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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 × 2 × 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 $Fm3m$, 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 $Fm3m$ 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 $Fm3m$ 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 $Pm3m$ (2 2 1) space group, a reduced-symmetry subgroup of $Fm3m$. 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 $P4/mmm$ (1 2 3), which is a reduced-symmetry subgroup of $Pm3m$ (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 × 2 × 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	*Pm3m* (2 2 1)	*Fm3m* (2 2 5)	*Pm3m* (2 2 1)	*P4/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).

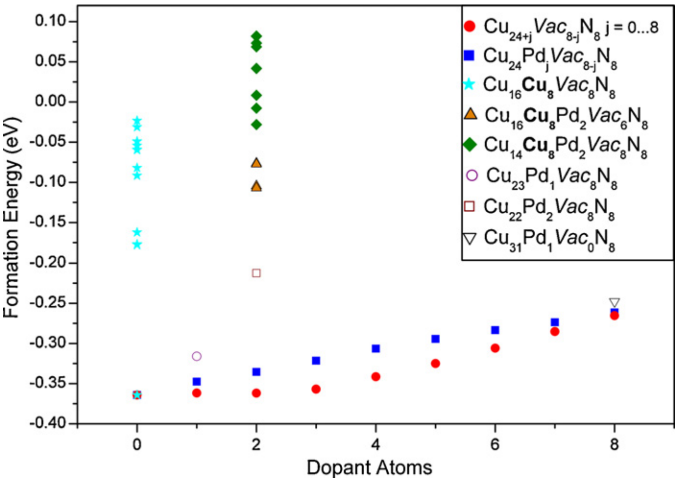

Fig. 2. Formation energies for the copper nitride series.

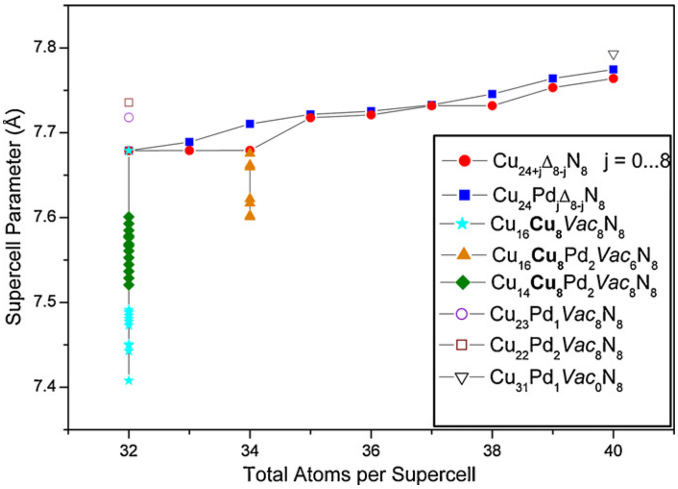

Fig. 3. Super-cell parameters versus total atoms for all copper nitrides series.

3. Results and discussion

3.1. The filling of metallic vacancies without altering the ordering

In this subsection we study the filling of the *Vac* – vacancies with Cu and Pd atoms in the following configurations: **A**. $Cu_{24+j}Vac_{8-j}N_8$, and **B**. $Cu_{24}\,Pd_jVac_{8-j}N_8$ with $j = 0–8$. As mentioned before, all structures were fully relaxed with respect to both atomic positions and lattice constants, and here we present the results of the optimized geometries.

The formation energy as function of the number of extra Cu (Pd) atoms in the copper nitride super-cell is shown in Fig. 2, and summarized in Table 2. The configurations $Cu_{24}\,Pd_jVac_{8-j}N_8$ ($j = 0–8$) are denoted by squares, while the $Cu_{24+j}Vac_{8-j}N_8$ ($j = 0–8$) by circles. The metallic vacancies (8r spaces), at the center of each of the eight cubes that form the super-cell, were filled one by one as j increases from 1 up to 8. For both, Cu and Pd atoms, there is an increase in the formation energy as the number of dopant atoms rises. However in the case of Cu, the rate is not uniform, and as shown in Fig. 2, for a small number (1–3) of extra Cu atoms, the formation energy is very similar to the one of ideal Cu_3N. On the other hand, when the dopant atom is Pd, the energy of these compounds increases almost linearly with respect to the number of dopant atoms. In the limit case, when all the 8r WS are filled with Cu or Pd atoms, the formation energy of both systems are very similar (they differ by 0.015 eV), indicating that Cu_4N ($Cu_{24+j}Vac_{8-j}N_8$ with $j = 8$) and Cu_3PdN ($Cu_{24}Pd_jVac_{8-j}N_8$ with $j = 8$) have almost the same probability to exist (Fig. 2).

