CMD Workshop 32 : Spintronics course
in Center for Spintronics Research Network (CSRN),
Graduate School of Engineering Science, Osaka University.

February 28, 2018

Spintronic Interface design
(スピントロニクス・インターフェース・デザイン)

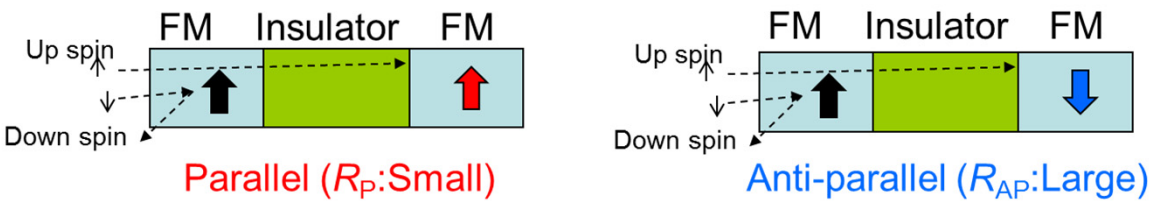
Yoshio Miura

Kyoto Institute of Technology (KIT)

Instroduction

Magnetic tunnel junction (MTJs)

(FM: Ferromagnetic metal)

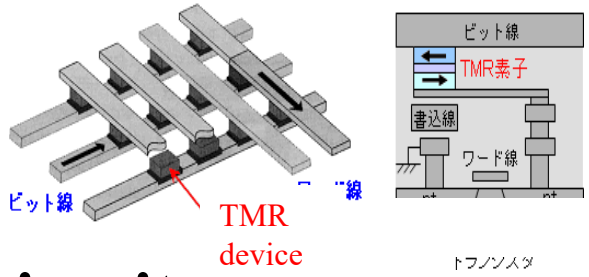


Tunneling magnetoresistance (TMR)

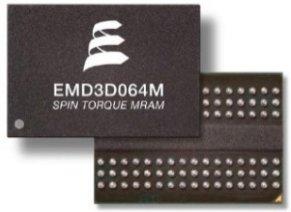
$$\text{TMR ratio} = \frac{R_{AP} - R_P}{R_{AP}}$$

Magnetoresistive Random Access Memory (MRAM)

- Non volatile memory
- Fast writing speed (10～50ns)
- Low electricity consumption (～30μW)
- Long endurance (10 years)



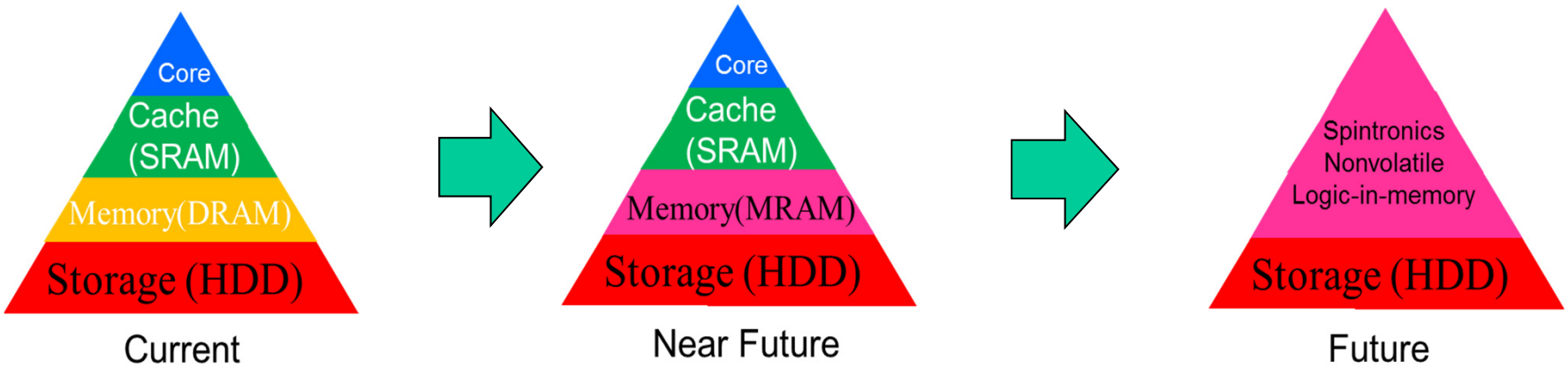
Everspin
64Mbit MRAM



Very Large-Scale Integrated (VLSI) circuit

Drastically reduce power consumption due to static power by replacing volatile DRAM and SRAM

H. Ohno, *et al.*, IEDM pp. 218-221 (2010).

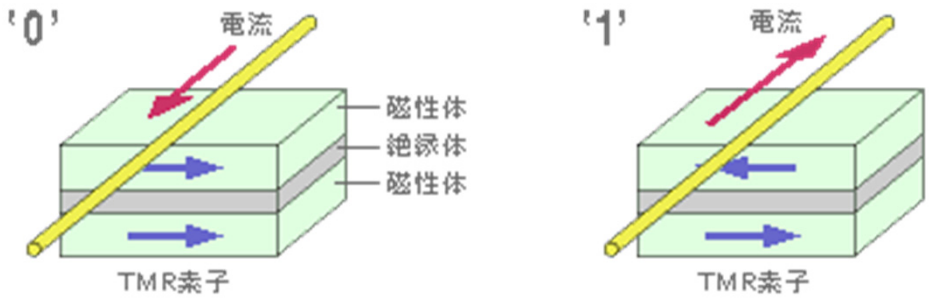


Magnetization reversal method in writing

1. Magnetic field by current

problem：・complicate circuit.
・current∝1/device-size

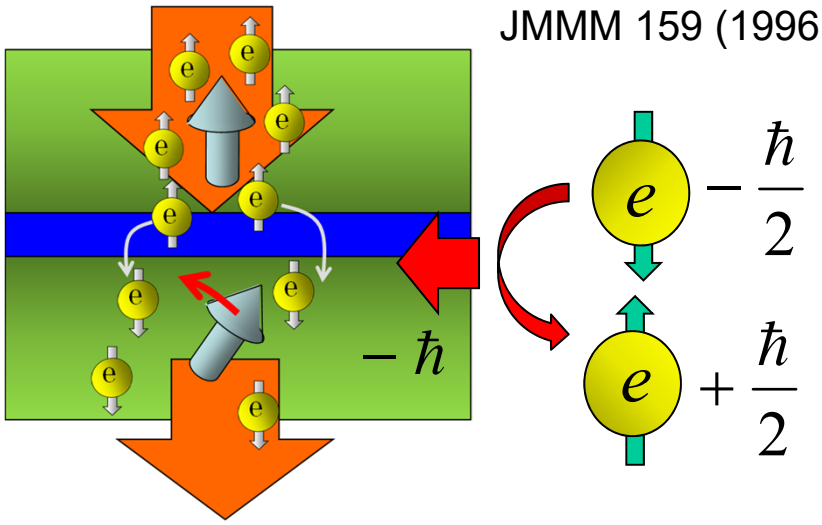
Effects of demagnetizing field increase the critical current for writing with decreasing size of device

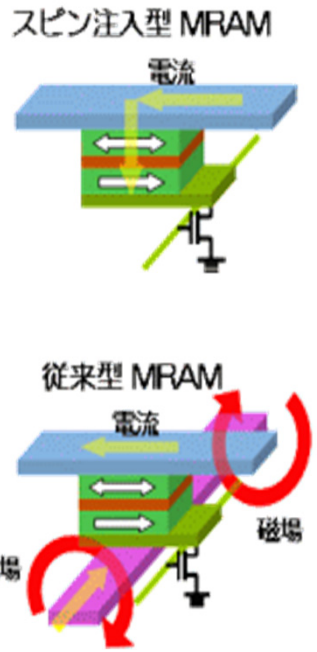


2. Spin transfer torque（spin-RAM）

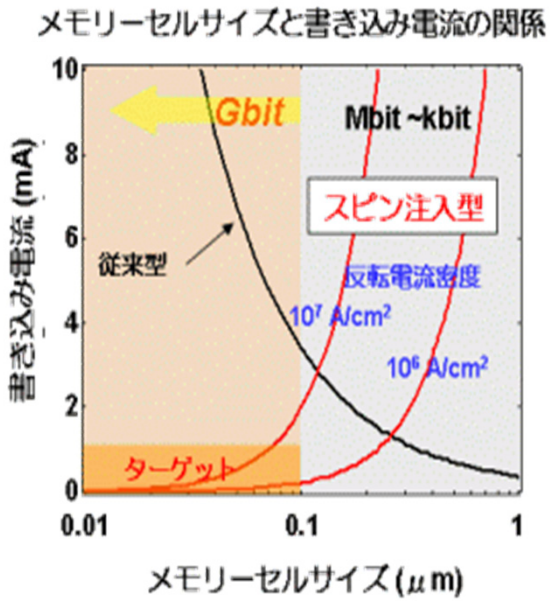
The spin flip of conductive electron give the torque to the local spin moment due to the angular momentum conservation

J.C. Slonczewski, JMMM 159 (1996) L1.



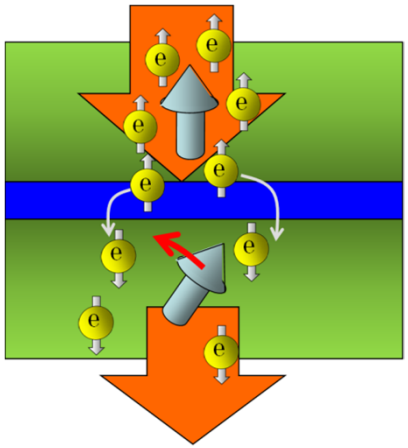


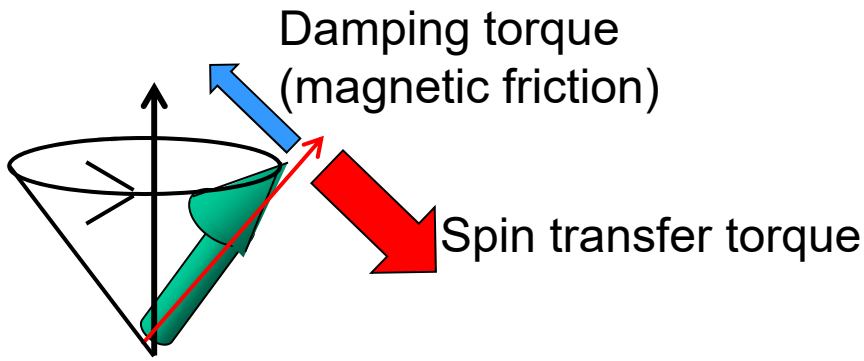
Tohoku Univ. Ando lab. HP



・simple circuit
・current∝device-size

Magnetization reversal by spin transfer torque (STT)





Reduction of critical current density (J_{c0})

(10^7A/cm^2⇒10^5A/cm^2)

$$J_{c0} \propto \alpha M_S \left[H_{anti} \pm 2\pi M_S \right] t / P$$

J.C. Slonczewski, JMMM 159 (1996) L1.

α: Magnetic damping constant
M_S: Saturation Magnetization
$H_{anti} \pm 2\pi M_S$: Effective anisotropy field
P: Spin polarization
t: Thickness of FM layer

1. High spin polarization (P) with low resistance

2. Low damping constant(α) with perpendicular magnetic anisotropy(PMA)

   Usually strong perpendicular magnetic anisotropy (PMA) is originated to the large spin orbit interaction leading to large damping α

3. Small magnetization (M_s) with high Curie temperature

   Ferrimagnetic materials

Contents

1. Spin-dependent transport in magnetic tunnel junctions with half-metallic Heusler alloys

Y. Miura, *et al*., Phys. Rev. B **83,** 214411 (2011).

2. Spin-dependent tunneling conductance in magnetic tunnel junctions with spinel-type $MgAl_2O_4$ barrier

Y. Miura, *et al*, PRB, **86**, 024426 (2012).
K. Masuda and Y. Miura, PRB **96**, 054428 (2017)

3. Electric field dependence of magnetic damping constant of Fe(001) surface

YM, M. Tsujikawa, M. Shirai, in preparation.

4. Magneto-crystalline anisotropy at interfaces of Fe(001) with various non-magnetic metals

Y. Miura, M. Tsujikawa, M. Shirai, J. Appl. Physics, **113**, 233908/1-6 (2013).

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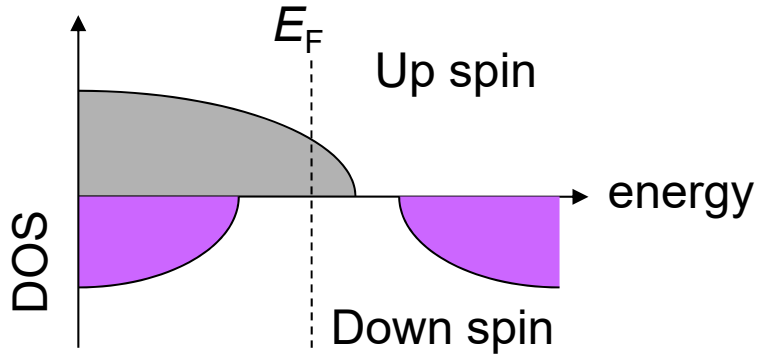
Introduction: Half-metallic ferromagnetic

Julliere model

$$\mathrm{TMR} = \frac{G_{\mathrm{P}} - G_{\mathrm{AP}}}{G_{\mathrm{P}}} = \frac{2P_{\mathrm{L}} \cdot P_{\mathrm{R}}}{1 - P_{\mathrm{L}} \cdot P_{\mathrm{R}}}$$

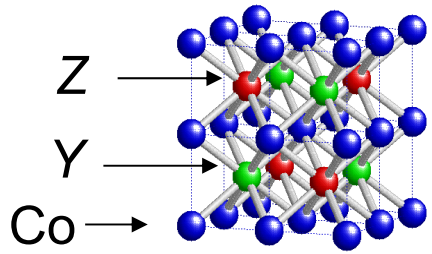
Spin-polarization at E_F $$P_{\mathrm{L(R)}} = \frac{D^{\uparrow}_{\mathrm{L(R)}} - D^{\downarrow}_{\mathrm{L(R)}}}{D^{\uparrow}_{\mathrm{L(R)}} + D^{\downarrow}_{\mathrm{L(R)}}}$$

The Half-metallic ferromagnets

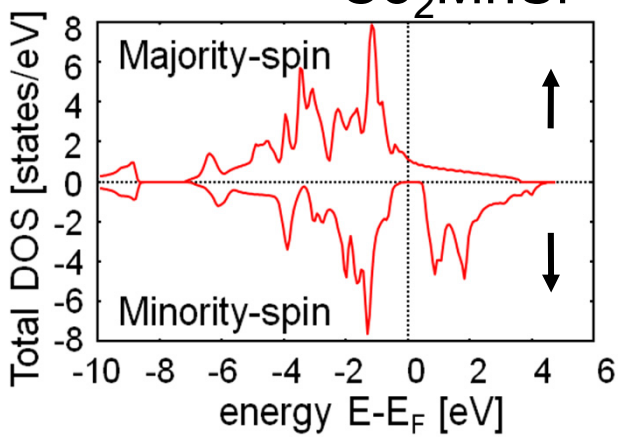


Co-based full Heusler alloys Co_2YZ (Y=Fe,Mn,Cr : Z=Si,Ge,Al,Ga)

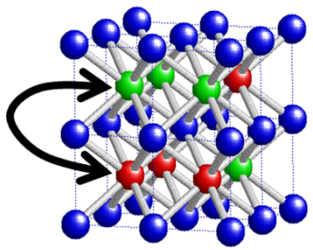
$L2_1$-structure



Co_2MnSi

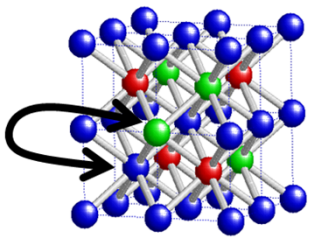


(1) B2-type disorder



$Co_2(Mn_{1-y}Si_y)(Si_{1-y}Mn_y)$

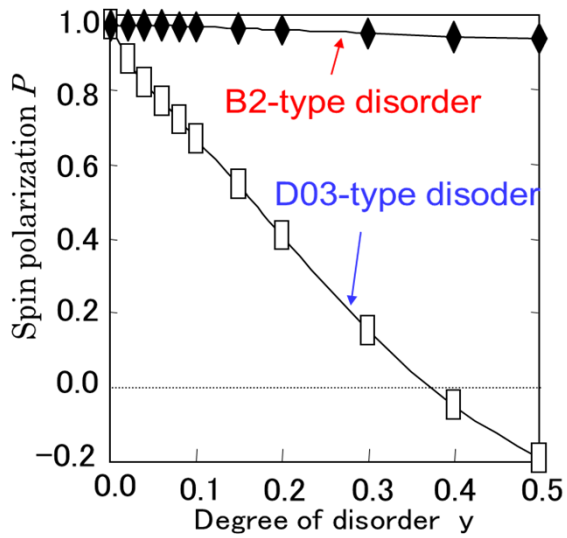
(2) D03-type disorder



$(Co_{2-y}Mn_y)(Mn_{1-y}Co_y)Si$

High Curie temperature (900K)

