First-principles verification of $CuNNi_3$ and $ZnNNi_3$ as phonon mediated superconductors*

Chen Jian-Yong(陈建勇)[a)†] and Wang Xing(王 星)[b)]

[a)] *Faculty of Science, Guilin University of Aerospace Technology, Guilin* 541004, *China*
[b)] *Bowen College of Management, Guilin University of Technology, Guilin* 541006, *China*

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Very recently, a new Ni-based antiperovskite nitride superconductor $CuNNi_3$ has been successfully synthesized. We investigate the electronic structures, phonon dispersions, and electron–phonon interactions of $CuNNi_3$ and the isostructual $ZnNNi_3$ by first-principles approach. By analyzing the Eliashberg function we obtain the superconducting transition temperature T_c 3.16 K (3.53 K), which is in good agreement with corresponding experimental T_c 3.2 K (3 K) for $CuNNi_3$ ($ZnNNi_3$). They can be verified as conventional phonon-mediated superconductors.

Keywords: transition temperature, Ni-based antiperovskite nitride, first-principles

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1. Introduction

Since $MgCNi_3$ was discovered to be superconducting near 8 K,[1] much attention has been focused on the isostructural cubic antiperovskites, with formula $XCNi_3$ (X is a group II or III element). They are possible candidate with high superconducting transition temperature and other significant technological characteristics. A super-conducting ($T_c \sim 3$ K) nitrogen-containing anti-perovskite, which has been successfully prepared by reacting Zn with Ni powders in NH_3 gas,[2] is very attractive. In the framework of the rigid-band view, $ZnNNi_3$ anti-perovskite can be considered as a one-electron-doped superconducting $MCNi_3$ (M is divalent cation), in which the Fermi level should be located far from the Ni 3d peak, i.e., in the region of extremely low density of states (DOS), which is not inclined to superconductivity. In addition, as far as we know, $ZnNNi_3$ is the first nitrogen-containing superconducting material in the Ni-based anti-perovskite series. In all known similar structures, namely in superconducting oxide perovskites, superconductivity is based on the electron–hole states of the oxygen atoms occupying 3c-type positions (0, 1/2, 1/2). In $CuNNi_3$, these positions are occupied by Ni atoms; this means that the mechanism of superconductivity probably is radically different. The fact that superconductivity rather than ferromagnetism occurs in compound where much nickel is present is surprising and suggests that $CuNNi_3$ is an unconventional superconductivity. Helal and Islam have studied the elastic and electronic properties of $SnNNi_3$ and $CuNNi_3$, by first-principles approach,[3] and showed that their metallic properties are like those of superconductor $ZnNNi_3$. Mechanical stability and thermal properties of $ZnNNi_3$ under pressure were also studied.[4] Very recently $CuNNi_3$ has been successfully synthesized and exhibits its superconductivity as the second nitride superconductor in the Ni-based antiperovskites with a transition temperature of 3.2 K, and the estimated electron–phonon coupling strength is 0.53, which means weak coupling.[5] There is no literature discussing superconductivity of $Cu(Zn)NNi_3$ from the viewpoint of lattice dynamics and elctron–phonon interaction through theoretical calculation. Using first-principles calculation, we obtain knowledge of electronic and dynamic properties of $Cu(Zn)NNi_3$ to preliminary explore the superconductivity.

The rest of this article is organized as follows. In Section 2 we present all the computational details. In Section 3 we describe the crystal structure, electronic state, crystal vibration, and electron–phonon interaction properties. Some conclusions are drawn from the present study in Section 4.

