Electric Field as a Switching Tool for Magnetic States in Atomic-Scale Nanostructures

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(Received 14 July 2010; published 18 January 2011)

One of the most promising candidates for the construction of ultrahigh-density storage media is low-dimensional atomic-scale magnetic nanostructures exhibiting magnetic bi- or multistability. Here we propose a novel route of locally controlling and switching magnetism in such nanostructures. Our *ab initio* studies reveal that externally applied electric field can be used for this purpose.

DOI: 10.1103/PhysRevLett.106.037202 PACS numbers: 75.75.−c, 73.22.−f, 75.30.Et, 75.30.Hx

Modern nanoscience and information technology demand ever new solutions in order to maintain their continued progress. Recently, the interest in low-dimensional magnetic nanostructures (atomic-scale clusters, wires, molecular magnets) has been rekindled by the prospect of using atomic-size magnets as information storage units in spintronic applications [1–4]. Among the most promising candidates for the construction of magnetic nanodevices are atomic-scale units that exhibit magnetic bi- or multistability. This property is peculiar to magnets that have two or more stable magnetic states characterized by a relatively small energy difference between them (of the order of tens of meV). The existence of magnetic bistability was discovered in experiments on molecular magnets: $Mn_{12}O_{12}$-acetate molecules [2–4]. First principles calculations gave a proper description of magnetic properties of these magnets in a free space [5,6] and on surfaces [7]. Other theoretical studies revealed that the phenomenon of magnetic bistability is general: it arises in nanostructures of different sizes and geometries, as has been evidenced for supported Mn clusters on Ag (Ref. [8]) and for Mn and V clusters on Cu (Ref. [9]) surfaces.

Switching a unit from one magnetic state to another can be performed by means of thermal activation [3,10], magnetic field, pressure, or light radiation [10]. These techniques, however, have an undesirable side effect: they act nonlocally. As a result, magnetic states of neighboring units are influenced as well. Here we reveal an alternative and novel route of controlling magnetism and switching between different magnetic states in low-dimensional nanostructures with bi- and multistability: we show that an external electric field (EEF) is a unique candidate, which could be exploited for this purpose. Such a field can be applied locally, e.g., by means of a scanning tunneling microscope tip.

Recent studies have shown that an EEF indeed dramatically affects physical properties of surface adsorbates. It has been revealed that such a field modifies not only adsorption energetics of individual atoms [11], but the surface kinetics of adatoms [12,13] and molecules [14] as well. An EEF controls the structure, dimensionality, and reactivity of supported metal nanoclusters [15]. Nonmagnetic supported metal thin films [16] and freestanding nanoparticles consisting of tens of atoms [17] exhibit ferromagnetism when exposed to an EEF. There have been experimental [18,19] and theoretical [20,21] hints that the magnetocrystalline anisotropy of thin magnetic films [18–20] and monolayers [21] can be manipulated by an EEF via the modification of their band structures.

In this Letter we reveal a general phenomenon: applying an EEF it is possible to switch a nanostructure with bi- and multistability between its different magnetic states. As an example, we consider the behavior of compact transition-metal dimers on a metal substrate in an EEF [22]. We first examine a system exhibiting magnetic bistability, a Mn dimer on a nonmagnetic Ag(001) substrate, and reveal that under a negative (positive) electric field ferromagnetic (FM) [antiferromagnetic (AFM)] configuration of the dimer is the ground state. We show that this effect is originated by the different behavior of electrons of the FM and AFM dimers in an EEF. Then we generalize our statements by extending the reasoning onto the case of a multistable system, a Mn dimer on a magnetic Ni(001) surface. We demonstrate that by applying an EEF one can rotate the direction of atomic spins for a certain magnetic state of a nanostructure.

All results are obtained using the projector augmented-wave technique [25] as implemented in VASP code [26] within the local Ceperly-Alder exchange and correlation functional (LDA) [27], as parametrized in Ref. [28]. We also tested functionals formulated in the generalized-gradient approximation (GGA) (PW91 [29], PBE [30]) and included the on-site Coulomb interaction (LDA + U) [31] to check the stability of the results. The principal scheme of our computational experiment is shown in Fig. 1(a) [32]. An EEF is oriented normally to a surface and is assumed to be positive when it is directed downwards. Effects of an EEF are studied introducing a planar dipole layer into the vacuum [33]. The dipolar correction has been included.

First we examine a compact Mn dimer oriented along the [010] crystallographic direction of Ag(001) [Fig. 1(a)].

