

Prediction of Superconductivity in 3d Transition-Metal Based Antiperovskites via Magnetic Phase Diagram

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(Received December 10, 2013; accepted March 5, 2014; published online April 10, 2014)

We theoretically studied the electronic structure, magnetic properties, and lattice dynamics of a series of 3d transition-metal antiperovskite compounds AXM_3 by density function theory. Based on the Stoner criterion, we drew the magnetic phase diagram of carbon-based antiperovskites ACM_3 . In the phase diagram, compounds with non-magnetic ground state but locating near the ferromagnetic boundary are suggested to have high $N(E_F)$ that may cause sizeable electron–phonon coupling and make the compounds superconducting. To approve this deduction, we systematically calculated the phonon spectra and electron–phonon coupling of a series of Cr-based antiperovskites ACr_3 and $ANCr_3$. The results show that $AlCCr_3$, $GaCCr_3$, and $ZnNCr_3$ could be moderate coupling BCS superconductors. The influence of spin fluctuation on superconductivity are discussed. Furthermore, other potential superconducting AXM_3 including some new Co- and Fe-based antiperovskite superconductors are predicted from the magnetic phase diagram.

1. Introduction

Since superconductivity (SC) was found by Onnes,¹⁾ researchers have made a lot of efforts to figure out its mechanism. The BCS theory^{2–4)} pointed out two electrons with opposite spins can pair with each other via electron–phonon coupling (EPC). Therefore, magnetism or spin fluctuation (SF) may break the pair and be harmful to SC. The discovery of unconventional superconductors such as cuprate oxide superconductors,^{5,6)} iron based superconductors,^{7,8)} Sr_2RuO_4 ,⁹⁾ $Na_xCoO_2 \cdot yH_2O$,¹⁰⁾ etc., challenges the EPC mechanism. For the unconventional superconductors, SF may play an important role in the superconducting mechanism, which makes researchers reconsider the relation between magnetism and SC.

Superconducting $MgCNi_3$,¹¹⁾ containing a high concentration of magnetic element Ni, attracted a lot of attentions on the role of SF. $MgCNi_3$ has a so-called antiperovskite structure, in which Mg atom locates at the corner, and six Ni atoms at the face-center together with one C atom at the body center form the C–Ni₆ octahedron. A van Hove singularity locates just below Fermi level (E_F), leading to large density of states (DOS) at E_F ($N(E_F)$).^{12–14)} It makes the compound strongly exchange-enhanced and unstable toward to ferromagnetism (FM) upon hole doping.^{12,13)} Experimentally speaking, due to the high volatility of Mg and the relatively poor reactivity of C, it is extremely difficult to synthesize stoichiometric $MgCNi_3$.^{15–17)} The atomic deficiencies in the antiperovskite system may strongly affect the properties^{18,19)} and lead to some contradictory results in the reported polycrystalline samples.¹⁵⁾ Recently, the single crystal samples have been prepared.^{16,17,20–24)} The physical property measurements demonstrate the conventional EPC mechanism, but the reported EPC strengths of these samples are contradicted.^{17,20–22,25,26)} Moreover, it has not been successful so far to induce FM instability by preparing hole-doped compounds such as $Mg_{1-x}Na_xCNi_3$ and $Mg_{1-x}Li_xCNi_3$. The interplay between SC and SF in $MgCNi_3$ is still unclear and in debate.²⁷⁾

Nowadays, lots of 3d transition-metal based antiperovskite AXM_3 (A usually is main group element; X = B, C, and N;

M = 3d transition-metal elements) have been experimentally synthesized.²⁸⁾ However, the reported physical property measurements are mainly focused on the Ni- and Mn-based antiperovskites. In Ni-based antiperovskites, $CdCNi_3$ and $ZnNNi_3$ were reported to show SC behavior.^{29,30)} Various magnetic structures and functionalities exist in Mn-based antiperovskites.^{31–36)} Moreover, superconducting trace has been found in $InBSc_3$.³⁷⁾ Some theoretical predictions suggest that SC may exist in some Sc- and Cr-based antiperovskites.^{38–41)} Indeed, due to the high concentration of 3d transition-metal atoms, one can imagine that more interesting properties exist in other antiperovskite AXM_3 . The investigation of them will be very important, both in the search for new superconductors and in the pursuit of a better understanding of the interplay between SC and magnetism.²⁷⁾

In the present work, we offer an approach to explore new 3d transition-metal based antiperovskite superconductors. In order to have an overall understanding of the magnetism in AXM_3 , we calculated the electronic structures of a series of 3d transition-metal based antiperovskites AXM_3 and concluded the doping effects of each atom. From the analysis of these doping effects, we can evaluate the variation of $N(E_F)$ of different AXM_3 . We drew a magnetic phase diagram of ACM_3 based on the Stoner criterion $N(E_F)I > 1$. From the phase diagram, we predict that the materials locating near FM boundary may have sizeable EPC and could show SC. To confirm this deduction, we systematically investigated the formation energies, electronic structures, lattice dynamic properties, and EPC of a series of Cr-based $AXCr_3$. For comparison, such properties of $MgCNi_3$ are also calculated. Our results confirm the strong EPC for $MgCNi_3$ and suggest that $AlCCr_3$, $GaCCr_3$, and $ZnNCr_3$ are moderate coupling BCS superconductors. The depairing effects from SF are also discussed. Furthermore, some potential superconducting antiperovskites such as new Co- and Fe-based superconductors are suggested.

2. Methods

The structural relaxation and electronic structure calculations were performed using projected augmented-wave (PAW)^{42,43)} method as implemented in the ABINIT

Table I. The $N(E_F)$ (states/eV/spin) in NM ground state (above “/”) and Stoner parameter I (under “/”) of ACM_3 ($A = \text{Na, Mg, Al, and Si}$, $M = 3d$ transition metal elements).

A↓	M→	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Na		3.66/0.26	3.19/0.22	1.51/0.50	4.17/0.32	7.84/0.37	7.61/0.30	3.83/0.41	7.45/0.33	0.44/0.74
Mg		5.30/0.30	1.64/0.40	4.28/0.23	2.86/0.34	5.47/0.35	6.20/0.32	3.69/0.41	2.57/0.28	0.41/0.79
Al		0.26/0.29	1.491/0.05	4.31/0.32	2.22/0.32	4.87/0.45	5.53/0.39	0.77/0.74	1.13/0.58	1.04/0.20
Si		1.26/0.42	2.23/0.25	6.38/0.21	3.06/0.27	6.20/0.47	1.35/0.31	3.87/0.42	1.68/0.19	0.75/0.72

code.^{44–46}) Electronic wavefunctions are expanded with plane waves up to an energy cutoff (E_{cut}) of 1200 eV. Brillouin zone sampling is performed on a Monkhorst–Pack (MP) mesh⁴⁷ of $16 \times 16 \times 16$. The self-consistent calculations were considered to be converged when the total energy of the system was stable within 10^{-6} Ha. Non-magnetic (NM) and FM states were tested in the study.

The calculations of phonon spectra and EPC were based on the frame work of the self consistent density functional perturbation theory (DFPT)⁴⁸) using planewaves and ultrasoft pseudopotentials⁴⁹) with Quantum-Espresso.⁵⁰) We use an $8 \times 8 \times 8$ grid for zone integration in the self-consistent calculations, while a denser $16 \times 16 \times 16$ grid was used in the EPC calculations. We have calculated dynamical matrices at a uniform $4 \times 4 \times 4$ grid of q -points.

To ensure our calculation reliability, we cross-checked the results given by the above two DFT codes and found them to be in close agreement. And for consistency, we used the same GGA-PBE⁵¹) exchange–correlation potential in both cases.

3. Results and Discussion

3.1 Doping effects of AXM_3

As Rosner et al.¹²) mentioned, the A-site atom only plays the role as an effective valent electrons supplier. The most common A-site atoms of the antiperovskite compounds can be divided into four groups according to the effective valence electrons: Cu and Ag (A^{1+}); Mg, Zn, and Cd (A^{2+}); Al, Ga, and In (A^{3+}); Ge and Sn (A^{4+}). Clearly, the effective valence electrons of A-site atoms are usually in the range from 1 to 4. For simplification, we chose Na^{1+} , Mg^{2+} , Al^{3+} , and Si^{4+} atoms as the A-site atoms of the antiperovskites we investigated.

