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Electronic and magnetic properties at the edges of nanostructures in an electric field: *ab initio* study

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Abstract

State of the art *ab initio* calculations of the electronic and magnetic properties at the edges of magnetic nanostructures in an external electric field are presented in this paper. Our results for the Fe stripes on Fe(0 0 1) reveal the existence of spin-polarized edge states. A spatially inhomogeneous electronic structure is found at the edge. We demonstrate that the spin-dependent screening density varies greatly at the atomic scale. Tuning of the spin-polarization by the external electric field is demonstrated.

Keywords: relaxation, magnetic nanostructures, edges effects, electric field

(Some figures may appear in colour only in the online journal)

1. Introduction

Precise control over electronic and magnetic properties down to the atomic level is central to the engineering of new magnetic nanostructures. In recent years considerable progress has been made regarding a direct observation of spin-dependent phenomena in metal nanostructures with an atomic-scale resolution [1–8]. Tuning of magnetic states is possible by means of hydrostatic pressure, thermal activation, a magnetic field or light irradiation [9]. However, in such experiments the effect of the external stimulus is nonlocal. An alternative route of controlling magnetism at a local scale is an external electric field (EEF) [10, 11]. There have been important experimental and theoretical studies that revealed the effects of EEF on the magnetic anisotropy [12–14], the Curie temperature [15] and exchange interactions [16] in magnetic nanostructures. Despite these studies, our understanding of how the electronic field affects the electronic and magnetic properties of nanoislands on metal surfaces remains very limited. With a decreasing size of nanostructures, the influence of edge atoms on their physical properties becomes very important. The reduced coordination of edge atoms leads to their specific electronic and magnetic properties. For example, the magnetic anisotropy of Co islands on Pt(1 1 1) is mainly caused by edge atoms alone [17]. The drastic difference between electronic states at the edges and in an internal region of nanoislands has been revealed [2, 18, 19]. For Co nanoislands on Cu(1 1 1) spin-polarized rim states have been identified by experiments and *ab initio* calculations [2, 18]. Magnetic properties such as spin polarization, tunnel magnetic resistance and magnetic anisotropy exhibit strong changes at rims [18, 20]. Last but not least, a reduced number of bonds at edges results in shorter interatomic distances. This, in turn can profoundly influence physical properties at the edges. An inhomogeneous distribution of bonds over nanoislands was predicted and confirmed by experiments [21–24]. This implies that electronic and magnetic properties can significantly vary across the island.

Very recent experiments performed by means of spin-polarized scanning tunneling microscopy (SP-STM) [25] have demonstrated the effect of the EEF on the magnetic anisotropy (MA) of nanoislands consisting of only a few atoms. In such small magnets, edge atoms could play a decisive role in the coupling between the electric field and magnetic properties. Therefore, we believe that *ab initio* studies of electronic and magnetic properties of atomic-size magnetic nanostructures

in an EEF is the main focus of ongoing experimental and theoretical research in spintronics. In this paper we present, to the best of our knowledge, the first such study. As a model system, we consider the edge of Fe nanoislands on Fe(0 0 1). We have revealed the existence of the spin polarized rim states at the edge which play an important role in the screening of the EEF. We demonstrate tuning of the spin-polarization (SP) of the electron density by the EEF. Our results provide compelling evidence for a spatial and spin dependent response of the edge area of nanostructures to the EEF.

2. Computational details

Our *ab initio* study is based on the density functional theory. We apply the generalized gradient approximation (GGA–PBE) [26] and use the Vienna *ab initio* simulation package (VASP) [27]. The projector augmented wave method was exploited in our calculations [28, 29]. We mimic the edge of 1 ML high Fe nanoislands on Fe(0 0 1) by an infinite stripe of atoms four rows wide. The Fe substrate is approximated by a slab of eight layers. The step has an orientation of (1 0 0) (figure 1). The distance between the stripes is about 15 Å. Due to the periodic boundary condition implemented in VASP we used only one stripe in the computational cell. Test calculations with different numbers of layers (more then six) were also performed. The results of these calculations have shown that the size of our stripe is sufficient to get robust results. For geometry optimization a criterion of force-on-nuclei convergence to within 0.005 eV $Å^{-1}$ was chosen. An energy cutoff of 500 eV for the plane wave expansion and a $12 \times 4 \times 1$ Monkhrost-Pack grid for k-point sampling were used. We performed test calculations with the energy cutoff 600 eV and with different k-point meshes. These calculations have demonstrated that a $12 \times 4 \times 1$ mesh is large enough to obtain robust results. A static electric field was introduced by a planar dipole layer method and was applied perpendicular to the surface [30]. A positive field was directed towards the surface. The magnetic moments of atoms were calculated by integrating the magnetization density $m(\vec{r})$ inside the corresponding atomic Wigner–Seitz (WS) spheres [31].