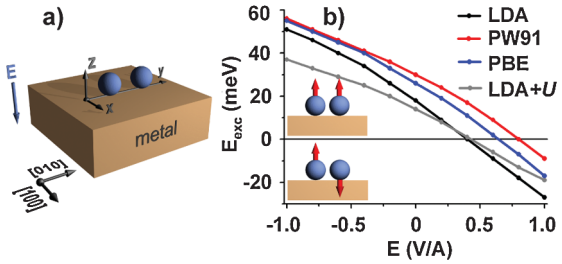

FIG. 1 (color). (a) The principal scheme of the computational experiment: a (001) surface is in an external electric field. (b) Energy difference $E_{\mathrm{exc}} = E_{\mathrm{AFM}} - E_{\mathrm{FM}}$ between two stable magnetic states (FM and AFM) of a Mn dimer on Ag(001) as a function of intensity of electric field E. For the LDA + U calculations we have used $U = 3$ eV, $J = 1$ eV.

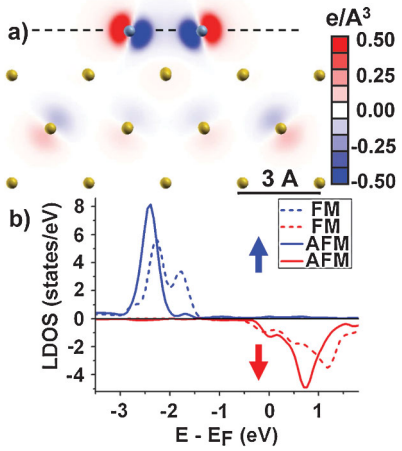

FIG. 2 (color). (a) Difference between the spatial distributions of electron density of the FM and the AFM Mn dimers on Ag (001) in the absence of an EEF. A crosscut by a plane $x = 0$ [see the coordinate system in Fig. 1(a)] is shown. Yellow balls are Ag atoms; blue balls are Mn atoms. The dashed line crosses the nuclei of the FM and the AFM dimers [36]. (b) The spin-polarized LDOS of 3d electrons of a Mn atom within the FM dimer (dashed lines) and the AFM one (solid lines).

The magnetism of the dimer is determined by the direct exchange interaction between the Mn atoms and is characterized by a collinear spin alignment with two magnetic states: FM and AFM. Let us now report on LDA results. For the fully relaxed geometry, the FM state is more stable, and the energy difference $E_{\mathrm{exc}} = E_{\mathrm{AFM}} - E_{\mathrm{FM}} = 18$ meV. The magnetic moments of Mn atoms are $3.92\mu_B$ and $3.87\mu_B$ in the FM and the AFM cases, respectively. To trace the effect of an EEF on the relative stability of two magnetic states of the dimer, we plot in Fig. 1(b) (black curve) E_{exc} as a function of the field intensity E. Negative EEF strengthens the FM coupling, while positive EEF, on the contrary, decreases the magnitude of E_{exc} and at a threshold value of $E \approx 0.4$ V/Å a reversal of the stability occurs [34]. For $E > 0.4$ V/Å an AFM dimer is the ground state [35].

An EEF affects positions of Mn atoms. Negative EEF lifts the dimers, since the positively charged Mn nuclei with the core electrons shift along the direction of an EEF. For $E = -1.0$ V/Å, vertical separations of the FM and the AFM dimers from the surface are changed from $z_F = 1.64$ Å and $z_A = 1.62$ Å to $z_F = 1.75$ Å and $z_A = 1.74$ Å, respectively. Positive field induces sinking of the dimers: for $E = 1.0$ V/Å, $z_F = 1.63$ Å and $z_A = 1.61$ Å. On the other hand, $E > 0$ attracts electrons from the surface into the vacuum, thus increasing bonding between Mn atoms and decreasing the bond length in dimers (y_F and y_A), and vice versa. We find that y_F are 2.72, 2.67, 2.65 Å and y_A are 2.59, 2.49, 2.45 Å for electrical fields E of -1.0, 0, 1.0 V/Å, respectively.