2. Computational details

We calculate both $CuNNi_3$ and $ZnNNi_3$ under the same condition. Electronic properties and lattice dynamics are performed with density functional theory (DFT)[6] and density functional perturbation theory (DFPT) respectively.[7] The full potential WIEN2k package[8] is utilized for calculating the electronic structure with plane wave function expand to $R_{MT}K_{max}$ equal to 7.0 (K_{max} is the magnitude of the largest reciprocal lattice vector and R_{MT} is the smallest in all the muffin-tin sphere radii), muffin-tin radii are automatically determined to be 1.249 Å, 1.275 Å, 0.831 Å, and 0.937 Å for Cu, Zn, N, and Ni atoms respectively.[9,10] A modified tetrahedron method[11] is adopted for Brillouin zone integration with A $18\times18\times18$ k-mesh to reach the convergence of to-

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†Corresponding author. E-mail: glcjyong@guat.edu.cn
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tal energy. For phonon band structure and electron–phonon coupling calculation, the Quantum ESPRESSO package[12] is applied with plane wave pseudopotential method and generalized gradient approximation of Perdew, Burke and Ernzerhoff (GGA-PBE) for exchange–correlation interaction. Ultrasoft pseudo-potentials[13] are well checked and employed. The energy cutoff of plane-wave basis wavefunction is set to be 544 eV. Full Brillouin zone phonon spectra are obtained from a Fourier interpolation of dynamical matrices calculated on a cubic $(4\times4\times4)$ q-point mesh. A 36×36×36 k-mesh, with a Methfessel–Paxton Gauss smearing of 0.408 eV is taken for double δ function integration for the Eliashberg function calculation (see Subsection 3.4).[14]

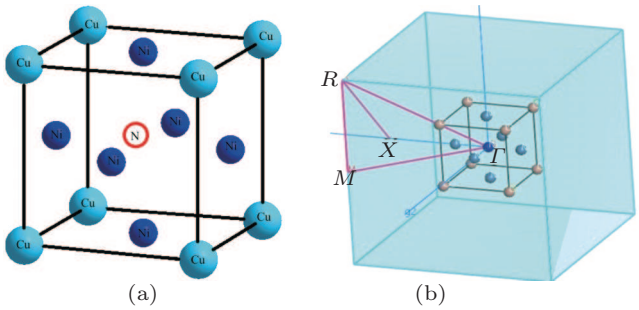


Fig. 1. (color online) Crystal structure of (a) $CuNNi_3$ and (b) Brillouin zone.

3. Results and discussion

3.1. Structure properties

The Ni-based Cu(Zn)NNi_3 antiperovskite superconductor possesses the cubic space group $Pm\bar{3}m$ (No. 221). The Wyckoff positions are Cu(Zn): 1a (0, 0, 0); N: 1b (1/2, 1/2, 1/2); Ni: 3c (1/2,1/2,0) (Fig. 1). In this structure, there are six Ni atoms at the face-centered positions of each unit cell forming a three-dimensional (3D) network of Ni octahedron. Each N atom is located at the body-centered cubic position surrounded by Ni octahedron cage. Spin-polarized ferromagnetic calculation performed for equilibrium geometry of Cu(Zn)NNi_3 converges to non-magnetic ground state, and the equilibrium lattice constant of $CuNNi_3$ is 3.7423 Å, which is in good accordance with the experimental value 3.742(2) Å. The optimized lattice constant of $ZnNNi_3$ is 3.769 Å. The optimized lattice parameter from GGA is slightly larger than the experimental lattice parameter, which is typical behavior in DFT calculations. Comparisons with the available experimental[2,5] and theoretical data[3,4] are shown in Table 1.

Table 1. Values of equilibrium lattice parameter (Å) and transition temperature (K) of $ZnNNi_3$ and $CuNNi_3$.

	Lattice constant	Transition temperature
$ZnNNi_3$	3.769	3.53
	3.756[a]	~ 3[a]
	3.765[c]	
$CuNNi_3$	3.7423	3.16
	3.742(2)[b]	3.2[b]
	3.761[d]	

[a]Ref. [2] (experiment); [b]Ref. [5] (experiment); [c]Ref. [4]; [d]Ref. [3].

3.2. Electronic structure studies

Our calculated band structures of $CuNNi_3$ and $ZnNNi_3$ agree fairly well with those in previous work,[3,9] $CuNNi_3$ exhibits nearly identical band structure with $ZnNNi_3$ except a few differences (Fig. 2). For instance, there is no overlap of conduction band and valence band at M point for $CuNNi_3$. Three bands go across the Fermi energy which contributes most to electron–phonon interaction. The most remarkable feature of the electronic density of states is a sharp van Hove peak less than 500 meV down from fermi energy (Fig. 3) which arises from antibonding bands relating to the Ni d orbitals. They are very narrow due to the linear Ni coordination, two nitrogen atoms become nearest neighbors of Ni, and thus it is expected that Ni 3d and N 2p electrons are strongly hybridized. Main contribution to states near fermi energy comes from Nid_{xz}, d_{yz} and Ni $d_{x^2}-d_{y^2}$ as can be seen from partial density of states (Fig. 3).

