Voltage- and temperature-dependence of the magnetic anisotropy of interfacial rare-earth local moments

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\textbf{Abstract.} The control of magnetic materials and devices by voltages without electric currents holds the promise of power-saving nano-scale devices. Here we study the temperature-dependent voltage control of the magnetic anisotropy caused by rare-earth (RE) local moments at an interface between a magnetic metal and a non-magnetic insulator, such as Co(RE)|MgO. Based on a Stevens operator representation of crystal and applied field effects, we find large dominantly quadrupolar intrinsic and field-induced interface anisotropies at room temperature. We suggest improved functionalities of transition metal tunnel junctions by dusting their interfaces with rare earths.

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1. Introduction

The magnetic order can be actuated by magnetic fields, spin [12] and heat [33, 34] currents, mechanical rotations and sound waves [5, 6], optical fields in cavities [7, 8], and electric fields [9, 10, 11]. The last effect, voltage-control of magnetic anisotropy (VCMA), avoids electric currents and thereby Joule heating. A time-dependent applied electric field can both switch magnetization [12, 13] and excite the ferromagnetic resonance [10, 14]. However, the tuning of the exchange interactions [27, 28, 29, 30, 31, 32], and the control of magnetic properties by electric fields has also been demonstrated or proposed in magnetoelectric materials [20, 21, 22], by proximity effects [23, 24, 25], nuclear spin resonance in single-molecule magnets [26], and the tuning of the exchange interactions [27, 28, 29, 30, 31, 32].

The electrostatic environment of a local moment affects its magnetic energy via the spin-orbit interaction (SOI) [33, 34]. In transition-metal atoms such as Fe, Co, and Ni with partially filled 3d subshells, the electrostatic interaction with neighboring atoms, \( E_{CF} \sim 1 \text{ eV} \) is much larger than the SOI \( E_{SOI} \sim 0.05 \text{ eV} \) [33], which implies that the orbital moment of transition-metal ions is easily quenched and the relatively large 3d orbital radius favors band formation and itinerant magnetism. The opposite occurs for the lanthanide series, i.e., atoms from lanthanum (La with atomic number 57) to lutetium (Lu with atomic number 71). The rare earths also include scandium (Sc) and yttrium (Y). Sc, Y, La, Eu, and Lu are not magnetic in their ground-state manifold. The half-filled subshell of the magnetic atom Gd lacks orbital moment and, therefore, SOI. For the rest of the rare earths, the 4f SOI \( E_{SOI} \sim 0.2 \text{ eV} \) is much stronger than crystal-field energies \( E_{CF} \sim 0.01 \text{ eV} \) [33], so their orbital moments are atomic-like and not quenched. The magnetism of lanthanide-containing compounds can be understood by models that proceed from an atomic picture. Nevertheless, since the crystal fields lock to their spin-orbit induced anisotropic charge distributions, large magnetocristalline anisotropies can be achieved.

A mechanism for the VCMA of rare earth (REs) moments is the electric field-induced torque on an anisotropic 4f charge distribution and the rigidly coupled magnetic moment by the electric quadrupolar coupling [35]. This torque is communicated to the magnetic order via the exchange interaction.

Here, we predict that an interfacial RE dusting enhance its VCMA efficiency. We study the temperature dependence of the VCMA of rare earth (REs) moments, as well as the role of higher-order anisotropy constants. The latter issue has been addressed in transition-metal systems [18, 19], where the first- and second-order contributions partially cancel in the total VCMA. We calculate the magnetic anisotropy constants (MACs) of a rare-earth ion in the presence of an electric field, assuming a strong exchange coupling with the system magnetization. The effect is strongest for a RE at an interface between a magnetic metal and a non-magnetic insulator, such as Co/MgO. The Hamiltonian of the local moment in an angular momentum basis leads to so-called Stevens operators that can be easily diagonalized. We extract the intrinsic and field-induced MACs from the corresponding temperature-dependent free energy as a function of temperature.

