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Review Article

Research Progress on Ni-Based Antiperovskite Compounds

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The superconductivity in antiperovskite compound $MgCNi_3$ was discovered in 2001 following the discovery of the superconducting MgB_2. In spite of its lower superconducting transition temperature (8 K) than MgB_2 (39 K), $MgCNi_3$ 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 $MgCNi_3$ were synthesized and the physical properties were investigated, which enriches the physics of the Ni-based antiperovskite compounds and help understand the superconductivity in $MgCNi_3$. 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 $MgCNi_3$ with the transition temperature $T_C \sim 8$ K (Figure 1) [2]. The superconductivity in $MgCNi_3$ 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 $MgCNi_3$ 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 $MgCNi_3$. 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 $MgCNi_3$ single crystals and on the synthesis and physical properties of neighbor compounds of $MgCNi_3$, 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

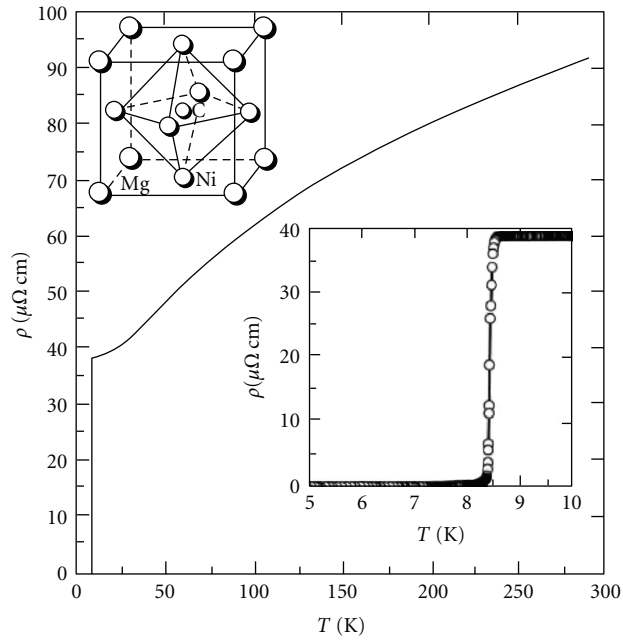

Figure 1: The temperature-dependent resistivity for polycrystalline $MgCNi_3$ [Adapted by permission from Macmillan Publishers Ltd: Nature. He et al., Nature, 411, 6833 (2001), copyright 2001]. The up and low insets show the antiperovskite crystal structure and superconducting transition, respectively.

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 $MgCNi_3$

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 $MgCNi_3$ single crystal up to date, was reported in 2007 [17] by Lee et al., five years after the discovery of superconductivity in polycrystalline $MgCNi_3$.

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°C under 4.25 GPa for 12 hours. The resulted sample is a mixture of single crystalline $MgCNi_3$ 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 $MgCNi_{2.8\pm0.05}$. As displayed in Figure 3, the transition temperature is found to be 6.7 K, slightly lower than the T_C for polycrystalline $MgCNi_3$. Even so, the entire sample quality was greatly improved compared with the crystalline samples. For example, the 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].

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) γ, Debye temperature Θ_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 $MgCNi_3$ single crystal from [17–20]. The values of $N(E_F)$ are from theoretical calculations reported in [4, 28, 42].

	$MgCNi_3$	$CdCNi_3$	$ZnNNi_3$
a (Å)	3.812/3.8125	3.844	3.756
T_C (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
γ (mJ·mol^{-1} K^{-2})	30.1	18	13
Θ_D (K)	284/132	352	336
$2\Delta/k_BT_C$	(3.75–5)/4	—	—
$N(E_F)$ (states eV^{-1}/f·u)	4.99	3.82	2.813

In order to clarify the nature of the superconductivity in single crystal $MgCNi_3$, 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 high-precision 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 strong-coupling 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

