# Lattice and Magnetic and Electronic Transport Properties in Antiperovskite M<sub>3</sub>AX Compounds

Guest Editors: Cong Wang, Koshi Takenaka, Laifeng Li, and Yuping Sun



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### Editorial

# Lattice and Magnetic and Electronic Transport Properties in Antiperovskite M<sub>3</sub>AX Compounds

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In the past 50 years, perovskite ABO3 oxides have been extensively studied, specially in electronic transport for the example of high-Tc cuprate superconductors with aberrant perovskite structure and in correlation between spin ordering and electronic transport for the example of giant magnetoresistance RMnO<sub>3</sub> (R: rare earth) compounds. However, another kind of compounds M<sub>3</sub>AX (M: magnetic elements, Mn, Ni, Fe, etc.; A: transition and main group elements, Ga, Cu, Sn, and Zn; X: N, C, and B), which was first discovered in 1930 by Morral as metallic perovskite, is lacking in systematical studies. The kind of compounds M<sub>3</sub>AX, with the so-called antiperovskite structure due to the reverse occupancy of metal and nonmetal elements (such as N and C) in cubic body corner and body center positions, has also exhibited a wide range of interesting physical properties, such as superconductivity (SC), giant magnetoresistance (GMR), negative/zero thermal expansion (NTE or ZTE) and nearly zero temperature coefficient of resistivity (NZ-TCR), magnetostriction and piezomagnetic effects, and magnetocaloric effect (MCE) due to the strong correlation among lattice, spin, and charge. Therefore, these compounds have attracted great attention. Early reports suggested that the physical properties of these materials are mainly originated from the complex magnetostructure and the induced variable band structure. The strong coupling among crystal structure, magnetic, and even electric ordering parameters and/or fields is also of great interest for the design of novel magnetoelectronic devices. The ability to control and tune the electronic transport,

magnetic transition, and abnormal thermal expansion behaviors of these materials makes it worthy to be studied for fundamental research as well as for potential applications.

Abnormal lattice variation has been one of the studied hot points in condensed matter physics. People have been searching for negative thermal expansion and nearly zero thermal expansion materials for many actual applications, which are very important in optical, microelectronic devices and spacecraft. Nowadays, the important phenomena were widely found in the series of antiperovskite compounds. However, the control of abnormal thermal expansion behaviors has been difficult, and how to design and obtain the nearly zero thermal expansion materials is still not clear. Materials with tunable magnetostructural correlations which may induce the lattice variation are very important. Such control over the magnetostructure and lattice variation has a great impact on material science.

This special issue deals with comprehensive contents in the field of condensed matter and materials physics, and it is interesting to the physicists and material researchers, who are studying on antiperovskite structured  $M_3AX$  compounds or relevant functional materials. This special issue brings together some of the latest developments in this field of research. Many of them contain new and original results which we acknowledge with thanks.

The seven articles in the special issue can address but a small subset of these fields. P. Tong and Y. P. Sun presented a review paper on the Ni-based antiperovskite compounds. In more detail, they reported the recent research progress on the experimental investigations of superconducting MgCNi<sub>3</sub> single crystals and the synthesis and physical properties of the neighbor compounds of MgCNi<sub>3</sub>. Moreover, a universal phase diagram of these compounds is presented, which suggests a phonon-mediated mechanism for the observed superconductivity. We know that it is still not clear whether the mechanism for MgCNi<sub>3</sub> superconductivity is conventional or not. The central issue is if and how the ferromagnetic spin fluctuations contribute to the cooper paring. The paper by S. Lin, B. S. Wang, P. Tong et al. reported the magnetic and electrical properties of  $GaCFe_{3-x}Cr_x$  ( $0 \le x \le 0.9$ ), and a magnetic/electrical phase diagram was plotted. Furthermore, the Fermi-liquid behavior was obtained below 70 K in the sample. In another paper, they theoretically investigated the antiperovskite chromium-based carbides ACCr<sub>3</sub> by the first principles calculation based on density functional theory (DFT). Y. Sun et al. reported the magnetic, calorimetric, and electronic transport properties of Mn<sub>3</sub>SbN. The lattice distortion from the high-temperature cubic structure to the roomtemperature tetragonal structure, which accompanies a ferrimagnetic transition, introduces a large transition entropy of 10.2 J mol<sup>-1</sup> K<sup>-1</sup> near 353 K. Y. Yin et al. reported the magnetic and electronic transport properties of Mn<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>N. The absolute value of  $d\rho/dT$  of Mn<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>N is much lower which is close to zero. The paper by T. Yamazaki et al. reported that the micrometer-scaled ferromagnetic ZnN<sub>v</sub>Ni<sub>0.6</sub>Co<sub>2.4</sub> domains are formed and embedded within a superconductive ZnNNi<sub>3</sub> bulk, which shows a chemical phase separation of superconductive ZnNNi<sub>3</sub> and ferromagnetic ZnN<sub>y</sub>Ni<sub>0.6</sub>Co<sub>2.4</sub>, reflecting the existence of a miscibility gap in  $ZnN_vNi_{3-x}Co_x$  for the samples with x < 2. B. Y. Qu et al. reported the giant negative thermal expansion in the Ge-doped antiperovskite Mn<sub>3</sub>CuN compound, which was theoretically studied using the first principles calculations. The giant negative thermal expansion was attributed to a magnetic phase transition from  $\Gamma_{5g}$  phase to the PM phase. In detail, they thought that these donated conduction electrons polarize the local electrons and change the local magnetic moments of Mn ions, leading to the volume contraction of the compound.

#### Acknowledgment

We would like to thank all contributors for their very hard work and patience in bringing out this special issue. We also expect that the special issue will stimulate the continuing efforts to deepen the investigation on the antiperovskite  $M_3AX$  compounds.

Cong Wang Koshi Takenaka Laifeng Li Yuping Sun

# Research Article

# Synthesis, Magnetization, and Electrical Transport Properties of Mn<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>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  $T_N \sim 163$  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  $(d\rho/dT)_{Mn_3Zn_0N}$  in transition temperature range, the absolute value of  $(d\rho/dT)_{Mn_3Zn_0N}$  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, *la* (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 la(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<sub>3</sub>ZnXN 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<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>N by solid state reaction and magnetic, electrical transport properties were investigated. It is found that Mn<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>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  $T_{\rm N} \sim 163$  K. Substitution of Cu for Zn favors FM state and weakens AFM ground state in Mn<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>N. Under high external fields (10 kOe–50 kOe), AFM-PM transition feature remains robust where FM phase is completely suppressed. Further, Mn<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>N exhibits a good metallic behavior except for a slope change around  $T_{\rm N}$  and shows a normal Fermi liquid behavior in a low temperature range from 5 K to 80 K. While compared with  $(d\rho/dT)_{\rm Mn_3ZnN}$  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<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>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 *Pm3 m*. It is less than that of Mn<sub>3</sub>ZnN (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  $T_{\rm N}$  ~163 K, although  $T_{\rm N}$  obtained in the FC cycle shifts to a lower temperature from ZFC cycle by about 8K. The thermal hysteresis in M(T) curves, particularly near  $T_N$ , implies a first-ordered magnetic transition in Mn<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>N. Similar result has been observed in Mn<sub>3</sub>ZnN 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  $2.0 \times 10^{-4}$  emu/(g·K) to  $0.8 \times 10^{-4}$  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<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>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  $T_{\rm N}$  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  $T_{\rm N}$ , 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<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>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<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>N from 10 K to 300 K under 0 kOe, 10 kOe, and 50 kOe, respectively. Mn<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>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  $\rho$  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<sub>3</sub>ZnN as reported in [6]. Previous investigations have shown that there exists an unusual conduction property, namely, low temperature coefficient of resistivity (TCR) in Mn<sub>3</sub>CuN 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<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>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  $\rho$  and  $T^2$  below 80 K, which agrees well with the following equation:

$$\rho = \rho_0 + AT^2, \tag{1}$$

where  $\rho_0$  is residual resistivity and *A* is constant; this result implys a Fermi liquid behavior that exists in Mn<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>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  $\rho$ -*T* indicates that electronphonon 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  $T_N \sim 163$  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<sub>3</sub>Zn<sub>0.9</sub>Cu<sub>0.1</sub>N exhibits a good metallic behavior except for a slope change around  $T_{\rm N}$ , which is closely related to AFM-PM magnetic transition. Compared with first differential of resistivity with respect to temperature for Mn<sub>3</sub>ZnN( $d\rho/dT$ )<sub>Mn<sub>3</sub>ZnN</sub> in transition temperature range, the absolute value of  $(d\rho/dT)_{\rm Mn_3Zn_0,sCu_{0.1}N}$  is much lower and is close to zero.

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# Research Article

# The Magnetic/Electrical Phase Diagram of Cr-Doped Antiperovskite Compounds $GaCFe_{3-x}Cr_x$ ( $0 \le x \le 0.9$ )

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We report the effect of Cr doping on the structural, magnetic, and electrical transport properties in Cr-doped antiperovskite compounds  $GaCFe_{3-x}Cr_x$  ( $0 \le x \le 0.9$ ). With increasing the Cr content *x*, the lattice constant increases while both the Curie temperature and the saturated magnetization decrease gradually. The electrical resistivity shows different behaviors as a function of *x*. For  $x \le 0.6$ , there exists a semiconductor-like behavior below a certain temperature which decreases with increasing *x*. In contrast, for  $0.7 \le x \le 0.9$ , the resistivity shows a metallic behavior in the whole temperature measured (2–350 K). In particular, the Fermi-liquid behavior is obtained below 70 K. Finally, based on the magnetic and electrical properties of  $GaCFe_{3-x}Cr_x$  ( $0 \le x \le 0.9$ ) a magnetic/electrical phase diagram was plotted.

#### 1. Introduction

Since MgCNi<sub>3</sub> was firstly reported as a new superconductor with the antiperovskite structure [1], the antiperovskite compounds AXM<sub>3</sub> (A = Ga, Al, Sn, Zn, Cu, In, Ge, Ag; X = C, N; M = Mn, Fe, Ni) have been extensively investigated [2–13]. Particularly, plenty of theoretical and experimental studies were performed for the Ni-based and Mn-based antiperovskite compounds [2–12]. Based on previous theoretical investigations [14, 15], the antiperovskite compounds AXM<sub>3</sub> have similar electrical band structure which determines the basical physical properties, indicating that all these antiperovskite compounds (e.g., Mn-, Fe-, or Ni-based) may exhibit similar physical properties.

Recently, considerable attention has been paid to the Fe-based antiperovskite compounds due to their interesting physical and mechanical properties, such as low temperature coefficient of resistance (LTCR) [16], magnetocaloric effect (MCE) [13, 17, 18], and good corrosion resistance [19, 20]. GaCFe<sub>3</sub> has been investigated for several decades as a typical Fe-based antiperovskite compound. It is a ferromagnetic (FM) material with the FM Curie temperature ( $T_C$ ) of 510 K

as reported previously [15]. Very recently, the studies of chemical doping at Ga site in GaCFe<sub>3</sub> have been reported, and some interesting physical properties such as extremely LTCR and large room-temperature MCE have been observed [13, 16, 17]. Based on the previous investigations of Mnor Ni-based antiperovskite compounds, the chemical doping has been proved to be an effectual method to manipulate the basic physical properties [6, 10, 21-24]. As reported previously in antiperovskite compounds  $GaCMn_{3-x}Ni_x$  [25],  $GaCMn_{3-x}Fe$  (or Cr or Co)<sub>x</sub> [26, 27], and  $SnCMn_{3-x}Fe_x$ [28], the chemical doping at Mn site can affect the magnetic and electrical transport properties significantly. Similarly, the chemical doping at Fe site for GaCFe<sub>3</sub> may be performable. However, no report was found on the chemical substitutions for the Fe site of Fe-based antiperovskite compound GaCFe<sub>3</sub>. As reported previously [14, 15], the density of states at the Fermi level  $E_F[N(E_F)]$  is mainly from Fe 3d electrons in AXFe<sub>3</sub>. As we know, the Cr  $(3d^54s^1)$  has one less 3d electron than Fe (3d<sup>6</sup>4s<sup>2</sup>) atom. Meanwhile, the Cr atom is bigger in size than that of Fe. The influences of hole doping and the change of lattice constant on the physical properties in  $GaCFe_{3-x}Cr_x$  will be thus interesting.



FIGURE 1: (Color online) (a) Room-temperature X-ray powder diffractions for  $GaCFe_{3-x}Cr_x$  ( $0 \le x \le 1$ ); the green vertical dashed line is a guide to the eye and the open triangle stands for the peak of chromium. (b) The lattice parameter *a* as a function of *x* for  $GaCFe_{3-x}Cr_x$  ( $0 \le x \le 1$ ).

In this paper, the structural, magnetic, and electrical evolutions with doping level *x* in GaCFe<sub>3-x</sub>Cr<sub>x</sub> ( $0 \le x \le 0.9$ ) were investigated. It is found that the lattice expands while both the Curie temperature and the saturated magnetization decrease gradually as *x* increases. For GaCFe<sub>3-x</sub>Cr<sub>x</sub> with  $x \le 0.6$ , the electrical resistivity exhibits a semiconductor-like behavior at low temperature while displaying a metallic behavior at elevated temperature. As the doping level *x* is above 0.7, the resistivity is metallic with a  $T^2$  temperature dependence below 70 K. Finally, a magnetic/electrical phase diagram of GaCFe<sub>3-x</sub>Cr<sub>x</sub> ( $0 \le x \le 0.9$ ) was presented.

#### 2. Experimental Details

Polycrystalline samples GaCFe<sub>3-x</sub>Cr<sub>x</sub> ( $0 \le x \le 1.0$ ) were prepared as described in our previous paper [13]. Powder X-ray diffraction (XRD) data was collected at room temperature using an X-ray diffractometer with Cu  $K_{\alpha}$  radiation (PHILIPS,  $\lambda = 0.15406$  nm). The data of XRD was refined using a standard Rietveld technique to determine the crystal structure parameter and the purity of phase. Magnetic measurements were performed on a superconducting quantum interference device magnetometer (SQUID 5T, Quantum Design) and on a vibrating sample magnetometer (VSM, Quantum Design). The electrical resistivity and specific heat were carried out on a physical property measurement system (PPMS 9T, Quantum Design). The electrical transport properties were measured by the standard four-probe method to eliminate the contact resistivity.

#### 3. Results and Discussion

Figure 1(a) shows the room-temperature XRD patterns for the samples  $GaCFe_{3-x}Cr_x$  (x = 0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4,

0.5, 0.6, 0.7, 0.8, 0.9, and 1.0). Obviously, all GaCFe<sub>3-x</sub>Cr<sub>x</sub> are single phase with a cubic antiperovskite structure (space group: Pm3m) except for a small amount of chromium (marked by open triangle) for x = 1.0. Moreover, according to the vertical bars the central position of peak (200) of GaCFe<sub>3-x</sub>Cr<sub>x</sub> shifts to lower angles with an increase of Cr content, suggesting that the lattice constant expands with increasing *x*. The Rietveld refinements of XRD patterns were performed for all samples to determine the lattice parameter. As shown in Figure 1(b), the refined lattice parameter increases with *x*, which is consistent with the shift of peak (200) in Figure 1(a). The expansion of lattice can be attributed to the larger atom radius of Cr than that of Fe.

Figure 2(a) presents temperature-dependent magnetization M(T)/M(5 K) curves for GaCFe<sub>3-x</sub>Cr<sub>x</sub> (0  $\leq x \leq 0.9$ ) at 100 Oe under zero-field-cooled (ZFC) process. Obviously, each M(T) curve exhibits an FM-PM transition as reported in GaCFe<sub>3</sub> [15]. The Curie temperature  $(T_C)$  (determined by the minimal value of dM/dT, shown in Figure 2(b)) is presented in Figure 2(d). It displays that the value of  $T_C$ decreases with increasing Cr content x. In order to investigate the magnetic ground state of  $GaCFe_{3-x}Cr_x$ , the isothermal M(H) curves at 5 K are measured and plotted in Figure 2(c). Apparently, all the M(H) curves display similar Hdependent behavior: with increasing the magnetic field, the magnetization increases initially and then tends to saturation above 10 kOe. Here, the value of saturated magnetization  $(M_{\rm S})$  is obtained by the extrapolation of the high field (10-45 kOe) M(H) curve to M-axis, which is shown in Figure 2(c) (the green dash line). As shown in Figure 2(d), the  $M_{S}$ decreases with increasing x.