Figure 1 shows the lattice parameters and magnetic moment of a series of carbon-based ACM_3 . As expected, the lattice parameter varies with the same trend of variation of the atom radius. The ground states of these compounds are determined by comparing the total energies of the NM and FM states. The $ACMn_3$ and most $ACFe_3$ show FM state, which coincides with the experimental results. Surprisingly, SiCFe_3 and AlCCo_3 show NM state. Comparing the magnetic moments with the $N(E_F)$ (Table I), one can see that all the compounds with FM ground state have quite large $N(E_F)$ in NM state. It is corresponding to the Stoner’s itinerant magnetism: the higher $N(E_F)$ in NM state, the easier a system becomes spin-polarized. The magnetism of these compounds will be discussed below.

In order to have an overall understanding of the $3d$ transition-metal based antiperovskites AXM_3 , the doping/substitution effects of each atom on the electronic structure must be investigated. We start from reviewing the electronic structure of MgCNi_3 . Figure 2 shows the calculated DOS of

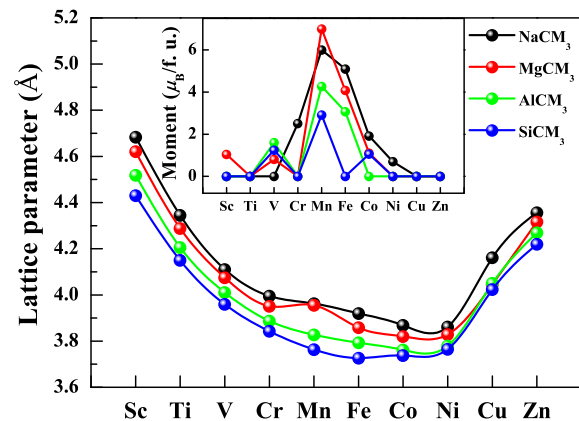


Fig. 1. (Color online) Lattice parameters and magnetic moments of ACM_3 ($A = \text{Na, Mg, Al, and Si}$, $M = 3d$ transition metal elements).

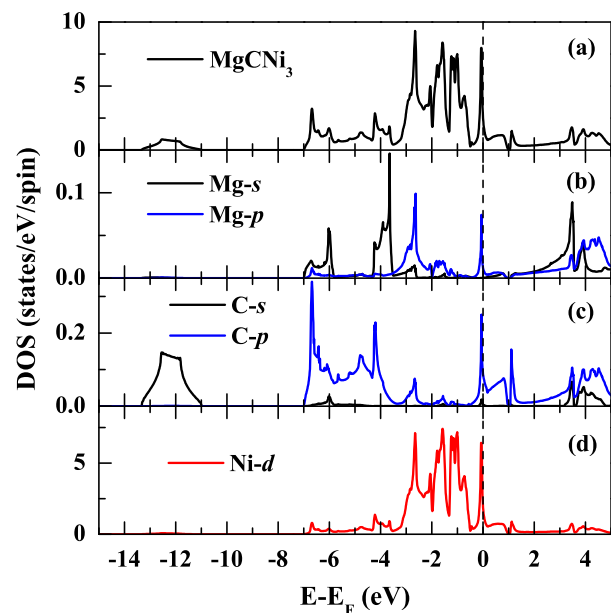


Fig. 2. (Color online) Total and atom-orbital-projected DOS of MgCNi_3 .

MgCNi_3 . It can be seen that the total DOS near E_F are mainly contributed by Ni- $3d$ electrons. From -7 to -4 eV and near E_F , C- $2p$ electrons hybridize strongly with Ni- $3d$ electrons. The π^* anti-bonding state locates just below E_F , which leads to the van Hove singularity, yielding the high $N(E_F) = 2.57$ states/eV/spin. We calculated the Stoner parameter I using the methods mentioned by Rosner et al.¹²) The result shows that $I = 0.28$, and Stoner enhancement factor $S = [1 - N(E_F)I]^{-1} = 3.57$, indicating the strong SF exists in MgCNi_3 . Our results are very close to the previous theoretical reports,^{12–15}) which proves the validity of present calculations.

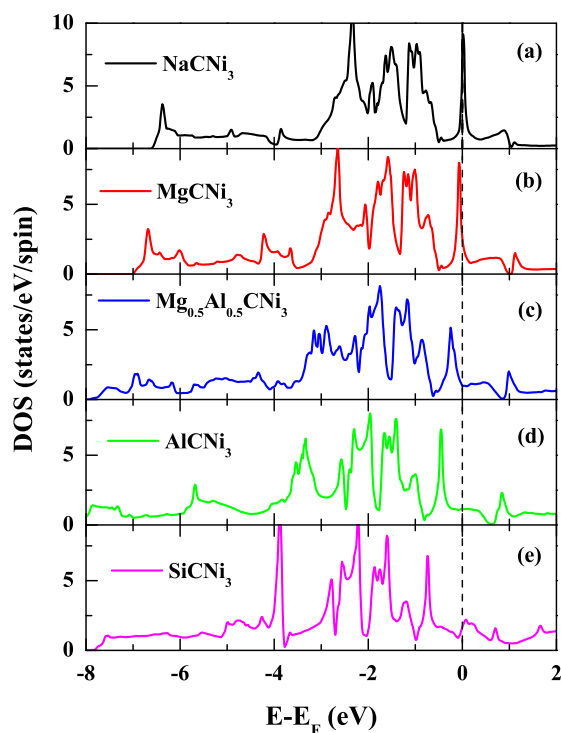


Fig. 3. (Color online) DOS of (a) NaCNi₃, (b) MgCNi₃, (c) Mg_{0.5}Al_{0.5}CNi₃, (d) AlCNi₃, and (e) SiCNi₃.

We firstly studied the A-site doping effect by investigating the electronic structures of NaCNi₃, MgCNi₃, AlCNi₃, and SiCNi₃. Using a doubled supercell, we also calculated the electronic structure of Mg_{0.5}Al_{0.5}CNi₃. As shown in Fig. 3, the doping of A-site atoms does not change the overall shape of DOS of ACNi₃ near E_F . The main change is the E_F moving with the variation of the amount of electrons. Thus the doping effect of A-site atom of AXM₃ can be evaluated by the rigid band approximation. For NaCNi₃, it can be seen as doped MgCNi₃ by a hole, which causes E_F decreasing. The E_F just locates at the DOS peak, leading to very large $N(E_F)$, which makes NaCNi₃ satisfied with the Stoner criteria $N(E_F)I > 1$. Therefore, spin polarization appears in NaCNi₃.

Next we consider the X-site doping effect. Figure 4 shows the DOS of MgBNi₃, MgCNi₃ and MgNNi₃. Since the X-2p electrons strongly hybridize with Ni-3d electrons, the change of X-site atoms is expected to strongly influence the shape of DOS. The evaluation of X-site doping effect needs to investigate the X-M hybridization besides the E_F moving. For instance, replacing the carbon atom in MgCNi₃ by boron atom, E_F moves to the DOS peak. On the other hand, the B-Ni hybridization makes the peak smeared, which does not lead to very large $N(E_F)$. Therefore MgBNi₃ is still in the NM ground state. The calculated $N(E_F)$ of MgBNi₃ is 2.58 states/eV/spin, which can be comparable to that of MgCNi₃. For MgNNi₃, the DOS peak is smeared, too. Meanwhile E_F moves away from the DOS peak, leading to small $N(E_F) = 1.36$ states/eV/spin.

According to our calculation, except for Ni- and Cu-based AXM₃, all the other compounds have similar character that the bonding and anti-bonding states are far from E_F . That means for most AXM₃ compounds, there exists weak X-M hybridizations at E_F . Figure 5 shows the DOS of AlCCr₃ and AlNCr₃. The shapes of DOS near E_F are very similar. The

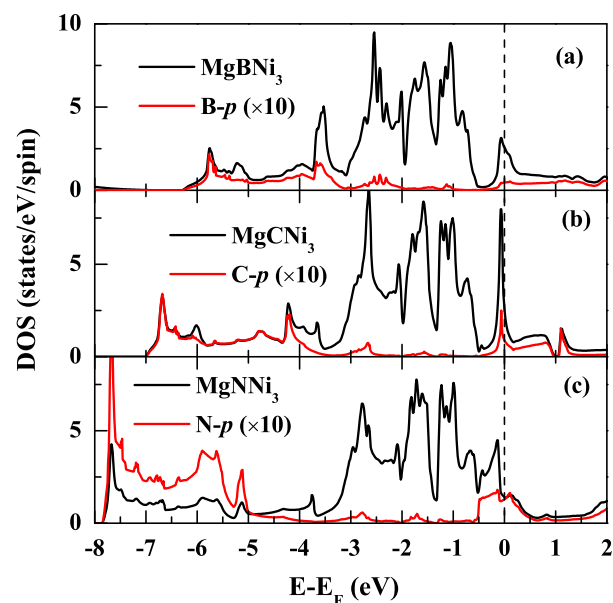


Fig. 4. (Color online) DOS of (a) MgBNi₃, (b) MgCNi₃, and (c) MgNNi₃.

