PHYSICAL REVIEW B **73**, 174434 (2006)

Magnetic interactions of Mn clusters supported on Cu

Anders Bergman,[1,*] Lars Nordström,[1] Angela Burlamaqui Klautau,[2] Sonia Frota-Pessôa,[3] and Olle Eriksson[1]
[1]*Department of Physics, Uppsala University, Box 530, Sweden*
[2]*Departamento de Física, Universidade Federal do Pará, Belém, PA, Brazil*
[3]*Instituto de Fisica, Universidade de Sao Paulo, CP 66318, Sao Paulo, SP, Brazil*

(Received 22 December 2005; revised manuscript received 25 April 2006; published 31 May 2006)

It is demonstrated that the magnetic interactions can be drastically different for nanosized systems compared to those of bulk or surfaces. Using a real-space formalism we have developed a method to calculate noncollinear magnetization structures and hence exchange interactions. Our results for magnetic Mn clusters supported on a Cu(111) surface show that the magnetic ordering as a rule is noncollinear and cannot always be described by using a simple Heisenberg Hamiltonian. We argue that the use of *ab initio* calculations allowing for noncollinear coupling between atomic spins constitutes an efficient and reliable way of analyzing nanosized magnets.

DOI: 10.1103/PhysRevB.73.174434 PACS number(s): 75.75.+a, 73.22.−f, 75.10.−b

I. INTRODUCTION

The effort of shrinking materials and devices to nanosizes is fueled both by scientific curiousity and industrial requirements. Applications are found in most scientific fields (photonics and electronics,[1] biotechnology,[2] information technology,[3] materials science,[4] and energy applications[5]) and devices based on nanotechnology are rapidly becoming a natural part of our daily life (e.g., in personal computers). The best way to characterize a nanomaterial is, apart from its size reaching nanometer dimensions, that finite size or quantum effects dominate, yielding new interactions and different functionality.

Small clusters supported on a surface are of special interest since they have the potential of increasing the density in information storage. One may envision that future magnetic hard disks with information carried by magnetic clusters, will have a storage density two orders of magnitude larger than those used today. The properties of such systems may be measured by means of scanning tunneling microscopy (STM),[6] where information is acquired on an atomic scale and atoms are imaged directly. This technique represents an enormous experimental development, and it has been applied to several nanomagnets,[7] but it must be followed by complimentary theoretical methods. The complication lies in that, due to the nanosize of these systems, traditional theoretical models based on bulk magnetism are often inappropriate. This calls for a method adapted for supported clusters where the constraint to fix the spin arrangement in a collinear way must be released so that complex noncollinear magnetic structures can be analyzed.

In this paper we present a first principles method for treating noncollinear magnetic configurations of supported clusters. As a demonstration, the technique is applied to Mn clusters supported on a Cu(111) surface. We have studied a large body of Mn clusters with different geometries. For practical reasons we present here only the results for a selection of the considered Mn clusters.

II. DETAILS OF CALCULATIONS

In order to correctly describe the physics of isolated clusters supported on surfaces in an efficient way, the theoretical method should preferably be real-space (RS) based, or at least not depend on translational symmetry. While the theory of noncollinear magnetism[8,9] has been implemented in several methods capable of treating periodic systems and free clusters, very few methods capable of treating noncollinear ordering in supported clusters[10–12] have been reported so far in the literature. The method used in this work differs from these previous methods by being a fully parameter-free density functional method.[13] The self-consistent noncollinear real space method used in this study is based on the Haydock recursion method[14] and the linear muffin-tin orbital atomic sphere approximation (LMTO-ASA) technique.[15] Besides being formulated completely in real space, our method also has the advantageous feature of having the computational cost scaling linearly with the number of inequivalent atoms in the system, and can thus be used for calculations of large systems. The RS-LMTO-ASA, a collinear version of this method, has successfully been used extensively for various types of electronic structure calculations earlier, and a more elaborate description of the collinear implementation can be found in Refs. 16 and 17.

