Magnetic and electrical properties of antiperovskite Mn$_3$InN synthesized by a high-pressure method

Y. S. Sun$^1$, Y. F. Guo$^1$, X. X. Wang$^{2,3}$, W. Yi$^1$, J. J. Li$^{2,3}$, S. B. Zhang$^1$, C. I. Sathish$^{2,3}$, A. A. Belik$^1$, K. Yamaura$^{2,3,4}$

$^1$International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044 Ibaraki, Japan
$^2$Department of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan
$^3$Superconducting Properties Unit, National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044 Ibaraki, Japan
$^4$JST, Transformative Research-Project on Iron Pnictides (TRIP), Tsukuba, 305-0044 Ibaraki, Japan

E-mail: SUN.Ying@nims.go.jp

Abstract. Mn$_3$InN antiperovskite is synthesized under high-pressure conditions, followed by measurements of magnetic susceptibility, isothermal magnetization, electrical resistivity, and specific heat. Multiple magnetic interactions are observed between 2 K and 400 K: the paramagnetic state turns to an antiferromagnetic state at 300 K on cooling, and a weak ferromagnetic contribution appears at 175 K by further cooling. Below 50 K, an enhanced ferromagnetic contribution is obvious. Although a long-range antiferromagnetic order is clearly established at room temperature, the material retains a good metallic conduction over a wide temperature range (the Sommerfeld coefficient is 43.3 mJ mol$^{-1}$ K$^{-2}$), suggesting a possible use of the material in spintronics applications.

1. Introduction

Interest in antiperovskite material with the formula Mn$_3$XN ($X$ = Ga, Zn, Cu, Ge, and Sn) has been renewed in recent years largely owing to the discovery of various phenomena such as giant magnetoresistance [1], superconductivity [2], and magnetostriction [3], those hopefully provide technical uses. In addition, associated crystallographic and magnetic properties of the materials are highly intriguing in connection with mutual interactions among those freedom of lattice, spin, and charge [4]. The band structure of Mn$_3$XN is significantly mediated by chemical bonding of MnN$_6$ octahedra, which forms a relatively narrow band [5]. This probably results in rich varieties of electronic properties of the materials because the conduction band of $X$ highly overlap with the narrow band [6] and the proximity of the Fermi level to singularities of the narrow band may lead intense coupling among localized electrons, non-localized electrons, and the phonons [7].

So far studies on large numbers of antiperovskite materials seem to reveal additional unusual electronic features; for instance large negative thermal expansion (NTE) in the Ge-doped Mn$_3$CuN [8, 9], and a near zero temperature coefficient of resistivity (TCR) above 150 K in Mn$_3$CuN [10] and Mn$_3$NiN [11]. Besides, Lukashev et al. recently reported frustrated spin density waves under mechanical stress of the Mn-based antiperovskites [12]. Song et al. reported spin-glass behaviors of Mn$_3$GaN [13]. The entire results, however, seems to somewhat controversial in part, hampering better understanding of the electronic properties of the materials, unfortunately. To solve the issues and make progress toward possible applications of the materials, additional studies including search for novel antiperovskite are still highly required.
As far as we know, a member of the family Mn$_3$InN was yet unstudied. We thus carefully conducted synthesis and primary characterizations of the electronic properties and structure of the antiperovskite Mn$_3$InN in this study.

2. Experimental

Polycrystalline Mn$_3$InN was prepared from powders of Mn$_2$N and In (99%) as follows. The binary precursor Mn$_2$N was prepared by firing Mn powder (99.99%) in nitrogen at 800 °C for 60 hr. The stoichiometric powders were thoroughly mixed and sealed into an Au capsule with a BN inner, which avoids direct reactions between the powder and Au. The assembled capsule was heated in a belt-type apparatus which is capable of maintain 6 GPa during heating at 1250 °C for 1 hr. The capsule was then quenched to ambient temperature before releasing the pressure.

Sample purity was investigated by powder X-ray diffraction (XRD). Panalytical X’Pert Pro multipurpose x-ray diffractometer with Cu-K$_\alpha$ radiation was used in the 2$\theta$ range from 5° to 90° with step size of 0.2°. DC magnetic susceptibility ($\chi$) of loosely gathered sample powder was measured in a magnetic property measurements system (Quantum Design) between 2 K and 400 K in an applied magnetic field of 100 Oe under both the zero-field-cooling (ZFC) and field-cooling (FC) conditions. Isothermal magnetization was measured between −50 and 50 kOe at 10 K, 100 K, and 200 K in the same apparatus. Measurements of resistivity ($\rho$) and specific heat ($C_p$) were conducted in a physical properties measurements system (Quantum Design) between 2 K and 400 K. A conventional four-probe technique was used for the $\rho$ measurement. $C_p$ was measured by a time-relaxation method in the same apparatus.

