Electronic structures of antiperovskite superconductors: MgXNi₃ (X=B,C,N)

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We have investigated electronic structures of a newly discovered antiperovskite superconductor MgCNi₃ and related compounds MgBNi₃ and MgNNi₃. In MgCNi₃, a peak of very narrow and high density of states is located just below E_F, which corresponds to the π* antibonding state of Ni-3d and C-2p but with the predominant Ni-3d character. The prominent nesting feature is observed in the Γ-centered electron Fermi surface of an octahedron-cage-like shape that originates from the 19th band. The estimated superconducting parameters based on the simple rigid-ion approximation are in reasonable agreement with experiment, suggesting that the superconductivity in MgCNi₃ is described well by the conventional phonon mechanism.

71.25.Pi, 74.25.Jb, 74.70.Ad

Recently, He et al. have discovered a new intermetallic superconductor MgCNi₃ with the transition temperature T_C of 8K, which has the antiperovskite structure. Because it has a large proportion of Ni per unit cell, it is expected that the magnetic fluctuation would be important in determining the superconducting behavior. This system is reminiscent of another Ni-based superconductors LnNi₃B₂C (Ln = Y, Tm, Er, Ho, Lu). The band calculations indicate that very large and narrow energy peak in the density of states (DOS) is located just below the Fermi energy E_F which has mainly the Ni 3d character. The behavior of the upper critical field H_C2(T) can be well fitted with the conventional BCS expression, whereas the zero-bias conductance peak observed below T_C suggests that MgCNi₃ is likely to be a non-s wave superconductor.

With Cu doping (electron doping) on Ni-site, T_C decreases systematically, but with Co doping (hole doping), the superconductivity disappears abruptly for doping of only 1%. In the case of Co doping, there is no evidence that the quenching of superconductivity is related to magnetism. Furthermore, it is observed that the superconductivity of MgC₂Ni₃ is sensitive to the content of C; it disappears between x=0.96 and x=0.90.

To understand the mechanism of the superconductivity in MgCNi₃, we have investigated systematically the electronic structures of MgXNi₃ (X=B, C and N), which have different number of valence electrons, but have the similar band structures. Using the linearized muffin-tin orbital (LMTO) band method in the local density approximation (LDA), we have obtained band structures, DOSs, and Fermi surfaces, and discussed the bonding characters. Muffin-tin orbitals up to d-states for Mg, C, and up to f-states for Ni are included in the LMTO band calculations. We have also estimated superconducting parameters based on the rigid-ion approximation. We have considered cubic MgCNi₃ with the lattice constant of 3.81Å and employed the atomic radii of 3.20, 1.54 and 2.49 Å for Mg, C and Ni, respectively. The same structural parameters are used for all MgXNi₃.

MgCNi₃ has the cubic antiperovskite structure: Mg at (0 0 0), C (0.5 0.5 0.5), and Ni at (0.5 0.5 0), (0.5 0.5 0) and (0 0.5 0.5). It is called as an antiperovskite structure because the transition metals are located at the corners of the octahedron cage in contrast to the ordinary perovskite structure. Without C located at the center of cubic cell, MgNi₃ is a simple ordered intermetallic compound with fcc structure (Ca₃Au-type). Without C, the Ni-3d band of MgNi₃ is very narrow, leading to a magnetic ground state with Ni magnetic moment of 0.43μ_B. By inserting C, two carbons become nearest neighbors of Ni, and thus it is expected that Ni-3d and C-2p electrons are strongly hybridized.

Total and projected local DOS of MgCNi₃ are provided in Fig. 1. The overall shape of the total DOS is similar to those of Hayward et al. and Dugdale and Jarlborg. The peaks near −7eV and 4eV correspond to σ bonding and antibonding states, respectively, of Ni-3d and C-2p states. On the other hand, the peaks near −4eV correspond to π bonding states of Ni-3d and C-2p. The π* antibonding states are located just below E_F, yielding the high DOS at E_F (N(E_F)) of 5.34 [states/eV]. The contribution of Ni-3d states to the DOS at E_F is as much as 76%. Small amount of C-2p states are hybridized with Ni-3d states. Because the peak just below E_F is very high and narrow, this system is expected to be unstable by small perturbation. The peak is located ~ 60meV below E_F and about 0.5 electrons are occupied between the peak and E_F. The stoner parameter S, defined as S ≡ N(E_F)I_{XC} with I_{XC} denoting the intra-atomic exchange-correlation integral, is 0.64. Indeed the filling of holes in a rigid band scheme produces the magnetic instability. That is, replacing Ni by a virtual atom with atomic number 27.93 (corresponding to Co 7% doping) yields the stoner parameter larger than 1.0.