The recursion method is, in its original formulation, designed to calculate the local density of states (LDOS), which corresponds to the diagonal terms of the imaginary part of the local Green's function $\mathcal{G}(\epsilon)=(\epsilon-\mathcal{H})^{-1}$ for specified atoms and orbitals, where $\mathcal{H}$ is the Hamiltonian and ϵ is the energy. For a correct treatment of noncollinear magnetism, an evaluation of off-diagonal parts of the Green's function are needed, which, in principle, are possible to extract using recursion methods. However, this is quite cumbersome and can be circumvented by using a unitary transformation $\mathcal{U}$ on the Hamiltonian $\mathcal{H}$, $\mathcal{H}'=\mathcal{U}\mathcal{H}\mathcal{U}^\dagger$. The Green's function is transformed in the same way; $\mathcal{G}'=\mathcal{U}\mathcal{G}\mathcal{U}^\dagger$. Using the relation $\mathcal{U}^\dagger\mathcal{U}=1$ and the fact that cyclic permutations of matrix multiplications conserve the trace of the product, the magnetic density of states $\boldsymbol{m}(\epsilon)$, can be written as

$$\boldsymbol{m}(\epsilon)=-\frac{1}{\pi}\text{Im}\,tr\{\boldsymbol{\sigma}\mathcal{U}^\dagger\mathcal{U}\mathcal{G}\mathcal{U}^\dagger\mathcal{U}\}=-\frac{1}{\pi}\text{Im}\,tr\{\boldsymbol{\sigma}'\mathcal{G}'\}, \quad (1)$$

where $\boldsymbol{\sigma}$ are the Pauli matrices, $(\sigma_x,\sigma_y,\sigma_z)$ and $\boldsymbol{\sigma}'$ is a Pauli matrix after the unitary transformation. The transformation matrix $\mathcal{U}$ is different for the tree directions, and chosen so that, $\mathcal{U}\sigma_j\mathcal{U}^\dagger=\sigma_z'$, for $j=x,y,z$, to yield a diagonal representation. The unitary transformation corresponds to a spin rotation where $\mathcal{U}$ can be calculated using the spin-$\frac{1}{2}$ rotation matrices. These transformations can then be applied to the original Hamiltonian for calculating the LDOS along the three orthogonal directions. With the Hamiltonian decomposed in a spin-dependent part, $\mathbf{B}$, and a spin-independent component, H, $\mathcal{U}$ operates only on the spin-dependent part,

$$\mathcal{H}' = H + \boldsymbol{B}\cdot\mathcal{U}\boldsymbol{\sigma}\mathcal{U}^\dagger. \tag{2}$$

From the transformed Hamiltonians $\mathcal{H}'$, the LDOS for the different directions are obtained using the recursion method, the local magnetization axis is calculated, and the LDOS for the local spin axis is constructed. Compared with the collinear case, the computational cost is tripled since the recursion is now performed for three directions, but it stills scales linearly with the number of atoms. Since our Hamiltonians are constructed within an *ab initio* LMTO-ASA formalism, all calculations are fully self-consistent, and the spin densities are treated within the local spin density approximation (LSDA).[18] No external parameters are thus needed to perform the calculations within our scheme. It can be noted that the choice of exchange and correlation potential is for some systems, e.g., for γ-Fe,[19] important for obtaining the correct magnetic structure. However, the choice of an exchange correlation potential typically becomes important only when one considers extremely small energy differences between different magnetic configurations (e.g., of order μ Ry/atom between ferromagnetic and antiferromagnetic). Furthermore, it is often the case for transition metal systems[20] that differences in the magnetic structure, when calculated with LSDA potentials compared to using gradient corrected potentials, are foremost an effect of the fact that the equilibrium volumes depend on the choice of exchange and correlation potentials. In this work, equilibrium volumes are not calculated, a fact which substantially diminishes the effect of which form of exchange correlation that is used, i.e., gradient corrections compared to LSDA. The importance of gradient corrections in the case of Mn structures on Cu surfaces has earlier been a matter of controversy,[21] but it is not believed that a gradient corrected potential would change the conclusions of this work, since as we shall see below, the energies relevant to this study are of order m Ry/atom.

