Effect of adsorbed H atoms on magnetism in monoatomic Fe wires at Ir(100)

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By means of *ab initio* calculations based on density-functional theory we demonstrate that magnetism in monoatomic Fe wires deposited on nanostructured Ir(100) surface can be tuned by their functionalization with hydrogen. The pristine monoatomic Fe wires deposited on nanostructured Ir(100) surface partially covered by H atoms are antiferromagnetic. However, the type of exchange interaction between Fe atoms can be changed by increasing H coverage. At fully hydrogenated Ir surface the Fe wires themselves are decorated with hydrogen, which gives rise to the ferromagnetic coupling between adjacent Fe atoms.

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I. INTRODUCTION

With the emergence of nanotechnology it becomes clear that the adsorbates can be used to create new nanostructured materials with unique properties, which can be exploited in various technological applications. The examples of self-organized growth of the adsorbates at metal surfaces include highly ordered arrays of monoatomic Cu wires on the Pd(110) surface[1] or fabrication of Ag nanoislands on the Pt(111) (Ref. 2) through nucleation of deposited metal atoms on carefully prepared substrates. Apart from self-assembly at the support, the adsorbates can also restructure the host surface. The O chemisorption at Cu(110), Ni(110), or Pd(110) surfaces leads to the formation of relatively simple missing or added row structures at Cu(110), Ni(110), or Pd(110) surfaces,[3] as well as much more complex surface oxides at Pd(100), Pd(111), or Rh(110) surfaces.[4,5] Recently Tao *et al.*[6] reported on nanostructuring of hex-Pt(100) surface induced by adsorbed carbon monoxide. The size of produced Pt islands vary in the range from 0.5 to 3.5 nm. Hydrogen adsorption on another metal surface with similar structure, the hex-Ir(100), leads to the formation of periodic one-dimensional nanostructures.[7]

The adsorbate can also be used to tailor more sophisticated properties of low-dimensional systems then just their atomic structure. Baldereschi *et al.*[8] adsorbed CO molecules on Ni(110) surface and accounted for a significant reduction in magnetic moments on Ni atoms with adsorbed molecules. The reduction or quenching in the magnetic moment of NO molecules adsorbed on a Pd_3Mn alloy surface is studied by Delbecq and Sautet.[9] They offered a nice explanation of observed effects performing the orbital interaction analysis. Manipulation of the magnetic properties at the level of a single molecule deposited on a metal surface was achieved by Zhao *et al.*[10] Through the dehydrogenation of the periphery of the cobalt phthalocyanine (CoPc) molecule deposited on Au(111) surface they were able to induce marked changes in molecular structure and consequently the magnetic behavior of the central Co atom in the CoPc molecule.

In the present study we use the density-functional theory (DFT) to demonstrate that the adsorbate can be employed to tailor magnetic order in monoatomic wires fabricated at metal surfaces. As a metal support we consider hydrogenated Ir(100) surface with self-organized microscopically long monoatomic Ir wires. As in experiments,[7] this surface is used as a template to grow microscopically long one-dimensional Fe structure, an approach alternative to standard methods of fabrication of monoatomic wires at vicinal metal surfaces.[11,12] Experimentally produced one-dimensional magnetic structures are composed of monoatomic Fe wires deposited on both sides of the Ir chains. The study of the role of H adsorbates on magnetic properties of the Fe-Ir-Fe sandwiched wires is a complicated task due to ample of possible magnetic configurations. In addition to the problems of the determination of the most favorable type of magnetic order within each Fe chain as a function of H coverage, the number of relevant magnetic configurations is further increased due to the non-negligible magnetic coupling between Fe chains. Hence, in order to simplify the investigation of the effect of H adsorbates on the magnetism in one-dimensional Fe structures, we consider as a model system *single* monoatomic Fe wires deposited on nanostructured Ir(100) surface. The results obtained using this simpler model are the essential step toward the first-principles description of more complex magnetic properties of the experimentally produced Fe-Ir-Fe sandwiched structures.

