Computational Materials Design (CMD®) Workshop

Spintronic Design Course

Spintronic · Design · Magnetic control II

Materials Design based on band structures

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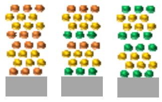
Outline
- Introduction
- Electronic structures and magnetism in transition-metals
- Electronic structures and magnetism at surfaces/thin films
- Control of magnetism by tuning atomic-layer alignments
- Control of magnetism by external electric field
- Summary

Role of materials in spintronics

Magnetic thin films



Artificial multilayer thin-films

Spin-related properties

Magnetization
Perpendicular MA
Magnetic (tunnel) resistivity
Spin (Hall) current
Spin Seebeck/peltier effect
Spin (orbital) torque
…

Required high-performance

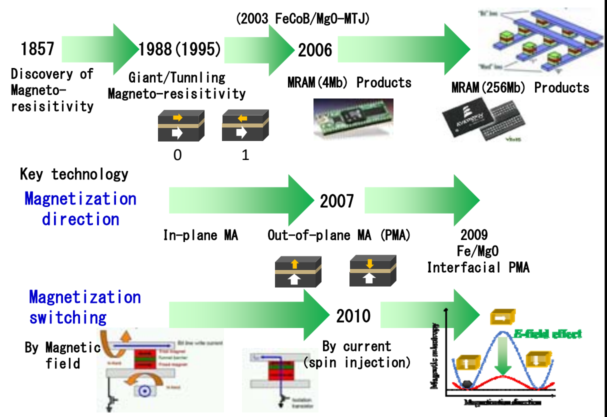
Magnetic field
Electric field
Heat
Light
Pressure
Current

External field response

Spintronic devices

HDD
MRAM
Magnetic domain memory
Spin microwave/ mill-meter wave oscillator
Spin diode/ transitor
…

An example of spintronic development

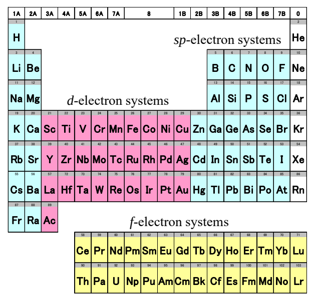


Role of first principles calculations in materials design

•Quantum mechanics !
•No use of empirical parameters !
•High accuracy in computations !

•Interpretation of experiments
•Understanding
•Prediction
with no restriction of materials

Unresolved issues
Strong correlated systems,
Exited states, etc.



Goal: Prediction of material properties from the periodic table

First principles calculations

①Kohn-Sham equation

$$\left[-\nabla^2 + V_c(\mathbf{r}) + V_{\mathrm{eff}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

exchange correlation potential

$$E_{xc}^{\mathrm{LDA}}[n] \approx \int n(\mathbf{r})\varepsilon_{ex}^{\mathrm{LDA}}(n(\mathbf{r}))$$

Coulomb potential
wave function (basis)

②Total energy

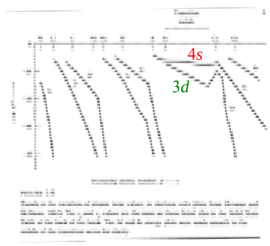
$$E_{\mathrm{total}} = \sum_{i=1,\varepsilon_i<E_F}^{N} \varepsilon_i - \frac{1}{2}\left[\int V_C(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \sum_\sigma \int \left(v_\sigma^{xc}(\mathbf{r}) - \varepsilon_\sigma^{xc}(\mathbf{r})\right)n_\sigma(\mathbf{r})d\mathbf{r}\right] - \frac{1}{2}\sum_\mu Z_\mu V_{C,\mu}(\mathbf{R}_\mu)$$

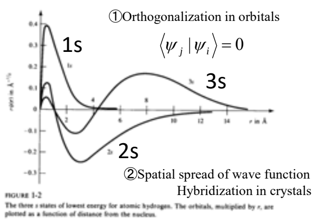
Kohn-Sham eigenvalues
(band structure, density of states)

double counting term

Eigenvalues and eigenstates of electron orbitals in atoms

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}$$





①Orthogonalization in orbitals

$$\langle \psi_j | \psi_i \rangle = 0$$

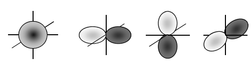
②Spatial spread of wave function
Hybridization in crystals

