Prediction of superconductivity of 3d transition-metal based antiperovskites via magnetic phase diagram

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We theoretically studied the electronic structure, magnetic properties, and lattice dynamics of a series of 3d transition-metal antiperovskite compounds AXM3 by density function theory. Based on the Stoner criterion, we drew the magnetic phase diagram of carbon-based antiperovskites ACM3. In the phase diagram, compounds with non-magnetic ground state but locating near the ferromagnetic boundary are suggested to yield sizeable electron-phonon coupling and behave superconductivity. To approve this deduction, we systematically calculated the phonon spectra and electron-phonon coupling of a series of Cr-based antiperovskites ACCr3 and ANCr3. The results show that AlCCr3, GaCCr3, and ZnNCr3 could be moderate coupling BCS superconductors. The influence of spin fluctuation on superconductivity are discussed. Furthermore, other potential superconducting AXM3 including some new Co-base and Fe-based antiperovskite superconductors are predicted from the magnetic phase diagram.

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I. INTRODUCTION

Since superconductivity (SC) was found by Onnes, researchers have made a lot of efforts to figure out its mechanism. The BCS theory2–4 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 superconductors25, iron based superconductors26, Sr3RuO4, Na2CoO2·2H2O18, 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 MgCNi311, containing a high concentration of magnetic element Ni, attracted a lot of attentions on the role of SF. MgCNi3 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 (EF), leading to large density of states (DOS) at EF (N(EF)). It makes the compound strongly exchange-enhanced and unstable toward to ferromagnetism (FM) upon hole doping12,13. Experimentally speaking, due to the high volatility of Mg and the relatively poor reactivity of C, it is extremely difficult to synthesize stoichiometric MgCNi314,15. The atomic deficiencies in the antiperovskite system may strongly affect the properties18,19 and lead to some contradictory results in the reported polycrystalline samples15,16. Recently, the single crystal samples have been prepared16,17,20,24. The physical property measurements demonstrate the conventional EPC mechanism, but the reported EPC strengths of these samples are contradict17,20,24,25,26.

Moreover, it has not been successful so far to induce FM instability by preparing hole-doped compounds such as Mg1−xNa2CNi3 and Mg1−xLi2CNi3. The interplay between SC and SF in MgCNi3 is still unclear and in debate27.

Nowadays, lots of 3d transition-metal based antiperovskite AXM3 (A usually is main group element; X = B, C, and N; M = 3d transition-metal elements) have been experimentally synthesized28. However, the reported physical property measurements are mainly focused on the Ni- and Mn-based antiperovskites. In Ni-based antiperovskites, CdCNi3 and ZnNNi3 were reported to show SC behavior29,30. Abundant magnetism appears in Mn-based antiperovskites (see recent review article Ref. 31). Moreover, superconducting trace has been found in InBSC32. Some theoretical predictions suggest that SC may exist in some Sc-based and Cr-based antiperovskites33,34. Indeed, due to the high concentration of 3d transition-metal atoms, one can imagine that more interesting properties exist in other antiperovskite AXM3. 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 magnetism27.

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 AXM3, we calculated the electronic structures of a series of 3d transition-metal based antiperovskites AXM3 and concluded the doping effects of each atom. From the analysis of these doping effects, we can evaluate the variation of N(EF) of different AXM3. We drew a magnetic phase diagram of ACM3 based on the Stoner criterion N(EF)I > 1. From the phase diagram, we predict that the materials locating near FM boundary may have sizeable EPC and could show SC. To con-
firm this deduction, we systematically investigated the formation energies, electronic structures, lattice dynamic properties, and EPC of a series of Cr-based AXM₃. For comparison, such properties of MgCNi₃ are also calculated. Our results confirm the strong EPC for MgCNi₃ and suggest that AlCCr₃, GaCCr₃, and ZnGCr₃ 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.