As shown in Fig. 3, where we plot the lattice parameter vs. the total number of atoms, the cells that contain Pd atoms are slightly larger than those with Cu. Again squares and filled circles denote extra Pd and Cu atoms respectively. The increase in the lattice parameter is about 1.1% and 1.2% for $Cu_{24+j}Vac_{8-j}N_8$ and $Cu_{24}\,Pd_jVac_{8-j}N_8$ ($j = 8$) respectively (see Table 2 and Fig. 3). These values are in good agreement with previous theoretical [14–15] and experimental values [14]. In particular, experiments on the ternary Cu_3NPd_x alloy [16] show a slight increase in the lattice parameter from $a = 3.83$ Å for the pure Cu_3N to $a = 3.85$ Å for $Cu_3NPd_{0.175}$.

To understand the electronic structure of our systems, we have calculated the density of states (DOS) of the copper nitride super-cell for all the considered configurations. Fig. 4a and b show the DOS for the series $Cu_{24+j}Vac_{8-j}N_8$ with $j = 0–8$, and $Cu_{24}\,Pd_jVac_{8-j}N_8$ with $j = 0–8$. From Fig. 4(a) we observe the disappearing of the gap when the first Cu is added to the super-cell, and the material behaves as an n-type semiconductor. When all center sites are filled

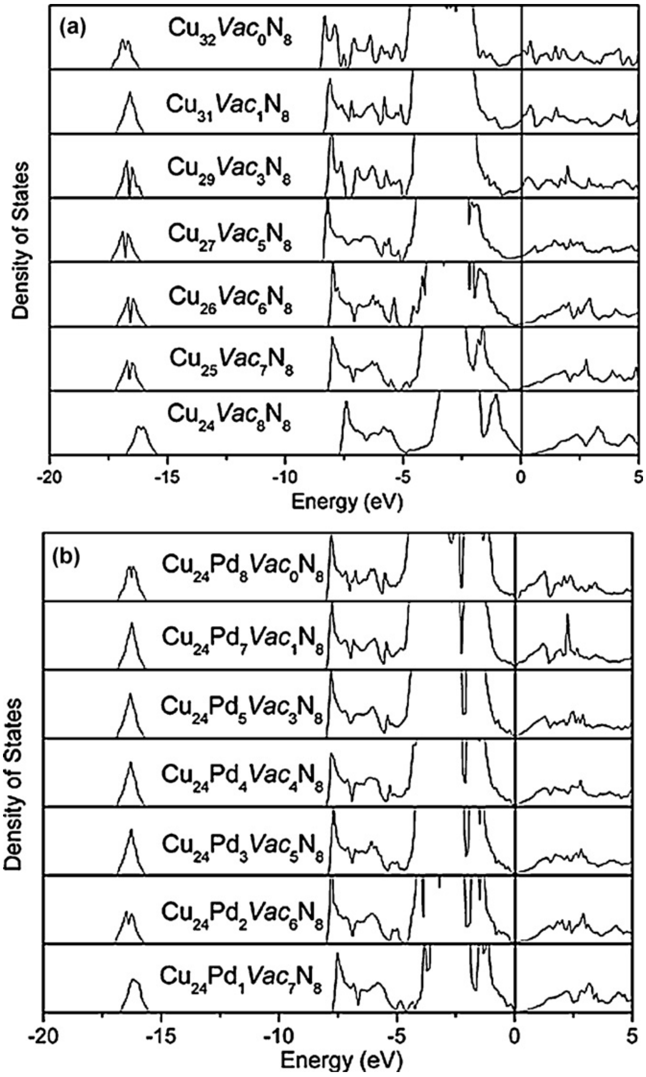

Fig. 4. Density of States for: (a) $Cu_{24+j}Vac_{8-j}N_8$, (b) $Cu_{24}\,Pd_jVac_{8-j}N_8$ ($j = 0–8$).

