Computational Materials Design (CMD®) Workshop

Spintronic Design Course

Spintronic · Design · Magnetic control II

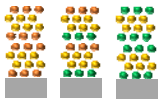
Materials Design based on band structures

Kohji Nakamura
Mie University

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 effect
- Spin (orbital) torque
- …

Required high-performance

Spintronic devices

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

Magnetic field, Electric field, Heat, Light, Pressure, Current

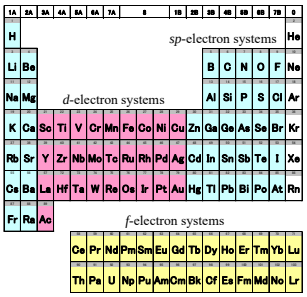
External field response

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

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

Coulomb potential

wave function (basis)

②Total energy

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

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

double counting term

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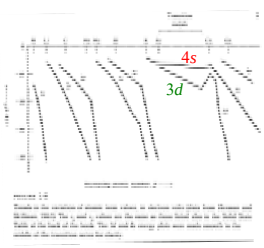
Eigenvalues and eigenstates of electron orbitals in atoms



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

①Orthogonalization in orbitals

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

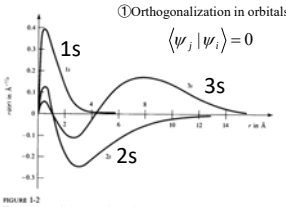


FIGURE 1-2
The three s states of lowest energy for atomic hydrogen. The orbitals, multiplied by r, are plotted as a function of distance from the nucleus.

Li : $1s^2 2s$

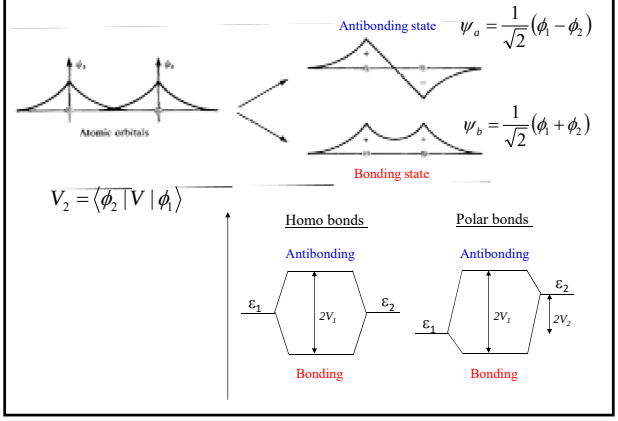
Na : $1s^2 2s^2 2p^6 3s$

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

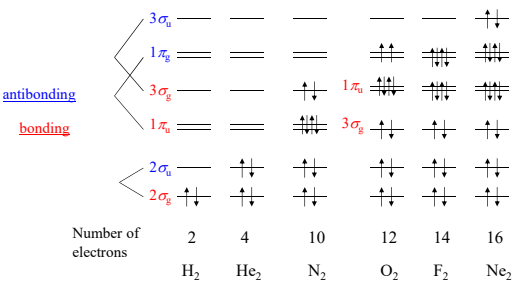
Atomic core

②Spatial spread of wave function
Hybridization in crystals

Hybridization : bonding and anti-bonding orbitals

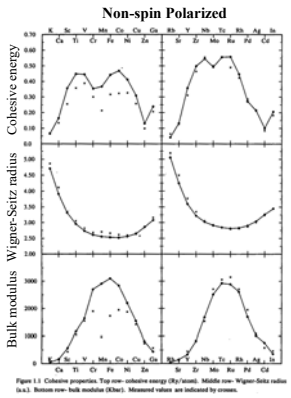


Valence electrons and electron configurations



Valence top (Fermi level) is determined by the number of electrons

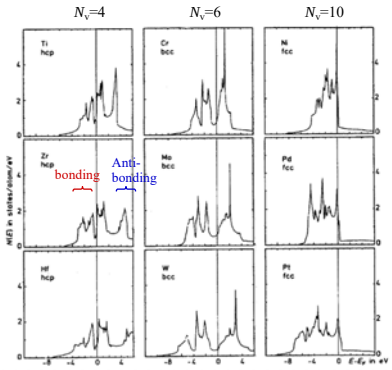
Cohesive energy and spin polarization in transition-metals