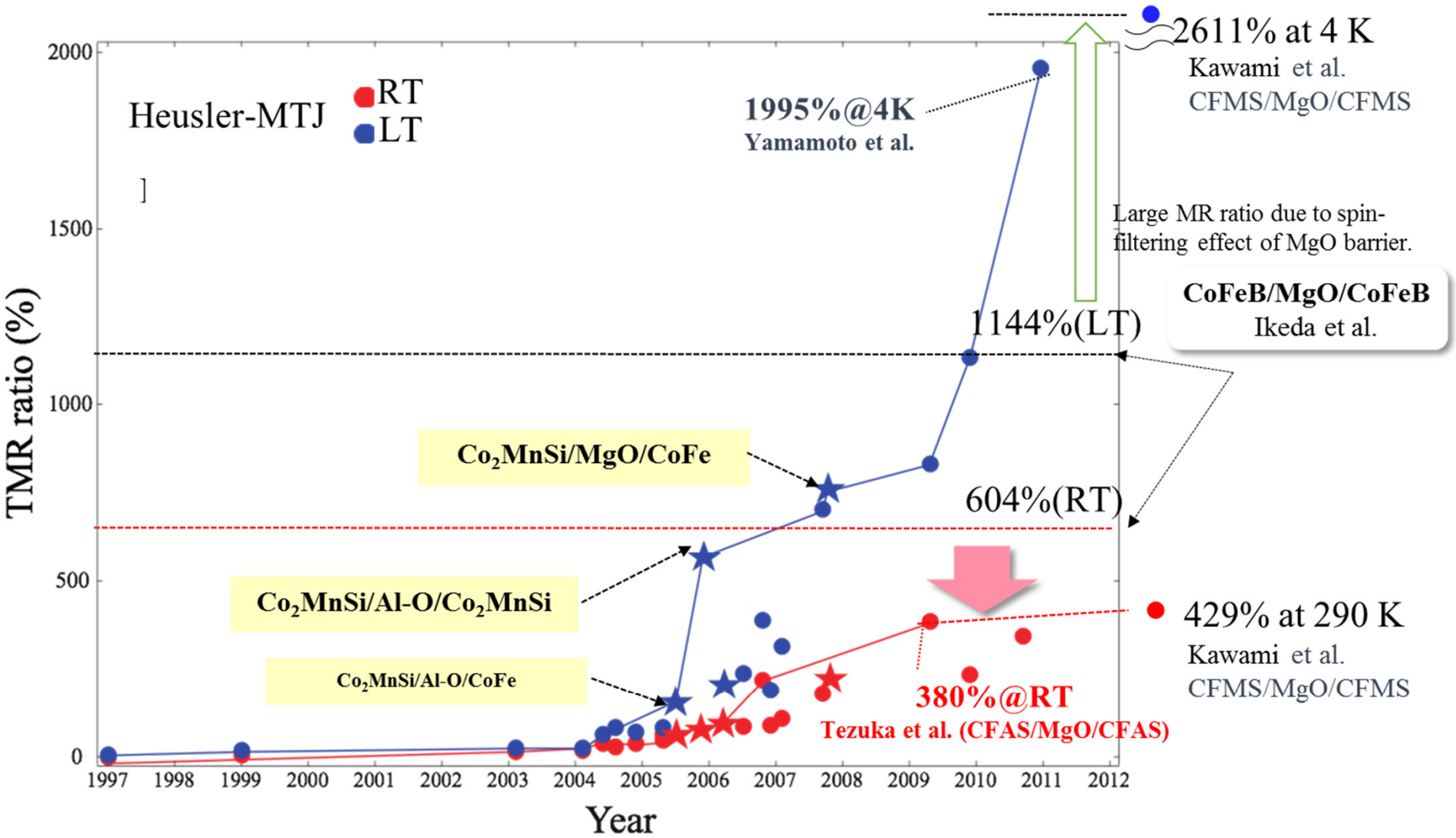
Simple fabrication process



Y. Miura, *et al.*, PRB, 69 (2004) 144413.

Progress of TMR ratio in half-metallic Heusler-based MTJs

Courtesy of Dr. Sakuraba

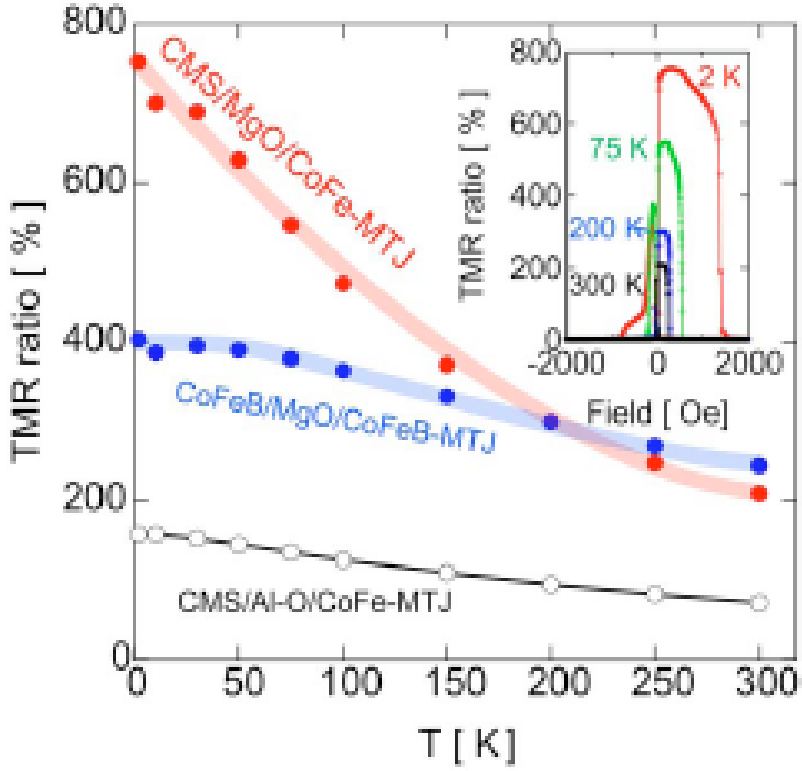


Heusler-based MTJ : Large temperature dependence of MR ratio is still a serious problem especially in CMS.

CMS: Co_2MnSi CFAS: $Co_2Fe(AlSi)$ CFMS: $Co_2(FeMn)Si$

Temperature dependence of TMR in half-metallic Heusler-based MTJs

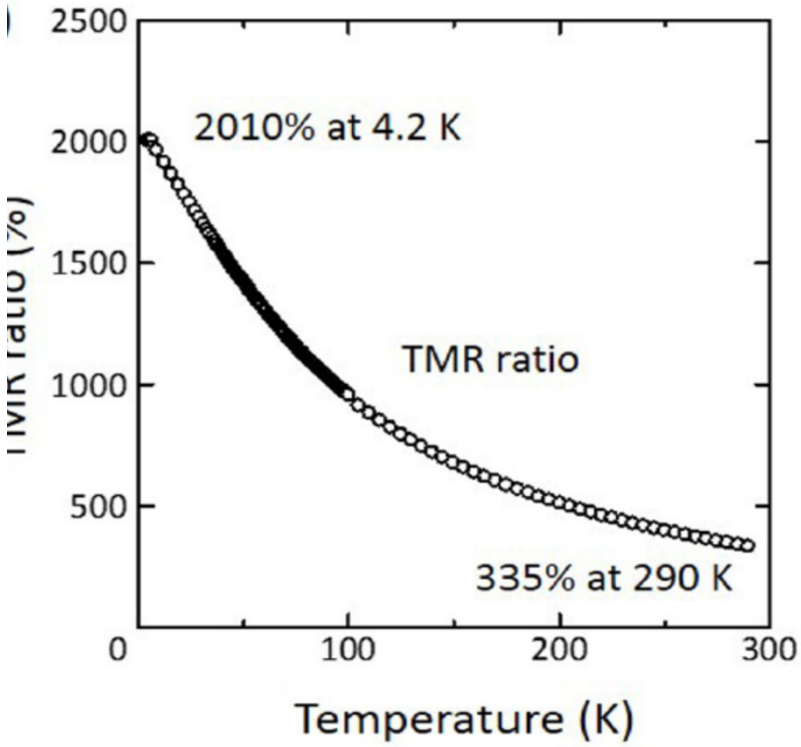
TMR ratio of MTJs with Co_2MnSi(CMS)



S. Tsunegi, *et al.*, APL 93 (2008) 112506.

CMS/MgO/CMS(001)

B. Hu, et al., PRB **94** (2016) 094428.



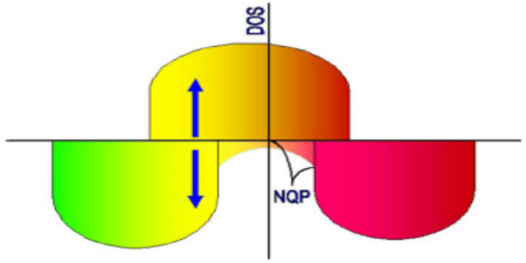
Present top data

Problem: Reduction of the TMR ratio at room temperature

in spite of high curie temperature of Co2MnSi: 985K

Introduction (theory)

1. Temperature dependence of bulk density of states owing to non-quasiparticle

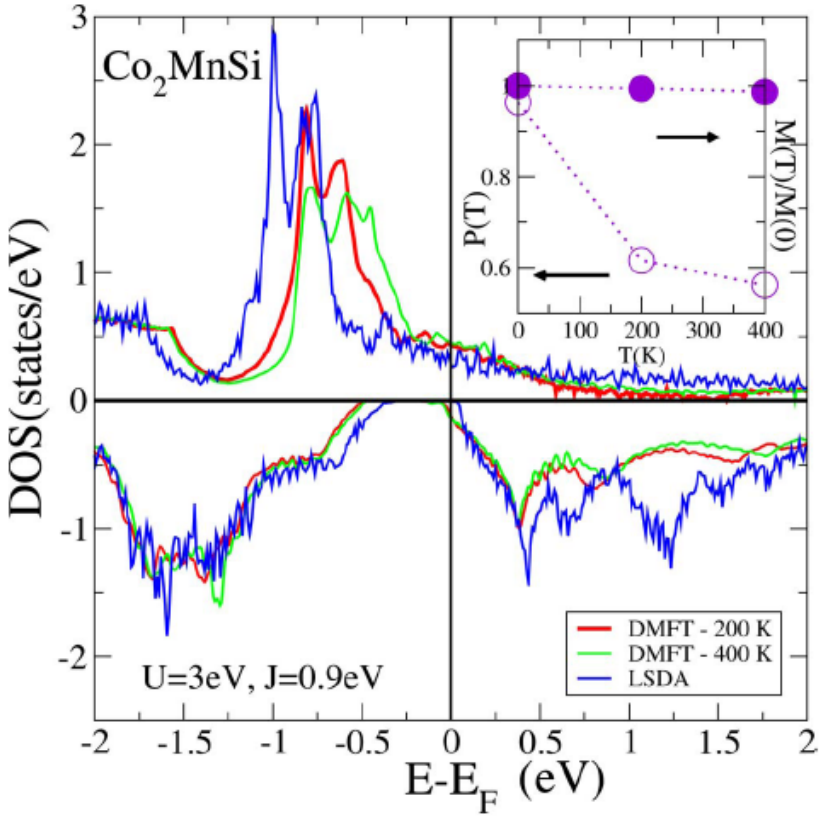


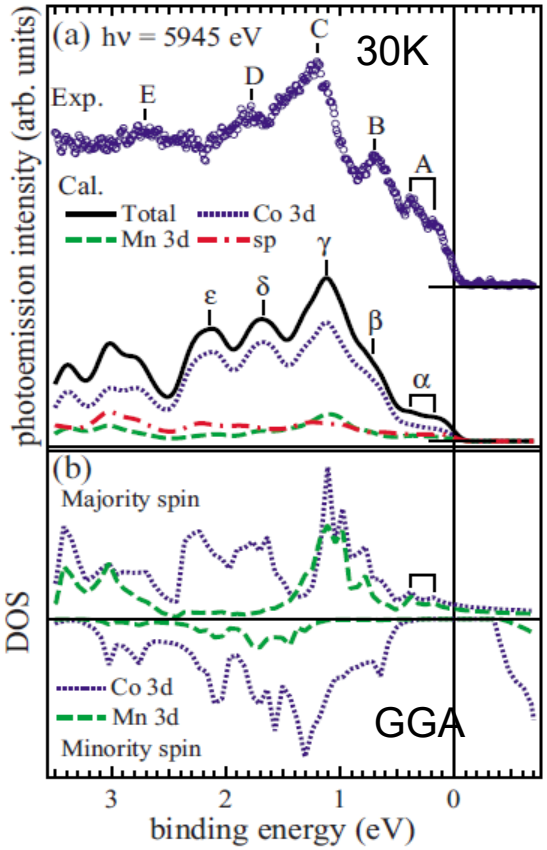
M. I. Katsnelson, *et al*., Rev. Mod. Phys. **80**, 315 (2008).

X-ray photoelectron spectroscopy of bulk CMS

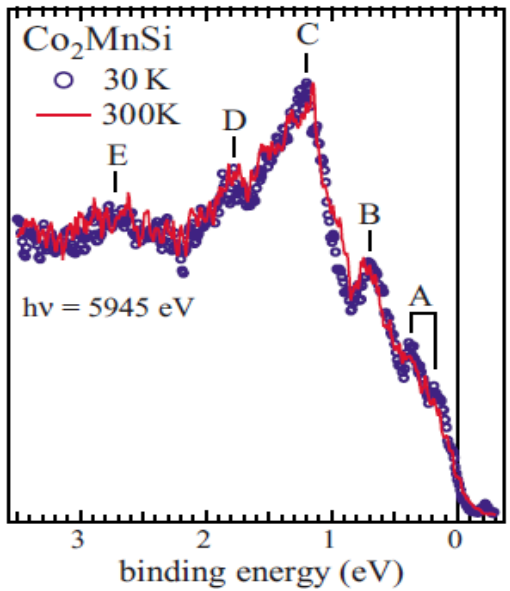
K. Miyamoto, *et al*., PRB. **79**, 100405(R) (2009).

