

## Electronic structure of superconducting non-oxide perovskite $\text{MgCNi}_3$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 L595

(<http://iopscience.iop.org/0953-8984/13/26/102>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 94.79.44.176

The article was downloaded on 13/05/2010 at 03:42

Please note that [terms and conditions apply](#).

## LETTER TO THE EDITOR

# Electronic structure of superconducting non-oxide perovskite $\text{MgCNi}_3$

Andrzej Szajek

Institute of Molecular Physics, Polish Academy of Sciences, M Smoluchowskiego 17,  
60-179 Poznań, Poland

E-mail: szajek@ifmpan.poznan.pl

Received 18 May 2001

## Abstract

The recently discovered superconductor  $\text{MgCNi}_3$  crystallizes in the classical cubic perovskite structure. The electronic structures of the  $\text{MgCNi}_{3-x}\text{M}_x$  ( $\text{M} = \text{Co}, \text{Cu}; x = 0, 0.5, 1.0$ ) system have been calculated using the self-consistent tight-binding linear muffin-tin orbital method. The calculations showed that the Fermi level for  $\text{MgCNi}_3$  is located in the slope descending from a sharp peak originating from d states of Ni atoms. Electron (Cu) and hole (Co) doping of  $\text{MgCNi}_3$  reconstructs its band structure but does not lead to magnetic order.

## 1. Introduction

From the early 1970s until 1986 when the high-temperature superconductors based on  $\text{CuO}_2$  layers were discovered [1] the highest superconducting critical temperature  $T_c$  was 23 K in the A15 pseudobinary system  $\text{Nb}_3\text{Al}_{1-x}\text{Ge}_x$  [2, 3]. Between 1986 and 2000, in addition to the mainstream HTcS activities, other research was carried out that resulted in the discovery of four classes of superconductors that have members with critical temperatures higher than the highest known in 1986. In chronological order, these classes are typified by the representatives  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  [4–6],  $\text{Cs}_3\text{C}_{60}$  [7],  $\text{YPd}_2\text{B}_2\text{C}$  [8, 9] and  $\text{Na}_x\text{HfNCl}$  [10], with maximum critical temperatures of 35, 40, 23 and 25 K, respectively. These new superconductors are somewhat different from the older superconductors, and certainly different from the layered cuprates. The discovery of superconductivity with  $T_c \approx 39$  K in  $\text{MgB}_2$  was announced in January 2001 [11, 12]. The recently discovered superconductor  $\text{MgCNi}_3$  crystallizes in the classical cubic perovskite structure with a critical temperature of 8 K [13]. This material is the three-dimensional analogue of the  $\text{LnNi}_2\text{B}_2\text{C}$  ( $\text{Ln} = \text{Y}, \text{Tm}, \text{Er}, \text{Ho}, \text{Lu}$ ) family of superconductors, which have critical temperatures up to 16 K (for  $\text{Ln} = \text{Lu}$ ) [14]. The fact that superconductivity rather than ferromagnetism occurs in a compound where so much nickel is present is surprising, and suggests that  $\text{MgCNi}_3$  is a candidate for exhibiting unconventional superconductivity.

In this work *ab initio* electronic structure investigations, using the self-consistent tight-binding linear muffin-tin (TB LMTO) method, are presented. The effect of electron (Cu) and hole (Co) doping is analysed.

## 2. Computational details

The band structure of the  $\text{MgCNi}_3$  system was calculated by the TB LMTO method in the atomic sphere approximation (ASA) [15, 16]. In this approximation, the crystal is divided into space-filling spheres, therefore with slightly overlapping spheres centred on each of the atomic sites. In the calculations reported here, the Wigner–Seitz (WS) sphere radii are such that the overlap is below 10%. The average WS radius ( $S_{av}$ ) was scaled such that the total volume of all spheres is equal to the equilibrium volume of the unit cell with the lattice constant  $a = 3.812\,21\text{ \AA}$  [13]. The WS radii are collected in table 1.