To get a deeper understanding of the LDA results presented in Fig. 1(b) (black curve), we analyze the electronic properties of the dimers. The FM and the AFM dimers have different spatial distributions of the valence electrons (4s, 4p, 3d). Figure 2(a) displays the cross section of the electron density difference between the FM and the AFM dimers by a plane (100) containing the dimer [i.e., by a plane $x = 0, [n_{\mathrm{FM}}(x, y, z) - n_{\mathrm{AFM}}(x, y, z)]_{x=0}$; see Fig. 1(a)] in the absence of an EEF. The red (blue) color marks areas where the electron density of the FM dimer is larger (smaller) than that of the AFM one. Blue and red spots are situated differently with respect to the dashed horizontal line, which crosses the nuclei of the Mn dimers [Fig. 2(a)] [36]. This indicates that the electrons of the FM dimer are less localized near the surface and reach farther into the vacuum than those of the AFM dimer. Our analysis shows that the major contribution to the difference between the spatial distributions of electron density around the FM and the AFM dimers is introduced by 3d electrons. This difference can be understood from the electronic structure of the dimers. The spin-polarized local density of states (LDOS) of a Mn atom within the AFM dimer is shown with solid lines in Fig. 2(b): the majority electrons exhibit one single-atom-like peak at -2.4 eV and are localized in the central region of the dimer. The LDOS of a Mn atom within the FM dimer is shown with dashed lines in Fig. 2(b): density of states of the majority electrons are split into two levels at -2.3 and -1.8 eV. This result correlates with the Alexander-Anderson model [37], which predicts a splitting of states in a FM dimer into bonding and antibonding orbitals. The bonding state is more tightly bound [37], which is reflected in the LDOS peak at -2.3 eV. The antibonding state is destabilized energetically (the peak at -1.8 eV) and localized in the outer region of the dimer [37]. These electrons penetrate deeper into the vacuum than those of the AFM dimer. The amount of minority electrons of a Mn atom in the dimers is small, and the difference between their LDOS [Fig. 2(b)] for $E < E_F$ is insignificant; thus, they are out of the scope of the further discussion.

Since the majority 3d electrons of the FM Mn dimer are destabilized energetically and penetrate into the vacuum

more than those of the AFM dimer, they are more sensitive to external influences. To prove this, we compare in Figs. 3(a) and 3(b) the LDOS of $3d$ electrons for the AFM and FM dimers at two extreme values of E. If E switches from 1.0 to -1.0 V/Å, the single peak in the LDOS of a Mn atom within the AFM dimer shifts by ≈ 70 meV towards lower energies [Fig. 3(a)]. This happens since negative EEF [see Fig. 1(a)] pushes the upper part of the electron clouds of the dimer towards the Mn nuclei, thus decreasing the potential energy of electrons. The peaks' shifts for the FM dimer are different: the low-energy peak shifts by ≈ 70 meV, while the high-energy peak shifts by ≈ 150 meV [Fig. 3(b)]. The sensitivity to an EEF of the antibonding states in the FM case and their stronger shift towards higher energies at $E > 0$ leads to the higher total energy of the FM dimer, while the stronger shift towards the lower energies at $E < 0$ causes the lower total energy of the FM dimer.

Despite the fact that the Ag(001) substrate was not involved in the discussion explicitly, its role is dramatic. A freestanding Mn dimer is a weakly bonded van der Waals molecule with binding energy of the order of tens of meV [38]. A Mn dimer on Ag(001) is a strongly bonded pair of atoms (binding energy 0.7 eV) with direct overlap of localized d orbitals. This enables control of a magnetic ground state effecting the spatial distribution of electron density of the dimers by an EEF.

To be convinced that our results are stable with respect to the chosen approximation to the exchange and correlation potential, we have calculated E_{exc} as a function of an EEF for the Mn dimer on Ag(001) within GGA using PW91 [29] and PBE [30] functionals and tested the effect of the on-site Coulomb interaction [31]. Since the proper value of the screened Coulomb interaction U in the examined system is unknown, we have set U to 3 eV, while the exchange energy J was set to 1 eV (Ref. [6]). The results are summarized in Fig. 1(b). In all the cases the trend is the same: an EEF affects E_{exc}, switching the dimer between the FM and the AFM states. Let us comment in more detail on the LDA + U results [Fig. 1(b), gray curve]. The on-site Coulomb interaction "locks" Mn d electrons on their orbitals; thus, the bonding between Mn atoms is decreased.

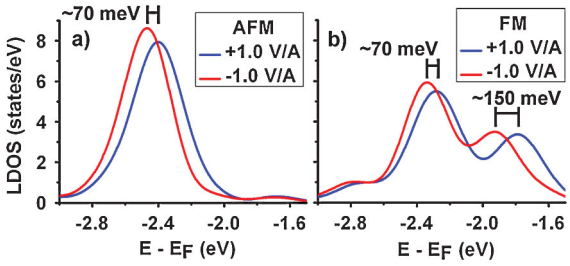

FIG. 3 (color). The LDOS of the majority $3d$ electrons of a Mn atom within (a) the AFM and (b) the FM dimer at two extreme values of field intensity (red curves, $E = -1.0$ V/Å; blue curves, $E = 1.0$ V/Å).

