Available online at www.sciencedirect.com
ScienceDirect
Solid State Sciences 9 (2007) 166–172
Solid State Sciences
www.elsevier.com/locate/ssscie

First-principles calculations of the structural and electronic properties of Cu_3MN compounds with M = Ni, Cu, Zn, Pd, Ag, and Cd

Ma. Guadalupe Moreno-Armenta*, William López Pérez[1], Noboru Takeuchi

Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, Apartado Postal 2681, Ensenada, Baja California, Mexico

Received 14 August 2006; received in revised form 14 November 2006; accepted 6 December 2006
Available online 5 January 2007

Abstract

We have performed accurate ab initio total energy calculations using the full-potential linearized augmented plane wave (FP-LAPW) method to investigate the structural and electronic properties of copper-transition metal nitrides. In its ground state, Cu_3N crystallizes in an anti-ReO_3 type cell and it is a semiconductor material with a small indirect gap. In this paper, we report a study of Cu_3MN compounds with M = Ni, Cu, Zn, Pd, Ag, and Cd. In the calculations, we have used the same anti-ReO_3 type cell of Cu_3N, but with the extra transition metal atom at the center of the cube. In particular, our calculated lattice parameters for copper nitride ($a = 3.82$ Å) and copper palladium nitride ($a = 3.89$ Å) are in excellent agreement with the experimental values of $a = 3.807$ Å and $a = 3.86$ Å, respectively. In all the cases we have studied, the addition of the transition metal atom modifies the electronic structure of Cu_3N, turning all copper-transition metal nitrides into metals.

Keywords: Transition metal nitrides; Copper nitride; Ab initio

1. Introduction

Transition metal nitrides have attracted widespread experimental and theoretical interest due to their excellent physical properties such as high hardness and melting points [1]. Many of these materials are binary compounds, and most of them crystallize in the rock salt structure [2]. They can be either metals or semiconductors [2–4]. In recent years Cu_3N has been extensively studied, motivated by its possible applications in the optoelectronic industry. Zachwieja and Jacobs [5] were able to obtain single crystals of Cu_3N using a high pressure high temperature growth technique in an ammoniac atmosphere. The compound is metastable at room temperature and it decomposes into copper and molecular nitrogen at 470 °C [6,7]. X-ray diffraction of the crystals showed that the structure was of anti-ReO_3 type (space group $Pm3m$), with a simple cubic unit cell of lattice constant $a = 3.807$ Å [8]. In this configuration, copper atoms occupy the middle of the cubic edges whereas nitrogen atoms occupy the corners of the cell. This arrangement is peculiar, since Cu atoms do not occupy the face-centered cubic close-packing sites. As a consequence, this crystal structure has many vacant interstitial sites. If additional copper or other transition metal atoms are contained within these sites, the electrical and optical properties of the nitride may differ from those of the ideal Cu_3N. That is, like WO_3, the Cu_3N has the possibility of being an inorganic host material even under high pressure conditions [9]. Electronic structure calculations have shown that Cu_3N is a semiconductor with a small indirect band gap [10].

In recent years, it has been possible to grow copper nitride thin films, and they have been investigated experimentally by different methods [11–16]. In some cases the films were semiconductors, while in other cases they showed a metallic behavior. In a previous work, we have shown that Cu_3N is indeed a semiconductor with a small indirect band gap, but the

* Corresponding author. CCMC-UNAM, P.O. Box 439036, San Ysidro, CA 92143-9036, USA.
E-mail addresses: moreno@ccmc.unam.mx (Ma.G. Moreno-Armenta), wlopez@uninorte.edu.co (W.L. Pérez), takeuchi@ccmc.unam.mx (N. Takeuchi).
[1] Permanent address: Departamento de Física, Grupo de Física de la Materia Condensada, Universidad del Norte, km. 5, Vía Puerto Colombia, Colombia.

1293-2558/$ - see front matter © 2007 Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.solidstatesciences.2006.12.002

insertion of an extra Cu atom in the middle of the cell results in a metallic behavior [17]. Our results find a larger lattice constant for the compound with the extra copper atom, in good agreement with experimental results, and supporting the idea that the metallic behavior of Cu_3N is due to an extra Cu atom [9,17,18].

Zachwieja and Jacobs have also successfully synthesized the compound Cu_3Pd_xN with x values $0.020 \leq x \leq 0.989$. Their X-ray analysis of a single-crystal showed a perovskite-type structure with the same space group *Pm*3*m*. The lattice constant obtained for $Cu_3Pd_{0.989}N$ was $a = 3.854$ Å and $a = 3.810$ Å for $Cu_3Pd_{0.02}N$. While copper nitride is a dark green semiconductor, $Cu_3Pd_{0.02}N$ and $Cu_3Pd_{0.989}N$ are silver-colored electrical conductors. The compounds are metastable at room temperature and decompose at 470 °C to give Cu_3Pd_x and N_2. Hahn and Weber studied the electronic structure of Cu_3N and Cu_3NPd, focusing mainly on the chemical-binding mechanisms of these materials. They concluded that Cu_3N is a semiconductor with an energy gap of 0.23 eV, while Cu_3PdN should exhibit a metallic behavior [10].

