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Ferromagnetism of Pd(001) substrate induced by antiferromagnetic CoO

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ABSTRACT

Our first-principles study has revealed unexpected spin polarization of the Pd(001) substrate in contact with antiferromagnetic CoO overlayers. We give an evidence that the ferromagnetism of Pd is caused by the zigzag positions of Co atoms with respect to the Pd interface, resulted from the lattice-mismatch driven structural relaxation. Because of the itinerant nature of its 4*d* electrons, we see that the ferromagnetic properties of Pd are highly sensitive to the local environment and can be enhanced further by increasing the thickness of CoO overlayer film or/and by applying an additional uniaxial pressure along c-axis exerted externally on the bottom layers of the Pd substrate. Our finding provides new functionality for the interfacial moments of the CoO/Pd system, which can be accessed experimentally, e.g., by the magneto-optical Kerr effect (MOKE) or/and by element-resolved X-ray magnetic circular dichroism (XMCD) measurement.

Magnetism at interface is a fascinating field of research [1–4]. The reduced dimensionality and the substrate induced effects, such as epitaxial strain, charge transfer and electronic hybridization, often exhibit extremely fascinating effects that are of fundamental interest and technological importance, largely for magnetic data storage and nanoelectronics [5,6].

In particular, the interface effects and the ability to precisely engineer them can enable making a nonmagnetic material magnetic and switching its magnetism on and off, which are the holy grails of spintronics. The fact that the magnetism emerges from a nonmagnet being in touch with ferromagnet is expected [1], but the same arising from a nonmagnet by contact with an antiferromagnet is puzzling since one thinks of antiferromagnets as magnetically neutral.

Since palladium is an element very close to fulfill the so-called Stoner criterion of ferromagnetism [7], it makes nonmagnetic Pd a good candidate for such studies. Much attention has been paid to the magnetic properties of Pd: it was shown that the effect of ferromagnetism in Pd can be achieved by reduced dimensionality [8,9] and/or by quantum well states formed in ultrathin Pd films [10]. It is also well known that the neighboring 3*d*-ferromagnet can spin-polarize a nonmagnetic metal like Pd [11]. Many different experimental techniques and theoretical studies have been applied to investigate various combinations of ferromagnet/Pd systems not only to understand the mechanism behind such spin-polarization effect but also for possible applications [12–14]. Especially, the magneto-optical Kerr effect (MOKE) measurements provide valuable information about such systems because the magneto-optical response from the ferromagnet/Pd interface is large [14–17].

Already, upon placing antiferromagnet on a ferromagnet the effects of enhanced coercivity and exchange bias have been reported [2–4]. Now, when antiferromagnet is interfaced with a nonmagnet, it is highly exciting to see whether the same behavior can be met, i.e., whether exchange bias can be observed in the interface between antiferromagnet and originally nonmagnetic material. From application point of view, it would be extremely interesting to switch on magnetism and simultaneously pin the magnetization through the exchange bias to an antiferromagnetic layer.

The polarization of Pd by AFM was considered for the first time in NiO/Pd multilayers [18]. Manago et al. [18–20] suggested that the ferromagnetic properties of such multilayers are related to the induced magnetic moment of Pd of $0.59\,\mu_B$ per interface Pd atom, which persists over a dozen monolayers (ML) away from the Pd/NiO interface. In comparison, the theoretical calculation for FM/Pd systems shows that both the magnetic moments and the number of polarized Pd atomic layers are much smaller [21]. Later on, Hoffmann et al. [22] investigated $(NiO/Pd)_N$ systems, in a form of bilayers ($N = 1$) and multilayers, grown on different substrates by applying polarized neutron reflectometry. In each of the cases, no effect of ferromagnetic Pd was observed. It should be emphasized, however, that Manago et al. and Hoffmann et al. studied the polarization of Pd in systems consisting of thin Pd films, and

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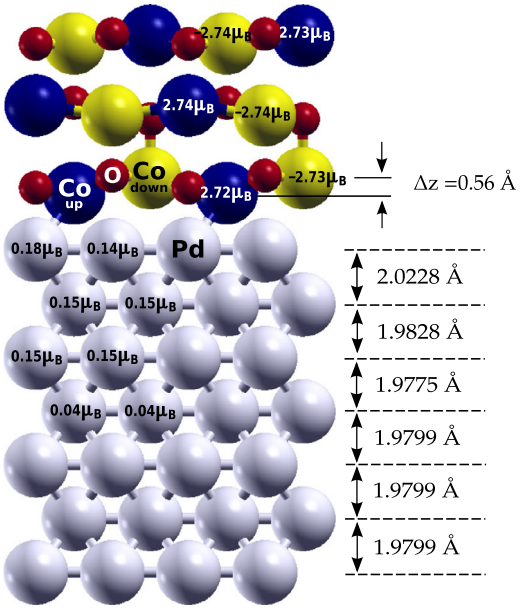

Fig. 1. (Color online.) Pictorial side view of the calculated structure for 3 ML of CoO on Pd(001) substrate. Our structural relaxation, which allows selectively dynamics along z-axis, suggests that, at the interface overlayer, the lattice misfit-induced strain brings Co-up much closer to Pd substrate than Co-down. The interlayer distances, magnetic moments of Co as well as induced magnetic moments of Pd are specified.

with the NiO/Pd sequence repeated many times. In such cases, the structural parameters (crystallographic orientation, lattice constant, quality of the film) cannot be represented by the model system. In particular, such structural modifications can be crucial for the spin-polarization effect, as it will be discussed in this letter.

