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Research Article

Synthesis, Magnetization, and Electrical Transport Properties of $Mn_3Zn_{0.9}Cu_{0.1}N$

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We synthesized $Mn_3Zn_{0.9}Cu_{0.1}N$ by solid state reaction, and magnetic as well as electrical transport properties were investigated. It is found that $Mn_3Zn_{0.9}Cu_{0.1}N$ exhibits a first-order antiferromagnetism (AFM) to paramagnetic (PM) transition with the Néel temperature T_N ~163 K, and substitution of Cu for Zn would favor ferromagnetism (FM) state and weaken AFM ground state, leading to a convex curvature character of *M(T)* curve. With high external fields 10 kOe–50 kOe, magnetic transition remains a robust AFM-PM feature while FM phase is completely suppressed. Thermal hysteresis of *M(T)* under 500 Oe is also suppressed when the magnetic field exceeds 10 kOe. $Mn_3Zn_{0.9}Cu_{0.1}N$ exhibits a good metallic behavior except for a slope change around T_N, which is closely related to AFM-PM magnetic transition. Compared with the first differential of resistivity with respect to temperature for $(d\rho/dT)_{Mn_3ZnN}$ in transition temperature range, the absolute value of $(d\rho/dT)_{Mn_3Zn_{0.9}Cu_{0.1}N}$ is much lower which is close to zero.

1. Introduction

The Mn-based antiperovskite compounds Mn_3XN (X = Cu, Zn, Ga, Sn, and so on) have attracted considerable attentions because of the discoveries of interesting properties such as non-Fermi liquid behavior [1, 2], magnetoresistance [3, 4], negative thermal expansion (NTE) [5–7], zero thermal expansion (ZTE) [8, 9], spin-glass behavior [10], and large negative magnetocaloric effect (MCE) [11–14].

As a typical member of Mn_3XN, Mn_3ZnN has been intensively investigated, and some novel properties have been observed like unusual phase separation and resistive switching phenomenon around antiferromagnetism (AFM) to paramagnetic (PM) transition [15, 16]. More interestingly, it has been confirmed that properties of Mn_3ZnN can be sensitively influenced by partial substitution at Zn sites, 1*a* (0,0,0) by other elements or even vacancies. For example, Sun et al. found that an obvious NTE phenomenon appears in $Mn_3Zn_{0.5}Ge_{0.5}N$ and ZTE behavior in $Mn_3Zn_{0.7}Sn_{0.3}N$, while abrupt lattice contraction near magnetic transition does not appear in Mn_3ZnN [17]. Very recently, Wang et al. demonstrated that NTE features in Mn_3Zn_xN can be induced and tuned by modulating the Zn occupancy [9].

It is of great interests to further probe the intrinsic relation between properties and substitution element or V_{Zn}, at 1*a* (0,0,0) sites, and understanding the novel properties origin is useful in attaining new insight on the magnetic mechanism in such a strong related system. All these make the further extensive experimental investigations on Mn_3ZnXN highly desirable for solving these puzzles. To this end, we choose Cu element as another attempt to address this issue. In this paper, we synthesized $Mn_3Zn_{0.9}Cu_{0.1}N$ by solid state reaction and magnetic, electrical transport properties were investigated. It is found that $Mn_3Zn_{0.9}Cu_{0.1}N$ exhibit