According to the previous theoretical studies [14, 15, 29], the density of states at the Fermi level  $E_F$  [ $N(E_F)$ ] is mainly from Fe 3d electrons in AXFe<sub>3</sub>. Generally, the change of  $N(E_F)$  can be caused by many factors such as



FIGURE 2: (Color online) (a) Temperature-dependent magnetization M(T)/M(5 K) curves under ZFC process at 100 Oe for GaCFe<sub>3-x</sub>Cr<sub>x</sub> ( $0 \le x \le 0.9$ ). (b) Temperature dependence of dM/dT for GaCFe<sub>3-x</sub>Cr<sub>x</sub>. (c) Magnetic field dependence of magnetization M(H) curves for GaCFe<sub>3-x</sub>Cr<sub>x</sub> at 5 K; inset shows the enlargement of M(H) curves at positive H. (d) The *x*-dependent  $T_C$  and  $M_S$  for GaCFe<sub>3-x</sub>Cr<sub>x</sub>.

expansion/shrinkage of lattice, Fe/Cr 3d-C 2p hybridization effect, and band filling effect. In a conventional scheme, the expansion of lattice constant may give rise to the increasing of  $N(E_F)$  due to the decrease of bandwidth [13, 16]. However, another important factor is associated with the detailed electronic structure at Fermi level. In GaCFe<sub>3</sub>, the calculation of band structure suggests that the position of  $E_F$  is located at the left hand of a sharp peak [14]. Considering the electronic structure of Cr  $(3d^54s^1)$  and Fe  $(3d^64s^2)$ , the Cr substitution for Fe can be considered as hole doping. Assuming a rigid band model, it will shift the  $E_F$  to lower energy side. As a result, the value of  $N(E_F)$  in GaCFe<sub>3-x</sub>Cr<sub>x</sub> is reduced with increasing x. Based on the Stoner model of itinerant ferromagnetism, the reduced



FIGURE 3: (Color online) (a) Isotherm magnetization M(H) curves for GaCFe<sub>2.6</sub>Cr<sub>0.4</sub> between 180 and 390 K with external magnetic fields up to 45 kOe. (b) The Arrott plots deduced from M(H) curves in (a). (c) Isotherm magnetization M(H) curves for GaCFe<sub>2.2</sub>Cr<sub>0.8</sub> between 100 and 250 K. (d) The Arrott plots deduced from M(H) curves in (c).

 $N(E_F)$  will lead to a decrease in the magnetization [30]. Therefore, x-dependent  $M_S$  could be understood based on the above discussions. Now, how can the Cr-doping reduce the  $T_C$ ? In itinerant ferromagnetism the main contribution to the magnetism is the itinerant electrons. Here, in GaCFe<sub>3</sub> the itinerant electrons are mainly 3d electrons of transition element. With the Cr doping level increasing, the 3d electrons decrease, which leads to a decrease in the exchange integral J. Correspondingly, the value of  $T_C$  decreases with increasing x. In a word, the evolutions of  $T_C$  and  $M_S$  are mainly attributed to the cooperation of the lattice expansion and changes of electronic structure by chemical doping.

In order to investigate the type of magnetic transition for  $GaCFe_{3-x}Cr_x$ , we measured the M(H) curves around the corresponding  $T_C$  for the selected samples. Figure 3(a) displays the isothermal magnetization M(H) curves measured between 180 and 390 K with the magnetic fields up to

45 kOe for GaCFe<sub>2.6</sub>Cr<sub>0.4</sub>. The M(H) curves were measured under the increasing/decreasing field processes around  $T_C$ (~305 K). As shown in Figure 3(a), all the M(H) curves around  $T_C$  are reversible during the increasing/decreasing field processes without any hysteresis, indicating a secondorder magnetic transition [9]. In addition, the Arrott plots derived from M(H) around  $T_C$  are presented in Figure 3(b). For GaCFe<sub>2.6</sub>Cr<sub>0.4</sub>, it is evident that the slope of H/Mversus  $M^2$  curve at high magnetic fields is positive for each temperature measured, confirming a second-order magnetic transition again [9, 23]. Analogously, for GaCFe<sub>2.2</sub>Cr<sub>0.8</sub>  $(T_{\rm C} \sim 165 \,{\rm K})$ , the M(H) curves and the Arrott plots in a temperature range of 100-250 K were shown in Figures 3(c) and 3(d), respectively, which confirm a second-order magnetic transition too. It is reasonable to conclude that the FM-PM transition is of second order for the left compositions in serial GaCFe<sub>3-x</sub>Cr<sub>x</sub>.



FIGURE 4: (Color online) (a)-(b) Temperature-dependent electrical resistivity at zero magnetic field in a temperature range of 2–350 K for  $GaCFe_{3-x}Cr_x$  ( $0 \le x \le 0.9$ ). (c) The resistivity as a function of temperature at zero magnetic field and 5 T for GaCFe<sub>3</sub>.

Figures 4(a) and 4(b) illustrate the temperature dependence of resistivity  $\rho(T)$  at zero magnetic field (2–350 K) for  $GaCFe_{3-x}Cr_x$ . All the magnitude of resistivity is comparable with other isostructural compounds [9, 22, 31, 32]. Figure 4(c) presents the temperature-dependent resistivity at both zero magnetic field and 5 T. Obviously, both curves are almost overlapped. The MR value (defined as  $(\rho(H) - \rho(0T))/\rho(0T)$ ) is positive and very small ( $\leq 1\%$ ) even at 5 T, suggesting that the magnetic field has little impact on the resistivity in  $GaCFe_{3-x}Cr_x$ . Figure 5(a) shows the normalized resistivity  $\rho(T)/\rho(350 \text{ K})$  for GaCFe<sub>3-x</sub>Cr<sub>x</sub> between 2 and 350 K. There exists a minimal resistivity ( $\rho_{\min}$ ) and the corresponding temperature  $T_{\rho_{\min}}$  decreases with increasing x (to see Figure 5(b)) for low-doping samples. In high-doping samples (0.7  $\leq$  $x\,\leq\,$  0.9), the  $\rho_{\rm min}$  disappears, which can be seen clearly in Figure 5(c). As shown in Figure 5(d), the low-T resistivity was well fitted by the formula  $\rho = \rho_0 + AT^2 (\rho_0 \text{ and } A$ represent the residual resistivity and  $T^2$ -term coefficient of the resistivity, resp.) up to about 70 K, indicating a Fermiliquid behavior for  $GaCFe_{3-x}Cr_x$  (0.7  $\leq x \leq$  0.9) at lower temperatures. That is to say, the electron-electron scatterings are dominant at lower temperature (5-70 K) [5, 9]. Furthermore, the fitting parameter A decreases with increasing x, which is shown in the left inset of Figure 5(d). However, at the elevated temperatures (100-270 K),  $\rho(T)$  increases almost linearly with temperature for the samples with  $0.7 \le x \le 0.9$  according to the fitting results (see the inset of Figure 5(c)), meaning that the contributions of electron-phonon scatterings exceed those of the electron-electron scatterings [9, 16]. In addition, the slope of linear part decreases with increasing x as displayed in the right inset of Figure 5(d). The above results can be simply understood as follows: with increasing the temperature, the number of excited phonons increases quickly, resulting in the enhancement of the phonon scatterings [9].

Figures 6(a)–6(c) show the specific heat  $C_P(T)$  for GaCFe<sub>3-x</sub>Cr<sub>x</sub> (0.7  $\leq x \leq$  0.9) measured between 7 and 70 K at zero field. As shown in the inset of Figures 6(a)–6(c), the data below 20 K is plotted as  $C_P(T)/T$  versus  $T^2$  which can be well expressed by using the following equation [5]:

$$\frac{C_P(T)}{T} = \gamma + \beta T^2 + \delta T^4, \tag{1}$$

where  $\gamma$  (Sommerfeld constant) is the electronic contribution,  $\beta$  is the phonon contribution, and  $\delta$  is deviations from

\_\_\_\_

x = 0.9

136

 $\Theta_D$ 

(K)

593

517

487

 $2.79 imes 10^{-4}$ 



FIGURE 5: (Color online) (a) The normalized resistivity  $\rho(T)/\rho(350 \text{ K})$  dependence of temperature at zero field between 2 and 350 K for  $GaCFe_{3-x}Cr_x$  ( $0 \le x \le 0.9$ ). (b) The temperature of minimal resistivity as a function of x for  $GaCFe_{3-x}Cr_x$  ( $0 \le x \le 0.6$ ). (c) Temperature dependence of resistivity at zero magnetic field for GaCFe<sub>3-x</sub>Cr<sub>x</sub> (0.7  $\leq x \leq 0.9$ ); inset displays the linear fits of  $\rho(T)$  for the samples with  $0.7 \le x \le 0.9$  between 100 and 270 K. (d) The lower- $T \rho(T)$  data plotted as  $\rho(T)$  versus  $T^2$  for the samples with  $0.7 \le x \le 0.9$ ; the left and right insets show fitted parameters A and k as a function of x, respectively (see text for details).

GaCFe <sub>3-x</sub> Cr <sub>x</sub>	$ ho_0$	Α	γ	β	σ	
	$(\mu\Omega cm)$	$(10^{-6} \mathrm{m}\Omega \mathrm{cm/K}^2)$	$(mJ/mol K^2)$	$(mJ/mol K^4)$	$(mJ/mol K^6)$	
x = 0.7	239	2.26	76.3	0.046	$3.66 \times 10^{-4}$	
x = 0.8	217	2.18	79.3	0.071	$2.99 \times 10^{-4}$	

81.7

0.085

1.57

TABLE 1: The fitting parameters of  $\rho_0$ , A,  $\gamma$ ,  $\beta$ ,  $\sigma$ , and  $\Theta_D$  for GaCFe<sub>3-x</sub>Cr<sub>x</sub> (0.7  $\leq x \leq$  0.9), respectively.



FIGURE 6: (Color online) (a)–(c) Temperature-dependent heat capacity  $C_P(T)$  at zero magnetic field for GaCFe<sub>3-x</sub>Cr<sub>x</sub> (0.7  $\le x \le 0.9$ ) between 6.7 and 70 K; inset shows the plots of  $C_P(T)/T$  versus  $T^2$  below 20 K and the solid line represents the fitting results according to (1). (d) The fitting parameter  $\gamma$  as a function of x for GaCFe<sub>3-x</sub>Cr<sub>x</sub>; the left and right insets show the parameters  $\beta$  and  $\delta$  as a function of x, respectively.

the linear dispersion of the acoustic modes in extended temperature range. The fitted parameters  $\gamma$ ,  $\beta$ , and  $\delta$  as a function of x are shown in Figure 6(d) and the insets of Figure 6(d), respectively. With x increasing, the  $\gamma$  and  $\beta$  increase while the  $\delta$  decreases. Accordingly, the Debye temperature  $\Theta_D = ((n \times 1.94 \times 10^6) / \beta)^{1/3}$  (where *n* is the number of atoms in a unit cell and equal to 5 for GaCFe<sub>3-x</sub>Cr<sub>x</sub> (0.7  $\leq x \leq$ 0.9)) is derived from the value of coefficient  $\beta$ . The detailed results of  $\rho_0$ , A,  $\gamma$ ,  $\beta$ ,  $\delta$ , and  $\Theta_D$  for GaCFe<sub>3-x</sub>Cr<sub>x</sub> (0.7  $\leq$  $x \leq 0.9$ ) are summarized in Table 1. Generally, the value of Kadowaki-Woods (KW) ratio  $A/\gamma^2$  is the well-known measure of electron-electron correlation [3, 16]. By taking the values of A and y listed in Table 1, the KW ratio was calculated for GaCFe<sub>3-x</sub>Cr<sub>x</sub> ( $0.7 \le x \le 0.9$ ). For x = 0.7, 0.8, and 0.9 the values of KW ratio are  $2.70 \times 10^{-7} \mu\Omega \text{ cm/(mJ/mol K)}^2$ ,  $3.46 \times$  $10^{-7} \mu\Omega \text{ cm}/(\text{mJ/mol K})^2$ , and 2.38×10<sup>-7</sup>  $\mu\Omega \text{ cm}/(\text{mJ/mol K})^2$ , respectively, which are much less than the universal value

 $a_0 = 10^{-5} \mu\Omega \text{ cm/(mJ/mol K)}^2$  of for strong electron-electron system [3], meaning a weak electron-electron correlation.

Finally, based on the data of magnetic and electrical transport properties, the magnetic/electrical phase diagram for  $GaCFe_{3-x}Cr_x$  ( $0 \le x \le 0.9$ ) is plotted in Figure 7. As for the magnetic phase diagram there are FM and PM regions; and the metallic, semiconducting, and Fermi-liquid areas are shown in electrical phase diagram.

#### 4. Conclusion

In summary, we present the magnetic/electrical phase diagram of  $GaCFe_{3-x}Cr_x$  ( $0 \le x \le 0.9$ ). The influences of the Cr doping on the structure, magnetic, and electrical transport properties have been investigated systematically. With increasing the Cr content x, the lattice parameter increases while both the  $T_C$  and  $M_S$  decrease gradually. For the samples with  $x \le 0.6$ , the resistivity curves show a



FIGURE 7: (Color online) The magnetic/electrical phase diagram for  $GaCFe_{3-x}Cr_x$  ( $0 \le x \le 0.9$ ).

semiconductor-like behavior below a certain temperature, which decreases as *x* increases. On the contrary, for  $x \ge 0.7$  the semiconductor-like behavior disappears, and the metallic behavior is dominant in the whole temperature range (2–350 K). Particularly, the samples with  $x \ge 0.7$  show a Fermi-liquid behavior at low temperatures. In addition, we confirm that the FM-PM transition in the serial GaCFe<sub>3-x</sub>Cr<sub>x</sub> is of second order.

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# Research Article

# Thermodynamic, Electromagnetic, and Lattice Properties of Antiperovskite Mn<sub>3</sub>SbN

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The physical properties of polycrystalline  $Mn_3SbN$  were investigated using measurements of the magnetic, calorimetric, and electronic transport properties. At room temperature, the phase crystallizes in a tetragonal structure with P4/mmm symmetry. A remarkably sharp peak in the heat capacity versus temperature curve was found near 353 K. The peak reaches 723 J mol<sup>-1</sup> K<sup>-1</sup> at its highest, which corresponds to a transition entropy of 10.2 J mol<sup>-1</sup> K<sup>-1</sup>. The majority of the large entropy change appears to be due to lattice distortion from the high-temperature cubic structure to the room-temperature tetragonal structure and the accompanying Ferrimagnetic transition.

#### 1. Introduction

Antiperovskite compounds with the formula Mn<sub>3</sub>XN or Mn<sub>3</sub>XC (X = Cu, Zn, Ga, Cu, In, or Sn) were discovered in the middle of the last century [1]. Recently, interest in these materials has intensively renewed owing to discoveries of new, potentially useful properties [2-4] such as the giant magnetoresistance of Mn<sub>3</sub>GaC [5], negative thermal expansion (NTE) of Mn<sub>3</sub>Cu(Ge)N [6] and Mn<sub>3</sub>Zn(Ge)N [7], magnetostriction of Mn<sub>3</sub>CuN [8] and Mn<sub>3</sub>SbN [9], and nearzero temperature coefficient of the resistivity of Mn<sub>3</sub>CuN [10] and Mn<sub>3</sub>NiN [11]. Specifically, Takenaka and Takagi found that Ge-doped Mn<sub>3</sub>CuN compound has a large NTE (NTE parameter =  $-25 \times 10^{-6} \text{ K}^{-1}$ ) [12]; using neutron diffraction, the broad NTE was determined to be associated with the local  $T_4$  structure [6]. Asano et al. discovered large magnetostriction in tetragonal Mn<sub>3</sub>CuN; it expands 0.2% and shrinks 0.1% in the directions parallel and perpendicular to an external 90 kOe magnetic field, respectively [8]. In previous studies, we found a peculiar phase separation and accompanying anomaly in the electronic transport properties of  $Mn_3ZnN$  [13, 14], while further study indicated that the thermal expansion properties of  $Mn_3ZnN$  can be controlled by introducing Zn vacancies [15]. In addition, Song et al. observed a canonical spin-glass state in  $Mn_3GaN$  below the spin-freezing temperature of 133 K [16]. Lukashev et al. systematically studied the spin density of the spin-frustrated state of a Mn-based antiperovskite under mechanical stress [17].

The above-mentioned properties enable a variety of potential applications for this type of material. Although the prospective industrial markets are expected to be large and much effort has already been devoted to studying their structural, electromagnetic, and transport properties, further investigations on antiperovskite materials are still required. In this study, the thermodynamic, electromagnetic, and electronic transport properties of  $Mn_3SbN$  are investigated. In particular, we focused on the notable transition entropy that



FIGURE 1: Rietveld refinement of the synchrotron XRD pattern of  $Mn_3SbN$ . The crosses and solid lines represent the observed and calculated profiles, respectively, and the difference between the curves is shown at the bottom. Bragg positions are marked by small ticks (upper: Mn3ZnN, lower: MnO).

accompanies the magnetic and crystal structure transition above room temperature.

#### 2. Experimental Details

A polycrystalline  $Mn_3SbN$  sample was prepared via the solid-state reaction of fine powders of Sb (99.99%, Rare Metallic Co.) and  $Mn_2N$ , which was synthesized by firing Mn powder (99.99%, Sigma Aldrich Co.) in nitrogen at 800°C for 60 h. Stoichiometric amounts of the starting materials were thoroughly mixed, and the mixture was pressed into a pellet. The pellet was sealed in an evacuated quartz tube, heated in a box furnace at 800°C for three days, and then slowly cooled to room temperature in the furnace.

The crystal structure of Mn<sub>3</sub>SbN was analyzed by synchrotron X-ray diffraction (SXRD) using a large Debye-Scherrer camera at the BL15XU NIMS beam line of the SPring-8 facility in Hyogo, Japan. The SXRD data were collected for  $2\theta$  ranging from 2° to 60° at intervals of 0.003°. The incident beam was monochromatized at  $\lambda = 0.65297$  Å. The evolution of the Mn<sub>3</sub>SbN crystal structure with temperature was also determined via the measurement of the SXRD patterns.

The temperature dependence of magnetization was measured between 2 and 400 K with applied magnetic fields of 0.1 and 5 kOe using a Magnetic Property Measurements System (Quantum Design). The measurements were conducted on loosely gathered powder under both zero-field cooling (ZFC) and field cooling (FC) conditions. The isothermal magnetization curve was recorded at 10 K between -50 and 50 kOe.