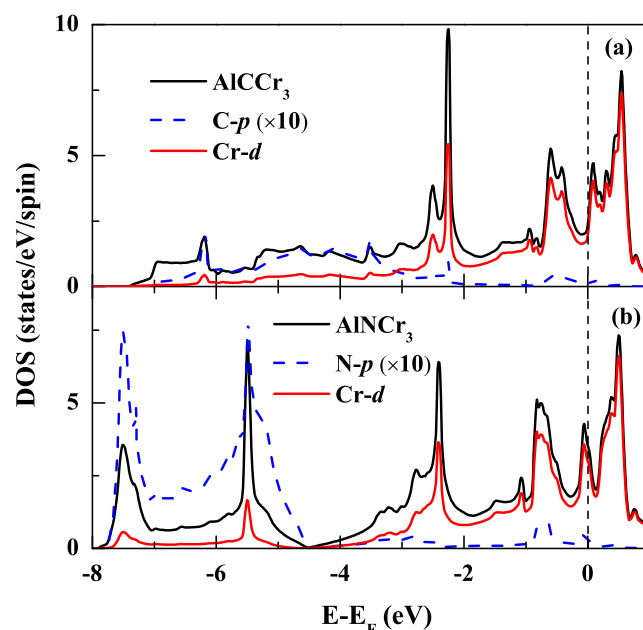


Fig. 5. (Color online) DOS of (a) AlCCr₃ and (b) AlNCr₃.

only difference is the location of E_F decided by total electrons. Thus for most AXM₃ (except for Ni- and Cu-based ones) the influence of electronic structure by changing X-site atom can be approximately evaluated as hole or electron doping.

Now we study the M-site doping effect on the electron structure. Figure 6 shows the DOS of MgCM₃. The shape of the DOS of MgCZn₃ is quite different from those of other MgCM₃. It is possibly due to that all the orbitals of Zn are fulfilled, which makes electrons of Zn atom localized. From MgCSc₃ to MgCCu₃, E_F moves towards to high energy as total electrons increase, and the shapes of DOS keep similar feature. Can we just deduce the M-site doping effect using rigid band approximation? The answer is negative.

We further investigated the electronic structure of doped MgCNi₃ by Co [i.e., MgC(Ni,Co)₃]. The calculated DOS in

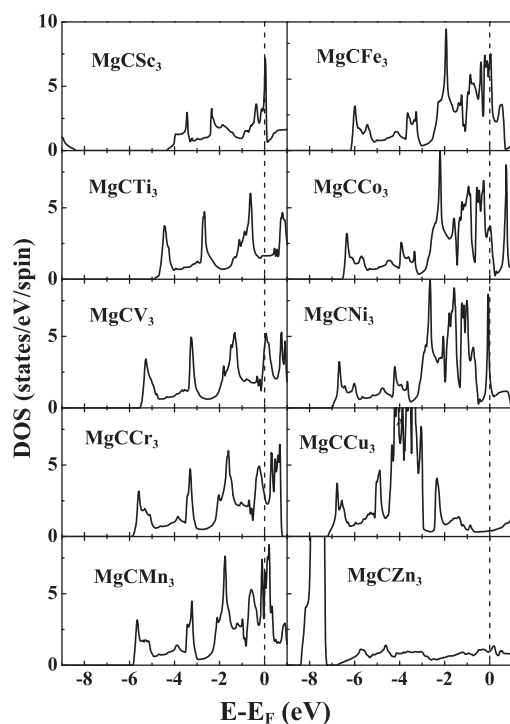


Fig. 6. DOS of MgCM_3 ($M = 3d$ transition metal elements).

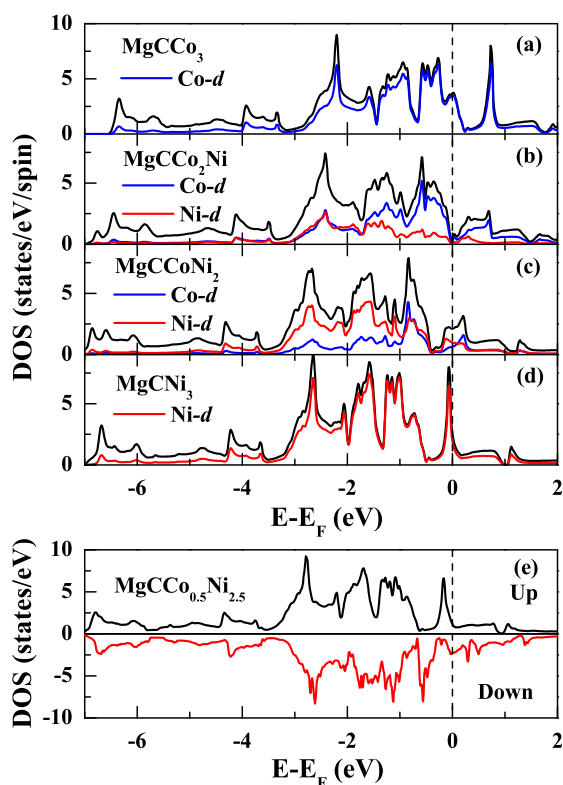


Fig. 7. (Color online) DOS in NM state of (a) MgCCo_3 , (b) MgCCo_2Ni , (c) MgCCoNi_2 , (d) MgCNi_3 , and (e) DOS in FM state of $\text{MgCCo}_{0.5}\text{Ni}_{2.5}$.

NM state of the doped MgCNi_3 by one, two, and three cobalt atoms are shown in Figs. 7(a)–7(d). E_F of MgCCo_3 locates at a DOS peak, which makes MgCCo_3 be in FM ground state. For MgCCoNi_2 and MgCCo_2Ni , the DOS near E_F can be seen as the sum of the DOS of Ni-3d electrons and Co-3d electrons. The small $N(E_F)$ of MgCCoNi_2 and MgCCo_2Ni

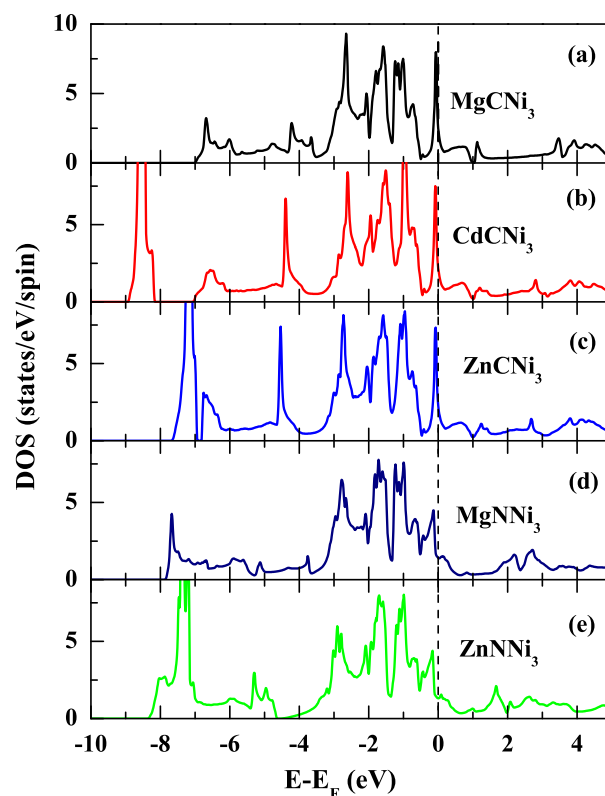


Fig. 8. (Color online) DOS of (a) MgCNi_3 , (b) CdCNi_3 , (c) ZnCNi_3 , (d) MgNNi_3 , and (e) ZnNNi_3 .

lead them to show NM ground state. The DOS peak (van Hove singularity) splits into two peaks contributed by π^* anti-bonding states of C–Ni and C–Co, respectively. The Co doping decreases the total electrons, which reduces E_F and makes the π^* anti-bonding state of C–Ni unoccupied. On the other hand, the Co doping weakens the DOS peak of Ni-3d electrons and enhances the DOS peak of Co-3d electrons. From the above discussion, one can deduce that as MgCNi_3 is doped by a small Co content, the DOS peak of Ni-3d electrons can still has considerable strength. Meanwhile E_F moves through the peak, which will lead to very large $N(E_F)$. According to Stoner criteria $N(E_F)I > 1$, the system will become FM state. The calculation of $\text{MgCCo}_{0.5}\text{Ni}_{2.5}$ proves the deduction [Fig. 7(e)]. However such a FM state has not been observed in experiments,¹⁵ might due to a high doping content or an inaccurate stoichiometry. Similarly, the variations of $N(E_F)$ and magnetic properties of M-site doping in other AXM_3 can be evaluated, too.

