Magnetic anisotropy of single 3d spins on CuN surface

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First-principles calculations of the magnetic anisotropy energy for Mn- and Fe-atoms on CuN/Cu(001) surface are performed making use of the torque method. The easy magnetization direction is found to be different for Mn and Fe atoms in accord with the experiment. It is shown the magnetic anisotropy has a single-ion character and mainly originates from the local magnetic moment of Mn- and Fe-atoms. The uniaxial magnetic anisotropy constants are calculated in reasonable agreement with the experiment.

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Recent scanning tunneling microscopy (STM) measurements of the spin-excitation energies in a magnetic field [1] for individual Fe and Mn atoms on CuN/Cu(001)-c(2x2) substrate report large values of the axial and transverse magnetic anisotropy energies (MAE) for a single magnetic atom. The STM experiments are complemented by density-functional theoretical calculations. These calculations reveal that the magnetic atoms become incorporated into a covalent CuN matrix, so that their electronic and magnetic character differs from the gas-phase transition metal atoms.

These STM experiments [1] along with previously reported XMCD measurements [2] for a single Co atom and small Co clusters on the Pt(111) surface show that just a few atom size nanostructures can maintain a stable magnetic orientation at low temperature due to the large magnetic anisotropy energy (MAE). What makes these atomic-scale magnetic structures technologically relevant is their large MAE which provides the means of reducing the size of the magnetic bits above the superparamagnetic limit, i.e. the ratio of the MAE to the thermal energy $k_B T$. Understanding of the atomic-scale MAE in nanomagnets is essential in the determination of the minimum feasible magnetic memory bit size, and can assist in further increase of the magnetic recording density.

In the work reported here we make use of ab initio numerical calculations of the MAE to analyze the key physical quantities determining the anisotropic magnetic characteristics of single 3d-metal atoms on CuN/Cu(001)-c(2x2) substrate. Similar to the theory of Ref. [1], we use a supercell model. The supercell consists of three Cu(001) layers and a single Cu$_2$N atomic layer with c(2x2)/N-Cu(001) arrangement given in [3]. The in-plane c(2x2) dimensional unit cell is doubled (Cu$_2$N$_2$), and the 3d-atom (Mn and Fe) is placed on the top of Cu-atom. The supercell is shown schematically in Fig. 1. The vacuum is modeled by the equivalent of four empty Cu layers.

The structure relaxation is performed employing the standard VASP method [4] without spin-orbit coupling (SOC) and making use of the generalized gradient approximation. Placing 3d atom on the top of the Cu atom in the CuN surface makes a substantial rearrangement of the atomic structure (see Fig. 1). The Cu atom right below the adatom moves toward the bulk and the relaxed distance between this atom and magnetic atom is decreasing from 4.42 Bohr for the Mn atom to 4.27 Bohr for the Fe atom. Other Cu atoms in the CuN top-layer change slightly their positions with the change of the magnetic atom. Overall relaxed atomic positions are qualitatively consistent with the picture given in Ref. [1].

![FIG. 1: A schematic crystal structure used to represent the 3d-atom on the c(2x2)N-Cu(001) surface. The actual atomic positions correspond to the case of the Mn atom on the c(2x2)N-Cu(001) surface.](image-url)
be valid for itinerant metallic systems.

The spin $M_S$ and orbital $M_L$ magnetic moments for the magnetization directed along the $z$-axis are given in Table I. for the Mn and Fe atoms. Small spin and orbital moments are also induced on neighboring Cu sites and quickly decay away from the magnetic Mn or Fe atom. The spin-resolved projected density of states (PDOS) for the Mn and Fe atoms is shown in Fig. 2. The spin-majority manifold is practically fully occupied for both Mn and Fe. For Mn atom, the spin-minority channel is almost empty and the orbital $M_L$ moment is almost zero. The spin-minority occupation is increased for the Fe-atom while the spin splitting and spin moment $M_S$ are decreasing. The detailed inspection of $m_{l}$-projected PDOS shows that non-zero orbital $M_L$ moment for the Fe atom originates from $|m_s = \frac{1}{2}; m_l = \pm 2\rangle$ orbitals near Fermi edge. The major contribution to $M_L$ is brought about mainly by in-plane $xy$ and $x^2 - y^2$ spin-minority orbitals. The $3z^2 - r^2$ orbital is the least localized due to the strong overlap with 3$d$ electrons of the Cu atom beneath.

Next we turn to a salient aspect of our investigation, the MAE calculations. The anisotropic energy $E_A(\theta, \phi)$ dependence (including the second order terms) on the magnetization direction reads,

$$E_A(\theta, \phi) = K^\perp_2 \mathbf{e}^2 + K^{||}_2 (\mathbf{e}^2 - \mathbf{e}_z^2),$$

$$E_A(\theta, \phi) = K^\perp_2 \cos^2(\theta) + K^{||}_2 \sin^2(\theta)(\cos^2(\phi) - \sin^2(\phi))$$

where $K^\perp_2$ and $K^{||}_2$ are the uniaxial MAE constants, and $\mathbf{e}_{x,y,z}$ are the cartesian coordinates of the normalized magnetization vector $\mathbf{M}/||\mathbf{M}|$. The $\theta$ and $\phi$ are the polar angles in the reference frame which is chosen as follows: the $x$-axis is along the in-plane hollow direction, the $y$-axis is along the in-plane N-chain direction, and $z$-axis is along the out-of-plane direction (see Fig. 1).