Up to now no theoretical investigations have shown how the AFM-film can drive ferromagnetism when it is in direct contact with a non-ferromagnetic metal like Pd. Motivated by these considerations, we show for the first time how the AFM thin film (of CoO) induces ferromagnetism in a nonmagnetic substrate [of Pd(001)]. Our finding provides new functionality for the interfacial moments of the AFM(CoO)/FM(Pd) system which can be accessed experimentally, e.g., by MOKE or/and by element-resolved X-ray magnetic circular dichroism (XMCD) measurement.

The crystallographic and spin structure of antiferromagnetic CoO can be described as follows: each Co atom has a spin that is antiparallel to the next Co atom (see Fig. 1), where AFM–Pd could be expected rather than FM–Pd. Therefore, to understand the ferromagnetic behavior of Pd, we study the CoO/Pd(001) system theoretically, using the VASP [23] implementation of DFT, with projector augmented wave (PAW) potentials [24]. We adopt the exchange-correlation functional of Perdew–Wang (PW91) [25] for the generalized gradient approximation (GGA) and an effective Hubbard U [26] of 6.1 eV for Co. Kohn–Sham wave functions are represented using a plane-wave basis truncated at an energy cutoff of 40 Ry and the Brillouin zone integrations are done on a uniform Monkhorst–Pack [27] grid of $19 \times 19 \times 1$. We use supercell geometry with a vacuum of 10 Å in the z direction to ensure negligible interaction between its periodic images. Selected structural relaxation is carried out so as to minimize the forces acting on each of the atoms using a conjugate-gradient algorithm.

The Pd(001) substrate is simulated by a 7-layer slab with the interlayer distances of the three bottom-most layers keeping fixed in its bulk GGA-optimized value of 1.9799 Å (see Fig. 1). Pd(001) has a primitive square net with an in-plane lattice spacing of 2.80 Å, which does not match to that of CoO (3.01 Å). This large in-plane lattice mismatch causes an elastic strain. This strain, as well as the presence of dissimilar neighbor such as those found at the interface and the absence of some neighbors such as those found at the surface, leads to structural relaxations resulting in considerable structural inhomogeneities. Our structural relaxation, which selectively allows dynamics along z-axis, suggests that the lateral registry between substrate and overlayer, where O atoms sit on top of the outermost Pd atoms and Co in fourfold hollow sites, is energetically favorable. This relaxation results in substantially distorted bond angles, different bond lengths and interlayer distortion as evident from Fig. 1 and Fig. 2. At the interface overlayer, this interlayer distortion brings Co-up much closer to Pd substrate (0.56 Å) than the Co-down atoms.

Such structural inhomogeneities evidently influence both the local and the long-range magnetic orderings of the CoO overlayers, resulting in a complex magnetic pattern. For example, an uncompensated magnetic configuration near the interface overlayer