2. Single-ion magnetic anisotropy

The 4f atomic radius is small compared to that of other filled atomic shells, which isolates the 4f electrons from other atoms in compounds [33]. Consequently, the crystal fields that would quench the orbital moment of 3d transition metals only slightly affect 4f electron ground-state configurations. The 4f subshell is characterized by a spin (S), an orbital moment (L), and a total angular moment (J = L + S). In the basis \(|S, L, J, J_z\rangle\),

\[ S^2|S, L, J, J_z\rangle = \hbar^2 S(S + 1)|S, L, J, J_z\rangle, \]
\[ L^2|S, L, J, J_z\rangle = \hbar^2 L(L + 1)|S, L, J, J_z\rangle, \]
\[ J^2|S, L, J, J_z\rangle = \hbar^2 J(J + 1)|S, L, J, J_z\rangle, \]
\[ \hat{J}_z|S, L, J, J_z\rangle = \hbar J_z|S, L, J, J_z\rangle, \]

where S and L are governed by Hund’s first and second rules, respectively. The third rule determines the multiplet \( J = L \pm S \), where the – and + is for the light (i.e., less than half-filled 4f shell with an atomic number less than 64) and heavy REs, respectively. We list the S, L, and J for the whole 4f series in table [1].

In the following, we focus on the ground-state manifold with constant S, L, and J numbers. This multiplet of \( J = L \pm S \) has 2J + 1 states that are degenerate in the absence of electromagnetic fields. Also,

\[ S = (g_J - 1)J, \]
\[ L = (2 - g_J)J, \]
\[ L + 2S = g_J J, \]

where \( g_J = 3/2 + [S(S + 1) - L(L + 1)]/[2J(J + 1)] \) is the Landé g-factor. The projections of S, L, and L + 2S on J for lanthanide atoms manifests itself also in the crystal-field Hamiltonian, as shown in the next subsection.
Table 1. Ground-state manifold of the tri-positive 4f ions. S, L, and J are the quantum numbers associated with S², L², and J², respectively. g_J is the Landé g-factor.

| Ion  | 4fⁿ | S  | L  | J   | g_J |
|------|-----|----|----|-----|-----|
| Ce³⁺ | 4f¹ | 1/2| 3  | 5/2 | 6/7 |
| Pr³⁺ | 4f² | 1  | 5  | 4   | 4/5 |
| Nd³⁺ | 4f³ | 3/2| 6  | 9/2 | 8/11|
| Pm³⁺ | 4f⁴ | 2  | 6  | 4   | 3/5 |
| Sm³⁺ | 4f⁵ | 5/2| 5  | 5/2 | 2/7 |
| Eu³⁺ | 4f⁶ | 3  | 3  | 0   | -  |
| Gd³⁺ | 4f⁷ | 7/2| 0  | 7/2 | 2   |
| Tb³⁺ | 4f⁸ | 3  | 6  | 3/2 | -  |
| Dy³⁺ | 4f⁹ | 5/2| 5  | 15/2| 4/3 |
| Ho³⁺ | 4f¹⁰| 2  | 6  | 8   | 5/4 |
| Er³⁺ | 4f¹¹| 3/2| 6  | 15/2| 6/5 |
| Tm³⁺ | 4f¹²| 1  | 5  | 6   | 7/6 |
| Yb³⁺ | 4f¹³| 1/2| 3  | 7/2 | 8/7 |

Table 2. Projection constants for the Stevens’ operators, set of Eqs. [39]. The nearly ellipsoidal 4f electron density causes a hierarchy of projection constants, i.e., most ions obey the scaling |ψ₂| ~ 10⁻², |ψ₄| ~ 10⁻³, and |ψ₆| ~ 10⁻⁵, so the quadrupole contribution dominates. Some use the notation α_j = ψ₂, β_j = ψ₄, and γ_j = ψ₆.

$$h^4 \hat{O}_4^{(0)} = 35\hat{j}_z^4 - 30\hat{j}_z^2 \hat{j}_x^2 + 25\hat{j}^4 - 6\hat{j}_y^2 + 3\hat{J}^4,$$  
$$h^6 \hat{O}_6^{(0)} = 231\hat{j}_z^6 - 315\hat{j}_z^4 \hat{j}_x^2 + 735\hat{j}_y^4 + 105\hat{j}_z^2 \hat{j}_y^2 - 5\hat{J}^2,$$  