II. METHODS

The structural relaxation and electronic structure calculations were performed using projected augmented-wave (PAW) method as implemented in the ABINIT code. 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) mesh 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. 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) using plane waves and ultrasoft pseudopotentials with QUANTUM-ESPRESSO. We use an 8 × 8 × 8 grid for zone integration in the self-consistent calculations, while a denser 16 × 16 × 16 grid was used in the EPC calculations. We have calculated dynamical matrices at a uniform 4 × 4 × 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-PBE exchange-correlation potential in both cases.

III. RESULTS AND DISCUSSIONS

A. Doping effects of AXM₃

As Rosner et al. 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 (A²⁺); Mg, Zn, and Cd (A²⁺); Al, Ga, and In (A³⁺); Ge and Sn (A⁴⁺). Clearly, the effective valence electrons of A-site atoms are usually in the range from 1 to 4. For simplification, we chose Na³⁺, Mg²⁺, Al³⁺, and Si⁴⁺ 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 ACM₃. 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 ACM₉₃ and most ACM₉₃ show FM state, which coincides with the experimental results. Surprisingly, SiCC₃ and AlCC₃ 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 AXM₃, the doping/substitution effects of each atom on the electronic structure must be investigated. We start from reviewing the electronic structure of MgCNi₃. Figure 2 shows the calculated DOS of MgCNi₃. It can be seen that the total DOS near E_F are mainly contributed by Ni-3d electrons. From -7 eV to -4 eV and near E_F, C-2p electrons hybridize strongly with Ni-3d electrons. The π* antibonding 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. 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 MgCNi₃. Our results are very close to the previous theoretical reports, which proves the validity of present calculations.

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 Mg₂₅Al₂₅CNi₃. As shown in figure 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-
TABLE I. The $N(E_F)$ (states/eV/spin) in NM ground state (above “/”) and Stoner parameter $I$ (under “/”) of ACM$_3$ ($A =$ Na, Mg, Al, and Si, $M = 3d$ transition metal elements).

|     | 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  | 1.49/0.05  | 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  |

![FIG. 2. Total and atom-orbital-projected DOS of MgCNi$_3$.](image)

Next we consider the X-site doping effect. Figures 4 shows the DOS of MgBNi$_3$, MgCNi$_3$ and MgNNi$_3$. 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 MgCNi$_3$ 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 MgBNi$_3$ is still in the NM ground state. The calculated $N(E_F)$ of MgBNi$_3$ is 2.58 states/eV/spin, which can be comparable to that of MgCNi$_3$. For MgNNi$_3$, 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.

![FIG. 3. DOS of (a) NaCNi$_3$, (b) MgCNi$_3$, (c) Mg$_{0.5}$Al$_{0.5}$CNi$_3$, (d) AlCNi$_3$, and (e) SiCNi$_3$.](image)