Temperature dependence of total DOS of bulk CMS calculated from DMFT





Valence band electronic structures of bulk CMS

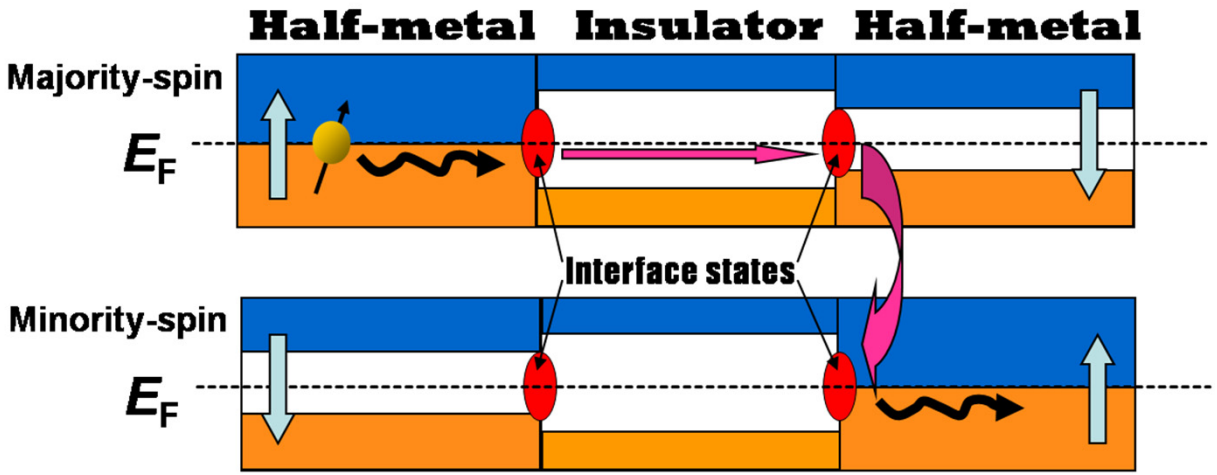


Introduction (theory)

2. Effects of the spin-flip scattering through the interface states promoted by magnetic excitation.

P. Mavropoulos, *et al*., PRB, 72 (2005) 174428.

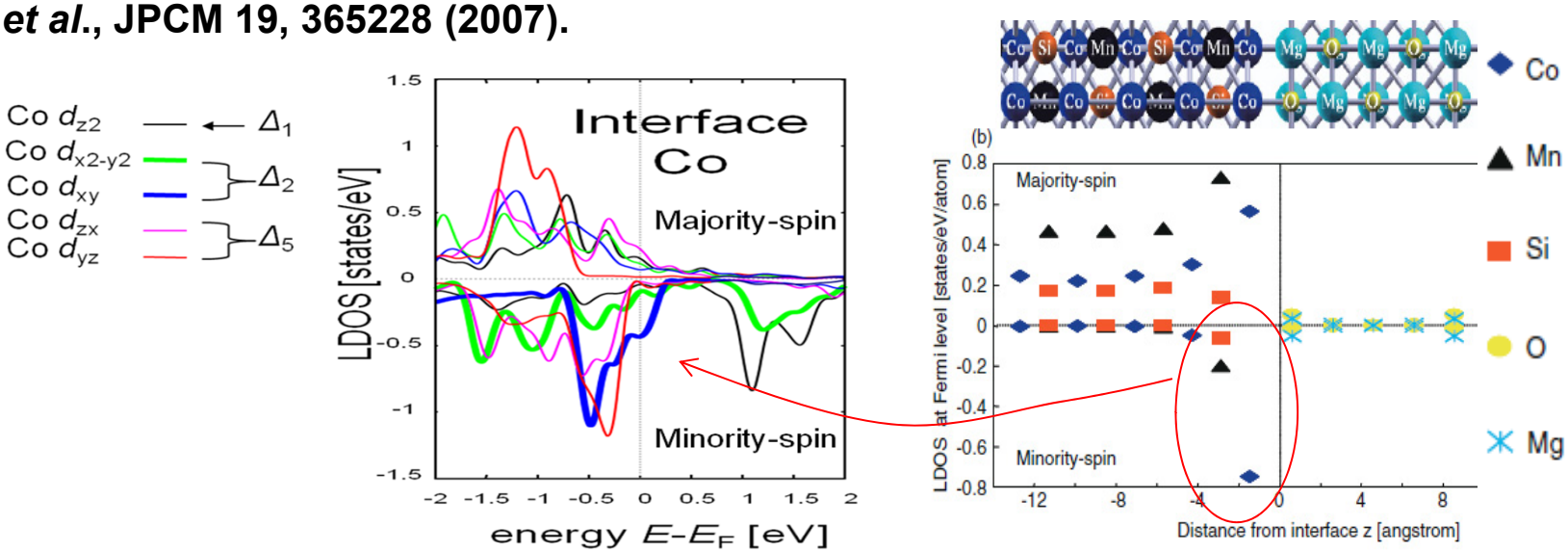
Anti-parallel magnetization



$Co_2MnSi/MgO(001)$

Y. Miura, *et al*., PRB 78, 064416 (2008).

Y. Miura, *et al*., JPCM 19, 365228 (2007).

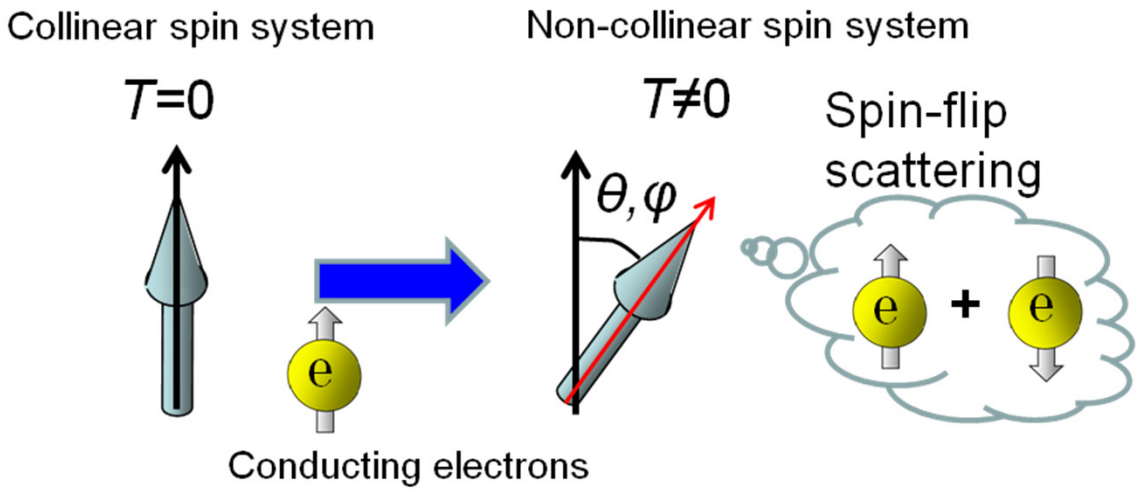


Purpose of this work

・To clarify a possible origin of reduction of TMR ratio at RT in MTJ with half-metallic Heusler alloys,

・We investigate effects of spin-flip scattering through the interface states at CMS/MgO junctions originating from non-collinear magnetic structures.

Thermal fluctuation of local spin-moments ⇒ Non-collinear magnetic structures



Calculation Method

Electronic structures

PWSCF http://www.pwscf.org/

- Plane-wave basis set
- Ultra-soft pseudopotential method
- GGA for Exchange-Correlation term

Transport calculations

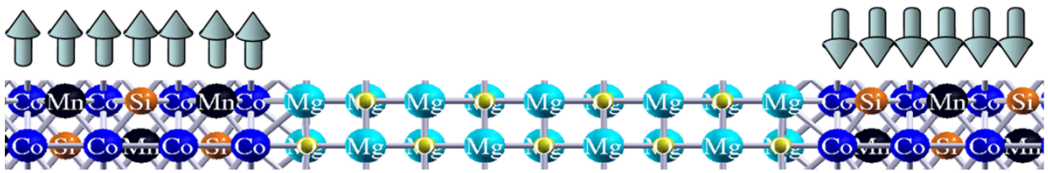
$$G = \frac{e^2}{h} \sum_i^N T_i$$

- Landauer formula
- Zero bias limet Ballistic Conductance

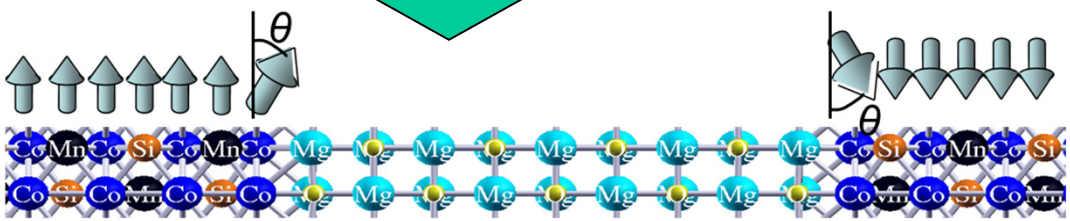
H. J. Choi and J. Ihm, PRB 59 (1999) 2267.
A. Smogunov, A. Dal Corso and E. Tosatti, PRB 70 (2004) 045417.

Conductance calculation in Non-collinear spin system

First, we perform electronic structure calculations in collinear spin system



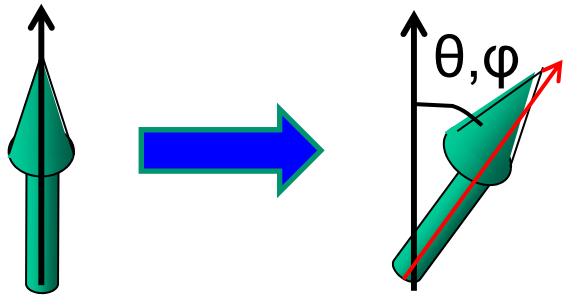
Then, we artificially rotate spin-quantum axis of local spin-moments to obtain density-matrix in non-collinear spin system.



The rotation of spin-quantum axis in NC spin system

The density matrix in non-collinear spin system is obtained from the inverse unitary transformation of spin-density in collinear spin system.

Collinear spin system($\mathbf{n}_i$) Non-collinear spin system($\mathbf{n}_{\alpha\beta}$)



$$n_{\alpha\beta}(\mathrm{r}) = \sum_{i=(\uparrow,\downarrow)} U^{+}_{\alpha i}\, n_i(\mathrm{r}) U_{i\beta}$$

$$U = \begin{pmatrix} \exp\left(\frac{1}{2}i\varphi\right)\cos\left(\frac{1}{2}\theta\right) & \exp\left(-\frac{1}{2}i\varphi\right)\sin\left(\frac{1}{2}\theta\right) \\ -\exp\left(\frac{1}{2}i\varphi\right)\sin\left(\frac{1}{2}\theta\right) & \exp\left(-\frac{1}{2}i\varphi\right)\cos\left(\frac{1}{2}\theta\right) \end{pmatrix}$$

J. Kubler et al., J. Phys. F: Met. Phys. **18**, 469 (1988).

Local potential in Collinear spin system

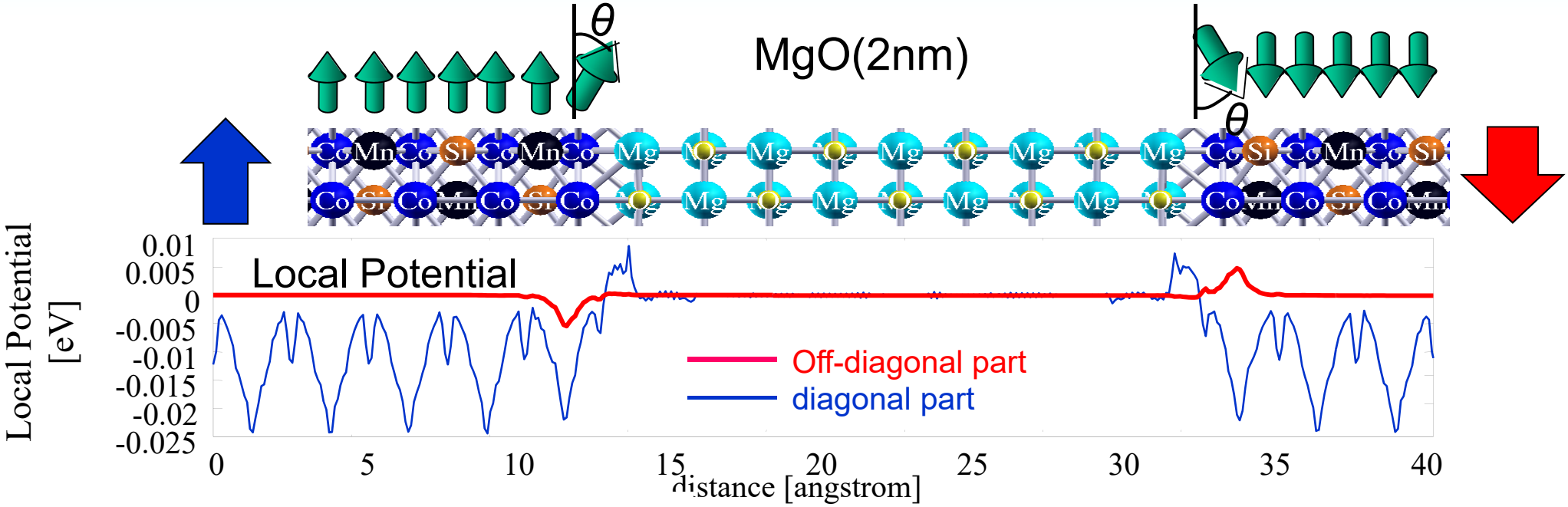
$$\begin{pmatrix} V_L(r)+V_H(r)+\frac{1}{2}\sum_{\alpha=(\uparrow,\downarrow)}\frac{\delta E_{XC}}{\delta n_\alpha}+\frac{1}{2}\left(\frac{\delta E_{XC}}{\delta n_\uparrow}-\frac{\delta E_{XC}}{\delta n_\downarrow}\right) & 0 \\ 0 & V_L(r)+V_H(r)+\frac{1}{2}\sum_{\alpha=(\uparrow,\downarrow)}\frac{\delta E_{XC}}{\delta n_\alpha}-\frac{1}{2}\left(\frac{\delta E_{XC}}{\delta n_\uparrow}-\frac{\delta E_{XC}}{\delta n_\downarrow}\right) \end{pmatrix}$$

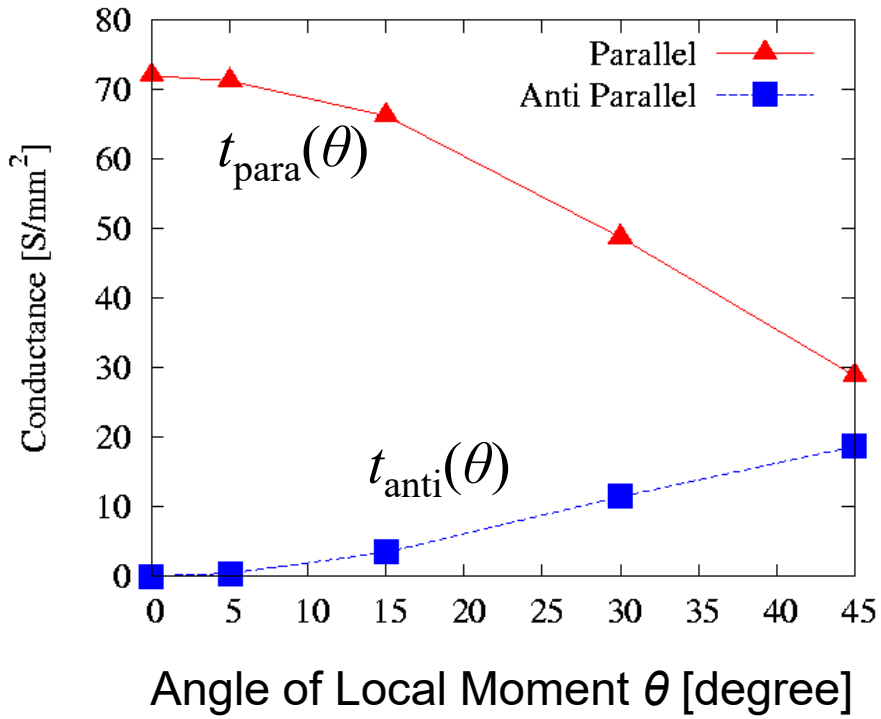
Local potential in Non-Collinear spin system

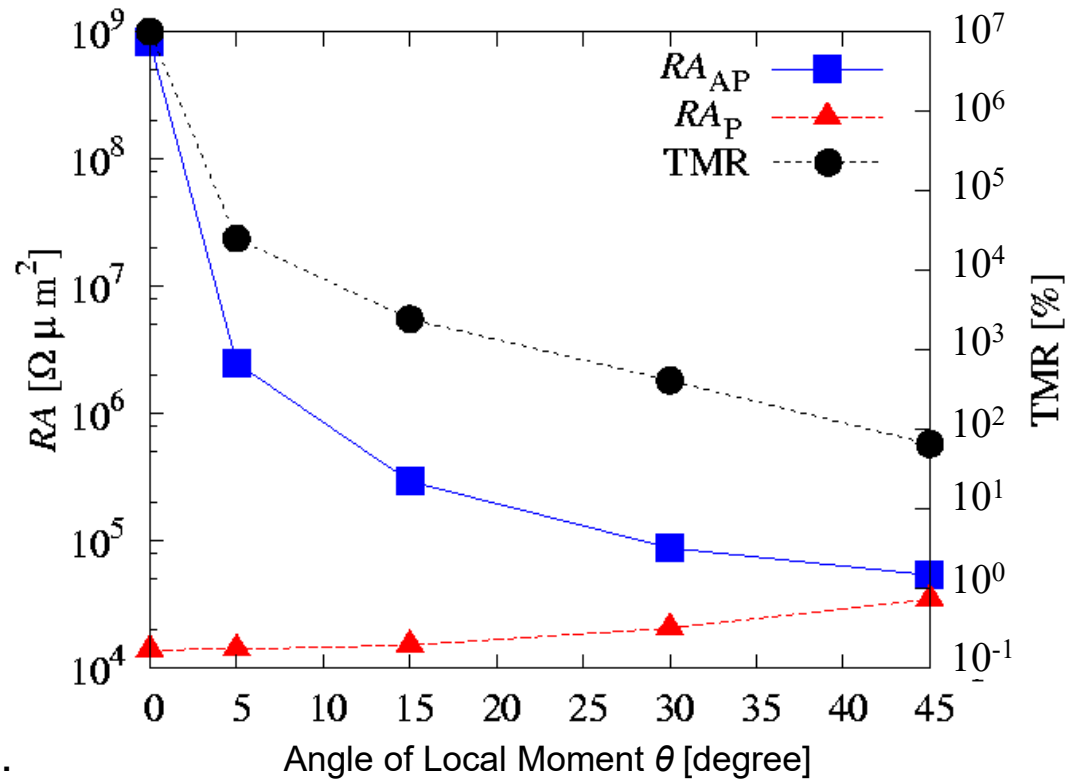
$$\begin{pmatrix} V_L(r)+V_H(r)+\frac{1}{2}\sum_{\alpha=(\uparrow,\downarrow)}\frac{\delta E_{XC}}{\delta n_\alpha}+\frac{1}{2}\left(\frac{\delta E_{XC}}{\delta n_\uparrow}-\frac{\delta E_{XC}}{\delta n_\downarrow}\right)\cos\theta & \frac{1}{2}\left(\frac{\delta E_{XC}}{\delta n_\uparrow}-\frac{\delta E_{XC}}{\delta n_\downarrow}\right)\sin\theta\cos\phi+\frac{i}{2}\left(\frac{\delta E_{XC}}{\delta n_\uparrow}-\frac{\delta E_{XC}}{\delta n_\downarrow}\right)\sin\theta\sin\phi \\ \frac{1}{2}\left(\frac{\delta E_{XC}}{\delta n_\uparrow}-\frac{\delta E_{XC}}{\delta n_\downarrow}\right)\sin\theta\cos\phi-\frac{i}{2}\left(\frac{\delta E_{XC}}{\delta n_\uparrow}-\frac{\delta E_{XC}}{\delta n_\downarrow}\right)\sin\theta\sin\phi & V_L(r)+V_H(r)+\frac{1}{2}\sum_{\alpha=(\uparrow,\downarrow)}\frac{\delta E_{XC}}{\delta n_\alpha}-\frac{1}{2}\left(\frac{\delta E_{XC}}{\delta n_\uparrow}-\frac{\delta E_{XC}}{\delta n_\downarrow}\right)\cos\theta \end{pmatrix}$$