Stevens operators for other symmetries are listed in [38, 39, 40]. The total crystal-field Hamiltonian reads

$$H_{CF} = -e \sum_{j=1}^{N_{4f}} V(\mathbf{r}_j) = \sum_{j=2,4,6} \psi_i \langle r^l \rangle A_i^{(0)} \hat{O}_i^{(0)}.$$  

2.1. Stevens operators

Let us consider a crystal site with a potential that is invariant to rotations around the z-axis, which can be expanded as

$$-eV(\mathbf{r}) = A_0^{(0)} (3z^2 - r^2) + A_4^{(0)} (35z^4 - 30r^2z^2 + 3r^4) + A_6^{(0)} (231z^6 - 315z^4r^2 + 105z^2r^4 - 5r^6),$$  

where A_i^{(0)} is a uniaxial crystal-field parameter associated to the Y_i^{(0)} spherical harmonic function (see Appendix A), usually expressed in units of temperature divided by a_0, where a_0 = 0.53 Å is the Bohr radius. For example, for the 4f states of Nd⁵⁺F₁₄B [37] A_2^{(0)} = 304 K/a_0⁶, A_4^{(0)} = -15 K/a_0⁴, and A_6^{(0)} = -2 K/a_0². The crystal-field parameters of the 4f and 4g states of other members of the (RE)₂F₁₄B family can be found in Ref. [37].

The electrostatic Hamiltonian of N₄f electrons in the subshell Hilbert space can be expanded into

$$\sum_{j=1}^{N_{4f}} (3z_j^2 - r_j^2) = \psi_2 \langle r^2 \rangle \hat{O}_2^{(0)},$$  
$$\sum_{j=1}^{N_{4f}} (35z_j^4 - 30r_j^2z_j^2 + 3r_j^4) = \psi_4 \langle r^4 \rangle \hat{O}_4^{(0)},$$  
$$\sum_{j=1}^{N_{4f}} h(\hat{r}_j, \hat{z}_j) = \psi_6 \langle r^6 \rangle \hat{O}_6^{(0)},$$  

where h(\hat{r}_j, \hat{z}_j) = 231z_j^6 - 315z_j^4\hat{r}_j^2 + 105z_j^2\hat{r}_j^4 - 5\hat{r}_j^6 and \hat{z}_j and \hat{r}_j are the operators of the z and the radial coordinates of the j-th electron, respectively. \langle r^l \rangle is the mean value of r^l calculated for a 4f (atomic) radial wave function. The projection constants \psi_l are listed in Table 2 while Stevens equivalent operators are

$$h^2 \hat{O}_2^{(0)} = 3\hat{j}_z^2 - \hat{J}^2,$$

$$h^6 \hat{O}_4^{(0)} = 35\hat{j}_z^4 - 30\hat{j}_z^2 \hat{j}_x^2 + 25\hat{j}^4 - 6\hat{j}_y^2 + 3\hat{J}^4,$$  
$$h^6 \hat{O}_6^{(0)} = 231\hat{j}_z^6 - 315\hat{j}_z^4 \hat{j}_x^2 + 735\hat{j}_y^4 + 105\hat{j}_z^2 \hat{j}_y^2 - 5\hat{J}^2,$$  

$$\psi_2 \langle r^2 \rangle \hat{O}_2^{(0)},$$  
$$\psi_4 \langle r^4 \rangle \hat{O}_4^{(0)},$$  
$$\psi_6 \langle r^6 \rangle \hat{O}_6^{(0)},$$  

2.2. Magnetic Anisotropy Constants

In several magnets, the exchange interaction strongly couples the 4f local moments to the magnetization \mathbf{m} = \sin \theta (\cos \varphi \mathbf{e}_x + \sin \varphi \mathbf{e}_y) + \cos \theta \mathbf{e}_z, where \mathbf{e}_j is the unit vector along the Cartesian axis j. Then, the Hamiltonian H of a single RE atom reads

$$H = H_{CF} + \frac{J_{ex} (g_J - 1) f(T)}{h} \mathbf{J} \cdot \mathbf{m},$$  

where J_{ex} > 0 is the exchange constant with units of energy. The exchange coupling favors the parallel alignment between the magnetization \mathbf{m} and the spin contribution to the 4f moment -\gamma_e (g_J - 1) \mathbf{J}, with -\gamma_e being the electron gyromagnetic ratio. Note that the 4f spin \mathbf{S} is antiparallel (parallel) to \mathbf{J} for the light (heavy) lanthanides because of g_J < 1 (g_J > 1).

