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Ab initio calculations of non-stoichiometric copper nitride, pure and with palladium

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ABSTRACT

We present first principles calculations of copper nitride by using periodic density functional theory within a plane-wave ultrasoft pseudopotential scheme. The insertions of extra Cu and/or Pd atoms in the empty sites, vacancy reorganization, and substitution of Cu by Pd atoms were studied. We have used an equivalent reduced-symmetry $2 \times 2 \times 2$ Cu_3N-like cubic super-cell. Small Cu and/or Pd concentrations and vacancy rearrangements in the copper sub-lattice were conveniently calculated in these low-symmetry cells. We cover probable situations like: the occupation of the initially empty copper sites by (1) copper atoms, and by (2) palladium; (3) the relocation of vacancies in the copper sub-lattice; and (4) the substitution of small quantities of copper by palladium atoms in the copper sub-lattice. The equilibrium volumes and energies after relaxing the atomic positions are compared to those of intrinsic copper nitride. We found that the most stable arrangement corresponds to the ideal stoichiometric Cu_3N. We also found that any deviation from this ideal configuration shift the semiconductor state to a metallic or semi-metallic one.

1. Introduction

Copper nitride is an interesting material for several reasons. As a technological material, copper nitride can be conductor or semiconductor and currently it is used as an optical engraving medium for optoelectronic devices [1–4]. Also, copper nitride is the most studied noble-metal-nitride (noble defined here in the sense of a nearly filled s- and d-shells), and some of its properties may be shared by other noble nitrides like gold, silver and platinum-group for which there are not definite structures. The experience acquired on copper nitride can be of help to elucidate the mechanisms of formation, the structures and the properties of these nitrides. As a transition metal nitride (TMN), it belongs to the family of non-stoichiometric interstitial compounds [5]. The distinctive features of non-stoichiometric interstitial compounds are a high concentration of atomic defects and a wide homogeneity region. In copper nitride, CuN_x, this region is from $0 \leq x \leq 1/3$ within the *Fm*3*m*, 2 2 5, space group. The lower limit extents down to zero because copper crystallizes in a cubic close-packed structure which also belongs to the *Fm*3*m* space group. This means that there is no phase transformation of the metallic sub-lattice as the nitride form. In the upper limit, it has been shown that increasing the nitrogen content beyond this limit greatly destabilizes the structure [6].

The nitrides that belong to the *Fm*3*m* group can be viewed as two interpenetrating face centered cubic (*fcc*) sub-lattices as in the NaCl type (B1) structure, where the metal atoms occupy the positions of one sub-lattice and the non-metal the positions of the other. Therefore, there are two kinds of vacancy (unoccupied) sites belonging to the metallic and the non-metallic sub-lattices. Considering the monovalent and trivalent states of copper and nitrogen respectively, Cu_3N can be considered as the stoichiometric structure of copper nitride. In this case, ¾ of the Cu sites and ¼ of the Nitrogen sites are occupied, and the point symmetry is reduced. The ordered structure for this particular state of copper nitride has been reported in the *Pm*3*m* (2 2 1) space group, a reduced-symmetry subgroup of *Fm*3*m*. The Wyckoff sites (WS) are occupied as follows: Cu atoms in 3d, vacancies for metal atoms correspond to 1b and N in 1a, as showed in Table 1. In this work we have used a super-cell model formed by eight Cu_3N unit cells that belongs to the space group *P*4/*mmm* (1 2 3), which is a reduced-symmetry subgroup of *Pm*3*m* (Table 1). This group preserves the symmetry of the system, and has many Wyckoff sites that can be used to accommodate metal atoms or to move vacancy positions.

Several questions can be raised: Can the remainder vacancies-sites be filled with copper or another metal? Can the vacant sites and occupied sites be interchanged? Is there another possible order of copper nitride? To try to answer these questions, we construct our $2 \times 2 \times 2$ super-cell, eight times the volume of the

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Table 1
Cell parameters and Wyckoff positions in relevant crystal lattice structures.

Cubic cell transformation				
Space group	*Pm*3*m* (2 2 1)	*Fm*3*m* (2 2 5)	*Pm*3*m* (2 2 1)	*P*4/*mmm* (1 2 3)
Cell volume	Original 55.612 Å^3	Eight-fold 444.894 Å^3	Eight-fold 444.894 Å^3	Eight-fold 444.894 Å^3
Axes	$x=y=z=a$ $\sigma=\beta=\gamma=90$	$x=y=z=2a$ $\sigma=\beta=\gamma=90$	$x=y=z=a$ $\sigma=\beta=\gamma=90$	$x=y=z=a$ $\sigma=\beta=\gamma=90$
Wyckoff positions				
Cu	3d	24e	6e, 6f, 12h	2g, 2h, 4o, 4i, 4m, 4n, 4l
N	1a	4a, 4b	1a, 1b, 3d, 3c	1a, 1b, 1d, 1c, 2e, 2f
Metallic vacancy	1b	8c	8g	8r

