Localization
of magnetocrystalline anisotropy energy:
Answering the Unanswerable

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Outline

MAE: What is it about

How to deal with an unanswerable question?

Quantifying the substrate contribution to MAE

Message to the mankind
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Message to the mankind
Magnetic Anisotropy Energy (MAE)

- Difference between total energies of a magnetic material for different orientations of the magnetization with respect to the crystal lattice:
  \[ E_{\text{MAE}} = E_x - E_z. \]

- Especially interesting
  - for layered composite systems (such as FePd or CoPt),
  - for adatoms, monolayers and generally nanostructures supported by non-magnetic substrates.

- Not only interesting but also relevant:
  For nanostructures, MAE is much larger than for bulk systems and could be significantly influenced by manipulating just few atoms.
Mechanism behind MAE

General fact: Magnetocrystalline contribution to MAE is due to the spin orbit coupling (SOC).
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Specific questions:

◮ For composite materials: What is the role of non-magnetic atoms?

◮ For supported nanostructures: What is the role of the substrate?

◮ Does MAE come only from the magnetic nanostructure (cluster, monolayer) or is there also a significant contribution from the substrate?
Where does the MAE come from? (1)

Relying on “technical means”, one can split MAE into adsorbate and substrate parts.

By decomposing the spatial integral in the expression for total energy into parts coming from different cells:

\[
E_{\text{total}} = \int \! \! dr \sum_n \psi_n^*(r) \left( -\frac{\hbar^2}{2m} \Delta \right) \psi_n(r) + \int \! \! dr \, n(r) \, V_{\text{nucl}}(r) + \ldots
\]

Tsujiwaka et al. PRL 102, 247203 (2009): Fe on Pt(001), FePt
Where does the MAE come from? (2)

Relying on “technical means”, one can split MAE into adsorbate and substrate parts.

- By assigning sum of band-energies to individual sites by decomposing the density of states into atom-resolved quantities:

\[
E_{\text{MAE}} = \sum_j \int_{-\infty}^{E_F} \text{d}E \ E \ [n_j(E; \hat{e}_1) - n_j(E; \hat{e}_2)].
\]

Burkert et al. PRB 71, 134411 (2005): bulk FePt, Fe₁₋ₓMnₓPt
Where does the MAE come from? (3)

Relying on “technical means”, one can split MAE into adsorbate and substrate parts.

- By relying on the Bruno formula, looking for anisotropies of orbital magnetic moments for each site:

\[ E_{\text{MAE}} = \sum_j \left[ \mu_{\text{orb}}^{(j),\parallel} - \mu_{\text{orb}}^{(j),\perp} \right] . \]

Duan et al. PRL 101, 137201 (2008): metallic films
Gimbert et al. PRB 86, 184407 (2012): Co/Ni (111) superlattices
Where does the MAE come from? (4)

Relying on “technical means”, one can split MAE into adsorbate and substrate parts.

- By comparing terms assignable to each site in the torque formula:

\[
E_{\text{MAE}} = \sum_j T_j^{(45^\circ)}.
\]

Schick et al. PRB 78, 054413 (2008): Mn monolayer on W(001)
Khmelevskyi et al. PRB 83, 224419 (2011): Mn\{Ni,Pd,Rh,Ir\}
Bornemann et al. PRB 86, 104436 (2012): adatoms on Ir, Pt, Au
Aas et al. JPCM 24, 406001 (2012): Pt monolayer inside Co
Where does the MAE come from? (5)

Is there some hard-line physics in such a separation?
Energy cannot be localized

- Energy is not an extensive quantity.
  - Energy of a system cannot be decomposed into sum of energies of its parts.

- Asking whether the MAE comes from the magnetic adsorbate or from the substrate is not well-defined, it has no exact meaning \( \Rightarrow \) it cannot be answered!
Energy cannot be localized

- Energy is not an extensive quantity.
  - Energy of a system **cannot be decomposed** into sum of energies of its parts.

- Asking whether the MAE comes from the magnetic adsorbate or from the substrate is not well-defined, it has no exact meaning \( \Rightarrow \) it cannot be answered!

- This solves the problem but **does not satisfy our curiosity**... 
  - We are not going to stop asking a question just because it cannot be answered.
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Way forward: Make the question answerable!