Specific heat  $(C_p)$  values were measured between 2 and 400 K with cooling using a Physical Properties Measurement System (Quantum Design). The sample was fixed on a stage using a small amount of grease; the heat capacity of the grease was measured first and subtracted from the total  $C_p$ .



FIGURE 2: Temperature dependence of magnetization in magnetic fields of 0.1 and 5 kOe. The left and right insets show the isothermal magnetization curve at 10 K and  $\chi^{-1}$  versus *T* plot of the FC data at 0.1 kOe, respectively.

The electrical resistivity ( $\rho$ ) was measured between 2 and 400 K with cooling and heating using a conventional fourprobe techniques with the same apparatus. The AC gauge current and frequency were 10 mA and 30 Hz, respectively. The electrical contacts were prepared on the surface of a barshaped piece of the pellet using silver paste and Pt wires.

#### 3. Results and Discussion

As shown in Figure 1, the synchrotron XRD pattern at room temperature fit well with a model pattern of the proposed structure (space group: P4/mmm). The structural parameters of Mn<sub>3</sub>SbN were refined by the Rietveld method using the RIETAN-FP program [18]. The occupancy factors of Sb, N, Mn1, and Mn2 were refined to be 1 (fixed), 1 (fixed), 0.97(1), and 0.99(1), respectively, while the isotropic atomic displacement parameters were 0.42(1), 0.84(5), 0.86(1), and 0.78(1) Å<sup>2</sup>, respectively. The lattice constants were calculated to be a = b = 4.17994(4) Å and c = 4.27718(5) Å. The final  $R_{\rm wp}$  and  $R_p$  reliability indexes were below 5.56% and 4.09%, respectively. The analysis revealed 1.91 mass% MnO in the sample as an impurity; as shown later, the magnetic,  $C_p$ , and  $\rho$  measurements suggest that the impurity does not significantly impact the measurements of Mn<sub>3</sub>SbN in this study.

Figure 2 displays the temperature dependence of magnetization of polycrystalline  $Mn_3SbN$ . The magnetization steeply increases upon cooling to around 353 K, which suggests the establishment of long-range magnetic order at the magnetic transition temperature ( $T_c$ ). In addition, a small hysteresis can be observed between the heating and cooling process, implying the first-order character of the magnetic transition. The remarkable bifurcation between the ZFC and FC curves may originate from the spontaneous alignment of random magnetic Mn moments in domain boundaries. It is worth noting that the hysteresis is less significant at a higher magnetic field of 5 kOe, which supports the domain picture.



FIGURE 3: Temperature dependence of the  $C_p$  of Mn<sub>3</sub>SbN. The left and right insets show a linear fit to the  $C_p/T$  versus  $T^2$  curve and an estimation of  $\Delta S$ , respectively.

To further study the magnetic properties, we applied the Curie-Weiss law to the paramagnetic portion. As shown in the right inset of Figure 2, the  $\chi^{-1}$ -T plot is well represented by the Curie-Weiss law, that is, the spin-only expression for magnetic susceptibility:  $\chi(T) = C/(T - \Theta_W)$ , where C is the Curie constant and  $\Theta_W$  is the Weiss temperature. The value of  $\Theta_W$  was determined to be 354 K, which suggests that ferromagnetic correlation is dominant in the spin system. The effective Bohr magneton  $(\mu_{\text{eff}})$  was estimated to be  $1.28 \,\mu_B/\text{Mn}$  from  $\mu_{\text{eff}} = 2.83 (\text{C}/\eta)^{0.5} \mu_B$ , where  $\eta$  is the number of magnetic atoms in the molecular formula ( $\eta = 3$ in the present case). The value of  $\mu_{\rm eff}$  is much lower than that of other antiperovskite manganese nitrides (e.g., 2.87  $\mu_B$  for Mn<sub>3</sub>ZnN [14]) and even lower than the expected moment for localized S = 1/2 spins, suggesting an itinerant character of the 3d electrons in Mn<sub>3</sub>SbN.

From the isothermal magnetization curve (see the inset of Figure 2), it was found that the magnetization at 50 kOe is ~0.35  $\mu_B$ /Mn, which is too small to be caused by full ferromagnetic order. The gap suggests that the spins of the Mn atoms are possibly Ferrimagnetically ordered. This Ferrimagnetic interaction is also suggested by the magnetization characteristics above 10 kOe, that is, the magnetization continuously increases with increasing magnetic field without approaching saturation. The Ferrimagnetic order of a related Mn-based antiperovskite compound was explained by a  $\Gamma^{4g}$ spin structure, where two of the three Mn magnetic moments are antiferromagnetically coupled and the third exhibits FM behavior [19]. It is possible that a similar magnetic structure is established in Mn<sub>3</sub>SbN below 353 K.

To further characterize the magnetic transition, the specific heat was measured from 400 to 2 K. As shown in Figure 3, the temperature dependence of  $C_p$  features a sharp and narrow peak around  $T_c$  ( $\Delta C_p/R = 87$  and  $\Delta T = 3$  K, where *R* is the ideal gas constant). This is indicative of a first-orderlike transition, as discussed in [20].



FIGURE 4: Temperature dependence of the magnetic entropy change when the magnetic field changes from 0 to 10, 20, 30, 40, and 50 kOe, respectively.

An estimation of entropy change is essential to understanding the nature of the transition of  $Mn_3SbN$ . The peak was roughly separated from the baseline using a polynomial function. Analysis indicates that the total transition entropy ( $\Delta S$ ) is ~1.23*R* (10.2 J/mol K). Since the total entropy change comprises all contributions, including the lattice, electronic, and magnetic changes [20], we evaluated each contribution independently.

For the present compound, the abrupt change of the magnetization at  $T_c$  may induce a large  $\partial M/\partial T$ ; therefore, a large magnetic entropy change  $(\Delta S_m)$  is expected. A series of magnetization curves with small temperature steps were measured; the data allow for a rough estimation of the magnetic entropy change via the thermodynamic Maxwell relation, as follows [21]:

$$\left(\frac{\partial S(T,H)}{\partial H}\right)_{T} = -\left(\frac{\partial M(T,H)}{\partial T}\right)_{H}.$$
 (1)

The magnetic entropy change,  $\Delta S_m(T, H)$ , can be calculated by

$$\Delta S_m(T,H) = S_m(T,H) - S_m(T,0) = \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH.$$
(2)

The temperature dependence of  $\Delta S_m$  calculated from (2) with fields of 10, 20, 30, 40, and 50 kOe is shown in Figure 4. The  $\Delta S_m$  is maximized around  $T_c$ , and the maximum is estimated to be ~2.1 J mol<sup>-1</sup> K<sup>-1</sup>, which implies that the lattice and electronic changes provide a fairly large contribution to the total entropy change.

To investigate the electronic contribution (i.e., the Sommerfeld coefficient or  $\gamma$ ), the  $C_p/T$  versus  $T^2$  plot below 10 K was analyzed by applying the approximate Debye model, as



FIGURE 5: Variation in (a) lattice parameters and (b) synchrotron XRD patterns with temperature for Mn<sub>3</sub>SbN.



FIGURE 6: Variation of  $\rho$  with temperature for Mn<sub>3</sub>SbN upon cooling and warming. The inset shows an enlarged view of the  $\rho$  variation around the magnetic transition.

follows:  $C(T)/T = \gamma + 2.4\pi^4 n N_0 k_B (1/\Theta_D^3) T^2$  ( $T \ll \Theta_D$ ), where *n* denotes the number of atoms per formula unit,  $k_B$ is the Boltzmann constant,  $N_0$  is the Avogadro constant, and  $\Theta_D$  is the Debye temperature. Fitting to the linear part of the  $C_p/T$  versus  $T^2$  plot using the least-squares method yielded  $\gamma$  and  $\Theta_D$  values of ~7.03(1) mJ mol<sup>-1</sup> K<sup>-2</sup> and 326(2) K, respectively. Compared with the parameters determined for other antiperovskite nitrides, Mn<sub>3</sub>SbN has a much lower  $\gamma$ , which indicates that the electronic correlation is somewhat weakened [20]. Thus, the electronic contribution might not be a dominant contributor to the total transition entropy.

In addition to the magnetic and electronic contributions, a possible lattice change may need to be investigated to analyze the total transition entropy. The variation of the synchrotron XRD pattern with temperature was measured. As shown in Figure 5(b). It can be seen that some typical reflections disappear with temperature, for example, the two reflections (002) and (200) for the *P4/mmm* lattice merge to one reflection. By the Rietveld analysis of the synchrotron XRD patterns, the structural change from tetragonal to cubic was defined, and the lattice constants were determined as a function of temperature, as shown in Figure 5(a). It is obvious that lattice parameter *c* increases slightly with increasing temperature, whereas *a* gradually decreases. When the temperature crosses  $T_c$ , the tetragonal structure completely transforms to an unidentified cubic structure. Hence, the lattice distortion must contribute to the total entropy change.

According to the thermodynamic relation, the magnetization (M) is equal to the first derivative of the magnetic free energy by the magnetic field, that is, df(M)/dH [22]. Therefore, the sharp transition indicates that the energy barrier in the free energy that separates the paramagnetic and ferromagnetic states is large. Accordingly,  $T_c$  and the energy barrier height probably correlate with the electronic density of states, which exhibits a sharp peak near the Fermi level [23]; therefore, the large entropy change is possibly related to the reconstruction of the electronic structure, which could induce the magnetic and structural transition. Since such an electronic reconstruction is often sharply reflected in a  $\rho$ -T curve, the electronic transport properties of Mn<sub>3</sub>SbN were carefully measured (shown in Figure 6). It is evident that an abnormal drop appears at  $T_c$  in the  $\rho\text{-}T$  curve, which is indicative of an electronic structure reconstruction. In addition, as shown in the inset of Figure 6, a small hysteresis was observed between the warming and cooling curves; this is in agreement with a first-order transition.

#### 4. Conclusions

In conclusion, the thermodynamic, electromagnetic, and transport properties of antiperovskite Mn<sub>3</sub>SbN were studied. The phase crystallizes in a tetragonal structure with a = b = 4.17994(4) Å and c = 4.27718(5) Å at room temperature. The  $C_p$  measurements revealed a sharp endothermic peak in the  $C_p$ -T curve at 353 K, which corresponds to a large

entropy change ( $\sim 10.2 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The present study clearly indicates that the entropy change is accompanied with a Ferrimagnetic transition and lattice distortion as well as a possible electronic structure reconstruction.

#### **Conflict of Interests**

The authors declare that they have no conflict of interests.

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# Research Article

# Structural, Elastic, and Electronic Properties of Antiperovskite Chromium-Based Carbides ACCr<sub>3</sub> (A = Al and Ga)

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We theoretically investigated antiperovskite chromium-based carbides ACCr<sub>3</sub> through the first-principles calculation based on density functional theory (DFT). The structure optimization shows that the lattice parameter of ACCr<sub>3</sub> is basically proportional to the radius of A-site elements. The calculated formation energies show that AlCCr<sub>3</sub> and GaCCr<sub>3</sub> can be synthesized at ambient pressure and are stable with nonmagnetic ground states. Based on the calculation of elastic constants, some elastic, mechanical, and thermal parameters are derived and discussed. AlCCr<sub>3</sub> and GaCCr<sub>3</sub> show ductile natures and may have similar thermal properties. From the analysis of the electronic structures, it was found that there are electron and hole bands that cross the Fermi level for AlCCr<sub>3</sub> and GaCCr<sub>3</sub>, indicating multiple-band natures. The Fermi level locates at the vicinity of the density of states (DOSs) peak, which leads to a large DOS at Fermi level dominated by Cr-3d electrons. The band structures of AlCCr<sub>3</sub> and GaCCr<sub>3</sub> are very similar to those of the superconducting antiperovskite MgCNi<sub>3</sub>. The similarity may make AlCCr<sub>3</sub> and GaCCr<sub>3</sub> behave superconductively, which needs to be further investigated in theoretical and experimental studies.

#### 1. Introduction

Recently, antiperovskite compounds AXM<sub>3</sub> (A, main group elements; X, carbon, boron, or nitrogen; M, transition metal) have attracted considerable attention. Due to the high concentration of transition metals in a cell, it can be deduced that interesting properties will be found in the family of compounds. In the antiperovskites family, nickelbased and manganese-based antiperovskites were extensively studied. Abundant physical properties were shown in the two kinds of compounds, such as superconductivity [1-3], giant magnetoresistance (MR) [4, 5], large negative magnetocaloric effect (MCE) [6, 7], giant negative thermal expansion [8, 9], magnetostriction [10], and nearly zero temperature coefficient of resistivity [11, 12]. But there are only a few reports about other 3d-metal-based antiperovskites so far. The difficulty restricting researchers is the exploration of new materials that can be experimentally synthesized. Therefore, theoretical investigations on these potential 3d-metal-based antiperovskites are useful to find the easily prepared stable materials and explore the new physical properties.

In the earlier years, researchers have found that in chromium compounds there are varieties of interesting physical properties. Many of chromium alloys such as Cr-Ru, Cr-Rh, and Cr-Ir alloys show superconductivity [13]. And it was found there is spin density wave antiferromagnetism that coexists with superconductivity in  $Cr_{1-x}Re_x$  (x > 0.17) [14],  $Cr_{1-x}Ru_x (x > 0.17)$  [15], and  $(Cr_{1-x}Mo_x)_{75}Ru_{75}$ (x = 0, 0.03, 0.06, and 0.10) [16]. For chromium-based antiperovskites, Wiendlocha et al. [17] discussed the possibility of superconductivity in GaNCr<sub>3</sub> and RhNCr<sub>3</sub>, and recent phonon and electron-phonon coupling calculation of RhNCr<sub>3</sub> [18] supports Wiendlocha et al.'s prediction. In the present work, we theoretically investigated antiperovskite chromium-based carbides ACCr<sub>3</sub> through the first-principles calculation based on density functional theory (DFT). The optimized lattice parameter of ACCr<sub>3</sub> is basically proportional to the radius of A-site elements. From the analysis of formation energies, we predict that only AlCCr<sub>3</sub> and GaCCr<sub>3</sub> can be synthesized at ambient pressure, and they are stable with nonmagnetic ground states. The elastic and electronic properties of the two compounds are specifically discussed.

TABLE 1: The coefficient  $A_2$  in (1) as combinations for second order elastic constant for cubic crystal.  $\eta_{\alpha}$  denotes the Lagrangian strain tensors in terms of  $\xi$ .

Strain type	$A_2$
$\eta_1 = (\xi, 0, 0, 0, 0, 0)$	C <sub>11</sub>
$\eta_2 = (\xi, \xi, 0, 0, 0, 0)$	$2C_{11} + 2C_{12}$
$\eta_3 = (\xi, \xi, \xi, 0, 0, 0)$	$C_{11} + 4C_{44}$

AlCCr<sub>3</sub> and GaCCr<sub>3</sub> show ductile natures and may have similar thermal properties. The electron and hole bands cross the Fermi level, implying the multiple-band nature of AlCCr<sub>3</sub> and GaCCr<sub>3</sub>. The Fermi level locates at the vicinity of the density of states (DOS) peak, which leads to a large DOS at Fermi level dominated by Cr-3d electrons. The bands properties of AlCCr<sub>3</sub> and GaCCr<sub>3</sub> are very similar to those of superconducting antiperovskite MgCNi<sub>3</sub>. The similarity may make AlCCr<sub>3</sub> and GaCCr<sub>3</sub> show superconductivity.

#### 2. Computational Details

The calculations were performed by projected augmentedwave (PAW) [19, 20] method using the ABINIT code [21-23]. The PAW method can lead to very accurate results comparable to other all-electron methods. For the exchangecorrelation functional, the generalized gradient approximation (GGA) according to the Perdew-Burke-Ernzerhof [24] parametrization was used. Electronic wavefunctions are expanded with plane waves up to an energy cutoff of 1200 eV. Brillouin zone sampling is performed on the Monkhorst-Pack (MP) mesh [25] of 16 × 16 × 16. The self-consistent calculations were considered to be converged when the total energy of the system was stable within  $10^{-6}$  Ha. Nonmagnetic, ferromagnetic (FM), and antiferromagnetic (AFM) states were tested in the study. For AFM states, we only considered the simplest case: the spins of Cr atom in [111] layers are parallel with each other in the same layer and are antiparallel with spins in the neighboring layers.

The elastic constants are evaluated according to the finitestrain continuum elasticity theory [26, 27]. The strain energy per unit mass can be expressed as a polynomial of the strain parameter  $\xi$  [28]:

$$\phi(\xi) = \frac{1}{2}A_2\xi^2 + \frac{1}{6}A_3\xi^3 + O(\xi^4), \qquad (1)$$

where the coefficients  $A_2$  and  $A_3$  are combinations of secondand third-order elastic constants of the crystal, respectively. For a cubic structure, there are three independent secondorder elastic constants ( $C_{11}$ ,  $C_{12}$ , and  $C_{44}$ ). Therefore, here we introduced 3 Lagrangian strain tensors labeled as  $\eta_{\alpha}$  in terms of  $\xi$ .  $\eta_{\alpha}$  and the corresponding coefficients  $A_2$  are listed in Table 1.

