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First-principles prediction of layered antiperovskite superconductors $A_2\text{CNi}_4$ ($A = \text{Al}, \text{Ga}, \text{and Sn}$)

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We theoretically designed and investigated the layered antiperovskite nickel carbides $A_2\text{CNi}_4$ with different A-site elements by using the first-principles calculation based on density functional theory (DFT). The calculated formation energies for a series of A-site elements show that Al_2CNi_4 , Ga_2CNi_4 , and Sn_2CNi_4 are stable and can be synthesized at ambient pressure. The elastic properties and electronic band structures were calculated and discussed. Similar to the superconducting MgCNi_3 , the three stable compounds show the non-magnetic ground states. The density of states at Fermi level $N(E_F)$, dominated by Ni-3d electrons, can be comparable with the $N(E_F)$ of MgCNi_3 . The electron and hole bands cross the Fermi level, indicating the multiple-band nature for $A_2\text{CNi}_4$ ($A = \text{Al}, \text{Ga}, \text{and Sn}$). Using the McMillan's formula, we approximately estimated the superconducting parameters such as electron-phonon coupling constants λ and superconducting transition temperatures T_C . Our present results show that the layered antiperovskite nickel carbides $A_2\text{CNi}_4$ ($A = \text{Al}, \text{Ga}, \text{and Sn}$) may be potential weak-coupling superconductors with T_C about 5~7 K. Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4769882>]

I. INTRODUCTION

Since the discovery of superconductivity by Onnes,¹ researchers are looking for a superconductor with high T_C that can be applied in real life. Until now, the highest T_C was found in layered cuprate oxide superconductors²⁻⁴ with layered structures based on perovskite templates. Most other high T_C superconductors have a layered structure as well, such as iron-based superconductors⁵ and MgB_2 .⁶ On the other hand, layered superconductors often proclaim new physics, such as p -wave spin-triplet superconductor Sr_2RuO_4 .⁷

In recent years, the antiperovskite carbides AXM_3 (X, carbon, boron or nitrogen; M, transition metal) have attracted considerable attention due to lots of interesting properties, such as superconductivity,^{8,9} non-Fermi liquid behavior,¹⁰ strong electron-electron correlation,¹¹ giant magnetoresistance (MR),^{12,13} large negative magnetocaloric effect (MCE),^{14,15} giant negative thermal expansion,^{16,17} magnetostriction,¹⁸ and nearly zero temperature coefficient of resistivity.¹⁹ Specially, in MgCNi_3 despite the strong expectation for ferromagnetism due to full occupancy of Ni, it shows superconductivity with a T_C about 8 K.⁸ Experiments and energy band calculations show that there is a van Hove singularity in the density of states (DOS) just below Fermi level (E_F), which leads to a large DOS at the E_F ($N(E_F)$), dominated by Ni-3d states.^{20,21} In the system, three dimensional

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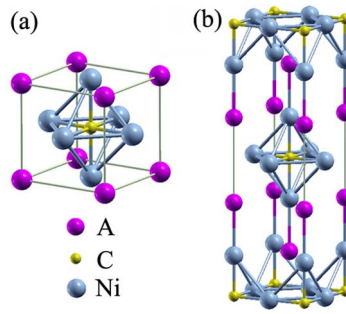


FIG. 1. The structures of (a) antiperovskite ACNi_3 and (b) layered antiperovskite A_2CNi_4 .

(3D) Fermi surfaces are composed of both electron and hole pockets. Experimental results^{22–24} have provided evidence for a medium to strong-coupling superconductivity driven by electron-phonon interactions. Further evidence for the phonon-mediated pairing mechanism is provided by theoretical estimates of electron-phonon coupling constant ranging from 0.8 to 1.5.^{25–27} Supposing that there is a family of layered materials with structures based on the ACNi_3 templates, new superconductivities and physics are expected in them.

In the present work, we theoretically designed layered antiperovskite nickel carbides A_2CNi_4 . The structure of A_2CNi_4 is similar to that of $(\text{La},\text{Sr})_2\text{CuO}_4$ ⁴ and Sr_2RuO_4 ,⁷ and can be seen as a stacking of ACNi_3 layers (Fig. 1). These kinds of materials were theoretically investigated through the first-principles calculation based on density functional theory (DFT). The formation energies for the series of A-site elements were calculated, and the results show that the A_2CNi_4 with $\text{A}=\text{Al}$, Ga, and Sn are stable and can be synthesized at ambient pressure. Similar to MgCNi_3 , A_2CNi_4 ($\text{A}=\text{Al}$, Ga, and Sn) have non-magnetic metallic ground states with large $N(E_F)$ and multiple-band natures. Using the McMillan's formula, we predicted some superconducting parameters such as electron-phonon coupling constants and superconducting transition temperatures. Our present results show that the layered antiperovskite nickel carbides A_2CNi_4 ($\text{A}=\text{Al}$, Ga, and Sn) may be potential weak-coupling superconductors with T_C about 5~7 K.