Additionally, the doping effect of some isovalent A-site atoms was also investigated. As shown in Fig. 8, changing Mg to the isovalent atoms Zn and Cd, the electronic structure near E_F rarely changes. It supports the A-site atoms only give the effective valence electrons as Rosner et al. proposed.¹² Thus the doping effects of A-, X-, and M-sites we concluded above can be generally applied to most 3d transition-metal based antiperovskites.

3.2 Magnetic phase diagram of ACM_3

We calculated the Stoner parameters I of a series of carbon-based ACM_3 (see Table I). Besides investigating the end members listed in Table I, we also performed DFT calculations for some doped samples with some typical

Table II. Lattice parameter a , formation energies ΔE , and magnetic moments per Cr atom M of ANCr_3 .

A	Zn	Ga	Al	Ag	Cd	Sn	Mg	In
a (Å)	3.861	3.868	3.878	3.861	3.91	3.944	3.956	3.918
ΔE_{NM} (eV/atom)	-0.1027	-0.2195	-0.2448	0.0972	0.0619	-0.0813	0.0173	0.0187
ΔE_{FM} (eV/atom)	-0.1027	-0.2206	-0.2455	0.0969	0.0626	-0.0831	0.0173	0.0186
M (μ_B/Cr)	0	0.23	0.22	0.06	0	0.69	0.03	0.4

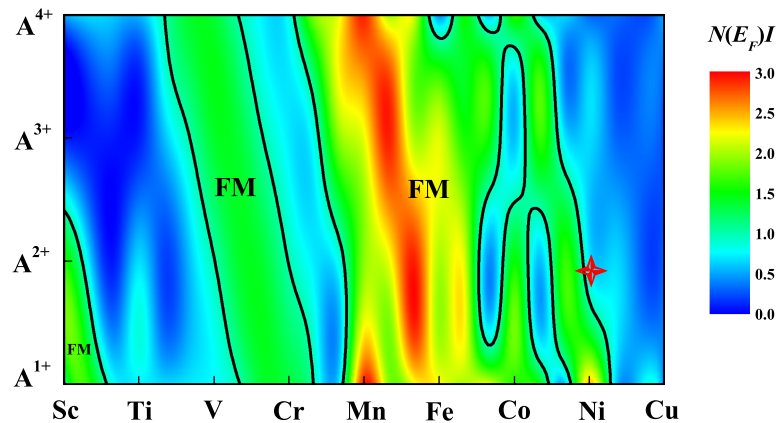


Fig. 9. (Color online) Magnetic phase diagram of ACM_3 . The black line is the NM-FM boundary. MgCNi_3 is highlighted using the red star.

doping concentrations (e.g., 50% for A-site, 33.3 and 66.7% for M-site in AXM_3). Using the factor $N(E_F)I$, we drew the magnetic phase diagram of carbon-based ACM_3 in Fig. 9. The details in the phase diagram between the calculated data points are obtained from the spline interpolation based on the doping effects concluded above. In the phase diagram, the A^{n+} atoms in y -axis stand for not only the Na, Mg, Al, and Si atoms, but also the atoms with n effective valence electrons. The ACM_3 locating in the areas with the colors green to red are satisfied with the Stoner criteria $N(E_F)I > 1$ and therefore show FM ground state.

All the Mn-based antiperovskites and most Fe-based antiperovskites show FM. Here we must point out that we only consider the NM and FM states. In reality, various magnetic structures, e.g., antiferromagnetism and non-collinear magnetism, are observed experimentally in the Mn-based antiperovskites.³¹ In this sense, our phase diagram can not present the real magnetism of such compounds. But in principle, if an itinerant system has very high $N(E_F)$ in NM state, this system is unstable and prefers to be spin-polarized. Accordingly, the magnetic ordering must occur to lower $N(E_F)$ to stabilize the system. If a compound locates in the FM area of our phase diagram, it means that the NM state does not favor the energy minimum and the magnetic ordering will emerge. Such phase diagram can help to explore new magnetic antiperovskites. Furthermore one can also predict the magnetic state of most boron- and nitrogen-based antiperovskites based on the magnetic phase diagram after considering the X-site doping effect as concluded above.

We highlighted MgCNi_3 using a red star in the phase diagram. Obviously, MgCNi_3 is very close to the FM state. One can imagine that there must be some interplay between FM and SC in MgCNi_3 . As mentioned above, in order to figure out such interplay, exploring more MgCNi_3 -like superconducting antiperovskites is necessary. We assume SC may appear in the area near the NM-FM boundary, since in

such area the compounds have sizeable $N(E_F)$ that can lead to a strong EPC.

3.3 Superconductivity in MgCNi_3 and AXCr_3

In the magnetic phase diagram, one can notice that some Cr-based antiperovskites locate in a small interval between two FM areas, which makes AXCr_3 as a good system to prove our deduction above. In this part, we investigated the potential SC in AXCr_3 . For comparison, the lattice dynamics and EPC property of MgCNi_3 were also calculated.

Previously, we calculated the formation energies and electronic structures of a series of Cr-based antiperovskite carbides ACCr_3 .⁵² Only AlCCr_3 and GaCCr_3 have negative formation energies and may be synthesized experimentally. Both the two compounds show the NM ground state. Because of the isovalent A-site atoms, the electronic structures near E_F of the two compounds are almost the same. Similar to MgCNi_3 , E_F of the two compounds locates at a slope of a DOS peak, which leads to large $N(E_F)$ and may generate sizeable EPC.

In present work, we also investigated a series of Cr-based antiperovskite nitrides ANCr_3 . The lattice parameters and the formation energies of NM and FM states are listed in Table II. It can be seen that the magnetic state of $A^{n+}\text{NCr}_3$ is almost the same as that of $A^{(n+1)+}\text{CCr}_3$, which accords with the X-site doping effect we concluded above. The calculated results show that ZnNCr_3 , AlNCr_3 , GaNCr_3 , and SnNCr_3 have negative formation energies and therefore may be synthesized under normal condition in experiments.

The overall shapes of DOS near E_F of ZnNCr_3 , AlNCr_3 , GaNCr_3 , and SnNCr_3 are very similar [see Figs. 10(a)–10(d)]. The calculated $N(E_F)$ and Stoner criteria $N(E_F)I$ are listed in Table III. It was previously suggested that GaNCr_3 may be a potential superconductor.^{39,41} According to our calculations, it can be seen that $N(E_F)I \approx 1$ for AlNCr_3 and GaNCr_3 , which means the two compounds just locate at the

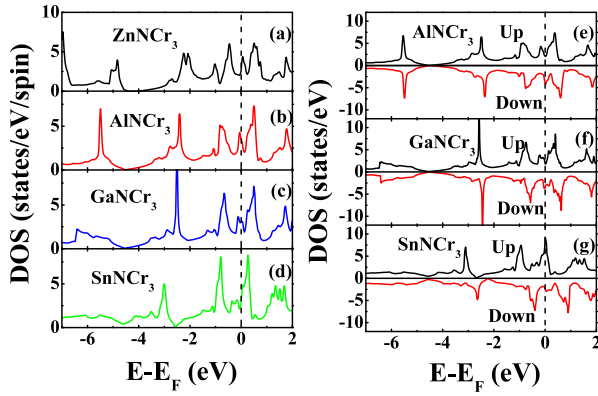


Fig. 10. (Color online) Left panel: DOS of (a) ZnNCr_3 , (b) AlNCr_3 , (c) GaNCr_3 , and (d) SnNCr_3 in NM state. Right panel: DOS of (e) AlNCr_3 , (f) GaNCr_3 , and (g) SnNCr_3 in FM state.