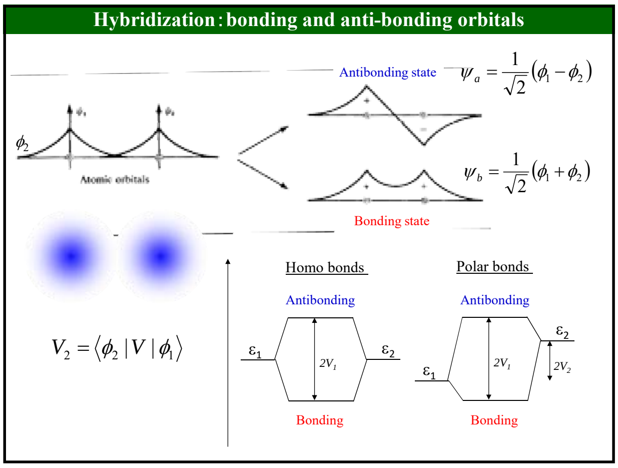
Li : $1s^2 2s$

Na : $1s^2 2s^2 2p^6 3s$

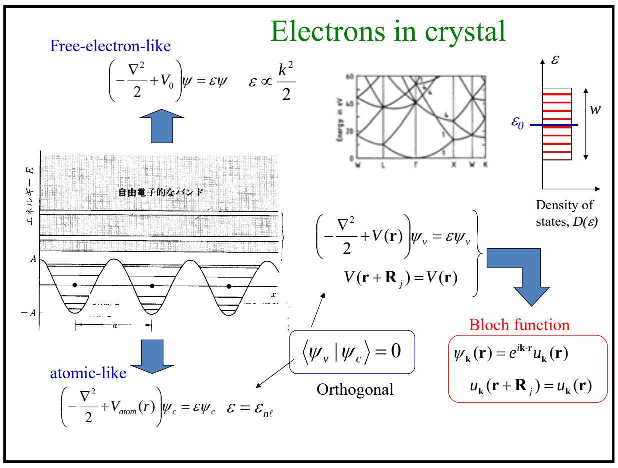
K : $1s^2 2s^2 2p^6 3s^2 3p^6 4s$

Atomic core

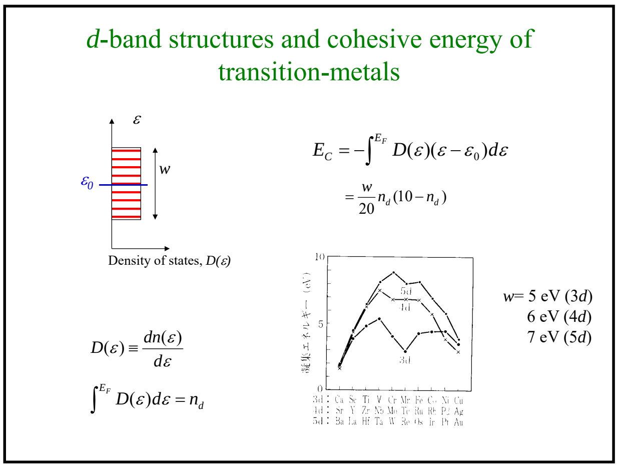




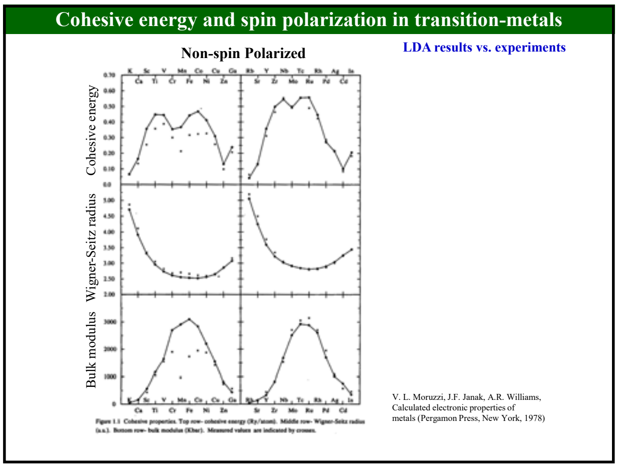
Hybridization : bonding and anti-bonding orbitals
Antibonding state
$\psi_a = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$
$\psi_b = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$
Bonding state
Atomic orbitals
ϕ_2
$V_2 = \langle \phi_2 | V | \phi_1 \rangle$
Homo bonds
Polar bonds
Antibonding
Antibonding
ε_1
ε_2
$2V_1$
$2V_2$
Bonding
Bonding