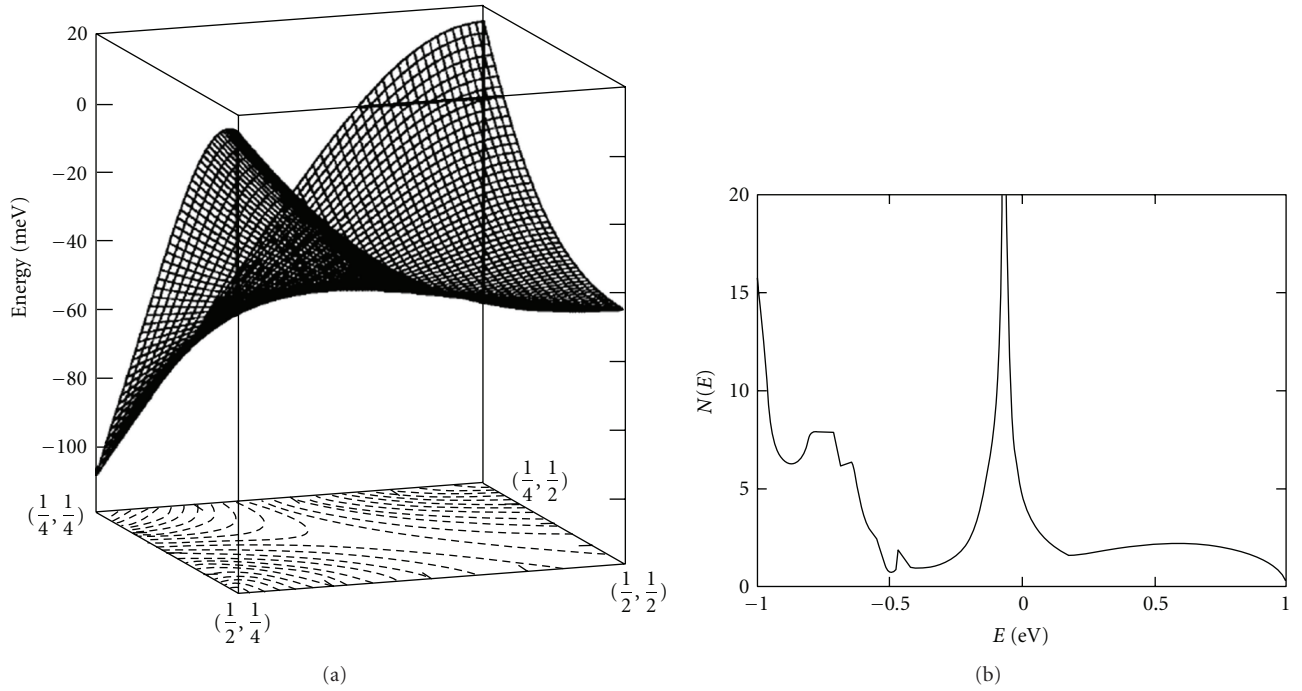

FIGURE 2: (a) Surface plot (and contour plot below) of the van Hove singularity in ε_k (relative to E_F) in the G-M-X plane, with M at the right-hand corner (planar coordinates are given in units of $2\pi/a$) [Reprinted with permission from H. Rosner et al., Phys. Rev. Lett. 88, 027001 (2002)]. (b) The 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)].

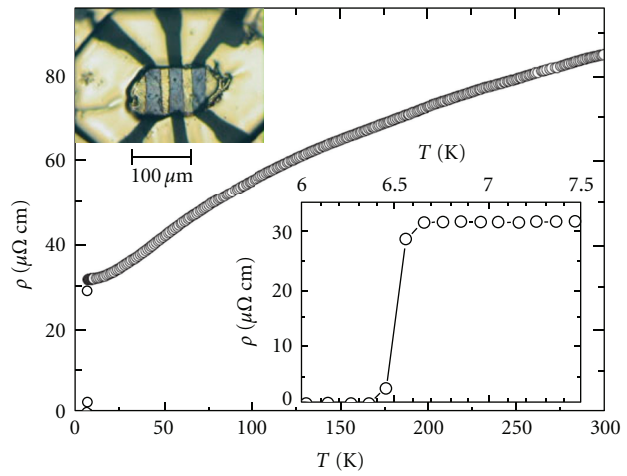

FIGURE 3: (Color online) Temperature-dependent resistivity of $MgCNi_{2.8}$ [Reprinted with permission from H. -S. Lee et al., Adv. Mater. 19, 1807-1809 (2007)]. The sample with four metallic leads is shown in the upper inset. The lower inset shows a magnified view of $\rho(T)$ near the superconducting 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 $MgCNi_3$. 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 $NbSe_2$. Also, the PE in $MgCNi_3$ was suggested be a dynamic phenomenon.

