

Induced effects by the substitution of Mg in MgCNi₃

Guohua Zhong, Jianglong Wang, Zhi Zeng*, Xiaohong Zheng
Key Laboratory of Materials Physics, Institute of Solid State Physics,

Chinese Academy of Sciences and Graduate School of the Chinese Academy of Sciences, Hefei 230031, China.

Haiqing Lin

*Department of Physics and Institute of Theoretical Physics,
The Chinese University of Hong Kong, Shatin, Hong Kong, China.*

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The electronic structures and magnetic properties induced by the substitution of Mg in MgCNi₃ were investigated by performing the first-principles density functional calculations. It is confirmed that AlCNi₃, GaCNi₃ and InCNi₃ are paramagnetic non-superconductors resulted from total energy, density of states at Fermi level and electron-phonon coupling constant. A large peak of density of states lies on the Fermi level resulting in ferromagnetism rather than superconductivity in NaCNi₃. The substitution of dual elements for Mg, such as Al_{0.5}Na_{0.5}CNi₃ and Al_{0.5}Li_{0.5}CNi₃, was inspected too. Evaluating the electron-phonon coupling interaction, the possible superconductivity exists in near ferromagnetism Al_{0.5}Na_{0.5}CNi₃.

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The discovery of superconductivity in MgCNi₃[1] has resumed the interest to search for new superconductors in intermetallic compounds because of its simple perovskite structure opposite to the oxide superconductors, though this T_c is only 8 K. Remarkably, there is no any oxygen and high Ni content in MgCNi₃, which usually results in magnetism rather than superconductivity. Many experimental and theoretical research works for MgCNi₃ superconductor and related compounds have been done. However, the debate on nature and microscopic origin of the superconducting states are still existent. The specific heat jump[1] $\Delta C(T_c)/kT_c \approx 1.9$ and nuclear spin-lattice relaxation rate[2] are consistent with conventional superconductivity. But the tunneling measurements[3–5] exhibit a non-*s*-wave BCS low-temperature behavior.

As an important method to investigate the superconducting mechanism, the doping effect has been extensively studied by substituting transition metals (Co, Cu, Fe and Mn) for Ni and substituting B, N atoms for C sites in past several years[6–8]. Recently, these compounds substituted for Mg in MgCNi₃, ZnCNi₃[9], AlCNi₃[10] and GaCNi₃[11] has been synthesized. Unfortunately, superconductivity has not been found among them. ZnCNi₃ exhibits the Pauli paramagnetic (PM) metallic behavior. A PM into weak ferromagnetism (FM) transition takes place at near 300 K in AlCNi₃. While a strong electron-electron correlation, being attributed to the instability FM order in GaCNi₃, are presented. The calculated electronic structures on ZnCNi₃[12] and AlCNi₃[13] indicated a decrease of density of states at Fermi level (N_{E_F}) although it is very similar to that of MgCNi₃. On the elements of periodic table, Ga and Al are in the same main group with equal outer valence

electrons. The recent results on GaCMn₃ showed rich magnetism and giant magnetoresistance[14, 15]. Therefore, it is worthwhile to examine the electronic structures and magnetic properties of GaCNi₃ as well as these compounds substituted single or dual elements (Al, In and Na, *etc.*) for Mg in detail.

It is our purpose in this work to clarify why not superconducting in these antiperovskite compounds and to seek new simple structural superconductors. Total energies, density of states (DOS) and electronic band structures were calculated by the highly precise full-potential linearized augmented plane-wave (FP-LAPW) method[16, 17] within the WIEN2k package[18]. The exchange-correlation contribution to the total energy was treated in the generalized gradient approximations (GGA) of PBE version[19]. The muffin-tin (MT) radii are 1.8 a.u. for Ni, 1.4 a.u. for C, and 2.0 a.u. for Ga (Al, In and Na). The LAPW basis set was defined by the cutoff $R_{MT}K_{MAX} = 7.0$, plus local orbital to relax the linearization errors. The *k*-points in the first Brillouin-zone (BZ), 10000 and 4000 for single and dual elements substitution for Mg, respectively, were adopted.