Table III. Calculated $N(E_F)$ (states/eV/spin) and Stoner criteria $N(E_F)I$ of ZnNCr_3 , AlNCr_3 , GaNCr_3 , and SnNCr_3 .

	ZnNCr_3	AlNCr_3	GaNCr_3	SnNCr_3
$N(E_F)$	2.81	3.53	3.08	3.01
$N(E_F)I$	0.76	1.09	1.01	1.29

FM quantum critical point. They show weak FM with small exchange splitting energies [Figs. 10(e) and 10(f)]. Therefore we did not consider the possibility of SC in AlNCr_3 and GaNCr_3 . It is worth noting that E_F of ZnNCr_3 locates very close to a DOS peak, which leads to large $N(E_F)$ and suggests a sizeable EPC.

We calculated the lattice dynamics and EPC properties of MgCNi_3 , AlCCr_3 , GaCCr_3 , and ZnNCr_3 . For reliability, we tested different exchange–correlation potentials and calculation parameters. The results are coincide with each other. The calculated phonon dispersion curves and the corresponding atom-projected phonon DOS are shown in Fig. 11. The ideal antiperovskite in cubic structure ($Pm\bar{3}m$) with five atoms per unit cell presents fifteen phonon modes including three acoustic and twelve optical modes. The highest three optical branches resulting mainly from the lighter C/N atom vibrations are well separated from the other phonon branches. The phonon modes in low-frequency region come mainly from the vibrations of Cr/Ni atoms with partial contribution of A and C/N vibrations.

Earlier calculations suggested lattice instabilities existing in MgCNi_3 ,^{53–56} which seem to be ruled out by the recent experimental and theoretical reports.^{24,25} According to our calculation, no imaginary frequency was found in MgCNi_3 , and the result is similar to the experimental one.²⁴ Soft longitudinal acoustic (LA) modes at M and R points are reproduced. Between X and R point, transverse acoustic (TA) mode of MgCNi_3 is significantly softened and very close to instability. In previous calculation by Tütüncü et al.,⁵⁶ imaginary frequency exists just in the same q -space path. Unfortunately, there are no existing experimental data about the phonon properties in such place. Additionally, in many previous calculations,^{53,54,56} strong softening or imaginary frequency is shown between Γ and R points. Our calculation reproduces such softening. However, experimental result only shows very small hints of the softening of TA mode

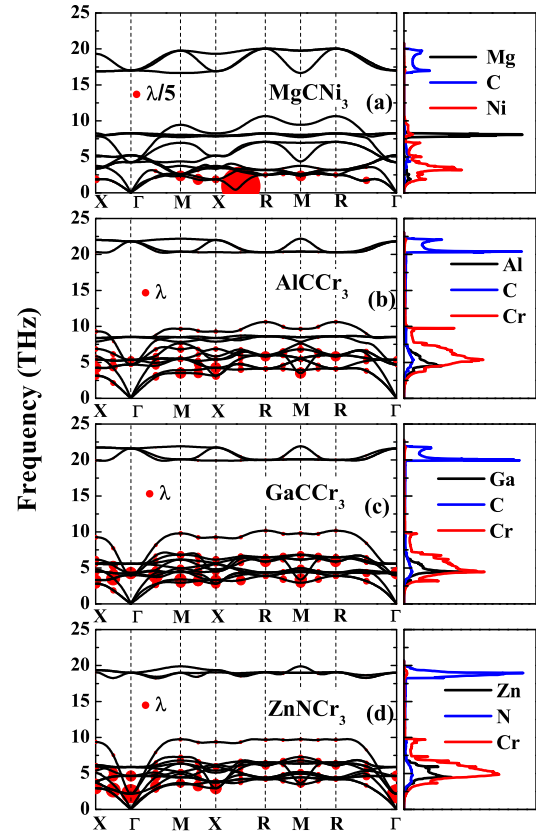


Fig. 11. (Color online) Phonon dispersions and phonon DOS of (a) MgCNi_3 , (b) AlCCr_3 , (c) GaCCr_3 , (d) ZnNCr_3 . The phonon dispersions are decorated with symbols, proportional to the partial EPC strength λ_{qv} .

between Γ and R points.²⁴ The differences between theoretical and experimental results may be due to the sample quality. As Heid et al.⁵⁴ pointed out, the lattice defects may play an important role in stabilizing the real structure. Indeed, the stoichiometry of the reported single crystals are deficient ($\text{MgCNi}_{2.8}$ and $\text{MgC}_{0.92}\text{Ni}_{2.88}$), which may be the reason of the absence of such soft-phonon anomaly in the experimental result. Such phonon mode softening is considered as the key role in the SC mechanism of MgCNi_3 .^{53,57,58} In experiments, single crystals with better quality are needed to figure out such puzzling anomalies.

For AlCCr_3 , GaCCr_3 , and ZnNCr_3 , the absence of imaginary frequency suggests the dynamic stability of the considered crystal structures of the three compounds. The acoustic modes are harder than those of MgCNi_3 , and no modes are close to instability. The optical phonons at Γ point belong to the following irreducible representations: $F(O_h) = 3F_{1u} + F_{2u}$ (see Fig. 12), which are infrared (IR) active (Table IV). The C/N related F_{1u}^1 mode and F_{1u}^3 mode of ZnNCr_3 are softer than those of AlCCr_3 and GaCCr_3 maybe due to the larger atomic mass of nitrogen. We did not observe the significant softening of F_{2u} mode that reported by Tütüncü et al. in RhNCr_3 and GaNCr_3 .^{40,41}

The calculated Eliashberg functions $\alpha^2F(\omega)$ of MgCNi_3 , AlCCr_3 , GaCCr_3 , and ZnNCr_3 are plotted in Fig. 13 according to the below formula:

$$\alpha^2F(\omega) = \frac{1}{N(0)} \sum_{\mathbf{k}, \mathbf{q}, \nu, n, m} \delta(\epsilon_{\mathbf{k}}^n) \delta(\epsilon_{\mathbf{k}+\mathbf{q}}^m) |g_{\mathbf{k}, \mathbf{k}+\mathbf{q}}^{\nu, n, m}|^2 \delta(\omega - \omega_{\mathbf{q}}^{\nu}), \quad (1)$$

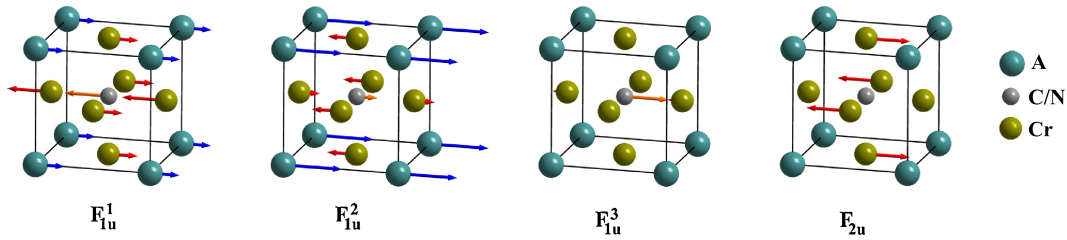


Fig. 12. (Color online) Schematic eigen displacements of zone-centre optical phonon modes in AXM₃. All phonon modes are infrared active.

Table IV. Optical phonon frequencies ω (THz) at Γ point, the calculated EPC strengths λ , and the logarithmically averaged phonon frequency $\omega_{\log}$ (K).