All previous theoretical studies of Ir supported Fe wires were performed exclusively for clean metal substrates. Spišák and Hafner[13] investigated reconstruction and dereconstruction of hex-Ir(100) surface upon Fe deposition, and reported on nonmagnetic state of biatomic Fe rows on quasi-hexagonal Ir(100). The magnetism of biatomic Fe rows on the same surface was carefully studied by Mazzarello and Tosatti.[14] They included the spin-orbit interaction effects and

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investigated stability of several noncollinear magnetic structures of the Fe wires. Yet, in these works the authors did not consider the presence of hydrogen, which is utilized in the experiments to fabricate nanostructured patterns at Ir(100) surface and can have a profound effect on the magnetism of deposited Fe wires. The focus of our investigation is to elucidate the role of adsorbed hydrogen atoms on magnetic properties of monoatomic Fe chains deposited on nanostructured Ir(100) surface. We demonstrate that the magnetic coupling between Fe atoms can be changed from antiferromagnetic (AFM) to ferromagnetic (FM) by varying H coverage at the surface. In addition, we provide detailed information regarding the H adsorption sites, and the corresponding binding energies, which enables us to identify the driving force leading to the nanostructuring of quasihexagonal topmost Ir layer.

The rest of the paper is organized as follows. A brief description of computational details, given in Sec. II, is followed by presentation of the main results in Sec. III. This section includes the study of surface reconstructing induced by adsorbed hydrogen, as well as magnetism of deposited Fe wires. Section IV is devoted to the discussion of presented results. The concluding remarks are given in Sec. V.

II. COMPUTATIONAL DETAILS

The calculations were performed with the computer code DACAPO,[15,16] using ultrasoft pseudopotentials[17,18] to describe core-valence interactions. The electron wave functions were expanded in plane waves with a cutoff energy of 25 Ry. For the augmented electron density an energy cutoff of 240 Ry was used. The electronic exchange-correlation effects are described via a generalized gradient approximation in the Perdew-Wang (PW91) functional form.[19] For all calculations we used the (5×2) surface cell. The surfaces are modeled by slabs of four fcc(100) layers placed in a supercell with at least 10 Å of vacuum. The Brillouin zone was sampled with 16 special **k** points.[20] The H atoms and two topmost Ir layers are fully relaxed while the rest of the atoms from the Ir slab are fixed in their bulk geometry. The H adsorption energies are referred to half the energy of the gas-phase H_2 molecule. The zero-point energy corrections are not included since they do not affect relative stability of individual adsorption configurations.[21] The spin-orbit interaction, although crucial for description of the properties such as orbital magnetism and magnetic anisotropy energy, is not included in the present calculations, since the spin-orbit related effects influence calculated total energy differences less than 1 meV per Fe atom.[14]

III. RESULTS

A. H induced reconstructing of quasihexagonal Ir(100)

We start the presentation of our results with a brief comparison of H binding at quasihexagonal [Fig. 1(a)] and nanostructured Ir(100) surfaces [Fig. 1(b)] to reveal the effect of adsorbed H atoms on their energetics. Previous studies showed the ability of the DFT to correctly reproduce structural properties of the clean[13,22] or partially hydrogenated quasihexagonal layer.[23] Comprehensive studies of H adsorption configurations at nanostructured and quasihexagonal Ir(100) surfaces are given in Refs. 21 and 24, respectively.

