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Catalysis Today 89 (2004) 375–378
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Supported magnetic Pd nanoclusters on Ag(0 0 1)

F. Amitouche [a], S. Bouarab [a,*], C. Demangeat [b]

[a] *Laboratoire de Physique et Chimie Quantique, Faculté des Sciences, Université Mouloud, Mammeri de Tizi-Ouzou, 15000 Tizi-Ouzou, Algeria*
[b] *Institut de Physique et Chimie des Matériaux de Strasbourg, 23 Rue du Loess, B.P. 43, F-67034 Strasbourg Cedex 2, France*

Abstract

A self-consistent tight-binding method has been used to calculate the electronic structure and magnetic properties of Pd islands on Ag(0 0 1) surface. We find a paramagnetic state for 21 Pd atoms ordered on one layer, whereas 33 atoms ordered on two atomic layers display a net magnetic moment. Surface effect and low atomic coordination do not lead necessarily to the onset of magnetism in Pd. More precisely, the present results show that the formation of the cluster (thickness and atomic aggregation) is one of the most important factor which could determine the magnetism of Pd systems.

Keywords: Pd nanoclusters; Ag(0 0 1) surface; Magnetic moment

1. Introduction

Adsorption of atomic clusters onto solid surfaces is a versatile surface-processing tool in the fabrication of model nanocatalysts. The electronic and magnetic properties, catalytic activity of the clusters depend on their geometrical structures and their size. In the field of catalysis, Pd supported clusters present very interesting catalytic properties [1]. However, their magnetic behavior are still subject to discussion [1,2] because Pd has very intriguing magnetic properties. Pd is paramagnetic in bulk as well in its atomic form with electronic structure ($4d^{10}5s^{0}$). However, in bulk, it is close to fulfill the Stoner criterion of magnetism because of its high paramagnetic susceptibility. One can expect onset of ferromagnetism in Pd by a lattice expansion of only 6% [3–5].

To study a possible onset of spin polarization in Pd, one could therefore investigate low dimensional structures such as Pd layers on Ag(0 0 1). The expectation is that the combined effect of lattice expansion on Ag substrate and the reduction of the coordination number should cause Pd to become magnetic. However, and contrary to this expectation, all the calculations [6–10] have shown non-magnetic state for 1 monolayer (ML) on Ag(0 0 1) in agreement with magneto-optical Kerr-effect experiments [11]. This unexpected result is somewhat intriguing since a bilayer on Ag(0 0 1) was found to be magnetic [10].

In this context, two of us have previously used a tight-binding (TB) Hubbard Hamiltonian within the unrestricted Hartee–Fock approximation to study the magnetism of Pd films on Ag(0 0 1) [8]. We have found that Pd films are magnetic in the range from $n = 3$ to 6 ML. As we have pointed out, such behavior cannot be surface effect but is related to the thickness of the Pd film. This surprising result was interpreted later by Mirbt et al. [12] in terms of quantum well states in Pd films. Indeed, these authors have performed local spin density calculation for fcc (0 0 1) surface of Ag covered up to 16 ML of Pd by means of scalar-relativistic spin-polarized Green's function technique. They found Pd at the Ag lattice spacing and at the interface magnetic with moment of the order of $0.3\mu_B$ excepted for coverages of 1–2 and 5–7 ML where magnetism is completely suppressed. Although these results are in qualitative agreement with our calculations [8] about the complete quenching of the magnetism for certain Pd coverages especially for 1 and 2 ML, they are somewhat in disagreement with those of Blügel [10] who found the bilayer ferromagnetic with a net magnetic moments of 0.17 and $0.11\mu_B$ at the surface and interface layer, respectively. We remind that, in our previous TB calculations [8], we have used a value of the integral exchange $J = 0.52$ eV which is slightly smaller than the LMTO value (0.65 eV) given by Christensen et al. [13]. For this value ($J = 0.65$ eV), a bilayer Pd is indeed ferromagnetic.

* Corresponding author. Tel.: +213-26-21-48-48; fax: +213-26-21-48-48.
E-mail address: sbouarab@yahoo.fr (S. Bouarab).

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doi:10.1016/j.cattod.2003.12.011

The aim of this work is therefore to carry on our earlier study performed on magnetic properties of thin Pd films on Ag(0 0 1) by considering lower dimensional systems consisting of supported Pd clusters on Ag(0 0 1) surfaces. This microscopic study is expected to clarify the interplay between the thickness effect and the atomic coordination on the magnetic properties of Pd. An important factor that makes atomic adsorbates different from complete thin films is the important reduction of the symmetry and the coordination.

