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Magnetic properties of Pd atomic chains formed during submonolayer deposition of 3d metals on Pd(110)

O V Stepanyuk[1,2], P A Ignatiev[2], N N Negulyaev[2], A M Saletsky[1] and W Hergert[3]

[1] Faculty of Physics, Moscow State University, Moscow 119899, Russia
[2] Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany
[3] Fachbereich Physik, Martin-Luther-Universität, Halle–Wittenberg, Friedemann-Bach-Platz 6, D-06099 Halle, Germany

E-mail: stepanyuk.ov@gmail.com

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Abstract
Recently, an unusual intermixing-driven scenario for the growth of atomic Pd chains on a Pd(110) surface during deposition of 3d metal atoms has been predicted (Stepanyuk 2009 *Phys. Rev.* B **79** 155410) and confirmed by STM and STS experiments (Wie *et al* 2009 *Phys. Rev. Lett.* **103** 225504). Performing *ab initio* calculations we demonstrate that Pd atomic chains grown above embedded Fe atoms exhibit magnetic properties which depend on the substrate mediated exchange interaction between the Fe atoms.

1. Introduction

Bulk palladium has a large susceptibility, but nevertheless it is a paramagnetic material [1]. The absence of magnetic order in Pd can be explained using the Stoner criterion [2]. Although the density of states $D(E_f)$ shows a sharp peak just below the Fermi level, the Stoner criterion [2] for ferromagnetism $D(E_f)I \geq 1$ is not satisfied as the Stoner parameter I is about 0.7 for Pd [1]. Nevertheless, Pd is close to a ferromagnetic instability [3]. The magnetic properties of Pd clusters and nanoparticles have been studied a lot in both theoretical [4–11, 13] and experimental [3, 12, 14, 15] investigations. It was revealed that the low dimension and lower coordination number of these clusters and nanoparticles results in enhancement of their magnetism. Another possibility to induce magnetism in palladium structures is the introduction of a weak concentration of a 3d impurity. Many years ago, Constant [16] and Gerstenberg [17] showed that dilute solutions of cobalt in palladium are ferromagnetic, and that the magnetic moment associated with one cobalt atom in palladium exceeds that of pure cobalt. Crangle [18] found ferromagnetism in solutions of iron in palladium as dilute as 1.25% iron. As Gerstenberg and Crangle pointed out, it must be concluded that some of the magnetic moment resides on the Pd atoms. Bozorth *et al* [19] showed that ferromagnetism existed in solid solutions of Co in Pd as dilute as 0.1% although the distance between Co atoms was about 10 Å indicating a ferromagnetic interaction between the Co atoms at these long distances. The above mentioned experiments suggested that the solute atom polarizes the surrounding Pd atoms to form a 'giant' magnetic moment. The total magnetic moment of a polarized cloud may be as much as 10 μ_B with average Pd moments of 0.05–0.4 μ_B [18, 20, 21]. Such a polarization cloud may consist of 200 host atoms [18]. The spatial extent of this cloud ranges from 10 to 50 Å. *Ab initio* calculations have revealed giant moments for 3d impurities in Pd [20]. Recently it has been predicted that an external electric field can induce a magnetic moment on a Pd surface [22]. Cheng and colleagues have shown that Pd–Fe multilayers have an average moment of 0.32 μ_B distributed to a depth of about 20 Å from the Pd/Fe interface [23]. In some cases the coupling between magnetic moments in Pd clusters could be antiferromagnetic as has been predicted by theory and *ab initio* calculations [8, 9]. Antiferromagnetic spin correlations in Pd–Fe alloys were also reported [24].