According to our calculation, except for Ni- and Cu-based AXM$_3$, all the other compounds have similar character that the bonding and anti-bonding states are far from $E_F$. That means for most AXM$_3$ compounds, there exists weak X-M hybridizations at $E_F$. Figure 5 shows the DOS of AlCCr$_3$ and AlNiCr$_3$. The shapes of DOS near $E_F$ are very similar. The only difference is the location of $E_F$ decided by total electrons. Thus for most AXM$_3$ (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 MgCM$_3$. The shape of the DOS of MgCZn$_3$ is quite different from those of other MgCM$_3$. It is possibly due to that all the orbitals of Zn are fulfilled, which makes electrons of Zn atom localized. From MgCSc$_3$ to MgCCu$_3$, $E_F$ 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 MgCNi$_3$ by Co (i.e. MgC(Ni,Co)$_3$). The calculated DOS in NM state of the doped MgCNi$_3$ by one, two, and three cobalt atoms are shown in figures 7 (a)-(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$_2$Ni, 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$_2$Ni lead them to show NM ground state. The DOS peak (van Hove singularity) splits into two peaks contributed by $\pi^*$ anti-bonding states of C-Ni and C-Co, respectively. The Co doping decreases the total electrons, which reduces $E_F$ and makes the $\pi^*$ 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 MgCCo$_{0.5}$Ni$_{2.5}$ proves the deduction (figure 7 (e)). However such a FM state has not been observed in experiments, 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 figure 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. Thus the doping effects of A-, X-, and M-sites we concluded above can be generally applied to most 3d transition-metal based antiperovskites.
served experimentally in the Mn-based antiperovskites antiferromagnetism and non-collinear magnetism, are observed in the Fe-based antiperovskites. In reality, abundant magnetisms, e.g. antiferromagnetism and non-collinear magnetism, are observed in the Fe-based antiperovskites. All the Mn-based antiperovskites and most Fe-based antiperovskites show antiferromagnetism and non-collinear magnetism. The ACMs located 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, abundant magnetisms, e.g. antiferromagnetism and non-collinear magnetism, are observed experimentally in the Mn-based antiperovskites. 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. Therefore, 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 MgNi$_3$ using a red star in the phase diagram. Obviously, MgNi$_3$ is very close to the FM state. One can imagine that there must be some interplay between FM and SC in MgNi$_3$. As mentioned above, in order to figure out such interplay, exploring more MgNi$_3$-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.

C. 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$_3$\cite{24}. 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 $A^{n+}NCr_3$ is almost the same as that of $A^{(n+1)+}CCr_3$, which accords with the X-site doping effect we concluded above. The calculated results show that ZnNCr$_3$, AlINCr$_3$, 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$_3$, AlINCr$_3$, GaNCr$_3$, and SnNCr$_3$ are very similar (see figures 10(a)-(d)). The calculated $N(E_F)$ and Stoner criteria $N(E_F)/I$ are listed in Table II. It was previously suggested that GaNCr$_3$ may be a potential superconductor\cite{34,35,54}. According to our calculations, it can be seen that $N(E_F)/I \approx 1$ for AlINCr$_3$ and GaNCr$_3$, which means the two compounds just locate at the FM quantum critical point. They show weak FM with small exchange splitting energies (figures 10(e) and (f)). Therefore, we did not consider the possibility of SC in AlINCr$_3$ 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$_3$, AlCr$_3$, GaCr$_3$, and ZnCr$_3$. 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 figure 11. The ideal antiperovskite in cubic structure (Pm3m) 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$_3$\cite{34,35}, which seem to be ruled out by the recent experimental and theoretical report\cite{24,54}. According to our calculation, no imaginary frequency was found in MgCNi$_3$, and the result is similar to the experimental one\cite{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 Tuittinci et al\cite{24}, 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, 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 between Γ and R point\cite{24}. The differences between theoretical and experimental results may be due to the sample quality. As Heid et al\cite{49} 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 (MgCN$_{2.8}$ and MgCr$_{0.92}$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$_3$\cite{34,48,49}. In experiments, single crystals with better quality are needed to figure out such puzzling anomalies.

For AlCCr$_3$, GaCCr$_3$, and ZnCCr$_3$, 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: $F(O_h) = 3F_{1u} + 2F_{2u}$ (see figure 12).
\[ \alpha \text{ figure 13 according to the below formula:} \]

\[ M_{\text{CNi}}(\lambda) = 1 \]

\[ \text{TABLE II. Lattice parameter } a, \text{ formation energies } \Delta E, \text{ and magnetic moments per Cr atom } M \text{ of ANCr}_3. \]