f(T) parameterizes the temperature dependence of the system magnetization [41, 42]

$$f(T) = \left[ 1 - s \left( \frac{T}{T_C} \right)^{3/2} - (1 - s) \left( \frac{T}{T_C} \right)^{1/3} \right]^1,$$  

$$H = H_{CF} + \frac{J_{ex} (g_J - 1) f(T)}{h} \mathbf{J} \cdot \mathbf{m},$$  

$$f(T) = \left[ 1 - s \left( \frac{T}{T_C} \right)^{3/2} - (1 - s) \left( \frac{T}{T_C} \right)^{1/3} \right]^1.$$
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where $T_C$ is the Curie temperature, and $s$ and $p$ (with $p > s$) are material dependent parameters. For example, for Co $T_C = 1385$ K, $s = 0.11$, and $p = 5/2$; for Fe, $T_C = 1044$ K, $s = 0.35$, and $p = 4$.

Empirical expression \(\mathcal{E}\) describes the temperature dependence between Bloch’s law \(1 - (s/3) (T/T_C)^{3/2}\) for $T \to 0$ and the critical scaling \((1 - T/T_C)^{1/3}\) for $T \to T_C$. Equation \(\mathcal{E}\) is all we need to know about the magnetic host.

The Helmholtz free energy \(\mathcal{J}\)

\[
F = -\frac{1}{\beta} \ln \left[ \sum_{n=1}^{2J+1} e^{-\beta E_n} \right],
\]

where $\beta = 1/(k_B T)$, $k_B = 8.617 \times 10^{-5}$ eV/K is Boltzmann’s constant, $T$ is temperature, and $E_n$ is the $n$-th eigenvalue of Eq. \(\mathcal{A}\). The uniaxial anisotropy energy density can be expanded as \(\mathcal{B}\) and \(\mathcal{C}\).

The applied electric field modifies not only the exchange interaction, with small electric field corrections.

The exchange interaction dominates the term splittings with small electric-field induced corrections.

In the following, we numerically compute the temperature-dependent MACs induced by electric fields at an insulator\(\text{metal}\) interface, also considering that crystal fields at interfaces may substantially differ from that in bulk crystals. We assume uniaxial symmetry and denote the interface crystal field parameters by $A_l^{(0)}$. An applied voltage can give rise to locally large electric fields $E_0$ normal to a metal\(\text{insulator}\) interface (along the $z$-axis), which contributes as $\Delta A_l^{(0)}$ with total $\Delta A_l^{(0)} = \bar{A}_l^{(0)} + \Delta A_l^{(0)}$.

3. Electric field dependent magnetic anisotropy

The applied electric field $E_0$ is screened on the scales of the Thomas-Fermi length $d_{TF} \sim 1$ Å on the metal side, so $E = E_0 e^{-z/d_{TF}} e_z$ for $z > 0$, with $z = 0$ being the interface position. Close to $z = 0$ and using the expressions from Appendix A,

\[
\Delta A_l^{(0)} = -\frac{e E_0}{6d_{TF}},
\]

\[
\Delta A_4^{(0)} = -\frac{e E_0}{840d_{TF}^2},
\]

\[
\Delta A_6^{(0)} = -\frac{e E_0}{166320d_{TF}^3}.
\]

Therefore, the electric field modifies not only the second-order uniaxial anisotropy but also higher-order terms. With this set of crystal-field parameters, we can diagonalize the atomic Hamiltonian \(\mathcal{D}\), evaluate the free energy \(\mathcal{E}\), and the MACs \(\mathcal{F}\). Numerical details are in Appendix B.