Once the single-crystal elastic constants are calculated, the related elastic and mechanic parameters may also be evaluated. Using the Voigt-Reuss-Hill approximation [29], bulk modulus B and shear modulus G of cubic crystal can be defined as

$$B = \frac{C_{11} + 2C_{12}}{3},\tag{2}$$

$$G = \frac{G_V + G_R}{2},\tag{3}$$

where the subscripts V and R denote the Voigt, and Reuss average, respectively. In (3),

$$G_{V} = \frac{C_{11} - C_{12} + 3C_{44}}{5},$$

$$G_{R} = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}.$$
(4)

Thus Young's modulus *E* and Poisson's ratio  $\sigma$  can be obtained using the relations

$$E = \frac{9BG}{3B+G},$$

$$\sigma = \frac{3B-2G}{2(3B+G)}.$$
(5)

Using the calculated bulk modulus *B*, shear modulus *G*, and Young's modulus *E*, the Debye temperature  $\Theta_D$  can be determined as

$$\Theta_D = \frac{h}{k_B} \left(\frac{3n\rho N_A}{4\pi M}\right)^{1/3} v_m,\tag{6}$$

where h,  $k_B$ , and  $N_A$  are Planck's, Boltzmann's constants, and Avogadro's number, respectively.  $\rho$  is the mass density, M is the molecular weight, and n is the number of atoms in the unit cell. The mean sound velocity is defined as

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{1/3},\tag{7}$$

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where  $v_l$  and  $v_t$  are the longitudinal and transverse sound velocities, which can be obtained from bulk modulus *B* and shear modulus *G*:

$$v_l = \left(\frac{3B + 4G}{3\rho}\right)^{1/2},$$

$$v_t = \left(\frac{G}{\rho}\right)^{1/2}.$$
(8)

#### 3. Results and Discussion

3.1. Ground State and Formation Energy. The structures were fully optimized with respect to lattice parameter and atomic positions. The optimized lattice parameters of  $ACCr_3$  for different A-site elements are listed in Table 2. The results show that the lattice parameter of  $ACCr_3$  is basically proportional to the radius of A-site elements (see Figure 1).

The common technique for producing antiperovskite carbides is the solid-state synthesis from the parent materials.

	а	$\Delta E_{ m NM}$	$\Delta E_{ m FM}$	$M_{ m FM}$	$\Delta E_{ m AFM}$	$M_{ m AFM}$
	(Å)	(eV/atom)	(eV/atom)	$(\mu_B/\mathrm{Cr})$	(eV/atom)	$(\mu_B/\mathrm{Cr})$
CuCCr <sub>3</sub>	3.869	0.214	0.212	0.396	0.205	1.006
ZnCCr <sub>3</sub>	3.894	0.125	0.126	0.127	0.115	1.020
GaCCr <sub>3</sub>	3.891	-0.019	-0.019	0.001	-0.019	0.099
MoCCr <sub>3</sub>	3.898	0.105	0.105	0.053	0.105	0.240
AlCCr <sub>3</sub>	3.887	-0.0479	-0.0478	0.034	-0.0478	0.212
AgCCr <sub>3</sub>	3.936	0.286	0.292	0.544	0.268	1.649
CdCCr <sub>3</sub>	3.973	0.256	0.257	0.341	0.213	2.102
SnCCr <sub>3</sub>	3.981	0.082	0.0786	0.400	0.082	0.000
MgCCr <sub>3</sub>	3.952	0.220	0.219	0.173	0.195	1.824
InCCr <sub>3</sub>	3.999	0.187	0.189	0.406	0.188	0.006
YCCr <sub>3</sub>	4.088	0.269	0.268	0.611	0.270	0.000
LaCCr <sub>3</sub>	4.122	0.496	0.362	1.8101	0.497	0.002
CaCCr <sub>3</sub>	4.083	0.539	0.541	0.3311	0.539	0.001
SrCCr <sub>3</sub>	4.155	0.795	0.795	0.402	0.796	0.002
BaCCr <sub>3</sub>	4.246	1.166	0.998	1.957	1.166	0.002

TABLE 2: Lattice parameter *a*, magnetic moments per Cr atom *M*, and the formation energies  $\Delta E$  of ACCr<sub>3</sub>.

TABLE 3: Elastic constants and derived quantities for  $ACCr_3$  (A = Al and Ga).

	$C_{11}$ (GPa)	$C_{12}$ (GPa)	$C_{44}$ (GPa)	Α	$C_p$ (GPa)	B (GPa)	G (GPa)	B/G	E (GPa)	σ	$\Theta_D(\mathbf{K})$
AlCCr <sub>3</sub>	448.18	297.98	68.31	0.91	229.67	348.04	70.95	4.90	199.30	0.40	532.43
GaCCr <sub>3</sub>	480.81	314.43	64.63	0.78	249.80	369.89	71.51	4.40	201.53	0.41	497.12



FIGURE 1: Relation between the lattice parameter a and the radius of A-site elements  $r_A$ .

Therefore we assumed that the antiperovskite chromiumbased carbides ACCr<sub>3</sub> could be synthesized in the same routine. We analyze the stability of compounds by calculating the formation energies  $\Delta E$ , which is defined as the difference between the total energies of initial reagents (elements) and final compounds:

$$\Delta E = E_{\text{tot}}^{\text{ACCr}_3} - \left( E_{\text{tot}}^{\text{A}} + E_{\text{tot}}^{\text{C}} + 3E_{\text{tot}}^{\text{Cr}} \right).$$
(9)

Here,  $E_{\text{tot}}^{\text{A}}$ ,  $E_{\text{tot}}^{\text{C}}$ , and  $E_{\text{tot}}^{\text{Cr}}$  are the total energies of the initial reagents.

According to the definition of  $\Delta E$ , negative values indicate that the formation of compounds from the initial components is energetically favorable and the compounds are stable with respect to a mixture of the initial elements. Conversely, if  $\Delta E > 0$ , the compounds are unlikely to be synthesized under normal conditions.

The calculated  $\Delta E$  for the series of A-site elements with different magnetic configurations are listed in Table 2. Except for AlCCr<sub>3</sub> and GaCCr<sub>3</sub>, all other compounds show positive  $\Delta E$ . For AlCCr<sub>3</sub> and GaCCr<sub>3</sub>, the values of  $\Delta E$  for different magnetic configurations are very close, and the magnetic moments per Cr atom for the FM and AFM states are very small, which implies the nonmagnetic ground states of AlCCr<sub>3</sub> and GaCCr<sub>3</sub>. From the analysis of formation energies, it seems that ACCr<sub>3</sub> can be synthesized only when A = Al and Ga. The elastic and electronic properties of the two compounds will be discussed later.

3.2. Elastic and Mechanical Properties. In order to obtain accurate elastic constants,  $\xi$  is varied with a step of 0.0025 in every case for  $\eta_{\alpha}$ . As an example, the strain energies for AlCCr<sub>3</sub> and the fitted polynomials are shown in Figure 2. The calculated elastic constants at ambient pressure and other derived mechanical parameters are listed in Table 3. From the calculated values of the elastic constants, one can find that they satisfy the mechanical stability criteria for a cubic crystal, that is,  $C_{11} > C_{12}$ ,  $C_{44} > 0$ , and  $C_{11} + 2C_{12} > 0$  [30], which indicates that the compounds are mechanically stable.



FIGURE 2: The strain-energy relation of AlCCr<sub>3</sub>.

Cracks in crystals are directly related to the anisotropy of thermal and elastic properties [31]. The elastic anisotropy factor *A* of cubic crystal can be described as

$$A = \frac{2C_{44}}{C_{11} - C_{12}}.$$
 (10)

For a complete isotropic system, the anisotropy factor A takes the value of unity, and the deviation from unity measures the degree of elastic anisotropy [32]. The elastic constant  $C_{44}$ represents the shear resistance in a [100] direction, which is related to the C–Cr bonding. The values of  $C_{44}$  for the two compounds are almost the same, which implies the similar C–Cr bonding nature of the two compounds.  $C_{11} - C_{12}$  turns out to be the stiffness associated with a shear in a [110] direction, which can be connected with the bonding between A-Cr bonding. Although A-M bonding is usually very weak in antiperovskite ACM<sub>3</sub>, it still can influence the anisotropy of the material. The anisotropic factors A are listed in Table 3. The different A-Cr bondings of the two compounds lead to different anisotropy. For AlCCr<sub>3</sub>, A = 0.91 indicates that AlCCr<sub>3</sub> is almost isotropic. However, GaCCr<sub>3</sub> seems like more anisotropic (A = 0.78).

Young's modulus E defines the ratio between the linear stress and strain. The larger the value of E, the stiffer is the material. In general, as Young's modulus increases, the covalent nature of the compound also increases, which further has an impact on the ductility of the compounds. The values of E for AlCCr<sub>3</sub> and GaCCr<sub>3</sub> are very close to each other, suggesting the similar covalent nature of the two compounds.

The Cauchy's pressure  $C_p$  is defined as the difference between the two particular elastic constants  $C_p = C_{12} - C_{44}$ . It is considered to serve as an indication of ductility:  $C_p > 0$ suggests that the material is expected to be ductile; otherwise, the material is expected to be brittle [33]. As shown in Table 3, the values of  $C_p$  for AlCCr<sub>3</sub> and GaCCr<sub>3</sub> are positive,

which is a clear indication for the compounds to be ductile. Another index of ductility is the ratio B/G. According to Pugh [34], the ductile/brittle properties of materials could be related empirically to the ratio B/G. If B/G > 1.75, the material would be ductile; otherwise the material behaves in a brittle manner. For  $ACCr_3$  (A = Al and Ga), all the calculated B/G ratios are much larger than 1.75, which clearly highlights the ductile nature of  $ACCr_3$  (A = Al and Ga). Poisson's ratio generally quantifies the stability of the crystal against shear and takes the value between -1 and 0.5, which are the lower and the upper bounds. The lower bound is where the material does not change its shape, and the upper bound is where the volume remains unchanged. The calculated  $\sigma$  of ACCr<sub>3</sub> (A = Al and Ga), listed in Table 3, are very close to the typical  $\sigma$  value of 0.33 for ductile metallic materials [35]. All the parameters clearly show the ductility of  $ACCr_3$  (A = Al and Ga).

Using bulk modulus *B*, shear modulus *G*, and Young's modulus *E*, the Debye temperature  $\Theta_D$  can be calculated. As a matter of fact, a higher  $\Theta_D$  would imply a higher thermal conductivity associated with the material [36]. For the present calculation, the  $\Theta_D$  are estimated to be 532.43 K and 497.12 K for AlCCr<sub>3</sub> and GaCCr<sub>3</sub>, respectively. The similar values of  $\Theta_D$  suggest the similar thermal characteristics of the two compounds.

3.3. Electronic Properties. The calculated electronic band structures along the high symmetry directions in the Brillouin zones together with the total and site-projected *l*-decomposed DOS at equilibrium lattice parameters for ACCr<sub>3</sub> (A = Al and Ga) are shown in Figures 3 and 4. The band structures of the two compounds are very similar. Bands from -13 eV to -10 eV are mainly from the C-2s and Cr-3d states with strong hybridizations characteristic. From -8 eV to 2 eV, there are hybridizations between C-2p and Cr-3d states, and the Cr-3d states contribute dominantly to the bands, which suggests the itinerant nature of Cr-3d electrons. From Figure 4, it can be seen the Fermi level locates at the vicinity of the DOS peak, which leads large DOS at the Fermi level  $N(E_F)$  with values of 4.79 states/eV for AlCCr<sub>3</sub> and 5.62 states/eV for GaCCr<sub>3</sub>.

The Fermi surfaces of the two compounds are similar (see Figure 5). There are four bands that cross the Fermi level. Hole pockets surrounding  $\Gamma$  point come from the lower two bands (denoted with red and green colors in Figure 3). Electron pockets surrounding R point come from the upper two bands (denoted with blue and purple colors in Figure 3). The differences of the Fermi surface of the two compounds come from the band denoted with blue color in Figure 3. It crosses the Fermi level at the vicinity of M point for AlCCr<sub>3</sub>, which makes the electron pockets surround the corners of the Brillouin zones connected to each other at M point. However, for GaCCr<sub>3</sub>, it crosses the Fermi level in the place between  $\Gamma$ and M points, which forms a cubic cage-like electron pocket surrounding  $\Gamma$  point and connecting with the corner-centered electron pockets. The presence of electron and hole bands crossing the Fermi level indicates the multiple-band natures for AlCCr<sub>3</sub> and GaCCr<sub>3</sub>.



FIGURE 3: The band structures for (a) AlCCr<sub>3</sub> and (b) GaCCr<sub>3</sub>. The colored lines denote the bands crossing the Fermi level.



FIGURE 4: The density of states of (a) AlCCr<sub>3</sub> and (b) GaCCr<sub>3</sub>.

In order to understand the bonding nature among the atoms in AlCCr<sub>3</sub> and GaCCr<sub>3</sub>, we plot the contour maps of the charge density of the two compounds in Figure 6. The C–Cr bonds are very strong, which coincides with the strong hybridization between C-2p and Cr-3d electrons shown in DOS figures. The similarity of the bonding nature for the two compounds coincides with the similar Young's modulus *E* discussed before.

The electronic properties of AlCCr<sub>3</sub> and GaCCr<sub>3</sub> are very similar to those of the superconducting antiperovskite MgCNi<sub>3</sub> [37], for which the Fermi level locates at the vicinity of the DOS peak as well, and there is multiple-band nature present. The similarity possibly makes AlCCr<sub>3</sub> and GaCCr<sub>3</sub> potential superconductors. According to McMillan's coupling theory [38], the electron-phonon coupling constant  $\lambda$  can be calculated from the following expression  $\lambda = \sum_{\alpha} (\eta_{\alpha}/M_{\alpha} \langle \omega_{\alpha}^2 \rangle)$ , where  $M_{\alpha}$  is the atomic mass and  $\langle \omega_{\alpha}^2 \rangle$  is the averaged phonon frequency and can be approximated as  $\langle \omega_{\alpha}^2 \rangle = \Theta_D^2/2$ . For superconducting MgCNi<sub>3</sub>, there is a peak (a van Hove singularity) in DOS just below Fermi level, which leads to a large  $N(E_F)$ . The  $N(E_F)$  is not large enough to lead magnetic instability, but it can lead to a large electron-phonon coupling constant [39]. To the best of our knowledge, except for the superconducting nickel antiperovskites, there are no



FIGURE 5: (a) Brillouin zone of ACCr<sub>3</sub>. Fermi surfaces of (b) AlCCr<sub>3</sub> and (c) GaCCr<sub>3</sub>.



FIGURE 6: The contour map of electron charge density of (a) AlCCr<sub>3</sub> and (b) GaCCr<sub>3</sub>.

other antiperovskites that have such a nature. Wiendlocha et al. [17] pointed out that in chromium systems, chromium atoms have very large values of the McMillan-Hopfield parameters [38], which may lead to a very strong electron-phonon coupling. The recently reported work about RhNCr<sub>3</sub> [18] supports Wiendlocha et al.'s prediction. The phonon and electron-phonon coupling calculations show that RhNCr<sub>3</sub>, which has a large  $N(E_F)$ , is a strong coupling superconductor with Tc above 16 K. Therefore, we consider that there is possibility for superconductivity appearing in AlCCr<sub>3</sub> and GaCCr<sub>3</sub>. Phonon and electron-phonon coupling calculations will be carried out in the future to confirm the possibility.

#### 4. Conclusion

In conclusion, we theoretically investigated the antiperovskite chromium-based carbides ACCr<sub>3</sub> through the first-principles calculation based on density functional theory. The optimized lattice parameter of ACCr<sub>3</sub> is basically proportional to the radius of A-site elements. Only AlCCr<sub>3</sub> and GaCCr<sub>3</sub> have negative formation energies, implying that the two compounds can be synthesized at ambient pressure and are stable with nonmagnetic ground states. AlCCr<sub>3</sub> and GaCCr<sub>3</sub> show ductile natures, and they may have similar thermal properties. Similar to superconducting antiperovskite MgCNi<sub>3</sub>, there are electron and hole bands that cross the Fermi level for AlCCr<sub>3</sub>

and GaCCr<sub>3</sub>, indicating multiple-band natures. The Fermi level locates at the vicinity of the DOS peak, which leads to a large  $N(E_F)$  dominated by Cr-3d electrons. These similarities possibly make AlCCr<sub>3</sub> and GaCCr<sub>3</sub> show superconductivity, which needs to be further investigated from theoretical and experimental studies.

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### Research Article

# Chemical Phase Separation of Superconductive and Ferromagnetic Domains in ZnNNi<sub>3-x</sub>Co<sub>x</sub>

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Various  $ZnN_yNi_{3-x}Co_x$  compounds with differing Co content, *x*, were synthesized, and their magnetic properties were investigated. Uniform solid solutions could not be obtained at low Co content (x < 0.75); instead micrometer-scaled ferromagnetic  $ZnN_yNi_{0.6}Co_{2.4}$  domains formed embedded within a superconductive  $ZnNNi_3$  bulk, showing chemical phase separation of superconductive  $ZnNNi_3$  and ferromagnetic  $ZnN_yNi_{0.6}Co_{2.4}$ . At intermediate levels of Co concentration (0.75 < x < 2), this two-phase separation might persist, and the superconductive behavior was strongly suppressed in this composition region. Only at high Co concentration (x > 2) the uniform ferromagnetic solid solution  $ZnN_yNi_{3-x}Co_x$  (with most likely y = 0.5) formed. The phase separation behavior is intrinsic to the system, reflecting the existence of a miscibility gap in  $ZnN_yNi_{3-x}Co_x$  for the samples with x < 2, and was shown not to be attributable to incomplete synthesis. In the two-phased samples, high-quality granular contact between the superconductor and ferromagnet has been realized, suggesting that the production of useful devices requiring high-quality contacts between superconductors and ferromagnets may be possible by making use of this two-phase situation.