**Table 1.** The crystallographic parameters used in the calculations ( $S_{av} = 2.6135\text{ au}$ ).

Atoms	WS radii $S_A$ (au)	$S_A/S_{av}$
Mg	3.66997	1.4042
C	1.94737	0.7451
Ni(Cu, Co)	2.21136	0.8461

The input electronic configurations were taken as: core[Ne] +  $3s^2$  for the Mg atom, core[He] +  $2s^2 2p^2$  for the C atom, core[Ar] +  $3d^8 4s^2$  for the Ni atom and for impurities: core[Ag] +  $3d^{7(10)} 4s^{2(1)}$  for Co (Cu) atoms. As the WS sphere for Mg atoms is very large, the f states were included in the calculations on Mg [17]. The Perdew–Wang [18] potential with gradient corrections was used in the calculations and the spin–orbit interactions were taken into account in the form proposed by Min and Jang [19]. The combined correction terms [15] were included to compensate for errors due to the ASA. The Brillouin zone  $k$ -point integrations were carried out using the tetrahedron method [20] on a grid of 816 and 2176  $k$ -points in the irreducible part of the hexagonal Brillouin zone (1/48 and 1/16 for undoped and doped systems, respectively), which corresponds to 27 000  $k$ -points throughout the Brillouin zone. The iterations were repeated until the energy eigenvalues of consecutive iteration steps were the same within an error of 0.01 mRyd.

## 3. Results

The site-projected,  $l$ -decomposed and total densities of states (DOS) for  $\text{MgCNi}_3$  are presented in figure 1. The results are consistent with those obtained by Hayward *et al* [21]. The Fermi level ( $E_F$ ) is located close to a peak provided mainly by Ni d electrons (77%). The Mg and C atoms (s and p electrons) provide a contribution to the DOS at about 1 eV below  $E_F$ . For  $\text{MgCNi}_3$ ,  $\text{DOS}(E = E_F) = 5.264\text{ states eV}^{-1}/\text{f.u.}$  The individual contributions to the DOS for  $E = E_F$  are collected in table 2. The experimental data [21] showed very limited solubility of Cu in  $\text{MgCNi}_{3-x}\text{Cu}_x$ ,  $x \leq 0.1$ ; then  $T_c$  decreases systematically from 6 to 7 K.

**Table 2.** Densities of states at the Fermi level (states  $\text{eV}^{-1}/\text{f.u.}$ ).

Electrons	Atoms		
	Mg	C	Ni
s	0.006	0.017	0.142
p	0.291	0.425	0.223
d	0.036	0.017	4.036
Total	0.385	0.459	4.420