The electronic and magnetic properties of such islands are calculated by using a tight-binding Hubbard Hamiltonian within the unrestricted Hartree–Fock approximation. This model was already used successfully to study magnetic thin films [8,14], free-standing clusters [15], or supported clusters [16]. Here, we consider Pd islands adsorbed on Ag(0 0 1) surface through a study on two types of atomic arrangements: the first one is formed by one layer thick cluster of 21 atoms, whereas the second consists of two atomic planes of 21 atoms at the interface with Ag and 12 atoms at the surface. The model Hamiltonian used is presented in Section 2. The discussion of the results is reported in Section 3, whereas Section 4 reports the main conclusions of the work.

2. Computational details

The spin-polarized electronic structure is determined by solving self-consistently a tight-binding Hamiltonian for d valence electrons in the unrestricted Hartree–Fock approximation:

$$H = \sum_{i\sigma} \varepsilon_{i\sigma} n_{i\sigma} + \sum_{\substack{\sigma \\ i \neq j}} t_{ij} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma}, \tag{1}$$

where $\hat{c}^{\dagger}_{i\sigma}$ and $\hat{c}_{j\sigma}$ are the operators for the creation and annihilation of d electrons with spin σ at the atomic site i, and $n_{i\sigma}$ the corresponding number operator. The hopping integrals t_{ij} between neighboring atoms i and j are assumed to be spin-independent and are fitted to reproduce the d-band width of Varma and Wilson [17]. The variation of the hopping integrals with the interatomic distance r_{ij} is assumed to follow a power law [18]:

$$t_{ij} = t^0_{ij} \left(\frac{r_0}{r_{ij}} \right)^5 \tag{2}$$

where t^0_{ij} are the hopping integrals at the bulk equilibrium distance r_0. At the Pd–Ag interface the hopping $t_{\mathrm{Pd–Ag}}$ is given by

$$t_{\mathrm{Pd–Ag}} = \sqrt{t_{\mathrm{Pd–Pd}} \times t_{\mathrm{Ag–Ag}}}. \tag{3}$$

The spin-dependent diagonal terms include the electron–electron interaction through a correction shift of the energy levels:

$$\varepsilon_{i\sigma} = \varepsilon^0_i - \tfrac{1}{2}(J)\mu_i + \Omega_i. \tag{4}$$

The energy ε^0_i is the paramagnetic metallic d level of species i. The second term is the shift due to the spin polarization of the electrons at site i ($\mu_i = \langle N_{i\uparrow} \rangle - \langle N_{i\downarrow} \rangle$). The spin-dependent local electronic occupations $N_{i\sigma}$ are self-consistently determined from the local densities of states $n_{i\sigma}$:

$$\langle N_{i\sigma} \rangle = \int_{-\infty}^{\varepsilon_{\mathrm{F}}} n_{i\sigma}(\varepsilon)\, \mathrm{d}\varepsilon, \tag{5}$$

which are calculated at each iteration by using the recursion method [19]. The self-consistent correction Ω_i assures the local charge d electronic occupation which was fixed to 9.52 electrons for Pd in agreement with ab initio calculations [3–5] and to 10 electrons for Ag. The exchange integral J for Pd is deduced from the value (0.65 eV) derived by Christensen et al. [13] within the LMTO method by taking into account the modification of the lattice parameter of Pd atoms epitaxially grown on Ag substrate. Indeed, the lattice parameter of Ag being bigger than that of Pd, the hopping integral between Pd atoms in the Pd cluster is now 0.52 eV by using Eq. (2). One can notice that the value of the exchange integral $J = 0.52$ eV used here is below the value 0.58 eV necessary to lead to the onset of magnetism in bulk Pd with the lattice parameter of Ag (epitaxial growth). In this way we underestimate somewhat the onset of spin polarization in Pd systems.

This model is very useful to study nanostructured materials without translation of symmetry since the calculations are performed in real space. Even if it is extremely crude, the model gives interesting general trends which are always confirmed by ab initio calculations [8,14–16,20].

3. Results and discussion

The clusters considered here (Fig. 1) consist either of one layer of 21 Pd atoms or of two layers of 21 atoms at the interface and 12 atoms at the surface. Both clusters are ordered at ideal lattice positions of Ag(0 0 1) surface. By considering such sufficiently thin small atomic layers we place ourselves in the situation of low coverages where the Ag lattice constant is generally maintained in Pd. Let us point out that the interlayer relaxation has been studied in detail for Ru and Rh overlayers on Ag(0 0 1) by Wu and Freeman [21] within full-potential linearized augmented plane wave (FLAPW) method. The overlayer relaxation was found to be very small and to have no significant effect on the magnetic properties.