Although the experimental results measured on the single crystal samples suggest that $MgCNi_3$ 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 $InCNi_3$, 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 $MgCNi_3$ single crystal. Therefore, a theoretical comparison between the Ni-deficient $MgCNi_{3-\delta}$ and perfect $MgCNi_3$ would resolve the problem. Moreover, growth of single crystals without Ni deficiencies is needed to end the ten-year debate on whether $MgCNi_3$ is unconventional superconductor.

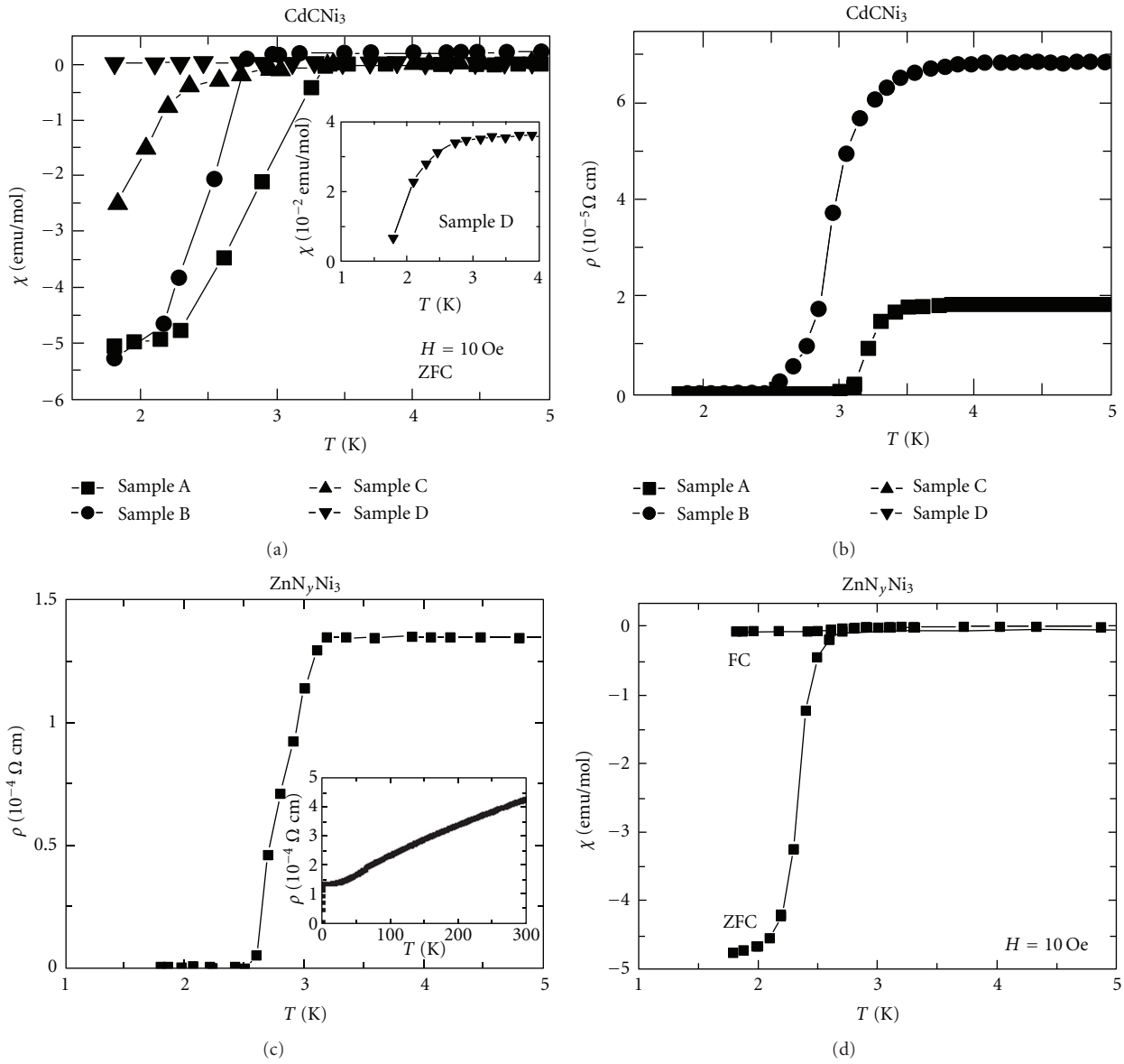

Figure 4: Temperature dependence of magnetic susceptibility (a) and electrical resistivity (b) for different $CdCNi_3$ samples [Reproduced with permission from M. Uehara et al., J. Phys. Soc. Jpn. 76, 034714 (2007)]. Temperature dependence of electrical resistivity (c) and magnetic susceptibility (d) for ZnN_yNi_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 $MgCNi_3$

The purpose of investigating the materials which are closely related to $MgCNi_3$, that is, $AXNi_3$ (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 $MgCNi_3$. Up to date, there are more than ten compounds neighboring to $MgCNi_3$ were synthesized and the physical properties investigated. These newly synthesized Ni-based antiperovskite compounds can be grouped into three types, that is, carbides $ACNi_3$, nitrides $ANNi_3$, and borides $ABNi_3$.

$CdCNi_3$ with the same number of valence electrons as $MgCNi_3$ is another superconductor in the carbides $ACNi_3$. 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 γ is 18 mJ/(mol K^2), smaller than that of $MgCNi_3$. However, the theoretical calculation shows the $N(E_F)$ value is slightly larger than $MgCNi_3$, while the calculated e-p coupling coefficient (0.8) is nearly half that of the corresponding value of 1.5 for $MgCNi_3$ [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, $ZnCNi_3$ with the same number of valence electrons, as $MgCNi_3$ and $CdCNi_3$, is found to be a Pauli