#### 1. Introduction

He et al. discovered a new antiperovskite superconductor MgCNi<sub>3</sub> that has a superconducting transition temperature  $(T_c) \sim 8 \text{ K}$  [1]. This compound has attracted attention in the context of the relationship between superconductivity and ferromagnetism, because the material includes large amounts of ferromagnetic Ni and has structural similarities with f.c.c. elemental Ni. Some researchers have supposed that the ferromagnetic correlation is associated with the superconductivity of MgCNi<sub>3</sub>. A theoretical calculation has pointed out that the emergence of ferromagnetism may be induced by hole doping [2].

In order to reveal the superconducting gap symmetry and to clarify the microscopic origin of the superconductivity in MgCNi<sub>3</sub>, various types of experiments have been carried out [3–14]. However, a rigid consensus has not been obtained yet about the origin of superconductivity in MgCNi<sub>3</sub>. Stimulated by the discovery of MgCNi<sub>3</sub>, several new antiperovskite compounds have been synthesized including two new superconductors, CdCNi<sub>3</sub> and ZnNNi<sub>3</sub>, and complementary theoretical studies have been performed, especially for these new superconductors [15–33].

In this study we synthesized and investigated the physical properties of the  $ZnN_yNi_{3-x}Co_x$  system composed of superconductive  $ZnNNi_3$  and ferromagnetic  $ZnN_yCo_3$ .  $ZnNNi_3$  is a superconductor with  $T_c \sim 3$  K that has the same antiperovskite structure as MgCNi\_3 [34, 35].  $ZnN_yCo_3$  is a ferromagnet with a Curie temperature above room temperature. It should be mentioned that the nitrogen content *y* of  $ZnN_yCo_3$  is about half of that in  $ZnNNi_3$  ( $y \sim 0.5$ ), which seems to be the only stable nitrogen content of this material [36]. The nitrogen content of  $ZnN_yCo_3$  has been confirmed by measuring the weight change before and after sintering.

These two compounds have the same antiperovskite structure and almost the same lattice constant (3.756 and 3.758 Å for ZnNNi<sub>3</sub> and ZnN<sub>v</sub>Co<sub>3</sub>, resp.), which make them

likely to form a  $ZnN_yNi_{3-x}Co_x$  solid solution with a whole value of *x*. However the chemical phase separation of superconductive  $ZnNNi_3$  and ferromagnetic  $ZnN_yNi_{0.6}Co_{2.4}$ domains has been observed. In this paper, we report the synthesis and the two-phase separation of superconductivity and ferromagnetism in the  $ZnN_yNi_{3-x}Co_x$  system in detail.

#### 2. Experimental

The samples were prepared from elemental Zn, Ni, and Co powders. The powders were weighed and mixed to a nominal composition of  $Zn_{1.05}Ni_{3-x}Co_x$  and were then pressed into pellets. Extra Zn powder was added to compensate for loss due to vaporization. The pellets were sintered in NH<sub>3</sub> gas in the following temperature sequence: (1) 400°C for 3 h, (2) 520°C for 5 h, and (3) 550–600°C for 5 h several times with intermediate grinding steps. The NH<sub>3</sub> gas decomposes to chemically active hydrogen and nitrogen at high temperatures, and the active nitrogen penetrates into the sample to nitrify the sample. This has been shown to be an effective method for forming 3d-transition metal nitrides [37–39].

X-ray diffraction patterns were obtained using Cu K $\alpha$  radiation. The magnetization measurements were performed using a Quantum Design SQUID magnetometer. Magnetization was measured with zero-field cooling (ZFC). In order to investigate the homogeneity of the sample, an electron probe microanalyzer (EPMA) was used.

#### 3. Results and Discussion

Figure 1 shows the powder X-ray diffraction patterns obtained for various  $ZnN_yNi_{3-x}Co_x$  samples. All of the diffraction patterns indicate a cubic structure with Pm3m space group. No impurity peaks were detected, showing singlephased samples. The lattice parameters were determined to be a nearly constant value of 3.756 Å for all samples, and systematic changes in the lattice constant were not observed as the Ni : Co ratio was varied.

Figure 2 shows the temperature dependence of the magnetic susceptibility for  $ZnN_yNi_{3-x}Co_x$  with x = 0, 0.25, 0.5, and 0.75 samples. All samples show superconductive behavior. The onset of  $T_c$  was seen to slightly decreased as the Co content (x) was increased. Though the superconducting volume fraction (SVF) decreases as x increases, the SVF values are large enough for bulk superconductivity up to x = 0.5 (SVF = 12% estimated from magnetization value at 1.8 K). The bulk superconductivity disappears in samples with x above 0.75 (data with x > 0.75 not shown).

Figure 3 shows the field dependence of magnetization curves at 1.8 K and 3.5 K with (a) x = 0.25 and (b) x = 0.5. Below  $T_c$  (1.8 K), the magnetization curves show superconducting character but overlap with ferromagnetic character for both samples. The ferromagnetic character becomes more obvious for the sample with larger Co content (compare x = 0.5 data in Figures 3(a) and 3(b) at 1.8 K). At the lower temperature, superconductivity seems to coexist with ferromagnetism, but above  $T_c$  (3.5 K), the superconductive character disappears and only the ferromagnetism survives (see 3.5 K data of Figures 3(a) and 3(b)). In order to clarify



FIGURE 1: Powder X-ray diffraction pattern for ZnNNi<sub>3-x</sub>Co<sub>x</sub>.



FIGURE 2: Temperature dependence of magnetic susceptibility,  $\chi$ , normalized by  $1/4\pi$  for ZnNNi<sub>3-x</sub>Co<sub>x</sub> under 10 Oe between 1.8 K and 5 K obtained by the ZFC method.

the origin of this coexistence, we analyzed the samples using EPMA.

Figures 4(a) and 4(b) show the elemental mapping analysis for Ni (Figure 4(a)) and Co (Figure 4(b)) over a  $230 \times 230 \,\mu\text{m}^2$  area of the x = 0.25 sample obtained using an acceleration voltage of 15 kV and probe diameter of 1  $\mu$ m. In Figure 4(a), darker blue colors indicate areas deficient in Ni content. From this figure, it can be seen that there are some blue islands that are tens of micrometers in size and have much less Ni content than the surrounding areas. On the other hand, in Figure 4(b), areas with brighter red colors indicate that the Co content is enhanced in those regions. Comparing these two figures, it is seen that within the islands with very small Ni content seen in Figure 4(a), the Co content is very large. The chemical composition of these islands was revealed to be  $ZnN_yNi_{0.6}Co_{2.4}$  and the volume fraction of the islands can be estimated from image



FIGURE 3: Magnetic field dependence of magnetization at 1.8 and 3.5 K for  $ZnNNi_{3-x}Co_x$  with (a) x = 0.25 and (b) x = 0.5.



FIGURE 4: Elemental quantity mapping analysis for (a) Ni and (b) Co over a  $230 \times 230 \mu m^3$  area for the x = 0.25 sample with an acceleration voltage of 15 kV and probe diameter of 1  $\mu$ m. The red-colored area on the left side of Figure 4(a) is due to instrumental noise.

mapping to be about 5%. Except for these  $ZnN_yNi_{0.6}Co_{2.4}$ islands, the overall chemical composition was found to be nearly pure superconductive  $ZnNNi_3$ . In order to clarify the magnetic property of  $ZnN_yNi_{0.6}Co_{2.4}$ , we synthesized a  $ZnN_yNi_{0.6}Co_{2.4}$  sample and measured its field-dependent magnetization at 1.8 K (Figure 5(a)). As clearly seen in Figure 5(a),  $ZnN_yNi_{0.6}Co_{2.4}$  is ferromagnetic. In Figure 5(b),  $ZnN_yNi_{0.6}Co_{2.4}$  magnetization data is superimposed with the 1.8 K data shown in Figure 3(a); the  $ZnN_yNi_{0.6}Co_{2.4}$ magnetization data was scaled by 0.05, corresponding to the volume fraction of  $ZnN_yNi_{0.6}Co_{2.4}$  (5%) estimated from the EPMA mapping data. It is clear that the ferromagnetic character seen in the x = 0.25 sample is well explained by the 5% reduced magnetization behavior of  $ZnN_yNi_{0.6}Co_{2.4}$ . It appears that the origin of the coexistence of superconductive and ferromagnetic behavior arises from a chemical phase separation where ferromagnetic  $ZnN_yNi_{0.6}Co_{2.4}$  regions are embedded within the superconductive  $ZnNNi_3$  background. It should be noted that the overall average composition of this 95%-ZnNNi\_3/5%-ZnN\_yNi\_{0.6}Co\_{2.4} sample is  $ZnN_yNi_{2.88}Co_{0.12}$ , which corresponds to only half the Co content of the nominal composition of  $ZnNNi_{2.75}Co_{0.25}$ . We suspect that the discrepancy may be explained by the existence of small or thin  $ZnN_yNi_{0.6}Co_{2.4}$  portions in the  $ZnNNi_3$  grain boundary areas, which we failed to adequately detect by mapping analysis. These small portions may lose



FIGURE 5: (a) Magnetic field dependence of magnetization at 1.8 K for  $ZnN_yNi_{0.6}Co_{2.4}$ . (b) Magnetic field dependence of magnetization at 1.8 K for  $ZnN_yNi_{0.6}Co_{2.4}$ . The magnetization data is scaled by a factor of 0.05 and superimposed with the 1.8 K data from Figure 3(a).



FIGURE 6: Temperature-dependent magnetic susceptibilities of x = 0.5 samples with various numbers of sintering cycles. The inset shows  $\chi$  at 1.8 K as function of sintering cycle number.

their long range ferromagnetic coherence because of their nonbulk morphology. In order to clarify this point, more detailed chemical analysis is needed.

There remains a question of whether the phase separation comes from the intrinsic nature of this compound or from incomplete sample preparation. In Figure 6, the temperature-dependent magnetic susceptibility of x = 0.5samples prepared after different numbers of sintering cycles in process (3) 550–600°C for 5 h (see Section 2) is shown. From this figure, it can be seen that the magnetization value at 1.8 K increases with increasing number of sintering cycles and almost saturates for the sample after 17 sintering cycles. This indicates that the chemical reaction has gone to completion and that the sample has reached a thermodynamic equilibrium state. Therefore, in this system, more than 17 sintering cycles are enough to achieve complete chemical reaction. The samples used in this study were synthesized with more than 17 sintering cycles; therefore, the two-phase separation cannot be attributed to incomplete synthesis but instead must be intrinsic to the system. It seems that Co ions cannot be substituted into Ni sites in the x = 0.25and 0.5 samples, instead, two-phase separation of ZnNNi<sub>3</sub> and ZnN<sub>y</sub>Ni<sub>0.6</sub>Co<sub>2.4</sub> arises. In other words, a miscibility gap exists in  $ZnN_{\nu}Ni_{3-x}Co_x$  systems for at least x = 0.25 and 0.5. In an Mn-doped ZnNNi<sub>3-x</sub>Mn<sub>x</sub> system synthesized by the same recipe used in the present study, the superconductivity completely disappeared with a tiny amount (x = 0.05) of doping, which indicated the formation of a uniform solid solution, even with small doping concentrations [40]. This experimental result also reinforces the peculiar character of the Co-doping system and supports the existence of a miscibility gap. Why does not a uniform solid solution of  $ZnN_{\nu}Ni_{3-x}Co_{x}$  form between the ZnNNi<sub>3</sub> and ZnN<sub>{\nu}</sub>Co<sub>3</sub> which have nearly the same crystal structures? As already mentioned, it has been recognized that, in the preset synthesis conditions, the nitrogen content y of  $ZnN_yCo_3$ must be about 0.5 [36] unlike  $ZnN_yNi_3$  (y = 1). Strictly speaking, the crystal structure of ZnNNi<sub>3</sub> is different than ZnN<sub>v</sub>Co<sub>3</sub> from the viewpoint of nitrogen content. Therefore, it is reasonable to imagine that ZnN<sub>0.5</sub>Co<sub>3</sub> cannot dissolve into ZnNNi<sub>3</sub>, even though the overall crystal structure and lattice parameters are almost the same. In contrast, for high x



FIGURE 7: SVF (a),  $T_c$  (b), and M (c) as a function of Co content, x.

values, homogeneous solid solutions of  $ZnN_{\nu}Ni_{3-x}Co_{x}$  may be realized because the islands of ZnN<sub>v</sub>Ni<sub>0.6</sub>Co<sub>2.4</sub> observed by EPMA mapping seem to be homogeneous within their islands. The nitrogen content y of  $ZnN_{y}Ni_{0.6}Co_{2.4}$  is inferred to be 0.5 due to the compositional proximity to ZnN<sub>0.5</sub>Co<sub>3</sub>. A lower nitrogen content ZnN<sub>0.5</sub>Ni<sub>3</sub> phase can be synthesized under 50%-H<sub>2</sub>+50%-NH<sub>3</sub> conditions (For synthesizing ZnN<sub>0.5</sub>Ni<sub>3</sub>, the concentration of NH<sub>3</sub> gas has to be diluted down to 50% by H<sub>2</sub> gas, while for the case of ZnNNi<sub>3</sub>, 100%-NH<sub>3</sub> gas is needed.) and may exist as a pseudostable phase under the present synthesis conditions using 100%-NH<sub>3</sub> gas. Therefore, it can be supposed that small amounts of ZnN<sub>0.5</sub>Ni<sub>3</sub> could dissolve into ZnN<sub>0.5</sub>Co<sub>3</sub> to form the solid solution  $ZnN_yNi_{3-x}Co_x$  at high x concentrations, with a most likely value of y = 0.5. If appropriate synthesis conditions were found that allowed the N content to be 1 for  $ZnN_{\nu}Co_3$ , the formation of uniform solid solutions at all x values could be possible. For example, this may be accomplished by using NH<sub>3</sub> gas at more than 1 atm.

In Figure 7, SVF,  $T_c$ , and magnetization values obtained in a 1 *T* field at 1.8 K (*M*) are shown as a function of the Co content, *x*. The SVF value decreases linearly as Co content increases up to about 0.5. This behavior is consistent with a two-phase situation. With linearly increasing *x*, the relative ratio of the superconducting region linearly decreases.  $T_c$ is nearly constant and suddenly disappears at x = 1. *M* increases linearly up to about 2 and strongly increases above x = 2. This implies that the two-phase situation extends up to x = 2, and at x > 2 the uniform solid solution  $\text{ZnN}_y \text{Ni}_{3-x} \text{Co}_x$ forms and shows ferromagnetism. However this hypothesis contradicts the experiment because the superconductivity disappears below x = 2. This discrepancy might be explained by the influence of the magnetic field made by ferromagnetic ZnN<sub>y</sub>Ni<sub>0.6</sub>Co<sub>2.4</sub> regions adjacent to the superconductive ZnNNi<sub>3</sub> region under the two-phase situation, which may strongly suppress or wholly destroy the superconductive behavior. In order to clear this point, further investigations employing NMR or  $\mu$ SR experiments are needed.

Finally, it should be mentioned that in the two-phase situation a prototype of a ferromagnet-superconductor granular contact device is naturally realized. The nature of the ferromagnet-superconductor grain boundary is expected to be good because the ferromagnetic ZnNyNi0.6Co2.4 and superconductive ZnNNi3 have almost the same crystal structure and lattice constant. This indicates the possibility for use in  $\pi$ -junction quantum bit and magnetoresistance devices and similar applications by tuning the morphological characteristics of the contact boundary, such as contact strength, shape of the boundary, and each domain size. These parameters may be controllable within conventional solid state reaction techniques by optimizing synthesis conditions such as temperature, sintering time, and nitrogen partial pressure, without the special equipment used in producing thin film devices.

#### 4. Conclusion

It has been revealed that, in  $ZnN_yNi_{3-x}Co_x$  systems with 0 < x < 0.75, instead of forming uniform solid solutions, micrometric scale ferromagnetic  $ZnN_yNi_{0.6}Co_{2.4}$  domains

embed within a superconductive ZnNNi<sub>3</sub> bulk, showing chemical phase separation of superconductive ZnNNi<sub>3</sub> and ferromagnetic ZnN<sub>y</sub>Ni<sub>0.6</sub>Co<sub>2.4</sub>. Our results suggest that, for 0.75 < x < 2, two-phase separation persists, but the superconducting region is strongly suppressed or almost destroyed possibly by the magnetic field produced by surrounding ferromagnetic regions. Above x > 2, the uniform solid solution  $ZnN_{y}Ni_{3-x}Co_{x}$  (with most likely y = 0.5) forms, and in this compositional region the system shows long range ferromagnetism. The two-phase separation nature is intrinsic to the system, reflecting the existence of a miscibility gap in  $ZnN_yNi_{3-x}Co_x$  with 0 < x < 0.75 and suggestively with 0.75 < x < 2. The origin of this unexpected chemical phase separation is probably due to the differences in stable nitrogen content between  $ZnN_{y}Ni_{3}$  (y = 1) and  $ZnN_{\nu}Ni_{0.6}Co_{2.4}$  ( $\nu = 0.5$ ). By taking advantage of this twophase situation, useful devices requiring high-quality granular contacts between superconductors and ferromagnets could be produced.