II. COMPUTATIONAL DETAILS

The real crystal structures of A_2XM_4 type compounds can usually be described in three space groups of $I4/mmm$ (tetragonal), $Abma$ and $Fmm2$ (orthorhombic), in which the later two structures are so-called distorted A_2XM_4 .²⁸ In this work, we only consider the tetragonal nickel carbides A_2CNi_4 . We chose the A-site elements corresponding to the following rules: (a) The metal elements usually existing in the real antiperovskites ACM_3 ; and (b) Generally speaking, the magnetic elements are harmful for conventional superconductivity, so A-site elements should be non-magnetic. The positions of atoms in the conventional cell are as follows: A (0, 0, z_1), C (0, 0, 0), Ni_1 (0.5, 0, 0), Ni_2 (0, 0, z_2).

The calculations were performed by projected augmented-wave (PAW)^{29,30} formalism implemented in the ABINIT code.^{31–33} The PAW method can lead to very accurate results comparable to other all-electron method. The exchange-correlation functions are treated by using the generalized gradient approximation (GGA) according to the Perdew-Burke-Ernzerhof³⁴ parametrization. Electronic wave functions 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) mesh³⁵ of $14 \times 14 \times 8$. The self-consistent calculations were considered to be converged when the total energy of the system was stable within 10^{-6} eV per atom. Non-magnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM) states were tested in the study. For AFM states, we considered the simplest configuration: the spins of Ni atom in the same ACNi_3 layer are paralleled with each other, and are anti-paralleled with spins in the neighboring ACNi_3 layers.

TABLE I. Predicated layered antiperovskite carbides (A_2CM_4) and nitrides (A_2NM_4) with different A-site and M-site elements according to the structure factors constraints. The values in brackets are the atom radius of elements. ■ means distorted A_2CM_4 , □ means tetragonal A_2CM_4 , ▲ means distorted A_2NM_4 , △ means tetragonal A_2NM_4 , × means non-existent compounds.

A→ M↓	Cu (1.28)	Zn (1.34)	Ga (1.35)	Al (1.43)	Ag (1.44)	Cd (1.51)	Sn (1.58)	Mg (1.6)	In (1.66)	Y (1.8)	Ca (1.97)
Ti (1.47)	▲	■▲	■△	□△	□△	□△	□△	□△	□△	×	×
V (1.34)	▲	■△	□△	□△	□△	□△	□△	□△	□	×	×
Cr (1.28)	▲	■△	□△	□△	□△	□△	□△	□△	□	×	×
Mn (1.27)	▲	■△	■△	□△	□△	□△	□△	□△	□	×	×
Fe (1.26)	▲	□△	□△	□△	□△	□△	□△	□△	□△	×	×
Co (1.25)	▲	■△	□△	□△	□△	□△	□△	□△	□	×	×
Ni (1.24)	▲	■△	□△	□△	□△	□△	□△	□△	×	×	×

III. RESULTS

A. Stability of A_2CNI_4

1. Structural criterion analysis

For perovskites AXM_3 or layered perovskite A_2XM_4 , the tolerance factor t is defined as

$$t = \frac{r_A + r_M}{\sqrt{2}(r_X + r_M)}, \quad (1)$$

where r is the atom's radius. For the known A_2XM_4 compounds, in distorted structures, the t factor changes in $0.8 \leq t \leq 0.9068$, and in tetragonal structure, the t factor changes in $0.9068 \leq t \leq 1$.²⁸ The empirical t factor takes into account the structural properties of the crystals if the size of octahedral voids in the close-packed AM_3 array is sufficient for embedding X atoms.