Table 2

Lattice parameters, and formation energies for the calculated configurations.

Compounds		a (Å)	Wyckoff sites that are occupied for:			Formation energy (eV)	Energy differences
			Cu atoms	Pd atoms	Vacancies (*Vac*)		
A.							
$\mathrm{Cu}_{24}\mathrm{Cu}_1\mathit{Vac}_7\mathrm{N}_8$	$\mathrm{Cu_3Cu_{0.125}N}$	7.68	2h, 2g, 4o, 4i, 4l, 4m, 4n	1	8r-1	−0.362	0.002
$\mathrm{Cu}_{24}\mathrm{Cu}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Cu_{0.25}N}$	7.68	2h, 2g, 4o, 4i, 4l, 4m, 4n	2	8r-2	−0.362	0.002
$\mathrm{Cu}_{24}\mathrm{Cu}_3\mathit{Vac}_5\mathrm{N}_8$	$\mathrm{Cu_3Cu_{0.375}N}$	7.72	2h, 2g, 4o, 4i, 4l, 4m, 4n	3	8r-3	−0.357	0.007
$\mathrm{Cu}_{24}\mathrm{Cu}_4\mathit{Vac}_4\mathrm{N}_8$	$\mathrm{Cu_3Cu_{0.5}N}$	7.72	2h, 2g, 4o, 4i, 4l, 4m, 4n	4	8r-4	−0.341	0.023
$\mathrm{Cu}_{24}\mathrm{Cu}_5\mathit{Vac}_3\mathrm{N}_8$	$\mathrm{Cu_3Cu_{0.625}N}$	7.73	2h, 2g, 4o, 4i, 4l, 4m, 4n	5	8r-5	−0.325	0.039
$\mathrm{Cu}_{24}\mathrm{Cu}_6\mathit{Vac}_2\mathrm{N}_8$	$\mathrm{Cu_3Cu_{0.75}N}$	7.73	2h, 2g, 4o, 4i, 4l, 4m, 4n	6	8r-6	−0.306	0.058
$\mathrm{Cu}_{24}\mathrm{Cu}_7\mathit{Vac}_1\mathrm{N}_8$	$\mathrm{Cu_3Cu_{0.875}N}$	7.75	2h, 2g, 4o, 4i, 4l, 4m, 4n	7	8r-7	−0.285	0.079
$\mathrm{Cu}_{24}\mathbf{Cu_8}\mathit{Vac}_0\mathrm{N}_8$	$\mathrm{Cu_4N}$	7.76	2h, 2g, 4o, 4i, 4l, 4m, 4n	8r	–	−0.265	0.099
B.							
$\mathrm{Cu}_{24}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.68	2h, 2g, 4o, 4i, 4l, 4m, 4n	–	8r	−0.364	0
$\mathrm{Cu}_{24}\mathrm{Pd}_1\mathit{Vac}_7\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.124}N}$	7.69	2h, 2g, 4o, 4i, 4l, 4m, 4n	1	8r-1	−0.348	0.017
$\mathrm{Cu}_{24}\mathrm{Pd}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.25}N}$	7.71	2h, 2g, 4o, 4i, 4l, 4m, 4n	2	8r-2	−0.335	0.029
$\mathrm{Cu}_{24}\mathrm{Pd}_3\mathit{Vac}_5\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.375}N}$	7.72	2h, 2g, 4o, 4i, 4l, 4m, 4n	3	8r-3	−0.321	0.043
$\mathrm{Cu}_{24}\mathrm{Pd}_4\mathit{Vac}_4\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.5}N}$	7.73	2h, 2g, 4o, 4i, 4l, 4m, 4n	4	8r-4	−0.306	0.058
$\mathrm{Cu}_{24}\mathrm{Pd}_5\mathit{Vac}_3\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.625}N}$	7.73	2h, 2g, 4o, 4i, 4l, 4m, 4n	5	8r-5	−0.294	0.070
$\mathrm{Cu}_{24}\mathrm{Pd}_6\mathit{Vac}_2\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.75}N}$	7.75	2h, 2g, 4o, 4i, 4l, 4m, 4n	6	8r-6	−0.283	0.081
$\mathrm{Cu}_{24}\mathrm{Pd}_7\mathit{Vac}_1\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.875}N}$	7.76	2h, 2g, 4o, 4i, 4l, 4m, 4n	7	8r-7	−0.274	0.091
