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Band gap evolution of bulk Cu_3N and monolayer Cu_2N under nonhydrostatic strain

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ABSTRACT

Structural and electronic properties of bulk Cu_3N and monolayer Cu_2N under *ab*-plane strain have been evaluated from first principles. Furthermore, the electronic structure of a layered $AgCu_2N$ system was studied. Structural optimizations were performed within the GGA approach, and band structures were obtained with the modified Becke-Johnson (MBJLDA) exchange-correlation potential. Compressive strain leads to a decrease of a band gap in the Cu_3N parent compound and Cu_2N atomic sheet, whereas tensile strain causes an opposite effect on band structures of these systems. Furthermore, some transitions between direct and indirect band gaps, induced by tensile strain, are revealed in these materials. The monolayer Cu_2N is found semimetallic. The hypothetical $AgCu_2N$ compound is predicted to be a semiconductor with the degenerate indirect *R*-Γ and *R*-*M* gaps, which are close in value to the direct *R*-*R* gap. The findings presented here suggest that tensile strain and a doping with Ag atoms are promising tools for band gap engineering in Cu_3N-based materials, thin films and heterostructures in particular.

1. Introduction

A cubic copper nitride is a promising material for optoelectronic devices [1–15]. Other various applications of Cu_3N systems have been considered, such as a component in Li-ion batteries [16,17], catalyst nanoparticles in alkaline fuel cells [17], and thin films as a barrier layer in low resistance magnetic tunnel junctions [18] or a resistive-switching material [19].

A wide range of indirect band gaps (E_g) was revealed in experimental studies of Cu_3N systems. For instance, the values of E_g from ≈ 1.2 up to ≈ 1.7 eV, depending on the growing conditions, crystallite size and lattice parameters, were obtained in the recent work [11]. Meantime, the modern DFT-based calculations yielded fundamental gaps between the *R* and *M* points of the cubic Brillouin zone (BZ), which are only 0.42 (PBE0) and 0.56 eV (MBJGGA) [20].

Theoretical investigations of the Cu_3N band structure in strain conditions (under hydrostatic pressure and for an increased lattice parameter *a*) [20–23], are insufficient for clarification of a significant variation of band gaps in different samples of Cu_3N materials. This issue may be connected with the Burstein-Moss shift [25,24], however, the DFT-based predictions suggested a very high concentration of defects, i.e., oxygen atoms [26], required for such a significant rise of a band gap. In spite of all, the gap $E_g = 1.2$ eV, which is relatively high when compared with the narrow $E_g = 0.65$ eV of InN system in equilibrium conditions [27], was obtained in high optical quality InN films due to the presence of strain and the Burstein-Moss effect [28]. Because the modern DFT-based calculations provide satisfactory band structures for InN (e.g. [29]), one may consider that high quality Cu_3N materials exhibit a significantly lower fundamental gap than those reported experimentally up to now.

Numerous theoretical investigations were devoted to magnetic properties of some 3*d* transition metal atoms deposited on the Cu_3N surface [30–38]. Such systems are predicted to be a promising environment for an exploration of the magnetic interactions between single addatoms, dimers, and in some atomic chains.

The DFT-based studies of structural, elastic and electronic properties of transition metal doped Cu_3N systems showed that the location of additional atoms in the empty space of Cu_3N host lattice leads to the metallic character of resultant materials [39–45].

In this work, structural and electronic properties of the *ab*-plane strained Cu_3N unit cell, two-dimensional Cu_2N atomic sheet, as well as layered tetragonal $AgCu_2N$ system are investigated from first principles. The main aim of this study is a careful examination of band structure of Cu_3N under nonhydrostatic pressure, which is a model system for thin films grown on various lattice-mismatched substrates. Next, the electronic structure of a hypothetical Cu_2N layer is predicted. Finally, a tetragonal $AgCu_2N$ compound, formed by Cu_2N sheets separated by Ag atoms is considered as a promising material with a direct band gap, in contrast to the parent Cu_3N system.

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2. Computational details

The electronic structure calculations have been performed with the use of the Abinit [46,47] and Wien2k [48] packages. First, the equilibrium and *ab*-plane strained geometries were found via stresses/forces relaxation in the Abinit code for PAW atomic datasets taken from the JTH table [49] with the Perdew-Burke-Ernzerhof [50] parametrization of the exchange-correlation energy. The calculations were performed for 30 Ha energy cutoff for the plane wave basis and the $8 \times 8 \times 8$ **k**-point mesh with two shifts: (0,0,0) and (0.5,0.5,0.5). Next, the band structures were calculated with the full-potential Wien2k code within the MBJLDA (TB09) approach [51]. The RK_{max} of 7 was selected. The $12 \times 12 \times 12$ and $12 \times 12 \times 1$ **k**-point meshes were employed for bulk systems and the atomic sheet, respectively.

This complex calculation scheme was necessary to obtain reasonable results of structural parameters and stress under nonhydrostatic strain conditions (Abinit), and accurate MBJLDA band structures (Wien2k). It is worth noting that the agreement between the results of computations using various modern DFT-based packages is generally satisfactory [52]. Particularly, for the PAW (Abinit) and FPLAPW (Wien2k) approaches, which are related to each other.

The equilibrium structure of Cu_3N compound was obtained for the cubic anti-ReO_3 primitive cell (space group no. 221) whereas other systems were modeled with the relative tetragonal structures (space group no. 121). As depicted in Fig. 1, one of Cu atoms in Cu_3N system was substituted with an Ag atom in the hypothetical $AgCu_2N$ material, which leads also to a tetragonal unit cell (u.c.). Meantime, the Cu_2N atomic sheet was similarly obtained with a removal of one of Cu atoms from the Cu_3N parent system. Such Cu_2N monolayers were separated with a vacuum region of 10 Å.