3. Results and discussion

First, we demonstrate that new spin-polarized electronic states (rim states) are developed at the edge of the Fe nanostructures. We calculated the spin-dependent local density of states (LDOS) on Fe(0 0 1) and at the edge sites. The LDOS around the Fermi energy is mainly determined by the minority states of the Fe atoms. Therefore, we present in figure 2 only the minority component of d-states. It is clearly seen that the LDOS at the edge atom (atom 2) exhibits a peak near the Fermi energy which is absent on Fe(0 0 1). This localized peak is mainly determined by d_{xz} and d_{yz} states and, as will be shown later, significantly affects a spin-dependent screening of the EEF at the edge. Similar to rim states found for the Co nanoisland on Cu(1 1 1) [2, 18] we expect that SP rim states at the edge of Fe nanostructures could give rise to an enhanced zero bias conductance.

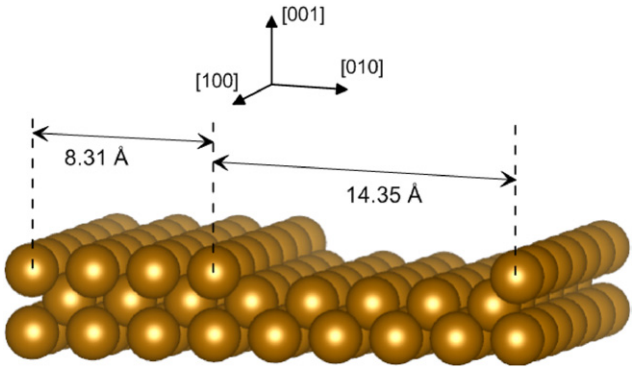

Figure 1. The geometry of system.

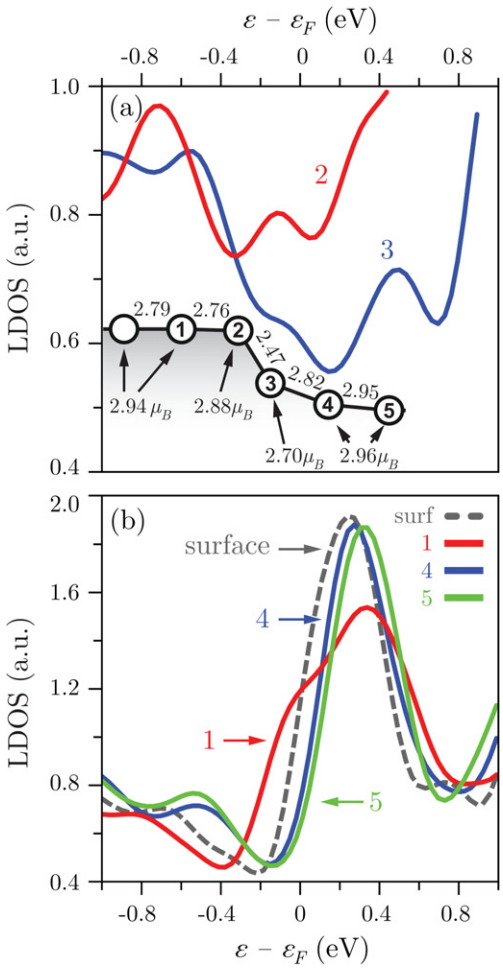

Figure 2. The LDOS of the minority components of d-states for various atoms near the edge. Bond lengths between atoms (insert in figure 2(a)) are given in Angstroms. Magnetic moments are given for each atom of the edge. The curves presented in figures 2(a) and (b) correspond to atoms shown in the insert in figure 2(a). Minority d-LDOS on the Fe(0 0 1) is also shown in figure 2(b) (surface).