In this study we have considered a large number of clusters with different shapes and sizes supported on a Cu(111) surface. The calculations of the Mn clusters have been performed by embedding the clusters as a perturbation on a previously self-consistently converged "clean" Cu(111) surface. The cluster atoms and neighboring Cu atoms are then recalculated self-consistently while the electronic structure for atoms far from the cluster are kept unchanged. As is usually the case for LMTO-ASA methods, the vacuum outside the surface needs to be simulated by having a number of layers of empty spheres above the Cu surface in order to provide a basis for the wave function in the vacuum and to treat charge transfers correctly. Structural relaxations have not been included in this study, so surface and cluster sites have been placed on a regular fcc lattice with the experimental lattice parameter of Cu. Structural relaxations can, in certain cases,[23] play an important role for the magnetic properties of supported clusters but cannot be obtained within the ASA. A complete structural relaxation is, however, not relevant for the systems considered in this study since in an experimental situation, various geometries would most likely be placed at nonequilibrium positions by means of, e.g., a STM tip. The only relevant relaxation one might consider is the binding distance between the cluster atoms and the substrate atoms. Since the Cu and Mn atoms have a similar size we have used the interatomic distance of bulk Cu as the distance between nearest neighbor Mn and Cu atoms and between Mn and Mn atoms. The clean Cu(111) surface has been modeled by a large (>5000) slab of atoms and the continued fraction, that occurs in the recursion method, have been terminated with the Beer-Pettifor[22] terminator after 25 recursion levels.

III. RESULTS

In Fig. 1 we show Mn clusters with a particularly complex magnetic structure. The local magnetic moments for the Mn atoms in the clusters depend strongly on the number of Mn neighbors with values between $4.7\mu_B$ for the single adatom and $2.7\mu_B$ when six Mn neighbors are present. In Fig. 1(a) the magnetic moments of a linear chain of Mn atoms is shown. Each Mn atom couples its magnetic moment antiparallel to its neighbor in a collinear way. This is in accordance with a Heisenberg Hamiltonian with antiferromagnetic nearest neighbor interactions.

In Fig. 1(b) the three atoms have been moved to form a triangular geometry and the magnetization profile then becomes a noncollinear structure. This is the result of a well-known phenomenon; magnetic frustration.[24] In a triangular geometry two magnetic moments with antiferromagnetic interactions can couple antiparallel, but the third moment cannot simultaneously be antiparallel to the first two, so it becomes "frustrated." Instead each moment forms an equal angle of 120° to its neighbor, and the calculated magnetization profile in Fig. 1(b) [and 1(a)] is the consequence of antiferromagnetic Mn-Mn interactions.

In Figs. 1(c) and 1(d) a more interesting scenario is found. First six Mn atoms forming a hexagonal ring structure were studied [1(c)]. The antiferromagnetic nearest neighbor interaction cause a magnetic order where every second atom has its magnetic moment pointing up and every other has a moment pointing down, and the magnetic order is collinear. However, for the cluster with one extra atom in the center of the hexagonal ring, Fig. 1(d), a different magnetic order, with a noncollinear component, is found. The atoms at the edge of the cluster have a canted antiferromagnetic profile, with a net moment pointing antiparallel to the magnetization direction of the atom in the center of the cluster. The magnetic moment of the central atom is almost perpendicular (~100°) to the atoms at the edge of the cluster and with a magnetic momentof $2.7\mu_B$. The edge atoms have a magnetic moment of $4\mu_B$ per atom that has an angle of ~165° to neighboring edge atoms and is parallel to its second nearest neighbors.

In Fig. 1(e), the magnetic order of a cluster with rhombic shape is shown. A noncollinear magnetic structure, as is