	$\omega(F_{1u}^1)$	$\omega(F_{1u}^2)$	$\omega(F_{1u}^3)$	$\omega(F_{2u})$	λ	$\omega_{\log}$
MgCNi ₃	4.26	5.21	17.01	8.28	1.34	115.77
AlCCr ₃	4.87	8.57	21.84	5.48	0.60	291.51
GaCCr ₃	4.19	5.62	21.63	4.44	0.78	253.91
ZnNCr ₃	2.45	5.92	18.98	4.82	0.67	260.27

where ω_q^v are phonon frequencies, ϵ_k^n electronic energies, and $g_{k,k+q}^{v,n,m}$ EP matrix elements. The total EPC strength is

$$\lambda = \sum_{q,v} \lambda_q^v = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega. \quad (2)$$

The calculated λ_q^v are visualized as red circles in Fig. 11. For MgCNi₃, the absence of imaginary frequency allows the direct calculation of the quantitative EPC contribution details from the lowest acoustic mode. Obviously for MgCNi₃ the EPC originates mainly from acoustic phonon modes softening. For AlCCr₃, GaCCr₃, and ZnNCr₃, optical modes are playing an important role. The EPC distributes throughout some low-frequency phonon modes. One can note that a larger λ_q^v always exists at the frequencies at which large Cr-phonon DOS present. At the zone center, the F_{1u}^1 and F_{2u} modes mainly contribute to EPC. For the two modes, Cr atoms vibrate strongly against each other (Fig. 12). Such vibrations can make large change in the overlap of 3d orbitals between neighbouring Cr atoms, leading to strong coupling. Comparing the EPC strength from different phonon modes of GaCCr₃ and ZnNCr₃, it can be found that the softening of F_{1u}^1 mode can strongly enhance λ .

The integrated EPC strengths $\lambda(\omega)$ are calculated using Eq. (2), and are plotted in Fig. 13. The EPC comes mainly from the $\alpha^2 F(\omega)$ peaks at low frequencies, which are mostly related to the vibrations of Ni/Cr atoms. For the peaks at high frequencies related to the vibrations of C/N atoms, their contributions to λ are less than 6%.

The calculated λ of MgCNi₃ is 1.34, implying very strong EPC. However, the calculated λ of AlCCr₃, GaCCr₃, and ZnNCr₃ are less than 1.0 and about 0.6–0.8 (Table IV), implying moderate EPC. The difference of λ for AXCr₃ can be described qualitatively using Hopfield expression

$$\lambda = \frac{N(E_F)I^2}{M\langle\omega^2\rangle}, \quad (3)$$

where I is mean square EPC matrix element averaged over Fermi surface, M is the ion mass, and $\langle\omega^2\rangle$ is the average

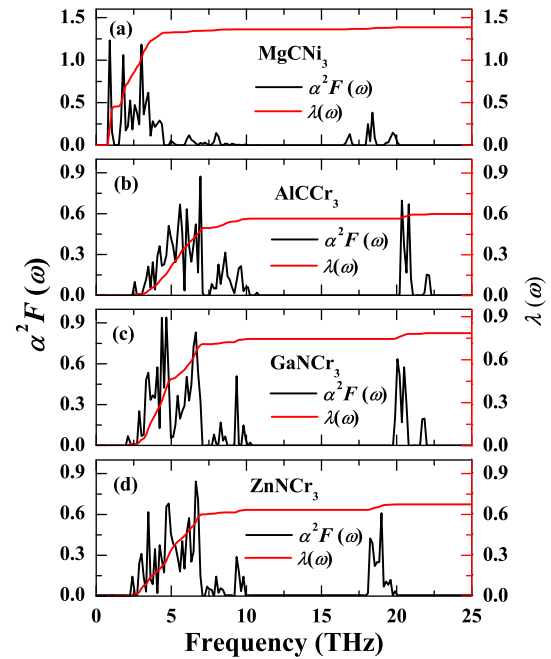


Fig. 13. (Color online) Eliashberg functions (left) and frequency-dependent EPC strength λ (right) of (a) MgCNi₃, (b) AlCCr₃, (c) GaCCr₃, and (d) ZnNCr₃.

squared phonon frequency. The higher $N(E_F)$ and the lower phonon frequency make GaCCr₃ has the larger λ .

To calculate T_C , we used the Allen–Dynes equation^{59–61)}

$$T_C = \frac{\omega_{\log}}{1.20} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*} \right], \quad (4)$$

where μ^* is Coulomb pseudopotential and the logarithmically averaged characteristic phonon frequency $\omega_{\log}$ is defined as

$$\omega_{\log} = \exp \left(\frac{2}{\lambda} \int \frac{d\omega}{\omega} \alpha^2 F(\omega) \log \omega \right). \quad (5)$$

At the absence of SF, using a typical $\mu^* = 0.1$, we can get T_C with the values of 11.82, 6.67, 11.29, and 8.23 K for MgCNi₃, AlCCr₃, GaCCr₃, and ZnNCr₃, respectively. According to the experimental results of MgCNi₃ single crystals,^{16,17,20–24)} the observed T_C is around 7 K. It seems that our calculation overestimates T_C of MgCNi₃. Therefore we need to consider the influence of SF in the system.

We firstly considered the purely static pair breaking due to SF by varying the Coulomb pseudopotential μ^* . The SF-induced repulsion can be times larger than the conventional Coulomb pseudopotential.^{62–64)} In Fig. 14(a), one can note

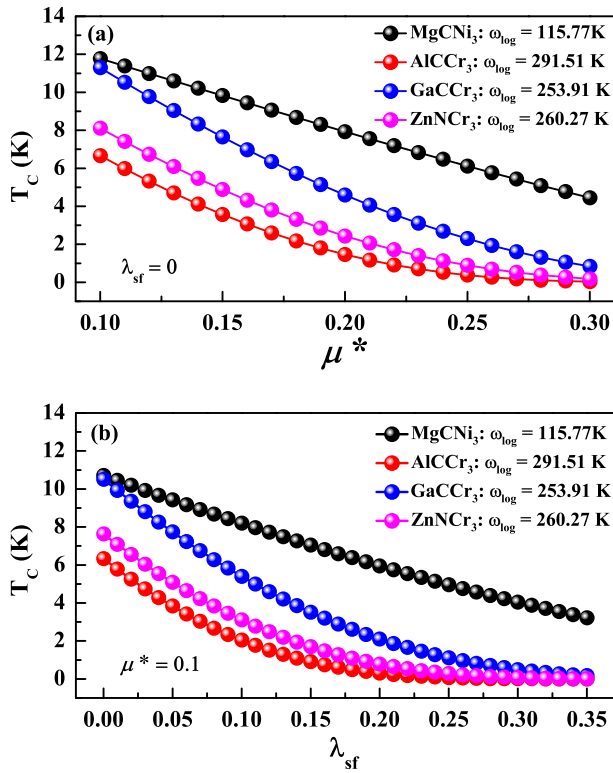


Fig. 14. (Color online) (a) Variation of T_C with μ^* (purely static pair breaking); (b) Variation of T_C with λ_{sf} (electron-paramagnon coupling).

that the increasing μ^* significantly depresses T_C . As T_C around 7 K, we can get $\mu^* \approx 0.23$. Such a value is smaller than the previous derivations of $\mu^* = 0.33$ ⁵³ and $\mu^* = 0.41$,⁵⁷ but still larger than the typical values $\mu^* = 0.1$ – 0.15 for the absence of SF.

It is better to discuss the influence of SF in terms of electron-paramagnon coupling strength λ_{sf} .⁵³ In that case, the effective coupling strength should be $\lambda_{\Delta} = \lambda - \lambda_{sf}$. The effective mass of the carriers should be enhanced by the factor $1 + \lambda_Z = 1 + \lambda + \lambda_{sf}$. And Eq. (4) should be changed as^{58,65}

$$T_C = \frac{\omega_{\log}}{1.45} \exp \left[-\frac{1 + \lambda_Z}{\lambda_{\Delta} - \mu^* \left(1 + 0.5 \frac{\lambda_{\Delta}}{1 + \lambda_Z} \right)} \right]. \quad (6)$$

Figure 14(b) shows the calculated T_C using Eq. (6) with different λ_{sf} (here the Coulomb pseudopotential is fixed to the typical value $\mu^* = 0.1$). When T_C is around 7 K, we can get $\lambda_{sf} \approx 0.15$. Although the obtained parameter is small, it still implies that SC in the system is partially suppressed by depairing effect from SF.^{57,58} The influence of SF on T_C of AlCCr_3 , GaCCr_3 , and ZnNCr_3 is also present in Fig. 14. If we consider the same SF influence as in MgCNi_3 , using Eq. (4) with $\mu^* = 0.23$ and $\lambda_{sf} = 0$, we can get $T_C = 0.70$, 3.11, and 1.40 K for AlCCr_3 , GaCCr_3 , and ZnNCr_3 , respectively; using Eq. (6) with $\mu^* = 0.1$ and $\lambda_{sf} = 0.15$, we can get $T_C = 0.91$, 3.52, and 1.69 K for AlCCr_3 , GaCCr_3 , and ZnNCr_3 , respectively.