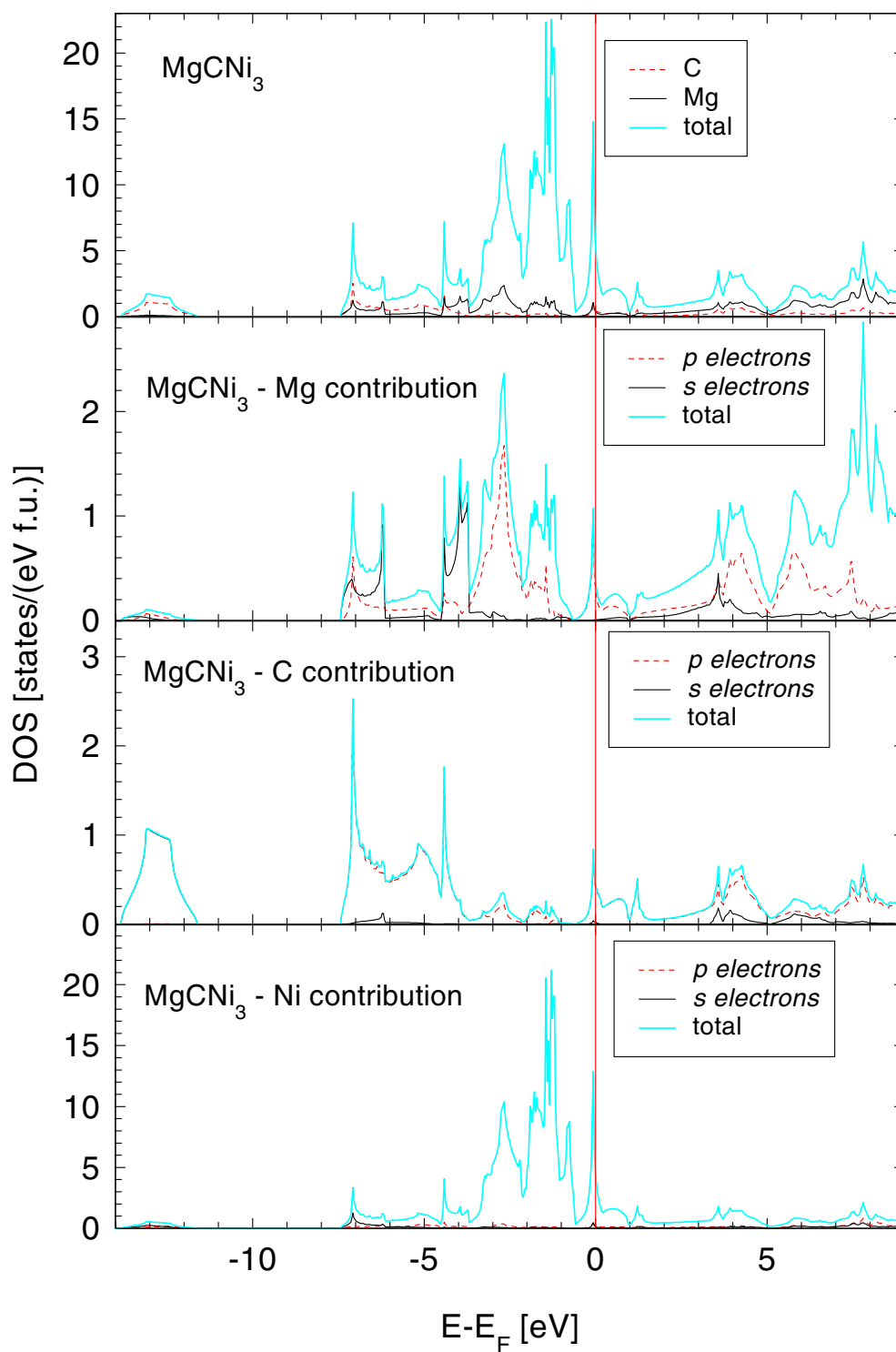


Figure 1. Total, site-projected and *l*-decomposed DOS for  $\text{MgCNi}_3$ .

In  $\text{MgCNi}_{3-x}\text{Co}_x$ , the solubility of Co is much more extensive, but bulk superconductivity disappears for Co doping of  $x = 0.03$  [21]. Our calculations were performed for (for both Co and Cu)  $x = 1$  and  $0.5$ . In all cases one of the Ni atoms is replaced by a Co or Cu atom. For  $x = 0.5$  a double perovskite supercell was used in the calculations. The lattice constants of the doped systems were the same as in the case of  $\text{MgCNi}_3$ .

The total and site-projected DOS are presented in figure 2. As the 3d band of Cu is filled, d states locate considerably below the Fermi level, between  $-2$  and  $-4$  eV. In contrast, for Co doping, Co d states are located between  $-4$  eV and  $E_F$ . In the case of Cu doping the Fermi level is shifted towards higher energies, the peak originating from Ni d states preserves its narrow shape and  $\text{DOS}(E = E_F)$  decreases to the values 2.206 and 2.343 states  $\text{eV}^{-1}/\text{f.u.}$  for  $x = 0.5$  and  $1.0$ , respectively. For Co doping, the Fermi level goes to lower energies and initially  $\text{DOS}(E = E_F)$  increases. However, increasing broadening of the peak near  $E_F$  compensates for this tendency. The values of  $\text{DOS}(E_F)$  are the following: 6.535 and 4.083 for  $x = 0.5$  and  $1.0$ , respectively. The value of  $\text{DOS}(E_F)$  for  $\text{MgCNi}_{5/2}\text{Co}_{1/2}$  obtained here directly from *ab initio* calculations is lower by a factor of about two than the value estimated by Hayward *et al* [21]. These changes versus concentration of impurities are plotted in figure 3.