The MACs $\Delta K_l$ from $\Delta A_l^{(0)}$ are proportional to the applied electric field $E_0$. $\Delta K_1$ has a negative slope for the oblate (pancake-shaped) ions Ce$^{3+}$, Pr$^{3+}$,
Nd\(^{3+}\), Tb\(^{3+}\), Dy\(^{3+}\), and Ho\(^{3+}\), and a positive slope for the prolate (cigar-shaped) ions Pm\(^{3+}\), Sm\(^{3+}\), Er\(^{3+}\), Tm\(^{3+}\), and Yb\(^{3+}\), consistent with previous results [35]. Figure 2 shows the VCMA contributions of a set of RE atoms at an interface at low temperatures with \(n_{RE} = 1 \text{ nm}^{-2}\), and \(J_{ex} = 0.1\) eV. We use \(d_{TF} = 1\) Å and the Co parameters for the magnetization, \(\{t_{c}, s, p\} = \{1385 \text{ K}, 0.11, 5/2\}\) in Eq. 7, assuming that they are not affected much by the interface. The MACs in units of energy density result from dividing the surface MACs by the thickness of the magnetic film. For example, dusting the interface with one Tm atom per nm\(^2\) with a field of \(E_0 \sim 1\) V/nm = 10\(^4\) kV/cm creates an energy volume density of 1 MJ/m\(^3\) in a 1 nm-thick Co film. Figure 2 illustrates that the VCMA of rare earths is governed only by \(K_1\), while \(K_2\) and \(K_3\) are negligibly small. This hierarchy differs from that of transition metals, where \(K_1\) and \(K_2\) are of the same order of magnitude and partially compensate each other [33, 34, 42]. This difference can be understood as follows. The \(l\)-th order MAC divided by the characteristic electrostatic energy, \(eE_0d_{TF}\), scales as \(\Delta K_j/(eE_0d_{TF}) \propto |\vartheta_{j2}(-z^2)|/|\vartheta_{6j}|\). The 4f subshell envelope is nearly ellipsoidal, which is accounted for by the hierarchy of the projections constants \(|\vartheta_{2j}| \ll |\vartheta_{4j}| \ll |\vartheta_{6j}|\). The transition metal 3d shells are more polarizable and can be more easily deformed by the crystal fields than the lanthanides. A consequence is that the quadrupole contribution of the voltage-controlled anisotropy \(\Delta K_1\) of rare earths is much larger than \(\Delta K_2\) and \(\Delta K_3\).

The temperature dependence of rare-earth magnetic anisotropies in bulk materials has been extensively studied [33, 34, 42]. Here we calculate the temperature dependence of the VCMA for rare-earth atoms at an interface between a non-magnetic insulator (such as MgO) and a magnetic metal, such as Fe or Co. Figure 3 illustrates the temperature-dependence of \(K_1\) for all lanthanides with a finite orbital moment in the temperature range 0 K \(\leq T \leq 1400\) K for \(n_{RE} = 1\) nm\(^{-2}\). \(K_1\) at room temperature, \(T = 300\) K, is specified inside each graph. The room-temperature VCMA is largest for Tb\(^{3+}\) and Dy\(^{3+}\) with \(\Delta K_1 = -9.6\) \(\mu\)J/m\(^2\) and \(\Delta K_1 = -9.1\) \(\mu\)J/m\(^2\), respectively.

In the absence of exchange coupling between the 4f angular momentum (\(J\)) and the magnetization (\(m\)), REs do not contribute to the anisotropy, so the VCMA...
strength vanishes for $J_{ex} \to 0$. This tendency is shown in Fig. 4 for 0.01 eV ≤ $J_{ex}$ ≤ 10 eV at $T = 300$ K. Results are not very sensitive to the value of typical exchange constants, 0.1 eV ≤ $J_{ex}$ < 1 eV, as long as they are larger than the anisotropy induced by the crystal fields or applied voltages (∼ 0.01 eV [33]).

4. Intrinsic interface magnetic anisotropy

The intrinsic (zero-electric field) magnetic anisotropy at the interface cannot be easily computed. Simple approaches, such as the point-charge model, are not adequate for metals due to the efficient screening by conduction electrons [44]. The screened-charge model of metals [43] has been used to characterize interfacial anisotropies in metallic multilayers [45]. However, this model is not valid for metal/insulator interfaces due to the inhomogeneous nature of the electron-gas density, which may render the screening less efficient and could create a magnetic anisotropy by itself.