In order to evaluate the MAE from Eq. (1), we make use of the torque method [7]. It can be formulated as follows. We solve the Kohn-Sham equations for a two-component spinor $|\Phi_i\rangle = \left(\begin{array}{c} \Phi_i^\uparrow \\Phi_i^\downarrow \end{array}\right)$.

$$\sum_{\beta} \left(-\mathbf{\nabla}^2 + \hat{V}_{eff} + \xi (\mathbf{i} \cdot \mathbf{s})\right) \Phi^\beta_i (\mathbf{r}) = e_{\beta} \Phi^\alpha_i (\mathbf{r}), \quad (2)$$

where the $\hat{V}_{eff} = V(\mathbf{r}) \mathbf{I} + \mathbf{A} \cdot \mathbf{B}(\mathbf{r})$ matrix consists of the sum of the scalar potential $V$ and “exchange” field $B$ parallel to the spin moment $M_S$, and $\hat{H}_{SO} = \xi (\mathbf{i} \cdot \mathbf{s})$ is the SO coupling operator. When the magnetic force theorem [8] is used to evaluate the magnetocrystalline anisotropy energy, the $M_S$ is rotated and a single energy band calculation is performed for the new orientation of $M_S$. The MAE results from SO coupling induced changes in the band eigenvalues $E_A(\theta, \phi) = \sum_{\epsilon} \epsilon_i(\theta, \phi)$. Alternatively, the torque $T(\theta, \phi) = \partial E_A(\theta, \phi)/\partial \theta$ can be evaluated making use of the linear response theory:

$$T(\theta, \phi) = \sum_{\epsilon} \frac{\partial \epsilon_i}{\partial \theta} \Phi_i^\uparrow (\mathbf{r}) \mathbf{I} \cdot \mathbf{s} \Phi_i^\downarrow + \Phi_i^\downarrow (\mathbf{r}) \mathbf{I} \cdot \mathbf{s} \Phi_i^\uparrow |\Phi_i^\downarrow \rangle \quad (3)$$

where the $\mathbf{U}(\theta, \phi)$ is a conventional spin rotation matrix and $|\Phi_i\rangle = \mathbf{U}(\theta, \phi)|\Phi_i\rangle$. An advantage of this approach is that it allows the total MAE separation into the element-specific contributions from different atoms in the unit cell. The torque method has been first implemented in FP-LAPW basis in Ref. [10]. Also, it has been employed recently in the Korringa-Kohn-Rostocker calculations [11].

The torque $T(\theta, \phi)$ angular dependence is shown in Fig. 3 for both Mn and Fe-atoms on CuN/Cu(001). A set of 784 $k$-points in the full 2D-BZ which is equivalent to 3136 $k$-points in the full 2D-BZ of Cu(001)) is used in these calculations. The uniaxial MAE constants $K^\perp_2$ and $K^{||}_2$ can be evaluated from the torque $T(\theta, \phi)$ angular dependence, shown in Fig. 3 and angular derivative

| Atom | $M_S^{Tot}$ | $M_S$ | $M_L$ |
|------|-----------|------|------|
| Mn   | 4.379     | 3.758| 0.004|
| Fe   | 3.654     | 2.917| 0.076|

TABLE I: Total spin moment per unit cell ($M_S^{Tot}$), spin ($M_S$) and orbital ($M_L$) magnetic moments on 3d-adatom (in Bohr magnetons) for the magnetization directed along the $z$-axis.

FIG. 2: Spin-resolved PDOS for Mn and Fe adatoms. Also shown PDOS for the Fe atom $x^2 - y^2$ and $3z^2 - r^2$ spin-minority orbitals.
of Eq.(1).

\[
T(\theta, \phi) = \left[-K^z_2 + K^x_2\right] \cos(2\phi) \sin(2\theta). \tag{4}
\]

For the Mn atom, the values of the uniaxial MAE constants are: \(K^z_2=0.20\) meV and \(K^x_2=0.17\) meV. The Mn atom contribution in \(K^z_2 = -0.16\) meV, and \(K^x_2=-0.12\) meV. For the Fe atom, \(K^z_2=0.16\) meV and \(K^x_2=0.93\) meV, and the Fe atom specific contributions in \(K^z_2 = -0.04\) meV, and \(K^x_2=0.97\) meV. Also, we found that higher order anisotropy is much less (at least by an order of magnitude) than the uniaxial anisotropy.