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# Review Article Research Progress on Ni-Based Antiperovskite Compounds

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The superconductivity in antiperovskite compound MgCNi<sub>3</sub> was discovered in 2001 following the discovery of the superconducting MgB<sub>2</sub>. In spite of its lower superconducting transition temperature (8 K) than MgB<sub>2</sub> (39 K), MgCNi<sub>3</sub> has attracted considerable attention due to its high content of magnetic element Ni and the cubic structure analogous to the perovskite cuprates. After years of extensive investigations both theoretically and experimentally, however, it is still not clear whether the mechanism for superconductivity is conventional or not. The central issue is if and how the ferromagnetic spin fluctuations contribute to the cooper paring. Recently, the experimental results on the single crystals firstly reported in 2007 trend to indicate a conventional *s*-wave mechanism. Meanwhile many compounds neighboring to MgCNi<sub>3</sub> were synthesized and the physical properties were investigated, which enriches the physics of the Ni-based antiperovskite compounds and help understand the superconductivity in MgCNi<sub>3</sub>. In this paper, we summarize the research progress in these two aspects. Moreover, a universal phase diagram of these compounds is presented, which suggests a phonon-mediated mechanism for the superconductivity, as well as a clue for searching new superconductors with the antiperovskite structure. Finally, a few possible scopes for future research are proposed.

#### 1. Introduction

To explore new superconductors is one of the central issues of material science and condensed matter physics. The discovery of high-temperature (high- $T_C$ ) superconductivity in cuprates has attracted a lot of attention in the past decades [1]. In 2001, Professor R. J. Cava from the University of Princeton reported the superconductivity in antiperovskite compound MgCNi<sub>3</sub> with the transition temperature  $T_C \sim$ 8 K (Figure 1) [2]. The superconductivity in MgCNi3 is unusual in view of the large content of the magnetic element Ni, which often favors a magnetic ground state. A prominent feature of the electronic structure is an extended van Hove singularity as shown in Figure 2(a), giving rise to a large density of states (DOS) just below the Fermi level  $(E_F)$  [see Figure 2(b)] [3]. A similar feature has been observed in some high- $T_C$  superconductors. Moreover, the DOS peak is mainly attributive to the Ni 3d states [4, 5]. Structurally, the cubic symmetry recalls the high- $T_C$  cuprates superconductors with perovskite structures. Thus the central question was raised, whether the superconductivity in MgCNi<sub>3</sub> is exotic. In other

words, the answer to the question lies in clarifying the roles of the spin fluctuations or ferromagnetic (FM) correlations probably from the dominant Ni content in MgCNi<sub>3</sub>. However, the experimental results based on polycrystalline samples by different techniques (such as NMR [6], London penetration depth [7, 8], critical current behavior [9], tunneling spectra [10, 11], carbon isotope effect [12], specific heat [13, 14], µSR [15] and so on) from different groups are controversial. A detailed summary on the experimental and theoretical results published before 2004 can be found in the review paper [16] written by Mollah. From then on, the researchers have been focusing on two main scopes in this field, namely, the experimental investigations on MgCNi<sub>3</sub> single crystals and on the synthesis and physical properties of neighbor compounds of MgCNi<sub>3</sub>, which have never been included in any review papers. In this paper, we focus on these two topics, as well as give a phase diagram based on the available data of the lattice constant, the Debye temperature and the density of state at the Fermi level,  $N(E_F)$ , for the Ni-based antiperovskite compounds. The phase diagram supports that the superconductivity observed in the Ni-based



FIGURE 1: The temperature-dependent resistivity for polycrystalline MgCNi<sub>3</sub> [Adapted by permission from Macmillan Publishers Ltd: Nature. He et al., Nature, 411, 6833 (2001), copyright 2001]. The up and low insets show the antiperovskite crystal structure and superconducting transition, respectively.

antiperovskite compounds is rather phonon-mediated than unconventional. The phase diagram also helps explore new superconductors in Ni-based antiperovskite compounds. Some possible future research scopes were proposed in the end of this paper.

#### 2. Experimental Results on Single Crystalline MgCNi<sub>3</sub>

The experiments on single crystal are desirable for eliminating the discrepancies in the experimental results based on polycrystalline samples. However, the first, also the only successful synthesis of MgCNi<sub>3</sub> single crystal up to date, was reported in 2007 [17] by Lee et al., five years after the discovery of superconductivity in polycrystalline MgCNi<sub>3</sub>.

In [17], Lee et al. employed a self-flux method with the aid of high pressure. The mixtures of Mg, C, and Ni powders with the ratio 1:1:3 were ground, pressed into a pellet, and then loaded into a high pressure cell. Then the sample was heated at  $1200^{\circ}$ C under 4.25 GPa for 12 hours. The resulted sample is a mixture of single crystalline MgCNi<sub>3</sub> with the size of hundreds of micrometers and some fluxes. Unlike the polycrystalline samples, the single crystal does not contain C or Mg deficiencies. Instead, Ni is found to be deficient. The real composition turns out to be MgCNi<sub>2.8±0.05</sub>. As displayed in Figure 3, the transition temperature is found to be 6.7 K, slightly lower than the  $T_C$  for polycrystalline MgCNi<sub>3</sub>. Even so, the entire sample quality was greatly improved compared with the crystalline samples. For example, the

TABLE 1: The lattice constant *a*, superconducting transition temperature  $T_C$ , low critical field  $H_{C1}(0)$ , up critical field  $H_{C2}(0)$ , coherence length  $\xi(0)$ , penetration depth  $\lambda(0)$ , Ginzgurg-Landau parameter  $\kappa(0)$ , electronic specific heat coefficient (Sommerfeld constant)  $\gamma$ , Debye temperature  $\Theta_D$ , coupling ratio  $2\Delta/k_BT_C$ , and the density of state at the Fermi level  $E_F$ ,  $N(E_F)$ , for the Ni-based antiperovskite superconductors. The parameters are mainly from [41]. The parameters under the "/" are for MgCNi<sub>3</sub> single crystal from [17–20]. The values of  $N(E_F)$  are from theoretical calculations reported in [4, 28, 42].

	MgCNi <sub>3</sub>	CdCNi <sub>3</sub>	ZnNNi <sub>3</sub>
a (Å)	3.812/3.8125	3.844	3.756
$T_C(\mathbf{K})$	7.6/7.3	3.2	3
$H_{C1}(0) (mT)$	10	8.6	6.9
$H_{C2}(0)$ (T)	14.4/12.8	2.2	0.96
$\xi(0)$	46/51	122	185
$\lambda(0)$ (Å)	2480/2300	2767	3089
$\kappa(0)$	54/44	23	17
$\gamma (mJ \cdot mol^{-1} K^{-2})$	30.1	18	13
$\Theta_D(\mathbf{K})$	284/132	352	336
$2\Delta/k_BT_C$	(3.75–5)/4	—	—
$N(E_F)$ (states eV <sup>-1</sup> /f·u)	4.99	3.82	2.813

residual resistivity ratio is 2.7, larger than the values ever reported for the crystalline samples. Moreover, the single crystal was homogeneous and free of microscopic regular arrays observed in the high-resolution transmission electron microscopy (TEM) images for polycrystalline samples [17].

In order to clarify the nature of the superconductivity in single crystal MgCNi<sub>3</sub>, further measurements have been performed on the samples from Lee's group. Based on the resistance measured as functions of the temperature and the applied magnetic field, it is found that the normal state resistivity can be explained by using only electron-phonon (e-p) scattering mechanism, indicating a conventional BCS behavior [18]. It is further supported by the linear behavior of  $H_{C2}(T)$  near  $T_C$ . The low-temperature electronic specific heat  $C_p(T)$  in superconducting state shows a classical exponential decrease confirming s-wave pairing with a moderate e-p coupling in this material [19, 20]. However, the  $C_p(T)$  at normal state cannot be well described by the usual  $T^3$  term of phonon contribution. A higher phonon-term probably due to the softening of the lowest acoustic Ni phonon modes is needed to interpret the deviation [20]. It is consistent with the magnetic penetration depth measured by highprecision tunnel diode oscillator technique and Hall probe magnetization, which shows that the superconducting gap is fully open over the whole Fermi surface [21]. Moreover, the ratio  $2\Delta/k_BT_C \approx 4$  and high specific-heat jump at  $T_C$ in zero field,  $\Delta C(T_C)/\gamma_n T_C \approx 1.96$ , indicating a strongcoupling mechanism. This scenario is supported by the direct gap measurements via the point-contact spectroscopy [20]. The reported superconducting parameters are summarized in Table 1. The availability of single crystal specimens also allows a detailed phonon-dispersion mapping which is



FIGURE 2: (a) Surface plot (and contour plot below) of the van Hove singularity in  $\varepsilon_k$  (relative to  $E_F$ ) in the G-*M*-*X* plane, with *M* at the right-hand corner (planar coordinates are given in units of  $2\pi/a$ ) [Reprinted with permission from H. Rosner et al., Phys. Rev. Lett. 88, 027001 (2002)]. (b) The peak structure in the electronic density of state around  $E_F$  [Reprinted with permission from D. J. Singh et al., Phys. Rev. B 64, 140507 (2001)].



FIGURE 3: (Color online) Temperature-dependent resistivity of MgCNi<sub>2.8</sub> [Reprinted with permission from H. -S. Lee et al., Adv. Mater. 19, 1807-1809 (2007)]. The sample with four metallic leads is shown in the upper inset. The lower inset shows a magnified view of  $\rho(T)$  near the superconducting transition.

closely related to the superconducting mechanism. By applying inelastic X-ray scattering (IXS), the phonon mapping was reported by Hong et al. [22]. The IXS result implies that there are no phonon anomalies that could support any exotic mechanisms for superconductivity in MgCNi<sub>3</sub>. This result was verified by a late *ab initio* calculation [23]. In addition, Jang et al. [24] observed the collapse of the peak effect (PE), namely a sudden increase in the critical current near the end of superconductivity. As the AC driving frequency increases, the PE was collapse and observable flux creep was developed in contrast to the result observed in the well-studied NbSe<sub>2</sub>. Also, the PE in MgCNi<sub>3</sub> was suggested be a dynamic phenomenon.

Although the experimental results measured on the single crystal samples suggest that MgCNi<sub>3</sub> is a conventional BCS-type superconductor with mediate or strong e-p coupling, it is yet arbitrary to exclude the contribution from spin fluctuations or FM instability. The reason is relative to the single crystalline sample itself. All the experiments were performed on the crystals prepared by the same group. Moreover, the crystal is Ni-deficient [17] though its superconducting parameters are close to those determined on polycrystalline samples (see Table 1). Theoretically, for another Ni-based antiperovskite compound InCNi<sub>3</sub>, it is proved that the excess of Ni, or say, deficiency of In can tune the system to the FM instability [25], even to a FM order [26]. It is natural to expect stronger spin-fluctuations given a perfectly stoichiometric MgCNi3 single crystal. Therefore, a theoretical comparison between the Ni-deficient MgCNi<sub>3- $\delta$ </sub> and perfect MgCNi<sub>3</sub> would resolve the problem. Moreover, growth of single crystals without Ni deficiencies is needed to end the ten-year debate on whether MgCNi3 is unconventional superconductor.



FIGURE 4: Temperature dependence of magnetic susceptibility (a) and electrical resistivity (b) for different CdCNi<sub>3</sub> samples [Reproduced with permission from M. Uehara et al., J. Phys. Soc. Jpn. 76, 034714 (2007)]. Temperature dependence of electrical resistivity (c) and magnetic susceptibility (d) for  $ZnN_{\nu}Ni_3$  [Reproduced with permission from M. Uehara et al., J. Phys. Soc. Jpn. 78, 033702 (2009)].

#### 3. Research Progress on Ni-Based Antiperovskite Compounds other than MgCNi<sub>3</sub>

The purpose of investigating the materials which are closely related to MgCNi<sub>3</sub>, that is, AXNi<sub>3</sub> (A = Zn, Al, Ga, In, Cd and so on; X = C, N, B), is two sided to explore new superconductors and to shed light on the superconducting mechanisms for MgCNi<sub>3</sub>. Up to date, there are more than ten compounds neighboring to MgCNi<sub>3</sub> were synthesized and the physical properties investigated. These newly synthesized Ni-based antiperovskite compounds can be grouped into three types, that is, carbides ACNi<sub>3</sub>, nitrides ANNi<sub>3</sub>, and borides ABNi<sub>3</sub>.

CdCNi<sub>3</sub> with the same number of valence electrons as MgCNi<sub>3</sub> is another superconductor in the carbides ACNi<sub>3</sub>. As shown in Figures 4(a) and 4(b), the transition temperature  $T_C$  is around 3.2 K, varying with fabrication conditions [27]. The superconducting parameters are listed in Table 1. The specific heat Sommerfeld constant  $\gamma$  is 18 mJ/(mol K<sup>2</sup>), smaller than that of MgCNi<sub>3</sub>. However, the theoretical calculation shows the  $N(E_F)$  value is slightly larger than MgCNi<sub>3</sub>, while the calculated e-p coupling coefficient (0.8) is nearly half that of the corresponding value of 1.5 for MgCNi<sub>3</sub> [28]. This is argued to be associated with a softening behavior of the lowest acoustic phonon branch along the X-R symmetry direction [28]. The large Wilson ratio  $R_W = (\pi^2 \kappa_B^2 / 3\mu_B^2)(\chi_0/\gamma) \sim 12$  and the well suppressed upper critical

field  $H_{c2}(0) \sim 2.2$  T, compared with the Pauli limit (14 T) indicate the existence of strong FM correlations. Surprisingly, ZnCNi<sub>3</sub> with the same number of valence electrons, as MgCNi<sub>3</sub> and CdCNi<sub>3</sub>, is found to be a Pauli paramagnetic (PM) metal without signals of superconductivity down to 2 K [29]. The value of  $\gamma$  is only 6.77 mJ/(mol K<sup>2</sup>), much smaller than those of MgCNi<sub>3</sub> and CdCNi<sub>3</sub> (see Table 1), indicating a very weak e-p coupling that explains the disappearance of superconductivity. However, it was theoretically suggested that the experimental ZnCNi<sub>3</sub> is carbon deficient, while the stoichiometric compound should be superconducting [30].

The polycrystalline ACNi<sub>3</sub> (A = Al, Ga, In) series with one more valence electron than MgCNi<sub>3</sub> were prepared by solid state reaction and detailed studies of their basic properties were performed. For GaCNi<sub>3</sub>, a  $T^2$  temperature dependence of resistivity was observed. The large values of the Kadowakiwoods ratio  $A/\gamma^2 \sim 7.2 \ (\mu\Omega \text{ cm/K}^2)$  and the Wilson ratio  $R_W \sim 9.2$  suggest a highly correlated Fermi liquid behavior [31]. The large electron-electron correlation was suggested to be caused by the proximity of FM order from the side of exchange-enhanced Pauli paramagnet, evidenced by the remarkable enhancements in both the specific heat Sommerfeld constant y and the temperature-independent magnetic susceptibility  $\chi_0$ . As to AlCNi<sub>3</sub> compound, the magnetic properties also show it is a strongly exchangeenhanced Pauli paramagnet in the very vicinity of FM order [32]. However, the low-temperature resistivity is nearly linear temperature-dependent, indicating a possible non-Fermiliquid behavior which is in sharp contrast with GaCNi<sub>3</sub>. The low-temperature electronic specific heat reveals that the spin fluctuations in AlCNi<sub>3</sub> are strongly enhanced when compared with the superconducting MgCNi<sub>3</sub>, while the e-p couplings are comparable in both compounds. The Wilson ratio  $R_W$  is about 2.4 and the dimensionless ratio that connects the low-temperature Seebeck coefficient with the Sommerfeld specific heat constant indicate that AlCNi<sub>3</sub> can be considered as a modest electron-correlated material. Consistently, the enhanced spin fluctuations were confirmed using <sup>27</sup>Al NMR measurement in AC<sub>x</sub>Ni<sub>3</sub> with  $x \ge 0.1$  where the FM order was suppressed and the system is in the vicinity of FM order [33, 34]. On the contrary, an early experimental report shows AlCNi<sub>3</sub> is a weak ferromagnet with the FM-PM transition at 300 K [35]. The nonmagnetic ground state for AlCNi<sub>3</sub> and GaCNi<sub>3</sub> was confirmed by many theoretical reports [36-39], though the predicted FM correlations or spin fluctuations are weaker than experimentally measured [37]. The existence of carbon deficiencies to various extents may account for this divergence, as suggested by Sieberer et al. [37]. As to the InCNi<sub>3</sub>, it was found that the reduction of Indium ratio in the mixture of the raw powders helps make pure antiperovskite type compound [26]. The resulted composition from the optimum synthesis is  $In_{0.95}CNi_3$ . It behaves as a FM metal below the Curie temperature (577 K) [26]. It was suggested that the appearance of ferromagnetism originates from the deviation of the Ni/In atomic ratio from the ideal case. Theoretically, it is found the ideally stoichiometric InCNi<sub>3</sub> is a nonmagnetic metal and far away from a long-range magnetic order [25, 40]. Both In vacancies

and substitutional Ni on In site were found to be able to lead to a spin-polarized ground state. Energetically, the latter scenario is more preferable to generate a FM ground state [25].