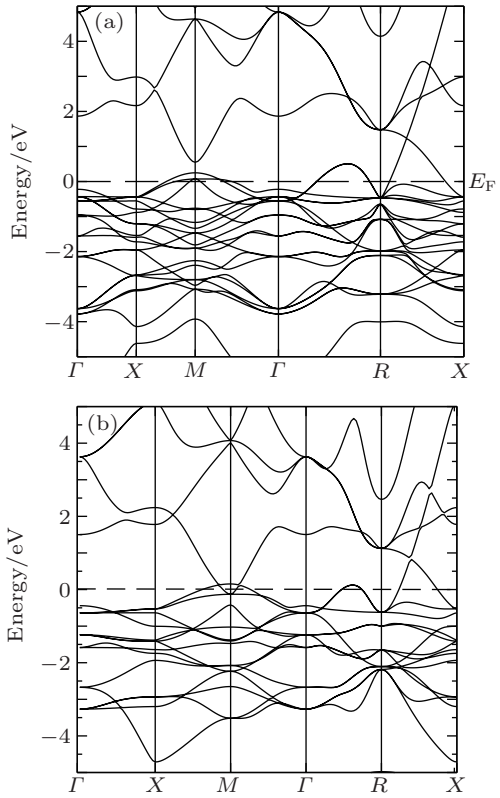


Fig. 2. Ultrasoft GGA-PBE band structures of (a) $CuNNi_3$ and (b) $ZnNNi_3$.

DOS at the Fermi level is dominated by the Ni d-states: it is not large enough to induce magnetic instabilities.[15] However, the DOS is sufficiently large to produce strong electron–phonon coupling. $CuNNi_3$ can be considered as a hole-doped $ZnNNi_3$, DOS of $CuNNi_3$ at E_F is higher than $ZnNNi_3$ suggesting that it is favorable for superconductivity.

