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Palladium magnetism induced by external electric field in Pd/BaO/Au structure

© A.S. Korshunov[1], Yu.B. Kudasov[1,2], V.N. Pavlov[1]

[1] Russian Federal Nuclear Center, All-Russia Research Institute of Experimental Physics,
Sarov, Russia
[2] Sarov Physics and Technology Institute of the National Research Nuclear University „MEPhI“,
Sarov, Nizhny Novgorod oblast, Russia
E-mail: korshunov@ntc.vniief.ru

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Since palladium is a nearly ferromagnetic paramagnet, a strong electric field in the layered metal/insulator/metal nanostructure can convert it into a ferromagnetic state. The electronic structure calculation of modified solid nanocell Pd/BaO/Au type under external electric field has performed. The structure relaxation was taken into account. The difference of Pd electronic structure was analyzed in structures with Pd and Au slabs in external electric field. The calculation of nanocell was done in spin-orbit and spin-polarized cases. It has been shown that in a structure with alternating layers of palladium and a more electronegative metal, e.g. gold, the threshold electric field required for the transition to a ferromagnetic state is reduced.

Keywords: Magnetism, Nanostructure, Density functional theory, Induced electric field, Density of state.

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1. Introduction

Controlling the magnetic state of matter using an electric field is one of the main directions in the development of promising memory elements with low energy consumption [1]. Both multiferroics, including those in the nanostructured state [2], and nanostructures with alternating dielectric or ferroelectric interlayers and magnetic layers are used to create them [3]. Moreover, the magnetic material must be sensitive either directly to the electric field or to deformations caused by the reverse piezoelectric effect in the dielectric.

Pure palladium belongs to the so-called almost ferromagnetic metals [4]. Its paramagnetic susceptibility χ turns out to be almost an order of magnitude higher than the susceptibility χ_0, which would be expected for non-magnetic metals within the framework of the collectivized electron model. According to Stoner's theory [5],

$$\chi = \frac{\chi_0}{1 - I\rho(\varepsilon_F)}, \tag{1}$$

where I is the parameter of the interelectronic interaction, $\rho(\varepsilon_F)$ is the density of states (DOS) at the Fermi level. This leads to the Stoner criterion for the transition to the ferromagnetic phase: $I\rho(\varepsilon_F) > 1$. Thus, even a slight increase in DOS at the Fermi level (on the order of 10 %) should lead to the transition of paramagnetic palladium to the ferromagnetic phase. Therefore, relatively weak effects can initiate ferromagnetic ordering in palladium: magnetic impurities, structural distortions (for example, in the amorphous phase it turns out to be ferromagnetic [6]), a nanostructured state, etc. It should be noted that palladium is widely used in chemical catalysis [7], including in the form of magnetic nanoparticles [8].

A mechanism for controlling palladium magnetism in a Pd/dielectric/Pd type nanostructure under the action of a potential difference applied to alternating palladium layers was proposed in Ref. [9]. A strong electric field, which can be created in nanostructures, forms excessive or reduced concentrations of electrons in the surface layers of the metal, and thereby changes the density of charge carrier states. It should be noted that in recent decades, the method of electrostatic doping of interface layers and ultrathin films with an electric field has become widespread [10], in particular, for controlling their magnetization [11,12]. There is a peak in the density of states just below the Fermi level in bulk palladium, so a decrease in the electron concentration is equivalent to a decrease in the Fermi level, i. e., its displacement to the peak region [13]. Thus, the condition of transition to the ferromagnetic state can be achieved.

The effect of excess electric charge in surface layers on magnetic susceptibility has been experimentally observed in nanocrystalline palladium particles [13]. Calculations in Ref. [9] have shown that in order to achieve the Stoner criterion in a layered Pd/dielectric/Pd nanostructure, very strong electric fields (of the order of 1 V/nm) are required, which can lead to dielectric breakdown. In this regard, the authors have considered special methods to reduce the threshold electric field. In particular, it was proposed to apply a ruthenium monolayer to the palladium-insulator interface to change the partial DOS on palladium. Modification of the magnetism of the PdCo film by an electric field was demonstrated in Ref. [14], and a thin layer of electrolyte was used to enhance the field effect. Later, the possibility of such a transition was shown experimentally already in a nanostructure with layers of pure palladium [15], where a nanolayer of an ionic liquid was used to enhance the efficiency of the electric field. For practical applications in microelectronics, it is desirable to create a „dry“ nanostructure without adding films in the liquid phase.