LDA results vs. experiments

V. L. Moruzzi, J.F. Janak, A.R. Williams, Calculated electronic properties of metals (Pergamon Press, New York, 1978)

Band structures of transition-metals



Band structure

$D^{3d}(E_F) > D^{4d}(E_F) > D^{5d}(E_F)$

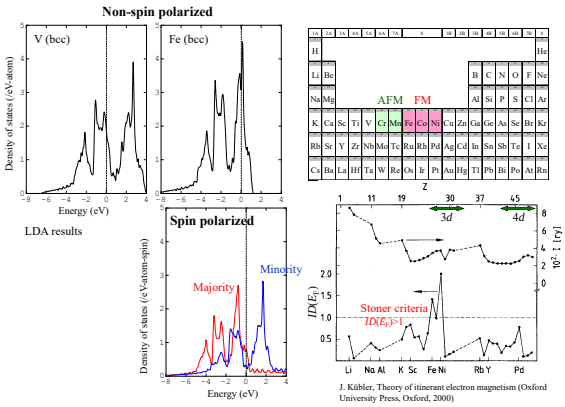
$W^{3d} > W^{4d} > W^{5d}$

Fermi level

$E_F^{Ti} < E_F^{Cr} < E_F^{Ni}$

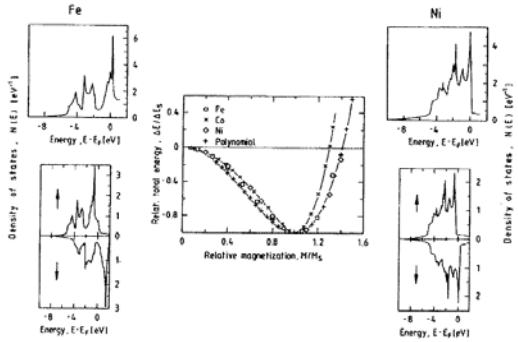
J. Kübler, Theory of itinerant electron magnetism (Oxford University Press, Oxford, 2000)

Magnetism in transition metals



J. Kübler, Theory of itinerant electron magnetism (Oxford University Press, Oxford, 2000)

Stability of magnetic structures



J. Kübler, Theory of itinerant electron magnetism (Oxford University Press, Oxford, 2000)

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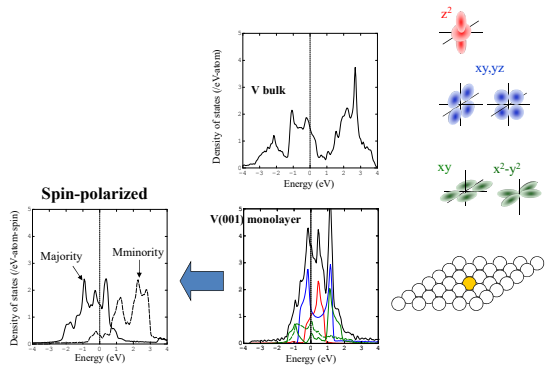
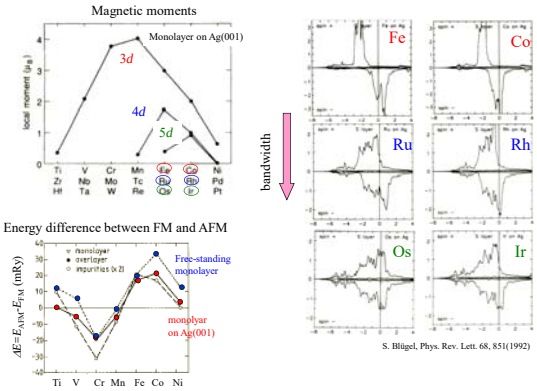
Band structures and spin polarization in transition metal monolayers