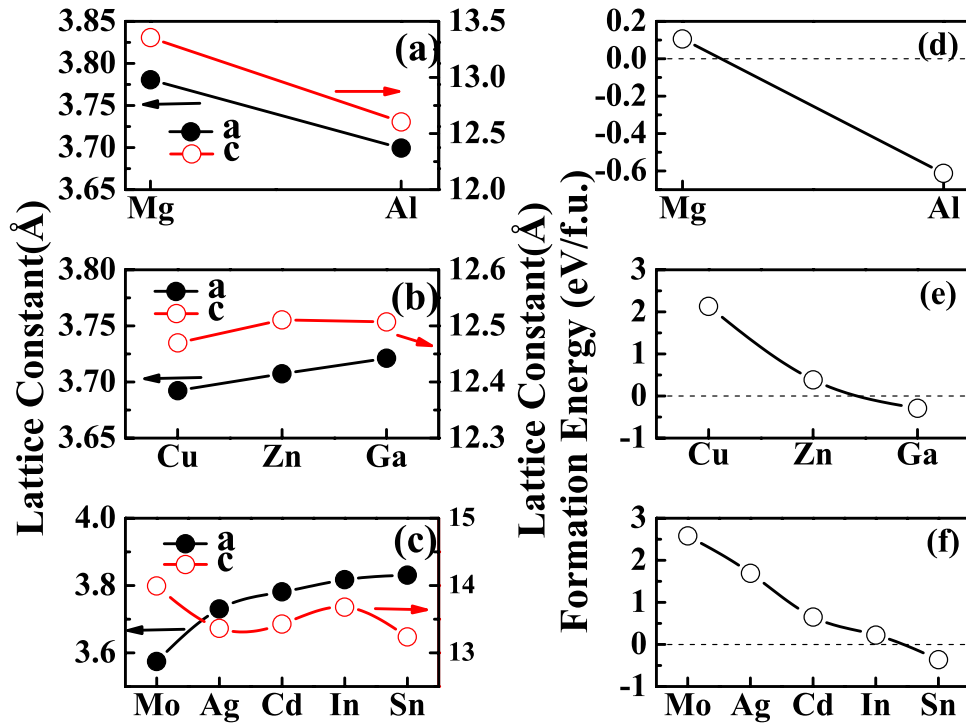
According to the criterion, in Table I we listed the stable structure of A_2CM_4 and A_2NM_4 , where M are 3d transition metal elements, and A are non-magnetic metal elements usually existing in ACM_3 . It can be found that Cu and In are the boundary of possible A-site elements.

Of course, the approach used here is based only on the radius of the atoms and does not take into account the specific features of formation energy, electronic structure, mechanical properties of the crystals, but it still can be applied to choose proper elements to design possible structures. The properties of A_2CNI_4 following the tolerance factor criterion will be discussed later.

2. Ground state and Formation energy

The structures were fully optimized with respect to lattice parameters and atomic positions for different magnetic configurations. The self consistent field (SCF) calculations show that the non-magnetic structure has the lowest total energy. Moreover, the obtained magnetic moments of each atom in FM and AFM states are quite small (lower than $10^{-3}\mu_B/\text{atom}$). Thus we considered non-magnetic state should be more stable. The calculated lattice parameters are shown in Fig. 2(a)–2(c). When A-site elements belong to the left area of period tables (e.g. Mg), A-site atoms have larger atom radius, thus A_2CNI_4 show larger lattice parameters. The smaller lattice parameters of A_2CNI_4 obtained as A-site elements locating in the middle of period table. However, when A-site elements change from the middle to the right of period table, the lattice parameters slightly increase. Bannikov *et al.*³⁶ reported the similar trends. In their work the calculated lattice parameters of $ACNi_3$ (A is 4d metal) decrease along the sequence $YCNi_3$ to $RuCNi_3$ and slightly increase along $RhCNi_3$ to $AgCNi_3$ at the end of the 4d row.

The common technique for producing antiperovskites is solid-state synthesis from the parent materials. We analyse the stability of compounds by calculating the formation energies ΔE , which is defined as the difference between the total energies of initial reagents (elements) and final

FIG. 2. Lattice parameters and formation energies for A_2CNi_4 .

compounds:

$$\Delta E = E_{tot}^{A_2CNi_4} - (2E_{tot}^A + E_{tot}^C + 4E_{tot}^{Ni}). \quad (2)$$

Here, E_{tot}^A , E_{tot}^C , and E_{tot}^{Ni} are the total energies of the initial reagents.

According to the definition of ΔE , negative values indicate that the formation of compounds from the initial components is energetically favorable and the compounds are stable with respect to a mixture of the initial elements. Conversely, if $\Delta E > 0$, the compounds are unlikely to be synthesized under ambient pressure. In order to verify our calculation methods, we firstly calculated the lattice parameters and formation energies for $ACNi_3$. Our results are perfectly matched with the previously reported results^{25–27,36–38} (not shown here).