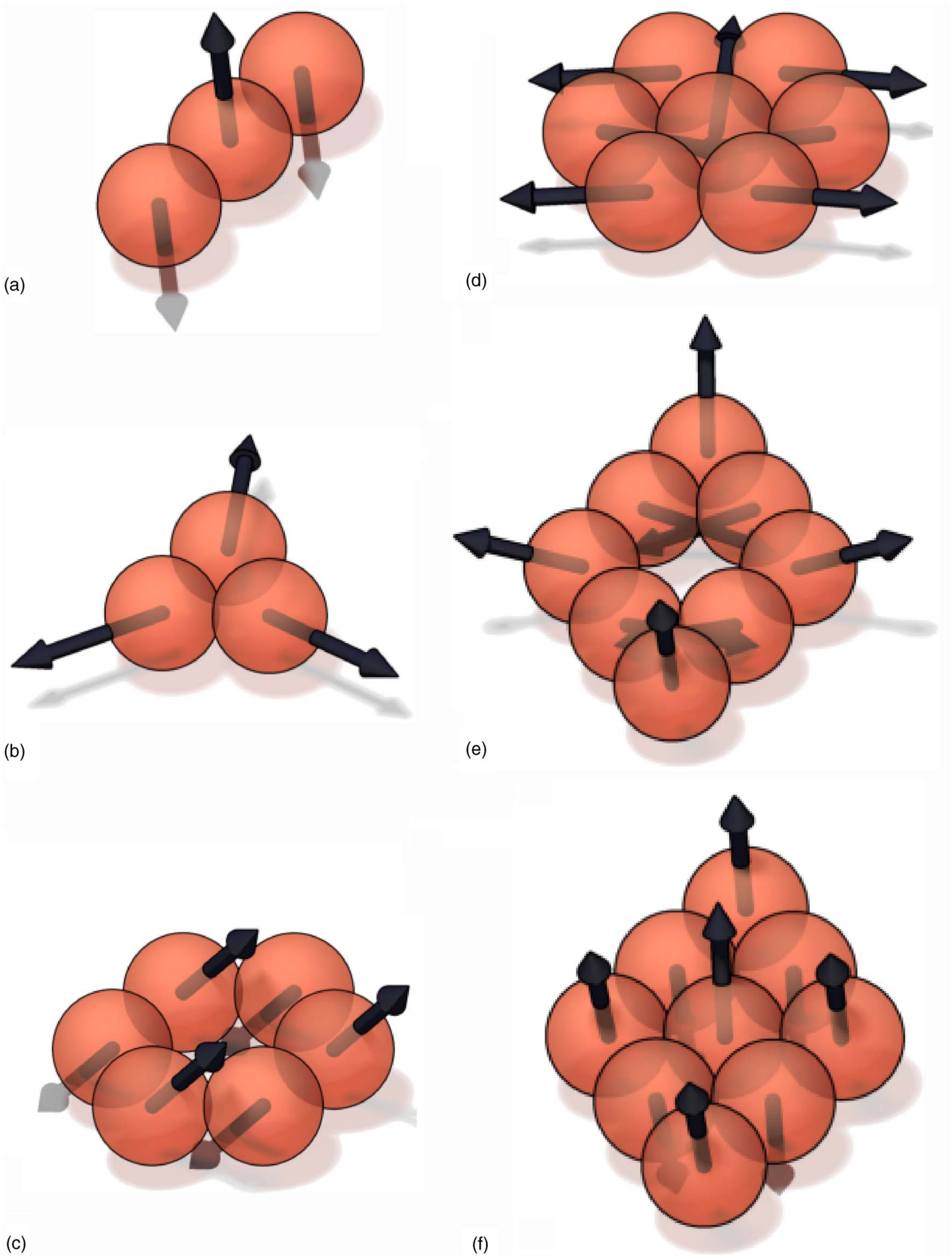

FIG. 1. (Color online) The magnetic ordering for Mn clusters on a Cu(111) surface.

shown in the figure, is found to be metastable in our calculations, and a collinear antiferromagnetic solution has a somewhat lower energy of $\sim 40\ \mathrm{meV/cluster}$. It should be noted here that, in general, it is possible that supported clusters can exhibit several local minima for different magnetization configurations, much in the same way as one might encounter in bulk materials. This situation is as a matter of fact also similar to the structural properties of matter, as a function of, e.g., pressure. In Fig. 1(f) we show the moment profile of the rhombic cluster with one extra atom in the middle of the cluster. The most stable magnetic configuration for this cluster is noncollinear with a slightly canted antiferromagnetic structure.