Y. Miura, et al., Phys. Rev. B **83,** 214411 (2011).

Transport in non-collinear spin MTJs

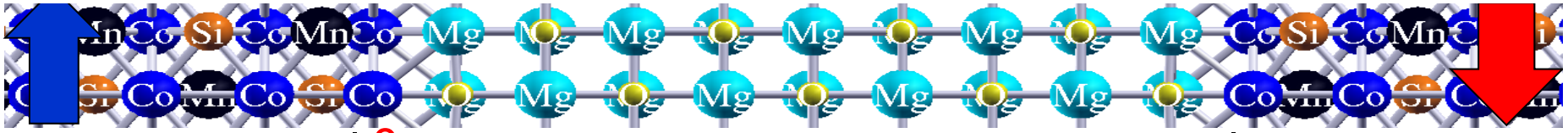


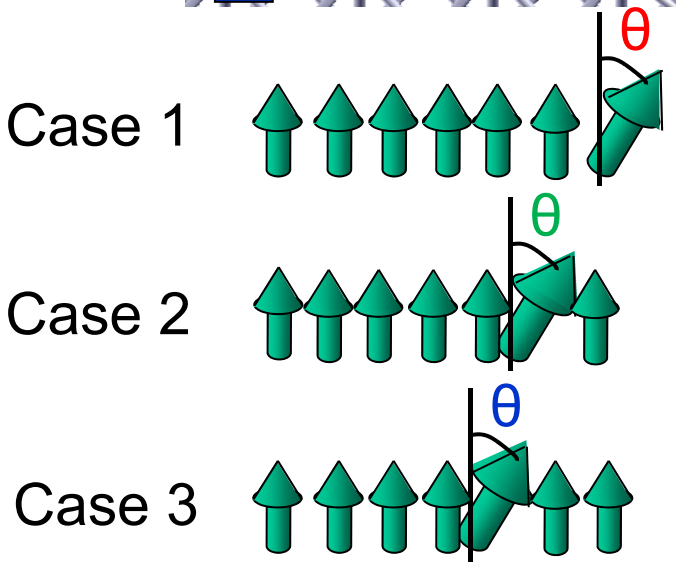


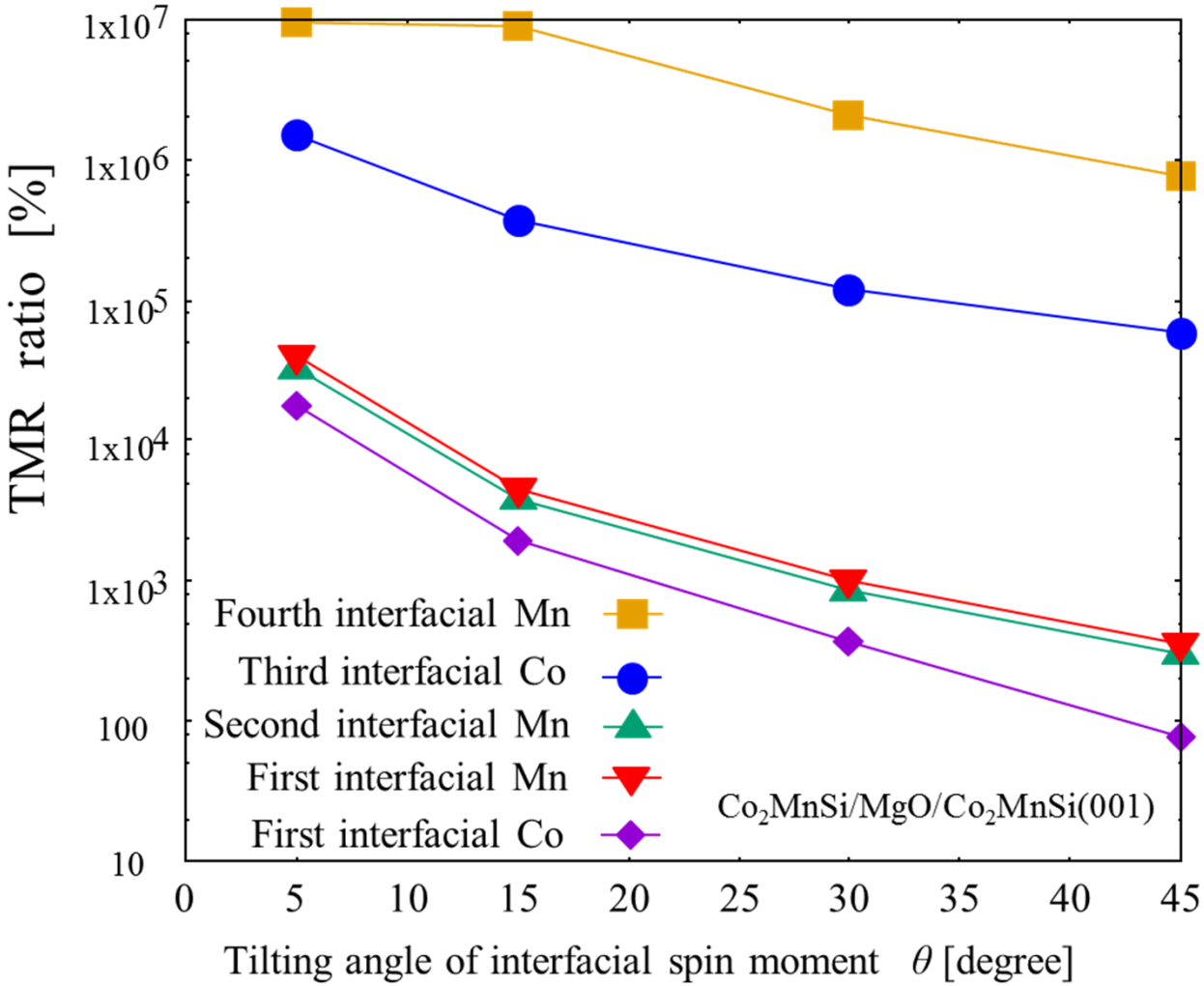


Y. Miura, et al., Phys. Rev. B **83,** 214411 (2011).

Effects of sub-interfacial non-collinear spin to TMR







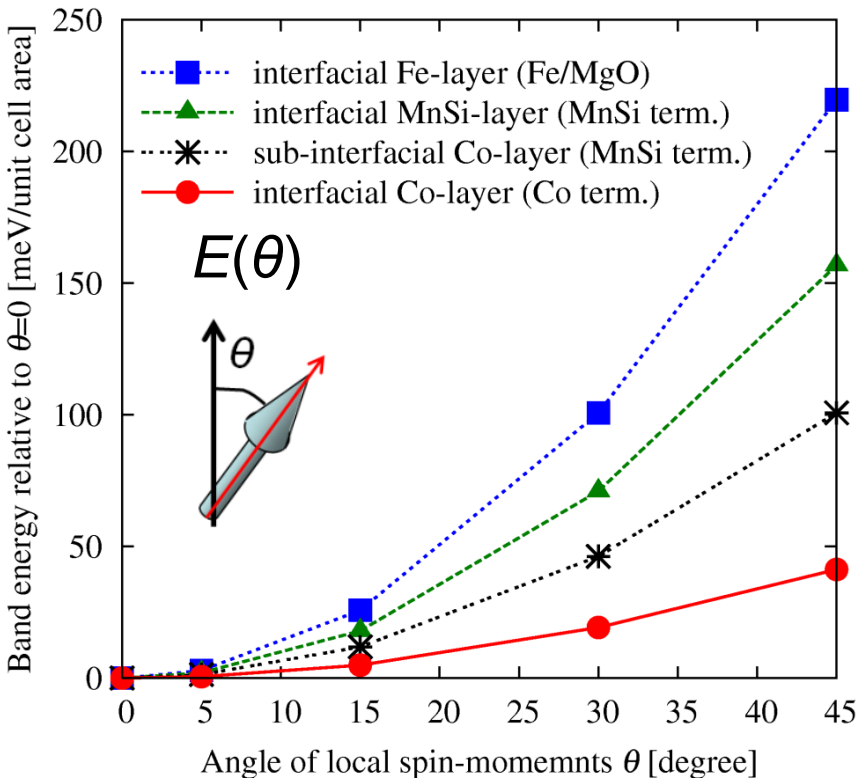
Noncollinear magnetic structures of the first and the second interfacial layer strongly reduce TMR.

Noncollinear magnetic structure of the third and forth interfacial layer show relatively small reduction of TMR.

Exchange stiffness constant at CMS/MgO(001)

Increase of band energy of Non-collinear Spin ⇒ Strength of exchange coupling

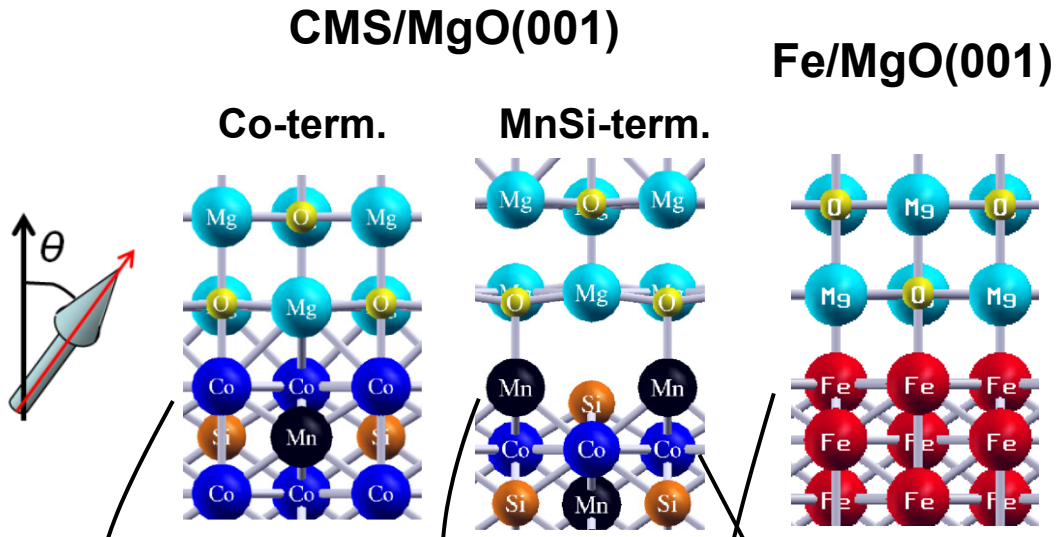
$E(\theta)=A(1-\cos\theta)$ $A \propto JM^2$



A. Sakuma, *et al.*, JAP **105**, 07C910 (2009).

Off-diagonal part of local potential

$$V_{\alpha\beta(\alpha\neq\beta)}(\mathrm{r})=\left(\frac{\delta E_{XC}}{\delta n_{\uparrow}}-\frac{\delta E_{XC}}{\delta n_{\downarrow}}\right)\sin\theta$$



Exchange stiffness of interfacial atoms

A [meV/u.c.a.]	Co^1	Mn^1	Fe^1	Co^2
Bulk (CMS or Fe)	414	529	600	414
MgO interface	145	565	753	347
ΔA [meV/u.c.a.]	−269	+34	+153	−67

Interfacial local spin-moment

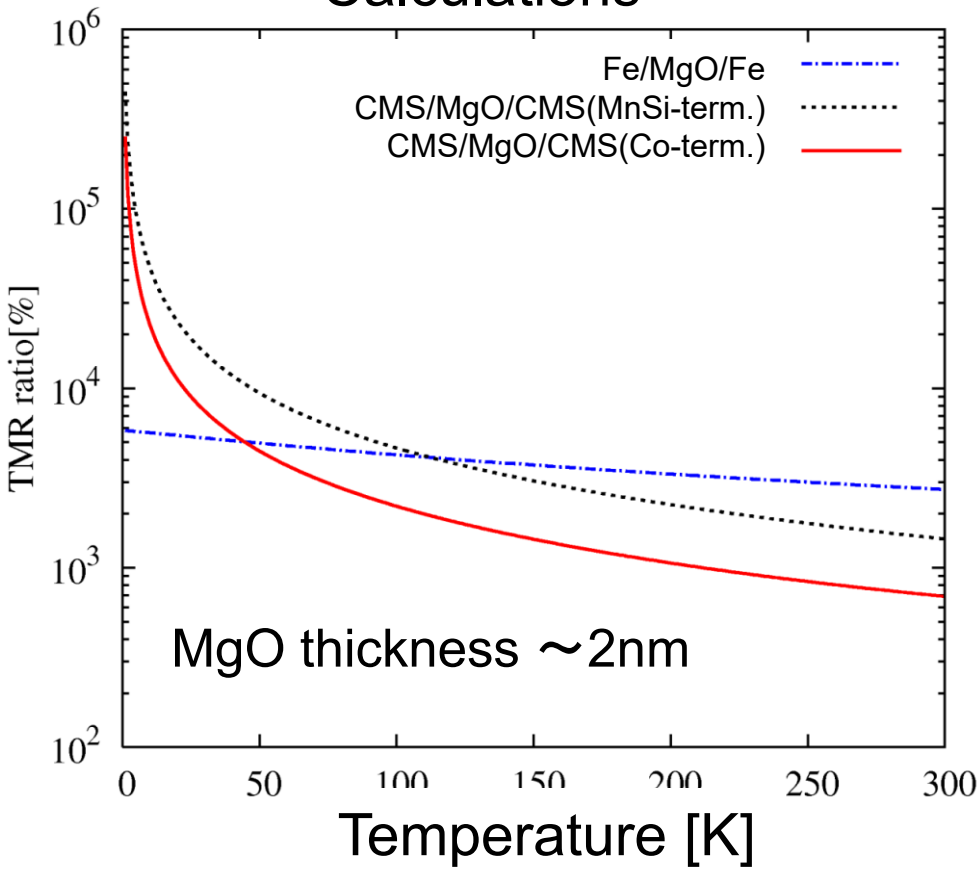
M [μ_B]	Co^1	Mn^1	Fe^1
Bulk (CMS or Fe)	0.93	3.31	2.35
MgO interface	0.54	4.06	2.98
ΔM [μ_B]	−0.39	+0.75	+0.63