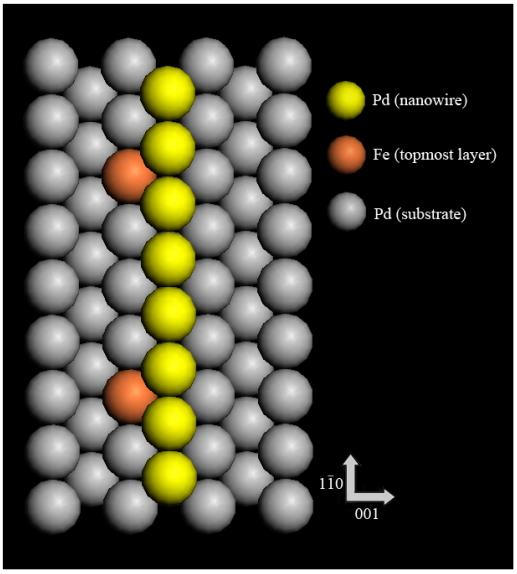

Figure 1. 1.3 × 10 × 7 Pd(110) elementary cell structure (top view).

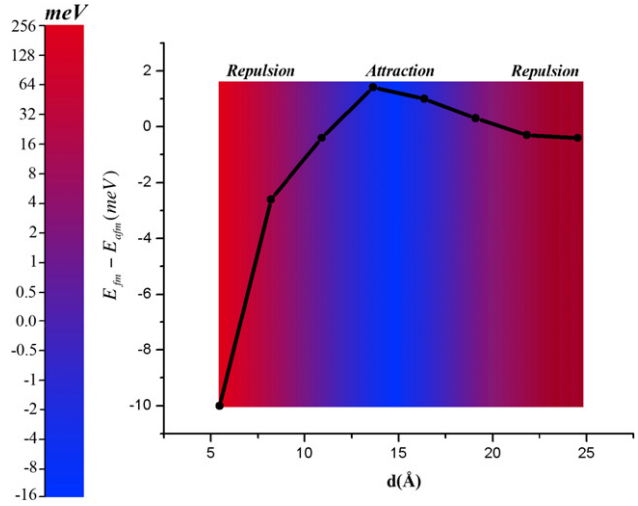

Figure 2. The exchange interaction between Fe impurities embedded in the Pd surface. The color map corresponds to the interaction energy values.

The direct antiferromagnetic exchange interaction between Fe atoms was proposed to lead to such correlations.

Our recent *ab initio* studies and Monte Carlo simulations have revealed an intermixing-driven scenario for the growth of Pd chains on Pd(110) [25]. It has been found that the deposited 3d atoms incorporate into the topmost substrate layer. Formation of a disperse array of 3d atoms within the topmost Pd layer has been demonstrated. Quite surprisingly growth of atomic chains consisting mainly of the expelled Pd atoms has been predicted. This unusual scenario of self-assembly of Pd chains has been confirmed by experiments [26]. In this paper we present *ab initio* studies of the interaction between the Fe atoms in the Pd(110) surface and the magnetic properties of the Pd chains formed during the deposition of 3d adatoms. Our study shows that the Pd chains can be in both ferro- and antiferromagnetic states stabilized by the substrate mediated exchange interaction between embedded magnetic atoms. To the best of our knowledge, our work demonstrates for the first time the possibility of magnetism in Pd chains on metal surfaces.

2. Method

In our calculations we use the Korringa–Kohn–Rostoker (KKR) Green's function method in the atomic spheres approximation [10, 27]. This method is based on the density functional theory in the local spin density approximation. The KKR approach exploits the properties of the Green's function of the Kohn–Sham equation, in particular the fact that the electronic density can be expressed through the imaginary part of the energy-dependent Green's function of the system. An arbitrary system can be regarded as the perturbation of an ideal one with a known Green's function: the Green's functions of these two systems can be linked through the Dyson equation [28]. We treat a surface as a 2D perturbation of an ideal crystal bulk with a slab of vacuum. Taking into account the translational symmetry of the surface geometry, the Green's function is formulated in momentum space. Adatoms and chains are considered as perturbations of the clean surface. These calculations are performed in real space. The exchange energies of compact systems (where the charge redistribution is significant) are calculated as the differences between the total energies of fully self-consistent ferromagnetic and antiferromagnetic solutions.