Taken together, the results in Fig. 1 show that as a rule noncollinear ordering is obtained for supported Mn clusters. Also, Fig. 1 shows that an analysis of the magnetism of supported clusters based upon conventional theoretical models, such as the Heisenberg model, may be cumbersome to

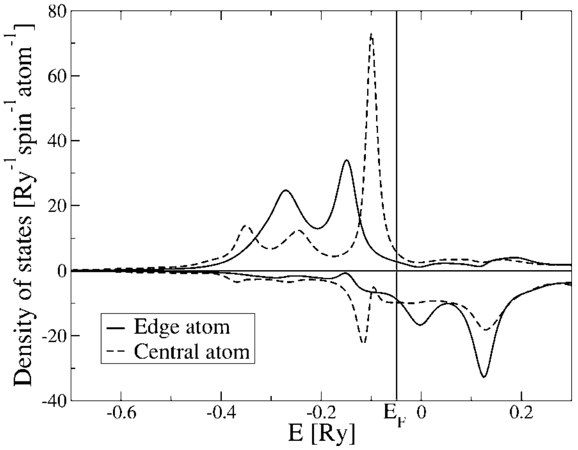

FIG. 2. Local density of states for a central and an edge atom in the cluster in 1(d).

perform for more complicated geometries. Due to differences in the local symmetry, the electronic structure at different atoms in the cluster becomes unique and different from the neighboring atoms, which can be seen in Fig. 2 where the LDOS for the central atom and an edge atom of the cluster in Fig. 1(d) is shown. As an effect of the difference in the electronic structure, the exchange interactions between atoms in the cluster depends strongly on the position of the atom in the cluster. This means that it is inappropriate to use the same magnetic moment and exchange parameters of, e.g., a Heisenberg Hamiltonian for all atoms in the analysis of the magnetism of the cluster in Fig. 1(d). To describe the magnetic properties accurately, noncollinear first principles theory is a very good alternative.

In our calculations, both the exchange interactions within each cluster as well as between the clusters appear naturally. This has been used for examining the distance dependence of intercluster interactions of triangular Mn clusters supported on a Cu(111) surface. In Fig. 3, the two triangular clusters are connected, forming a single, six atom, cluster. As expected, this single cluster shows a noncollinear order due to its frustrated geometry. The magnetic moments and angles between moments for the atoms in the cluster displayed in Fig. 3 are shown in Table I where the atoms are labeled according to Fig. 3(b). The magnetic moments for the atoms in the cluster depend on the number of nearest Mn neighbors where fewer neighbours yield higher magnetic moment.

Figure 4 shows the magnetic order of the clusters as they are separated from each other with an increasing distance. When the distance between the clusters is very large one expects that the moment profile within each cluster would be identical to that in Fig. 1(b). The magnetic order of the clusters in Fig. 4(a) is indeed close to the noninteracting cluster order with only a few degrees deviation of the magnetic moments. The magnetic moments for the clusters in Fig. 4(b) are even closer to the magnetic order found for the noninteracting case. It can also be noted that the two cluster-cluster distances in Figs. 4(a) and 4(b) give very similar magnetization geometries. This demonstrates that the intracluster interaction is much larger than the intercluster interaction, even for short cluster-cluster distances. As a measure of the intercluster exchange for this geometry, total-energy calculations show that the energy needed to flip the spins by 180° in one of the clusters, in Fig. 4(a), is in the range of a few meV.

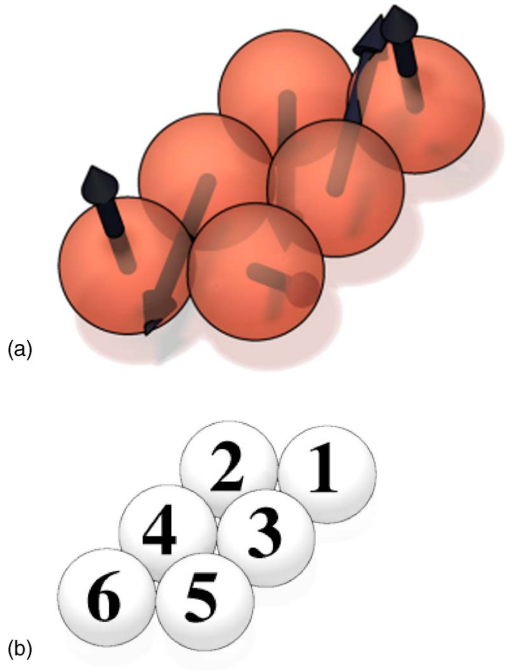

FIG. 3. (Color online) Magnetic moments for two triangular Mn clusters connected to each other, resulting in a single, six atom, cluster. The angles between the magnetic moments are given in Table I, where the atoms are labeled according to the figure to the right.