Here we estimate the order of magnitude of the intrinsic interfacial RE magnetic anisotropy by the model of a local moment in a metal at the origin surrounded by four oxygen atoms with Cartesian coordinates ($\pm d_{ox}, 0$, $-d_{ox}$)/\(\sqrt{2}\) and (0, \(\pm d_{ox}, 0$)/\(\sqrt{2}\) and five transition-metal atoms (such as Co or Fe) at positions ($\pm d_{TM}$, 0, 0), (0, $\pm d_{TM}$, 0) and (0, 0, $d_{TM}$), as shown in Fig. 5. The uniaxial crystal-field parameter [33, 34, 44] reads

\[
\tilde{A}_2^{(0)} = \sum_j A'_j \left( 3 \cos^2 \theta_j - 1 \right),
\]

where $j$ labels the ligand, $\cos \theta_j$ is the $z$-component of the $j$-th site position ($r_j$), and $A'_j$ depends on the distance $d_j = |r_j|$

\[
A'_j (d_j) = -\frac{eQ_j e^{-d_{j}/d_{TF}}}{4\pi\varepsilon_0 2d_j^2} \left[ 1 + \frac{d_j}{d_{TF}} + \frac{1}{3} \left( \frac{d_j}{d_{TF}} \right)^2 \right],
\]

where $\varepsilon_0$ is the vacuum permittivity. We adopt the bulk effective (or crystal-field) ligand charges for $Q_j$. Using $d_{ox} = 6$ Å, $d_{TM} = 5$ Å, and $d_{TF} = 1$ Å, and $A'_j/k_B$ for iron and oxygen of the order of magnitude of 90$K_a^{-2}$ and 20$K_a^{-2}$, respectively, $\tilde{A}_2^{(0)} \sim -2 \times 10^{18}$ eV/m\(^2\) is of the same order as that produced by an electric field of $E_0 = 1.2$ V/nm.

For the present interface model, prolate (oblate) ions characterized by $\vartheta_2 > 0$ ($\vartheta_2 < 0$) favor an perpendicular (in-plane) magnetization. Doping a transition-metal layer with prolate rare-earth ions enhances the perpendicular interface anisotropy, which is important for STT-MRAM applications, but also requires higher voltages for VCMA-induced magnetization switching. We note that in traditional VCMA experiments on transition metals, the total magnetic anisotropies are small, and electric-field effects easily dominate. A quantitative description of the intrinsic interface rare-earth anisotropy as a function of interface structure and morphology requires ab initio calculations.

5. Conclusions and discussion

We studied the temperature-dependent voltage-controlled magnetic anisotropy of rare-earth atoms at a magnetic metal/non-magnetic insulator interface. Our findings differ from the conventional wisdom based on transition metals. In rare earths, only the lowest-order uniaxial constant can be efficiently modulated by a voltage because of the small 4f radius and rigid ellipsoidal shape of the 4f shell electron density. To leading order, the magnetic anisotropy constants change linearly with the applied electric field, with a negative slope for the oblate (pancake-like) Ce\(^{3+}\), Pr\(^{3+}\), Nd\(^{3+}\), Tb\(^{3+}\), Dy\(^{3+}\), and Ho\(^{3+}\), and a positive one for the prolate Pm\(^{3+}\), Sm\(^{3+}\), Er\(^{3+}\), Tm\(^{3+}\), and Yb\(^{3+}\) moments.

Figure 4. Magnetic Anisotropy constant $\Delta K_1$ for $J_{ex} = 10$ eV (solid line), $J_{ex} = 1$ eV (crosses), $J_{ex} = 0.1$ eV (open circles), and $J_{ex} = 0.01$ eV (full circles). This graph uses $T = 300$ K, $E_0 = 10$ mV/nm, and a density $n_{eff} = 1$/nm\(^2\) at a Co surface. The thin horizontal line $\Delta K_1 = 0$ is just for visual guidance.

Figure 5. Sketch of the ligands of a RE atom at a metal/insulator interface.
trinsic (i.e., independent of the applied electric field) magnetic anisotropy, the oblate (prolate) ones favoring a perpendicular (in-plane) equilibrium magnetizations.

Our model assumes metallic screening, i.e., a drop of the electric field over atomic distances at the interface which hosts the rare earth moments. This assumption might break down at non-ideal interfaces, so it should be confirmed by experimentally or ab initio methods.