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

\[ \text{TABLE III. Calculated } N(E_F) \text{ (states/eV/spin) and Stoner criteria } N(E_F)I \text{ of ZnNCr}_3, \text{ AlNCr}_3, \text{ GaNCr}_3, \text{ and SnNCr}_3.} \]

|       | 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 | 1.39 |

\[ \text{TABLE IV. Optical phonon frequencies } \omega \text{ (THz) at } \Gamma \text{ point, the calculated EPC strengths } \lambda, \text{ and the logarithmically averaged phonon frequency } \omega_{\text{log}} \text{ (K).} \]

|       | \(\omega(F_{1u}^\alpha)\) | \(\omega(F_{2u}^\alpha)\) | \(\omega(F_{1u}^\beta)\) | \(\omega(F_{2u}^\beta)\) | \(\lambda\) | \(\omega_{\text{log}}\) |
|-------|----------------|----------------|----------------|----------------|-------------|----------------|
| 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 |

which are infrared (IR) active (table IV). The C/N related \(F_{1u}^\alpha\) mode and \(F_{1u}^\beta\) 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 T"ut"unc"u et al. in RhNCr\(_3\) and GaNCr\(_3\).\(^{35,36}\)

The calculated Eliashberg functions \(\alpha^2F(\omega)\) of MgCNi\(_3\), AlCCr\(_3\), GaCCr\(_3\), and ZnNCr\(_3\) are plotted in figure 13 according to the below formula:

\[ \alpha^2 F(\omega) = \frac{1}{N(0)} \sum_{k,q,n,m} \delta(\epsilon^n_k) \delta(\epsilon^m_{k+q}) |g^{\nu,n,m}_{k,k+q}|^2 \delta(\omega - \omega^\nu_{q}), \]

where \(\omega^\nu_{q}\) are phonon frequencies, \(\epsilon^n_k\) electronic energies, and \(g^{\nu,n,m}_{k,k+q}\) EP matrix elements. The total EPC strength is

\[ \lambda = \sum_{\nu,q} \lambda^\nu_{q} = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega. \]

The calculated \(\lambda^\nu_{q}\) are visualized as red circles in figure 13. For MgCNi\(_3\), the absence of imaginary frequency allows the direct calculation of the quantitative EPC contribution details from the lowest acoustic mode. Obviously for MgCNi\(_3\) the EPC originates mainly from acoustic phonon modes softening. For AlCCr\(_3\), GaCCr\(_3\), and ZnNCr\(_3\), optical modes are playing an important role. The EPC distributes throughout some low-frequency phonon modes. One can note that a larger \(\lambda^\nu_{q}\) always exists at the frequencies at which large Cr-phonon DOS present. At the zone center, the \(F_{1u}\) and \(F_{2u}\) modes mainly contribute to EPC. For the two modes, Cr atoms vibrate strongly against each other (figure 12). Such vibrations can make large change in the overlap of 3d orbitals between neighboring Cr atoms, leading to strong coupling. Comparing the EPC strength from different phonon modes of GaCCr\(_3\) and ZnNCr\(_3\), it can be found that the softening of \(F_{1u}\) mode can strongly enhance \(\lambda\).

The integrated EPC strengths \(\lambda(\omega)\) are calculated using equation (2), and are plotted in figure 13. The EPC comes mainly from the \(\alpha^2F(\omega)\) peaks at low frequen-
λ strong EPC. However, the calculated than 6%.

FIG. 12. Schematic eigen displacements of zone-centre optical phonon modes in AXM$_3$. All phonon modes are infrared active.

cies, 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 $\lambda$ are less than 6%.

The calculated $\lambda$ of MgCNi$_3$ is 1.34, implying very strong EPC. However, the calculated $\lambda$ of AlCCr$_3$, GaCCr$_3$, and ZnNCr$_3$ are less than 1.0 and about 0.6 $\sim$ 0.8 (table IV), implying moderate EPC. The difference of $\lambda$ for AXCr$_3$ can be described qualitatively using Hopfield expression

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

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 squared phonon frequency. The higher $N(E_F)$ and the lower phonon frequency make GaCCr$_3$ has the larger $\lambda$.