The calculated formation energies of A_2CNi_4 are shown in Fig. 2(d)–2(f). As the A-site elements are in the same period in periodic table, the formation energies decrease with increasing atomic numbers. The formation of a material accompanies with the transfer of electrons of outer shells of atoms, in another word, ionization. It turns out the changes of formation energies of A_2CNi_4 correspond to the changes of ionization energies of A-site elements. The results indicate that the principal possibility of the successful synthesis of a compound needs to choose initial reagents which have proper radius and lower ionization energy. Bannikov *et al.*³⁶ reported similar trends of the variation of formation energy of $ACNi_3$ (A is 4d metals).

From the analysis of formation energies, we qualitatively conclude that A_2CNi_4 can be synthesized when A = Al, Ga, and Sn. In the following we will specially discuss the properties of the three potentially stable compounds.

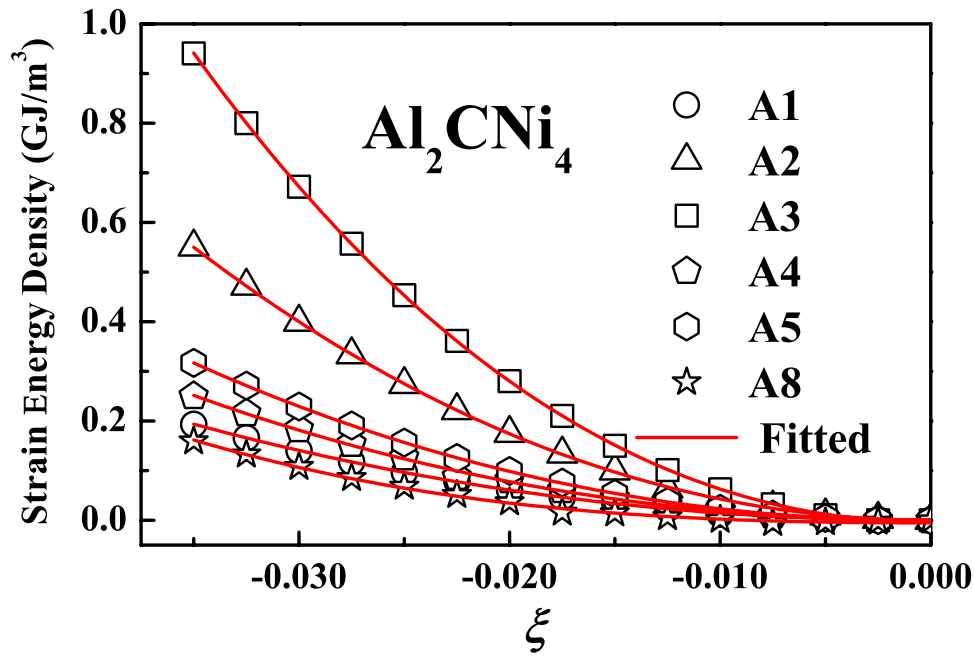
B. Elastic and mechanical properties

The elastic constants are evaluated according to the finite-strain continuum elasticity theory.^{39,40} The strain energy per unit mass can be expressed as a polynomial of the strain parameter ξ ,⁴¹

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

TABLE II. The coefficient A_2 in Eq. (3) of corresponding Lagrangian strains as combinations of second order elastic constant for tetragonal crystal.

Strain type	A_2
$J_A = (\xi, 0, 0, 0, 0, 0)$	C_{11}
$J_B = (\xi, \xi, 0, 0, 0, 0)$	$2C_{11} + 2C_{12}$
$J_C = (\xi, \xi, \xi, 0, 0, 0)$	$2C_{11} + C_{33} + 4C_{13} + 2C_{12}$
$J_D = (\xi, 0, 0, 2\xi, 0, 0)$	$C_{11} + 4C_{44}$
$J_E = (\xi, 0, 0, 0, 0, 2\xi)$	$C_{11} + 4C_{66}$
$J_F = (0, 0, 0, 0, 0, \xi)$	C_{33}

FIG. 3. The strain-energy relation of Al_2CNi_4 .TABLE III. Elastic constants and derived quantities for A_2CNi_4 ($\text{A}=\text{Al}$, Ga , and Sn).

	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)	C_{66} (GPa)	B (GPa)	G (GPa)	B/G	E (GPa)	σ	Θ_D (K)
Al_2CNi_4	293.14	123.44	80.57	102.24	16.64	44.08	119.42	34.86	3.43	80.96	0.41	356.59
Ga_2CNi_4	269.52	135.09	86.11	340.32	30.97	31.95	165.93	49.49	3.35	114.36	0.40	375.00
Sn_2CNi_4	319.83	99.58	83.63	310.8	42.51	41.97	164.81	63.75	2.59	137.91	0.38	385.63

where the coefficients A_2 and A_3 are combinations of second- and third-order elastic constants of the crystal, respectively. In a tetragonal structure, there are six independent second-order elastic constants (C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , and C_{66}). Therefore, here we introduced 6 Lagrangian strain tensors labeled as J_α in terms of ξ . J_α and the corresponding coefficients A_2 are listed in Table II.