LDA results

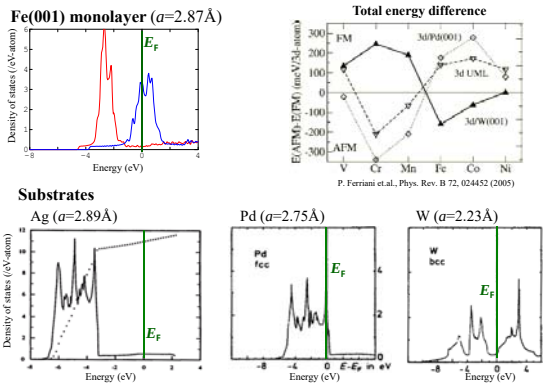


Ferromagnetism in transition metal monolayers



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)

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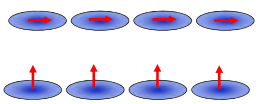
First principles calculations of MCA energy

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

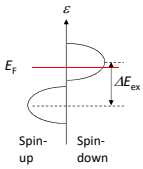
$$\approx \{E[\rho_0, \mathbf{m}_0(\rightarrow)] - E[\rho_0, \mathbf{m}_0(\uparrow)]\}$$

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

Very sensitive to band structures !!

Perturbation method of MCA energy

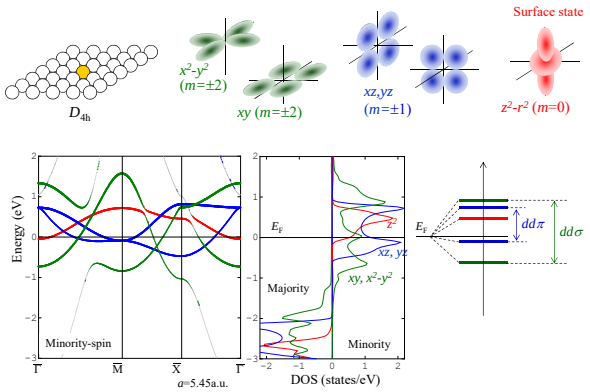
$$E_{MCA}(\sigma) = E^{SOC}(x) - E^{SOC}(z)$$
$$\approx \Delta E^{dd} + \Delta E^{ud}$$



$$\Delta E^{dd} = E^{dd}(x) - E^{dd}(z)$$
$$= \xi^2 \sum_{o_-}\sum_{u_-} \frac{|\langle o_- | \mathbf{L}_z | u_- \rangle|^2 - |\langle o_- | \mathbf{L}_x | u_- \rangle|^2}{\varepsilon_{u_-} - \varepsilon_{o_+}}$$

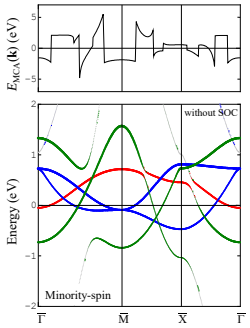
$$\Delta E^{ud} = E^{ud}(x) - E^{ud}(z)$$
$$= \frac{\xi^2}{\Delta E_{ex}} \sum_{o_-} \langle o_- | 3\mathbf{L}_z^2 - \mathbf{L}^2 | o_- \rangle$$

Band structure of Fe monolayer

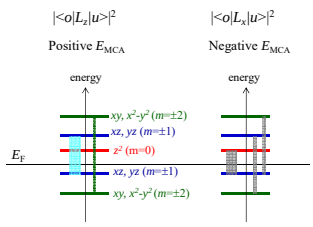


Rule in the origin of MCA

E_{MCA} = 0.19 meV/atom



Simple picture from perturbation theory



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

PMA arises from SOC between m=±1 orbitals

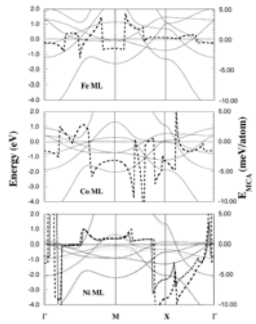
MCA energy in 3d transition metal monolayers