paramagnetic (PM) metal without signals of superconductivity down to 2 K [29]. The value of γ is only 6.77 mJ/(mol K^2), much smaller than those of $MgCNi_3$ and $CdCNi_3$ (see Table 1), indicating a very weak e-p coupling that explains the disappearance of superconductivity. However, it was theoretically suggested that the experimental $ZnCNi_3$ is carbon deficient, while the stoichiometric compound should be superconducting [30].

The polycrystalline $ACNi_3$ (A = Al, Ga, In) series with one more valence electron than $MgCNi_3$ were prepared by solid state reaction and detailed studies of their basic properties were performed. For $GaCNi_3$, a T^2 temperature dependence of resistivity was observed. The large values of the Kadowaki-woods ratio $A/\gamma^2 \sim 7.2$ ($\mu\Omega$ 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 γ and the temperature-independent magnetic susceptibility χ_0. As to $AlCNi_3$ compound, the magnetic properties also show it is a strongly exchange-enhanced Pauli paramagnet in the very vicinity of FM order [32]. However, the low-temperature resistivity is nearly linear temperature-dependent, indicating a possible non-Fermi-liquid behavior which is in sharp contrast with $GaCNi_3$. The low-temperature electronic specific heat reveals that the spin fluctuations in $AlCNi_3$ are strongly enhanced when compared with the superconducting $MgCNi_3$, 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 $AlCNi_3$ can be considered as a modest electron-correlated material. Consistently, the enhanced spin fluctuations were confirmed using ^{27}Al NMR measurement in AC_xNi_3 with $x \geq 0.1$ 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 $AlCNi_3$ is a weak ferromagnet with the FM-PM transition at 300 K [35]. The nonmagnetic ground state for $AlCNi_3$ and $GaCNi_3$ 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 $InCNi_3$, 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 $InCNi_3$ 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].