3. Results and discussion

The equilibrium lattice parameter $a = 3.824$ Å, obtained here for the cubic Cu_3N compound, is in good agreement with previous results of GGA calculations and experimental data taken from literature, as gathered in Table 1.

Because the recent study [20] suggested that the anti-ReO_3 phase of Cu_3N is stable under hydrostatic pressures up to 30 GPa (in contrast to the previous work [22]), we consider a wide range of biaxial stress (P) for this system (from − 10 to 30 GPa). As presented in Fig. 2, the *ab*-plane stress of 30 GPa corresponds to the lattice parameter $a = 3.470$ Å, whereas the tensile stress of 10 GPa yields the u.c. with $a = 4.210$ Å. It is worth noting that this kind of strain changes the symmetry of the u.c., and leads to the relaxation of the perpendicular lattice parameter (labeled here as c). Then the c/a ratio of the Cu_3N system increases or decreases for compressive or tensile strain, respectively. Such conditions are present in thin films deposited on lattice mismatched substrates.

The calculated (MBJLDA) band structures of Cu_3N in equilibrium and stress conditions are presented in Fig. 3. In equilibrium, the

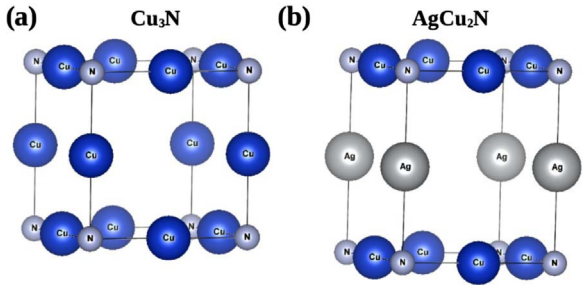

Fig. 1. The unit cells of cubic Cu_3N (a) and tetragonal $AgCu_2N$ (b) depicted with the VESTA package [53].

Table 1
Equilibrium lattice parameters (GGA) and band gaps (MBJLDA) calculated for Cu_3N and $AgCu_2N$. Experimental data for Cu_3N are taken from Refs. [9–11,45].

	a (Å)	c (Å)	E_g (eV)
Cu_3N			
this work	3.824^{GGA}	–	0.44^{MBJLDA}
Ref. [20]	3.829^{GGA}	–	0.56^{MBJGGA}
Ref. [20]	3.829^{GGA}	–	0.42^{PBEO}
Ref. [21]	3.82^{GGA}	–	0.25^{GGA}
Experimental	3.80–3.85	–	–
$AgCu_2N$			
this work	3.770^{GGA}	4.469	0.65^{MBJLDA}

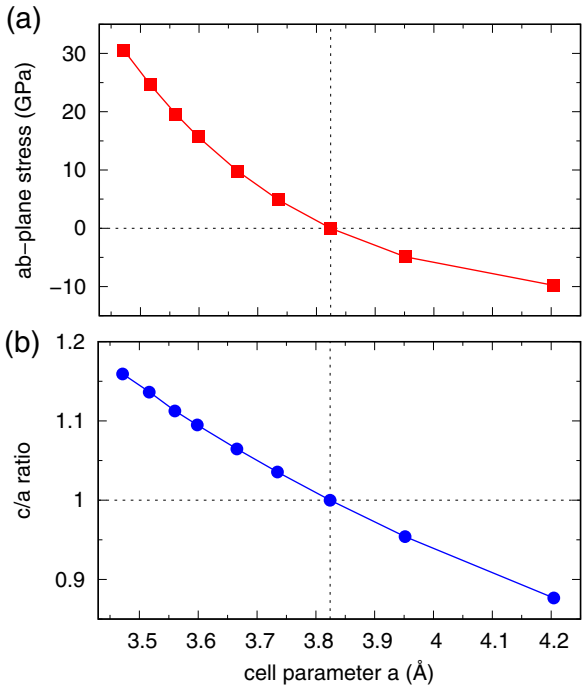

Fig. 2. Stress/strain relations (a) and c/a ratios (b) calculated (GGA) for *ab*-plane strained unit cell of Cu_3N. The equilibrium lattice parameter a is marked by a vertical dashed line.

indirect band gap (R-M) of 0.44 eV was found. As seen in Table 1, it is lower than the previous MBJGGA result (0.56 eV), however, it is close to that calculated with the PBE0 hybrid exchange functional (0.42 eV) [20].

The value of the indirect E_g (R-M) decreases in compressively strained Cu_3N systems [21,20]. As presented in Fig. 3 (a), the zero E_g was obtained for $P = 25$ GPa, corresponding to $a = 3.52$ Å, which differs strongly from that derived from band structures obtained with the GGA approach ($a = 3.71$ Å) [21]. This discrepancy is related to the well-known underestimation of E_g in standard DFT-based calculations. Meantime, the tensile strain leads to an increase of indirect E_g in Cu_3N. A significant elongation of the lattice parameter a may cause a transition between the R-M and R-Γ band gaps in this system, as presented in Fig. 3(c).

A careful analysis of the valence band maximum (VBM) and conduction band minimum (CBM) for high symmetry points in the Brillouin zone of the strained u.c. of Cu_3N is presented in Fig. 4 (a). One may notice that the tensile strain leads to an increase of the CBM energy at points R and M, whereas an opposite effect is revealed at points Γ and X. As presented in Fig. 4 (b), the indirect R-M and direct