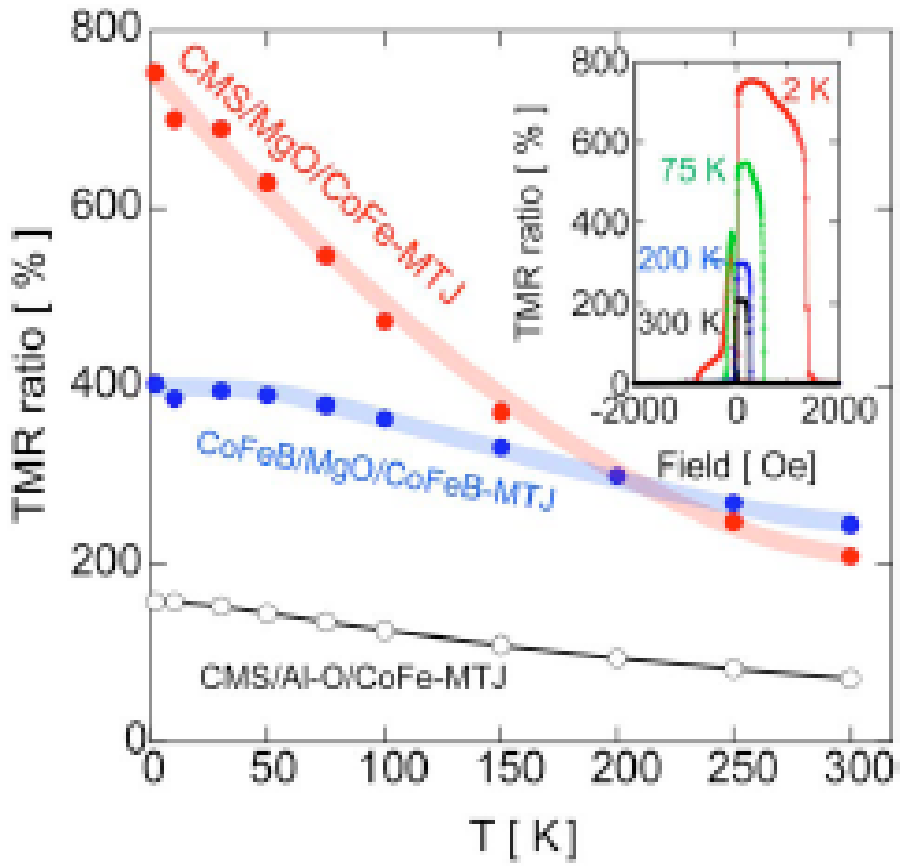
TMR ratio at finite temperature

Boltzmann average of tunneling conductance

$$t^{(\mathrm{para,anti})}(T) = \frac{\int t_{(\mathrm{para,anti})}(\theta)\exp[-2E(\theta)/k_B T]\sin\theta d\theta}{\int \exp[-2E(\theta)/k_B T]\sin\theta d\theta}$$

Calculations

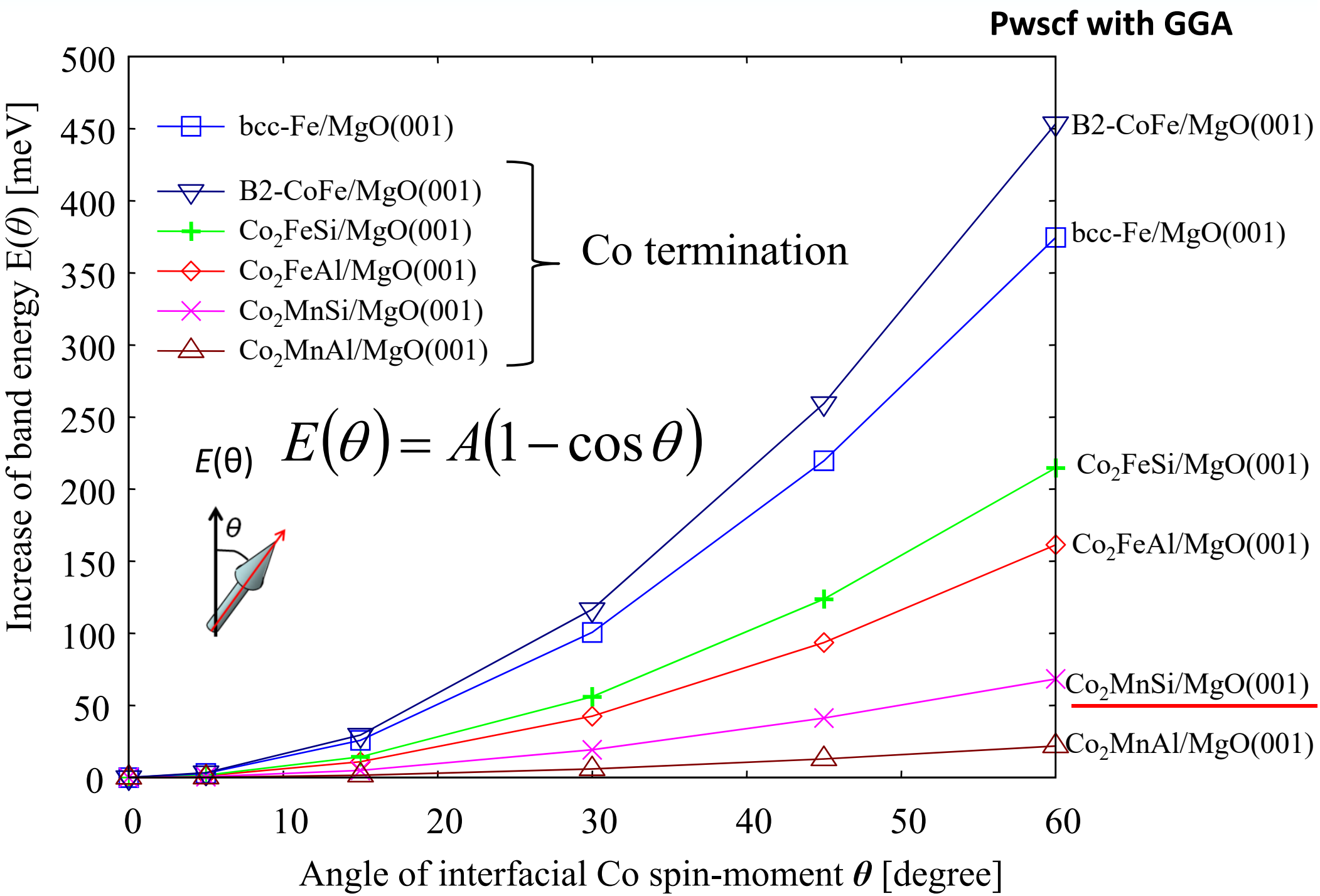




S. Tsunegi, *et al.*, APL 93 (2008) 112506.

Reduction TMR ratio at RT in CMS/MgO/CMS MTJ can be attributed to a spin-flip scattering at interfacial region caused by thermal fluctuation.

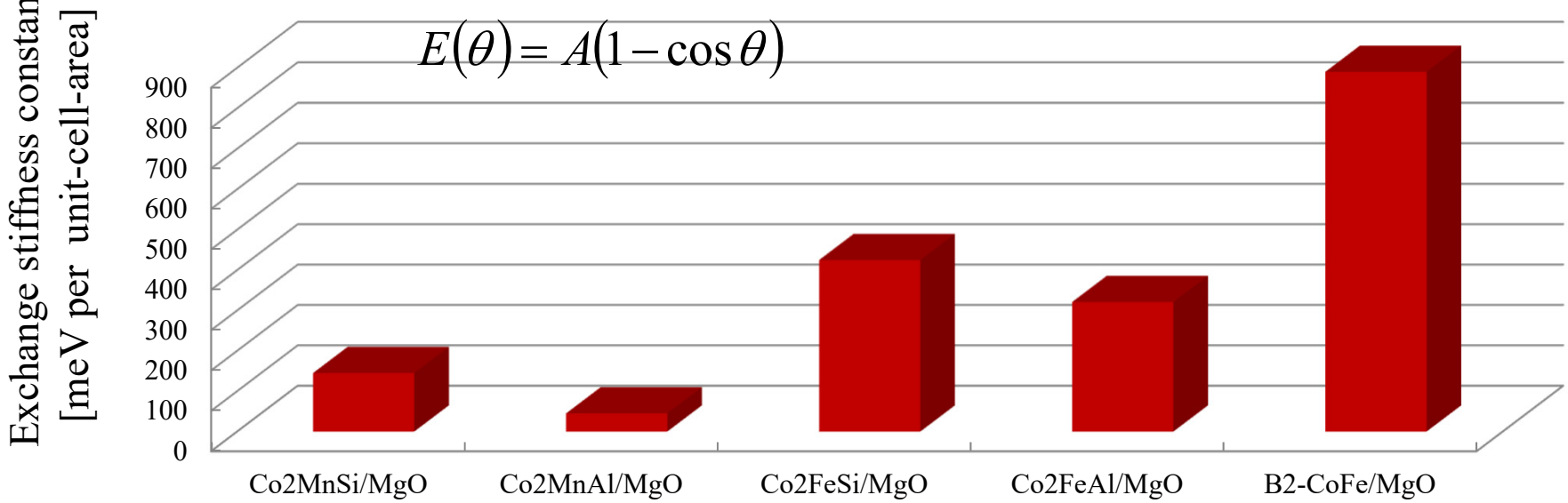
Exchange coupling for other Heusler alloys



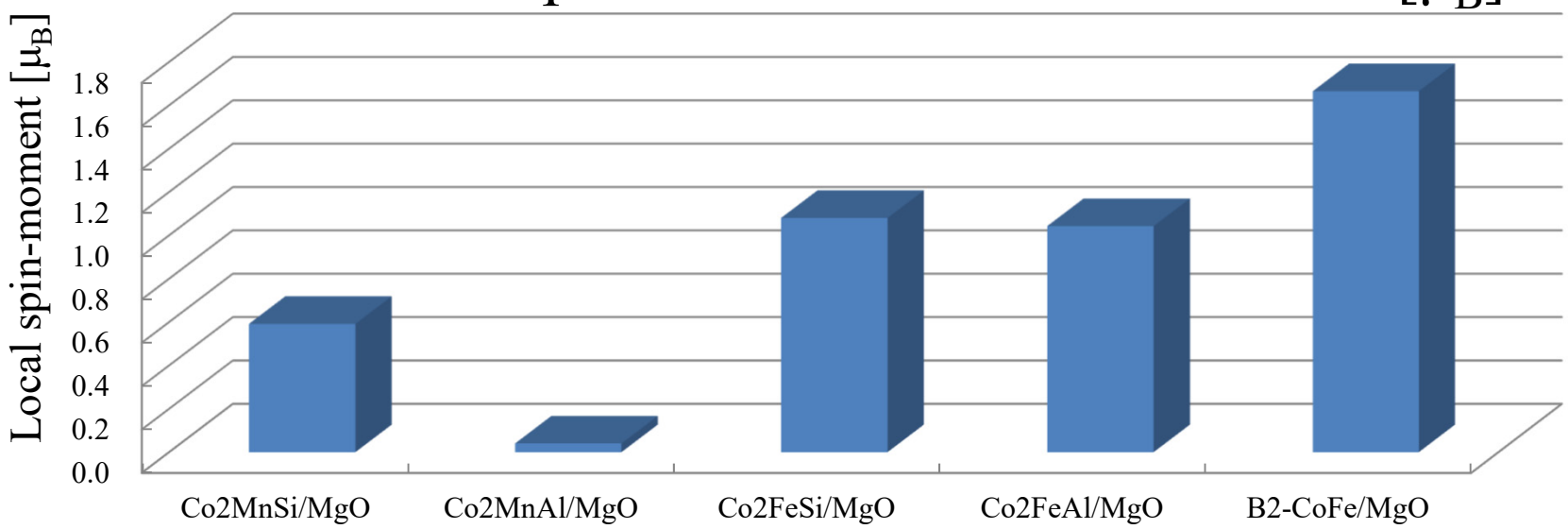
$$E(\theta) = A(1-\cos\theta)$$

Exchange stiffness constant at Co termination

Inter-atomic layer exchange stiffness constant A [meV/cell area]



Interfacial Co spin-moment at Co termination [μ_B] $A \propto JM^2$



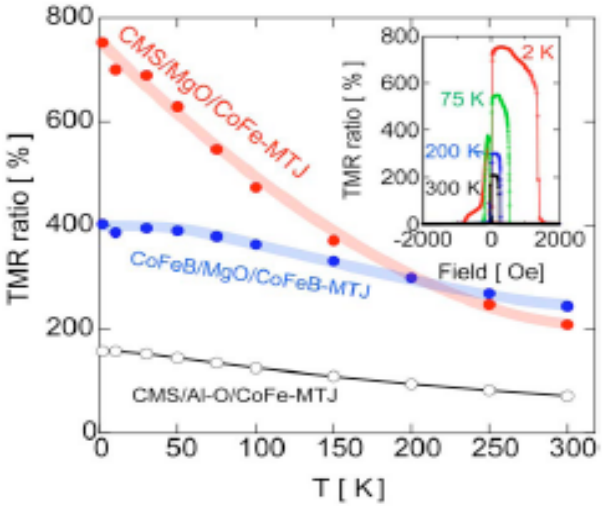
Enhancement of interfacial Co spin-moment is effective to obtain large exchange coupling.

Comparison with Experimental results on TMR at LT and RT

$Co_2MnSi/MgO(001)$

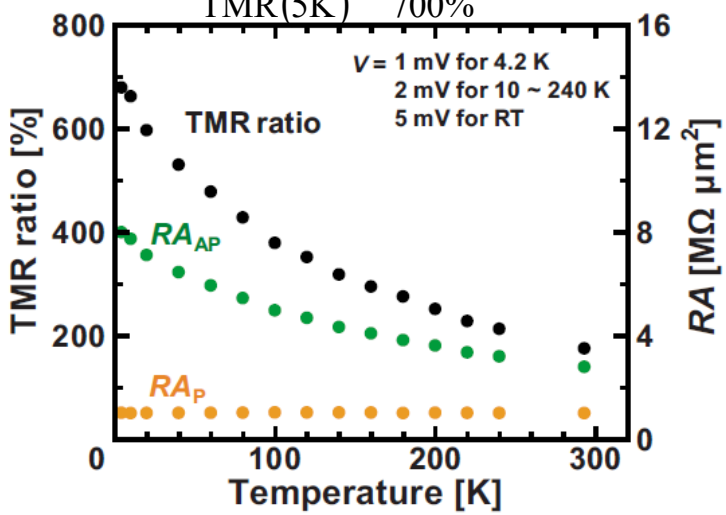
S. Tsunegi, *et al*., APL 93 (2008) 112506.

$$\frac{TMR(RT)}{TMR(2K)} = \frac{217\%}{753\%} = 0.29$$



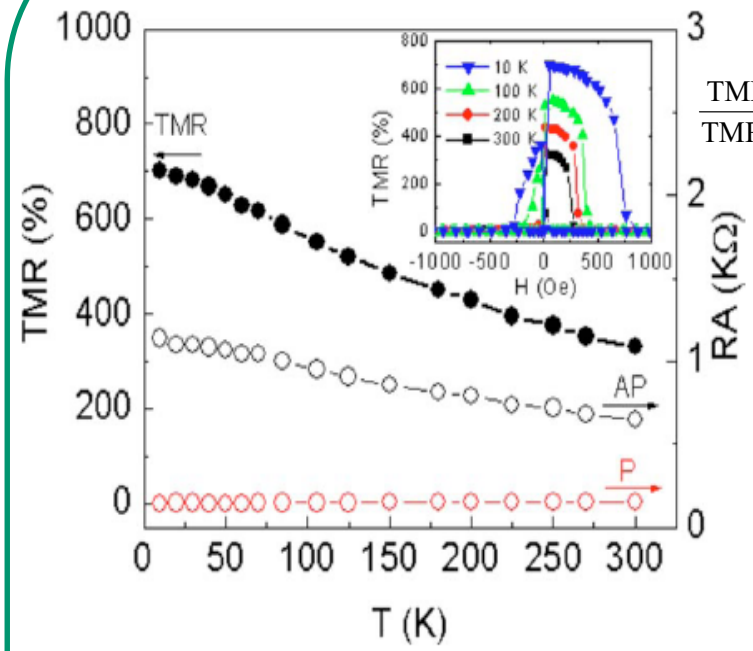
T. Ishikawa, *et al*., APL 94 (2009) 092503.