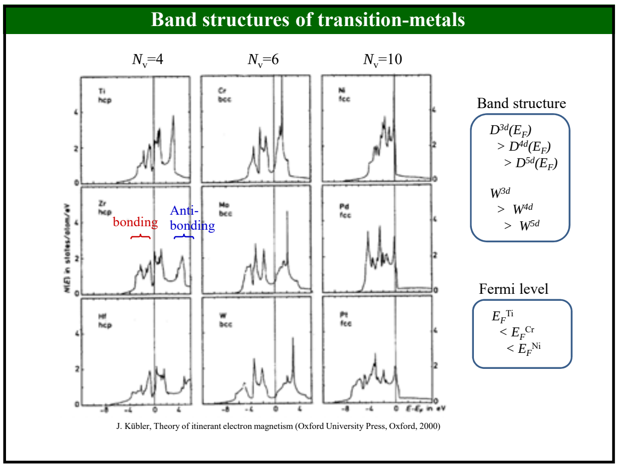
Electrons in crystal
Free-electron-like
$\left(-\frac{\nabla^2}{2} + V_0\right)\psi = \varepsilon\psi \quad \varepsilon \propto \frac{k^2}{2}$
自由電子的なバンド
$\left(-\frac{\nabla^2}{2} + V(\mathbf{r})\right)\psi_v = \varepsilon\psi_v$
$V(\mathbf{r} + \mathbf{R}_j) = V(\mathbf{r})$
ε_0
w
Density of states, $D(\varepsilon)$
Bloch function
$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$
$u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_j) = u_{\mathbf{k}}(\mathbf{r})$
$\langle \psi_v | \psi_c \rangle = 0$
Orthogonal
atomic-like
$\left(-\frac{\nabla^2}{2} + V_{atom}(r)\right)\psi_c = \varepsilon\psi_c \quad \varepsilon = \varepsilon_{n\ell}$



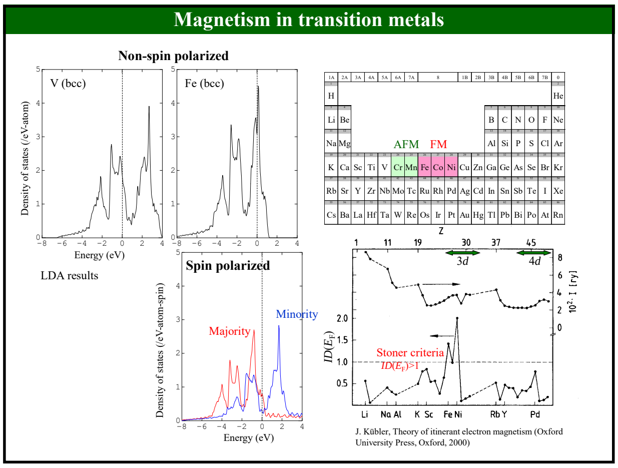
d-band structures and cohesive energy of transition-metals
ε
ε_0
w
Density of states, $D(\varepsilon)$
$E_C = -\int^{E_F} D(\varepsilon)(\varepsilon - \varepsilon_0) d\varepsilon$
$= \frac{w}{20} n_d (10 - n_d)$
$D(\varepsilon) \equiv \frac{dn(\varepsilon)}{d\varepsilon}$
$\int^{E_F} D(\varepsilon) d\varepsilon = n_d$
w = 5 eV (3d)
6 eV (4d)
7 eV (5d)



Cohesive energy and spin polarization in transition-metals
Non-spin Polarized
LDA results vs. experiments
Cohesive energy
Wigner-Seitz radius
Bulk modulus
V. L. Moruzzi, J.F. Janak, A.R. Williams, Calculated electronic properties of metals (Pergamon Press, New York, 1978)



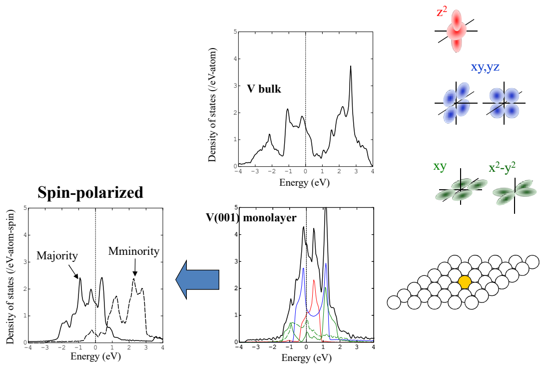
Band structures of transition-metals
N_v=4
N_v=6
N_v=10
bonding
Anti-bonding
Band structure
$D^{3d}(E_F) > D^{4d}(E_F) > D^{5d}(E_F)$
$W^{3d} > W^{4d} > W^{5d}$
Fermi level
$E_F^{Ti} < E_F^{Cr} < E_F^{Ni}$
J. Kübler, Theory of itinerant electron magnetism (Oxford University Press, Oxford, 2000)