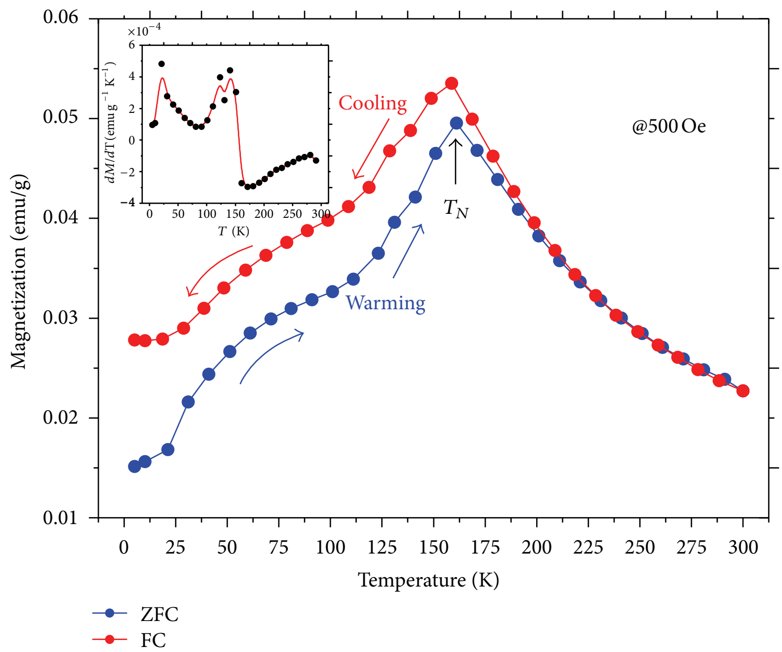

Figure 1: Temperature dependence of magnetization $M(T)$ under FC and ZFC processes measured at 500 Oe. Inset shows the temperature dependence of dM/dT.

a typical AFM-PM transition with the Néel temperature of T_N ~163 K. Substitution of Cu for Zn favors FM state and weakens AFM ground state in $Mn_3Zn_{0.9}Cu_{0.1}N$. Under high external fields (10 kOe–50 kOe), AFM-PM transition feature remains robust where FM phase is completely suppressed. Further, $Mn_3Zn_{0.9}Cu_{0.1}N$ exhibits a good metallic behavior except for a slope change around T_N and shows a normal Fermi liquid behavior in a low temperature range from 5 K to 80 K. While compared with $(d\rho/dT)_{Mn_3ZnN}$ in transition temperature range, the absolute value of $d\rho/dT$ is much lower and is close to zero.

2. Experiment

Sintered polycrystalline samples of $Mn_3Zn_{0.9}Cu_{0.1}N$ were prepared by a solid state reaction. Mn_2N (homemade, 99.9%), and high purity Zn (Alfa, 99.99%), high purity Cu (Alfa, 99.99%) were mixed in the stoichiometric proportion and pressed into a pellet. The pellet was wrapped by tantalum foil and placed into a quartz tube and then was vacuumized to 10^{-5} Pa. The quartz tube was sealed and heated at 850°C for 96 h. The as-synthesized sample was characterized by high-resolution X-ray diffraction diffractometer (XRD, Philips X'PERT MPD) with cell parameter calculated from Rietveld analysis of XRD pattern $a = 3.89965$ Å, space group $Pm3m$. It is less than that of Mn_3ZnN (ICDD-PDF: 23–0229, space group $Pm3m$). Magnetization measurements were performed with a commercial superconducting quantum interference device (SQUID). Both field-cooled (FC) and zero-field-cooled (ZFC) magnetizations were measured from 10 K to 300 K. The resistivity was measured using the standard four-probe technique in a physical property measurement system (Quantum Design, PPMS).

3. Results and Discussion

Temperature dependence of magnetization $M(T)$ measured in both FC and ZFC of $Mn_3Zn_{0.9}Cu_{0.1}N$ is shown in Figure 1. A clear AFM-PM transition can be seen in both sets of data around the Néel temperature T_N ~163 K, although T_N obtained in the FC cycle shifts to a lower temperature from ZFC cycle by about 8 K. The thermal hysteresis in $M(T)$ curves, particularly near T_N, implies a first-ordered magnetic transition in $Mn_3Zn_{0.9}Cu_{0.1}N$. Similar result has been observed in Mn_3ZnN by Kim et al. [18]. With decreasing the temperature, as shown in the inset, the absolute value of dM/dT decreases near $T = 125$ K from 2.0×10^{-4} emu/(g·K) to 0.8×10^{-4} emu/(g·K) and $M(T)$ curve shows an abnormal convex curvature from 125 K to 25 K, indicating an existence of FM state at low temperature. This result should be ascribed to the substitution of Cu in $Mn_3Zn_{0.9}Cu_{0.1}N$. It is well known that FM phase in low-T region is intrinsic property of Mn_3CuN [19, 20], thus Cu doping in $Mn_3Zn_{0.9}Cu_{0.1}N$ would favor FM state and weaken AFM ground state, and $M(T)$ curve correspondingly exhibits a convex curvature character.