Let us look back at the electronic structures of AlCCr_3 , GaCCr_3 , and ZnNCr_3 . The E_F locates between two DOS peaks, which suggests in the system both hole and electron doping can enhance the SF and lead to a transition from SC to magnetic instability. Considering it has not been successful

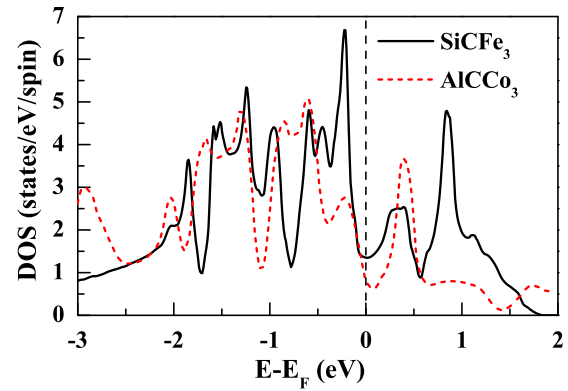


Fig. 15. (Color online) DOS near E_F of (a) SiCFE_3 and (b) AlCCO_3 .

so far to investigate such transition in doped antiperovskites such as $\text{Mg}_{1-x}(\text{A}^{1+})_x\text{CNi}_3$ due to the difficulty in experimental preparation of samples, AXCr_3 may be good candidates to figure out the relation between SC and magnetism in antiperovskites.

3.4 Other potential superconducting AXM_3

Since the discovery of SC in MgCNi_3 , researchers have made great efforts to explore other 3d transition-metal based antiperovskite superconductor.^{37–41,66} The observed superconducting trace at 4.5 K found in $\text{In}_{1.3}\text{B}_{0.7}\text{Sc}_3$ is encouraging.³⁷ Theoretically, InBSc_3 is close to weak FM and with an EPC superconducting mechanism.^{37,38} One should believe the Ni-based antiperovskite superconductor are not alone and other superconducting antiperovskites may be hidden behind them.

Indeed, our magnetic phase diagram shows that some AXSc_3 should be very close to FM, which may potentially be superconducting. There are also some other antiperovskite compounds close to FM, such as AXV_3 , for which the cubic phase has not been successfully prepared so far. Here we present two potential superconducting parent materials $\text{A}^{4+}\text{CFE}_3$ ($\text{A} = \text{Si}, \text{Ge}, \text{etc.}$) and $\text{A}^{3+}\text{CCO}_3$ ($\text{A} = \text{Al}, \text{Ga}, \text{etc.}$). The DOS near E_F of SiCFE_3 and AlCCO_3 are plotted in Fig. 15. One can notice that the E_F of the two compounds just locates at a DOS valley. Thus both electron and hole doping can move E_F to the DOS peaks nearby, and largely enhance $N(E_F)$ to yield strong EPC. Therefore, doped $\text{A}^{3+}\text{CCO}_3$ may be new Co-based superconductors besides $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$.¹⁰ And doped $\text{A}^{4+}\text{CFE}_3$ may be new Fe-based superconductors.

As we know, the role of EPC in the Fe-based superconductors is still puzzling. For instance, EPC mechanism can get a reasonable T_C of the hcp iron under pressure, but can not explain the rapid disappearance of SC above 30 GPa.^{7,67,68} For the iron pnictide superconductors,⁸ Boeri et al.^{69,70} and Mazin et al.⁷¹ pointed out that the EPC in the system is intrinsically weak, but can be enhanced strongly by magnetism.⁷² Although EPC is still not enough to explain the high critical temperature, it is strong enough to have a non-negligible effect on SC. On the other hand, in the similar system of nickel pnictide superconductors, it seems the EPC plays the main role.⁷⁰ One may connect nickel pnictide superconductors with MgCNi_3 by the similar EPC mechanism. The potential superconductivity in doped $\text{A}^{4+}\text{CFE}_3$ may

also help to figure out the superconducting mechanism, which needs to be further confirmed in experimental and theoretical works.

4. Conclusions

In this work, we theoretically investigated the electronic structure, magnetic properties, and lattice dynamics of the 3d transition-metal based antiperovskite compounds AXM_3 . Based on the analysis of the doping effect in AXM_3 , we drew the magnetic phase diagram of ACM_3 . We suggested that superconducting antiperovskites can be found in the NM area but very close to FM boundary. In order to prove the deduction, we investigated a series of Cr-based antiperovskite $AXCr_3$ ($X = C, N$). The results indicate that $AlCCr_3$, $GaCCr_3$, and $ZnNCCr_3$ are of NM ground state but very close to FM instability. Due to the large $N(E_F)$, these compounds have sizeable EPC. We calculated the phonon spectra and EPC of $MgCNi_3$, $AlCCr_3$, $GaCCr_3$, and $ZnNCCr_3$. Our results confirm the strong EPC in $MgCNi_3$, and show that $AlCCr_3$, $GaCCr_3$, and $ZnNCCr_3$ are moderate coupling BCS superconductors. Such compounds may be good candidates to figure out the role of SF. Moreover, some potential new antiperovskite Co- and Fe-based superconductors are suggested.

Up to date, there is no definite evidence of SF in $MgCNi_3$ single crystals.²⁰⁾ Since such single crystals are not stoichiometric, the interplay between SC and magnetism are still puzzling. Our phase diagram and predictions could offer new route to figure out the issue. In experiments one can try to prepare such potential antiperovskite superconductors we predicted. Furthermore, by doping we can control the physical properties and may observe the magnetic-superconducting transition through quantum critical point. We hope our phase diagram and predictions can help to explore more 3d transition-metal based antiperovskite superconductors and figure out the relation between SC and magnetism in the system.

Acknowledgments

This work was supported by the National Key Basic Research under Contract No. 2011CBA00111, and the National Nature Science Foundation of China under Contract Nos. 51171177, 11304320, 11274311, 11174295, and U1232139. The calculations were partially performed at the Center for Computational Science, CASHIPS.

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- 1) H. Onnes, *Commun. Phys. Lab. Univ. Leiden* **12**, 120 (1911).
- 2) L. N. Cooper, *Phys. Rev.* **104**, 1189 (1956).
- 3) J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **106**, 162 (1957).
- 4) J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).
- 5) J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).
- 6) M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, *Phys. Rev. Lett.* **58**, 908 (1987).
- 7) K. Shimizu, T. Kimura, S. Furomoto, K. Takeda, K. Kontani, Y. Onuki, and K. Amaya, *Nature* **412**, 316 (2001).
- 8) Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).

