Surface Magnetism of Fe(001)

First-principles calculations reveal that the magnetic moments of atoms at an Fe(001) surface are 33% larger than in the bulk. This enhancement is confined to the top layer, which demonstrates the highly localized character of the enhanced surface magnetism. The very rapid decay of the surface magnetization is superimposed by small Friedel-like oscillations.

Keywords: Magnetism, surfaces, iron, first-principles computations

1 Background

Magnetic properties are of critical importance for our information-based society. Tremendous amounts of data such as business and banking information, email communication, contact information, digital images and movies are stored on magnetic disks. Furthermore, permanent magnets are essential for all kinds of small and large electric motors, which may have significant impact on the performance of electric vehicles. Spintronics, *i.e.* the combined use of electronic and magnetic properties is emerging as a new technology in microelectronics. Related to this phenomenon was the discovery of the giant magneto-resistance effect by Peter Grünberg and Albert Fert in 1988, which brought about a breakthrough in gigabyte magnetic disks. For their work these researchers were awarded the Nobel prize in 2007.

First-principles calculations are a reliable source for predicting magnetic properties as demonstrated here for the prototypical case of an Fe(001) surface. Given the performance and continuing drastic increase in computing power, magnetic properties of increasing complex systems such as nanostructures can be predicted with high confidence, thus guiding the design of novel materials and devices.

With the development of accurate surface science techniques in the late 1960's, initial experimental data suggested "magnetically dead" layers on transition metal surfaces. By the late 1970's and early 1980's first-principles methods combined with the power of supercomputers of that time allowed for the first time accurate calculations of magnetic properties of surfaces. These calculations indicated enhanced magnetic moments at the Fe surfaces in contradiction to early experiments [2], [3]. There was no reason to doubt the reliability of these calculations. The discrepancy was later traced to surface contamination and further experiments reconciled the theoretical and experimental data as discussed in [4].

This application note serves to demonstrate how such calculations can be performed within the *MedeA*® [1] *Environment* and discusses the results in detail.

2 Method of Calculation

The first principles calculations as based on density functional theory were performed using MedeA-VASP [5], which uses projector-augmented (PAW) potentials and wave functions [6]. Exchange and correlation effects were included within the semilocal GGA as parametrized by the PBEsol scheme [7]. In a first step, a structural optimization of bulk

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[3] S. Ohnishi, A. J. Freeman, and M. Weinert, "Surface magnetism of Fe(001)", *Phys. Rev. B* **28**, 6741(1983) (DOI)

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APPLICATION NOTE

body-centered cubic Fe was performed and the electronic and magnetic properties calculated. Based on these results, a nine-layer slab was constructed using the surface-builder tool of MedeA, with the periodic slabs being separated by a vacuum region of about 14 Ångström thickness. Again, this was followed by structural optimization. However, in this case only the atomic positions were relaxed since it is well justified to assume that the in-plane lattice parameters adopt those of the bulk system. Finally, the electronic and magnetic properties were calculated and analyzed.

3 Computed Results

The calculated valence electron charge and spin densities of body-centered cubic iron are displayed in Figure 1. They serve as a reference for the surface calculations to be discussed below. Obviously, the charge density shows little asphericity whereas the shape of the spin-density iso-surfaces reflects the underlying cubic lattice.

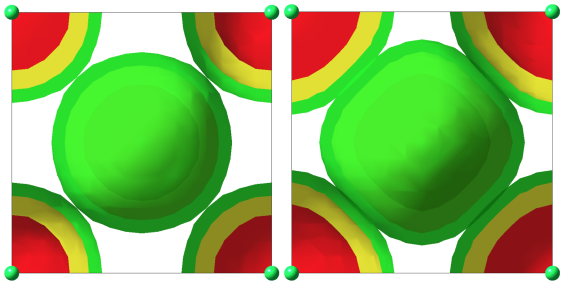

Figure 1: Valence-electron charge (left) and spin density (right) of bulk bcc Fe as viewed along the (100) direction. The plot shows the charge density as three-dimensional iso-surfaces at values of 0.4, 0.6, and 1.4 e/Ang and the spin density as three-dimensional iso-surfaces at values of 0.03, 0.1 and 0.5 e/Ang.

The spin-dependent electronic density of states (DOS) as plotted in Figure 2 is characterized by an almost rigid exchange splitting of the electronic states. Worth mentioning is the pronounced dip of the minority and majority DOS at the Fermi energy (indicated by the green line) and about 1.5 eV below, respectively, which separates bonding and antibonding 3d states and places ferromagnetic iron in the vicinity of the exciting class of halfmetallic ferromagnets such as CrO_2 [8]. The calculated magnetic moment amounts to 2.16μ_B, which is close to the experimental value of 2.12μ_B.

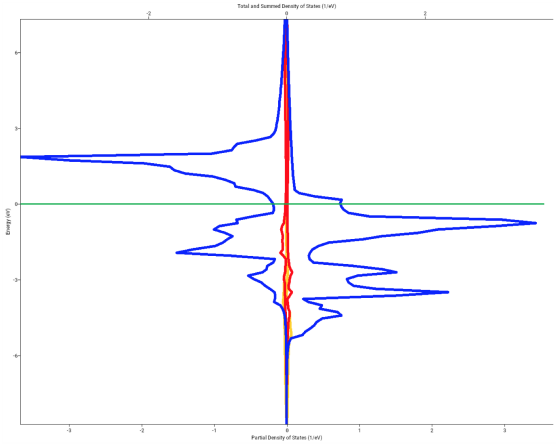

Figure 2: Electronic density of states of bulk bcc Fe. Spin minority and majority DOS are plotted to the left and right, respectively.