Interaction energy values for unrelaxed geometries have been calculated with the KKR method. These results have been checked by the VASP code [29]. The comparison has shown a good agreement between the results obtained by these two methods. Calculations of magnetic moments and interaction energies between Fe impurities in a Pd surface in a fully relaxed geometry have been performed by the VASP code [29] in the Perdew–Wang 1991 version of the generalized gradient approximation [30]. PAW pseudopotentials have been exploited in our calculations [31].

VASP simulations were performed on a periodical supercell constructed from seven 3 × 10 Pd (110) layers as shown in figure 1, where the four bottom layers were fixed to reproduce bulk properties. The calculations were performed using a 3 × 2 × 1 mesh in the Brillouin zone. The optimized atomic geometries were achieved when the forces were smaller than 0.01 eV $Å^{-1}$. Fe atoms were embedded into the topmost layer of the Pd(110) surface, and the Pd atoms lined up into surface nanowires, as was shown in our recent work [25].

3. Main results

First, we discuss the exchange interactions between embedded Fe impurities in the topmost layer of the Pd(110) surface. Our calculations have revealed that the iron atoms at the first neighbor positions exhibit strong ferromagnetic coupling, about 170 meV. Increasing the distance between Fe impurities

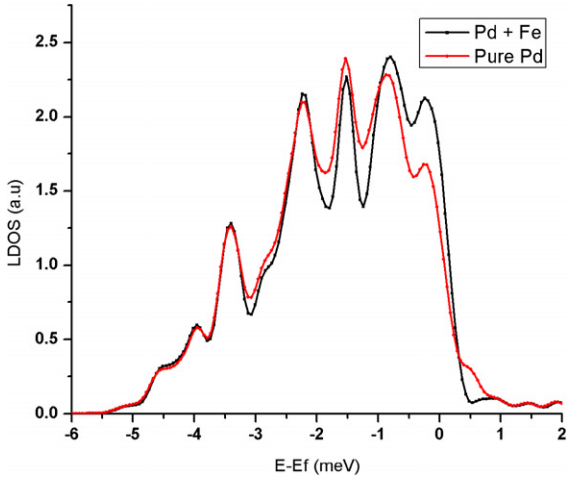

Figure 3. Surface chain Pd d-state density. The red graph corresponds to a configuration with a pure Pd surface under the chain, the black one describes chain Pd d-states when one Fe atom is embedded in the topmost layer under the chain. Zero energy corresponds to the Fermi energy.

leads to a reduction of the ferromagnetic interactions. For distances larger than 5 Å, the interaction is caused by the Pd electrons, i.e. it is a substrate mediated interaction. The exchange interaction exhibits oscillatory behavior. For distances between 11 and 18 Å the coupling between Fe impurities is antiferromagnetic and it becomes weakly ferromagnetic for distances larger than 20 Å.[4]

During deposition at low temperatures impurities can embed almost immediately at any position on the surface [25]. Therefore it is important to study interactions between Fe impurities for short, intermediate, and large separations.

Our *ab initio* results obtained in fully relaxed geometry (color map in figure 2) reveal that up to approximately 8 Å (third neighbor position) the interaction is repulsive, changing from 290 meV (first neighbor position) to a only few meV for 10 Å. For distances from 10 to approximately 17 Å the interaction between Fe impurities is attractive with a value of about 5–10 meV. For larger distances the interaction becomes repulsive again.

The above discussed results for the exchange interactions and interaction energies suggest that Pd chains grown above embedded Fe impurities [25] may exhibit interesting magnetic properties. First, we demonstrate that Pd atoms become magnetic in the presence of an Fe atom embedded in a surface. We have found that Pd atoms exhibit a magnetic moment of about 0.15 μ_B if they are in close proximity to the Fe atoms. To explain this result we apply the Stoner criterion [2]. According to the Stoner criterion we have to compare the paramagnetic DOSs of Pd atoms in the presence and absence of Fe impurities. Our calculations are presented in figure 3. Distinct increase of the DOS at the Fermi level could be observed for Pd atoms contacting Fe atoms. That fact proves that embedding of a 3d impurity into the Pd topmost layer triggers magnetic behavior of the surface Pd chains.