$\mathrm{Cu}_{24}\mathrm{Pd}_8\mathit{Vac}_0\mathrm{N}_8$	$\mathrm{Cu_3PdN}$	7.77	2h, 2g, 4o, 4i, 4l, 4m, 4n	8r	–	−0.261	0.103
C.							
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.49	4o, 4i,4l, 4n, 8r		2h, 2g, 4m	−0.177	0.187
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.47	4i, 4l, 4m, 4n, 8r		2h, 2g, 4o	−0.031	0.333
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.41	4o, 4l, 4m, 4n, 8r		2h, 2g, 4i	−0.162	0.202
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.48	4o, 4i,4l, 4m, 8r		2h, 2g, 4n	−0.177	0.187
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.48	4o, 4i, 4m, 4n, 8r		2h, 2g, 4l	−0.178	0.186
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.49	2g, 2h, 4o, 4i, 4m, 8r		4l, 4n	−0.049	0.315
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.44	2g, 2h, 4i, 4m, 4n, 8r		4o, 4l	−0.092	0.272
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.47	2g, 2h, 4o, 4m, 4n, 8r		4i, 4l	−0.060	0.304
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.45	2g, 2h, 4o, 4i, 4n, 8r		4l, 4m	−0.082	0.282
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.48	2g, 2h, 4o, 4l, 4m, 8r		4i, 4n	−0.059	0.305
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.49	2g, 2h, 4i, 4l, 4n, 8r		4o, 4m	−0.049	0.315
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.44	2g, 2h, 4o, 4i, 4l, 8r		4m, 4n	−0.082	0.282
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.45	2g, 2h, 4i, 4l, 4m, 8r		4o, 4n	−0.082	0.282
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.47	2g, 2h, 4l, 4m, 4n, 8r		4o, 4i	−0.054	0.310
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_3N}$	7.48	2g, 2h, 4o, 4l, 4n, 8r		4i, 4m	−0.023	0.341
D.							
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.25}}\mathit{Vac}_{0.75}\mathrm{N}$	7.62	4o, 4l, 4m, 4n, 8r	2g	2h, 4i	−0.104	0.260
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.25}}\mathit{Vac}_{0.75}\mathrm{N}$	7.60	4o, 4i, 4m, 4n, 8r	2g	2h, 4l	−0.107	0.257
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.25}}\mathit{Vac}_{0.75}\mathrm{N}$	7.60	4o, 4i, 4l, 4n, 8r	2g	2h, 4m	−0.107	0.257
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.25}}\mathit{Vac}_{0.75}\mathrm{N}$	7.68	4o, 4i, 4l, 4m, 8r	2g	2h, 4n	−0.076	0.288
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.25}}\mathit{Vac}_{0.75}\mathrm{N}$	7.66	4l, 4m, 4n, 8r	2g	2h, 4o	−0.077	0.287
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.25}}\mathit{Vac}_{0.75}\mathrm{N}$	7.62	4o, 4l, 4m, 4n, 8r	2h	2g, 4i	−0.105	0.260
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.25}}\mathit{Vac}_{0.75}\mathrm{N}$	7.68	4o, 4i, 4m, 4n, 8r	2h	2g, 4l	−0.076	0.288