$$\frac{TMR(RT)}{TMR(5K)} = \frac{180\%}{700\%} = 0.26$$



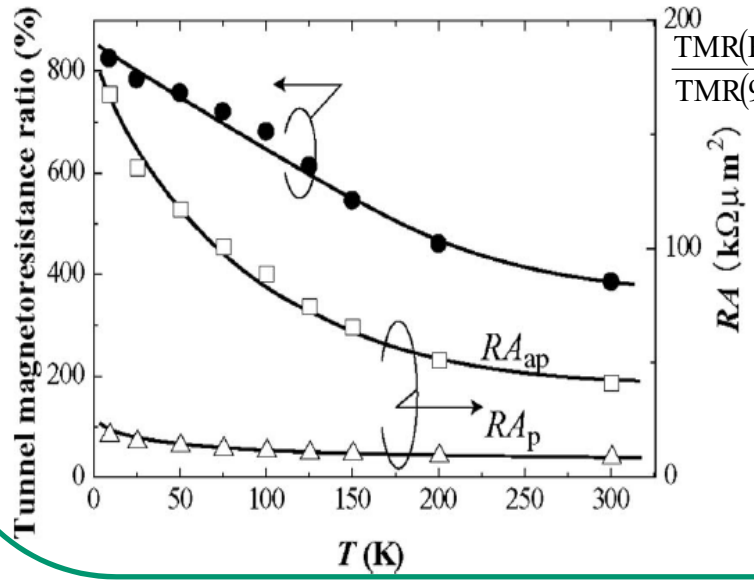
$Co_2Fe(Al,Si)/MgO(001)$

W. Wang, *et al*., APL 95 (2009) 182502.



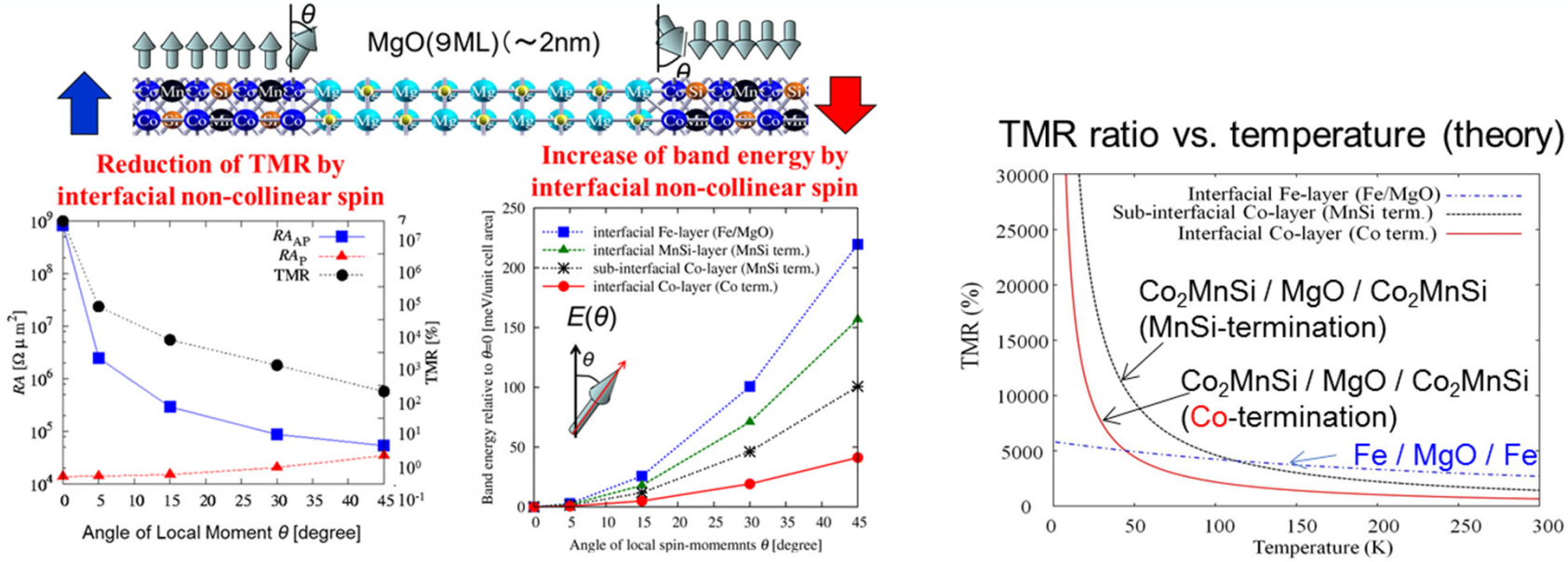
$$\frac{TMR(RT)}{TMR(10K)} = \frac{330\%}{700\%} = 0.47$$

N. Tezuka, *et al*., APL 94 (2009) 162504.



$$\frac{TMR(RT)}{TMR(9K)} = \frac{386\%}{832\%} = 0.46$$

Summary of the first topic



◇ Spin-flip scattering at 1ML of interfacial non-collinear magnetic structures strongly affect the spin-dependent conductance and TMR ratio.

◇ Interfacial Co-layer is easy to fluctuate at RT due to the small exchange stiffness at CMS/MgO(001) junctions.

◇ The reduction of the TMR ratio at RT can be attributed to spin-flip scattering at interfacial region caused by thermal fluctuation of interfacial Co-layers.

To raise the TMR ratio at RT, we have to insert Fe-layer to enhance the interfacial exchange stiffness of CMS/MgO junction.

Contents

1. Spin-dependent transport in magnetic tunnel junctions with half-metallic Heusler alloys

Y. Miura, *et al*., Phys. Rev. B **83,** 214411 (2011).

2. Spin-dependent tunneling conductance in magnetic tunnel junctions with spinel-type $MgAl_2O_4$ barrier

Y. Miura, *et al*, PRB, **86**, 024426 (2012).
K. Masuda and Y. Miura, PRB **96**, 054428 (2017)

3. Electric field dependence of magnetic damping constant of Fe(001) surface

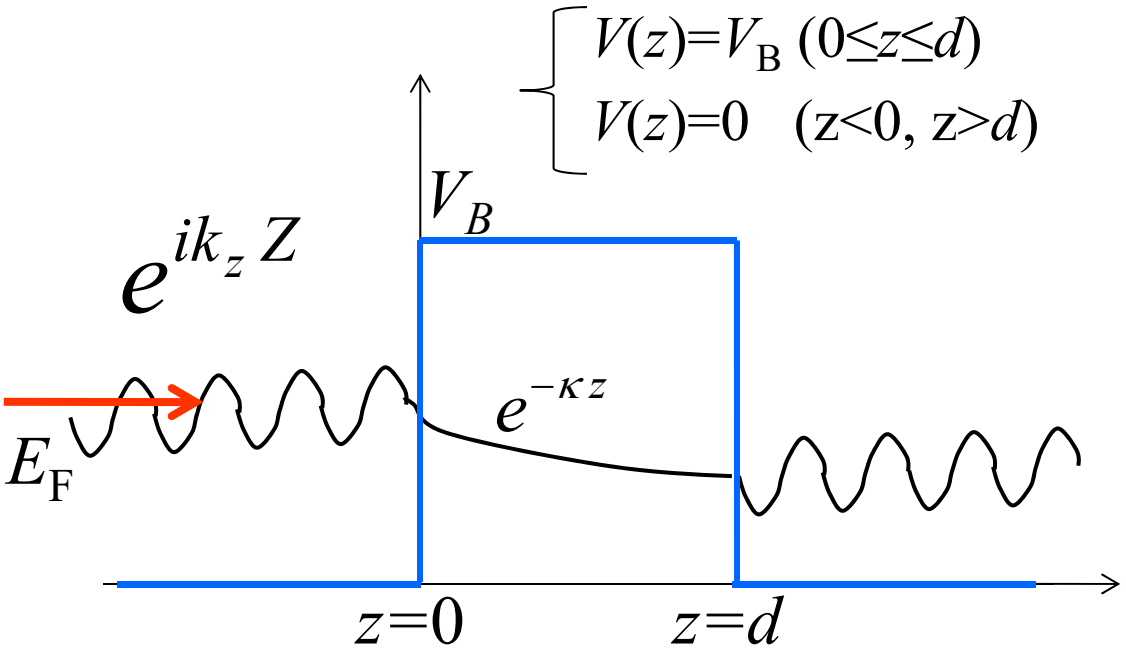
YM, M. Tsujikawa, M. Shirai, in preparation.

4. Magneto-crystalline anisotropy at interfaces of Fe(001) with various non-magnetic metals

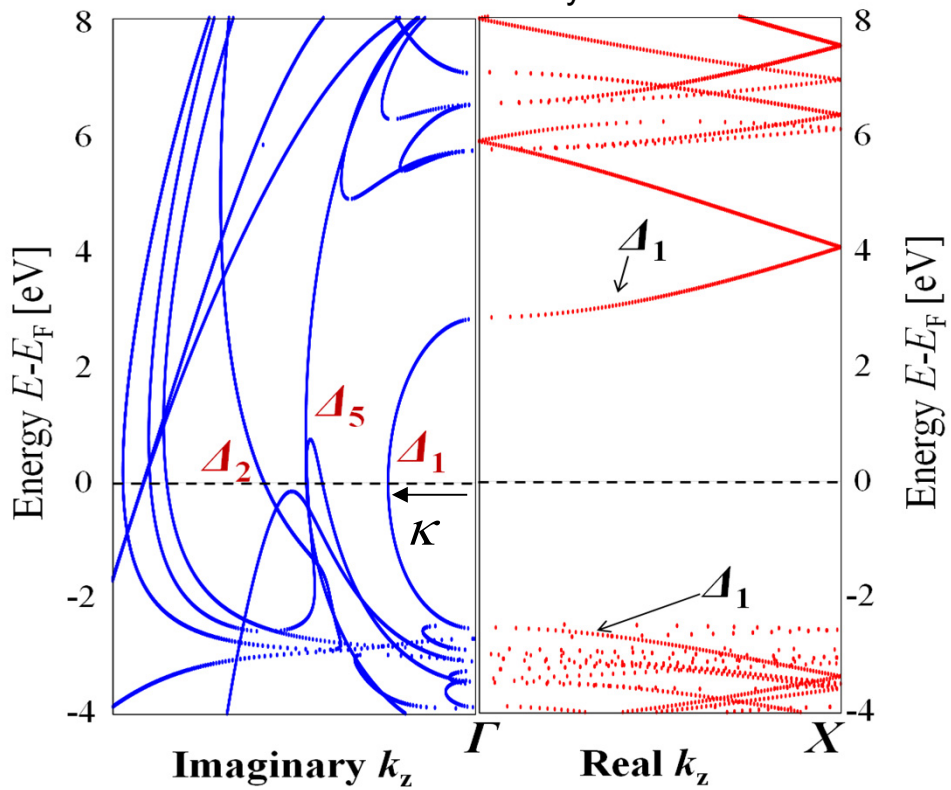
Y. Miura, M. Tsujikawa, M. Shirai, J. Appl. Physics, **113**, 233908/1-6 (2013).

Complex band structure of MgO and tunneling effects

- Transmission of 1D potential



MgO band at $(k_x,k_y)=(0,0)$



Imaginary part of complex band structure determines the decay rate of evanescent state in barrier

$$\kappa = \frac{\sqrt{2m(V_B - E_F)}}{\hbar}$$

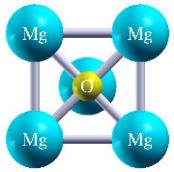
$$\left[-\nabla^2 + V(\mathbf{r}) - E\right]\Psi_k(\mathbf{r}) = 0$$

Complex band calculation

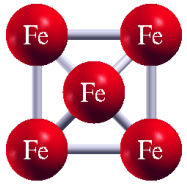
for given E

Coherent tunneling in Fe/MgO/Fe(001)

W. H. Butler, et al., PRB, **63** 054416 (2001).

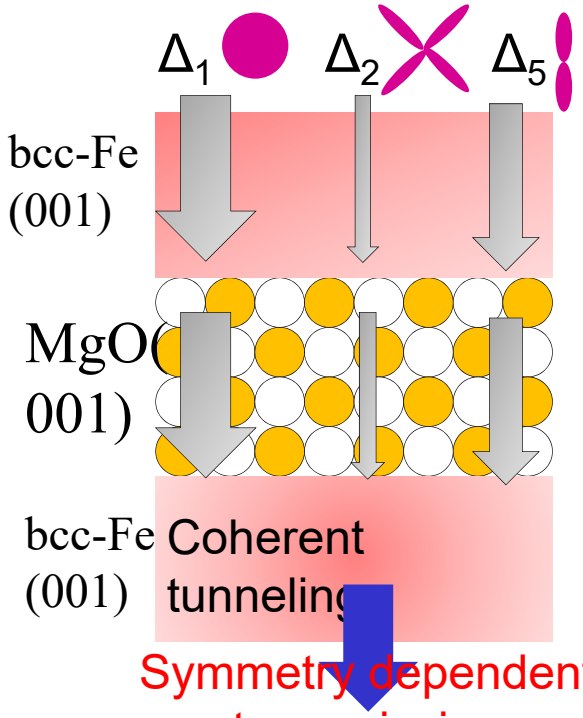


C_{4v} [001]



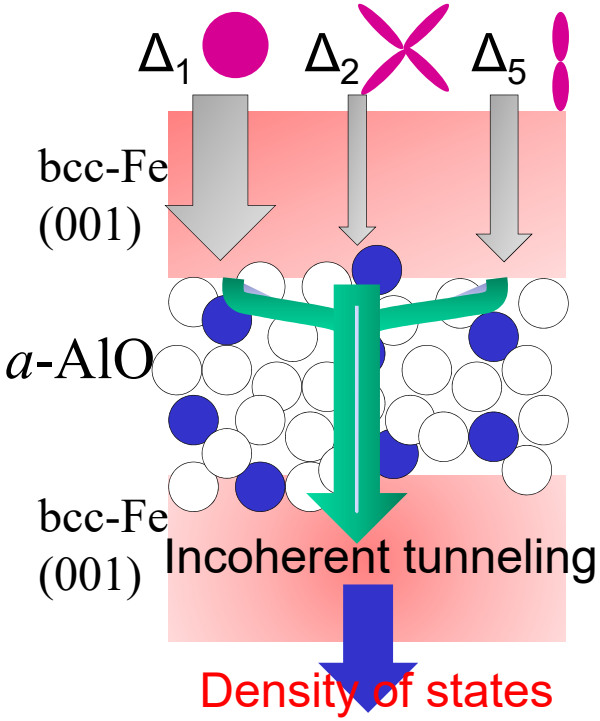
C_{4v}

Crystalline-MgO barrier MTJ



Symmetry dependent transmission

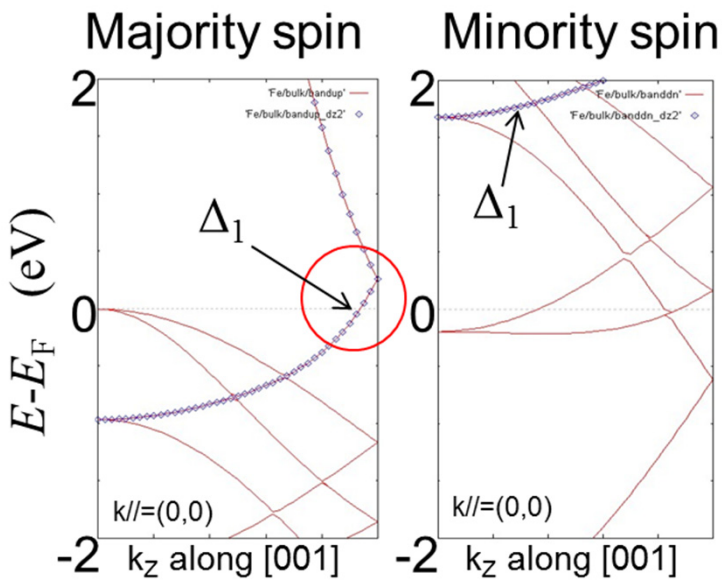
Amorphous Al-O barrier MTJ



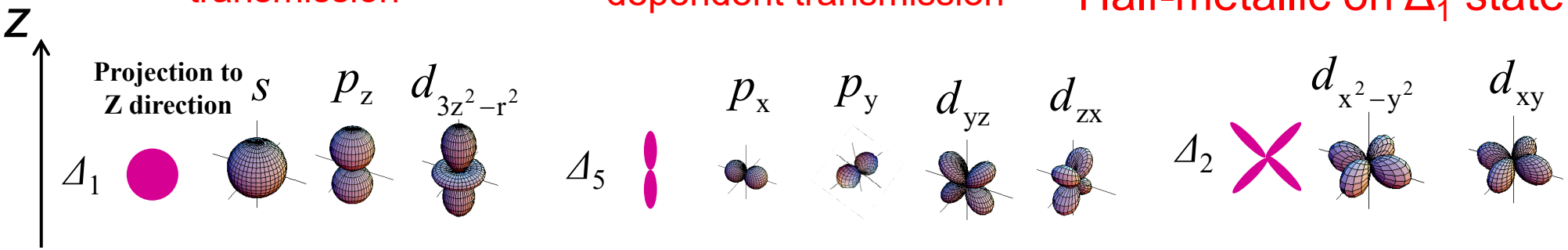
Density of states dependent transmission