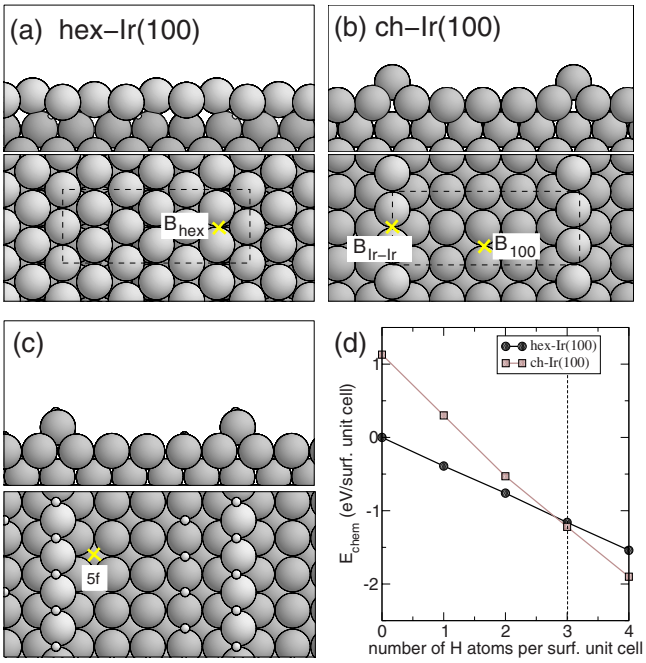

FIG. 1. (Color online) Side and top views of (a) quasihexagonal and (b) square Ir(100) surface with periodic monoatomic Ir wires; big gray and small white spheres represent Ir and H atoms, respectively. (c) The surface from Fig. 1(b) with 0.4 ML of H; (d) total H chemisorption energies E_{chem} as a function of the number of H atoms per (5×2) cell.

According to experiments,[7] upon H adsorption at temperatures above 180 K a quasihexagonal layer reconstructs to the fcc(100) layer, with an additional row of Ir atoms. They form parallel chains, separated on the average by five bulk interatomic Ir-Ir distances [Fig. 1(b)]. We refer to this *chain* iridium structure as the ch-Ir(100) surface. Comparing total energies of two surfaces we found that *clean* ch-Ir(100) is by 0.09 eV per surface atom less stable than the Ir(100)-(5×1)-hex surface. The driving force for the reconstructing is a pronounced difference in H binding at these two surfaces.

In agreement with Ref. 24, we found that the most favorable H adsorption site at hex-Ir(100) is the bridge site denoted as B_{hex} in Fig. 1(a). The calculated binding energy is 0.39 eV. The binding on top of an Ir atom and in the threefold hollow site is 0.32 eV and 0.27 eV, respectively.

The H adsorption at ch-Ir(100) is significantly stronger than at the quasihexagonal surface. The binding energy of a single H atom at bridge site of Ir chains [marked as the $B_{Ir\text{-}Ir}$ in Fig. 1(b)] is 0.83 eV, very close to the value reported in Ref. 21. For H adsorption at bridge sites on the terraces, denoted as B_{100} in Fig. 1(b), we calculated binding energy of 0.7 eV. Noticeable stronger H binding energies at the ch-Ir(100) than at the hex-Ir(100) surface give rise to the reconstruction of the hex-Ir(100) observed in the experiments. The evolution of the total chemisorption energies of H, calculated relative to the energy of clean hex-Ir(100) surface and half

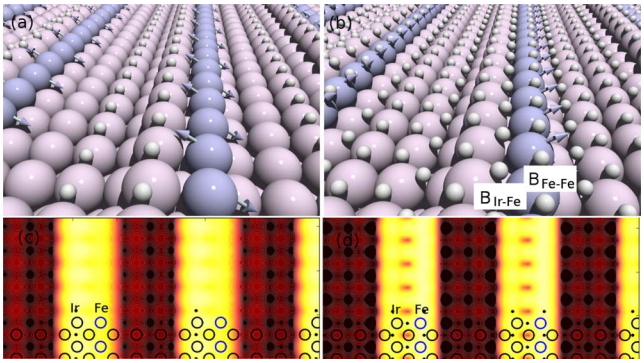

FIG. 2. (Color online) (a) Fe wires on the ch-Ir(100) surface with H coverage of 0.4 ML; (b) the same surface with H coverage of 1.4 ML; Fe atoms are shown as light blue (dark gray) spheres and H atoms are small white spheres; the arrows indicate magnetic moments of Fe atoms; [(c) and (d)] the simulated STM images of the structures in (a) and (b), respectively. H atoms in (c) and (d) are represented by small black spheres.

the energy of the corresponding number of H_2 molecules in gas phase, is plotted in Fig. 1(d). Our calculation show that for H coverages higher than 0.3 monolayers (MLs) the ch-Ir(100) surface becomes energetically more favorable.