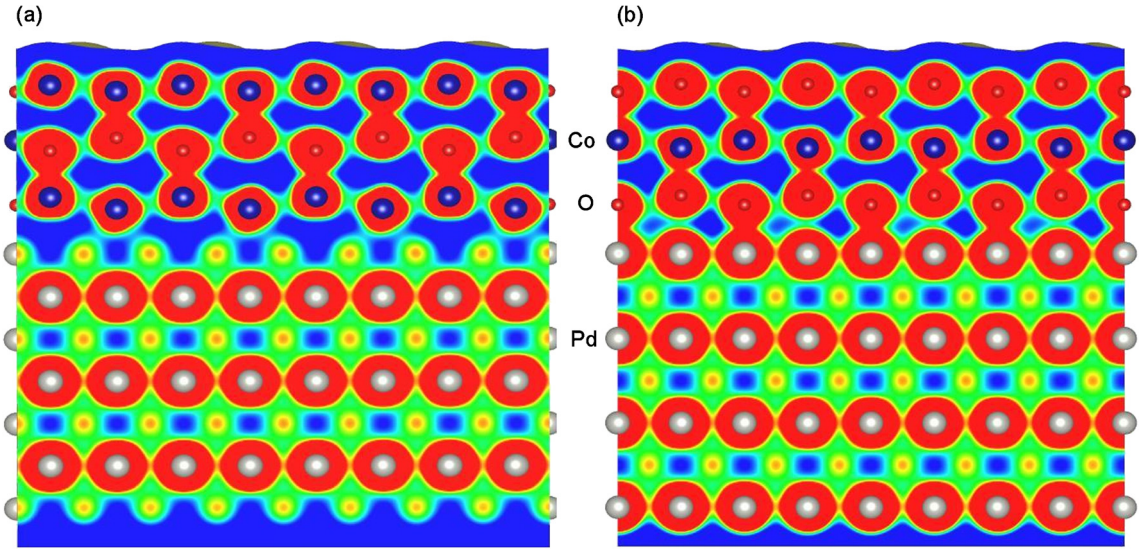

Fig. 2. (Color online.) (a) The color pattern of the calculated valence charge density distribution for 3 ML of CoO on Pd(001) with a cut by [100] plane through Co atoms at interface in order to show how Co atoms couple with Pd atoms at interface, and (b) the same with a cut by [100] plane through O atoms at interface in order to show how O atoms couple with Pd atoms at interface. Deep blue balls (dark and big) represent Co atoms, deep red balls (light and small) represent O atoms and grey balls represent Pd atoms. Besides balls, other blue (dark) represents low valence charge while other red (light) represents a high concentration of valence charge.

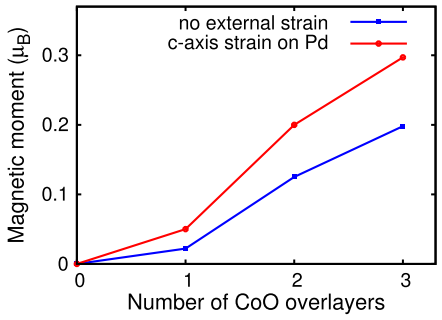

Fig. 3. (Color online.) The calculated induced magnetic moment on Pd interface atoms for (001) substrate as a function of the number of CoO overlayers is plotted. The blue curve (darker) is obtained when the Pd(001) substrate is simulated by a 7-layer slab with the interlayer distances of the three bottom-most layers keeping fixed in its bulk GGA-optimized value of 1.9799 Å, and the red curve (lighter) is for the same system but an additional uniaxial strain (about 1.7%) along c-axis is applied externally on the three bottom-most layers of the Pd substrate.

results from these structural inhomogeneities. When three overlayers of CoO are placed on the Pd substrate, the magnetic moments of Co become $2.72\,\mu_B$ (site up) and $-2.73\,\mu_B$ (site down) at the interface overlayer (I). For the layers $I+1$ and $I+2$, these values are $2.74\,\mu_B$, $-2.74\,\mu_B$ and $2.73\,\mu_B$, $-2.74\,\mu_B$, respectively. The magnetic moment is not completely compensated because the relaxed positions of the Co atoms are no longer equivalent by symmetry and show a zigzag configuration with respect to the Pd surface. The zigzag atom configuration causes spin uncompensation, which in fact induces magnetic moments in Pd layers near the interface, and turns an otherwise nonmagnetic Pd substrate into a ferromagnet.

Note, that, in the case of Ir(001) substrate, the CoO(111) monolayer, where the neighboring Co atoms have, at least partially, opposite magnetic moments, the polarization of the nearby Ir atoms is small [28]. The presence of ferromagnetism in Pd/CoO system is a key result of our study which can be attributed to a combination of several reasons. First of all, Pd is very close to fulfill the so-called Stoner criterion of ferromagnetism due to a high-density of electronic states near its Fermi energy. Secondly, metallic palladium itself is not ferromagnetically ordered, though its magnetic susceptibility is very large due to a high density of electronic states near its Fermi energy. Consequently, such spin induction can stabilize the ferromagnetic order in Pd. Furthermore, in Pd the large itinerant nature of its 4*d* electrons (its 4*d* electrons are much more delocalized than in Ir and Rh) causes a nearly-itinerant-electron like parabolic band structure [29]. This facilitates itinerant band ferromagnetism in Pd and makes its ferromagnetic properties a sensitive function of local environment. As a result, by changing the thickness of CoO overlayer or by reducing interlayer distance a bit for the three bottom-most Pd layers (which can be achieved by applying an external uniaxial pressure along c-axis on the bottom of the Pd substrate), its magnetic moment can be enhanced further, as shown in Fig. 3.

Finally, the spin-polarized Pd behaves like a ferromagnetic film in direct contact with an antiferromagnetic CoO layer. Thus, one can expect a presence of the exchange bias effect (a shift of the loops along the field axis by H_{EB}) and an increase of the coercivity field which is considered as an indication of coupling [30]. Note, however, that the AFM/FM interaction is very sensitive to interface conditions, and most of the parameters involved in such interaction (such as structural imperfection, domain formation and/or spin configuration) are difficult to control.

In conclusion, we demonstrate how the proximity of an AFM thin film (of CoO) drives magnetization to a nonmagnetic metal substrate [of Pd(001)], using a first-principles density functional theoretical investigation. We show that the ferromagnetism of Pd results from the zigzag positions of Co atoms caused by the strain-relief mechanism near the interface. We expect that this theoretical study will be of value in the context of experimental work, especially in MOKE and XMCD, to develop a better understanding of novel functionalities for the interfacial moments of the CoO/Pd(001) system, which furthermore could incite futuristic device applications based on the exciting ability to control the functionality for such interfacial moments.

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