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.25}}\mathit{Vac}_{0.75}\mathrm{N}$	7.66	4o, 4i, 4l, 4n, 8r	2h	2g, 4m	−0.077	0.287
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.25}}\mathit{Vac}_{0.75}\mathrm{N}$	7.60	4o, 4i, 4l, 4m, 8r	2h	2g, 4n	−0.107	0.257
$\mathrm{Cu}_{16}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_6\mathrm{N}_8$	$\mathrm{Cu_3Pd_{0.25}}\mathit{Vac}_{0.75}\mathrm{N}$	7.60	4i, 4l, 4m, 4n, 8r	2h	2g, 4o	−0.107	0.257
E.							
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.52	2h, 4o, 4i, 4n, 8r	2g	4l, 4m	−0.028	0.336
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.56	2h, 4o, 4m, 4n, 8r	2g	4l, 4i	0.0418	0.406
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.56	2h, 4o, 4l, 4n, 8r	2g	4m, 4i	0.0418	0.406
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.57	2h, 4i, 4l, 4m, 8r	2g	4o, 4n	0.0687	0.433
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.58	2h, 4i, 4l, 4n, 8r	2g	4o, 4m	0.0733	0.437
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.59	2h, 4o, 4l, 4m, 8r	2g	4i, 4n	0.0821	0.446
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.60	2h, 4l, 4m, 4n, 8r	2g	4o, 4i	0.0822	0.446
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.58	2h, 4o, 4i, 4m, 8r	2g	4l, 4n	0.0733	0.437
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.53	2h, 4i, 4m, 4n, 8r	2g	4l, 4o	0.0083	0.372
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.54	2h, 4o, 4i, 4l, 8r	2g	4n, 4m	0.0084	0.373
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.57	2g, 4o, 4i, 4n, 8r	2h	4l, 4m	−0.008	0.356
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.59	2g, 4o, 4m, 4n, 8r	2h	4l, 4i	0.0821	0.446
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.59	2g, 4o, 4l, 4n, 8r	2h	4m, 4i	0.0819	0.446
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.55	2g, 4i, 4l, 4m, 8r	2h	4o, 4n	0.0687	0.433
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.59	2g, 4i, 4l, 4n, 8r	2h	4o, 4m	0.0733	0.437
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.56	2g, 4o, 4l, 4m, 8r	2h	4i, 4n	0.0418	0.406
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.55	2g, 4l, 4m, 4n, 8r	2h	4o, 4i	0.0418	0.406
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.58	2g, 4o, 4i, 4m, 8r	2h	4l, 4n	0.0733	0.437
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.54	2g, 4i, 4m, 4n, 8r	2h	4l, 4o	0.0083	0.372
$\mathrm{Cu}_{14}\mathbf{Cu_8}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}}\mathit{Vac}\mathrm{N}$	7.53	2g, 4o, 4i, 4l, 8r	2h	4n, 4m	0.0084	0.373
F.							
$\mathrm{Cu}_{22}\mathrm{Pd}_2\mathit{Vac}_8\mathrm{N}_8$	$\mathrm{Cu_{2.75}Pd_{0.25}N}$	7.74	2h, 4o, 4i, 4l, 4m, 4n	2g	8r	−0.212	0.152