In order to obtain accurate elastic constants, ξ is varied with a step of 0.0025 in every case for J_α . As an example, the strain-energies for Al_2CNi_4 and the fitted polynomials are shown in Fig. 3. The calculated elastic constants at ambient pressure and other derived mechanical parameters are listed in Table III. It was known that the mechanical parameters are directly determined by the features of the average bond strength. For example, C_{33} is related to the unidirectional compression along the [001] direction. For Al_2CNi_4 , C_{33} is comparably smaller than C_{11} , which implying the weaker coupling between AlCNi_3 layers in the compound (see more discussions in next section).

From the elastic constants, one may obtain the bulk modulus B and shear modulus G using the Voight-Reuss-Hill approximation:⁴²

$$B = \frac{B_V + B_R}{2}, \quad (4)$$

and

$$G = \frac{G_V + G_R}{2}, \quad (5)$$

where the Voight average can be described as⁴²

$$B_V = \frac{2C_{11} + C_{33} + 4C_{13} + 2C_{12}}{9}, \quad (6)$$

and

$$G_V = \frac{2C_{11} + C_{12} - (C_{12} + 2C_{13})}{15}. \quad (7)$$

The Reuss average can be expressed as⁴³

$$B_R = \left[\frac{2}{C_{11} + C_{12} - 2C_{13}} + \frac{1}{C_{33} - C_{13}} \right]^{-1} + C_{13}, \quad (8)$$

and

$$G_R = \left[\frac{1}{5} \left(R + \frac{2}{C_{11} - C_{12}} + \frac{2}{C_{44}} + \frac{1}{C_{66}} \right) \right]^{-1}, \quad (9)$$

where $R = [(C_{11} + C_{12})C_{33} - 2C_{13}^2]/6B_V$.

Then we can get the Young's modulus E and the Poisson's ratio σ using the following standard relations:

$$E = \frac{9BG}{3(B + G)}, \quad (10)$$

and

$$\sigma = \frac{3B - 2G}{2(3B + G)}. \quad (11)$$

According to Pugh,⁴⁴ the ductile/brittle properties of materials could be related empirically to the ratio of bulk modulus B divided shear modulus G (B/G). If $B/G > 1.75$, the material would be ductile; otherwise the material behaves in a brittle manner. For $A_2\text{CNi}_4$ ($A=\text{Al}$, Ga , and Sn), all the calculated B/G ratios are larger than 1.75. The Young's modulus E also reflects the ductility. The larger the value of E , the stiffer is the material, and as the covalent nature of the compounds increases E also increases. Another important parameter describing the ductile nature of solids is the Poisson's ratio σ . For ductile metallic materials σ is typically around 0.33.⁴⁵ The calculated elastic and mechanical parameters are listed in Table III, which classify $A_2\text{CNi}_4$ ($A=\text{Al}$, Ga , and Sn) as ductile materials.

Debye temperature (Θ_D) is one of the most important parameters that determine the thermal characteristics of materials. It can be obtained in terms of the mean sound velocity v_m :

$$\Theta_D = \frac{h}{k_B} \left(\frac{3n\rho N_A}{4\pi M} \right)^{\frac{1}{3}} v_m, \quad (12)$$

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

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{\frac{1}{3}}, \quad (13)$$

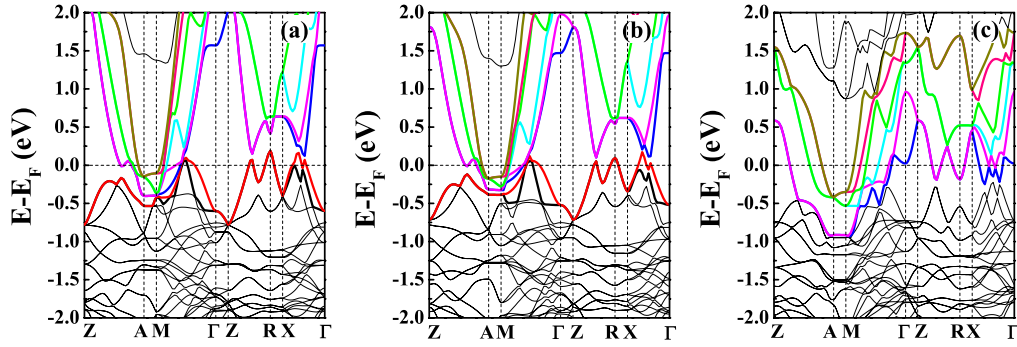


FIG. 4. Band structures of (a) Al_2CNi_4 , (b) Ga_2CNi_4 , and (c) Sn_2CNi_4 . The colored lines denote the bands crossing the Fermi level.