We study the structure of Pd/dielectric/Pd in this paper, as well as the structure with alternating layers of palladium and gold as a more electronegative metal. In this case, it can be expected that the built-in electric field reduces the concentration of electrons in the palladium surface layer. In this case, the Fermi level shifts to the region of the peak density of the states [9], which should lead to an increase in the density of states even in the absence of an external electric field. BaO was chosen as the insulator because its crystal lattice is in good agreement with the palladium lattice. The first-principle modeling of Pd/BaO/Pd and Pd/BaO/Au nanostructures with an electric potential applied to alternating metal layers is performed. At the same time, unlike the study in Ref. [9], in which the external electric field was taken into account through indirect estimates, in the current study, direct modeling of structures with an external potential applied to metal layers was carried out.

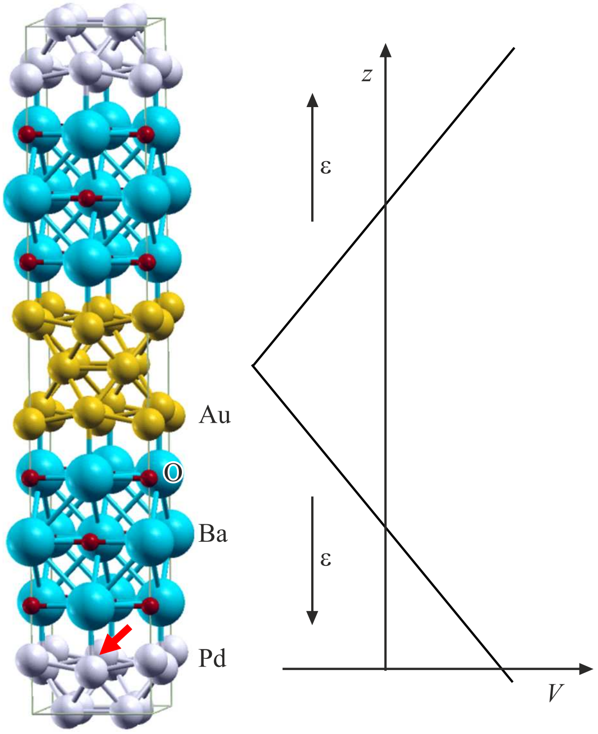

Figure 1. Calculated supercell (on the left) with layers of palladium, gold and insulator (Pd is shown with white balls, Ba — blue, Au — gold, O — red) and an applied electric field (on the right) in the form of a zig-zag potential [20].

2. Calculation method

The calculations were performed within the framework of the density functional theory using the full-potential method of coupled plane waves with local orbitals (FP-LAPW+lo), implemented in a specialized WIEN2k software package taking into account local orbitals [16,17]. The calculated grid in the Brillouin zone contained 2000 points (132 in the irreducible part); the exchange-correlation potential was calculated using the generalized gradient approximation in the Purdue-Burke-Ernzerhof formulation GGA-PBE [18]. The calculation of the states of localized electrons at deep levels (below the energy 7 Ry from the Fermi level) was completely relativistic in all cases. Calculations for valence electrons were performed in two versions: both taking into account the (SO) and without taking into account the (NSO) spin-orbit interaction. The spin-orbit interaction was included in the calculation only on palladium and gold atoms and was introduced as a secondary variational procedure using scalar-relativistic eigenfunctions as a basis. At the same time, the standard basis was extended by local orbitals $p_{1/2}$ [19]. In all calculations, the convergence in charge and energy was 10^{-4} electrons and 10^{-6} Ry per cell, respectively.

The supercell shown in Figure 1, consisting of alternating layers of palladium, gold, and a BaO insulator, was used for calculations. In fact, taking into account periodic boundary conditions for a supercell in the plane of the layers, the study was performed for a system of ultrathin 2D films (slabs) consisting of three monolayers Pd (seven unequal positions), three monolayers Au (seven unequal positions) and separating them three monolayers BaO. In total, the supercell contained 32 unequal positions of atoms. Since the applied external electric field was chosen in the form of a zig-zag potential [20], implemented in the Wien2k package, in order to meet the conditions for the periodicity of the structure, the unit cell must be doubled along the axis z (perpendicular to the layers). To estimate the change in the densities of states on Pd, two different calculations were performed — taking into account and without taking into account the external electric field.