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

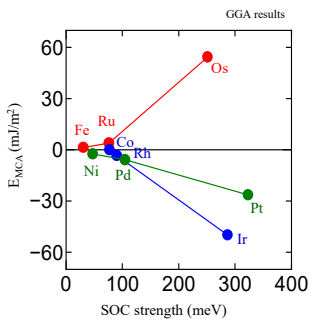
(a=a_{Cu})

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



MCA energy of 3d, 4d, and 5d transition metal monolayers

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt



1 meV/unit-area = 1.8 mJ/m^2

Effect of substrates to MCA in transition metal monolayers

Perpendicular MCA

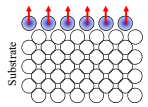


Table 2
Calculated MCA energies for selected transition magnetic thin films

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

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

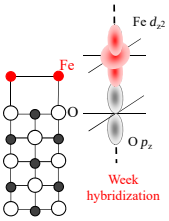
Perpendicular MCA of Fe thin film on MgO(001): Theory

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

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

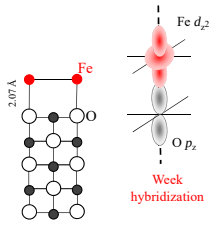
LDA

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



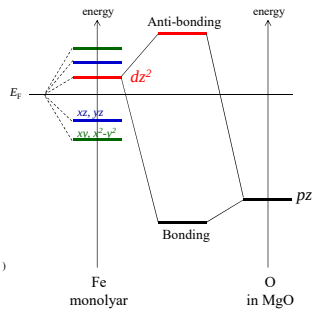
Origin of interfacial perpendicular MCA
Fe dz^2 - O pz hybridization

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)

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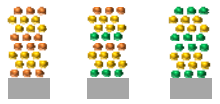
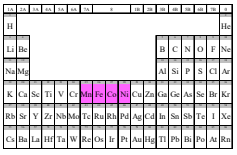
Control of MCA by tuning atomic-layer alignments

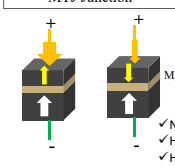
Interfaces, superlattices, multilayers



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

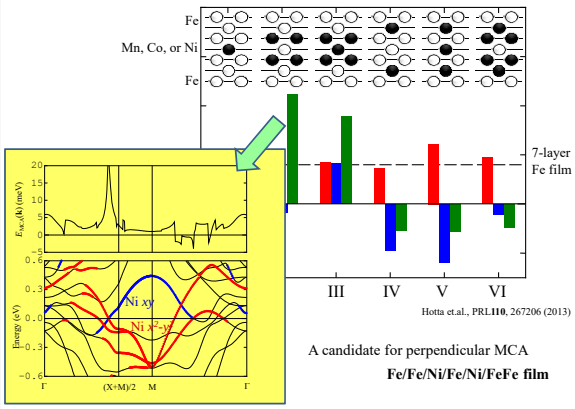


MTJ Junction



- ✓Nonvolatile
- ✓High capacity
- ✓High speed

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

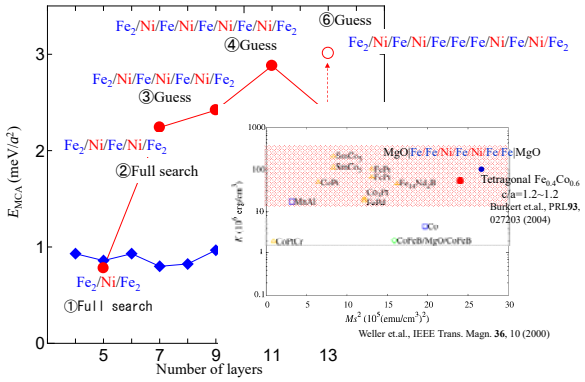


Hotta et.al., PRL**110**, 267206 (2013)