3. Results and discussion

The XRD pattern for Mn$_3$InN is shown in Figure 1. All Bragg reflections are well characterized by a cubic unit cell with $Pm\bar{3}m$ space group. Shown by the inset to Figure 1, the cubic cell consists of Mn atoms at the face-centered position and In atoms at the corner position and N atoms at the body-centered position. The lattice constant was calculated in the analysis to be 4.029(1) Å. Additional minute peaks are aroused from tiny amount of impurities of In and MnO. Absence of anomalies in $\chi$ and $C_p$ data shown later suggested that these impurities little hinder the characterizations of this study.

Figure 1. XRD pattern of Mn$_3$InN antiperovskite collected at room temperature.

Figure 2 depicts the temperature dependence of $\chi$ of Mn$_3$InN, measured in both the ZFC and FC processes in a dc magnetic field of 100 Oe. Above 300 K, the magnetic ground state is primarily paramagnetic (PM), while seen from the inset of Figure 2, $\chi(T)$ shows remarkably steep increase around 300 K and 175 K, indicating magnetic transitions. A plateau of $\chi(T)$ was observed in the temperature range between the two transitions. Additional magnetic anomaly was also observed around
50 K by further cooling. The characteristic magnetic behaviors are more sharply observed in the FC process. The difference between $M_{ZFC}$ and $M_{FC}$ curves may be microscopically understood as a result of competition between multiple magnetic interactions.

Figure 2. Temperature dependence of $\chi$ for antiperovskite Mn$_3$InN taken at 100 Oe.

Figure 3. Isothermal magnetization curves of antiperovskite Mn$_3$InN measured at 10K, 100K, and 200K.

To shed more light on the nature of the multiple magnetic transitions, we measured isothermal magnetization at various temperatures as shown in Figure 3. At 200 K, the $M(H)$ curve is almost linear, suggesting that the magnetic state between 300 K and 175 K is likely antiferromagnetic (AFM). Upon cooling, weak ferromagnetic (WFM) state seems to subsequently develop, accompanied by magnetic hysteresis with a coercive field of ~300 Oe (100 K). However, the magnetization does not saturate even at the highest limit 50 kOe. It still possesses linear $H$-dependence and far away from the expected saturation. The hysteresis loop obviously grows up larger with decreasing temperature (100 K-10 K), suggesting that the magnetic ground state is dominated by AFM correlations and minor WFM correlations. If the picture is true, the magnetization should be expressed by the form $M_F + \chi_{AF} H$, where $M_F$ is the FM component and $\chi_{AF}$ is the slope of $M(H)$ at high field. With temperature decreasing to 10 K, the coercive field remarkably grows remarkably to 2600 Oe, implying presence of an enhanced FM (EFM) ordering. After 50K, the WFM component becomes gradually stronger with decreasing temperature due to the triangular spin rearrangement, results in the occurrence of EFM. However, the AFM interactions are still dominant because the magnetization is still far below the expected saturation.
Combined with the magnetic susceptibility results, we propose the following picture for the magnetic properties of the antiperovskite Mn$_3$InN: three states at least exist in the range between 2 K and 300 K; at high temperature it is PM (> 300 K) and AFM correlations start developing at around 300 K on cooling, and at 175 K additional WFM interactions are established. Further cooling turns on the E FM state below approximately 50 K.

Figure 4 plots the resistivity of the polycrystalline Mn$_3$InN as a function of temperature. The curve shows continuous decrease upon cooling to 2 K from 400 K with a positive curvature ($d\rho/dT > 0$), indicating a metallic conduction. Independent measurement on warming coincides well with the cooling curve, suggesting well productivity of the result and absence of thermal hysteresis over the temperature range. Since any anomaly suggestive of impurity contributions is insignificant, the impurities such as In and MnO seems to play a trivial role during the transport. For more precise analysis, $d\rho/dT$ vs. $T$ is shown in the inset to Figure 4. It reveals two anomalies around 50 K and 300 K, corresponding to the appearance of AFM and the enhanced FM transition, respectively. This may be due to possible coupling between the magnetic order and the charge transport in this compound.

Figure 4. Temperature dependence of resistivity in the cooling and warming process, respectively. The inset shows the data of $d\rho/dT$ vs $T$.

Figure 5. Temperature dependence of specific heat of Mn$_3$InN. The inset shows the fit of $C_p/T$ vs $T^2$ at lowest temperature limit.