Since the bonding states are presented in a FM dimer, the strength of the FM coupling decreases, and in the absence of an EEF E_{exc} becomes smaller (14 meV) than in the case of the LDA (18 meV). The "locking" of electrons on the orbitals due to the on-site Coulomb interaction has another sequence: the modifications in the electronic structure in dimers become less sensitive to an EEF. Thus, the smaller inclination angle of the curve $E_{\mathrm{exc}}(E)$ is observed for the LDA + U than in the case of the pure LDA. It is worth noting that we have also tried other values of U (2 and 4 eV) within LDA + U calculations, and all our conclusions remain unchanged.

Having revealed that an EEF can switch an atomic-scale nanostructure with magnetic bistability between its two magnetic states, in the following we extend our investigations onto systems which have more than two states with close energies, i.e., multistable systems. Such a phenomenon is observed for a Mn dimer on a magnetic Ni(001) surface [Fig. 1(a)]. Ni bulk is magnetic, with the net magnetic moment of $0.65\mu_B$ per atom. Three stable magnetic solutions, shown in Fig. 4(a), exist in the system in the absence of an EEF [39]. (i) The ground state is the noncollinear (NC) configuration with an angle $2\alpha = 116°$ between the spins and a magnetic moment $\mu = 3.61\mu_B$ per Mn atom. This state is formed since two Mn atoms on Ni(001) prefer the AFM alignment, which is in competition with the FM coupling between the Mn and Ni atoms [39]. The vertical distance of the NC dimer from the surface z is 1.59 Å and the bond length y is 2.56 Å. (ii) The FM dimer with $\mu = 3.68\mu_B$ per Mn atom, $z = 1.61$ Å and $y = 2.70$ Å, is 2 meV less stable than the NC one. (iii) The ferrimagnetic (FI) dimer with the angles $\gamma = 4°$, $\beta = 2°$, with magnetic moments $\mu_1 = 3.60\mu_B$ and $\mu_2 = 3.50\mu_B$ for the left and the right atoms, respectively [Fig. 4(a)], and with $z = 1.57$ Å and $y = 2.48$ Å, is 28 meV less favorable than the NC one.

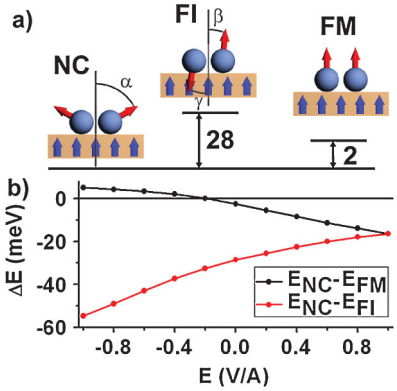

FIG. 4 (color). (a) Energy differences (in meV) between three stable magnetic configurations of a Mn dimer on Ni(001) in the absence of an EEF: noncollinear (NC), ferrimagnetic (FI), and ferromagnetic (FM). Red (blue) arrows schematically illustrate the spin directions of Mn (Ni) atoms. (b) Energy difference between them as a function of electric field strength.

The black curve in Fig. 4(b) shows the energy difference between the NC and FM configurations of the Mn dimer $E_{NC} - E_{FM}$ on Ni(001) as a function of the field strength. For $E < 0$, the transition from the NC to the FM ground state occurs at $E \approx -0.2$ V/Å. The physics behind this phenomenon is identical to the case of the Mn dimer on Ag (001). For $E > 0$, the NC dimer is the ground-state solution. The energy balance between the NC and the FI states is modified as a function of E as well [red curve in Fig. 4(b)]. At any $E < 1.0$ V/Å the FI solution remains the most unfavorable, while the reversal of the stability of the FI and the FM states takes place at $E = 1.0$ V/Å.

Last but not least, we observe one more intriguing phenomenon: the angle between individual spins in atomic-scale structures is rotated through the application of an EEF. The change of the spin orientation is essential for the NC state [Fig. 4(a)]: the angle 2α between Mn spins changes from 78° at $E = -1.0$ V/Å to 128° at $E = 1.0$ V/Å. At $E < 0$, the electrons of the outer shells of the Mn atoms within the NC dimer are pushed towards the substrate; thus, the intensity of the Mn-Mn interaction, which is AFM [39], decreases. The FM interaction between the Mn and Ni atoms starts to prevail, leading to smaller values of 2α. At $E > 0$, the strength of Mn-Mn interaction increases, leading to larger values of 2α. The angle between the spins in the FM and the FI dimers rotates slightly, being around 0° and 178°, respectively, at any E in the examined range of values.

In summary, we have revealed a novel phenomenon: an electric field can be used for local control of magnetism and realignment of individual spins in low-dimensional magnetic nanostructures on magnetic and nonmagnetic metal surfaces. Our work provides the promising theoretical prediction that it is feasible with the current technology to use an electric field as a switching tool for the magnetic states of atomic-scale nanostructures with magnetic bi- and multistability.

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