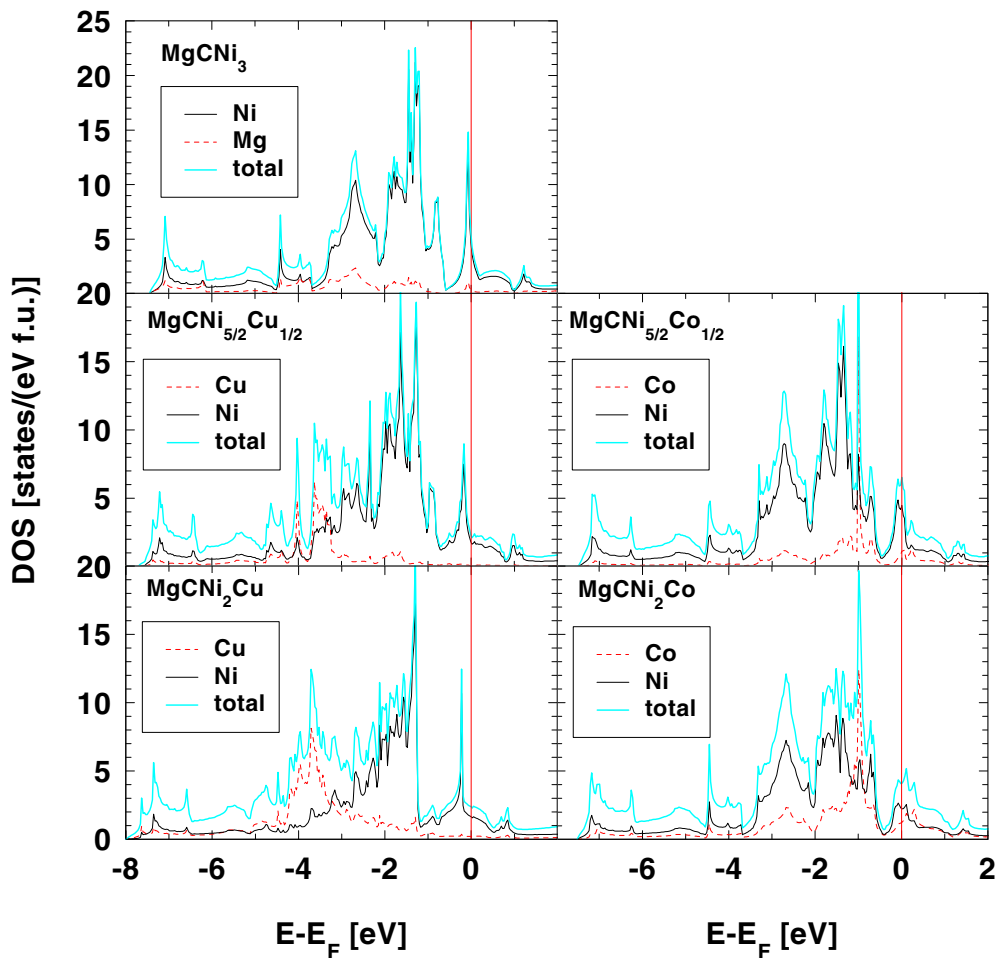


Figure 2. Total and site-projected DOS for  $\text{MgCNi}_{3-x}\text{M}_x$  ( $M = \text{Co}, \text{Cu}; x = 0, 0.5, 1.0$ ).

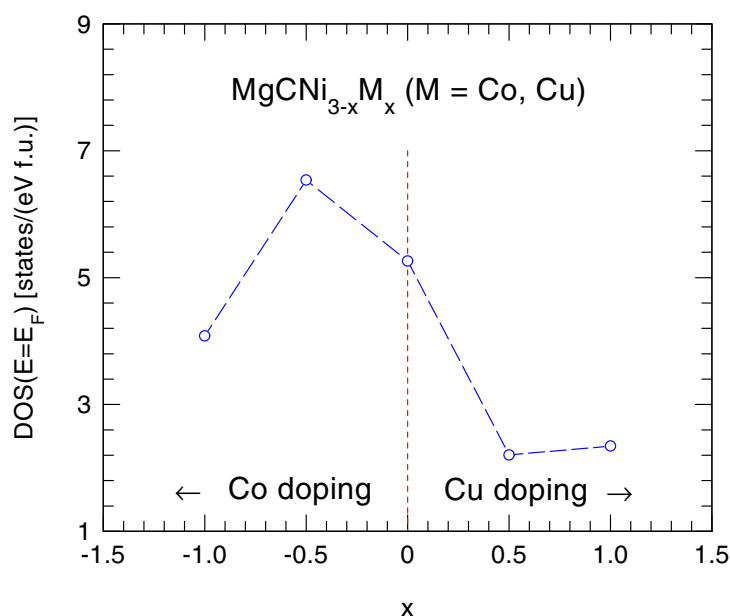


Figure 3. DOS( $E = E_F$ ) plotted as a function of the concentration of impurities.