Table 2 (*Continued*)

Compounds		a (Å)	Wyckoff sites that are occupied for:			Formation energy (eV)	Energy differences
			Cu atoms	Pd atoms	Vacancies (*Vac*)		
G. $Cu_{23}Pd_1Vac_8N_8$	$Cu_{2.87}Pd_{0.124}N$	7.72	2h, 1g, 4o, 4i, 4l, 4m, 4n	1g	8r	−0.316	0.048
H. $Cu_{31}Pd_1Vac_0N_8$	$Cu_{3.87}Pd_{0.124}N$	7.80	2h, 1g, 4o, 4i, 4l, 4m, 4n, 8r	1g	–	−0.248	0.116

with copper, the material has a metal behavior. When the dopant is palladium (Fig. 4b), we observe that the DOS diagrams around the Fermi energy has almost no variation with the increase of Pd atoms, and the material looks like a semimetal.

3.2. *The variation of vacancies ordering*

In this group we have included the series: **C**. $Cu_{16}\mathbf{Cu_8}Vac_8N_8$, and **D**. $Cu_{16}\mathbf{Cu_8}Pd_2Vac_6N_8$.

Again, in Fig. 2, we show the formation energies as function of the number of extra Cu (Pd) atoms, and the results are summarized in Table 2. The configurations $Cu_{16}\mathbf{Cu_8}Vac_8N_8$ (shown as solid stars) correspond to the shifting of 8 Cu atoms, one from each unit cell to its respective center. The configurations $Cu_{16}\mathbf{Cu_8}Pd_2Vac_6N_8$ (shown as solid triangles) are similar, but with the inclusion of two additional Pd atoms at center sites. We observe an increase in the formation energies, with a larger change in the later case.

We can observe from the structural parameters (Table 2), that the lattice constants decrease when copper atoms are moved from their original positions to the 8r sites. However, there is almost no difference if we insert the two extra palladium atoms in the super-cell. The lattice constant for $Cu_{16}\mathbf{Cu_8}Pd_2Vac_6N_8$ (with only 6 vacancies) show a very small increase with respect to the ones of $Cu_{16}\mathbf{Cu_8}Vac_8N_8$ (Cu_3N with 8 vacancies), even though the later configuration has 34 atoms instead of 32 atoms, indicating that there is big empty space at the center of the cube.

In Fig. 5 we plot the DOS for one representative compound of each series of configurations. The results in these calculations demonstrate the importance of the position of the vacancies. The ideal Cu_3N (Fig. 6a) which has all its vacancies in the WS 8r is semiconductor, whereas the same compound in which some Cu atoms are moved to the WS 8r sites is not (Fig. 6b). The addition of two Pd atoms in to WS 8r sites changes the DOS little (Fig. 6c). A small peak around −14 eV can be now observed, and it probably comes from a Pd contribution.

3.3. *Interchange of Cu by Pd atoms*

In this subsection we consider the substitution of small quantities of copper by palladium atoms in the copper sub-lattice. We have considered the series **E**. $Cu_{14}\mathbf{Cu_8}Pd_2Vac_8N_8$, and three additional configurations **F**. $Cu_{23}Pd_1Vac_8N_8$ G. $Cu_{22}Pd_2Vac_8N_8$, and **H**. $Cu_{31}Pd_1Vac_0N_8$.

Again, in Fig. 2, we show the formation energies as function of the number of extra Cu (Pd) atoms, and the results are summarized in Table 2. The configurations **E**. $Cu_{14}\mathbf{Cu_8}Pd_2Vac_8N_8$ (shown as solid rhombuses) correspond to the exchange of two Cu by Pd atoms. This series of configurations should be compared with **C**. and **D**. We observe a larger increase in the binding energy, indicating that the larger Pd atom do not fit very well in the Cu lattice, also resulting in a larger cell as shown in Table 2. The DOS for a representative compound of the series can be seen in Fig. 5d. Again, the system is now metallic, and the DOS is very similar to the one of configuration **D**. (Fig. 5c).

To confirm that the metallicity of configurations **C**. **D**. and **E**. is due to the occupation of some WS 8r sites, we have calculated three single configurations in which we substitute one and two Cu atoms by Pd in Cu_3N, and one Cu by a Pd atom in Cu_4N.

In Configuration **F**. $Cu_{23}Pd_1Vac_8N_8$, which is equivalent to the substitution of one Cu by a Pd atom in Cu_3N, we have calculated a single geometry in which a random Cu atom is substituted by a Pd atom, while all 8r vacancies were kept empty, resulting in a super-cell with 32 atoms. Its formation energy (shown as an empty circle in Fig. 2) is just ~0.05 eV higher than the one of Cu_3N. Although it is a small value, it is larger than the formation energy for the insertion of the Pd atom at the WS 8r site. The formation energy of configuration **G**. $Cu_{22}Pd_2Vac_8N_8$ (shown as an empty square in Fig. 2), with two Pd substituting Cu atoms, is ~0.05 eV higher than the one of Cu_3N. The formation energy of configuration **H**. $Cu_{31}Pd_1Vac_0N_8$ that corresponds to the substitution of one Cu by a Pd atom in Cu_4N is shown as an empty triangle in Fig. 2. It is slightly higher than the formation energy of Cu_4N by ~0.02 eV.