The results in Fig. 4 show that the “frustrated geometry” of the triangular clusters, with 120° between the different moments of each cluster, is very robust, even if the cluster-cluster distance becomes very small. Hence the intraexchange interaction is much stronger (and antiferromagnetic) than the interexchange interaction. This finding is important when one attempts to design cluster-based media for magnetic information storage where a bit stored in one cluster should not be allowed to interact and degrade the information in the nearest neighboring cluster.

We end this paper with a short discussion on the possibility to grow the clusters studied here and to measure their magnetic structures with atomic resolution. Recently small magnetic Cr clusters supported on a gold surface, with dif-

TABLE I. Magnetic moments (in μ_B) and angles between moments for the cluster displayed in Fig. 3. The numbers to the far left in the table refer to the numbering of the atoms in the cluster in Fig. 3 and the moments listed to the far right refer to atomic moments.

Atom	1	2	3	4	5	6	Moment
1	0	155	88	80	155	5	4.28
2	155	0	118	75	50	153	3.94
3	88	118	0	167	68	89	3.60
4	80	75	167	0	124	79	3.60
5	155	50	68	124	0	156	3.94
6	5	153	89	79	156	0	4.28

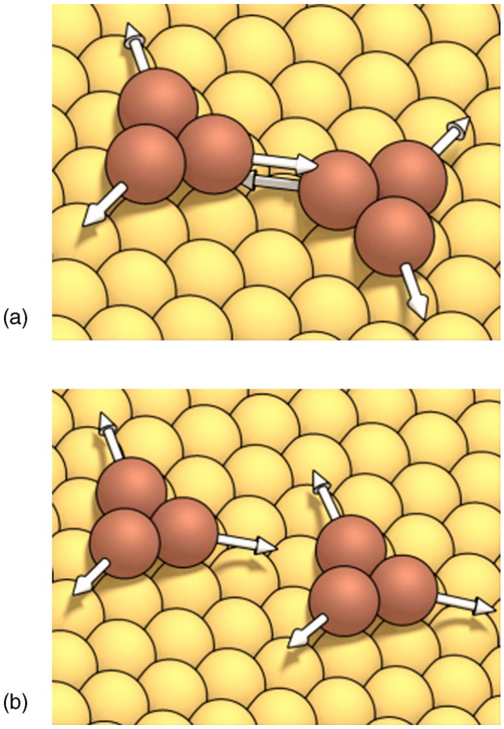

FIG. 4. (Color online) Magnetic moments for Mn atoms in exchange coupled clusters on a Cu(111) surface.

ferent geometries, have indeed been synthesized and studied with STM.[27] Different geometries were found to have different spinconfigurations, much in the same way as we discuss here. In general, spin-polarized (SP-STM) (Ref. 25) should be the best method to detect the magnetic structures proposed here, since it has been shown to have the necessary resolution to determine magnetization directions between different atoms in a nanostructure. This technique was also used to measure the g value and spin excitation at single absorbed Mn atoms on a substrate of Al_2O_3.[26] Hence, STM is the most promising experimental technique to verify the here predicted magnetic profiles. Examples of SP-STM determinations of atomic scale magnetism, including noncollinear coupling, may be found in Refs. 28 and 29.

ACKNOWLEDGMENTS

We acknowledge financial support from the Göran Gustafsson foundation, the Swedish Research Council, the Swedish Foundation for Strategic Research, Seagate Technology, and CNPq, Brazil. The calculations were performed at the high performance computing centers UPPMAX, NSC, and HPC2N within the Swedish National Infrastructure for Computing and at the computational facilities of the LCCA, University of São Paulo, and of the CENAPAD at University of Campinas, SP, Brazil.