The reduced number of bonds at the edge causes lower binding energy. Therefore edge atoms exhibit stronger relaxations. One can see (see figure 2(a)) that the bond lengths between the edge atom and its nearest neighbours are shorter than bond lengths on the top and bottom of the edge of the stripe. It is known that a decreasing interatomic distance usually tends to reduce magnetic moments. This

Table 1. Magnetic moments (MM) and bond lengths (BL) at the edge (positions of the atoms are shown in figure 2.).

Atom #	MM (relax) [μ_B]	MM (unrelax) [μ_B]	BL (relax) [Å]	BL (unrelax) [Å]
1	2.94	2.98	2.79	2.87
2	2.88	2.95	2.76	2.87
3	2.70	2.69	2.47	2.49
4	2.96	3.00	2.82	2.87
5	2.96	3.00	2.95	2.87

simple argument explains why magnetic moments at the edge and at the bottom (atoms 2 and 3, figure 2(*a*)) are reduced. At the same time, the decreasing coordination number tends to enhance magnetic moments. Therefore, the magnetic moment of the atom at the edge (atom 2, figure 2(*a*)) is larger than the moment of the bottom atom (atom 3, figure 2(*a*)). A strongly reduced bond length between atoms 2 and 3 compared to the bond length between atoms 1,2 and atoms 4,5 leads to a reduction of the magnetic moment of atom 2 compared to atoms 1,4 and 5 while it has a smaller coordination number. It is interesting to note that calculations for unrelaxed geometry show a similar distribution of the magnetic moments at the edge. These results are presented in table 1. One can see that relaxations of the bond lengths at the edge are rather small. Small differences between magnetic moments at the top of the step and at the bottom are caused by a spin-dependent charge-flow from the top to the bottom (spin-dependent Smoluchowski effect [6]). A strongly inhomogeneous bond length distribution at the edge leads to a site-dependent electronic structure. The spatial variation of the minority *d*-states depicted in figure 2 endorses this effect. It is clearly seen that the rim state is exclusively observed at the edge atom (atom 2) and the LDOS changes significantly at the scale of a few Angstroms. Our results indicate that at a distance of 6–7 Å from the edge, the LDOS is already very close to that on Fe(0 0 1). A strong broadening of the LDOS at the bottom (atom 3, figure 2(*a*)) is caused by an increased coordination and a reduced bond length due to atomic relaxations. It is interesting to note that the strong peak found on Fe(0 0 1) at ∼0.2 eV above the Fermi energy is of the d_{z^2} character surface state [32–34]. Our results show that this state is completely quenched at the edge and at the bottom atoms. This is in agreement with the STM experiments on Fe steps on Fe(0 0 1) [34].

Now we turn to a discussion of the effect of the EEF on the spin-dependent charge density at the nanostructure edge. It is important to recall several works devoted to the screening of the EEF at defects on nonmagnetic surfaces [35–38]. The field enhancement at kink sites, on top of step atoms, and adatoms has been demonstrated. A remarkable site specificity of screening charge density on stepped surfaces was revealed. In the case of magnetic substrates, screening of the EEF becomes spin-dependent [13, 39]. Therefore, the response of the minority and majority electrons to the EEF at the edges could be very different.

In order to get a deeper insight into an electron screening at the nanostructure edge we have calculated the spin-dependent induced electron charge density $\Delta\rho^{\downarrow\uparrow}(r) = \Delta\rho^{\downarrow\uparrow}(r, E) - \Delta\rho^{\downarrow\uparrow}(r, 0)$ at different sites at the edge (E—is the EEF). The