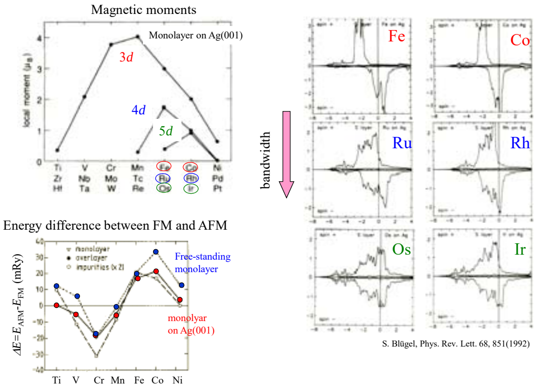
Magnetism in transition metals
Non-spin polarized
V (bcc)
Fe (bcc)
Density of states (/eV-atom)
Energy (eV)
LDA results
Spin polarized
Majority
Minority
Density of states (/eV-atom-spin)
AFM
FM
3d
4d
Stoner criteria
$ID(E_F)>1$
$ID(E_F)$
J. Kübler, Theory of itinerant electron magnetism (Oxford University Press, Oxford, 2000)

Band structures and spin polarization in transition metal monolayers

LDA results

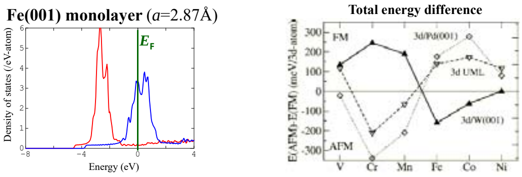


Ferromagnetism in transition metal monolayers



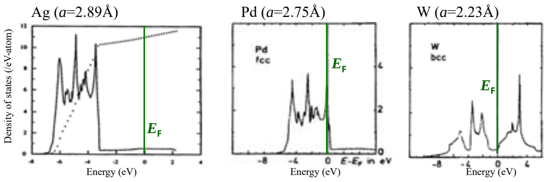
S. Blügel, Phys. Rev. Lett. 68, 851(1992)

Effect of substrates to magnetism in transition metal monolayers



P. Ferriani et.al., Phys. Rev. B 72, 024452 (2005)

Substrates



Magnetocrystalline anisotropy (MCA)

MTJ device

[1]

Ferromagnetic

Insulator

Ferromagnetic

✓Non-volatility
✓Large capacity
✓High-speed

Many Applications

- MRAM
- Magnetic sensor

[1] S. Yuasa, *et al.*, Nature Materials **3**, 868 (2004).

In-plane MCA

Large advance for applications

Out-of-plane MCA

We, here, design thin films with large MCA

First principles calculations of MCA energy

Spin-orbit coupling

$$H^{SOC} = \frac{1}{4c^2}\frac{1}{r}\frac{dV}{dr}\ell\cdot\boldsymbol{\sigma} = \xi(r)\begin{bmatrix}\ell_z & \ell_- \\ \ell_+ & -\ell_z\end{bmatrix}$$

Admixture of spin-up and down components

SOC strength, $\xi(r)$
~50 meV in
3*d*-metals

Magnetocrystalline anisotropy energy

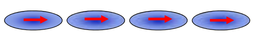
$$E_{MCA} = E_{total}(\rightarrow) - E_{total}(\uparrow)$$

Force theorem

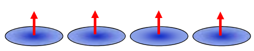
$$\approx \{E[\rho_0, \mathbf{m}_0(\rightarrow)] - E[\rho_0, \mathbf{m}_0(\uparrow)]\}$$

$$= \sum_{\mathbf{k}}\left[\sum_{i\in o'}\varepsilon_{\mathbf{k},i}(\rightarrow) - \sum_{i\in o'}\varepsilon_{\mathbf{k},i}(\uparrow)\right]$$

$E_{MCA} < 0$: in-plane MCA



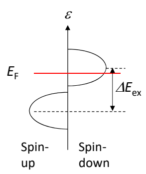
$E_{MCA} > 0$: Perpendicular MCA



Perturbation method of MCA energy

$$E_{MCA}(\sigma) = E^{SOC}(x) - E^{SOC}(z)$$

$$\approx \Delta E^{dd} + \Delta E^{ud}$$



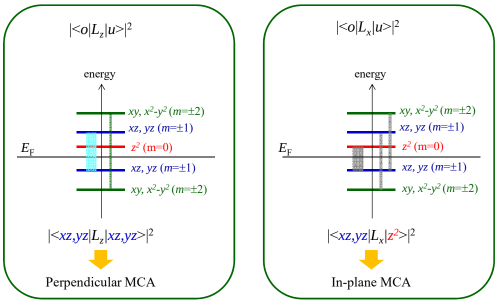
$$\Delta E^{dd} = E^{dd}(x) - E^{dd}(z)$$

$$= \xi^2\sum_{o_-}\sum_{u_-}\frac{|\langle o_- | \mathbf{L}_z | u_-\rangle|^2 - |\langle o_- | \mathbf{L}_x | u_-\rangle|^2}{\varepsilon_{u_-} - \varepsilon_{o_+}}$$