Higher values of DOS( $E = E_F$ ) do not lead to magnetic order. Band-structure calculations with spin polarization were performed for artificially split d bands of Co and Ni. With starting iterations hypothetically assigned magnetic moments of  $2 \mu_B/\text{atom}$ , the self-consistent values reach moments below  $10^{-5} \mu_B/\text{atom}$ .

The author is grateful to Professor J A Morkowski and Professor A Jezierski for stimulating discussions and for critically reading the manuscript. The band calculations were performed at the Supercomputer and Networking Centre in Poznań (PCSS).

## References

- [1] Bednorz G and Müller K A 1986 *Physica B* **64** 189
- [2] Gavalier J R, Janocko M A, Braginski A I and Roland G W 1975 *IEEE Trans. Magn.* **11** 192
- [3] Gavalier J R, Janocko M A and Jones C K 1974 *J. Appl. Phys.* **45** 3009
- [4] Mattheis L F, Gyorgy E M and Johnson D W Jr 1988 *Phys. Rev. B* **37** 3745
- [5] Cava R J, Batlogg B, Krajewski J J, Farrow R, Rupp L W Jr, White A E, Short K, Peck W F and Kometani T 1988 *Nature* **332** 814
- [6] Cava R J and Batlogg B 1989 *MRS Bull.* **14** 49
- [7] Palstra T T M, Zhou O, Iwasa Y, Sulewski P E, Fleming R M and Zegarski B R 1995 *Solid State Commun.* **93** 327
- [8] Cava R J, Takagi H, Batlogg B, Zandbergen H W, Krajewski J J, Peck W F Jr, van Dover R B, Felder R J, Siegrist T, Mizuhashi K, Lee J O, Eisaki H, Carter S A and Uchida S 1994 *Nature* **367** 146
- [9] Hossain Z, Gupta L C, Mazumdar C, Nagarajan R, Dhar S K, Godart C, Levy-Clement C, Padalia B D and Vijayaraghavan R 1994 *Solid State Commun.* **92** 341
- [10] Yamanaka S, Hotehama K and Kawaji H 1998 *Nature* **392** 580
- [11] Akimitsu J 2001 *Proc. Symp. on Transition Metal Oxides (Sendai, 10 January 2001)* at press
- [12] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 *Nature* **410** 63
- [13] He T, Huang Q, Ramirez A P, Haas M K, Slutsky J S, Inumara K, Zandbergen H W, Ong N P and Cava R J 2001 *Nature* **411** 54
- [14] Cava R J, Takagi H, Zandbergen H W, Krajewski J J, Peck W F Jr, Siegrist T, Batlogg B, van Dover R B, Felder R J, Mizuhashi K, Lee J O, Eisaki H and Uchida S 1994 *Nature* **367** 252

- 
- [15] Andersen O K 1975 *Phys. Rev. B* **12** 3060
  - [16] Krier G, Jepsen O, Burkhardt A and Andersen O K 1995 *The TB-LMTO-ASA Program* source code, version 4.7
  - [17] Kortus J, Mazin I I, Belashchenko K D, Antropov V P and Boyer L L 2001 *Preprint* cond-mat/0101446
  - [18] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 *Phys. Rev. B* **46** 6671
  - [19] Min B I and Jang Y-R 1991 *J. Phys.: Condens. Matter* **3** 5131
  - [20] Blöchl P, Jepsen O and Andersen O K 1994 *Phys. Rev. B* **49** 16223
  - [21] Hayward M A, Haas M K, Ramirez A P, He T, Regan K A, Rogado N, Inumaru K and Cava R J 2001 *Solid State Commun.* submitted (2001 *Preprint* cond-mat/0103296)