On the other hand, with such supported clusters, it is possible to clarify the effect of the atomic coordination through different inequivalent atoms on the onset of magnetism in Pd. In this way, we would like to check if the thickness effect displayed in the case of Pd complete adlayers on Ag(0 0 1) is maintained for low coverages (one and two incomplete atomic layers in our case).

For 21 Pd atoms ordered on one layer, we find a paramagnetic state, as in the case of one complete atomic layer [8]. The onset of magnetism in this island appears from a critical

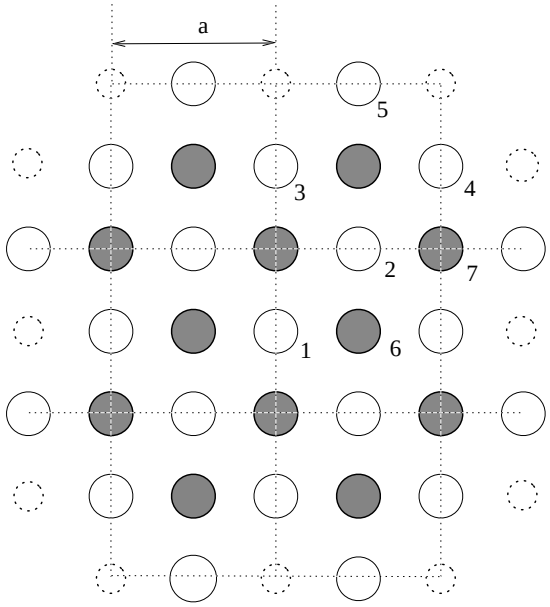

Fig. 1. Schematic view of the two islands of Pd considered at the Ag(0 0 1) surface. (i) 21 Pd atoms (circles) ordered on one layer (five inequivalent sites labeled 1–5); (ii) island of 33 atoms distributed on two layers: 21 atoms (circles) at the interface with Ag and 12 atoms (dark circles) at the surface (seven inequivalent sites labeled 1–7). All the atoms occupy ideal lattice positions of Ag atoms (dotted circles) given the parameter *a*.

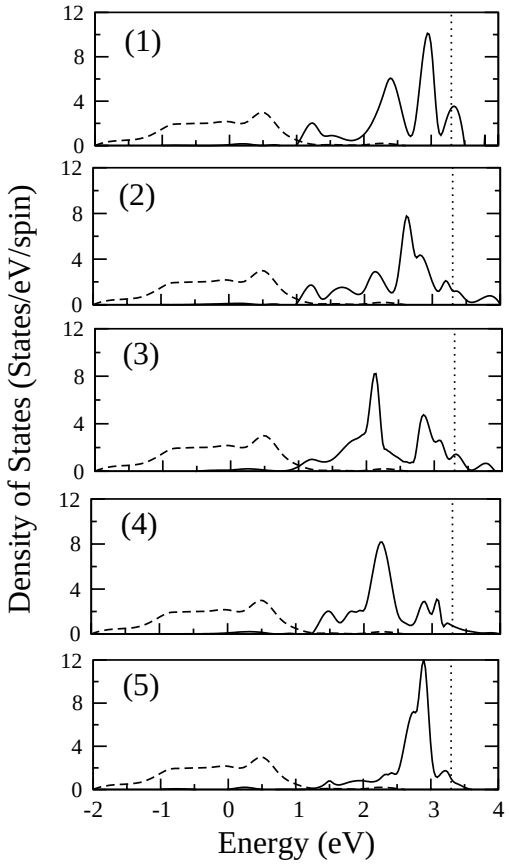

Fig. 2. Paramagnetic density of states calculated on each of five inequivalent atoms (1–5) of the island of 21 atoms ordered on one layer (Fig. 1). Full line corresponds to Pd DOS whereas dashed line is for Ag substrate. The vertical dotted line indicates the Fermi level.

value of the exchange integral $J_c = 0.78\,\text{eV}$ which is very high even with respect to the LMTO value of $J = 0.65\,\text{eV}$ calculated by Christensen et al. [13]. The absence of magnetism on the 21 Pd atoms can be explained by the calculated paramagnetic density of states (DOS) (Fig. 2) on each of the five inequivalent atoms of Fig. 1. Indeed the surface peak which appears on the DOS (Fig. 2) of atoms 1–5 fall far below the Fermi level giving rise to very low DOS at the Fermi energy (E_F). The Stoner like-criterion $J \times \text{DOS}(E_F) \geq 1$ is not satisfied anymore so that none of the five Pd atoms of the cluster is magnetic. From positions 1 to 5 of such atoms, the number of nearest and next-nearest neighbors decreases, but the highest coordinated atom (1) which has eight Pd neighbors in the first two coordination spheres displays a higher paramagnetic DOS at E_F than the less coordinated one (atom 5) which has only three next-nearest neighbors. This result confirms once more the peculiarity of Pd versus the onset of ferromagnetic behavior. The onset of magnetism in Pd systems cannot be related directly to the atomic coordination neither to the surface effect.