These results show that it is possible to change the electronic properties of Cu_3N by inserting an extra metal atom in the anti-ReO_3 cell. Using first-principles total energy calculations, we have studied the structural and electronic properties of bulk Cu_3MN with M = Ni, Pd (p-type), Cd, Zn (n-type), Cu and Ag. We have found that the metal interposition significantly modifies the electronic structure of Cu_3N.

2. Method

Our calculations were performed within the framework of density functional theory (DFT). At present, it is one of the most accurate methods to calculate the structural and electronic properties of the ground state of solids. We have used the full-potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN code [19]. The exchange and correlation effects were treated using the generalized gradient approximation (GGA) of Perdew et al. [20]. We have used muffin-tin radii of 1.7 a.u. for Cu, 1.5 for N, and 1.9 for Ag, Cd, Pd, Ni and Zn, angular momenta inside the muffin-tin sphere up to $l = 10$, and 56 k point in the irreducible part of the Brillouin zone (BZ).

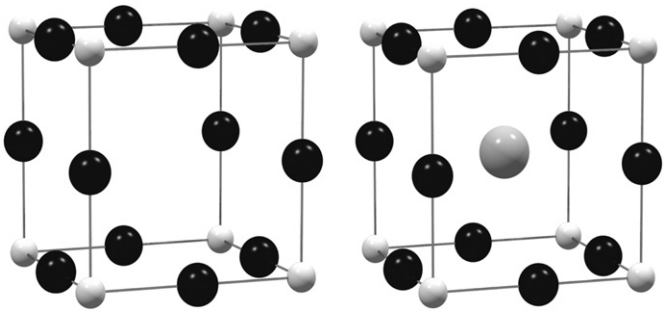

Fig. 1. Unit cell of (a) Cu_3N and (b) Cu_3MN. Black, light gray, and dark gray circles represent copper, nitrogen and transition metal atoms, respectively.

The calculations of Cu_3N in its ideal structure were done with a cubic anti-ReO_3 type of cell (space group *Pm*3*m*). In this configuration each nitrogen atom has six copper neighbors while two N atoms surround the copper atoms. It has been demonstrated that the Cu_3N cell can be filled by Pd to yield anti-perovskite-type Cu_3PdN, [6] in which Pd, N, and Cu have coordination numbers of 12, 6 and 2, respectively, corresponding to cubic close packed sites (Fig. 1).

In the present paper, we present a study of the bulk properties of Cu_3MN with M (M = Pd, Ni, Zn, Ag or Cd) in the body center of the Cu_3N structure. We have used an anti-perovskite structure type, which has the same *Pm*3*m* space group. In order to investigate the possibility that those compounds could be magnetic systems, we have performed both spin-unpolarized and spin-polarized calculations.

3. Results

In a previous work, the ground-state properties of copper nitride were obtained by minimization of the total energy with respect to the unit-cell volume [17]. Uniform compression and expansion of the lattice, with the relative positions within the unit cell held constant, were used to make isotropic variation of the cell volume. In Table 1 we summarized some of the structural parameters. Using the calculated lattice parameter obtained in Ref. [17], we have studied the electronic properties of Cu_3N in the ground state. The total and partial densities of states (DOS) are shown in Fig. 2, for copper and nitrogen atoms. The band structure is shown in Fig. 3.

Table 1
Calculated structural properties of Cu_3N in a cubic anti-ReO_3 type structure and with an extra metal atom at the center of the cell (experimental results are in parenthesis)

Structure	Cu_3N	Cu_3NiN	Cu_4N	Cu_3ZnN	Cu_3PdN	Cu_3AgN	Cu_3CdN
a (Å)	3.82 (3.807)	3.83	3.878	3.94	3.89 (3.86)	3.96	4.03
V (Å^3)	55.74	56.18	58.32	61.16	58.86	62.09	65.45
B_0 (GPa)	115.2	165.6	127	114.9	172.4	131.0	99.4
B_0	4.066	4.272	5.22	5.075	6.908	5.615	7.817
E_0	−19.45	−24.42	−24.20	−19.78	−23.92	−20.99	−18.74
d_{Cu-Cu} (Å)	2.70	2.707	2.74	2.78	2.75	2.80	2.85
d_{Cu-M} (Å)		2.707	2.74	2.78	2.75	2.80	2.85
d_{N-M} (Å)		3.31	3.36	3.41	3.368	3.429	3.49
d_{N-Cu} (Å)	1.91	1.915	1.939	1.97	1.945	1.98	2.015