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Electronic Structure of $Mg_2Ni_{1-x}Cu_x$

A. Jezierski[a], M. Jurczyk[b] and A. Szajek[a]

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

[b]Institute of Material Science and Engineering, Poznań University of Technology
pl. M. Skłodowskiej Curie 5, 60-965 Poznań, Poland

Nanocrystalline Mg_2Ni doped alloys are good materials for hydrogen storage. In this work we present the influence of the chemical disorder on the electronic structure of $Mg_2Ni_{1-x}Cu_x$ alloys for $0 < x < 0.2$. The electronic structure was calculated by *ab initio* full potential scalar relativistic local-orbital method in the coherent potential approximation. We observe the change of the density of states near the Fermi energy.

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1. Introduction

Magnesium-based systems are promising materials for hydrogen storage. The electronic and electrochemical properties of Mg_2Ni doped by transition elements were studied in the last years [1–5]. In this paper we paid our attention on the change of the electronic structure of $Mg_2Ni_{1-x}Cu_x$ alloys for $0 < x < 0.2$, during the substitution of Ni by Cu atoms. Mg_2Ni alloy crystallizes in the hexagonal $P6_222$ (space group No. 180) type structure. The primitive cell is presented in Fig. 1. Mg atoms are located at two positions: 6i (x, $2x$, 0) and 6f (0.5, 0, z) for $x = 0.162$ and $z = 0.1187$. Two nickel atoms are distributed at 3d (0, 0, 0.5) and 3b (0.5, 0, 0.5) positions in the unit cell. In the case of $Mg_2Ni_{1-x}Cu_x$ nickel atoms were replaced by copper atoms at 3d, 3b or partially in both positions. In this work we present *ab initio* calculations of the influence of chemical disorder on the electronic densities of states. The chemical disorder was taken into account based on the coherent potential approximation (CPA) and the local density approximation (LDA) scheme [6–9]. In the next section we present outline of the method and the results are reported in Sect. 3.

2. Method of calculations

The electronic properties of $Mg_2Ni_{1-x}Cu_x$ alloys for $x = 0.05$, 0.10, 0.15 and 0.20, were calculated by the first principle scalar relativistic full-potential local-orbital and coherent potential approximation (FPLO-CPA) methods [6–8]. The calculations were performed within the LDA [7]. The exchange correlation potential was used in the form of Perdew and Wang [10]. The self-consistent calculations were performed for 396 k-points in the irreducible Brillouin zone.

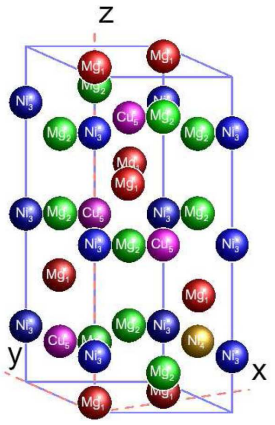

Fig. 1. Primitive unit cell of $Mg_2Ni_{1-x}Cu_x$.

In *ab initio* calculations the magnesium $7s$, $7p$, $6d$, and $5f$ states, the nickel $6s$, $6p$ and $5d$ states, as well as the copper $4s$, $4p$ and $3d$ states were treated as valence states. The calculations were performed for the experimental lattice parameter $a = 5.216$ Å and $c = 13.246$ Å [1]. For each distribution of copper atoms (at 3b or 3d sites) the total energy was calculated and we found that for the copper atom located at 3d position the system was the lower total energy, although the differences between different configurations were small.

3. Results and discussion

In Figs. 2 and 3 we present the total density of states (DOS) of $Mg_2Ni_{1-x}Cu_x$ alloys for the concentration of copper $x = 0.05$, 0.10, 0.15 and 0.20, respectively. The substitution of Ni by Cu atoms leads to increase in the number of electrons in the system and we observe the modification of the total densities of states.

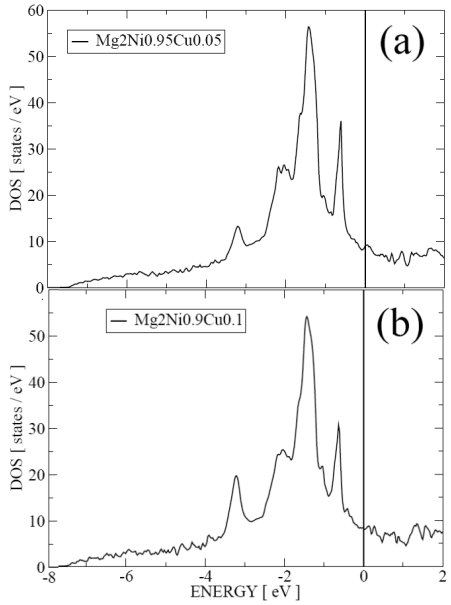

Fig. 2. Total and partial electronic DOS of $Mg_2Ni_{0.95}Cu_{0.05}$ (a) and $Mg_2Ni_{0.90}Cu_{0.10}$ (b) alloys. The Fermi energy is located at $E = 0$ eV.

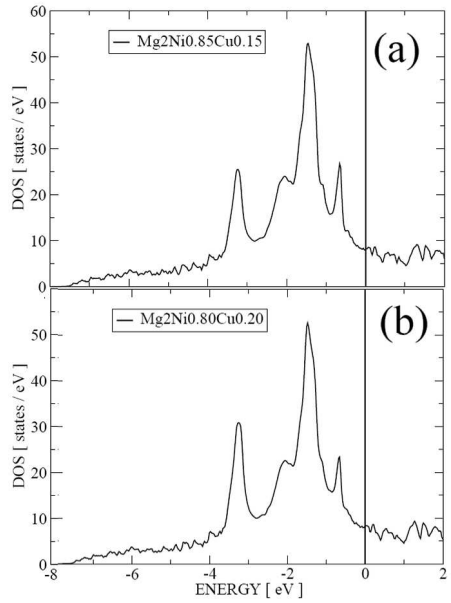

Fig. 3. Total and partial electronic DOS of $Mg_2Ni_{0.85}Cu_{0.15}$ (a) and $Mg_2Ni_{0.80}Cu_{0.20}$ (b) alloys. The Fermi energy is located at $E = 0$ eV.