Figure 2 presents the temperature dependence of magnetization $M(T)$ measured at several magnetic fields (10 kOe, 20 kOe, 30 kOe, 40 kOe, and 50 kOe). It can be seen that AFM-PM transition always located near T_N of ~163 K under different external fields, while the FM phase (as shown in Figure 1) has been completely suppressed beyond 10 kOe, implying that below T_N, the AFM phase is relatively robust

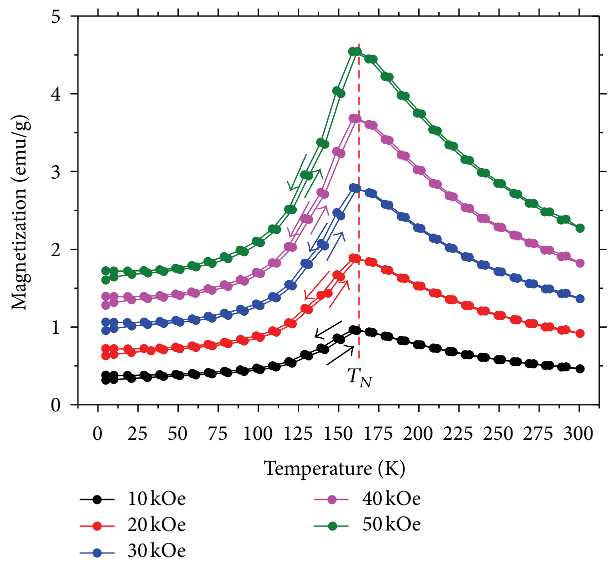

FIGURE 2: Temperature-dependent magnetization $M(T)$ of $Mn_3Zn_{0.9}Cu_{0.1}N$ measured during both FC and ZFC processes at several magnetic fields. The arrows indicate the direction of temperature circle.

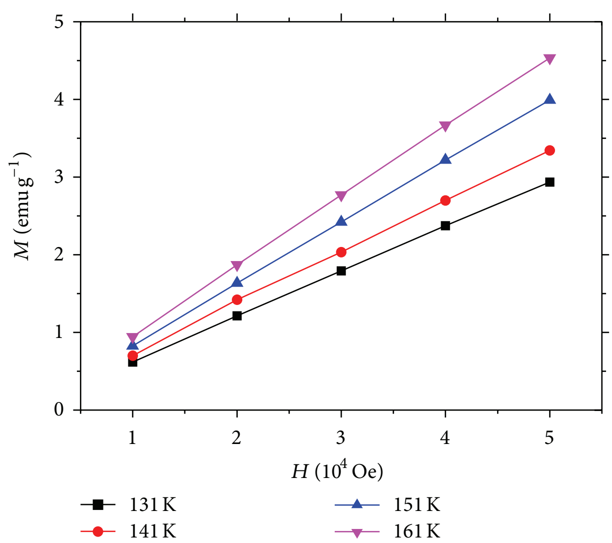

FIGURE 3: Magnetization versus magnetic field M versus H at several temperature around T_N for $Mn_3Zn_{0.9}Cu_{0.1}N$.

while FM phase is metastable in this case. Further, it is worthy to note that the thermal hysteresis of $M(T)$ curves displayed in Figure 1 is also suppressed when the magnetic field exceeds 10 kOe. It can be seen that magnetization is not saturated even when the external field H exceeds 50 kOe; to demonstrate this feature clearly, magnetization versus magnetic field (M versus H) around T_N is plotted in Figure 3, and the isotherms curves $M(H)$ are nearly linear with increasing of H.

Figure 4 illustrates the temperature dependence of resistivity $\rho(T)$ of $Mn_3Zn_{0.9}Cu_{0.1}N$ from 10 K to 300 K under 0 kOe, 10 kOe, and 50 kOe, respectively. $Mn_3Zn_{0.9}Cu_{0.1}N$ exhibits a typical metallic behavior except for a slope change around 162 K, which is closely related to AFM-PM transition, similar phenomena have been observed in other systems [21], where ρ decreases due to the orientation of magnetic moments from AFM ordering. However, no magnetoresistance appears during the whole temperature ranges in this study. Simultaneously, we note that the absolute value of $d\rho/dT$ in the transition temperature range of 140 K–162 K nearly decreases to zero, as shown in the bottom inset of Figure 4, which is lower than that of Mn_3ZnN as reported in [6]. Previous investigations have shown that there exists an unusual conduction property, namely, low temperature coefficient of resistivity (TCR) in Mn_3CuN above magnetic transition temperature; that is, the absolute value of $d\rho/dT$ is close to zero in this temperature range [22]. Moreover, in [23] it is assumed that Cu–N bonds serve as the key role to induce low TCR feature in nitrides. Therefore, it is