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



Weller et.al., IEEE Trans. Magn. **36**, 10 (2000)

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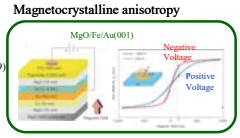
Control of magnetism of metal thin films by electric field

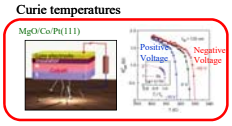
- Magnetocrystalline anisotropy (MCA)
  Weisheit et.al., Science 315, 349 (2007)
  Maruyama et.al., Nature Nanotech. 4, 349 (2009)
  Duan et.al., PRL**101**, 137201 (2008)
  Nakamura et.al., PRL**102**, 187201 (2009); PRB **80**, 172402 (2009)
  Tsujikawa et.al., PRL**102**, (2009)
  ….
- Curie temperature (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)

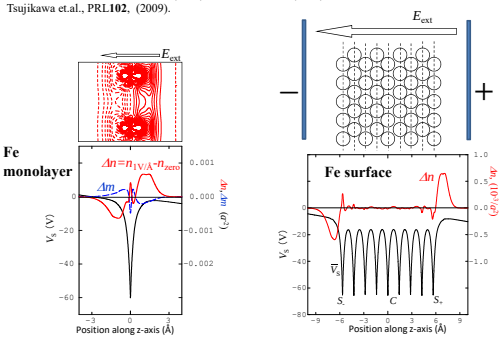
Curie temperatures



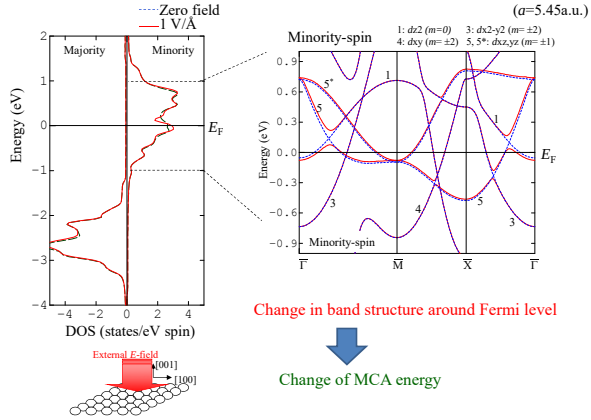
Chiba et.al., Nat. Mater. 10, 853-856 (2011)

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



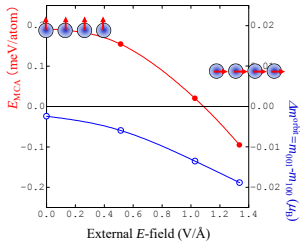
Change in band structure around Fermi level

Change of MCA energy

Modification of MCA energy of Fe monolayer

(a=5.45a.u.)

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

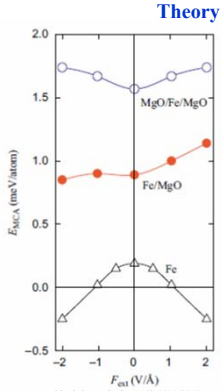


The MCA is modified by an *E*-field
due to the change in band structures around E_F.