Magnetic properties of Mn$_3$InN were further studied by measurements of $C_p$ between 2 K and 400 K. As shown in Figure 5, a notable peak corresponding to the PM-AFM transition was observed at $T\approx$300 K as the derived from $dC_p/dT$ is in good agreement with the derived from $d\rho/dT$ (not shown). The peak part was roughly separated from the body of the $C_p$ data by applying a polynomial function,
allowing us to estimate the entropy change to be 0.24R. In addition, anomalies corresponding to the other two magnetic transitions were undetected probably because the two transitions at low temperature solely result from a spin reorientation. At low temperature limit \( T << \Theta_D \), below 10 K, \( C_p \) was analyzed by using the approximate Debye model: \( \frac{C(T)}{T} = \gamma + 2.4\pi^4nN_0k_B(1/\Theta_D^3)T^2 \), where \( n \) denotes the number of atoms per formula unit, \( k_B \) is the Boltzmann constant, and \( N_0 \) is the Avogadro constant, respectively. Fitting to the linear part of \( C_p/T \) vs. \( T^2 \) by a least-squares method yielded the Sommerfeld coefficient \( \gamma \) (the electronic contribution to the heat capacity) and the Debye temperature \( \Theta_D \) (lattice contribution) to be 43.26(1) mJ mol\(^{-1}\) K\(^{-2}\) and 262(2) K, respectively. The obtained \( \gamma \) has higher value than the usual ones for pure 3d metals, indicating the existence of a high density of states near the Fermi level. Moreover, the \( \gamma \) value is slightly larger compared with that of Mn\(_3\)GaN (\( \gamma \): 38 mJ mol\(^{-1}\) K\(^{-2}\)) [17], suggesting that the electronic correlations of Mn\(_3\)InN is slightly enhanced.

In summary, antiperovskite Mn\(_3\)InN compound was synthesized under high pressure conditions probably for the first time, and the materials was systematically studied by measurements of magnetic susceptibility, isothermal magnetization, specific heat, and electrical resistivity. The compound clearly shows multiple magnetic transitions with continuously cooling from 400 K to 2 K. The materials hold a good metallic conduction below the bulk AFM transition at room temperature, suggesting technical possibilities toward practical uses in the field of spintronics.

Acknowledgements
This research was supported in part by the World Premier International Research Center from the Ministry of Education, Culture, Sports, Science and Technology, Japan; the Grants-in-Aid for Scientific Research (22246083) from Japan Society for the Promotion of Science; and the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program) from JSPS.

References
[1] K. Kamishima, T. Goto, and H. Nakagawa et al., Phys. Rev. B 63, 024426 (2000).
[2] T. He, Q. Huang, and A. P. Ramirez et al., Nature 411, 54 (2001).
[3] K. Asano, K. Koyama, and K. Takenaka1, Appl. Phys. Lett. 92, 161909 (2008).
[4] W. S. Kim, E. O. Chi, and J. C. Kim et al., Solid Sate Commun. 119, 507 (2001).
[5] M. Mekata, J. Phys. Soc. Jpn 17(5), 796-803 (1962).
[6] J. Garcia, A. Bianconi, and A. Marcelli et al., IL Nuovo Cimento 7D, 493 (1986).
[7] J. P. Jardin and J. Labbe, J. Solid State Chem. 46, 275 (1983).
[8] K. Takenaka and H. Takagi, Appl. Phys. Lett. 87, 261902(2005).
[9] S. Iikubo, K. Kodama, and K. Takenaka et al., Phys. Rev. Lett. 101, 205901 (2008).
[10] E. O. Chi. S. Kim, and N. H. Hur et al., Solid State Commun. 120, 307 (2001).
[11] Y. Sun, C. Wang, and L.H.Chi et al., Scripta Mater.62, 686 (2010).
[12] P. Lukashev, R.F. Sabirianov, and K. Belashchenko et al., Phys. Rev. B 78, 184414 (2008).
[13] B. Song, J.K. Jian, and H.Q. Bao et al., Appl. Phys. Lett. 92, 192511 (2008).
[14] E.F. Bertaut.,D. Fruchart and J.P. Bouchaud et al., Solid State Commun., 6, 251 (1968).
[15] D. Fruchart and E.F. Bertaut, J. Phys. Soc. Jpn 44(3), 781 (1978).
[16] W.J. Feng, D. Li, and W.J. Ren et al., J. Alloys Comp. 437, 27 (2007).
[17] J. García, J. Bartolomé and D. González et al., J. Chem. Thermodynamics 15, 465(1983).