B. Monoatomic Fe wires at nanostructured Ir(100)

Once we confirmed thermodynamic stability of partially hydrogenated ch-Ir(100) surface, for the H coverage of 0.4 ML, we added a chain of Fe as depicted in Fig. 2(a). This is the Fe adsorption geometry identified by scanning tunneling microscopy (STM) and found as the most favorable in our calculations.

The next step in our study is to examine H binding at the Fe wires. A careful investigation of different H adsorption sites at the Fe wires reveals two stable adsorption sites: one on Ir atoms near the bridge position between Ir and Fe wires [$B_{Ir\text{-}Fe}$ in Fig. 2(b)] and the another in the bridge between two Fe atoms [$B_{Fe\text{-}Fe}$ in Fig. 2(b)]. The H binding energy in the $B_{Ir\text{-}Fe}$ site is 0.49 eV, which is considerably larger than at the $B_{Fe\text{-}Fe}$ site, where we calculated binding energy of 0.26 eV. These results demonstrate that the H binding at Fe is significantly weaker that at Ir. Hence, the H adsorption on Fe wires will occur only upon full hydrogenation of Ir wires and terraces. Starting from the H coverage of 0.4 ML, we sequentially added H atoms to the ch-Ir(100) surface with deposited Fe chains and inspected several possible configurations.

Our test calculations and results from previous studies[21] indicate that, for H coverages in the range from 0.4 to 1.6 ML, only the bridge sites at the wires and the terraces will be occupied. This considerably restricts the number of favorable configurations. The configurations considered in the present study are shown in Fig. 3. By comparing different configurations with the same H coverage (Θ_H), we observed that the magnetic properties of Fe wires weakly depend on the H adsorption at Ir sites for $0.4 \leq \Theta_H \leq 1.2$ ML. The magnetic properties of Fe wires change significantly only when H atoms bind in the $B_{Fe\text{-}Fe}$ sites. This is demonstrated in Fig. 4(a), where we presented the evolution of energy difference between FM and AFM wires with Θ_H, calculated for the most favorable configurations at given coverage [i.e., the nH-(a) structures, $4 \leq n \leq 16$, in Fig. 3]. The corresponding evolution of Fe magnetic moments is shown in Fig. 4(b).[25] For H coverages up to 1.2 ML the AFM configuration is