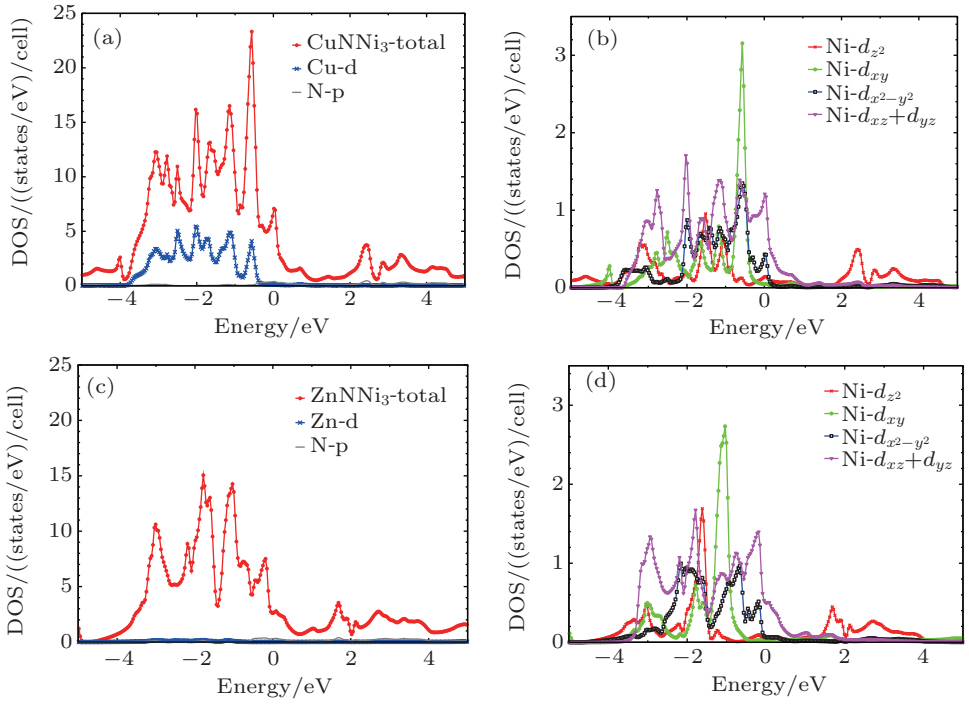


Fig. 3. (color online) Calculated total and projected electron DOSs of $CuNNi_3$ [(a) and (b)] and $ZnNNi_3$ [(c) and (d)].

3.3. Lattice dynamics

The phonon spectrum is shown in Fig. 4. There are 15 phonon branches in the full phonon dispersion including three acoustic and twelve optic phonon branches since the unit cell consists of five atoms. Owing to the large differences in mass,

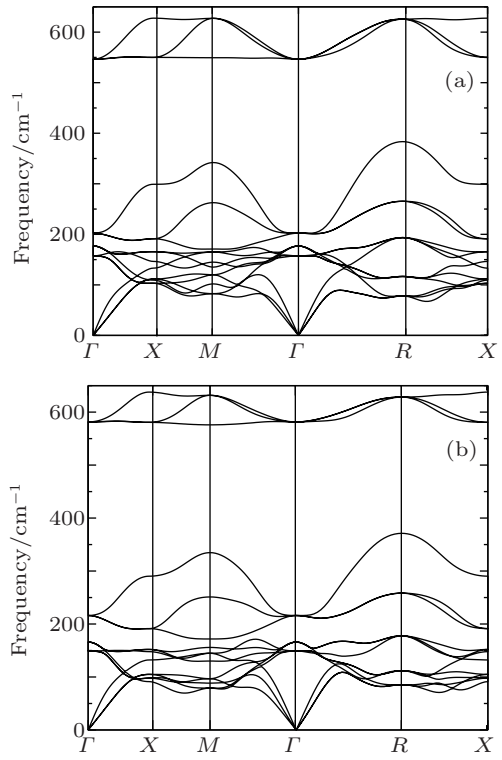


Fig. 4. Calculated phonon dispersions of (a) $CuNNi_3$ and (b) $ZnNNi_3$.

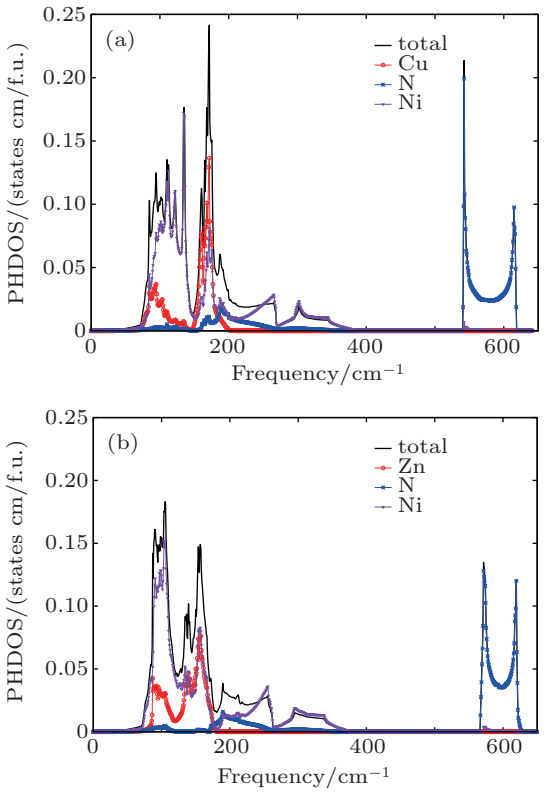


Fig. 5. (color online) Total and atom-projected PHDOSs of (a) $CuNNi_3$ and (b) $ZnNNi_3$.

the phonon band of $Cu(Zn)NNi_3$ decomposes well into two parts, a low-frequency region with predominant Ni and Cu modes and vibrations of the N atom around 600 cm^{-1} due to its small mass (Fig. 4). The stoichiometric compound is dynamically stable in the harmonic approximation since the

entire modes exhibit positive frequencies. We can conclude that at our optimized lattice constant Cu(Zn)NNi$_3$ lies at least in its local minimum of energy surface.