The structural parameters of configurations **F**. **G**. and **H**. are also summarized in Table 2 and plotted in Fig. 3, where it can be noticed that the biggest lattice parameter is when the palladium atom is in a copper site and all the center spaces are filled with copper ($Cu_{31}Pd_1Vac_0N_8$). In this stoichiometry the Cu_3N lattice is increased by 1.44%, which is the highest value obtained in this study.

As seen in Fig. 6(a and b), $Cu_{23}Pd_2Vac_8N_8$ and $Cu_{22}Pd_2Vac_8N_8$ are semiconductors, with a small gap at the Fermi level. On the other hand, the density of states of $Cu_{31}Pd_1Vac_0N_8$, a geometry in

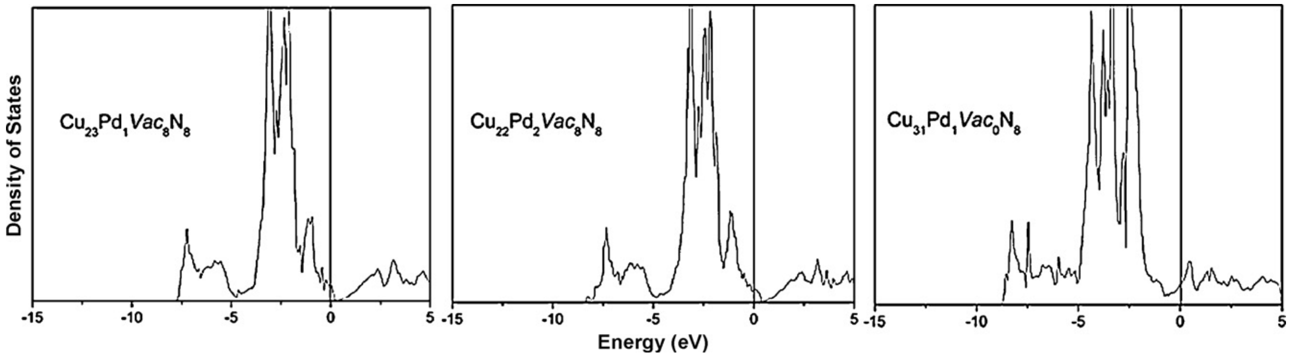

Fig. 5. Density of states for: $Cu_{22}Pd_2Vac_8N_8$, $Cu_{23}Pd_1Vac_8N_8$, and $Cu_{31}Pd_1Vac_0N_8$.