ZnNNi3 is the only superconductor observed so far in the nitrides ANNi<sub>3</sub> [41]. The  $T_C \sim 3$  K, as shown in Figures 4(c) and 4(d), is close to that of CdCNi<sub>3</sub>. The magnetic susceptibility shows a Pauli-like behavior with the magnitude much smaller than that of CdCNi<sub>3</sub>. It indicates the FM correlations in this material are not as enhanced as in CdCNi<sub>3</sub>. The obtained specific heat Sommerfeld constant y is  $13 \text{ mJ}/(\text{mol } \text{K}^2)$ , smaller than the value of  $18 \text{ mJ}/(\text{mol } \text{K}^2)$  for CdCNi<sub>3</sub>. Even so, the  $T_C$  is close to CdCNi<sub>3</sub> because the FM correlation which could suppress the  $T_C$  is weak in ZnNNi<sub>3</sub>. Compared with MgCNi<sub>3</sub>, a significantly reduced  $N(E_F)$  was theoretically observed in ZnNNi<sub>3</sub> [42], which accounts for the lower  $T_C$  in ZnNNi<sub>3</sub> than in MgCNi<sub>3</sub>. The CdNNi<sub>3</sub> and InNNi3 were also successfully synthesized by the same authors of [41] but neither is superconducting [43]. The  $\gamma$ value is  $12 \text{ mJ}/(\text{mol } \text{K}^2)$  and  $8 \text{ mJ}/(\text{mol } \text{K}^2)$  for CdNNi<sub>3</sub> and InNNi<sub>3</sub>, respectively, smaller than that for ZnNNi<sub>3</sub>. However, the temperature-independent magnetic susceptibility  $\chi_0$  for CdNNi<sub>3</sub> and InNNi<sub>3</sub> is larger than that of ZnNNi<sub>3</sub>, indicative of an enhanced contribution from the FM correlations in the former two compounds. It shows by theoretical calculations that the  $N(E_F)$  for CdNNi<sub>3</sub> is comparable with that for ZnNNi<sub>3</sub> [44], but the  $N(E_F)$  is much reduced in InNNi<sub>3</sub> [45]. Assuming that the e-p coupling is comparable in CdNNi<sub>3</sub> and ZnNNi<sub>3</sub>, it is possible to observe superconductivity in CdNNi<sub>3</sub> in case the FM correlations can be well suppressed. Very recently, He et al. reported two series of doped CdNNi<sub>3</sub>, that is,  $Cd_{1-x}In_xNNi_3$  ( $0 \le x \le 0.2$ ) and  $Cd_{1-x}Cu_xNNi_3$  ( $0 \le 0.2$ )  $x \leq 0.2$  [46]. These compounds show metallic resistivity and exhibit a Fermi liquid behavior at low temperatures. No superconductivity was found down to 2K. However, all samples exhibit very soft and weak ferromagnetism, in contrast to the PM behavior for CdNNi3reported previously by Uehara et al. [43].

Compared with the carbides ACNi<sub>3</sub> and nitrides ANNi<sub>3</sub>, little attention has been paid to the borides ABNi3. To the best of our knowledge, ScB<sub>0.5</sub>Ni<sub>3</sub> [47] is the only boron based Ni-based antiprovskite compound with its physical properties reported in the literatures. It shows a Pauli PM behavior without any superconducting signals observed down to 2 K. We tried to synthesize  $ABNi_3$  (A = Al, Ga, In, and so on) samples by solid state reaction [48]. The pure sample of InBNi3 with the antiperovskite structure (lattice constant a = 3.795 Å) was successfully synthesized and structural, magnetic, transport properties, and specific heat measurements performed. No superconductivity appears down to the lowest temperature by electric and magnetic measurements (5 K) as shown in Figure 5(a). The magnetization  $\chi(T)$  takes a typical Pauli PM behavior with a very small contribution from the FM spin fluctuations. As shown in the inset of Figure 5(b), the low-temperature specific heat data, plotted as C(T)/T versus  $T^2$ , can be well fitted using the following formula,  $C(T)/T = \gamma +$  $\beta T^2$ , where y is the Sommerfeld constant for electronic



FIGURE 5: (Color online) The physical properties for InBNi<sub>3</sub>. (a) dc magnetic susceptibility  $\chi(T)$  at H = 1 kOe. Inset shows the temperature dependence of resistivity measure at zero field. (b) Specific heat as a function of temperature. Inset shows a linear fit of C(T)/T versus  $T^2$  below 15 K.



FIGURE 6: (Color online) The Debye temperature,  $\Theta_D$ , and the DOS at  $E_F$ ,  $N(E_F)$  as a function of the lattice parameter *a* for Ni-based antiperovskite compounds. The crossing dashed lines indicate the trends of  $\Theta_D$  (downwards) and  $N(E_F)$  (upwards) with increasing the lattice constant *a*. The  $\Theta_D$  values are derived from specific heat data reported in [26, 29, 31, 32, 41]. The  $N(E_F)$  values are from theoretical calculations where corresponding calculated lattice constant is the closet to the experimental ones [4, 28, 30, 37, 39, 40, 42].

contribution and the second term represents the phonon contribution according to the Debye approximation [31, 32]. The fitted values of  $\gamma$  and  $\beta$  are equal to 11.33 mJ/(mol K<sup>2</sup>) and 0.32 mJ/(mol K<sup>4</sup>), respectively. The Debye temperature  $\Theta_D$  is estimated to be 311 K according to the formula,  $\Theta_D = (n \times 1.944 \times 10^6 / \beta)^{1/3}$ , where *n* is the number of atoms in a unit cell. The Wilson ration is estimated to be 0.93, very close to the free electrons, indicating weak FM correlations or

spin fluctuations in InBNi<sub>3</sub>. The value of *y* is smaller than the superconducting compounds in Table 1. So the e-p coupling is weak in this compound, accounting for the disappearance of superconductivity. Theoretically, the  $N(E_F)$  is only 1.47 states  $eV^{-1}/f \cdot u$  [49], consistent with the observed small *y*. Besides, the authors predicted that introduction of holes into InBNi<sub>3</sub> could make it superconducting, which has not been proved experimentally yet. Theoretically, it is predicted that AlBNi<sub>3</sub> is candidate for studying unconventional superconductivity, which has not been tested experimentally either [50].

#### 4. A Universal Phase Diagram

Thanks to the systematic studies in the past, it is possible to draw a uniform picture of the properties for the Ni-based antiperovskite compounds, thus to shed light on the unique superconductivity in MgCNi<sub>3</sub>. The Debye temperature  $\Theta_D$ obtained from specific heat measurements, the calculated density of state at Fermi level  $N(E_F)$  available in the published literatures are plotted as a function the lattice constant, as shown in Figure 6. Two main trends can be found, (1) the  $\Theta_D$  increases approximately as the lattice constant is reduced. (2) The shrinkage of lattice constant reduces the  $N(E_F)$ , which is more scattered than  $\Theta_D$  though.

The evolution of  $\Theta_D$  derived from experimental specific heat data with lattice constant can be understood as follows: the lattice contraction leads to the hardening of phonon mode, thus an increase of Debye temperature [29]. There exists a strong hybridization between X 2p and Ni 3d orbitals [4, 5, 16, 25, 30, 36, 37], playing important roles in determining the physical properties. The decrease of lattice constant reduces the Ni–C bond length, thus enhances the hybridization, leading to a decreased  $N(E_F)$ . It is more general that the DOS is inversely proportional to the band width W. for a cubic solid, the band width is related with the lattice constant a by the expression  $W \sim 1/a^3$  [29]. Therefore, the decrease of lattice constant will increase the band width, leading to a reduction of  $N(E_F)$ . In addition, the theoretical calculations show there is a peak structure in the DOS below the  $E_F$  for all Ni-based antiperovskite compounds AXNi<sub>3</sub>. For carbide compounds ACNi<sub>3</sub> (A = Al, Ga, In) or ZnNNi<sub>3</sub> that has more electrons than MgCNi<sub>3</sub>, could be interpreted as electron-doped MgCNi<sub>3</sub>, resulting in a downward shift of the position of the peak in the DOS from the  $E_F$ , consequently a reduced  $N(E_F)$  [39]. In a word, the  $N(E_F)$  is expected to increase as the lattice expands. It is basically followed by many compounds as shown in Figure 6. However, the real case may be too complex to be attributed to the above models. One example is InBNi<sub>3</sub> whose  $N(E_F)$  is extremely lower than expected. It is probably because the B 2p state in borides hybridizes with Ni 3d state more than the C 2p state in carbides ACNi<sub>3</sub> [51].

For a BCS theory, the e-p coupling constant can be estimated by the McMillan's formula [32],  $\lambda_{ph}$  $[N(E_F)\langle I^2\rangle/M\langle\omega\rangle]$ , where  $\langle I^2\rangle$  is the averaged electron-ion matrix element squared, M is an atomic mass, and  $\langle \omega^2 \rangle$  the averaged phonon frequency proportional to Debye temperature  $\Theta_D$ . Therefore, a combination of a large  $N(E_F)$  and small  $\Theta_D$  will lead to a strong e-p coupling, consequently a BCS-like superconductor. The Ni-based antiperovskite compounds seem to obey this raw. All discovered superconductors locate on the right side of the map in Figure 6, where the  $\Theta_D$  is relatively small, but the  $N(E_F)$  is relatively large. For instance, MgCNi<sub>3</sub> which shows the highest  $T_C$  has the largest  $N(E_F)$  and smallest  $\Theta_D$ . Figure 6 also suggests that the superconductivity observed in the Ni-based antiperovskite compounds is predominantly s-wave BCS type mediated by e-p coupling, though the other contributions, for example, from spin fluctuations, may not be excluded. We note that the  $\Theta_D$  for MgCNi<sub>3</sub> in the figure is from polycrystalline sample [27], while the value deduced from resistivity for single crystal MgCNi3 is surprisingly small (132 K) [18]. There is no clear trend for the relation between number of the valence electrons and  $N(E_F)$  or  $\Theta_D$ . Regardless of this, the phase diagram in Figure 6 provides a clue for searching new superconductors in Ni-based antiperovskite compound AXNi<sub>3</sub>, namely, the compounds with large lattice constant may be superconducting in terms of the BCS scenario.

#### 5. Future Outlook

In the future, the following works are worthy to be done.

- New MgCNi<sub>3</sub> single crystals with ideal 1:1:3 stoichiometry would finally close the long-time debate on the mechanism of superconductivity.
- (2) In order to clarify the divergences among the experimental and theoretical results for the Ni-based antiperovksite compounds other than MgCNi<sub>3</sub>, more extensive investigations on single crystal samples are desirable. The growth of single crystal AXNi<sub>3</sub> is a challenge. The successful growth of MgCNi<sub>3</sub> single

crystals would help, because the application of high pressure during heating can improve the solubility of carbon and suppresses the volatility of magnesium.

- (3) The AXNi<sub>3</sub> materials may serve as a platform for studying quantum critical phenomena (QCP) and quantum phase transitions (QPT) in simple material systems with three-dimensional cubic structure and none "f" elements. Previously, the QCP and QPT have been extensively studied in some "unique" systems [52], such as heavy fermions with "f" elements, magnetic systems with spin frustration, and so on. Taking the advantages of the single crystal samples, the possible quantum phase transitions can be explored in some AXNi<sub>3</sub>, such as AlCNi<sub>3</sub>, GaCNi<sub>3</sub>, and CdCNi<sub>3</sub>, driven by chemical alloying, external pressure, or magnetic field.
- (4) It is interesting to explore new superconductors with antiperovskite structure based the clues mentioned, for example, large lattice constant may favor BCS superconductivity. This clue may work for the antiperovskite compounds based on other 3d elements, such as Ti and Sc. The discovery of new superconductors can always cheer the superconductor society.

#### 6. Conclusion

We summarized the recent progress for Ni-based antiperovskite compounds closely related to the superconducting MgCNi<sub>3</sub>. A universal phase diagram is presented based on the published data, which would help design new superconductors with the antiperovskite structure. The synthesis and characterization on single crystals are desirable for future study in order to eliminate the divergences made by different authors or between the theoretical and experimental result.

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# Research Article Origin of the Giant Negative Thermal Expansion in Mn<sub>3</sub>(Cu<sub>0.5</sub>Ge<sub>0.5</sub>)N

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The giant negative thermal expansion in the Ge-doped antiperovskite Mn<sub>3</sub>CuN compound is theoretically studied by using the first principles calculations. We propose that such a negative thermal expansion property is essentially attributed to the magnetic phase transition, rather than to the lattice vibration of the Ge-doped compound. Furthermore, we found that the doped Ge atoms in the compound significantly enhance the antiferromagnetic couplings between the nearest neighboring Mn ions, which effectively stabilizes the magnetic ground states. In addition, the nature of the temperature-dependent changes in the volume of the Ge-doped compound was revealed.

#### 1. Introduction

Controlling the thermal expansion behavior of materials is eagerly required in modern advanced industries [1, 2]. Commonly, such control can be realized through mixing a kind of positive thermal expansion (PTE) materials with a kind of negative thermal expansion (NTE) materials whose volumes contract on heating. As we know, there are many PTE materials in the world, but the NTE ones rarely exist yet. Therefore, a challenging issue in controlling the thermal expansion behavior of the materials is to synthesize materials possessing NTE property.

Mn<sub>3</sub>CuN, a member of the anti-perovskite manganese nitride Mn<sub>3</sub>MN (M = Zn, Cu, etc.) [3–5], does not possess the negative thermal expansion property. However, recent experiments [6] reported that, with partial substitution of Ge for Cu in the Mn<sub>3</sub>CuN compound, the synthesized Mn<sub>3</sub>(Cu<sub>1-x</sub>Ge<sub>x</sub>)N compounds exhibited isotropic negative thermal expansion. Typically, the Ge-doped compound, Mn<sub>3</sub>(Cu<sub>1-x</sub>Ge<sub>x</sub>)N (x = 0.5), showed the NTE property in a wide temperature window of 316–386 K, together with a giant negative thermal expansion coefficient (The linear thermal expansion coefficient of a material is definited as  $\alpha = (1/L)(\Delta L/\Delta T)$ . Here, *L* is the length of the material at temperature  $T_0$ , and  $\Delta L$  is the change of the length when temperature has a change of  $\Delta T = T - T_0$ ) of  $\alpha_L = -16 \times 10^{-6} \text{ K}^{-1}$ . More importantly, the working temperature and the width of the temperature window as well as the negative thermal expansion coefficient of the Ge-doped compound were modulated through the introduction of Ge dopant.

Prompted by the pioneering research [6], many other groups have studied the doping effect on the NTE property for some counterparts of  $Mn_3(Cu_{1-x}Ge_x)N$ , typically like  $Mn_3(Cu_{1-x}Sn_x)N$  [7],  $Mn_3(Zn_{1-x}Ge_x)N$  [8],  $Mn_3(Cu_{0.6}Si_xGe_{0.4-x})N$  [9], and so on [10, 11]. All the efforts reported in these papers showed that it was the doped Ge that brought the NTE property into these antiperovskite compounds, just like that of the  $Mn_3(Cu_{1-x}Ge_x)N$ compound. Therefore, the doped Ge was regarded as a "magic element" for the observed NTE property in the class of the anti-perovskite manganese nitride compounds [6].

Recently, revealing the nature of such a "magic element" in the elegant performance of the NTE property has aroused many attractions, Matsuno and coworkers [12] proposed that the Ge dopant caused a local structural distortion in the  $Mn_3(Cu_{0.7}Ge_{0.3})N$  compound, leading to the negative thermal expansion of the system in a broad temperature range. This was supported by the neutron powder diffraction



FIGURE 1: The magnetic configurations of (a)  $\Gamma^{5g}$ , (b) C0, and (c) C1. The arrows in the figures indicate the orientations of the local magnetic moments at the ions.

and NMR measurements on  $Mn_3(Cu_{1-x}Ge_x)N$  [13]. On the other hand, through fitting the possible magnetic configurations to their experimental data, Kodama et al. [14] found that the ordering moment of the ground state known as the anti-ferromagnetic  $\Gamma^{5g}$  (seen in Figure 1(a)) of the  $Mn_3(Cu_{1-x}Ge_x)N$  compound gradually increased with decreasing temperature. This might also be responsible for the NTE property of the concerned compound. Even so, it is still unclear why the doped Ge atoms make the  $Mn_3(Cu_{1-x}Ge_x)N$  compound be of NTE property.

Usually, the thermal expansion property of a compound arises from different mechanisms, such as the lattice vibration, the temperature-excited magnetic phase transition, and the diffusion of ions/atoms between interstitial sites. Among these different mechanisms, both the lattice vibration and the phase transition are mainly responsible for the thermal expansion property of many materials. However, for our concerned  $Mn_3(Cu_{1-x}Ge_x)N$  compound, the relation between its thermal expansion behavior and the lattice vibration is still puzzling.

In this theoretical study, the  $Mn_3(Cu_{0.5}Ge_{0.5})N$  compound is selected as a representative, since it exhibited a striking NTE property in experiment. Our calculations indicate that the lattice vibration contributes to the positive thermal expansion, and the magnetic phase transition from anti-ferromagnetic phase to paramagnetic phase contributes to the negative thermal expansion. Both of the PTE and NTE are compensative to each other, resulting in the observed thermal expansion behavior of the  $Mn_3(Cu_{0.5}Ge_{0.5})N$  compound. Furthermore, a novel mechanism is proposed to explain the role of the doped Ge for the broad working temperature range of NTE in the  $Mn_3(Cu_{0.5}Ge_{0.5})N$  compound.

#### 2. Computational Details

In our calculations, a  $\sqrt{2} \times \sqrt{2} \times 2$  supercell consisting of 20 atoms is used to simulate the magnetic structures of Mn<sub>3</sub>(Cu<sub>0.5</sub>Ge<sub>0.5</sub>)N compound, where half of Cu atoms were replaced by Ge atoms. Based on the symmetry of the supercell, there are three kinds of distributions of Ge in it. These configurations are all optimized by using the VASP code [15, 16], in which the projector augmented wave (PAW) pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) parameterizations of the generalized gradient approximation [17] are adopted. The cut-off energy is 400 eV and a gammacentered k-point mesh of  $5 \times 5 \times 3$  is used for the geometry optimization. Optimizations are performed until the residual forces acting on the atoms are smaller than 0.01 eV/Å.