The band structure of MgCNi₃ along the symmetry line of the simple cubic Brillouin zone is shown in Fig. 1. The band near −12eV corresponds to C-2s states, while the dispersive bands in the range of −7eV to −4eV are due to C-2p states. Only two bands (the 18th and 19th bands), which have mainly Ni-3d character, cut the Fermi level. These two bands are confined between −0.5eV and 1.0eV, and available states in these bands are about four. Hence, in the rigid band scheme, small electron or hole doping will produce the carriers with the 18th and the 19th band character. The 18th band is relatively flatter.
than the 19th band, and so the Ni-3d character is stronger in
the 18th band.

Figure 3 presents the Fermi surfaces of the 18th (a) and
the 19th bands (b) in the simple cubic Brillouin zone.
The 18th band gives rise to a clover-like hole surface
centered at X of each cubic face and small hole pockets along
the (111) directions. With increasing the Fermi level
(electron doping), the areas of these hole Fermi surfaces
decrease, reducing \( N(E_F) \). In opposite, with decreasing
the Fermi level (hole doping), the Fermi surface areas in-
crease, enhancing \( N(E_F) \). When decreasing the Fermi
level further below the DOS peak, the crossing of each
hole surface occurs, converting it to electron surface and
decreasing Fermi surface. On the other hand, the 19th
band yields an octahedron-cage-like electron surface
centered at \( \Gamma \) and additional narrow electron surfaces along
the Brillouin zone edges (Fig. 3(b)). As compared to
the case of the 18th band, the 19th band shows a rather
small change in the Fermi surface topology with varying
the Fermi level position due to its more dispersive band
character. The Fermi surface topology obtained in the
present study is qualitatively similar to those of Dugdale
and Jarlborg[3].

The most notable in Fig. 3(b) is the prominent nesting
feature along the (110) direction observed in the ab
plane of the \( \Gamma \)-centered Fermi surface with the octahedron-
cage-like shape. In fact, this is contrary to the report by
Dugdale and Jarlborg[3] who have not observed the obvi-
ous nesting feature in the Fermi surface of the 19th band.
As mentioned above, the detailed shapes of the Fermi
surfaces are very sensitive to the position of the Fermi
level, because of the very sharp DOS peak near \( E_F \).
Presumably the difference between two results arises from
the different band parameters employed in the LMTO
band calculations, such as atomic radii, number of k-
points, energy parameters, and so on. In any case, the
present result reveals that the system is in the vicinity
of the Fermi surface nesting, if not complete in undoped
MgCNi3. It is well known that the system with the Fermi
surface nesting can be strongly correlated with various in-
stabilities: the structural transition (the charge density
wave instability) or the spin density wave instability. It is
thus expected that MgCNi3 may be susceptible to one
of the above instabilities. However, until now, any evi-
dence of magnetic or structure transition has not been
reported[3]. This aspect remains to be resolved.

We have seen that the DOS peak near \( E_F \) is pro-
duced by the hybridization of Ni-3d and C-2p states. In
MgCNi3, the bands from \(-0.5eV \) to \( 1.0eV \) are almost
half-filled: two electron states out of four available states
are occupied. To explore the doping effect with varying
the number of valence electrons, we have investigated
electronic structures of MgXNi3 (X= B, C, N) . Figure
2 provides the DOSs for MgXNi3. It is seen that the
effect of changing X is mainly a variance of the Fermi
level with respect to the DOS peak. The shape of DOS
is perturbed a little, which indicates that the rigid band
scheme would work well in this system.

The B-2p state in MgBNi3 is located higher in energy
than the C-2p state of MgCNi3, and so the hybridization
with Ni-3d is stronger. Hence the band is more dispersive
and accordingly the DOS peak becomes smeared. Al-
though the Fermi level in MgBNi3 is located very close
to the DOS peak, the DOS at \( E_F \), 4.79 [states/eV], is
comparable to that of MgCNi3 (5.34 [states/eV]) (Table
1). Hence the magnetic instability does not occur either
in MgBNi3. As described before, the effective hole dop-
ing in MgBNi3 converts a hole Fermi surface of the 18th
band to an electron Fermi surface, and an electron sur-
face of the 19th band is reduced. In MgNNi3, the
N-2p state is located a bit lower in energy than the C-2p
state of MgCNi3, yielding reduced bandwidths of both
the 18th and the 19th band. By the effective electron
doping in MgNNi3, the DOS at \( E_F \) is reduced to 3.63
[states/eV] (Table 1). The contribution of the 18th band
to the DOS at \( E_F \) is almost negligible and the Fermi sur-
face of the 19th band, which gives the main contribution
to the DOS at \( E_F \), is changed to a hole surface.