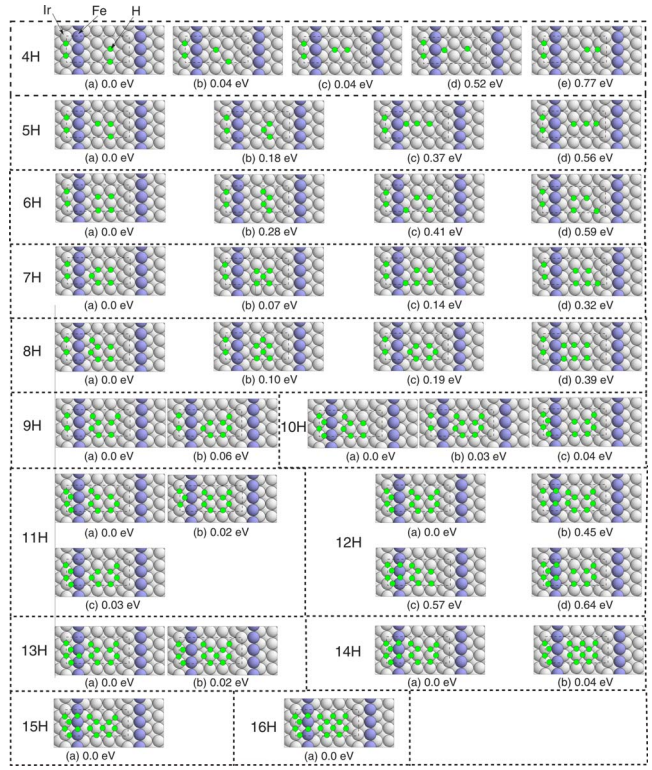

FIG. 3. (Color online) H adsorption configurations at nanostructured Ir(100) surface decorated with Fe wire. The H coverage is in the range from 0.4 to 1.6 ML [i.e., the number of H atoms per (5×2) cell varies from 4 to 16]. The energies of the structures with the same H coverage are given with respect to the most favorable configuration.

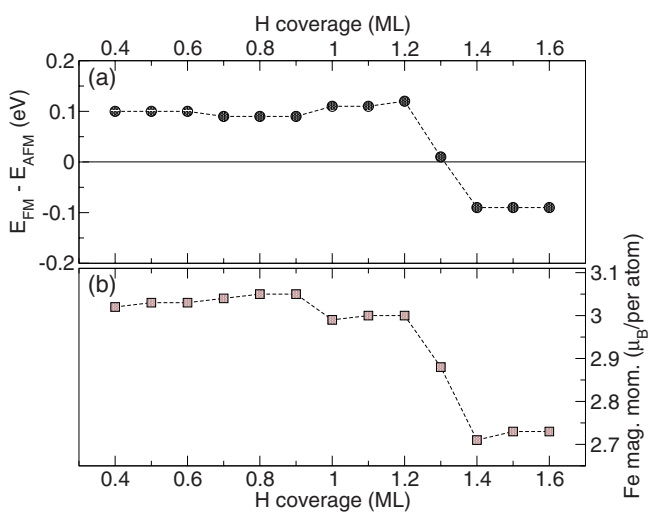

FIG. 4. (Color online) (a) Evolution of energy difference between FM and AFM wires with H coverage, calculated for the most favorable H configurations at given coverage; (b) Fe magnetic moments as a function of H coverage.

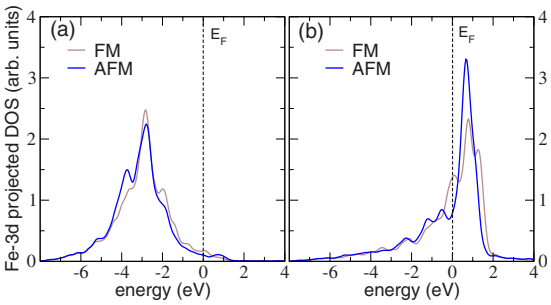

FIG. 5. (Color online) (a) Majority-spin and (b) minority-spin density of states projected on 3*d* orbitals of Fe atoms of pristine ferromagnetic and antiferromagnetic wires [cf. Fig. 2(a)].

0.1 ± 0.01 eV per Fe atom more favorable than the FM one while the magnetic moments at Fe atoms are in the range from 3.0 to $3.05\mu_B$.