By calculations, the energies of the supercell with three kinds of distributions of Ge in the compound are achieved, respectively. We find that the energy differences between the Ge distributions are less than 18 meV per unit cell. Such very small energy differences imply that these different distributions of Ge in  $Mn_3(Cu_{0.5}Ge_{0.5})N$  compound may exist at finite temperatures. Even so, we select the lowest-energy one to serve our following calculations.

#### 3. Results and Discussions

3.1. Vibrational Effect on the Variation of Volume. Structurally,  $Mn_3(Cu_{0.5}Ge_{0.5})N$  is composed of the corner-shared



FIGURE 2: The coefficient of the thermal expansion  $\alpha_L$  caused by the lattice vibration as a function of the temperature.

Mn<sub>6</sub>N octahedron, somewhat like the structural feature in the ZrW<sub>2</sub>O<sub>8</sub> compound [18], where an open-framework structure consisting of corner-linked rigid polyhedra associates with the transverse vibrational modes that cause NTE. Thus, it is necessary to examine the thermal expansion behavior induced by the vibrational modes. Within the quasiharmonic approximation, the thermal expansion coefficient  $\alpha_L$  is related to the vibrational modes of a material, which is calculated through the formula [19]

$$\alpha_L = \frac{k_B}{3BV} \sum_{j=1}^n \gamma_j \left(\frac{\hbar\omega_j}{k_BT}\right)^2 \frac{\exp(\hbar\omega_j/k_BT)}{\left[\exp(\hbar\omega_j/k_BT) - 1\right]^2}, \quad (1)$$

where  $\omega_j$  is the *j*th frequency, *B* the bulk modulus, *V* the volume of the system, and  $\gamma_j$  the Grüneisen parameter relevant to the *j*th vibrational mode. Here, the Grüneisen parameter is defined as

$$\gamma_j = -\left(\frac{\partial \ln \omega_j}{\partial \ln V}\right)_T.$$
 (2)

To evaluate the coefficient of the thermal expansion, we first compute the bulk modulus and all vibrational frequencies at  $\Gamma$  point for the supercell. Based on the obtained energy as a function of the volume of the system the bulk modulus of the concerned system is predicted to be about 128.2 GPa (to accurately achieve the vibrational modes, a larger supercell containing  $2 \times 2 \times 2$  chemical unit cells is selected in our calculations relevant to the vibrational modes.) Meanwhile, the dynamic matrix of the considered system is generated through the forces acting on each atom, with using the frozen phonon approximation. By solving the dynamic matrix, we obtain all of the vibrational frequencies and the related eigenmodes. According to the obtained eigenmodes and the bulk modulus, the thermal expansion coefficient  $\alpha_L$  is obtained, as shown in Figure 2. Apparently, the value of  $\alpha_L$  is very small at low temperature and then increases rapidly with increasing temperature. When the temperature reaches 100 K or so,  $\alpha_L$  almost converges to the value of  $11.50 \times 10^{-6} \text{ K}^{-1}$ .

This value is in good agreement with that  $(13 \times 10^{-6} \text{ K}^{-1})$  from experiment [6]. Such agreement indicates that the widely used frozen phonon approximation is also reliable to evaluate the dynamical property of the compound. More importantly, the calculated values of  $\alpha_L$  shown in Figure 2 are positive in the whole considered temperature range. This strongly predicts that the transverse motion from the rigid octahedron has no contribution to the observed NTE property in the Mn<sub>3</sub>(Cu<sub>0.5</sub>Ge<sub>0.5</sub>)N compound.

3.2. Magnetic Phase Transition versus the Variation of Volume. Experiments found the observed NTE behavior in the  $Mn_3(Cu_{0.5}Ge_{0.5})N$  compound accompanied with a magnetic transition from the low temperature  $\Gamma^{5g}$ -type antiferromagnetic (AFM) phase to the high temperature paramagnetic (PM) phase [6, 20]. However, such NTE behavior was not found in the Mn<sub>3</sub>CuN compound yet [6, 21]. Clearly, the observed NTE property of Mn<sub>3</sub>(Cu<sub>0.5</sub>Ge<sub>0.5</sub>)N does tightly couple with the doped Ge atoms. To understand the role of the doped Ge atoms in the concerned NTE behavior, it is valuable to study the Mn<sub>3</sub>CuN compound firstly.

For the undoped MnCuN compound, where the Mn ions contribute to local magnetic moments, showing noncollinear magnetic configuration. Its ground state was experimentally demonstrated to be ferromagnetic. Furthermore, a magnetic configuration (notated as C0, seen in Figure 1(b)) was suggested to explain the ground state [21]. Our calculations reproduce the magnetic configuration C0, with the ferromagnetic components of local magnetic moments of  $0.18 \,\mu_B$  and  $0.30 \,\mu_B$  for the Mn ions locating at two unequal planes, respectively, which are close to the values of  $0.20 \,\mu_B$ and  $0.65 \mu_B$  reported in experiment [21]. However, such agreement does not directly support C0 configuration as the ground state of the Mn<sub>3</sub>CuN compound. In fact, a ground state configuration should have the lowest energy among all of the possible magnetic configurations. To examine whether the configuration C0 is the ground state or not, we generate many kinds of magnetic configurations, followed by full relaxations. Among these considered magnetic configurations, a lowest-energy configuration (notated as C1, seen in Figure 1(c) is found, whose energy is lower by about 0.3 eV per primitive unit cell than that of the C0 configuration. Furthermore, we find that the configuration C1 characterizes the FM feature, and the ferromagnetic component averaged on Mn ions in this configuration is about  $0.1 \mu_B$ , being smaller than the experimental value of  $0.35 \,\mu_B$ .

Moreover, for this undoped compound, we find that these magnetic configurations have different energies, meaning that these magnetic configurations may be thermally excited at different temperatures. On the other hand, the equilibrium volumes of all considered magnetic configurations are very close to each other. Hence, the thermally excited transformation between different magnetic configurations does not change the volume of the compound nearly. In other words, the Mn<sub>3</sub>CuN compound does not show NTE on heating. This is consistent with the observation in experiment very well [6].

Then, we turn to the  $Mn_3(Cu_{0.5}Ge_{0.5})N$  compound. For this compound, the magnetic state at low temperature

0.2 0.2 Energy (eV/unit cell) Energy (eV/unit cell) 0.15 0.15 0.1 0.1 0.05 0.05 0 0 3.78 3.81 3.84 3.87 3.9 3.78 3.81 3.84 3.87 3.9 Lattice constant (Å) Lattice constant (Å) (a) (b)

0.25

FIGURE 3: (a) The energies of the considered magnetic configurations as a function of the lattice constant for  $Mn_3(Cu_{0.5}Ge_{0.5})N$ . The solid line represents the energy curve of  $\Gamma^{5g}$  and the dashed lines represent the energy curves of the magnetic metastable configurations. (b) The energies as a function of the lattice constant for the distorted  $\Gamma^{5g}$  configurations (dashed lines) and the perfect  $\Gamma^{5g}$  configuration (solid line). The energy at the equilibrium volume of the  $\Gamma^{5g}$  configuration is taken as a reference.

was demonstated to be AFM in experiment. Moreover, experiments suggested that a special AFM configuration named as  $\Gamma^{5g}$  just corresponded to the ground state of the compound [13]. On the theoretical side, it is necessary to clarify its magnetic ground state. To do this, we randomly generate about eighty magnetic configurations plus the  $\Gamma^{5g}$ configuration in this compound. After full relaxations of the spins and atomic positions for each concerned case, we only have twenty four inequivalent magnetic configurations. Figure 3(a) displays the energy as a function of the lattice constant for each magnetic configuration. From Figure 3(a), one can find that the lowest-energy magnetic configuration is  $\Gamma^{5g}$ , and its equilibrium lattice constant is evaluated to be 3.864 Å, in agreement with the experimental value of 3.910 Å [13]. Furthermore, our calculations indicate that the local magnetic moments of the Mn ions in the  $\Gamma^{5g}$  configuration are 2.63  $\mu_B$ , being in good consistent with the experimental value of 2.47  $\pm$  0.27  $\mu_B$  [21]. Such agreement supports that  $\Gamma^{5g}$  is really the magnetic ground state for Mn<sub>3</sub>(Cu<sub>0.5</sub>Ge<sub>0.5</sub>)N compound.

0.25

The experiments revealed that with raising temperature, the Mn<sub>3</sub>(Cu<sub>0.5</sub>Ge<sub>0.5</sub>)N compound exhibited a volume contraction. Basically, the temperature effect not only excites more magnetic configurations of the system, but also distorts each magnetic configuration to some extent. To qualitatively evaluate the distorted magnetic configurations, we randomly deviate the orientations of the local moments of Mn ions from their initial orientations for each magnetic configuration, and thus a series of the distorted configurations can be generated through controlling the deviating extent. The volume of the compound at each distorted configuration is optimized with fixing the orientations of the local moments. Our calculations show that the volume of the distorted magnetic configurations almost does not change, except for the  $\Gamma^{5g}$  configuration. As shown in Figure 3(b), with distorting the  $\Gamma^{5g}$  configuration seriously, the energy of the system increases significantly, and the volume of the lattice decreases largely. This predicts that the volume contraction on heating is actually contributed from the distorted  $\Gamma^{5g}$  configuration together with the thermal excited metastable configurations.

On the other hand, when the compound was heated up to the Neel temperature, it transfers from the AFM  $\Gamma^{5g}$  state to the PM state [13]. As we know, the PM state is a magnetic disorder state, which cannot be simply approximated to be either a non-magnetic state or a magnetic ordering state with lowmagnetic moment in a theoretical calculation. Since there are many different magnetic configurations in the compound, the PM state may be approximatively regarded as a mixture of many magnetic structures that can be thermally excited, when the compound is heated up above the Neel temperature. According to this, the volume of the compound at the PM state is expressed as the statistically averaged volume of many different magnetic structures including  $\Gamma^{5g}$ , by using the Boltzmann distribution function. Combining this consideration with the energy curves shown in Figure 3, we statistically compute the lattice constant (a(T)) at each considered temperature. Of these temperature-dependent lattice constants, the lattice constant at 500 K is selected as a reference, and thus we obtain the ratio of the lattice constant contraction,  $\Delta a/a = (a(T) - a(500 \text{ K}))/a(500 \text{ K})$ . As displayed in Figure 4(a), the lattice constant exhibits a



FIGURE 4: (a) The ratio of the lattice contraction caused by the magnetic interaction. (b) The ratio of the lattice change arising from the magnetic interaction and the lattice vibration.  $\Delta a$  represents the difference between the lattice constant at temperature *T* and the lattice constant at 500 K.

gradual decrement with increasing temperature. This implies that the considered magnetic interactions really cause the NTE property in the whole temperature range. To go further, combining this NTE behavior with the PTE behavior from the lattice dynamics shown in Figure 2, we find that the compound exhibits the NTE behavior only in a temperature range of 250-340 K, as seen in Figure 4(b), in consistent with the results reported in experiment [6]. Our calculations above reveal that the volume contraction from the magnetic couplings is actually compensated by the lattice vibrations to some extent. The effect of such compensation is strongly relevant to the temperature. Namely, when the temperature is either below 250 K or over 340 K, the volume change of the compound from the lattice vibration overpasses that from the magnetic interaction, showing the PTE behavior. And in the temperature range between 250 and 340 K, the NTE effect is much stronger than the PTE effect, so that the compound exhibits a net effect of NTE in such a temperature window.

3.3. The Role of the Doped Ge Atoms in the NTE Property. As mentioned above, it is the doped Ge atoms that cause the compound to be of NTE property. Meanwhile, the observed NTE property is stemmed from the magnetic interaction between ions in the  $Mn_3(Cu_{0.5}Ge_{0.5})N$  compound. So, the nature of the observed NTE property is essentially associated with how the doped Ge atoms affect the magnetic couplings between ions. Physically, the magnetic couplings between ions in a compound can be expressed by the exchange parameters between different ions within the framework of the classical isotropic Heisenberg theory [22-25]. In our concerned compound, three typical kinds of exchange parameters,  $J_1$ ,  $J_2$ , and  $J'_2$  are considered. Here,  $J_1$  is the coupling between an Mn ion and its nearest neighbor Mn;  $J_2$  is the super exchange between an Mn ion and its second neighbor Mn ion, separated by an N atom;  $J'_2$  is the coupling between an Mn ion and its second neighbor Mn ion, without any atom between them. Based on the classical isotropic Heisenberg theory [22-25], the energy gain from the magnetic couplings is expressed as  $24J_1 - 12J_2 - 24J'_2$  for  $Mn_3(Cu_{0.5}Ge_{0.5})N$  and  $8J_1 - 12J_2 + 8J'_2$  for  $Mn_3CuN$ .

TABLE 1: Exchange parameters (meV) for  $Mn_3CuN$  and  $Mn_3(Cu_{0.5}Ge_{0.5})N$  compounds.

Compound	I.	I.	Ľ
Compound	Л	J2	J <sub>2</sub>
Mn <sub>3</sub> CuN	-7.5	22.5	-4.9
$Mn_3(Cu_{0.5}Ge_{0.5})N$	-19.90	20.3	-8.8

Table 1 lists the calculated exchange parameters for both compounds. Among the three kinds of exchange parameters, the amplitude of  $J_1$  for the Mn<sub>3</sub>(Cu<sub>0.5</sub>Ge<sub>0.5</sub>)N compound is considerably bigger than that for the Mn<sub>3</sub>CuN compound. This indicates that the doped Ge strongly enhances the magnetic interaction between the nearest-neighboring Mn ions in the  $Mn_3(Cu_{0.5}Ge_{0.5})N$  compound. It is worth noting that in our concerned anti-perovskite manganese nitride compound, the couplings between the nearest-neighboring Mn ions form a triangular structure in space. Such a triangular feature is just responsible for the noncollinear antiferromagnetic configuration, which is the basic characteristic of the  $\Gamma^{5g}$  configuration. So, the doped Ge atoms effectively enhance the AFM  $\Gamma^{5g}$  configuration much more than the other configurations in the Mn<sub>3</sub>(Cu<sub>0.5</sub>Ge<sub>0.5</sub>)N compound. This is just corresponding to the fact that Mn<sub>3</sub>(Cu<sub>0.5</sub>Ge<sub>0.5</sub>)N has the ground state of  $\Gamma^{5g}$ , whereas Mn<sub>3</sub>CuN does not have yet [6, 21].

As reported in experiments, the doped Ge atoms not only caused the NTE property, but also made the NTE occurring in a broad temperature range for Mn<sub>3</sub>(Cu<sub>0.5</sub>Ge<sub>0.5</sub>)N. However, these features did not occur in the Mn<sub>3</sub>(Cu<sub>1-x</sub>M<sub>x</sub>)N (M = Zn, Si, and Ga) compounds. Basically, the different behaviors in NTE of the compounds caused by the different dopants tightly couple with the different electronic structures of the dopants. For the isolated atoms of Cu, Ge, Zn, and Mn, the energies of their highest occupied orbitals are in the order of  $E_{Zn}^{4s}(-5.93 \text{ eV}) < E_{Mn}^{4s}(-5.47 \text{ eV}) < E_{Cu}^{4s}(-4.98 \text{ eV}) < E_{Ge}^{4p}(-4.38 \text{ eV})$ . Clearly, the energy differences of the orbitals between Mn and M (M = Cu, Zn and Ge) are quite big. This means that the 4s orbital of either Cu or Zn and the 4p orbital of Ge do not significantly couple with the valence

orbital of Mn in the compound. So, in the compound, most electrons on these atomic orbitals are unpaired and thus locate at the unsaturated states which are almost at the Fermi level. Especially,  $E_{Ge^{4p}}$  is much higher than the others, and the number of electrons on Ge 4p is larger than the other orbitals considered above. Thus the doped Ge in the compound contribute more states at the Fermi level than the other cases. Meanwhile, the local density of states (LDOS) at the Fermi level from the Mn ions drops down largely when the content of Ge is 50% [26] in the compound. With rising temperature, more electrons from the Ge 4p orbital are thermally excited into the conduction band in such metallic systems. These conduction electrons may polarize some of local electrons in the compound, altering the magnetic couplings between Mn ions and the local magnetic moments accordingly. Namely, some of magnetic states in the Ge-doped compound is easily excited by temperature, even temperature rises slightly. As a result, the Ge-doped compound shows a gradually temperature-dependent change in volume. This is corresponding to the wide temperature range for the NTE working, as reported in experiments [6].

#### 4. Conclusion

We have investigated the lattice vibrations and the magnetic phase transition for the Ge-doped metallic anti-perovskite  $Mn_3(Cu_{0.5}Ge_{0.5})N$  compound, based on first-principles calculations. We find that the lattice vibrations contribute to the PTE property rather than the NTE property. Our calculations indicate that the observed NTE is actually resulted from the magnetic phase transition from the  $\Gamma^{5g}$  phase to the PM phase. Furthermore, we suggest that the thermal effect excites more valence electrons from the doped Ge atoms to the conduction bands in the compound. These donated conduction electrons polarize the local electrons and change the local magnetic moments of Mn ions, leading to the contraction of the compound in volume.

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