Due to the disperse distribution of Fe impurities embedded in the Pd surface, they could be found in regions of ferro- and antiferromagnetic coupling (see figure 4). We

[4] If the distance between nearest adatoms is larger than 5–10 Å (figure 2), the distance between next neighbor atoms is 10–20 Å. For such distances the effect of the second atom on the exchange interaction plays only a minor role due to very small values of the exchange energies.

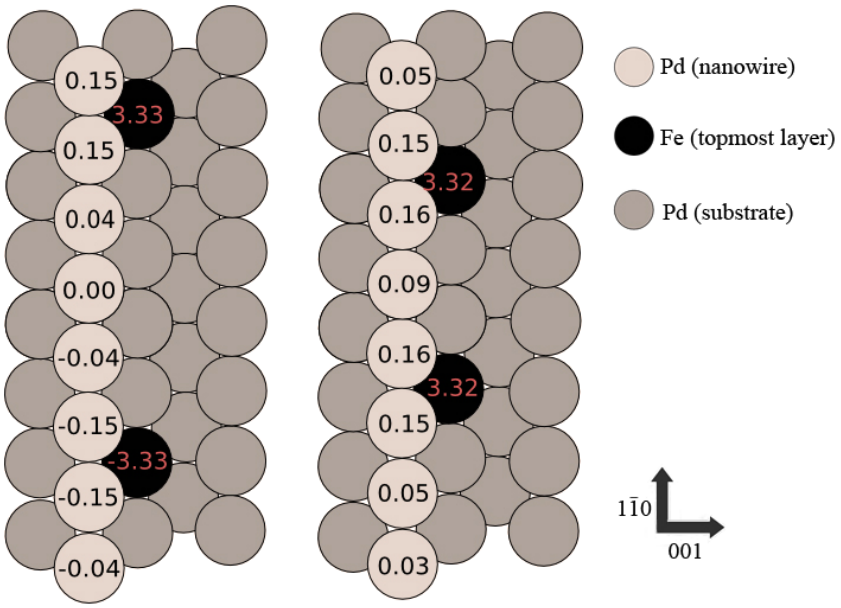

Figure 4. Magnetic moments (μ_B) of Pd nanowires grown atop embedded Fe atoms. The left (right) sketch illustrates the case of antiferromagnetically (ferromagnetically) coupled Fe impurities. In the case of antiferromagnetically coupled Fe impurities, the magnetic moments change their sign at the center of the Pd ad-chain.

performed calculations of the magnetic moments of Pd chains grown above Fe impurities in both cases—when the Fe atoms are coupled ferromagnetically, being located, for example, on a third neighbor position, and for antiferromagnetic coupling at fifth neighbors. In both cases the Pd is coupled ferromagnetically with neighboring Fe atoms. In the ferromagnetic configuration the magnetic moment of the embedded Fe is 3.32 μ_B, the magnetic moment of the first neighboring Pd atoms is about 0.15–0.16 μ_B, which decreases to 0.04 μ_B for the next atom in the chain, so the Pd atoms form a ferromagnetic chain. Considering the antiferromagnetic configuration of the embedded Fe atoms (3.33 μ_B), the first neighboring Pd atoms have a magnetic moment about 0.15 μ_B, which decreases to 0.04 μ_B for the next atoms in the chains. In that case, the Pd nanowire atoms exhibit spin alternation, i.e. the spin directions of the Pd atoms could be different along the chain.

In summary, we performed *ab initio* calculations of the magnetic properties of Pd chains on the Pd(110) surface in the presence of embedded Fe impurities. It was found that (i) the exchange interaction between Fe impurities exhibits an oscillatory behavior, (ii) the Pd atoms in the chain are coupled ferromagnetically with the nearest embedded Fe impurities, (iii) the Pd chains could be in the ferromagnetic state or exhibit spin alternation.

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