$$\Delta E^{ud} = E^{ud}(x) - E^{ud}(z)$$

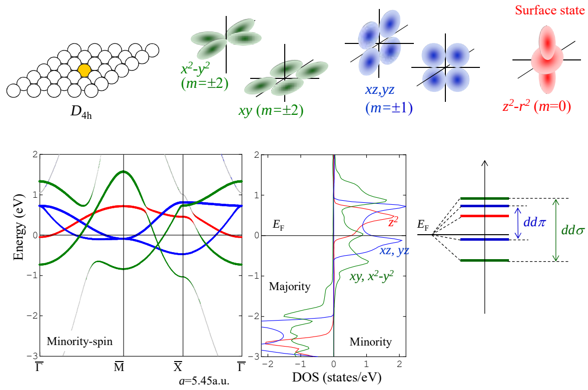
$$= \frac{\xi^2}{\Delta E_{ex}}\sum_{o_-}\langle o_- | 3\mathbf{L}_z^2 - \mathbf{L}^2 | o_-\rangle$$

Rule in origin of MCA

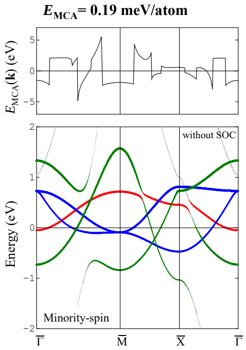


MCA depends sensitively on orbitals states between E_F

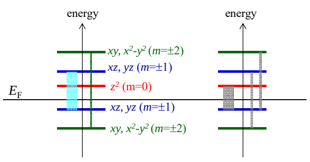
Band structure of Fe monolayer



Rule in the origin of MCA



Discussion from perturbation theory



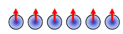
$|\langle xz,yz|L_z|xz,yz\rangle|^2$ > $|\langle xz,yz|L_x|z^2\rangle|^2$

Positive E_{MCA} Negative E_{MCA}

PMA arises from SOC between $m=\pm1$ orbitals

MCA energy in 3d transition metal monolayers

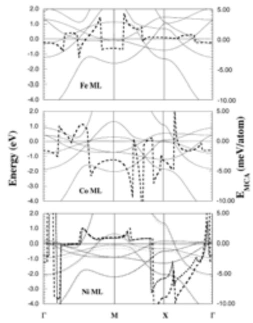
Perpendicular MCA



System	Method	E_{MCA}
★ Fe(0 0 1)	FLAPW-GGA	+ 0.50
	FLAPW-LDA	+ 0.21
Co(0 0 1)	FLAPW-GGA	− 1.49
	FLAPW-LDA	− 1.42
Ni(0 0 1)	FLAPW-GGA	− 0.77
	FLAPW-LDA	− 1.64

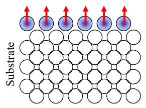
($a=a_{Cu}$)

R. Wu, A.J. Freeman, J. Magn. Magn. Mater. 200, 498(1999)



Effect of substrates to MCA in transition metal monolayers

Perpendicular MCA



R. Wu, A.J. Freeman, J. Magn. Magn. Mater. 200, 498(1999)

Table 2
Calculated MCA energies for selected transition magnetic thin films

System	Method	E_{MCA}
Co/Cu(0 0 1)	FLAPW-LDA-ST-UR [46]	− 0.38
	FLAPW-LDA-SC-RL [44,45]	− 0.36
	FLAPW-LDA-ST-RL [42,43]	− 0.09
	FLAPW-GGA-TQ-RL [41]	− 0.61
	SKKR-LDA-UR [47]	− 0.38
	Experiment [35]	− 0.37
★ Cu/Co/Cu(0 0 1)	FLAPW-LDA-ST-UR [46]	− 0.01
	FLAPW-GGA-TQ-RL [41]	+ 0.54
	SKKR-LDA-UR [48]	+ 0.85
	Experiment [35]	+ 0.1
Co/Cu(1 1 1)	FLAPW-LDA-ST-RL [48]	− 0.30
Co/Pd(0 0 1)	FLAPW-LDA-ST-RL [76]	− 0.91
★ Co/Pd(1 1 1)	FLAPW-LDA-ST-RL [76]	+ 0.25
★ Pd/Co/Pd(0 0 1)	FLAPW-LDA-ST-UR [118]	+ 0.56
Ni/Cu(0 0 1)	FLAPW-LDA-ST-UR	− 0.69
★ 2Ni/Cu(0 0 1)	FLAPW-LDA-ST-UR	+ 0.33
★ 3Ni/Cu(0 0 1)	FLAPW-LDA-ST-UR	+ 0.08
4Ni/Cu(0 0 1)	FLAPW-LDA-ST-UR	− 0.06
Cu/Fe/Cu(0 0 1)	SKKR-LDA [119]	− 0.41
	LMTO-LDA [120,121]	− 0.43
★ Fe/Au(0 0 1)	FLAPW-LDA [122]	+ 0.57
	SKKR-LDA [123]	+ 0.56