The calculated charge and spin densities of the nine-layer slab used to model the (001) surface as displayed in Figure 3 and Figure 4, respectively, are found in very close agreement with those presented by Ohnishi *et al.* [3]. Again, the charge and spin density display a much different behavior. While the charge density shows only little deviation from the shape observed for bulk Fe even in the surface layer, the spin density of the surface atoms reveals a much stronger distortion from the bulk spin density and assumes a more oval shape with considerable contributions extending into the vaccum region. In contrast, the spin density of the atoms already in the first subsurface layer strongly resembles that of the spin density observed for bulk Fe.

This behavior is reflected by the calculated layer-resolved spin-dependent electronic densities of states as displayed in Figure 5, which are in close agreement with previous results [2] [3]. The values of the atomic magnetic moments likewise show a strong decrease away from the surface. Specifically, the magnetic moment of the iron atom at the surface amounts to 2.87 μ_B. This values is by about 33% larger than that of bulk bcc Fe in

[8] F. Bisti, V. A Rogalev, M. Karolak, S. Paul, A. Gupta, T. Schmitt, G. Güntherodt, V. Eyert, G. Sangiovanni, G. Profeta, and V. N. Strocov, "Weakly-Correlated Nature of Ferromagnetism in Nonsymmorphic CrO_2Revealed by Bulk-Sensitive Soft-X-Ray ARPES", *Phys. Rev. X* **7**, 041067 (2017) (DOI)

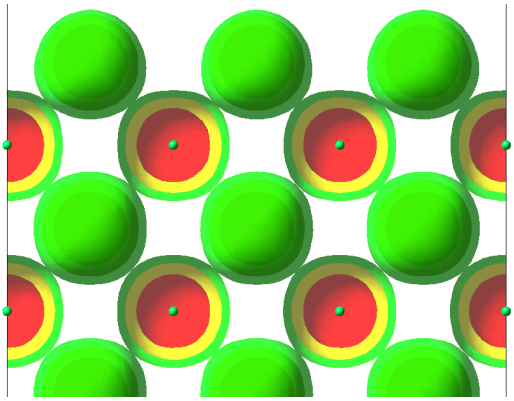

Figure 3: Valence-electron charge density at an Fe(001) surface as viewed along the (100) direction. The plot shows the charge density (of the upper half of the slab) as three-dimensional iso-surfaces at values of 0.4, 0.6, and 1.4 e/Ang.

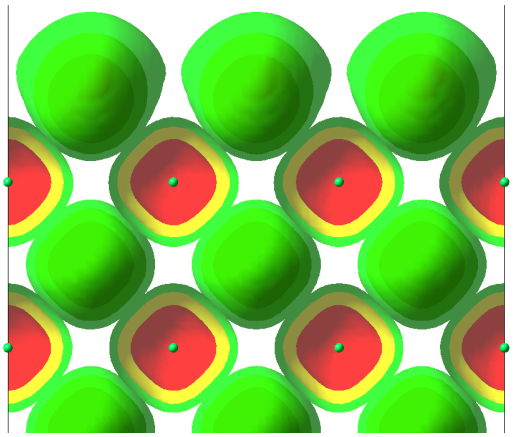

Figure 4: Valence-electron spin density at an Fe(001) surface as viewed along the (100) direction. The plot shows the spin density (of the upper half of the slab) as three-dimensional iso-surfaces at values of 0.03, 0.1 and 0.5 e/Ang.

good agreement with experimental data, *e.g.* from Mößbauer measurements (see [2] and references therein) and angle-resolved photoemission experiments [4]. However, already at the first subsurface layer the local magnetic moment has drastically decreased and assumes almost the bulk value. Hence, the increased magnetization forms an atomically thin surface layer. The rapid decrease of the layer-resolved densities of states is confirmed by the very close similarity of the local density of states of the atoms at the center of the slab (right-most plot in Figure 5) to that of bulk Fe as shown in Figure 2. In particular, the DOS of the center slab reproduces the distinct dip between the bonding and antibonding Fe 3d states already discussed for bulk Fe. Interestingly, this minimum of the partial DOS is filled at the surface layer for both the spin majority and minority states while it is clearly visible for all subsurface layers included in Figure 5.

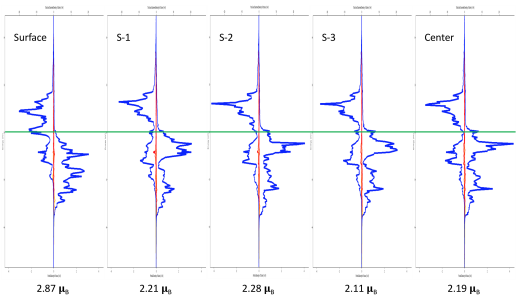

Figure 5: Layer-resolved spin-dependent electronic density of states of the surface layer, three subsurface-layers, and the central layer of a nine-layer slab of Fe. Spin minority and majority DOS are plotted to the left and right, respectively, of each subfigure.

4 Conclusion

The electronic and magnetic properties of slabs of ferromagnetic Fe as investigated by first-principles calculations reveal strong enhancement of the magnetization in the surface layer by about 33% as compared to the bulk magnetization. While the electronic charge density shows only minor changes at the surface, the spin density displays an oval-shape distortion with an eruptive extension into the vacuum region. Electronic surface states of both spin directions are found between the respective bonding and antibonding states. All calculated results are in very good agreement with experimental data and thus underline the predictive power of atomistic simulations as based on density functional theory. With the MedeA environment including the surface-builder tool, and MedeA VASP, calculations as those described here can be routinely and efficiently performed.

MedeA modules used in this application

- *MedeA Environment*
- *MedeA VASP*