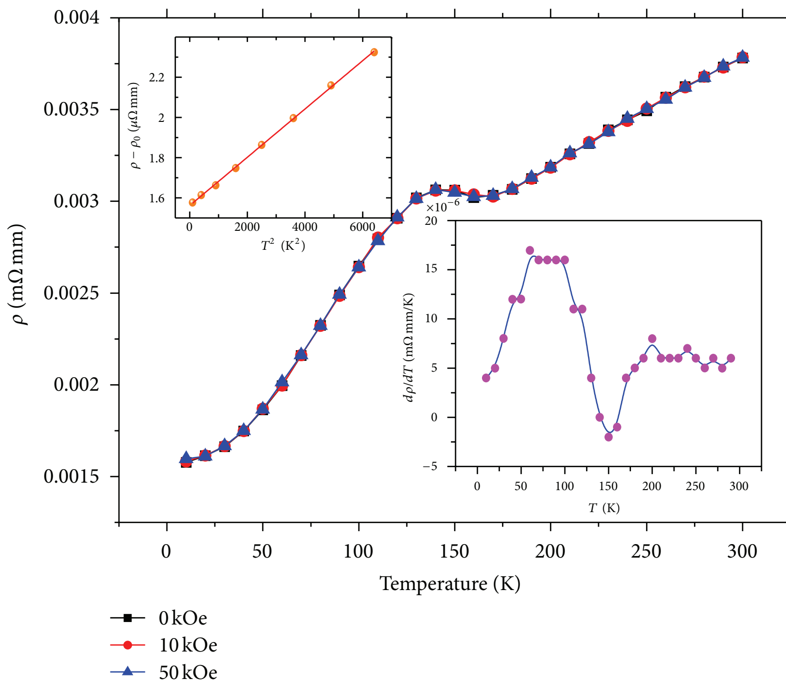

FIGURE 4: Temperature-dependent resistivity of $Mn_3Zn_{0.9}Cu_{0.1}N$ measured at $H = 0$ kOe, 10 kOe, and 50 kOe. The top inset: linear fitting of $\rho - \rho_0$ versus T^2 below 80 K according to (1). The bottom inset: temperature dependence of $d\rho/dT$.

reasonable to suggest the plateau-like $\rho(T)$ curve around T_N in $Mn_3Zn_{0.9}Cu_{0.1}N$ could be well understood in terms of partial doping effect induced by Cu. The top inset in Figure 4 shows a linear relationship between ρ and T^2 below 80 K, which agrees well with the following equation:

$$\rho = \rho_0 + AT^2, \quad (1)$$

where ρ_0 is residual resistivity and A is constant; this result implys a Fermi liquid behavior that exists in $Mn_3Zn_{0.9}Cu_{0.1}N$ in temperature range $T < 80$ K [1]. In this sense, we assumed that the electron-electron scatterings are dominant in this temperature range. However, with temperature increasing, the number of phonon sharply increases and phonon scatterings enhance accordingly, as one can see in temperature range 80 K $< T <$ 140 K and 162 K $< T <$ 300 K linear relationship between ρ-T indicates that electron-phonon scatterings exceed electron-electron scatterings in the temperature ranges mentioned above.

4. Conclusion

In summary, we synthesized $Mn_3Zn_{0.9}Cu_{0.1}N$ by solid state reaction, and magnetic as well as electrical transport properties were investigated. It is found that $Mn_3Zn_{0.9}Cu_{0.1}N$ exhibits a first-ordered antiferromagnetism (AFM) to paramagnetic (PM) transition with the Néel temperature T_N ~163 K, and substitution of Cu for Zn would favor FM state and weaken AFM ground state, leading to a convex curvature characterof $M(T)$ curve. Further, we found that under high external fields 10 kOe–50 kOe magnetic transition remains a robust feature of AFM-PM while FM phase is completely suppressed. Further, thermal hysteresis of$M(T)$ exhibited at 500 Oe is also suppressed when the magnetic field exceeds 10 kOe. $Mn_3Zn_{0.9}Cu_{0.1}N$ exhibits a good metallic behavior except for a slope change around T_N, which is closely related to AFM-PM magnetic transition. Compared with first differential of resistivity with respect to temperature for $Mn_3ZnN(d\rho/dT)_{Mn_3ZnN}$ in transition temperature range, the absolute value of $(d\rho/dT)_{Mn_3Zn_{0.9}Cu_{0.1}N}$ is much lower and is close to zero.

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