We observe important influence of H adsorbate only at coverages of 1.3 and 1.4 ML when H atoms occupy bridge or near-bridge sites at Fe wires. It turns out that the magnetism of Fe wires is very weakly affected by H adsorption on the $B_{Ir\text{-}Fe}$ sites. However, when H adsorbates bind at the $B_{Fe\text{-}Fe}$ positions, the magnetic properties of Fe wires change considerably. At the H coverage of 1.3 ML the AFM and FM structures are nearly degenerate with the Fe magnetic moment of $2.93\mu_B$. At the H coverage of 1.4 ML all $B_{Ir\text{-}Fe}$, as well as $B_{Fe\text{-}Fe}$ sites are occupied [Fig. 2(b)], which gives rise to the ferromagnetic coupling among Fe atoms in the chain. The antiferromagnetic order is 0.09 eV per Fe atom less favorable. We calculated the same magnetic moment of $2.70\mu_B$ per Fe atom for both the FM and AFM phases. Additional H atoms adsorbed at the surface with 1.4 ML of hydrogen bind at the Ir(100) terraces, with the binding energies of 0.19 eV and 0.28 eV, in the 15H-(a) and 16H-(a) structure in Fig. 3, respectively. However, the effect of last two adsorbed H atoms on magnetism of Fe wires is negligible. Hence, the analysis of magnetic properties of the fully hydrogenated Fe wires will be performed for the 14H-(a) structure in Fig. 3. The configurations with H coverages higher than 1.6 ML are not included in Fig. 3 since our calculations show that the binding of an additional H atom is negative.

IV. DISCUSSION

Our discussion will focus on the properties of Fe wires at the Ir surface with low (0.4 ML) and high (1.4 ML) H coverage. The structure of monoatomic Fe wires deposited on the nanostructured Ir(100) surface with 0.4 ML and 1.4 ML of H is depicted in Figs. 2(a) and 2(b), respectively.

We also included simulated STM images of the partially [Fig. 2(c)] and fully hydrogenated [Fig. 2(d)] surfaces. Simulated STM images were constructed as topographs of constant local density of states (LDOS), $\rho(x,y,z,E)=\rho_o$,[26] calculated at $\rho_o=5\times e^{-6}1/\text{Å}^3/\text{eV}$. This value of the LDOS is chosen in order to produce the corrugation in the surface topography similar to the one observed in the experiments.[7] According to the expectations, in the simulated STM images

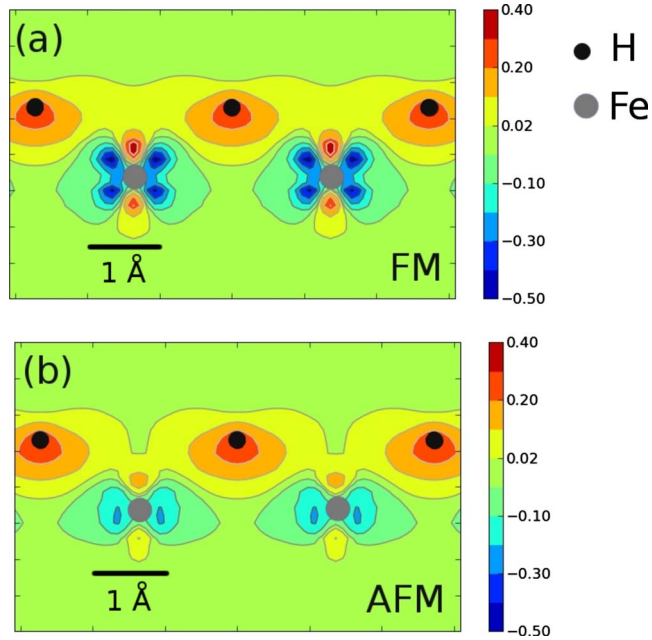

FIG. 6. (Color online) Electron density induced upon adsorption of two H atoms in the $B_{Fe\text{-}Fe}$ sites on (a) ferromagnetic and (b) antiferromagnetic Fe wire supported by fully hydrogenated ch-Ir(100) surface. The contour plots are given in the plane determined by Fe atoms and H atoms adsorbed in the $B_{Fe\text{-}Fe}$ sites. The horizontal axis is along direction of the Fe wire and the vertical one is at 67° with respect to the Ir(100) terraces.

the Ir and Fe wires are seen as periodic arrays of bright stripes separated by dark areas, corresponding to the Ir(100) terraces. The increase in H coverage from 0.4 to 1.4 ML results in modest changes in the simulated STM images The effect of the H adsorption is however much more pronounced if we follow magnetic properties of the wires.