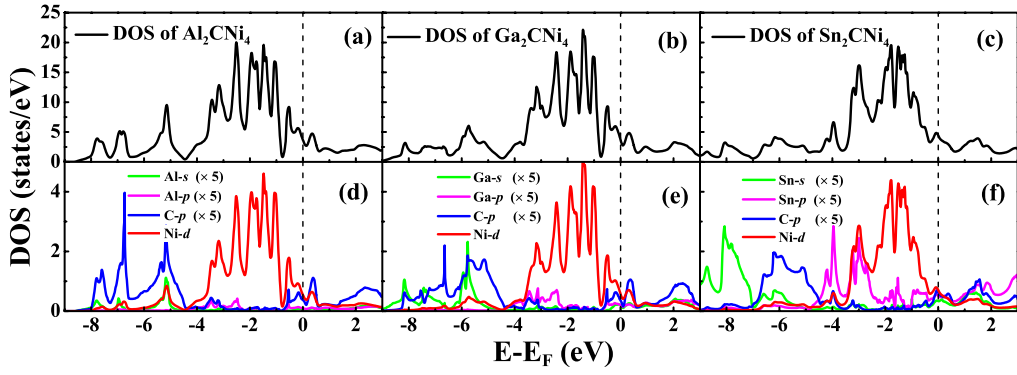


FIG. 5. Top panels: The density of states of (a) Al_2CNi_4 , (b) Ga_2CNi_4 , and (c) Sn_2CNi_4 . Bottom panels: The partial density of states of (d) Al_2CNi_4 , (e) Ga_2CNi_4 , and (f) Sn_2CNi_4 .

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

$$v_l = \left(\frac{3B + 4G}{3\rho} \right)^{\frac{1}{2}}, \quad (14)$$

and

$$v_t = \left(\frac{G}{\rho} \right)^{\frac{1}{2}}. \quad (15)$$

The estimated Debye temperatures (see Table III) of A_2CNi_4 ($A = \text{Al}$, Ga , and Sn) can be comparable with that of MgCNi_3 ,^{24,46,47} implying the similar averaged phonon frequencies.

C. Electronic and bonding properties

The calculated electronic band structures along the high symmetry directions in the Brillouin zones together with the total and site-projected I-decomposed DOS at equilibrium lattice parameters for A_2CNi_4 ($A = \text{Al}$, Ga , and Sn) are shown in Fig. 4 and 5. The band structures were calculated using a conventional cell with 14 atoms. The bands between -8 eV and -5 eV come mainly from the strong hybridization between C-2*p* electrons and Ni-3*d* electrons. And the bands between -5 eV and Fermi level are mainly from Ni-3*d* electrons, together with a mixture of A-*p* and C-2*p* electrons.

The band structures near Fermi level for A_2CNi_4 ($A = \text{Al}$, Ga , and Sn) are similar, except for the location of Fermi level. According to the rigid band model, the more electrons of Ga will lead the higher Fermi level of Ga_2CNi_4 than that of Al_2CNi_4 . On the other hand, the smaller lattice volume of Al_2CNi_4 will increase the Fermi energy level. So the Fermi energies of Al_2CNi_4 and Ga_2CNi_4

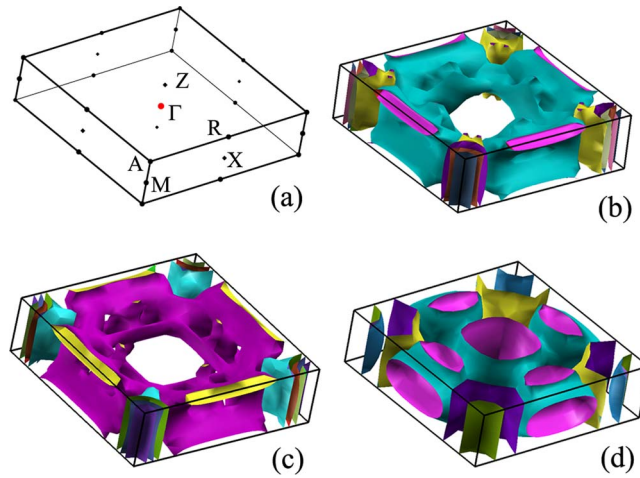


FIG. 6. (a) Brillouin zone of A_2CNI_4 conventional cell and Fermi surfaces of (b) Al_2CNI_4 , (c) Ga_2CNI_4 , and (d) Sn_2CNI_4 .