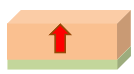
Perpendicular MCA at Fe/MgO(001) interface: Theory

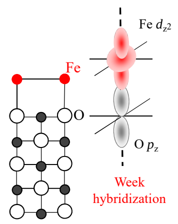
$$E_{MCA} = E^{SOC}(\rightarrow) - E^{SOC}(\uparrow)$$

	E_{MCA} (meV/a^2)
Free-standing Fe monolayer	0.19
Fe/MgO	1.28
Au_3/Fe_3/MgO	0.94

LDA

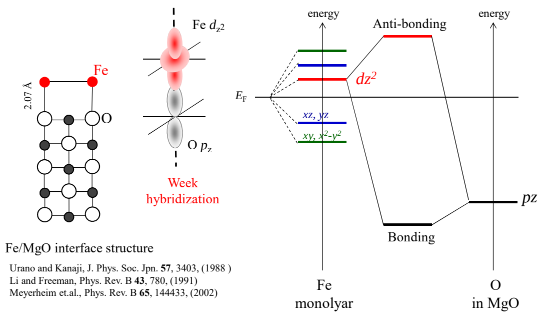
Nakamura et.al., PRB 81, 220409, (2010)





Origin of interfacial perpendicular MCA
Fe dz² - O pz hybridization

Fe d_{z2} – O p_z hybridization at Fe/MgO interface

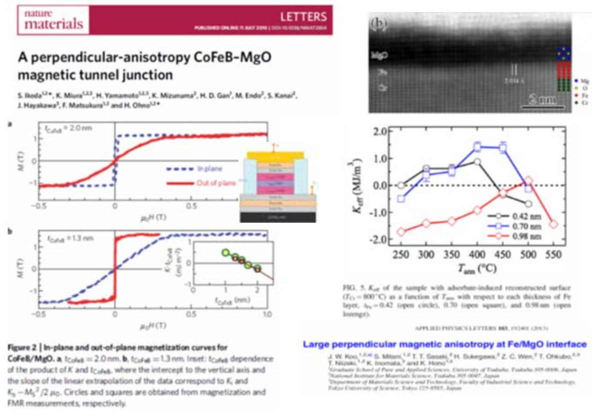


Fe/MgO interface structure

Urano and Kanaji, J. Phys. Soc. Jpn. **57**, 3403, (1988)
Li and Freeman, Phys. Rev. B **43**, 780, (1991)
Meyerheim et.al., Phys. Rev. B **65**, 144433, (2002)

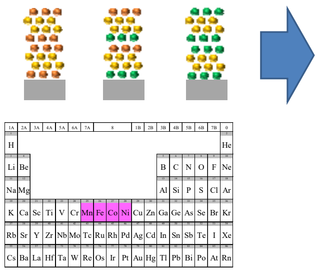
Shimabukuro, Physica E , **42**, 1014 (2010).
Nakamura et.al., PRB 81, 220409, (2010)

Perpendicular MCA of Fe thin film on MgO(001): experiments



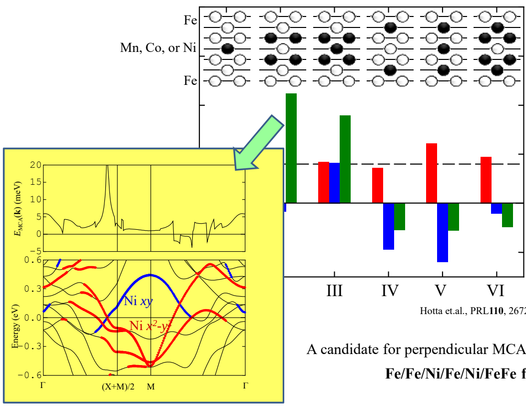
Control of MCA by tuning atomic-layer alignments

Interfaces, superlattices, multilayers



Thin films with large perpendicular MCA, consisting of only 3d metals

MCA of 3d transition metal thin films with seven-atomic-layer



7-layer Fe film

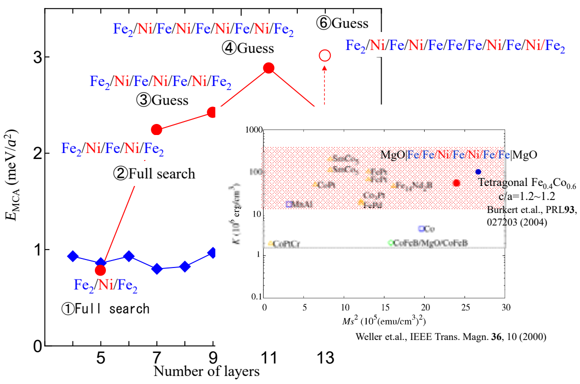
Hotta et.al., PRL**110**, 267206 (2013)