To rationalize the effect of the adsorbates on the magnetism in the wires, we first examined the electronic properties of hydrogen-free wires [Fig. 2(a)]. Since in the Fe wire grown on Ir substrate the distance between deposited Fe atoms is 2.73 Å, ~0.3 Å more than in the bulk crystal, the interaction between Fe atoms in the chain is very weak compared to the interaction of Fe with closest Ir atoms. To estimate the Fe-Ir interaction we adsorbed a single Fe atom at the 5*f* site of the ch-Ir(100) surface [Fig. 1(c)] and calculated the binding energy of 5.7 eV. The same binding energy is found for AFM Fe wires of Fig. 2(a). In the FM wire the binding energy is smaller by 0.1 eV per Fe atom. Thus, the interaction between ferromagnetically coupled Fe atoms is actually repulsive. The hybridization between 3*d* states of FM wire involves the orbitals centered on adjacent atoms, positioned at the same energy. The interaction between filled Fe 3*d* majority-spin states is repulsive since their antibonding combinations are not emptied [Fig. 5(a)]. For partially occupied minority-spin states of FM wire [Fig. 5(b)] the interaction is weakly attractive. We observed a central peak at ~1 eV above Fermi level and two "satellite" peaks corresponding to the bonding (lower in energy) and antibonding (higher in energy) coupling of the Fe minority-spin states located at adjacent atoms. The central peak originates from

the states not involved in the interaction due to symmetry reasons. Small energy gain in the FM wire caused by an increase in the occupation of the minority-spin states cannot compensate the repulsive interaction between filled Fe 3*d* majority-spin states.

The hybridization between 3*d* states, located at the neighboring Fe atoms with opposite magnetic moments, is much smaller in the AFM wire due to a big energy mismatch between the 3*d* states from the same spin channel. The interaction involves fully occupied orbitals from one Fe atom and partially filled states from the adjacent one. Hence, the repulsion observed in the FM wires does not occur in the AFM Fe chains. As a consequence, the center of Fe 3*d* majority-spin states in AFM wire is lower in energy by 0.15 eV than in the FM wire [Fig. 5(a)]. Another fingerprint of weak hybridization in the AFM wire is a single sharp peak in the Fe 3*d* minority-spin DOS, located ~1 eV above Fermi level [Fig. 5(b)].

The energy shift of the Fe 3*d* states of the FM wires, compared to those in the AFM chains, leads to the difference in their reactivity. According to the Hammer-Nørskov *d*-band model,[27] the reactivity of transition metals is enhanced when the center of their *d* bands is moved closer to the Fermi level,[27] as we observed for FM monoatomic wires. Higher reactivity of the FM wires is clearly seen in the plot of the electron-density displacement which occurs upon H adsorption on the monoatomic Fe wires supported by Ir(100) (Fig. 6). The stronger interaction of the H 1*s* states with the Fe 3*d* states from the FM wire than that from the AFM wire changes preferential magnetic order from the later to the former.

V. CONCLUSIONS

In the present study we demonstrated dual role of hydrogen atoms adsorbed on hex-Ir(100) surface. Already at the H coverage of 0.4 ML the quasihexagonal surface reconstructs, producing periodic Ir chains on a squared Ir(100) surface. The Fe monoatomic wires deposited on such a nanostructured surface are a rare example of a stable, pristine Fe structure with the antiferromagnetic order. The H atoms employed to fabricate nanostructured Ir(100) surfaces can be also used to manipulate the magnetism of deposited Fe wires. At the fully hydrogenated ch-Ir(100) surface Fe wires are decorated with H atoms, which leads to the ferromagnetic coupling between adjacent Fe atoms. Our study demonstrate the high potential of covalent functionalization as a tool for tailoring properties of nanostructures on the atomic scale.

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