data, plotted as $C(T)/T$ vs. T^2, can be well fitted linearly by using the expression, $C(T)/T=\gamma+\beta T^2$, where γ (the Sommerfeld constant) represents the electronic contribution, the second term is the lattice contribution according to the Debye approximation.[21] The obtained values of γ are 42.3 mJ/mol K^2 and 51.4 mJ/mol K^2 for $x=0$ and 0.15, respectively, indicating a larger DOS at E_F in $x=0.15$ than in $x=0$. This is in agreement with the larger carrier concentration in $x=0.15$ than that in $x=0$ at low temperatures, as shown in Fig. 3(d). By taking the formula, $\Theta_D=(n\times1.944\times10^6/\beta)^{1/3}$ (n, the number of atoms in a unit cell) and the fitted β value, the Debye temperature Θ_D is estimated to be 356 K and 318 K for $x=0$ and 0.15, respectively.

Now we turn back to the small or even negative TCR shown in Fig. 1 for $AgN_{1-x}C_xMn_3$. It is normal for semiconductors to show a negative TCR, where the electronic transport is dominated by thermally excited carriers. However,

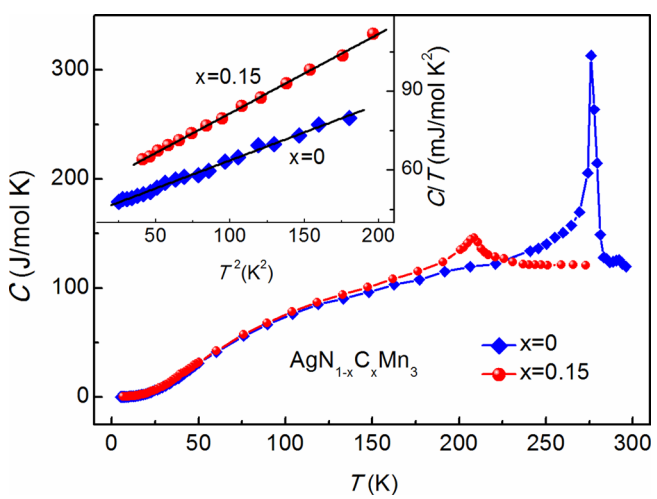

FIG. 4. Specific heat $C(T)$s for $AgN_{1-x}C_xMn_3$ with $x=0$ and 0.15. Inset shows the low-temperature $C(T)$ plotted as $C(T)/T$ vs. T^2 and a linear fitting (solid line) for both compounds.

the carrier density in $AgN_{1-x}C_xMn_3$ (e.g., $2.1 \times 10^{22}\,cm^{-3}$ for $x = 0.15$) is close to that of common metals (e.g., $8.45 \times 10^{22}\,cm^{-3}$ in copper), but it is a few orders of magnitude larger than that in conventional semiconductors (less than $10^{18}\,cm^{-3}$).[19] In fact, our initial optical absorption experiment did not show any signals of energy gap as a common semiconductor would show.[16] This indicates the scenario that the balance between opposing changes in carrier density and mobility causes a low TCR is not applicable here since it was initially proposed for semiconductors.[15] Then, how can a material with metal-like high concentration of charge carries take on a semiconductor-like negative slope of resistivity? Decades ago, Mooij studied the transport properties of a number of disordered metals and metallic alloys (~122 compounds) and found a ''universal'' relation between the resistivity and TCR, i.e., TCR decreases with the increase of residual resistivity and becomes negative if resistivity is above $150\,\mu\Omega\cdot cm$.[22] Later, Tsuei expanded Mooij's criterion to a range of $30\,\mu\Omega\cdot cm$–$400\,\mu\Omega\cdot cm$ on the basis of the data of more than 500 compounds.[23] Such a correlation between the high resistivity and negative TCR is mainly attributed to the competition between the quantum-mechanical effects of incipient localization (weak localization) due to disorders and classical Boltzmann electron transport.[23] It is natural that doping can introduce disorders because the dopant atoms statistically occupy sites in the host lattice. In $AgN_{1-x}C_xMn_3$, particularly for $x = 0.15$, the high residual resistivity ($\sim 360\ \mu\Omega\cdot cm$) is clearly larger than the Mooij's criterion and close to the upper bound of the criterion range proposed by Tsuei. The residual resistivity ratio (RRR) is reduced remarkably from 2.3 for $x = 0$ to 1.1 for $x = 0.15$, indicating an increasing magnitude of disorders. The disorders lead to a reduced mean free path for conduction carriers (l_e), and tend to reduce the TCR to a negative value.[1,23] Another key factor that could influence the slope of resistivity is the Fermi wave vector (k_F) which is related to the charge carrier density n by $n \sim {k_F}^3$. A small k_F value was considered to fulfill the disorder-induced negative TCR in quasicrystals.[24] Thus, as plotted in Fig. 3(d), the reduction of n at high temperatures due to carbon doping may account, at least partially, for the decrease in magnitude of TCR and the signal switch in terms of weak localization. Regardless of the above discussions, to get a thorough understanding of the negative TCR in current compounds or other antiperovskite manganese nitrides, a detailed investigation of the electronic structure is desirable.

IV. CONCLUSION

In summary, we have successfully synthesized the antiperovskite compounds $AgN_{1-x}C_xMn_3 (0 \le x \le 0.15)$. With the increase in x, the TCR above room temperature decreases and eventually changes the sign from positive to negative when $x \ge 0.1$. Meanwhile, the temperature range is gradually broadened. A very low TCR of 3.1 ppm/K between 280 K and 375 K can be observed in $x = 0.07$, which is close to the critical value of x where the TCR changes sign. Absolute Zero TCR is expected at an optimized doping level between $x = 0.07$ and 0.1, indicating a great potential for practical application as standard-resistor materials. The immunity of the resistivity and TCR to the external magnetic field as high as 50 kOe may exclude the magnetic scattering or short-range magnetic ordering as a possible mechanism for the observed low-TCR. As demonstrated by Hall effect measurement, the carrier density for $x = 0.15$ is slightly increased below 200 K while dramatically reduced by an order of magnitude at room temperature in comparison with that for the parent compound. The reduction of carrier density probably due to the reconstruction of electronic structure, along with the increasing intrinsic disorders, is suggested to be responsible for the decreasing TCR and its signal change with increasing x.

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