$ZnNNi_3$ is the only superconductor observed so far in the nitrides $ANNi_3$ [41]. The $T_C \sim 3$ K, as shown in Figures 4(c) and 4(d), is close to that of $CdCNi_3$. The magnetic susceptibility shows a Pauli-like behavior with the magnitude much smaller than that of $CdCNi_3$. It indicates the FM correlations in this material are not as enhanced as in $CdCNi_3$. The obtained specific heat Sommerfeld constant γ is 13 mJ/(mol K^2), smaller than the value of 18 mJ/(mol K^2) for $CdCNi_3$. Even so, the T_C is close to $CdCNi_3$ because the FM correlation which could suppress the T_C is weak in $ZnNNi_3$. Compared with $MgCNi_3$, a significantly reduced $N(E_F)$ was theoretically observed in $ZnNNi_3$ [42], which accounts for the lower T_C in $ZnNNi_3$ than in $MgCNi_3$. The $CdNNi_3$ and $InNNi_3$ were also successfully synthesized by the same authors of [41] but neither is superconducting [43]. The γ value is 12 mJ/(mol K^2) and 8 mJ/(mol K^2) for $CdNNi_3$ and $InNNi_3$, respectively, smaller than that for $ZnNNi_3$. However, the temperature-independent magnetic susceptibility χ_0 for $CdNNi_3$ and $InNNi_3$ is larger than that of $ZnNNi_3$, 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 $CdNNi_3$ is comparable with that for $ZnNNi_3$ [44], but the $N(E_F)$ is much reduced in $InNNi_3$ [45]. Assuming that the e-p coupling is comparable in $CdNNi_3$ and $ZnNNi_3$, it is possible to observe superconductivity in $CdNNi_3$ in case the FM correlations can be well suppressed. Very recently, He et al. reported two series of doped $CdNNi_3$, that is, $Cd_{1-x}In_xNNi_3$ ($0 \leq x \leq 0.2$) and $Cd_{1-x}Cu_xNNi_3$ ($0 \leq x \leq 0.2$) [46]. These compounds show metallic resistivity and exhibit a Fermi liquid behavior at low temperatures. No superconductivity was found down to 2 K. However, all samples exhibit very soft and weak ferromagnetism, in contrast to the PM behavior for $CdNNi_3$reported previously by Uehara et al. [43].

Compared with the carbides $ACNi_3$ and nitrides $ANNi_3$, little attention has been paid to the borides $ABNi_3$. To the best of our knowledge, $ScB_{0.5}Ni_3$ [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 $InBNi_3$ 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 γ is the Sommerfeld constant for electronic