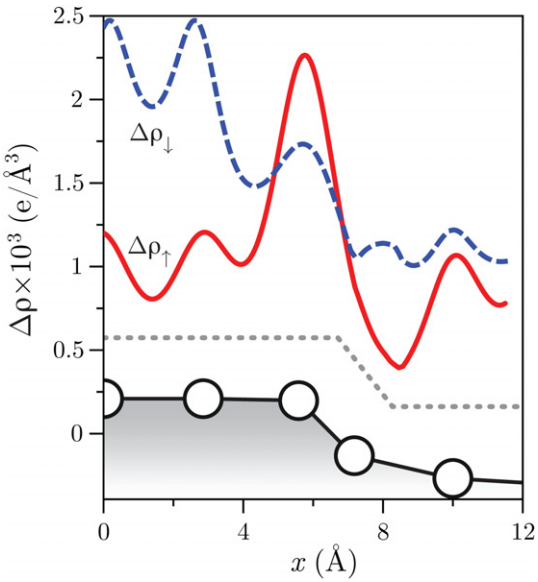

Figure 3. The influence of the EEF on the induced charge density on edge atoms. The majority and minority channels are presented. Calculations are performed at 1.5 Å above the edge (dotted line).

spatial distribution and full view of the screening electron density is shown in figures 3 and 4 for $E = 0.8\,\mathrm{V\,Å^{-1}}$ as an example. These results reveal that electron screening at the edge is a spin-dependent phenomenon. On can see that on the top of the stripe the minority electrons are more strongly affected be the EEF than the majority electrons. This finding is in line with recent calculations for Fe(0 0 1) [32]. It was demonstrated that a large number of the minority *d*-states at the Fe atom results in a LDOS in vacuum of *d*-character. In our case, the strong effect of the EEF on the minority states stems from d_{xz} and d_{yz} components of the *d*-LDOS which penetrate into the vacuum. At the same time, the screening minority charge density is reduced above the edge atom (atom 2, 1.5 Å above this atom see figure 3). The physical mechanism responsible for this effect is related to a rim *d*-states and atomic relaxations which increase the localization of the minority density at the edge. It is important to note that due to the strong localization of the minority rim *d*-states they are practically not affected by the EEF. These states lead to a strong spin-dependence of the induced charge-density (figures 3 and 4).

Our results provide clear evidence that the spin-dependent screening of the EEF primarily occurs on the top of the edge. Similar conclusions were made for nonmagnetic steps and prominences on surfaces [38, 40]. The induced charge density visualized in figure 4 clearly shows that the screening of the EEF is confined to the surface. Our results unambiguously reveal that the screening of the EEF at the edge exhibits a strong spatial dependence at the atomic scale and it is different for the majority and the minority electrons.

The above findings suggest the possibility of tuning the spin-polarization (SP) locally at the edge of a magnetic nanostructure by the EEF. To demonstrate this, we have calculated the SP of the charge density $\mathrm{SP}(r) = \frac{\rho^{\uparrow}(r)-\rho^{\downarrow}(r)}{\rho^{\uparrow}(r)+\rho^{\downarrow}(r)}\cdot 100\%$ as a function of EEF. As an example, we present in figure 5 our calculations for several positions at the edge. For

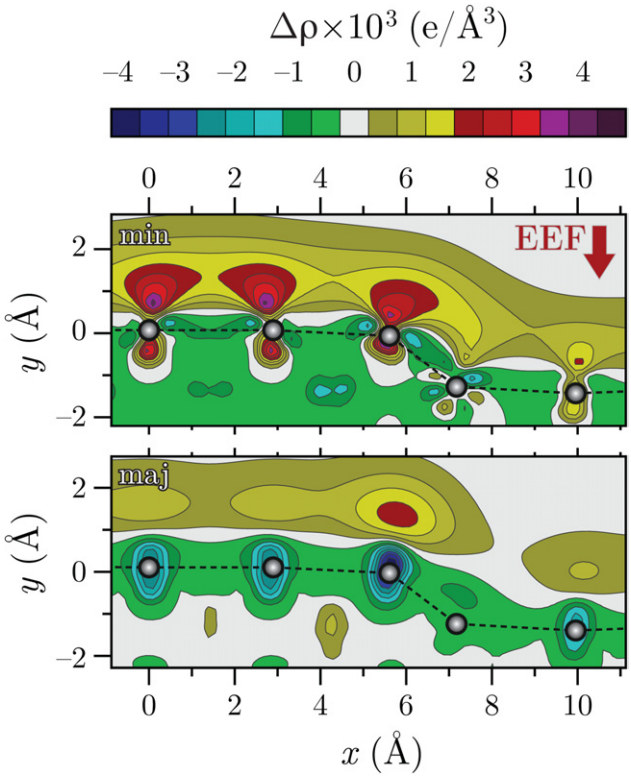

Figure 4. Full view screening electron density of the minority and majority electrons is presented. Positions of the atoms are shown as black balls.