Band dispersion of bcc-Fe

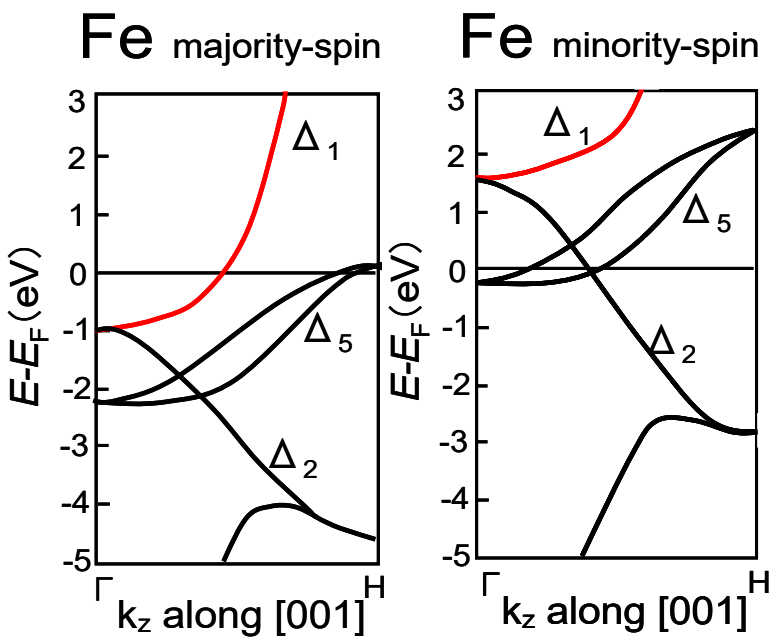
$(k_x,k_y)=(0,0)$



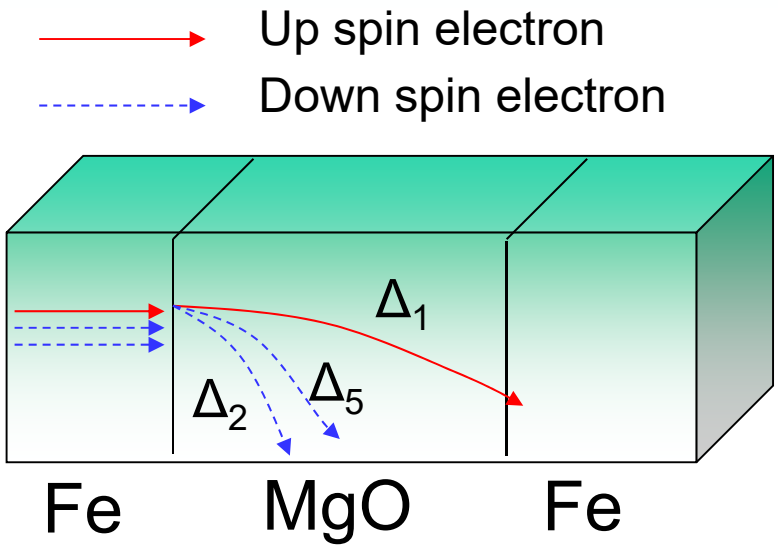
Half-metallic on Δ_1 state



Giant TMR in Fe/MgO/Fe(001)

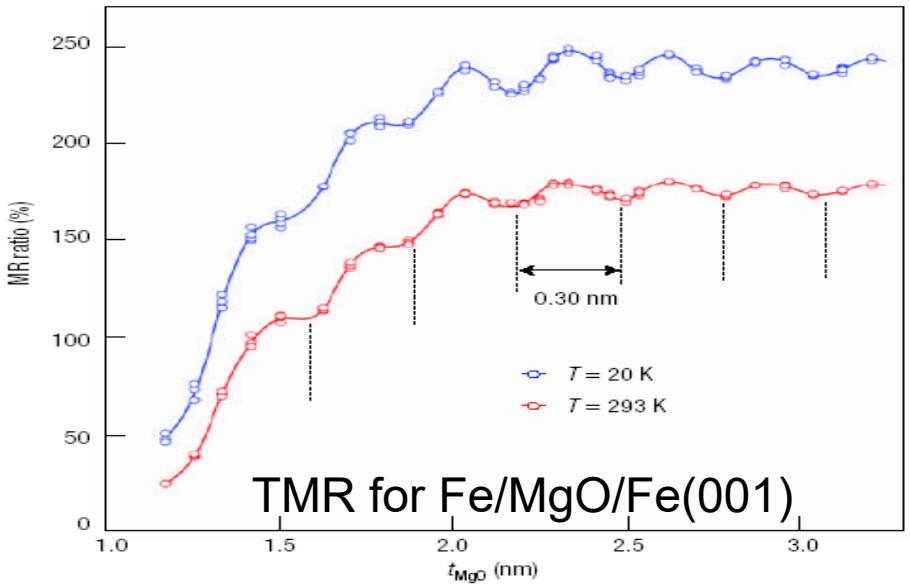


Half-metallic on Δ1 state in bcc-Fe (P=1)



Highly spin-polarized current

Theoretical TMR ratio⇒1500%
(MgO thickness～1nm)



TMR for Fe/MgO/Fe(001)

Experiment

S. Yuasa, *et al.*, JJAP, **43** L588 (2004).
S. Parkin, *et al.*, Nature Material, **3** 862 (2004).
S. Yuasa, *et al.*, Nature Material, **3** 868 (2004).

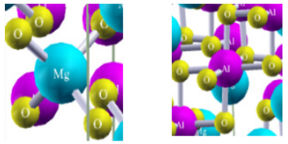
S.Ikeda,*et al* Appl.Phys. Lett. **93**, 082508 (2008).

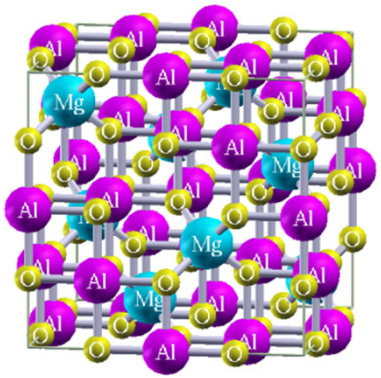
$Co_{20}Fe_{60}B_{20}$/MgO/$Co_{20}Fe_{60}B_{20}$ (TMR ～604% @300K)

Spinel Barrier

$MgAl_2O_4$

$Fd\bar{3}m$(No. 227)





Normal spinel structure

Tetrahedral A-site・・・Mg^{2+} fcc-sublattice ・・・O^{2-}

Octahedral B-site・・・Al^{3+} (u-parameter)

Advantage:

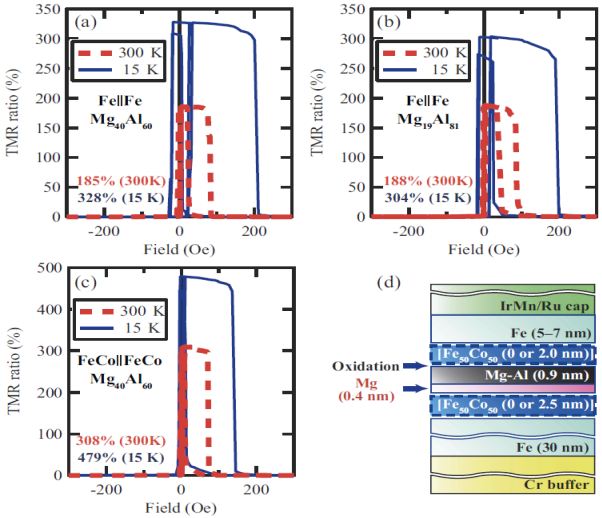
1. Very small lattice mismatch with bcc-Fe (<0.5%)

   Lattice constant : (8.09Å)/√2=5.72Å

2. Modulation of lattice constant by choosing cation atoms.

   $MgAl_2O_4$, $ZnAl_2O_4$, $SiMg_2O_4$, $TiZn_2O_4$, $SiZn_2O_4$, Al_3O_4, etc.

Experiments : MTJs with normal spinel $MgAl_2O_4$ barrier on Fe(CoFe)



TMR=160%@15K (120%@RT)

H. Sukegawa, *et al.*, APL 96, (2010) 212505.

TMR=328%@15K (188%@RT)

TMR=478%@15K (303%@RT)

H. Sukegawa, *et al.*, PRB **86**, 184401 (2012).

Calculation : bulk $MgAl_2O_4$

Y. Nian, *et al.*, PRB, 43 (1991) 4461.

R. Khenata, *et al.*, Physics Letters A, 344 (2005) 271.

Purpose of this work

- Coherent tunneling properties of spinel $MgAl_2O_4$–based MTJs
- Origin of the TMR effect in $Fe/MgAl_2O_4/Fe(001)$ MTJs.

Electronic and transport calculations of $Fe/MgAl_2O_4$-based MTJs together with Fe/MgO-based MTJs on the basis of the first-principles density functional method.

Calculation method

Electronic structure calculation

PWSCF http://www.pwscf.org/

- Ultra-soft pseudopotential
- GGA for exchange-correlation term

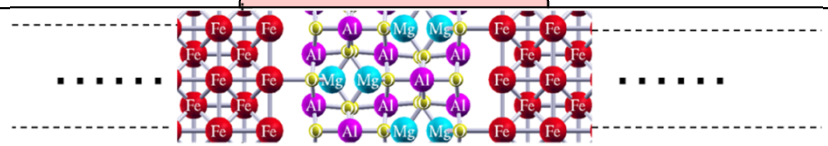
Conductance calculation

H. J. Choi and J. Ihm, Phys. Rev. B **59**, 2267 (1999).

A. Smogunov, A. Dal Corso, E. Tosatti, PRB, 70, 045417 (2004)

electrode region | Scattering region | electrode region

$$\Psi_L = \psi_k + \sum_{k' \in L} r_{k'k} \psi_{k'} \quad \Psi_S \quad \Psi_R = \sum_{k' \in R} t_{k'k} \psi_{k'}$$



Fe $MgAl_2O_4$ Fe

$$\left[-\nabla^2 + V_{loc}(\mathbf{r})\right]\psi_k(\mathbf{r}) + \sum_{I,mn} \tilde{D}^I_{mn} \left\langle \beta^I_n \middle| \psi_k \right\rangle \beta^I_m(\mathbf{r}) = E\psi_k(\mathbf{r})$$

- Landauer formula

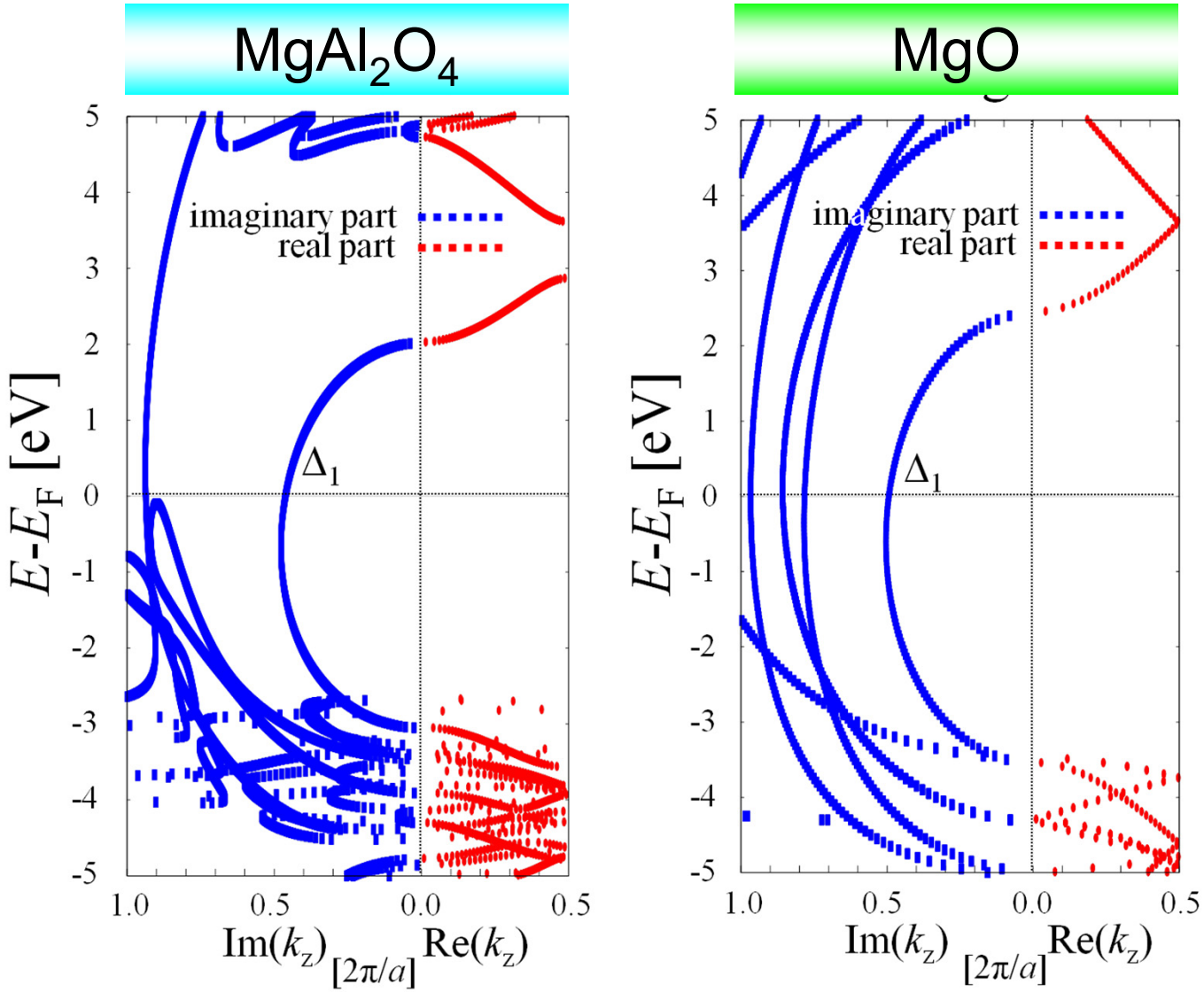
$$G = \frac{e^2}{h} \sum_i^N T_i$$

- **Fixed k//**
- **Fixed spin index**
- **Zero bias limit conductance**

Complex band structures of $MgAl_2O_4$

$k_{//}=(0,0)$

$k_z=k_z'+ik_z''$

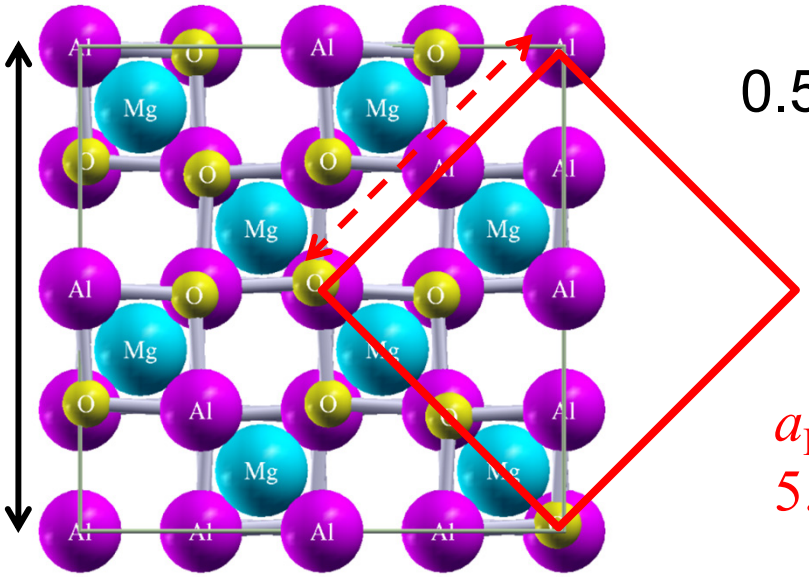


$MgAl_2O_4$ has the smallest imaginary part with the Δ_1 symmetry in the energy gap.