We have explored superconducting properties of
MgXNi3 based on the rigid-ion approximation[2]. We
have estimated the superconducting parameter \( \eta_{\alpha} =
N(E_F)(\langle P_{\alpha}^2 \rangle) \), where \( \langle P_{\alpha}^2 \rangle \) is the average electron-ion
interaction matrix element for the \( \alpha \)-th ion. Table 1 pro-
vides the calculated \( \eta_{\alpha} \) for each MgXNi3. It is seen that
the contribution of Ni-3d states to the superconductivity
is most important and \( \eta_{Ni} \) is the largest for MgCNi3.
This is consistent with the observed trend that both the
electron and hole dopings on MgCNi3 suppress the supercon-
ductivity. By increasing the atomic number from B, C to
N, the contribution of X-2p states increases, while that
of Ni-3d increases first and then decreases. Due to light
ionic masses of X, even the small increase in \( \eta_X \) affects
the superconducting property substantially. Therefore,
effectively electron doped system MgNNi3, once synthe-
sized successfully in the antiperovskite structure, would
have comparable \( T_C \) to MgCNi3.

One can evaluate the electron-phonon coupling con-
stant \( \lambda_{ph} \) by using the McMillan’s formula
\( \lambda_{ph} = \sum_x \eta_x / M_x (\omega_x^2) \), where \( M_x \) is the
ionic mass and \( \omega_x^2 \) is the relevant phonon frequency[2].
Since there has been no information on the relevant phonons, we instead use
the average phonon frequency \( \omega^2 \) as \( \Theta_D \) is the
Debye temperature. However, even the value of \( \Theta_D \) is
not available. Albeit very crude, one can estimate \( \Theta_D \)
from the specific heat data[2] \( C/T = 300 \) K from the graph of
\( C/T \) vs. \( T^2 \). Using these informations for MgCNi3, one
obtains \( \lambda_{ph} = 1.56 \), and then the McMillan’s \( T_C \)
formula with an effective electron-electron interaction parameter
\( \mu^2 = 0.13 \) gives rise to \( T_C = 23 K \). These values seem
to be too large, as compared to experimental \( T_C \) and
the estimated \( \lambda_{ph} \sim 0.8 \) from the specific heat data[2].
Note, however, that \( \lambda_{ph} \) strongly depends on the choice
of the Debye temperature. As shown in Table 1 with
a choice of larger \( \Theta_D = 400 \) K, one obtains \( \lambda_{ph} = 0.77 \)
and \( T_C = 11K \), which are in reasonable agreement with experiment. This suggests that the superconductivity in
this system can be described by the conventional phonon mechanism. For more precise estimations of $\lambda_{ph}$ and $T_c$, detailed information on the phonon spectra is prerequisite.

In conclusion, we have investigated electronic structures of the non-oxide antiperovskite superconductor MgCNi$_3$. The $\pi^*$ antibonding state of Ni-3$d$ and C-2$p$ is formed near $E_F$ with the mainly Ni-3$d$ character. Fermi surfaces are composed of two bands. The topology of hole Fermi surfaces coming from the 18th band is sensitively modified by the variance of the Fermi level position. The electron surface of the 19th band with an octahedron-cage shape tends to induce the Fermi surface nesting. By comparison of DOSs for MgXNi$_3$ (X=B,C,N), the doping effects are discussed. The estimation of $\lambda_{ph}$ and $T_c$ based on the rigid-ion approximation suggests that the superconductivity of MgCNi$_3$ is described well by the conventional phonon mechanism.

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![FIG. 1. Total and projected local DOS of MgCNi$_3$.](image)
**TABLE I.** Total and partial DOSs at $E_F$ (in states/eV) for MgXNi$_3$ (X = B, C, N).

|         | $N_{Mg}$ | $N_X$ | $N_{Ni}$ | $N_{total}$ |
|---------|----------|-------|----------|-------------|
| MgBNi$_3$ | 0.38     | 0.18  | 1.41     | 4.79        |
| MgCNi$_3$ | 0.22     | 0.42  | 1.57     | 5.34        |

FIG. 2. Band structure of MgCNi$_3$ along the symmetry lines of the simple cubic Brillouin zone.

FIG. 3. Fermi surfaces of MgCNi$_3$ in the simple cubic Brillouin zone coming from the 18th band (a) and the 19th band (b).

FIG. 4. Density of states of MgXNi$_3$ (X = B, C, N).
TABLE II. Comparison of $\eta$ (in eV/Å²) and $\lambda_{ph}$ for $\Theta_D = 300$K and 400K.

|       | $\eta_{Mg}$ | $\eta_X$ | $\eta_{Ni}$ | $\lambda_{ph}$ (300K) | $\lambda_{ph}$ (400K) |
|-------|------------|---------|-------------|----------------|----------------|
| MgBNi3 | 0.00       | 0.22    | 0.67        | 0.67           | 0.38           |
| MgCNi3 | 0.00       | 0.48    | 1.36        | 1.36           | 0.77           |
| MgNNi3 | 0.00       | 0.58    | 0.87        | 1.07           | 0.60           |