Figure 5 shows both the total and atom-projected phonon density of states (PHDOS). The acoustic modes are mainly of Ni characteristic with only a small hybridization of Cu modes. A remarkable feature from the PHDOS of CuNNi$_3$ and ZnNNi$_3$ is the significant mixed characteristic of phonons from different atoms particularly in a region from 150 cm^{-1} to 200 cm^{-1} which is responsible for the renormalized phonons arising due to the coupling between electrons and phonons.[16] This suggests that Cu(Zn)NNi$_3$ can be viewed as a moderately strong electron–phonon interaction substance, which will be discussed in detail below.

3.4. Electron–phonon interaction

We now discuss the interaction between electrons and phonons. The electron–phonon coupling (EPC) constant λ is usually extracted from the Eliashberg function $\alpha^2F(\omega)$ which describes the averaged coupling strength between the electrons of Fermi energy and the phonons of energy ω. It is used to derive the T_c of a conventional phonon-mediated superconductor as follows:[17–19]

$$\alpha^2F(\omega)=\frac{1}{2\pi N(\varepsilon_F)}\sum_{q\upsilon}\frac{\gamma_{q\upsilon}}{\omega_{q\upsilon}}\delta(\omega-\omega_{q\upsilon}), \tag{1}$$

where ε_F is the Fermi energy, $N(\varepsilon_F)$ is the electronic DOS per atom and per spin at the Fermi level, $\omega_{q\upsilon}$ is the phonon frequency indexed with wave vector q and mode number υ. The phonon linewidth $\gamma_{q\upsilon}$ is given by the Fermi "golden rule" as follows:

$$\gamma_{q\upsilon}=2\pi\omega_{q\upsilon}\sum_{kjj'}\left|g^{q\upsilon}_{k+qj',kj}\right|^2\delta(\varepsilon_{kj}-\varepsilon_F)\,\delta(\varepsilon_{k+qj'}-\varepsilon_F), \tag{2}$$

with ε_{kj} being the electron eigenvalue indexed with wave vector k and the band index j, the electron–phonon matrix element $|g^{q\upsilon}_{k+qj',kj}|$ can be defined as

$$g^{q\upsilon,j'j}_{k+qj',kj}=\sum_{R,\upsilon}\frac{\eta_{q\upsilon}(R,v)}{\sqrt{2M_R\omega_{q\upsilon}}}\left\langle k+q,j'\left|\frac{\delta V_{\rm eff}}{\delta R_\upsilon}\right|k,j\right\rangle. \tag{3}$$

Both ψ_{kj} and $\psi_{k+qj'}$ states have the Fermi energy ε_F, $\eta_{q\upsilon}(R,v)$ is the eigen-vectors of a $q\upsilon$ mode. M_R are the nuclei mass. $V_{\rm eff}$ is the one-electron potential due to the phonon distortion. The expression of EPC is also given in terms of the Eliashberg function:

$$\lambda=2\int\frac{{\rm d}\omega}{\omega}\alpha^2F(\omega)=\int{\rm d}\omega\lambda(\omega). \tag{4}$$

After λ is obtained from

$$\langle\omega\rangle_{\log}=\exp\left[\frac{2}{\lambda}\int_0^{\omega_{\max}}\alpha^2F(\omega)\frac{\ln(\omega)}{\omega}{\rm d}\omega\right], \tag{5}$$

the transition temperature can be calculated from the Allen-Dynes formula as follows:[20,21]

$$T_c=\frac{\langle\omega\rangle_{\log}}{1.2}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right], \tag{6}$$

where $\omega_{\max}$ is the maximum phonon frequency, μ^* is the screened Coulomb pseudopotential parameter with typical value in a range of 0.10–0.15.