- The only option left: amend the question so that it becomes well-defined and can be answered.
  - If you cannot make the people to change, make them to change the question they are asking.
Way forward: Make the question answerable!

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  - If you cannot make the people to change, make them to change the question they are asking.

Wanted:
An internally consistent formulation of the question about the localization of MAE.
Switch SOC and $B_{\text{ex}}$ in the substrate on and off

- To get MAE, one must have spin-orbit coupling (SOC) and magnetism, which is enhanced by the exchange field $B_{\text{ex}}$ ($B_{\text{ex}} = V_{\uparrow} - V_{\downarrow}$).

- We can selectively switch the SOC and $B_{\text{ex}}$ on and off in the substrate only, thereby assessing their influence on MAE of the whole system.

- If manipulating the substrate SOC and/or $B_{\text{ex}}$ does not change the calculated MAE, one can say that the substrate does not directly contribute the MAE.
We are not the first to play with SOC.

In some works, influence of SOC is also investigated (even though not in a systematic way):

Wang et al. PRB 48, 15886 (1993): Pd/Co/Pd sandwich
Daalderop et al. PRB 50, 9989 (1994): Co/Pd multilayer
Ravindran et al. PRB 63, 144409 (2001): \{Fe,Mn\}{Ni,Pd,Pt}
Burkert et al. PRB 71, 134411 (2005): bulk FePt, Fe_{1-x}Mn_xPt
Baud et al. PRB 73, 104427 (2006): Co wires on steps of Pt(111)
Subkow et al. PRB 84, 054443 (2011): Fe surfaces

...
Our playground

Co monolayers and Co adatoms on Cu, Ag, Au, Pd, Pt (111) surfaces
Our playground

Co monolayers and Co adatoms on Cu, Ag, Au, Pd, Pt (111) surfaces

Low polarizability: Cu, Ag, Au
High polarizability: Pd, Pt
Our playground

Co monolayers and Co adatoms on Cu, Ag, Au, Pd, Pt (111) surfaces

Low polarizability: Cu, Ag, Au

High polarizability: Pd, Pt

Small SOC: Cu

Large SOC: Pt, Au
Computational framework

- Spin polarized fully relativistic Green’s-function KKR formalism
- Manipulate SOC and $B_{\text{ex}}$ for the substrate only
- MAE evaluated via torque
- ASA potentials, bulk-like geometry
- Ebert, Ködderitzsch and Minár RPP 74, 096501 (2011) for more
Computational framework

- Spin polarized fully relativistic Green’s-function KKR formalism
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Definition: $E_{\text{MAE}} \equiv E_{||} - E_{\perp}$

$E_{\text{MAE}} > 0 \iff$ easy axis $\perp$ to surface

$\begin{align*}
\text{SOC} &\neq 0 \\
B_{\text{ex}} &\neq 0
\end{align*}$

$\begin{align*}
\text{SOC} &\neq 0 \\
B_{\text{ex}} &= 0
\end{align*}$

$\begin{align*}
\text{SOC} &= 0 \\
B_{\text{ex}} &\neq 0
\end{align*}$

$\begin{align*}
\text{SOC} &= 0 \\
B_{\text{ex}} &= 0
\end{align*}$
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What to expect?

MAE needs for its existence SOC and magnetism.

Conjecture:

1. Suppressing SOC in the substrate will decrease MAE.
2. Suppressing $B_{ex}$ in the substrate will decrease MAE.
3. For substrates with large SOC and/or $B_{ex}$, the role of the substrate will be more important.
4. For adatoms, the role of the substrate will be more important than for monolayers (more substrate atom per magnetic atom than for monolayers).
Results: MAE for Co adatoms [meV]

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Pd</th>
<th>Ag</th>
<th>Pt</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOC ≠ 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B_{ex}</td>
<td>13.2</td>
<td>6.6</td>
<td>15.9</td>
<td>8.7</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>13.2</td>
<td>6.5</td>
<td>15.9</td>
<td>8.7</td>
<td>14.7</td>
</tr>
<tr>
<td>SOC = 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B_{ex}</td>
<td>12.4</td>
<td>4.7</td>
<td>14.5</td>
<td>5.7</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>4.6</td>
<td>14.5</td>
<td>5.7</td>
<td>10.1</td>
</tr>
</tbody>
</table>