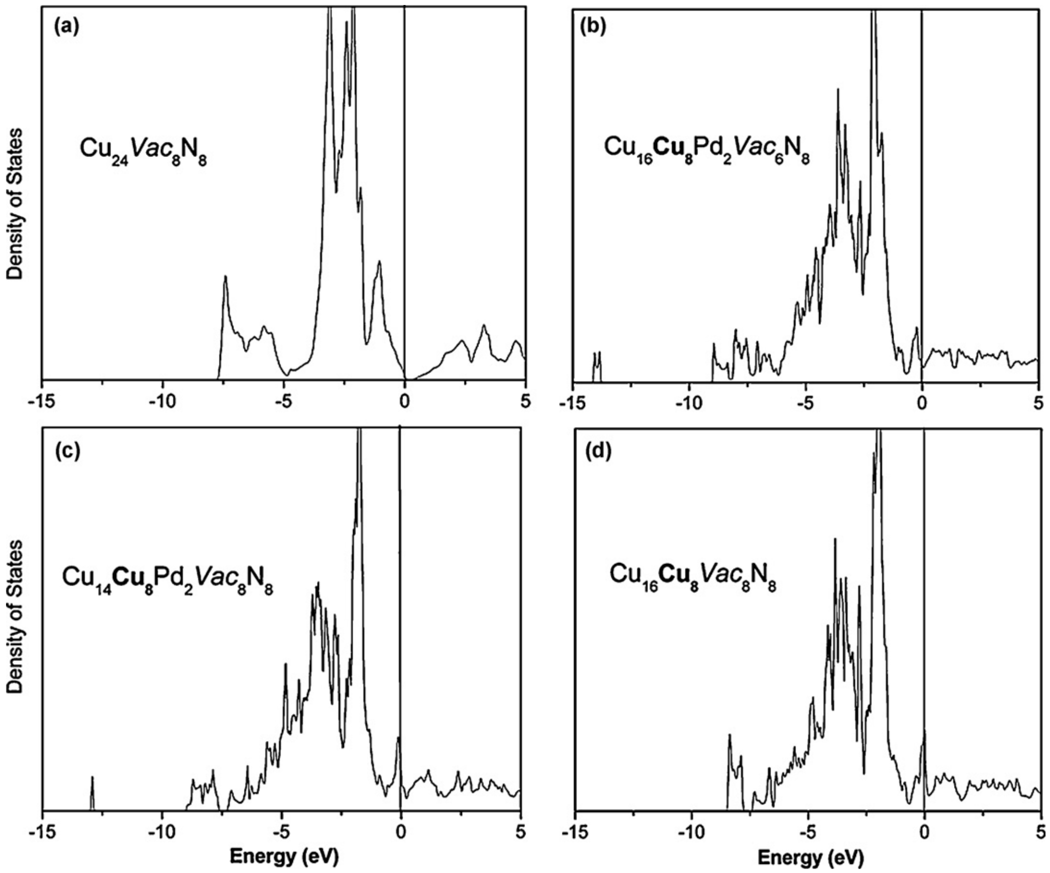

Fig. 6. Total density of states for: (a) Cu_3N, (b) $Cu_{16}\mathbf{Cu_8}Pd_2\mathit{Vac}_6N_8$, (c) $Cu_{14}\mathbf{Cu_8}Pd_2\mathit{Vac}_8N_8$, and (d) $Cu_{16}\mathbf{Cu_8}\mathit{Vac}_6N_8$.

which a Pd take the place of a Cu atom and all the center vacancies (WS 8r) are occupied for copper (Fig. 5c) has a metallic behavior.

We believe that the semiconductor state presented by Cu_3N (anti-ReO_3) is a consequence of the oxidation state of copper atoms which must be +1. When an extra Pd, Cu or any other metal atom is introduced at the center of the cubic cell (a site with coordination 12), they are in a reduced form Pd^0 or Cu^0 and induces the material to its metallic state.

4. Summary

Using Density Functional Theory calculations, with a plane wave pseudopotential approach, and within the generalized gradient approximation (GGA), we have reported the structural and electronic properties non-stoichiometric copper nitride, pure and with palladium. Specifically, we have study the series of configurations: $Cu_{24+j}\mathit{Vac}_{8-j}N_8$; Cu_{24} $Pd_j\mathit{Vac}_{8-j}N_8$ (with $j = 0.8$); $Cu_{16}\mathbf{Cu_8}\mathit{Vac}_8N_8$; $Cu_{16}\mathbf{Cu_8}Pd_2\mathit{Vac}_6N_8$; $Cu_{14}\mathbf{Cu_8}Pd_2\mathit{Vac}_8N_8$, and three fixed geometries: $Cu_{23}Pd_1\mathit{Vac}_8N_8$, $Cu_{22}Pd_2\mathit{Vac}_8N_8$, and $Cu_{31}Pd_1\mathit{Vac}_0N_8$.

We have found that in $Cu_{24+j}\mathit{Vac}_{8-j}N_8$ for one and two Cu atoms ($j = 1$–2) the energy is only a slightly higher than it is in the Cu_3N, in good agreement with experiments that show that it is possible to introduce a small amount of extra metal atoms in copper nitride. Instead, the formation energies for the other series are sensibly higher.

A study of the electronic properties has shown that in the compounds with the vacancies located at the WS 8r sites (at the center of the unit cell) unoccupied, the material is a semiconductor. On the other hand, when one or more of the WS 8r sites are occupied, the material becomes a metal.

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