The partial density of states for $x = 0.15$ is plotted in Fig. 4. The total DOS consists of the contributions from magnesium atoms (the broad band in the region of $-8 < E < 0$ eV), nickel atoms at 3b and 3d position in the region of $-4 < E < 0$ eV and copper atom (3d position) located between $-4 < E < -2$ eV. The change of copper concentration leads to the modification

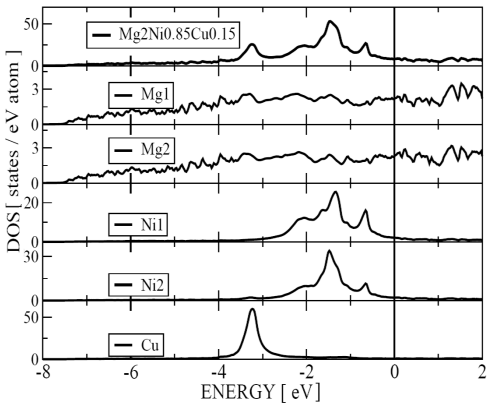

Fig. 4. Total and partial density of states of $Mg_2Ni_{0.85}Cu_{0.15}$ alloy. The Fermi level is located at $E = 0$ eV.

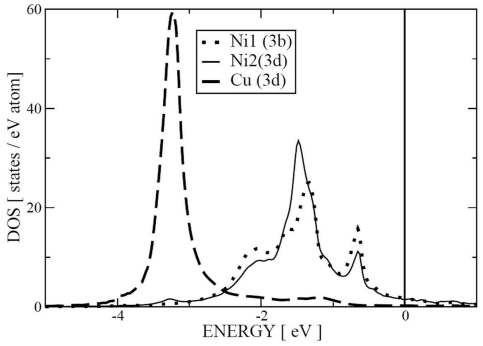

Fig. 5. Partial density of states of Ni1(3b), Ni2(3d) and Cu(3d) in $Mg_2Ni_{0.85}Cu_{0.15}$ alloy. The Fermi level is located at E = 0 eV.

of the shape of DOS in two regions of energy: the first region is near -3.2 eV and the second region is between $-2 < E < -0.5$ eV. In Fig. 5 we present the local DOS of d states of Cu (broken curve), Ni1 (dotted curve) and Ni2 (solid curve) atoms. The change of the concentration of copper atom leads to the modification of shape of three peaks of Ni2 atom. The change of the total density of states near the Fermi level is presented in Fig. 6. Up to $x = 0.15$ the values of $N(E_F)$ decrease, but for

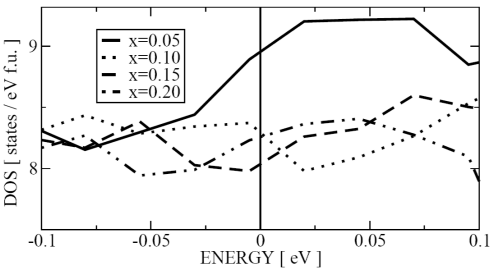

Fig. 6. Total electronic density of states of $Mg_2Ni_{1-x}Cu_x$ alloy near the Fermi energy.

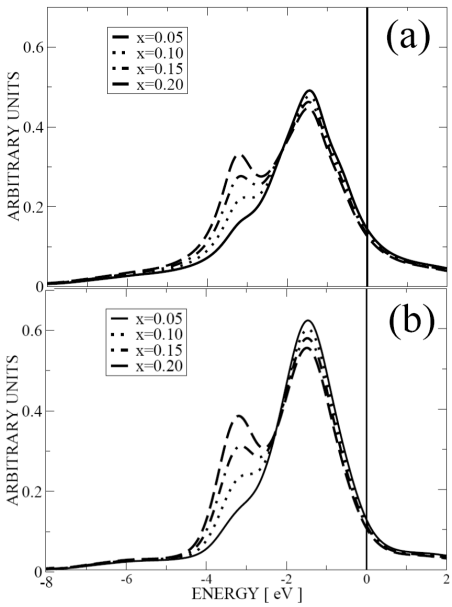

Fig. 7. The density of states convoluted with Lorentzians (a) and Gaussians (b) of FWHM = 0.4 eV.

$x = 0.2$ the values of $N(E_F)$ increase. The change of the electronic densities of states can be observed in the X-ray photoelectron spectroscopy (XPS) experiment. In Fig. 7a and b we plotted the density of states convoluted with Lorentzians (Fig. 7a) and Gaussians (Fig. 7b) of FWHM = 0.4 eV taking into account proper photoelectronic cross-section from [11]. Our theoretical XPS spectra indicate that there are two main peaks: one from 3d Ni states around $E = -2$ eV and the second peak near $E = -3$ eV which is connected to 3d states of Cu.

4. Conclusions

In this work we presented the electronic structure of $Mg_2Ni_{1-x}Cu_x$ alloys. The copper atoms were located at the 3d and 3b sites. We found that the position of Cu atoms in 3d sites is more stable, although the difference of the total energy between different configurations is small. The substitution of Ni by Cu modified the shape of the density of states at the Fermi energy. We observe mainly the modification of two peaks: one near $E = -3.2$ eV due to Cu 3d states and the second at –0.7 eV connected to 3*d* states of Ni atom.

Acknowledgments

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