The equilibrium lattice constant (a_0) of AlCNi₃ and GaCNi₃ obtained in our calculations are about 5% larger than the experimental values[10, 11]. This unusual overestimation from DFT calculation was also reported in the previous calculations[12, 13]. The bulk modulus B has such a relation of $B_{AlCNi_3}(210.72GPa) > B_{GaCNi_3}(209.35GPa) > B_{InCNi_3}(183.56GPa)$, which is in between the value of 251 GPa for ZnCNi₃ [9] and our calculated 175.46 GPa for MgCNi₃. For other compounds, no reported data are referenced.

The electronic structures of AlCNi₃ had been reported by Okoye[13]. Here we only specifically show the energy band structure along the high symmetry directions of BZ and the DOS of GaCNi₃ in Fig. 1. It is very visible that the GaCNi₃ exhibits metallic character. The width of

*E-mail: zzeng@theory.issp.ac.cn

valence band is about 9.0 eV. Ni 3d band, mainly contributing to the energy range of -4.0~ 1.0 eV, is splitted into d_{z^2} , d_{xy} , $d_{x^2-y^2}$ and $d_{xz}+d_{yz}$ because of the influence of two nearest-neighbor C atoms. The $d_{xz}+d_{yz}$ subband mixed with C 2p band crosses the E_F and forms the complicated Fermi surface along $X-M-\Gamma$ directions. Other two nonbonding subbands d_{xy} and $d_{x^2-y^2}$ stay below the E_F . Seen from total DOS and projected density of states (PDOS) in Fig. 1(b), electronic states near E_F almost completely consist of Ni-3d. A sharp peak (mainly resulted from Ni) is at 0.44 eV below E_F , which is larger than 0.08eV of MgCNi₃[8]. It is noted that the hybridizations between Ga 4s/4p and Ni 3d are at about -8.5, -6.5, -3.4, and 3.0 eV. And the charge density plot illustrates the ionic character of Ga-Ni bond with the charge transferring from Ga to Ni. The Ga 4p level is lower than the Al 3p level because of scalar relativistic effects, therefore this results in the small difference in the position of the corresponding hybridized states. The strong hybridization arises from C and ambient six Ni atoms. Three clear covalent bonding states between C 2p and Ni 3d form in the range of -9.0 ~ -3.5 eV and the antibonding states hybridized between Ni $d_{xz}+d_{yz}$ and C 2p along z -axis direction cross the E_F .

Although doped electrons increase from the dopant Al to Ga and then to In, the unit cell also correspondingly gathers volume. Therefore, the electronic structures of AlCNi₃ and InCNi₃ are very similar to these of GaCNi₃, especially, near the Fermi level. These results are even similar to those of ZnCNi₃ and MgCNi₃. The N_{E_F} , 2.23, 2.43 and 2.42 states/eV per unit cell, is almost the same for AlCNi₃, GaCNi₃ and InCNi₃, respectively. But these data are only about half of that of MgCNi₃. Comparing GaCNi₃ (AlCNi₃ and InCNi₃) with MgCNi₃, and ignoring the volume variation of unit cell, doping electrons leads to the increase of the E_F , which increases or decrease the areas of electron-type Fermi surface (e -FS) or hole-type Fermi surface (h -FS), respectively. From the band structures in Fig. 1(a), the bands shift towards lower energy due to a number of imported electrons, two bands cross the E_F in MgCNi₃ while only one band does in GaCNi₃. As a result, the h -FS disappears along $R-\Gamma$ direction as well as around X point. Hence a complicated Fermi surface is formed as h -FS along $X-M$ and $M-\Gamma$ directions, and e -FS around M point shown in Fig. 2. No obvious nesting character is observed at Fermi surface in GaCNi₃. AlCNi₃ and InCNi₃ have the analogous FS characteristics.

The magnetic stability was investigated by total energy and Stoner parameter (S). The calculated S parameters following H. Rosner[20] are 0.19, 0.31 and 0.58 for AlCNi₃, InCNi₃ and GaCNi₃, respectively, implying that PM ground state exists in these compounds. Such results somewhat differ from experiments[10, 11]. However, the calculated total energy disparity of different magnetic orders is negligible for these compounds.