To calculate $T_c$, we used the Allen-Dynes equation$^{54-56}$

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

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

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

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

FIG. 13. Eliashberg functions (left) and frequency-dependent EPC strength $\lambda$ (right) of (a) MgCNi$_3$, (b) AlCCr$_3$, (c) GaCCr$_3$, and (d) ZnNCr$_3$.

FIG. 14. (a) Variation of $T_c$ with $\mu^*$ (purely static pair breaking); (b) Variation of $T_c$ with $\lambda_{sf}$ (electron-paramagnon coupling).
MgCNi$_3$, AlCCr$_3$, GaCCr$_3$, and ZnNCr$_3$, respectively. According to the experimental results of MgCNi$_3$ single crystals$^{16,17,20–24}$, the observed $T_C$ is around 7 K. It seems that our calculation overestimates $T_C$ of MgCNi$_3$. 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 $\mu^*$. In figure 14 (a), one can note that the increasing $\mu^*$ 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 $\mu^* = 0.33^{48}$ and $\mu^* = 0.41^{48}$, but still larger than the typical values $\mu^* = 0.1 \sim 0.15$ for the absence of SF.

It is better to discuss the influence of SF in terms of electron-paramagnon coupling strength $\lambda_{sf}$.$^{48}$ In that case, the effective coupling strength should be $\lambda_{sf} = \lambda = \lambda_{sf}$. The effective mass of the carriers should be enhanced by the factor $1 + \lambda_{sf} = 1 + \lambda_{sf}$. And equation (4) should be changed as$^{53,57}$

$$ T_C = \frac{\omega_{0\alpha}}{1.45} \exp \left( \frac{(1 + \lambda_{sf})}{\lambda_{sf} - \mu^*(1 + 0.5 \frac{1}{1 + \lambda_{sf}})} \right). \tag{6} $$

Figure 14 (b) shows the calculated $T_C$ using equation (6) with different $\lambda_{sf}$ (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$^{52,53}$. The influence of SF on $T_C$ of AlCCr$_3$, GaCCr$_3$, and ZnNCr$_3$ is also present in figure 14. If we consider the same SF influence as in MgCNi$_3$, using equation (6) 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 equation (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 so far to investigate such transition in doped antiperovskites such as Mg$_{1-x}$($A^{1+}$)$_x$Ni$_3$ 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.

D. 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 superconductors$^{32–36,58}$. The observed superconducting trace at 4.5 K found in In$_{1.3}$B$_0.7$Sc$_3$ is encouraging$^{32}$. Theoretically, InBSc$_3$ is close to weak FM and with an EPC superconducting mechanism$^{32,33}$. 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 A$^{4+}$CCo$_3$ (A = Si, Ge, etc.) and A$^{3+}$CCO$_3$ (A = Al, Ga, etc.). The DOS near $E_F$ of SiCCo$_3$ and AlCCo$_3$ are plotted in figure 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 A$^{3+}$CCO$_3$ may be new Co-based superconductors besides Na$_x$CoO$_2$-yH$_2$O$^{32}$. And doped A$^{4+}$CCo$_3$ 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$^{59,60}$. For the iron pnictide superconductors$^{8}$, Boeri et al.$^{61,62}$ and Mazin et al.$^{63}$ pointed out that the EPC in the system is intrinsically weak, but can be enhanced strongly by magnetism$^{64}$. 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$^{62}$. One may connect nickel pnictide superconductors with MgCNi$_3$ by the similar EPC mechanism. The potential superconductivity in doped A$^{4+}$CCo$_3$ may also help to figure out the superconducting mechanism, which needs to be further confirmed in experimental and theoretical works.
IV. 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 ZnNCr\(_3\) 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 ZnNCr\(_3\). Our results confirm the strong EPC in MgCNi\(_3\), and show that AlCCr\(_3\), GaCCr\(_3\), and ZnNCr\(_3\) are moderate coupling BCS superconductors. Such compounds may be good candidates to figure out the role of SF. Moreover, some potential new antiperovskite Co-based 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.

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