original Cu_3N cell. This super-cell has 32 sites available for the metallic sub-lattice, which can be occupied by copper atoms or left empty as corresponding metal atom vacancies; and 32 non-metallic sub-lattice sites, which can be used by nitrogen atoms or left empty as corresponding non-metallic atom vacancies. The starting configuration $Cu_{24}Vac_8N_8Vac_{24}$, with a 3:1 metal to non-metal ratio, matchs the stoichiometric copper nitride. It contains 24 copper atoms, 8 metal atom related vacancies, 8 nitrogen atoms and 24 non-metallic atom related vacancies. Since the occupation of vacancies by nitrogen has been covered in a previous publication we will omit them here [6]. We consider probable situations like: the occupation of the initially empty copper sites by (1) copper atoms, and by (2) palladium; (3) the relocation of vacancies in the copper sub-lattice; and (4) the substitution of small quantities of copper by palladium atoms in the copper sub-lattice.

2. Method

Calculations were based on the periodic density functional theory as implemented in the Quantum-Espresso package [7]. Exchange and correlation potential energies were treated according to the generalized gradient approximation (GGA) with the gradient corrected Perdew, Burke, and Ernzerholf (PBE) [8] functional. Electron–ion interactions were described by the ultra-soft pseudo-potentials [9,10]. The electron states were expanded in plane waves with kinetic energy cutoffs of 30 and 240 Ry for the wave function and charge density, respectively.

All structures were fully relaxed with respect to both atomic positions and lattice constants. The ground-state properties of the Cu_3N structure were obtained by minimization of the total energy with respect to the unit cell volume (V). Uniform compression and expansion of the lattice were used to make isotropic variations of the volume. The $E(V)$ curve was fitted to the Murnaghan equation of state. The calculated lattice parameter for Cu_3N in the anti-ReO_3 structure was $a=3.84$ Å, in good agreement with the experimental value of $a=3.83$ Å [11].

We considered the filling of vacancies without altering the order by studying the following series of configurations:

- **A**. $Cu_{24+j}Vac_{8-j}N_8$ with $j=0$–8. This series represent the occupation of native metallic vacancies by additional copper.
- **B**. $Cu_{24}Pd_jVac_{8-j}N_8$ with $j=0$–8. This series represent the occupation of native metallic vacancies by palladium atoms.

We also study the variation of the order in the vacancies in these series of configurations:

- **C**. $Cu_{16}\mathbf{Cu_8}Vac_8N_8$. In this series an arbitrary group of eight (one in each primitive unit cell) Cu atoms are interchanged with native vacancies. The bold notation refers to the Cu atoms that are move to previously empty sites. Several nonequivalent combinations were tried.
- **D**. $Cu_{16}\mathbf{Cu_8}Pd_2Vac_6N_8$. Similar to the anterior series, but with the additional intercalation of two new Pd atoms in empty sites.

And finally we considered the interchange of Cu by Pd atoms in the following series of configurations:

- **E**. $Cu_{14}\mathbf{Cu_8}Pd_2Vac_8N_8$. Similar to the anterior series, but with the substitution of two Cu atoms by Pd atoms.
- Three additional configurations given by **F**. $Cu_{22}Pd_2Vac_8N_8$, **G**. $Cu_{23}Pd_1Vac_8N_8$ which are equivalent to 3–8% substitution of Cu by Pd in Cu_3N respectively, and **H**. $Cu_{24}Cu_7Pd_1Vac_0N_8$ which is equivalent to a 5% substitution of Cu by Pd in Cu_4N.

In Table 1 we summarize the transformations on the basic Cu_3N cubic cell needed to reproduce the super-cell used in our calculations. The WS occupied by copper atoms are: 2g, 2h, 4l, 4i, 4o, 4m, and 4n. The WS 8r correspond to the vacant sites (*Vac* – vacancies) in the cube center of the Cu_3N cell. The structure is showed in Fig. 1, where the Wyckoff sites (WS) inside of spatial group 1 2 3 are denoted by different colors.

The cohesive energy and density of states were calculated for the equilibrium structures. We calculated the formation energy according to the following equation [12,13].

$$E^{f} = \frac{(E^{tot}_{super-cell} - nE^{tot}_{Cu-bulk} - m\frac{1}{2}E^{tot}_{N_2})}{(n+m)}$$

where n, and m are respectively the number of metal and non-metal atoms used in the super-cell, and $E^{tot}_{super-cell}$, $E^{tot}_{Cu-bulk}$, and $E^{tot}_{N_2}$ are the calculated energies of the super-cells, bulk copper and free nitrogen molecule respectively. For the ternary compounds the equation is modified to

$$E^{f} = \frac{(E^{tot}_{super-cell} - nE^{tot}_{Cu-bulk} - oE^{tot}_{M-bulk} - m\frac{1}{2}E^{tot}_{N_2})}{(n+o+m)}$$

where o refers to the number of foreign atoms in the super-cell and E^{tot}_{M-bulk} is the energy obtained for the bulk metal (copper or palladium).

Fig. 1. (a) Copper nitride (2 × 2 × 2) super-cell. Cu and N atoms are shown as red and blue spheres respectively, while vacancies are shown as gray spheres. (b) Cu and vacancy Wyckoff positions are color coded (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).