A candidate for perpendicular MCA

Fe/Fe/Ni/Fe/Ni/FeFe film

Search for 3*d* thin films with giant perpendicular MCA

Upper limit for perpendicular MCA in 3*d* thin films



E-field-control of magnetism

Electrons

Electric field → Charge

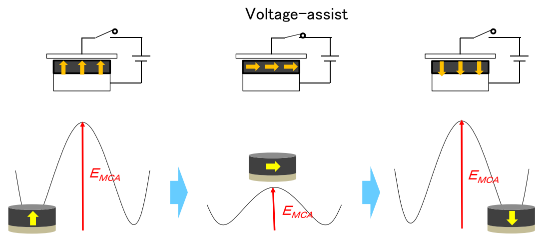
at the nano-scale with a low-energy power consumption

leading to semiconductor technology

Magnetic field Currents → Magnetization or spins

✓Non-volatile
✓Large capacity
✓High-speed
✓Low power

An example: Voltage-assist magnetization switching



E-field-induced modification of magnetocrystalline anisotropy

Experiment

Au/Fe/MgO [5]

FePt/Ionic riquid [1]
First observation

Au/FeCo/MgO [6], [7]
Demonstration of switching

Pt/Co/$Gd_{1-x}O_x$ [8], [9]
Giant *E*-field effects over 5000 fJ/Vm

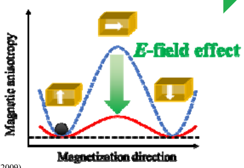
2007 2008 2009 2010 2012 2014 2016

Theory

3*d* transition-metal surfaces[2]

3*d* transition-metal monolayers[3]

Pt/Fe/Pt (001)[4]

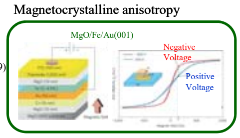


[1] M. Weisheit, *et al*., Science **315**, 349 (2007). [5] T. Maruyama, *et al*., Nat. Nanotech. **4**, 158 (2009).
[2] C.-G. Duan, *et al*., Phys. Rev. Lett. **101**, 137201 (2008). [6] T. Nozaki, *et al*., Appl. Phys. Lett. **96**, 022506 (2010). [9] U. Bauer, *et al*., Nat. Mater. , **14**, 174 (2015).
[3] K. Nakamura, *et al*., Phys. Rev. Lett. **102**, 187201 (2009). [7] Y. Shiota, *et al*., Nat. mater. **11**, 39 (2010). [10] T. Nozaki, *et al*., Phys. Rev. Appl. **5**, 044006 (2016).
[4] M. Tsujikawa, *et al*., Phys. Rev. Lett. **102**, 247203 (2009). [8] Chong Bi, *et al*., Phys. Rev. Lett. **113**, 267202 (2014).

Control of magnetism of metal thin films by electric field

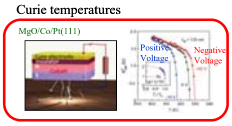
- Magnetocrystalline anisotropy (MCA)
  Weisheit et.al., Science 315, 349 (2007)
  Maruyama et.al., Nature Nanotech. 4, 349 (2009)
  Duan et.al., PRL**101**, 137201 (2008)
  Nakamura et.al., PRL**102**, 187201 (2009); PRB **80**, 172402 (2009)
  Tsujikawa et.al., PRL**102**, (2009)
  ….
- Curie temperature (T_C)
  Chiba et.al., Nat. Mater. 10, 853-856 (2011)
  Oba et.al., PRL**114**, 107202 (2015)
- Dzyaloshinskii-Moriya interaction (DMI)
  Nawaoka et.al., Appl. Phys. Express 8, 063004(2015)
  Nakamura et.al., (2015)
- Magnetic moments
  Obinata et.al., Sci. Rep. 5, 14303 (2015)
- Magneto-optical conductivity
  Hibino et.al., (2015)
  Nakamura et.al., J. Korean Phys. Soc. **63**, 612 (2013)
- Magnetic dumping
  Okada et.al., Appl. Phys. Lett. 105, 052415 (2014)
- Magnetic phase-transition (bcc Fe vs fcc Fe)
  Gerhard et.al., Nat. Nanotech., **5**, 792 (2010)
- etc.