- 9) Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, *Nature* **372**, 532 (1994).
- 10) K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, *Nature* **422**, 53 (2003).
- 11) T. He, Q. Huang, A. P. Ramirez, Y. Wang, K. A. Regan, N. Rogado, M. A. Hayward, M. K. Haas, J. S. Slusky, K. Inumara, H. W. Zandbergen, N. P. Ong, and R. J. Cava, *Nature* **411**, 54 (2001).
- 12) H. Rosner, R. Weht, M. D. Johannes, W. E. Pickett, and E. Tosatti, *Phys. Rev. Lett.* **88**, 027001 (2001).
- 13) D. J. Singh and I. I. Mazin, *Phys. Rev. B* **64**, 140507(R) (2001).
- 14) J. H. Shim, S. K. Kwon, and B. I. Min, *Phys. Rev. B* **64**, 180510(R) (2001).
- 15) S. Mollah, *J. Phys.: Condens. Matter* **16**, R1237 (2004).
- 16) H.-S. Lee, D.-J. Jang, H.-G. Lee, S.-I. Lee, S.-M. Choi, and C.-J. Kim, *Adv. Mater.* **19**, 1807 (2007).
- 17) R. T. Gordon, N. D. Zhigadlo, S. Weyeneth, S. Katrych, and R. Prozorov, *Phys. Rev. B* **87**, 094520 (2013).
- 18) M. Sieberer, P. Mohn, and J. Redinger, *Phys. Rev. B* **75**, 024431 (2007).
- 19) D. F. Shao, W. J. Lu, J. C. Lin, P. Tong, H. B. Jian, and Y. P. Sun, *J. Appl. Phys.* **113**, 023905 (2013).
- 20) H. S. Lee, D. J. Jang, H. G. Lee, W. Kang, M. H. Cho, and S. I. Lee, *J. Phys.: Condens. Matter* **20**, 255222 (2008).
- 21) Z. Pribulová, J. Kačmarčík, C. Marcenat, P. Szabó, T. Klein, A. Demuer, P. Rodiere, D. J. Jang, H. S. Lee, H. G. Lee, S.-I. Lee, and P. Samuely, *Phys. Rev. B* **83**, 104511 (2011).
- 22) P. Diener, P. Rodière, T. Klein, C. Marcenat, J. Kacmarck, Z. Pribulova, D. J. Jang, H.-S. Lee, H.-G. Lee, and S.-I. Lee, *Phys. Rev. B* **79**, 220508(R) (2009).
- 23) D.-J. Jang, H.-S. Lee, H.-G. Lee, M.-H. Cho, and S.-I. Lee, *Phys. Rev. Lett.* **103**, 047003 (2009).
- 24) H. Hong, M. Upton, A. H. Said, H.-S. Lee, D.-J. Jang, S.-I. Lee, R. Xu, and T.-C. Chiang, *Phys. Rev. B* **82**, 134535 (2010).
- 25) P. K. Jha, S. D. Gupta, and S. K. Gupta, *AIP Adv.* **2**, 022120 (2012).
- 26) P. Tong and Y. P. Sun, *Adv. Condens. Matter Phys.* **2012**, 903239 (2012).
- 27) C. Loison, A. Leithe-Jasper, and H. Rosner, *Phys. Rev. B* **75**, 205135 (2007).
- 28) D. Fruchart, R. Fruchart, P. L'heritier, K. Kanematsu, R. Madar, S. Misawa, Y. Nakamura, P. J. Webster, and K. R. A. Ziebeck, *Alloys and Compounds of D-Elements With Main Group Elements* (Springer, Berlin, 1988) Part 2, p. 186.
- 29) M. Uehara, T. Yamazaki, T. Kôri, T. Kashida, Y. Kimishima, and I. Hase, *J. Phys. Soc. Jpn.* **76**, 034714 (2007).
- 30) M. Uehara, A. Uehara, K. Kozawa, T. Yamazaki, and Y. Kimishima, *Physica C* **470**, S688 (2010).
- 31) P. Tong, B. S. Wang, and Y. P. Sun, *Chin. Phys. B* **22**, 067501 (2013).
- 32) K. Kamishima, T. Goto, H. Nakagawa, N. Miura, M. Ohashi, N. Mori, T. Sasaki, and T. Kanomata, *Phys. Rev. B* **63**, 024426 (2000).
- 33) K. Takenaka and H. Takagi, *Appl. Phys. Lett.* **87**, 261902 (2005).
- 34) S. Iikubo, K. Kodama, K. Takenaka, H. Takagi, M. Takigawa, and S. Shamoto, *Phys. Rev. Lett.* **101**, 205901 (2008).
- 35) K. Takenaka, *Sci. Technol. Adv. Mater.* **13**, 013001 (2012).
- 36) E. O. Chi, W. S. Kim, and N. H. Hur, *Solid State Commun.* **120**, 307 (2001).
- 37) B. Wiendlocha, J. Tobola, S. Kaprzyk, D. Fruchart, and J. Marcus, *Phys. Status Solidi B* **243**, 351 (2006).
- 38) B. Wiendlocha, J. Tobola, and S. Kaprzyk, *Phys. Rev. B* **73**, 134522 (2006).
- 39) B. Wiendlocha, J. Tobola, S. Kaprzyk, and D. Fruchart, *J. Alloys Compd.* **442**, 289 (2007).
- 40) H. M. Tütüncü and G. P. Srivastava, *J. Appl. Phys.* **112**, 093914 (2012).
- 41) H. M. Tütüncü and G. P. Srivastava, *J. Appl. Phys.* **114**, 053905 (2013).
- 42) P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- 43) M. Torrent, F. Jollet, F. Bottin, G. Zerah, and X. Gonze, *Comput. Mater. Sci.* **42**, 337 (2008).
- 44) X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J.-Y. Raty, and D. C. Allan, *Comput. Mater. Sci.* **25**, 478 (2002).
- 45) X. Gonze, *Z. Kristallogr.* **220**, 558 (2005).
- 46) X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Cote, T. Deutsch, L.

- Genovese, Ph. Ghosez, M. Giantomassi, S. Goedecker, D. R. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, M. Mancini, S. Mazevet, M. J. T. Oliveira, G. Onida, Y. Pouillon, T. Rangel, G.-M. Rignanese, D. Sangalli, R. Shaltaf, M. Torrent, M. J. Verstraete, G. Zerah, and J. W. Zwanziger, *Comput. Phys. Commun.* **180**, 2582 (2009).
- 47) H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- 48) S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* **73**, 515 (2001).
- 49) D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- 50) P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- 51) J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- 52) D. F. Shao, W. J. Lu, S. Lin, P. Tong, and Y. P. Sun, *Adv. Condens. Matter Phys.* **2013**, 136274 (2013).
- 53) A. Y. Ignatov, S. Y. Savrasov, and T. A. Tyson, *Phys. Rev. B* **68**, 220504(R) (2003).
- 54) R. Heid, B. Renker, H. Schober, P. Adelman, D. Ernst, and K.-P. Bohnen, *Phys. Rev. B* **69**, 092511 (2004).
- 55) P. K. Jha, *Phys. Rev. B* **72**, 214502 (2005).
- 56) H. M. Tütüncü and G. P. Srivastava, *J. Phys.: Condens. Matter* **18**, 11089 (2006).
- 57) A. Wälte, G. Fuchs, K.-H. Müller, A. Handstein, K. Nenkov, V. N. Narozhnyi, S.-L. Drechsler, S. Shulga, L. Schultz, and H. Rosner, *Phys. Rev. B* **70**, 174503 (2004).
- 58) O. V. Dolgov, A. A. Golubov, I. I. Mazin, and E. G. Maksimov, *J. Phys.: Condens. Matter* **20**, 434226 (2008).
- 59) W. L. McMillan, *Phys. Rev.* **167**, 331 (1968).
- 60) R. Dynes, *Solid State Commun.* **10**, 615 (1972).
- 61) P. B. Allen and R. C. Dynes, *Phys. Rev. B* **12**, 905 (1975).
- 62) N. F. Berk and J. R. Schrieffer, *Phys. Rev. Lett.* **17**, 433 (1966).
- 63) K. H. Bennemann and J. W. Garland, *AIP Conf. Proc.* **4**, 103 (1972).
- 64) D. A. Papaconstantopoulos and B. M. Klein, *Phys. Rev. Lett.* **35**, 110 (1975).
- 65) L. Ortenzi, S. Biermann, O. K. Andersen, I. I. Mazin, and L. Boeri, *Phys. Rev. B* **83**, 100505(R) (2011).
- 66) R. E. Schaak, M. Avdeev, W.-L. Lee, G. Lawes, H. W. Zandbergen, J. D. Jorgensen, N. P. Ong, A. P. Ramirez, and R. J. Cava, *J. Solid State Chem.* **177**, 1244 (2004).
- 67) I. I. Mazin, D. A. Papaconstantopoulos, and M. J. Mehl, *Phys. Rev. B* **65**, 100511(R) (2002).
- 68) S. K. Bose, O. V. Dolgov, J. Kortus, O. Jepsen, and O. K. Andersen, *Phys. Rev. B* **67**, 214518 (2003).
- 69) L. Boeri, O. V. Dolgov, and A. A. Golubov, *Phys. Rev. Lett.* **101**, 026403 (2008).
- 70) L. Boeri, O. V. Dolgov, and A. A. Golubov, *Physica C* **469**, 628 (2009).
- 71) I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, *Phys. Rev. Lett.* **101**, 057003 (2008).
- 72) L. Boeri, M. Calandra, I. I. Mazin, O. V. Dolgov, and F. Mauri, *Phys. Rev. B* **82**, 020506(R) (2010).