The enlargement of the cluster of 21 Pd atoms by adding a second layer of 12 atoms as shown in Fig. 1, gives rise to a completely different situation. The onset of the spin polarization is shifted to lower values of the exchange integral so that we obtain a magnetic moments from a critical value $J_c = 0.45\,\text{eV}$ which is much smaller than the value of $J = 0.52\,\text{eV}$ used here.

We report in Fig. 3a, the magnetic moments on each of the seven inequivalent atoms of the clusters of 33 atoms (Fig. 1): five atoms (labeled 1–5) at the interface with Ag and two atoms (6 and 7) at the surface. In Fig. 3b, we plot the corresponding paramagnetic DOS at the Fermi energy as well as that obtained for the five inequivalent atoms of the first cluster of 21 atoms. As we can see in Fig. 3b, the adsorption of the second layer on top of the first one is characterized by an enhancement of the paramagnetic DOS at E_F and therefore by an onset of magnetic moments relatively large.

Atoms 1, 4, 5 and 7 bear sizeable magnetic moments (0.15, 0.4, 0.17 and $0.21\mu_B$). The mean magnetic moment per atom is of the order of the value ($0.17\mu_B$) obtained in the case of bilayer on Ag(0 0 1) by Blügel [10]. However, it is difficult to deduce any simple connection between magnetism and atomic coordination in Pd systems. From the tendency of bulk Pd to develop magnetic moment upon expansion one could expect onset of magnetism on the first cluster of 21 atoms. However, this is clearly not true as we have seen in the case of the magnetic moments obtained in the case of the ML thick cluster of 21 atoms. Another interesting fact is the onset of magnetism when the thickness of the slab increases. It seems therefore that the formation of the cluster (thickness and atomic aggregation) is the most important factor which determine the magnetism

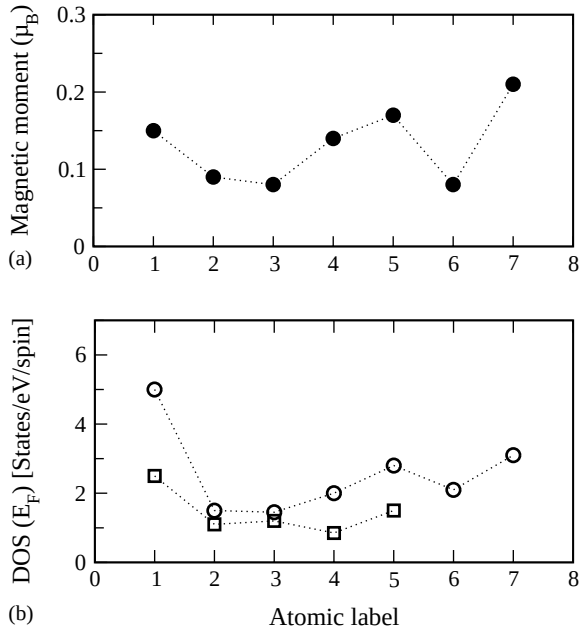

Fig. 3. Calculated magnetic moments (a) on the seven inequivalent atoms (1–7) of the island of 33 atoms ordered on two atomic layers (Fig. 1). The corresponding paramagnetic DOS at E_F (b) are also reported (circles) together with that obtained in the case of the island of 21 atoms with five inequivalent sites (1–5) ordered on one layer.

of Pd systems. This confirms the proposal of Bouarab et al. [22] in the case of free-standing Pd films concerning the appearance of bonding and anti-bonding d–d states which could modify the DOS at the Fermi level (Stoner criterion).

4. Conclusion

In this work, we have reported results concerning magnetic properties of adsorbed Pd clusters on Ag(0 0 1) surface which are consistent with the thickness effect on the onset of magnetism in Pd films. Indeed, some atomic aggregation is needed for Pd atoms in order to become magnetic. One layer of 21 atoms at lattice spacing of Ag is not magnetic, whereas an enlargement by adding 12 atoms on the top of the first 21 atoms shows a net magnetic moments. It seems clearly that the onset of magnetization is a competition between d–d bonding and anti-bonding and the positions of these peaks relative to the Fermi energy.

Acknowledgements

This work was supported by the Algerian project ANDRU/PNR3 (AU4 499 02) and by a collaborative program DEF-CNRS between the University Louis Pasteur of Strasbourg, France and the University Mouloud Mammeri of Tizi-Ouzou, Algeria.

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