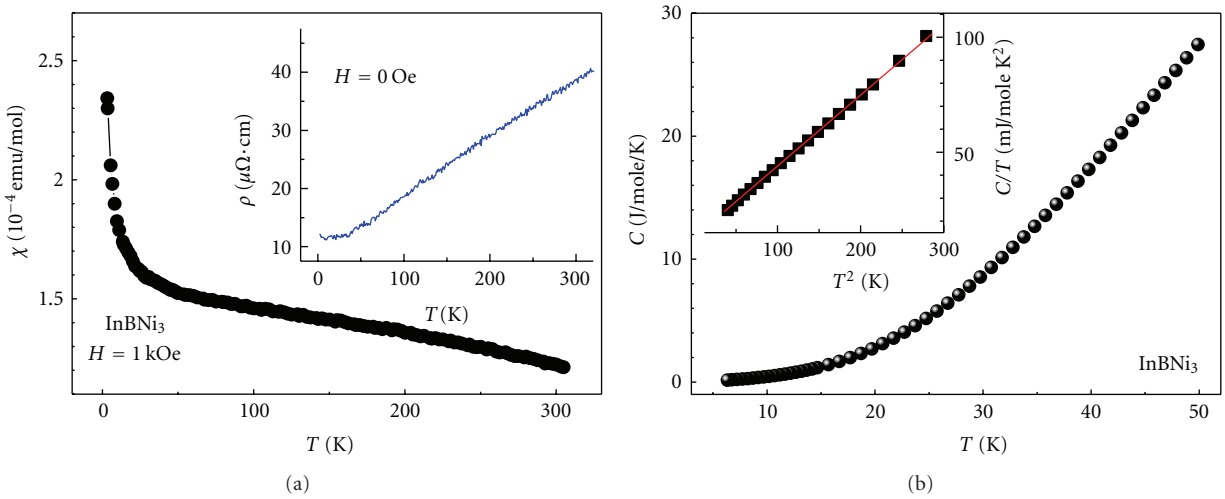

FIGURE 5: (Color online) The physical properties for $InBNi_3$. (a) dc magnetic susceptibility $\chi(T)$ at $H = 1$ kOe. Inset shows the temperature dependence of resistivity measure at zero field. (b) Specific heat as a function of temperature. Inset shows a linear fit of $C(T)/T$ versus T^2 below 15 K.

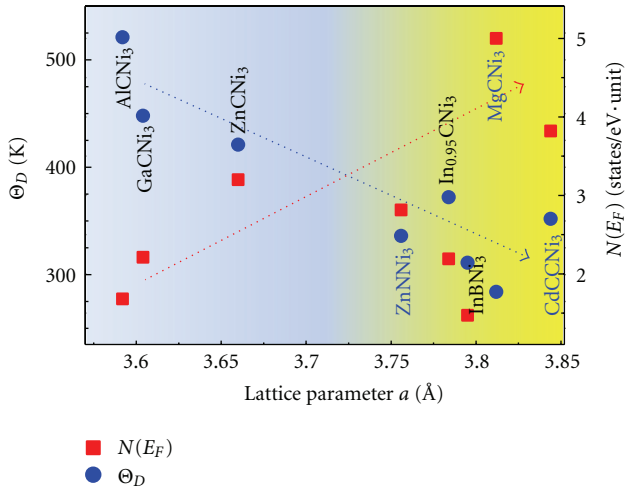

FIGURE 6: (Color online) The Debye temperature, Θ_D, and the DOS at E_F, $N(E_F)$ as a function of the lattice parameter a for Ni-based antiperovskite compounds. The crossing dashed lines indicate the trends of Θ_D (downwards) and $N(E_F)$ (upwards) with increasing the lattice constant a. The Θ_D values 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 γ and β are equal to 11.33 mJ/(mol K^2) and 0.32 mJ/(mol K^4), respectively. The Debye temperature Θ_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 $InBNi_3$. The value of γ 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·u [49], consistent with the observed small γ. Besides, the authors predicted that introduction of holes into $InBNi_3$ could make it superconducting, which has not been proved experimentally yet. Theoretically, it is predicted that $AlBNi_3$ 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 $MgCNi_3$. The Debye temperature Θ_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 Θ_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 Θ_D though.

The evolution of Θ_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 $AXNi_3$. For carbide compounds $ACNi_3$ (A = Al, Ga, In) or $ZnNNi_3$ that has more electrons than $MgCNi_3$, could be interpreted as electron-doped $MgCNi_3$, 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 $InBNi_3$ 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 $ACNi_3$ [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 Θ_D. Therefore, a combination of a large $N(E_F)$ and small Θ_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 Θ_D is relatively small, but the $N(E_F)$ is relatively large. For instance, $MgCNi_3$ which shows the highest T_C has the largest $N(E_F)$ and smallest Θ_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 Θ_D for $MgCNi_3$ in the figure is from polycrystalline sample [27], while the value deduced from resistivity for single crystal $MgCNi_3$ 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 Θ_D. Regardless of this, the phase diagram in Figure 6 provides a clue for searching new superconductors in Ni-based antiperovskite compound $AXNi_3$, 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.

(1) New $MgCNi_3$ 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 $MgCNi_3$, more extensive investigations on single crystal samples are desirable. The growth of single crystal $AXNi_3$ is a challenge. The successful growth of $MgCNi_3$ 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 $AXNi_3$ 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 $AXNi_3$, such as $AlCNi_3$, $GaCNi_3$, and $CdCNi_3$, 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 $MgCNi_3$. 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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