Magnetocrystalline anisotropy



Maruyama et.al., Nature Nanotech. 4, 349 (2009)

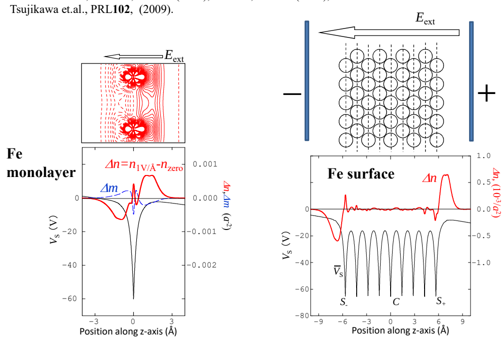
Curie temperatures



Chiba et.al., Nat. Mater. 10, 853-856 (2011)

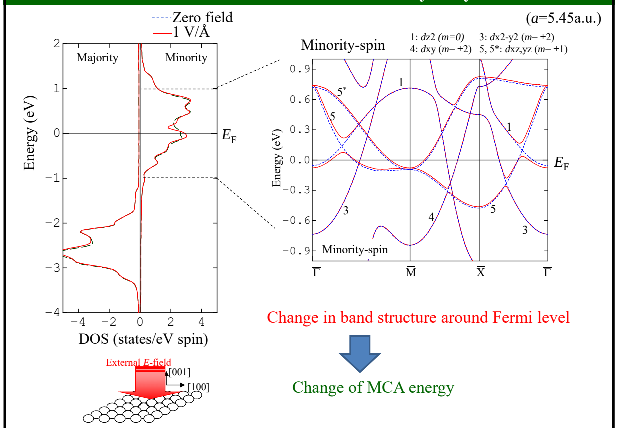
Electric-field-induced charges at surfaces

- ***Redistribution in charge/spin densities at surfaces/interfaces by E-field.***
  Duan et.al., PRL**101**, 137201 (2008),
  Nakamura et.al., PRL**102**, 187201 (2009); PRB **80**, 172402 (2009),
  Tsujikawa et.al., PRL**102**, (2009).



Modification of band structure of Fe monolayer by electric field

(*a*=5.45a.u.)

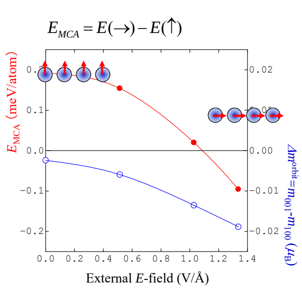


Change in band structure around Fermi level

Change of MCA energy

Modification of MCA energy of Fe monolayer

(*a*=5.45a.u.)

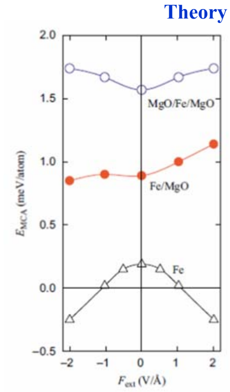


The MCA is modified by an *E*-field
due to the change in band structures around E_F.

Nakamura et.al., PRL**102**, 187201 (2009)

Modification of MCA energy at MgO/Fe interface

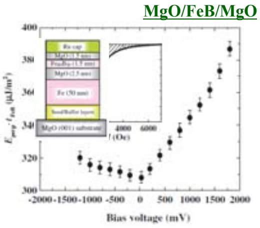
Theory



Shimabukuro, Physica E , **42**, 1014 (2010)

Experiments

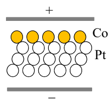
MgO/FeB/MgO

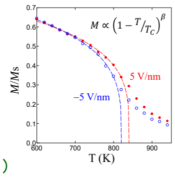


Nozaki et.al., Appl. Phys. Express **6**, 123001 (2013)

Comparison to experiments

Co/Pt(111)

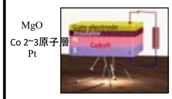




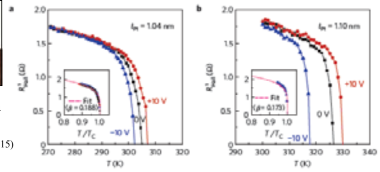
	Theory	experiments
T_C	~830	~320
ΔT_C	~20K	~10K
β	~0.26	~0.18

Agreed with experiments qualitatively

MgO/Co/Pt(111)



±0.2V/nm

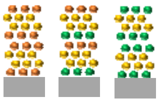


Oba et.al., PRL**114**, 107202 (2015)

Summary

Spintronic · Design · Magnetic control

Artificial multilayer thin-films



Importance of understanding electronic structures

magnetic properties

- ✓Perpendicular magnetization
- ✓Tunnel magneto resistance
- ✓Spin current and torque
- ✓etc.

Key ideas for PMCA

- Interface-induced PMCA
- Atomic-layer-alignment-tuned PMA (artificial multilayers)

- ➢ Crystal structures and atomic arrangements
- ➢ The number of valence electrons
- ➢ Eigenvalues and eigenstates of s, p, d, f orbitals
- ➢ d-d (d-sp) hybridization