Prior to calculations with the electric field, a preliminary optimization of the equilibrium positions of atoms inside the unit cell was carried out. The cell size along the axis z (perpendicular to the plane) was also minimized, since it was assumed that the lateral dimensions of the structure correspond to the equilibrium values for BaO. Structural relaxation was carried out from the initial positions of the atoms determined for the bulk crystal structure to forces not exceeding 10 mRy/Bohr. The initial values of the forces in the nonrelaxed structure reached 800 mRy/Bohr.

Several types of calculations were performed: Pd/BaO/Pd structures with and without electric field to obtain the initial state of the Pd electronic structure for further comparison, as well as Pd/BaO/Au structures in the SO and NSO variants with and without electron spin polarization. It should also be noted that one of the main difficulties in calculating the electronic structure due to the large number of unequal atomic positions and low symmetry due to the lack of a cell inversion center was the weak convergence of the total energy solution, especially in the absence of an external electric field, which significantly increased the calculation time.

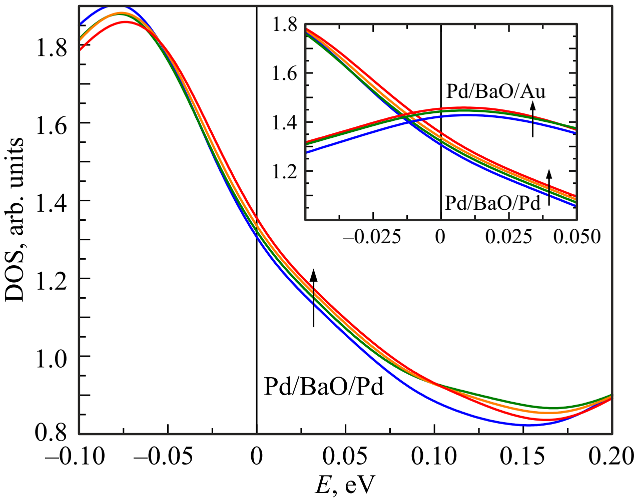

Figure 2. Partial density of palladium atom states in the Pd/BaO/Pd structure as a function of energy under applied external electric field $\varepsilon = 0$, 0.1, 0.3, 0.5. The energy is calculated from the Fermi level. The inset shows an enlarged fragment of the graph and the density of states on the palladium atom in the Pd/BaO/Au structure at $\varepsilon = -0.1$, 0, 0.1. The arrows show the order of the curves as the amplitude of the electric field increases.

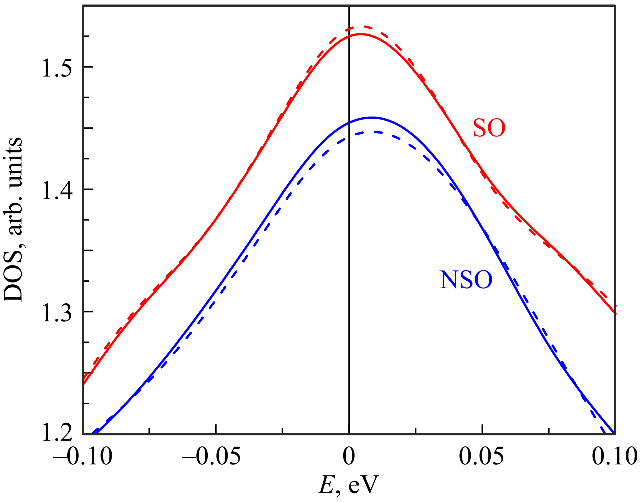

Figure 3. Comparison of partial DOS in the palladium layer in the Pd/BaO/Au structure without taking into account the spin-orbit interaction (NSO) and taking into account (SO). Dotted lines correspond to $\varepsilon = 0$, solid lines correspond to $\varepsilon = 0.1$.

3. Results and discussion

To compare the results, the densities of palladium's electronic states for the Pd/BaO/Pd supercellular were first calculated as a function of the potential difference between the metal electrodes. Partial palladium absorption curves normalized per atom are shown in Figure 2. Here and further, the results for the Pd atom in the center of the cell are shown as partial palladium DOS (shown by the bold red arrow in Figure 1). Partial DOS on other Pd atoms differed slightly. As expected, the electric field causes the Fermi level to shift to the peak region in the palladium layer. The electric field in Figure 2 is given in relative units: $\varepsilon = 1$ corresponds to approximately 8.7 V/nm. It can be seen that $\varepsilon = 0.5$ increases DOS by 5 %, i. e., approximately $\varepsilon = 1$ is needed to enter the ferromagnetic phase, which is consistent with the estimates in study [9]. In reality, the Stoner criterion is only a very approximate estimate of the critical field, since simultaneously with the shift in the Fermi level, the shape of the DOS also changes (Figure 2). Nevertheless, it is obvious that in order to achieve the Stoner criterion, it is necessary to apply a huge external electric field, which is unlikely to be realized experimentally without degradation and electrical breakdown of the BaO interlayer.