SOC ≠ 0
B_{ex} ≠ 0

SOC ≠ 0
B_{ex} = 0

SOC = 0
B_{ex} ≠ 0

SOC = 0
B_{ex} = 0
Results: MAE for Co monolayers [meV]

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Cu</th>
<th>Cu</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>-0.69</td>
<td>-0.69</td>
<td>-0.83</td>
<td>-0.83</td>
</tr>
<tr>
<td>Ag</td>
<td>-1.59</td>
<td>-1.62</td>
<td>-1.90</td>
<td>-1.90</td>
</tr>
<tr>
<td>Pt</td>
<td>0.08</td>
<td>0.15</td>
<td>-0.27</td>
<td>-0.34</td>
</tr>
<tr>
<td>Au</td>
<td>-0.62</td>
<td>-0.24</td>
<td>-0.63</td>
<td>-0.63</td>
</tr>
</tbody>
</table>

SOC ≠ 0

SOC ≠ 0

SOC = 0

SOC = 0

$B_{ex} ≠ 0$

$B_{ex} = 0$

$B_{ex} ≠ 0$

$B_{ex} = 0$
Pragmatist’s view: Contributions to the torque

When MAE is evaluated via the torque, one adds contributions which can be “mechanically” assigned to individual atoms: $E_{MAE} = \sum_j T_j^{(45^\circ)}$.

It is possible to see *mechanistically* which portion of the sum comes from substrate atoms (it is not a well-defined procedure but...):

<table>
<thead>
<tr>
<th>Co adatom</th>
<th>Co monolayer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td>0.02%</td>
</tr>
<tr>
<td>Pd</td>
<td>Ag</td>
</tr>
<tr>
<td>0.7%</td>
<td>0.01%</td>
</tr>
<tr>
<td>Pt</td>
<td>Au</td>
</tr>
<tr>
<td>0.1%</td>
<td>0.01%</td>
</tr>
</tbody>
</table>

(it is not a well-defined procedure but...)
Torque vers. SOC and $B_{ex}$ manipulation

Role of the substrate in generating MAE for Co adatoms and monolayers on noble metals as assessed by SOC and $B_{ex}$ manipulation and as assessed by comparing individual terms in the torque evaluation:

<table>
<thead>
<tr>
<th>adatoms</th>
<th>SOC</th>
<th>$T_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>and $B_{ex}$</td>
<td>terms</td>
</tr>
<tr>
<td>Cu</td>
<td>5.1%</td>
<td>0.02%</td>
</tr>
<tr>
<td>Ag</td>
<td>8.4%</td>
<td>0.00%</td>
</tr>
<tr>
<td>Au</td>
<td>31.1%</td>
<td>0.01%</td>
</tr>
<tr>
<td>Pd</td>
<td>30.7%</td>
<td>0.67%</td>
</tr>
<tr>
<td>Pt</td>
<td>34.8%</td>
<td>0.14%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>monolayers</th>
<th>SOC</th>
<th>$T_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>and $B_{ex}$</td>
<td>terms</td>
</tr>
<tr>
<td>Cu</td>
<td>-20.4%</td>
<td>-0.10%</td>
</tr>
<tr>
<td>Ag</td>
<td>-19.3%</td>
<td>-0.06%</td>
</tr>
<tr>
<td>Au</td>
<td>-142.5%</td>
<td>-0.39%</td>
</tr>
<tr>
<td>Pd</td>
<td>265.5%</td>
<td>24.7%</td>
</tr>
<tr>
<td>Pt</td>
<td>422.5%</td>
<td>190.9%</td>
</tr>
</tbody>
</table>
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Things to remember

- Substrate contribution to MAE of supported nanostructures can be isolated by manipulating SOC and $B_{ex}$ for the substrate.

- For adatoms, substrate contribution is relatively small. For monolayers, substrate contribution can be essential.

- Contribution from SOC is more important than contribution from the exchange field $B_{ex}$.
  - For adatoms, $B_{ex}$ has negligible effect even for highly-polarized hosts such as Pd or Pt (not so for monolayers...)
  - If SOC and $B_{ex}$ in the substrate are large, their effect is non-linear.

- For all five substrates, their contribution to MAE is in-plane.