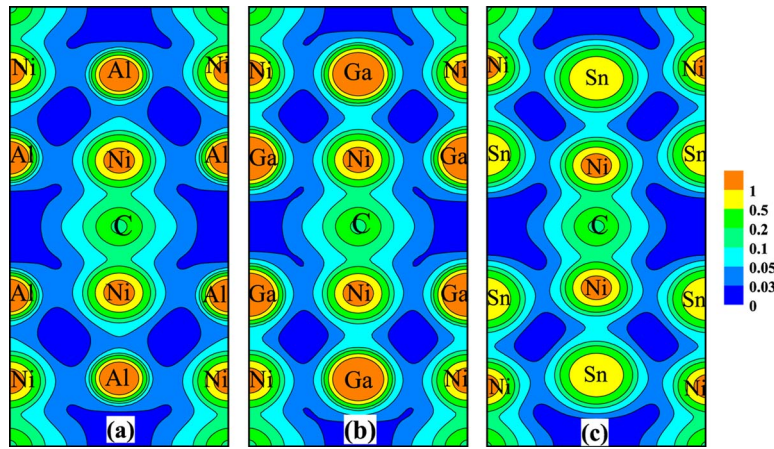


FIG. 7. The contour map of electron charge density of (a) Al_2CNI_4 , (b) Ga_2CNI_4 , and (c) Sn_2CNI_4 .

are very close, which leads to similar Fermi surface characters. For these two compounds, there are eight bands cross the Fermi level. Very complicated 3D-like hole pockets come from the lower two bands, and 2D-like electron sheets (along the k_z direction) around the corners of the Brillouin zone (Fig. 6(b) and 6(c)) come from the upper six bands. Sn has more electrons than Ga and Al, which increases the Fermi energy of Sn_2CNI_4 significantly. Six bands cross the Fermi level, the lower two bands form complicated 3D-like hole pockets, which form electron sheets for Al_2CNI_4 and Ga_2CNI_4 cases. The upper four bands still form 2D-like electron sheets (along the k_z direction) around the corners of the Brillouin zone (Fig. 6(d)). The presence of electron bands and hole bands crossing the Fermi level indicates the multiple-band natures for A_2CNI_4 ($A=Al, Ga, \text{ and } Sn$).

The DOS at Fermi energy level of the three compounds are dominated by Ni-3d electrons. The value of $N(E_F)$ are 3.67, 3.68, and 4.43 states/eV for Al_2CNI_4 , Ga_2CNI_4 , and Sn_2CNI_4 , respectively, which can be comparable with that of $MgCNI_3$.^{26,47,48} However, different from the case of $MgCNI_3$, there is no van Hove singularity in DOS near E_F .

In order to understand the bonding nature among the atoms in A_2CNI_4 , we plot the contour maps of charge density of the three compounds in Fig. 7. The C-Ni bonds are very strong, which coincides with the strong hybridization between C-2p and Ni-3d electrons shown in DOS figures. The adjacent $ACNI_3$ -layers are coupling with weaker A-Ni bond. For Ga_2CNI_4 , strong hybridization between Ga-4s and Ni-3d electrons (Fig. 5(e)) leads to strong Ga-Ni bonds, which make the elastic constant C_{33} bigger than that of the others. On the contrary, for Al_2CNI_4 , the hybridization between

TABLE IV. The DOS at Fermi energy level $N(E_F)$, Stoner parameter S , Coulomb pseudopotential parameter μ^* , McMillan–Hopfield parameters η_α , electron-phonon coupling constant λ , and the superconducting transition temperature T_C of $A_2\text{CNi}_4$ ($A = \text{Al, Ga, and Sn}$).

	$N(E_F)$ (states/eV)	S	μ^*	η_A (eV/Å ²)	η_C (eV/Å ²)	η_{Ni} (eV/Å ²)	λ	T_C (K)
Al_2CNi_4	3.67	0.20	0.09	0	0.11	0.45	0.59	5.9
Ga_2CNi_4	3.68	0.27	0.09	0	0.17	0.40	0.57	6.8
Sn_2CNi_4	4.43	0.43	0.10	0	0.13	0.42	0.55	5.5

Al and Ni is very weak, which leads to a weak coupling between the AlCNi_3 -layers and hence a small elastic constant C_{33} .