In addition, Na, Li, Be, Al_{0.5}Na_{0.5} and Al_{0.5}Li_{0.5} replacing Mg were also inspected to seek the new super-

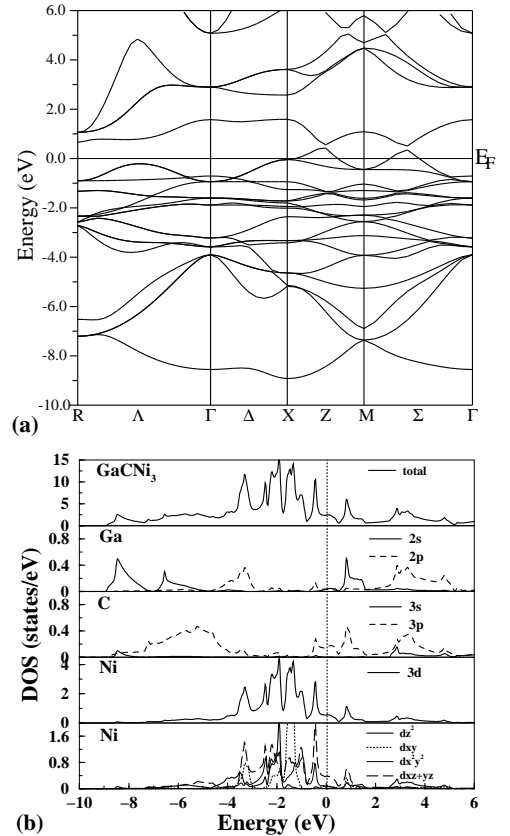


FIG. 1: (a) Electronic band structures. (b) Total and projected density of states on GaCNi₃.

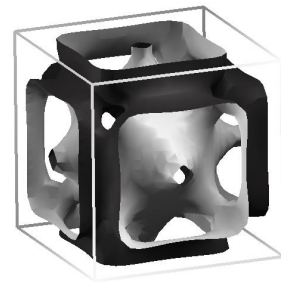


FIG. 2: The calculated Fermi surface of GaCNi₃.

conductor. Among these compounds, NaCNi₃ of holes doping, and Al_{0.5}Na_{0.5}CNi₃ of equal electrons substituting, are expected to hold superconductivity. However, a large N_{E_F} with the large $S = 2.06$ shows strong FM in NaCNi₃. Although $S = 0.93$, the magnetic instability occurs in Al_{0.5}Na_{0.5}CNi₃ because the total energy difference between PM and FM states is only 0.068 meV. A wide resonance peak of DOS resulted from the interaction between Al and Na bestrides the E_F , leading to the N_{E_F} of 5.95 states/eV per unit cell.

TABLE I: Comparison of η_α ($\text{eV}^2/\text{\AA}^2$), λ_{ph} and T_c (K) at Θ_D (K).

	η_X	η_C	η_{Ni}	λ_{ph}	T_c	Θ_D
MgCNi ₃	0.00	0.16	1.53	0.84	11	300
AlCNi ₃	0.01	0.09	1.62	0.44	1	400
GaCNi ₃	0.13	0.05	1.32	0.35	0.2	400
InCNi ₃	0.00	0.06	1.29	0.33	0.1	400
AlNaC ₂ Ni ₆	0.00	0.12	1.30	0.69	6	300

To examine whether these above materials are superconducting or not, the superconducting parameter η_α and the electron-phonon coupling constant λ_{ph} were evaluated by using the McMillan and Hopfield's formulae[21, 22], shown in Table I, in which the average phonon frequency $\langle\omega^2\rangle \simeq \Theta_D^2/2$ is used, where Θ_D is the Debye temperature. Comparing the data in Table I, the atomic contribution from Mg site to the λ_{ph} can be neglected except for Ga. For compound MgCNi₃, its $\Theta_D \simeq 300$ K results in $\lambda_{ph}=0.84$ and $T_c=11$ K with an effective electron-electron interaction parameter $\mu^*=0.13$, showing that the superconductivity in MgCNi₃ can be described by the conventional phonon mechanism. These results are in reasonable agreement with experiment and previous

calculation[1, 14]. However, for AlCNi₃, GaCNi₃ and InCNi₃, experiments evaluated the Θ_D to be around 400 K[10, 11]. As a result, T_c is expected to be lower than 2 K for AlCNi₃, GaCNi₃ and InCNi₃. While in the case of Al_{0.5}Na_{0.5}CNi₃, because its electronic structures are very close to those of MgCNi₃, its Θ_D could be close to 300 K. Thus, its T_c is near 6 K when ignoring the spin fluctuation as showing Table I.