Replacing palladium with a metal with a higher electronegativity [21] induces a built-in electric field in the gap between the conductive layers, which can be used to lower the threshold value of the electric field required to convert the palladium layer to a ferromagnetic state. To test this hypothesis, calculations of the Pd/BaO/Au structure were carried out, similar to those carried out above. It should be noted that the difference between the standard potentials of palladium and gold is about 0.7 V, which is a qualitative estimate of the potential difference between the metal electrodes Pd and Au. In a structure with three BaO monolayers, the built-in electric field strength is of the order of 1 V/nm, which, according to estimates by the Stoner criterion, is sufficient for the transition of the structure to a ferromagnetic state.

The inset in Figure 2 shows that replacing palladium with gold dramatically increases the density of states in the palladium layer. In addition, Figure 3 shows the role of the spin-orbit interaction, which also significantly increases DOS. As a result, it can be expected that in a Pd/BaO/Au structure with thin dielectric layers (three monolayers of BaO), the Stoner criterion can be achieved without an external electric field. Indeed, calculations with spin polarization (and spin-orbit interaction) have shown that palladium turns out to be weakly magnetic even in the absence of an external electric field. The magnetic moment is $0.15\,\mu_B$ (in Boron magnetons). This value is about three orders of magnitude higher than the criterion of convergence in charge (10^{-4} electrons), which makes it possible to confidently speak about the ferromagnetic state of palladium. The Pd/BaO/Pd structure remained nonmagnetic with a similar calculation (the magnetic moment did not exceed $2 \cdot 10^{-3}\,\mu_B$). Figure 4 shows the DOS spin splitting for the palladium atom, which also characterizes the

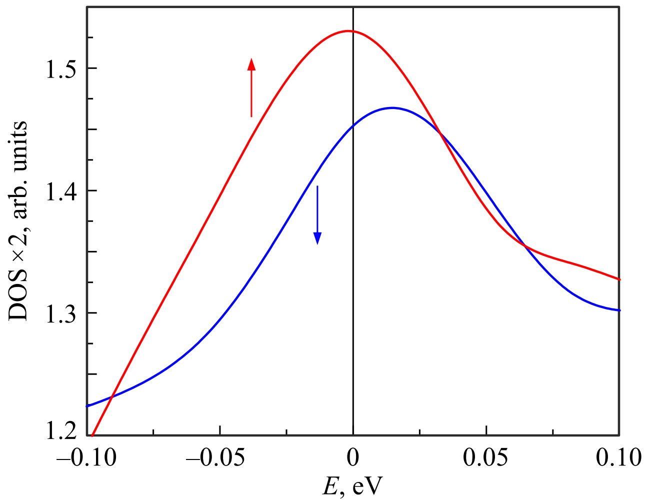

Figure 4. Spin cleavage of partial palladium DOS in Pd/BaO/Au at $\varepsilon = 0.1$. The DOS values have been doubled for convenience of comparison with calculations without spin polarization.

ferromagnetic state. Thus, despite the fact that the estimates according to the Stoner criterion require an electric field value approximately an order of magnitude higher than the field determined by the difference between the standard electrode potentials of gold and palladium, the Pd film in the Pd/BaO/Au structure appears to be in a ferromagnetic state. This may be due to the important role of dielectric polarizability (the relative permittivity of BaO is ~ 10) [9]. Above, we presented the results of calculating DOS for one of the palladium atoms. Other atoms are also in a spin-polarized state with similar DOS.

4. Conclusion

As a result of the simulation, we performed a numerical estimate of the electric field required to stimulate palladium surface magnetism in a layered structure of the Pd/BaO/Pd type. It is shown that when a palladium layer is replaced with gold, an internal effective electric field is created, which can lead to a significant change in the electronic structure of palladium and a decrease in the threshold external electric field. In the Pd/BaO/Au structure with very thin BaO layers (three monolayers, 0.8 nm), a weak spontaneous magnetization occurs in palladium layers even in the absence of an external field, which changes noticeably under the influence of an external electric field. Therefore, for experimental research, it is better to use structures with thickened BaO layers (up to ~ 1.6 nm) in which there is no spontaneous magnetization of palladium layers. The expected critical electric field in this case is 1 V/nm.

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Conflict of interest

The authors declare that they have no conflict of interest.

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