D. Evaluation of superconducting parameters

In order to assess whether these compounds are close to ferromagnetism or not, we performed fixed-spin-moment calculations, which allow for an estimation of the Stoner parameter S . The Stoner parameters can be obtained using the relation:^{21,49}

$$\Delta E = \frac{1 - S}{2N(E_F)} M^2, \quad (16)$$

where ΔE is the total energy difference between non-magnetic state and the ferromagnetic state with a fixed tiny spin moment M . If $S > 1$, the system should be of ferromagnetic stability. The calculated Stoner parameters S are listed in Table IV. All the calculated S is far below the ferromagnetic critical point, which proves the non-magnetic ground state of $A_2\text{CNi}_4$ ($A = \text{Al, Ga, and Sn}$).

Similar to MgCNi_3 , $A_2\text{CNi}_4$ ($A = \text{Al, Ga, and Sn}$) have non-magnetic metallic ground states with large $N(E_F)$ and multiple-band natures, which are typical characteristics of superconducting antiperovskite materials.^{25–27}

We discuss the possible superconductivity of $A_2\text{CNi}_4$ ($A = \text{Al, Ga, and Sn}$) using McMillan's coupling theory:⁵⁰

$$T_C = \frac{\Theta_D}{1.45} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]. \quad (17)$$

Coulomb pseudopotential parameter μ^* can be empirically obtained using the relation:⁵¹

$$\mu^* = 0.26 \frac{N(E_F)}{1 + N(E_F)}, \quad (18)$$

where $N(E_F)$ is expressed in states/eV/atom.

The electron-phonon coupling constant λ can be calculated from the following expression

$$\lambda = \sum_{\alpha} \frac{\eta_{\alpha}}{M_{\alpha} \langle \omega_{\alpha}^2 \rangle}, \quad (19)$$

where M_{α} is the atomic mass, $\langle \omega_{\alpha}^2 \rangle$ is the averaged phonon frequency and can be approximated as $\langle \omega_{\alpha}^2 \rangle = \Theta_D^2/2$. The McMillan–Hopfield parameters $\eta_{\alpha} = N(E_F) \langle I_{\alpha}^2 \rangle$,⁵⁰ where $\langle I_{\alpha}^2 \rangle$ is the average electron-phonon matrix element for the α th atom. First-principles evaluation of these matrix elements, often using rigid muffin-tin approach,⁵² which will most strongly depend on proper treatment of the screened electron-ion interaction, is a formidable task beyond the scope of this work. Since the $N(E_F)$ and Θ_D of $A_2\text{CNi}_4$ ($A = \text{Al, Ga, and Sn}$) can be comparable with those of MgCNi_3 , we used conservative values of $\langle I_{\alpha}^2 \rangle$ calculated by Shim *et al.*,²⁶ just in order to approximately estimate the superconducting transition temperatures. The estimated superconducting transition temperatures and other quantities are listed in Table IV. The results show that $A_2\text{CNi}_4$ ($A = \text{Al, Ga, and Sn}$) are weak-coupling superconductors with T_C about 5~7 K.

IV. CONCLUSION

In conclusion, we have theoretically designed and investigated layered antiperovskite nickel carbides $A_2\text{CNi}_4$ through the first-principles calculation based on density functional theory. The analysis of formation energies show that the $A_2\text{CNi}_4$ with $A=\text{Al}$, Ga, and Sn are stable and can be synthesized at ambient pressure. The DOS at Fermi energy level of the three compounds, dominated by Ni-3d electrons, can be comparable with that of MgCNi_3 . However, unlike MgCNi_3 , the studied $A_2\text{CNi}_4$ do not show the van Hove singularity in the DOS near E_F . Multiple bands cross the Fermi level, forming 2D-like electron sheets and complicated 3D-like hole pocket. The strong hybridization between C and Ni leads to a strong C-Ni bond. The adjacent ACNi_3 -layers are coupling with weaker A-Ni bond, which may lead to a small elastic constant related to the [001] direction. Because of their non-magnetic metal ground states, large $N(E_F)$, and multiple-band nature, we consider $A_2\text{CNi}_4$ ($A=\text{Al}$, Ga, and Sn) may have superconductivities similar with that of MgCNi_3 . Using the McMillan's formula, we approximately estimated some superconducting parameters. The results show that the layered antiperovskite nickel carbides $A_2\text{CNi}_4$ ($A = \text{Al}$, Ga, and Sn) may be weak coupling layered superconductors with T_C about 5~7 K. This work needs to be further confirmed by experimental studies.

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