In summary, we have investigated the electronic structures induced by the substitution of Mg in MgCNi₃. The decrease of electron-phonon interaction was used to explain the non-superconductor GaCNi₃ as well as AlCNi₃ and InCNi₃. Hole doped NaCNi₃ exhibits FM state rather than superconducting state. Al_{0.5}Na_{0.5}CNi₃ similar to MgCNi₃ is worthwhile to explore its superconductivity.

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- [1] T. He, Q. Huang, A.P. Ramirez, Y. Wang, K.A. Regan, N. Rogado, M.A. Hayward, M.K. Haas, J.J. Slusky, K. Inumara, H.W. Zandbergen, N.P. Ong, and R.J. Cava, Nature (London) **411**, 54 (2001).
- [2] P.M. Singer, T. Imai, T. He, M.A. Hayward, and R.J. Cava, Phys. Rev. Lett. **87**, 257601 (2001).
- [3] Z.Q. Mo, M.M. Rosario, K.D. Nelson, K. Wu, I.G. Deac, P. Schiffer, Y. Liu, T. He, K.A. Regan, and R.J. Cava, Phys. Rev. B **67**, 094502 (2003).
- [4] L. Shan, H.J. Tao, H. Gao, Z.Z. Li, Z.A. Ren, G.C. che, and H.H. Wen, Phys. Rev. B **68**, 144510 (2003).
- [5] R. Prozorov, A. Snezhko, T. He, and R.J. Cava, Phys. Rev. B **68**, 180502(R) (2003).
- [6] A. Szajek, J. Phys.: Condens. Matter **13**, L595 (2001).
- [7] In Gee Kim and Jae Il Lee, Phys. Rev. B **65**, 064525 (2002).
- [8] J.L. Wang, Y. Xu, Z. Zeng, Q.Q. Zheng, and H.Q. Lin, J. Appl. Phys. **91**, 8504 (2002).
- [9] Min-Seok Park, Jin-Soo Giim, Soo-Hyeon Park, Y.W. Lee, E.J. Choi, Supercond. Sci. Technol., **17**, 274 (2004).
- [10] A.F. Dong, G.C. che, W.W. Huang, S.L. Jia, H. Chen, and Z.X. Zhao, Physica C **422**, 65 (2005).
- [11] P. Tong, Y.P. Sun, X.B. Zhu, and W.H. Song, Phys. Rev. B **73**, 245106 (2006).
- [12] M.D. Johannes and W.E. Pickett, Phys. Rev. B **70**, 060507(R) (2004).
- [13] C.M.I. Okoye, Solid State Commun. **136**, 605 (2005).
- [14] J.H. Shim, S.K. Kwon, and B.I. Min, Phys. Rev. B **66**, 020406(R) (2002).
- [15] In Gee Kim, Ying Jiu Jin, and Jae Il Lee, Phys. Rev. B **67**, 060407(R) (2003).
- [16] O.K. Andersen, Phys. Rev. B **21**, 3060 (1975).
- [17] D. Singh, "Planewaves, pseudopotentials and the LAPW-method", Kluwer Academic Publishing (1994), ISBN 0-7923-9421-7
- [18] P. Blaha, K. Schwarz, P. Sorantin, and S.B. Trickey, Comput. Phys. Commun. **59**, 399 (1990).
- [19] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- [20] H. Rosner, R. Welt, M.D. Johannes, W.E. Pickett, and E. Tosatti, Phys. Rev. Lett. **88**, 027001 (2002).
- [21] W.L. McMillan, Phys. Rev. **167**, 331 (1968).
- [22] J.J. Hopfield, Phys. Rev. **186**, 443 (1969).