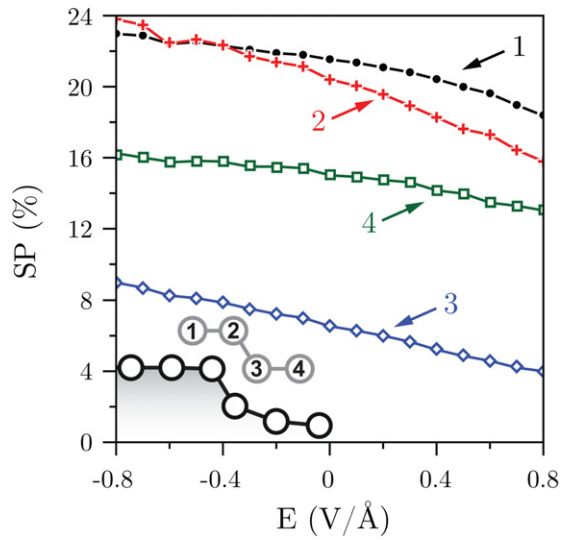

Figure 5. Tuning the spin-polarization at the edge by the EEF. Calculations were made for the points shown in the insert (1.5 Å above the edge). A similar SP was found in the area 3 Å above the surface.

both positive and negative electric fields, the largest SP is found on top of the stripe edge (curve 1, 2, figure 5). This is explained by a reduced spill-out of the minority electrons due to their hybridization with minority d-states of Fe surface atoms. Due to a reduced coordination of the edge atom (curve 2, figure 5) the spill-out of the minority electrons is enhanced. This increases $\rho^{\downarrow}(r)$ and reduces the SP. However, the difference in the SP between positions 1 and 2 is small due to the Smoluchowski effect [6] which reduces $\rho^{\uparrow}(r)$. With an increasing strength of the positive EEF the spill-out of the minority electrons increases leading to a decreasing of the SP. A strong suppression of the SP at the bottom (curve 3, figure 5) results from an increased coordination and decreased bond lengths. Both of these factors reduce the spill-out of the majority and minority electrons. The reduction of the SP on the terrace near the edge (position 4, figure 5) can be explained by the increased bond lengths in this area (see figure 2 insert). Using a tight-binding model [41], the shift of the band can be written as $\Delta E = \beta(r)F(\vec{k}, r)$ where $F(\vec{k}, r)$ is a positive sum of k-dependent cosine functions, $\beta(r)$—the overlap integral $\beta(r) = \beta_0 \exp(-qr)$; q—is a positive constant; $\beta_0 < 0$ for occupied states. For small changes of the bond length $r = r_0 - \delta r$, one can obtain $\Delta E \sim (1 + q\,\delta r)\beta_0 F(\vec{k}, (\delta r)^2)$ $(F(\vec{k}, (\delta r)^2) = 0$ for $\delta r = 0)$. Therefore, with an increasing bond length, the minority d-states are pushed to higher energies and become more delocalized. This leads to an enhancement of $\rho^{\downarrow}(r)$ and the reduction of the SP.

4. Conclusion

In summary we have presented *ab initio* studies of electronic and magnetic properties at the edge of a magnetic nanostructure in the EEF. Our findings give clear evidence for the existence of new spin-polarized states at the edge. We have shown that the electronic structure at the edge exhibits strong changes at the Angstrom-scale. A strongly inhomogeneous distribution of the spin-dependent screening density at the edge was revealed. Tuning of the SP by the EEF was demonstrated. Although we have used a particular system, the Fe stripes on Fe(0 0 1), we believe that the main conclusions of our work can be applied to different magnetic nanostructures on metal surfaces.

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