---

*Electronic address: Anders.Bergman@fysik.uu.se

[1] M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith, and C. M. Liebe, Nature (London) **415**, 617 (2002).

[2] C. C. Berry, J. Mater. Chem. **15**, 543 (2005).

[3] P. Gambardella, S. Rusponi, M. Veronese, S. S. Dhesi, C. Grazioli, A. Dallmeyer, I. Cabria, R. Zeller, P. H. Dederichs, K. Kern, C. Carbone, and H. Brune, Science **300**, 1130 (2003).

[4] M. W. Barsoum, T. Zhen, S. R. Kalidindi, M. Radovic, and A. Murugaiah, Nat. Mater. **2**, 107 (2003).

[5] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, and J-M. Tarascon, Nature (London) **407**, 496 (2000).

[6] G. Binnig and H. Rohrer, Helv. Phys. Acta **55**, 726 (1982).

[7] M. Bode, Rep. Prog. Phys. **66**, 523 (2003).

[8] L. M. Sandratskii, Adv. Phys. **47**, 91 (1998).

[9] L. Nordström and D. J. Singh, Phys. Rev. Lett. **76**, 4420 (1996).

[10] S. Uzdin, V. Uzdin, and C. Demangeat, Europhys. Lett. **47**, 556 (1999).

[11] C. C. Cornea and D. C. A. Stoeffler, J. Magn. Magn. Mater. **282**, 198 (1999).

[12] R. Robles, E. Martinez, D. Stoeffler, and A. Vega, Phys. Rev. B **68**, 094413 (2003).

[13] After the original submission of this paper, a noncollinear extension of the full potential Korringa-Kohn-Rostoker method was reported by S. Lounis, S. Mavrpoulos, P. H. Dederichs, and S. Blugel, Phys. Rev. B **72**, 224437 (2005).

[14] R. Haydock, *Solid State Physics* (Academic Press, New York, 1980), Vol. 35.

[15] O. K. Andersen, O. Jepsen, and D. Glötzel, *Highlights of Condensed-Matter Theory* (North-Holland, Amsterdam, 1985).

[16] S. Frota-Pessôa, Phys. Rev. B **46**, 14570 (1992).

[17] A. B. Klautau and S. Frota-Pessôa, Surf. Sci. **579**, 27 (2005).

[18] U. von Barth and L. A. Hedin, J. Phys. C **5**, 1629 (1972).

[19] M. Körling and J. Ergon, Phys. Rev. B **54**, R8293 (1996).

[20] See, e.g., R. Hafner, D. Spisák, R. Lorenz, and J. Hafner, Phys. Rev. B **65**, 184432 (2002); T. C. Leung, C. T. Chan, and B. N. Harmon, Phys. Rev. B **44**, 2923 (1991).

[21] D. Spisák and J. Hafner, Phys. Rev. B **61**, 12728 (2000) and following comment by P. Kurz, G. Bihlmayer, S. Blugel, K. Hirai, and T. Asada, Phys. Rev. B **63**, 096401 (2001).

[22] N. Beer and D. Pettifor, *The Electronic Structure of Complex Systems* (Plenum Press, New York, 1984).

[23] S. Pick, V. S. Stepanyuk, A. N. Baranov, W. Hergert, and P. Bruno, Phys. Rev. B **68**, 104410 (2003).

[24] S. T. Bramwell and M. J. O. Gingras, Science **294**, 1495 (2001).

[25] O. Pietzsch, A. Kubetzka, M. Bode, and R. Wiesendanger, Science **292**, 2053 (2001).

[26] A. J. Heinrich, J. A. Gupta, C. P. Lutz, and D. M. Eigler, Science **306**, 466 (2004).

[27] T. Jamneala, V. Madhavan, and M. F. Crommie, Phys. Rev. Lett. **87**, 256804 (2001).

[28] A. Wachowiak, J. Wiebe, M. Bode, O. Pietzsch, M. Morgenstern, and R. Wiesendanger, Science **298**, 577 (2002).

[29] S. Heinze, M. Bode, A. Kubetzka, O. Pietzsch, X. Nie, S. Blügel, and R. Wiesendanger, Science **288**, 1805 (2000).