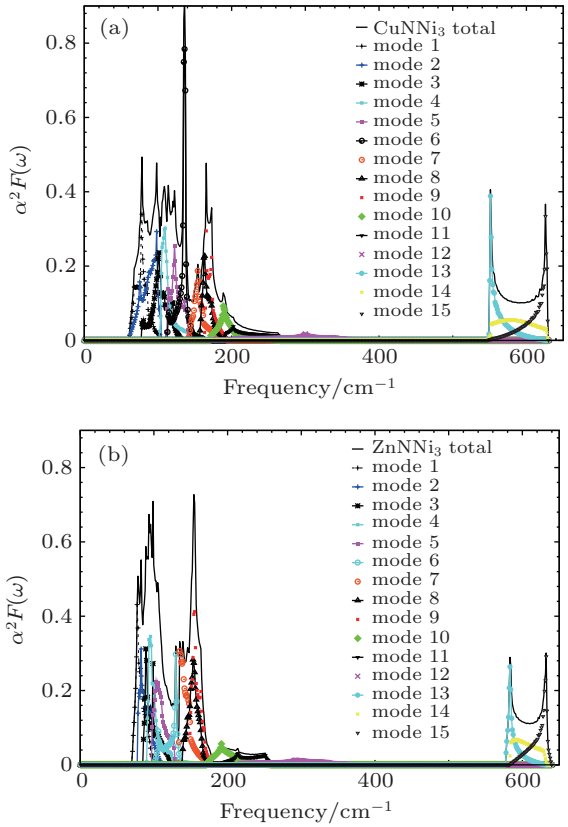


Fig. 6. (color online) Total and mode resolved Eliashberg functions of (a) CuNNi$_3$ and (b) ZnNNi$_3$.

Our calculated Eliashberg function is shown in Fig. 6. The deviation of the shape of $\alpha^2F(\omega)$ from that of PHDOS suggests that phonons with different energies almost make comparable contributions to $\alpha^2F(\omega)$, which suggests isotropical superconductors. They originate from the isotropical crystal structures and d electron distributions. However, the cases of MgB$_2$[22] and graphene[23] are very different: only two narrow peaks emerge in $\alpha^2F(\omega)$, which means that only several phonon modes involved in plane vibration have strong couplings. Comparing Fig. 5 with mode resolved $\alpha^2F(\omega)$ in Fig. 6 (colored lines), at lower energy (between 20 cm^{-1} and 180 cm^{-1}) each mode makes a larger contribution to $\alpha^2F(\omega)$ than the others. At higher energy (above 180 cm^{-1}) much less phonons are involved in the process of electron scattering. The λ characterizes correction magnitude of several physical parameters due to the electron–phonon coupling[24,25] such as quasi-particle energy, effective mass, electronic heat capacity, etc. The calculated value of λ is 0.6924, which means that the coupling strength between electrons and phonons in

$CuNNi_3$ is strong. As can be seen from Table 1, T_c is 3.16 K when selecting μ^* as a typical value of 0.13. The calculated value of T_c agrees excellently with 3.2 K measured in recent experiments.[5] For $ZnNNi_3$, the calculated value of λ is 0.6922 and T_c is 3.53 K, which fits well to experimental critical temperature $T_c \sim 3$ K.[2] This further demonstrates that the superconducting behavior of $Cu(Zn)NNi_3$ is described properly by the conventional BCS phonon-mediated mechanism. It is expected that the EPC strength and transition temperature can be enhanced by applying biaxial tensile strain which will significantly soften certain modes.[23]

4. Conclusions

Using first-principles calculation based on density functional theory, we study the electronic, lattice dynamics, electron–phonon coupling properties of Ni-based antiperovskite nitride superconductor $CuNNi_3$ and $ZnNNi_3$. Phonon dispersion calculation without negative frequency indicates that the optimized structure is in dynamic stability; furthermore $\alpha^2F(\omega)$ is obtained from electron–phonon interaction calculation. The low energy phonons are more involved in the process of scattering of electrons than the high energy phonons. The calculated transition temperatures are 3.16 K and 3.53 K for $CuNNi_3$ and $ZnNNi_3$ respectively, experimental results are 3.2 K and 3 K. This clarifies that the superconductivity is governed by the BCS mechanism. They can be categorized as a conventional phonon-mediated superconductor.

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