Nevertheless, we are confident about substantial effects at room temperature for even low densities of RE atoms (∼ 1/nm²). Since the electric field is strongly enhanced at metal/insulator interfaces, bulk doping of a magnet with rare earths is not very efficient. Still, the dusting of the interface between a tunnel barrier and a transition metal thin film can significantly enhance the switching efficiency of voltage-controlled tunnel junctions.

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Appendix A. Expansion into spherical harmonics

We focus on the axially symmetric potentials, −eV(r), that we decompose into the Spherical harmonics Y_l^0(θ)

\[ Y_l^0(\theta) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta), \quad (A.1) \]

where l = 2, 4, 6 and P_l is the l-th Legendre polynomial,

\[ P_2(x) = \frac{1}{2}(3x^2 - 1), \quad (A.2) \]
\[ P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3), \quad (A.3) \]
\[ P_6(x) = \frac{1}{16}(231x^6 - 315x^4 + 105x^2 - 5), \quad (A.4) \]

leading to a multipolar expansion up to the 6th order in r

\[ -eV(r) = 4\sqrt{\frac{\pi}{5}} Y_2^0(\theta)r^2 A_2^{(0)} + 16\sqrt{\frac{\pi}{9}} Y_4^0(\theta)r^4 A_4^{(0)} + 32\sqrt{\frac{\pi}{13}} Y_6^0(\theta)r^6 A_6^{(0)} + c_0(\theta), \quad (A.5) \]

where c_0(θ) collects the odd terms in z (dipolar-like contributions) that do not interact with a nearly ellipsoidal 4f subshell (i.e., the fields are not large enough to polarize/asymmetrize the subshell). Using the orthonormality of spherical harmonic functions,

\[ \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \left[ Y_l^m(\theta, \phi) \right]^* Y_{l'}^{m'}(\theta, \phi) = \delta_{l,l'}\delta_{m,m'}, \]

one gets

\[ A_2^{(0)} = -\frac{e}{4\pi^2} \sqrt{\frac{5}{\pi}} \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_2^0(\theta)V(r), \quad (A.6) \]
\[ A_4^{(0)} = -\frac{e}{16\pi^4} \sqrt{\frac{9}{\pi}} \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_4^0(\theta)V(r), \quad (A.7) \]
\[ A_6^{(0)} = -\frac{e}{32\pi^6} \sqrt{\frac{13}{\pi}} \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_6^0(\theta)V(r). \quad (A.8) \]

The single-electron 4f wave functions have principal and orbital quantum numbers n = 4 and l = 3, respectively. Consequently, the 4f charge distribution has non-vanishing multipoles up to the 2l = 6-th order.

Appendix B. Numerical Details

For convenience, we introduce dimensionless parameters for the MACs \( k_i = \Delta K_i/(n_{RE}J_{ex}) \), reciprocal thermal energy \( \beta \equiv J_{ex}/\beta \), and crystal-field parameters \( a_i = \hbar i (r^i) A_i^{(0)}/J_{ex} \). The reduced Helmholtz free energy \( F/J_{ex} = -\beta^{-1} \ln \sum e^{-\beta \epsilon_n} \), where \( \epsilon_n \equiv E_n/J_{ex} \) is the n-th eigenvalue of the dimensionless 4f Hamiltonian \( H/J_{ex} \). We approximate the radial 4f wave function by a Slater-type orbital, \( R(r) \propto r^i e^{-r/a} \), with \( a = 0.133 \) Å, such that the mean value \( \langle r \rangle = 0.6 \) Å. Then, \( \langle r^2 \rangle = 0.42 A^2 \), \( \langle r^4 \rangle = 0.24 A^4 \), and \( \langle r^6 \rangle = 0.19 A^6 \). We use the \( T_C \), \( s \) and \( p \) values of Co for the temperature dependence of the host magnetization. The derivatives of Eqs. (10), (11), and (12) are discretized using central schemes of order \( \Delta \theta^2 \), with the \( \theta \) step-size \( \Delta \theta = 0.1 \). A finer grid \( \Delta \theta = 0.05 \) and \( \Delta \theta = 0.01 \) leads to the same results.

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