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

Modification of MCA energy at MgO/Fe interface

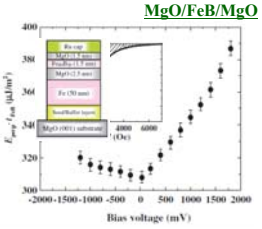
Theory



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

Experiments

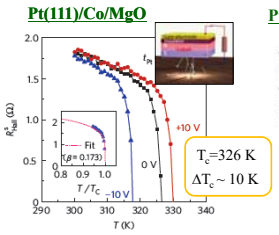
MgO/FeB/MgO



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

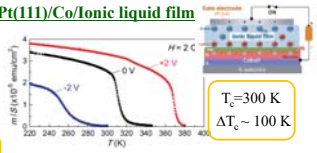
Control of Cure temperature by electric field

Pt(111)/Co/MgO



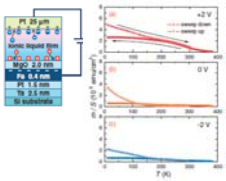
T_c=326 K
ΔT_c ~ 10 K

Pt(111)/Co/Ionic liquid film



T_c=300 K
ΔT_c ~ 100 K

Pt(111)/Fe/Ionic liquid film

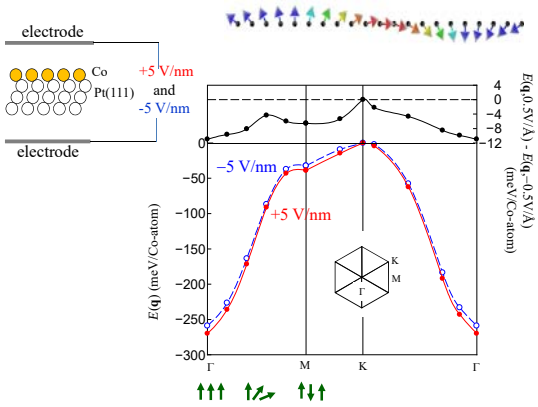


T_C in positive E-field is higher than that in negative E-field

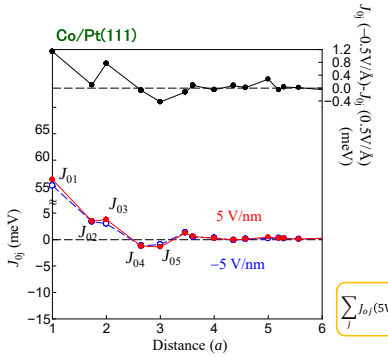
T_C (+V) > T_C (−V)

D. Chiba *et al*., Nat. Mater., **10**, 853-856 (2011).
K. Shimamura *et al*., Applied Physics Letters **100**, 122402 (2012).
M. Kawaguchi at.al. Appl. Phys. Express **5**, 063007 (2012).

Modification of frozen magnon (spin-spiral structure) dispersion



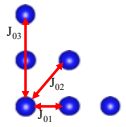
Modification of exchange interaction by electric field



Heisenberg model

$$H = -\sum_{i \neq j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j$$

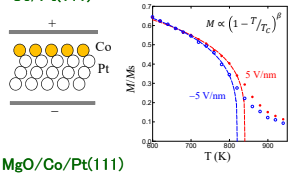
$$J_{0j} = \frac{1}{N} \sum_{\mathbf{q}} \exp(-i\mathbf{q} \cdot \mathbf{r}_{0j}) \Delta E(\mathbf{q})$$



$$\sum_j J_{0j}(5V/nm) - \sum_j J_{0j}(-5V/nm) = 10.3 \text{ meV}$$

Comparison to experiments

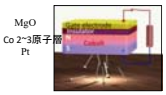
Co/Pt(111)



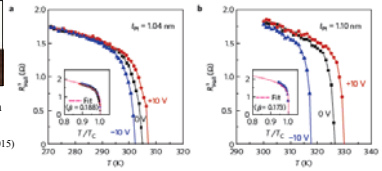
	Theory	experiments
T_C	~830	~320
ΔT_C	~20K	~10K
β	~0.26	~0.18

Agreed with experiments qualitatively

MgO/Co/Pt(111)



±0.2V/nm

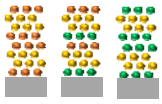


Oba et.al., PRL**114**, 107202 (2015)

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.

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