Now we evaluate the MAE defined as the energy \(E_A(\theta, \phi)\) difference for different directions of the magnetization \(M\). Using the torque \(T(\theta, \phi)\) angular dependence shown in Fig. 3, we obtain \(\text{MAE} = \int_{0}^{\pi/2} d\theta T(\theta, \phi)\).

The values of the MAE are shown in Table II. There is an increase of the MAE from Mn to the Fe atom case. For the Mn atom, the easy magnetization axis is directed along the surface normal \(z\) axis, in agreement with the experimental data [1]. For the case of Fe, the easy magnetization is along the N-chain, also in agreement with the experiment [1]. The anisotropic energy \(E_A(\theta, \phi)\) angular dependence for Mn and Fe atoms on CuN surface together with the easy magnetization axis orientation is illustrated in Fig. 4.

![Graph showing the torque for Mn and Fe atoms](image)

**FIG. 3:** The torque \(T(\theta, \phi)\) for the \(x - z\)-plane (\(\phi = 0^\circ\)) and \(y - z\)-plane (\(\phi = 90^\circ\)) as a function of \(\theta\). The total torque and leading contributions from the 3d-adatom are shown.

| Total MAE Mn Fe | \(\Delta E_A[z - x]\) | -0.03 -0.77 | \(\Delta E_A[z - y]\) | -0.37 1.08 | \(\Delta E_A[y - x]\) | 0.34 -1.86 |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|

**TABLE II:** The MAE (meV) for the Mn and Fe-adatoms, Here, \(\Delta E[i - j] = E_A[M||ji] - E_A[M||ij], i(j) = x, y, z\)

It is quite common to examine the correlation between the MAE and the orbital moment anisotropy (OMA). Approximate relation between the MAE and OMA is given by Bruno formula [12], [MAE \(\approx -\xi/4\) OMA], where \(\xi\) is the SOC constant. For the Mn atom case, the Bruno formula gives \(\Delta E_A[z - x]\) of -0.07 meV, \(\Delta E_A[z - y]\) of -0.02 meV, and \(\Delta E_A[y - x]\) of -0.05 meV. Comparison with the torque results of Table II. shows that Bruno formula predicts the correct easy \(z\)-axis but fails to describe the \(y - x\) plane transverse anisotropy. For the case of Fe atom, making use of Bruno formula we obtain the MAE of \(\Delta E_A[z - x]\) = -0.74 meV, \(\Delta E_A[z - y]\) = 1.46 meV, and \(\Delta E_A[y - x]\) = -2.19 meV in a good agreement with the torque results (see Table II.). The reason why Bruno formula works better for Fe atom than for Mn atom case is that it is not accurate enough to account for relatively small Mn atom MAE. For the stronger Fe atom MAE, validity of Bruno formula is improving on qualitative.

Now we turn to comparison with the experimental results of Hirjibehedin et al. [1]. The STM measures the spin-excitation energies in a magnetic field. These excitation spectra are then analyzed by the model Hamiltonian,

\[
\hat{H} = g_\mu_B \mathbf{B} \mathbf{S} + D S_z^2 + E (S_x^2 - S_y^2) \tag{5}
\]

In the Eq.(5), the \(z\)-axis is chosen along the easy magnetization direction. In order to compare our results with the experiment, we have to convert the data in Table II. into the reference frame chosen in Ref. [1] and re-normalize the anisotropy values by \(S^2\) (\(S = 5/2\) for Mn and \(S = 2\) for Fe). The results are shown in Table III. Our \emph{ab initio} results correctly reproduce the sign and order of magnitude of \(D\) and \(E\) experimental anisotropies.

It is quite surprising that the LSDA based calculations give quite reasonable values of the MAE constants for the systems which have been initially thought as being close to the atomic limit. The density functional theory is known to work reasonably well for the ground state
FIG. 4: The anisotropic energy $\{\theta, \phi\}$ angular dependence for Mn (top) and Fe (bottom) atoms on CuN surface. Here the length of radius vector forming the surface is equal to $[E_A(\theta, \phi) - E_A(easy axis)]$.

In conclusion, we have shown that the magnetic anisotropy energies for Mn- and Fe-atoms on CuN/Cu(001) can be semi-qualitatively reproduced by the first-principles LSDA FP-LAPW calculations. The easy magnetization direction is found in agreement with the experimental data for Mn and Fe atoms. It is shown the calculated MAE has a single-ion character and mainly originates from the well localized moment of Mn- and Fe-atoms. The uniaxial MAE constants are calculated in semi-quantitative agreement with the experiment.

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TABLE III: Comparison with experimental $D$ and $E$ (meV).

|        | Mn      | Exp. $\pm$ 0.001 | LSDA    |
|--------|---------|------------------|---------|
| $D$    | -0.039  | 0.007 ± 0.001    | 0.03    |
| $E$    |         |                   |         |

|        | Fe      | Exp. $\pm$ 0.01  | LSDA    |
|--------|---------|------------------|---------|
| $D$    | -1.55   | 0.31 ± 0.01      | -0.36   |
| $E$    |         |                   | 0.10    |

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