Structures of Fe/$MgAl_2O_4$(001) interface

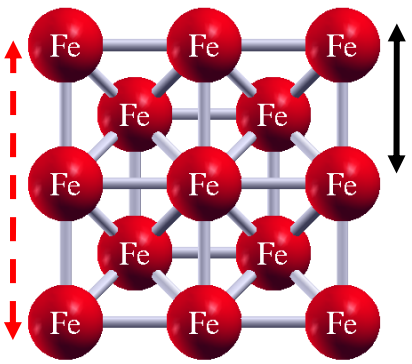
$a_{MgAl2O4}$=8.09[Å]

$a_{MgAl2O4}/\sqrt{2}$=5.72[Å]



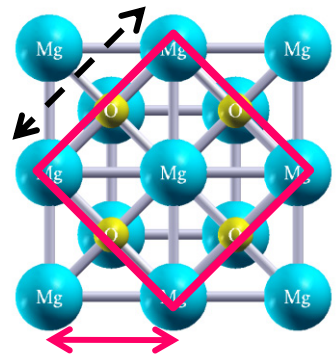
0.5% lattice mismatch

a_{Fe}=2.866[Å]



a_{Fe} × 2= 5.732[Å]

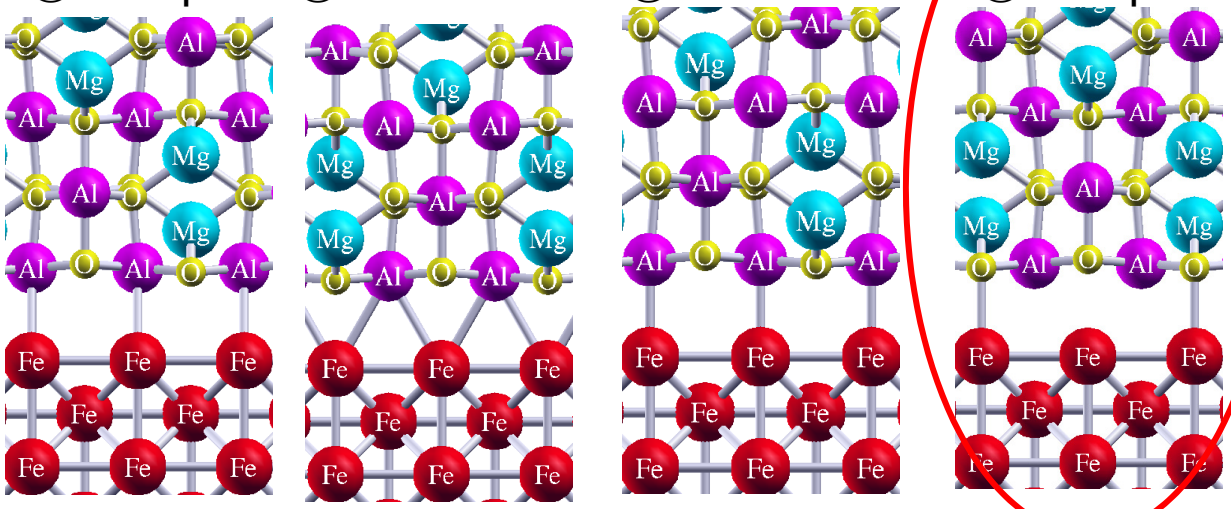
a_{MgO}=4.213[Å]



$a_{MgO}/\sqrt{2}$=2.979[Å]

Possible interfacial structures(B-site termination)

① Al-top ② Al-O hollow ③ Al-Al hollow ④ O-top



	Energy [eV/ucv]
① Al-top	0(基準)
② Al-O hollow	-0.1
③ Al-Al hollow	2.5
④ O-top	-3.2 Stable

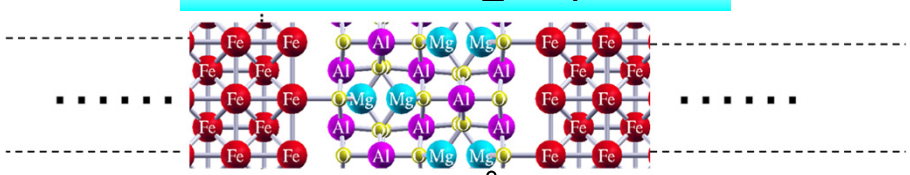
※ucv=unit cell volume

O-top configuration with B-site termination

TMR effect of $Fe/MgAl_2O_4/Fe(001)$ MTJ

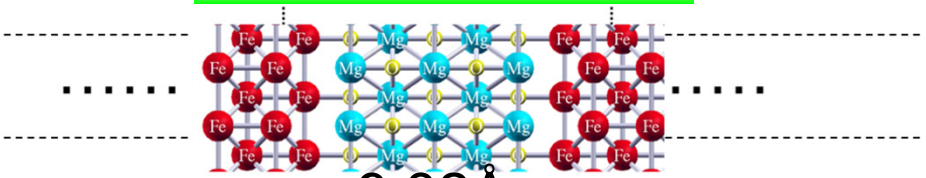
YM, *et al*, PRB, **86**, 024426 (2012).

$Fe/MgAl_2O_4/Fe$



9.56Å

$Fe/MgO/Fe$



9.32Å

$$\mathrm{TMR} = \frac{G_P - G_{AP}}{G_{AP}}$$

$Fe/MgAl_2O_4/Fe$	$Fe/MgO/Fe$
160%	**1600%**

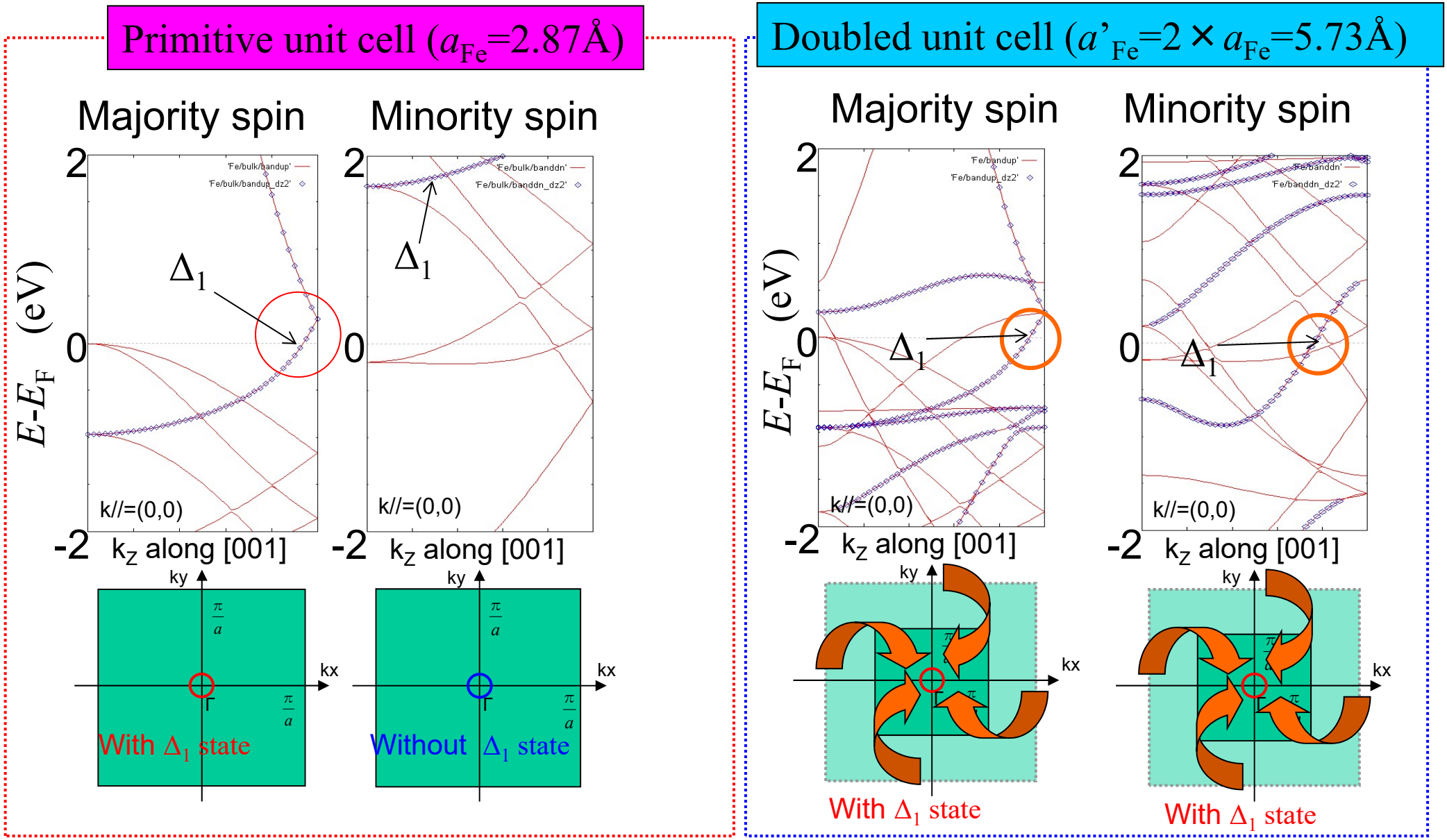
Conductance	$Fe/MgAl_2O_4/Fe$	$Fe/MgO/Fe$
G_P (parallel magnetization)	**0.52** ↑0.5 ↓0.02	**0.103** ↑0.1 ↓0.003
G_{AP} (Anti-parallel magnetization)	**0.2** ↑0.1 ↓0.1	**0.006** ↑0.003 ↓0.003

※unit $[S/\mu m^2]$

The large conductance in the anti-parallel magnetization, indicating appearance of new conductive channel in the Fe/MgAl2O4/Fe MTJs.

Band dispersion of bcc-Fe at $k_{//}$=(0,0)

s,p_z,d_{z2} ◇◇◇



The minority-spin states with the Δ_1 symmetry appear along Δ line due to the band folding effect.

Projection of the tunneling wavefunction

Projection of tunneling wavefunction at E_F

$$C_{\alpha lm} = \int d^3\mathbf{r}'[W^{\alpha}_{lm}(\mathbf{r}' - \boldsymbol{\tau}^{\alpha})]^* \Psi_s(\mathbf{r}')$$

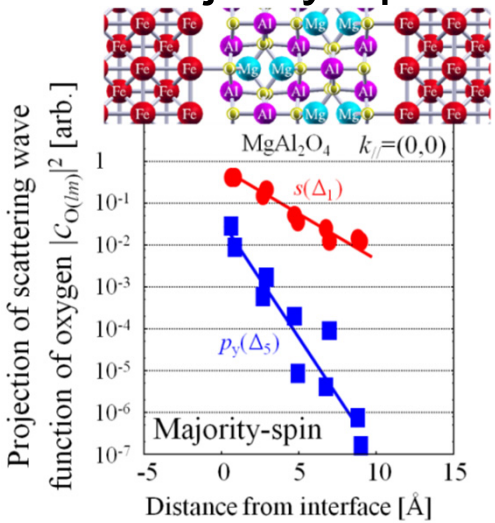
$\Psi_s(r')$: Tunneling wave function
W_{lm} : Local orbital
α : Atom index

Parallel magnetization

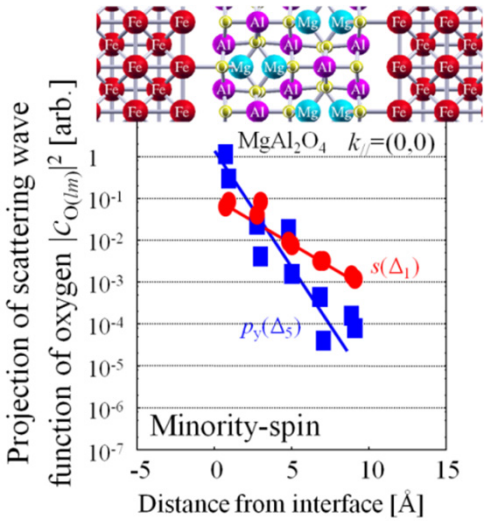
Choi and Ihm, Phys. Rev. B.,**59**(1998) 3.

$Fe/MgAl_2O_4/Fe$

Majority-spin

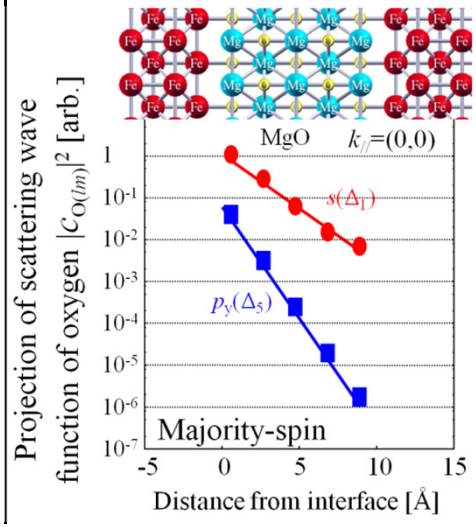


Minority-spin

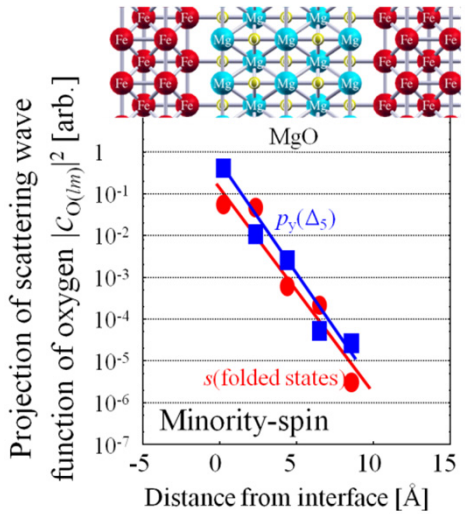


Fe/MgO/Fe

Majority-spin



Minority-spin



In minority-spin states, the Fe/spinel-based MTJ has the slow decay Δ_1 evanescent states due to the folded Fe-*s* channels.

YM, *et al*, PRB, **86**, 024426 (2012).

Comparison with experimental TMR of $Fe/MgAl_2O_4/Fe$

Calculation:

160% at 0K,

$Fe/MgAl_2O_4(1.2nm)/Fe$

$CoFe/MgAl_2O_4(1.2nm)/CoFe$

Experiments:

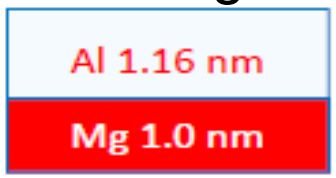
Fe/Mg-Al-O(1.1nm)/Fe	165% at 15K	APL 96, (2010)
Fe/Mg-Al-O(1.2nm)/Fe	328% at 15K	PRB **86**, (2012).
CoFe/Mg-Al-O(1.2nm)	479% at 15K	

H. Sukegawa, *et al.*, APL 96, (2010) 212505.

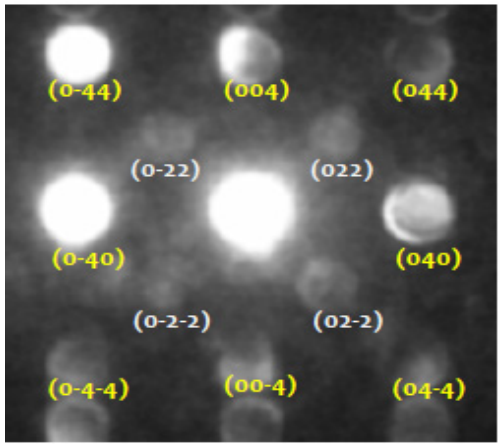
A:TMR≈165%

$a_{barrier}$≈8.0Å

Oxidation of Al on Mg



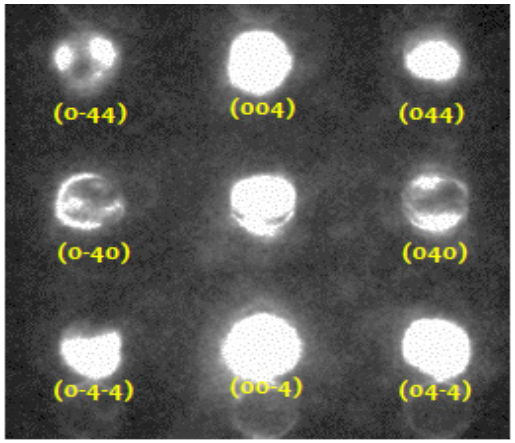
Presence of {022} spot indicating ordered spinel structure



$a_{barrier}=a_{spinel}$

B:TMR≥300%

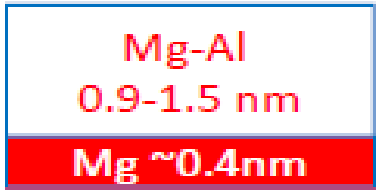
$a_{barrier}$≈4.0Å



$a_{barrier}=a_{spinel}/2$

H. Sukegawa, *et al.*, PRB **86**, 184401 (2012).

Oxidation of magnalium (Mg-Al)



Absence of {022} spot indicating ordered spinel structure

Due to the reduction of the lattice constant, the band folding and appearance of new conductive channel in minority-spin states were suppressed in the MTJs.

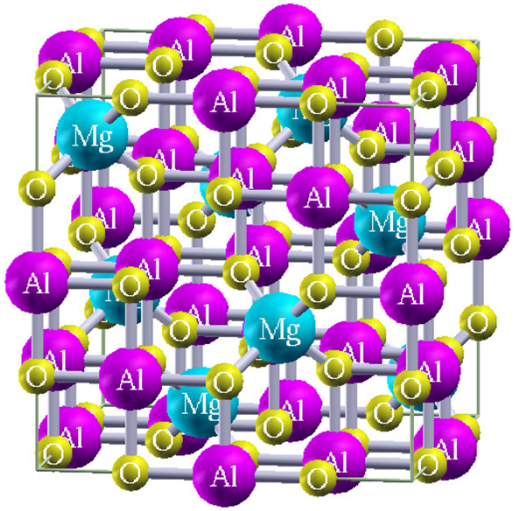
Why unit-cell size of Mg-Al-O barrier reduces?

The Mg^{2+} - Al^{3+} swapping in two different cation sites just transforms the normal spinel to the inverse spinel, and it does not affect the unit-cell size and its space group.

Cations must randomly occupy octahedral and tetrahedral sites including vacant sites.

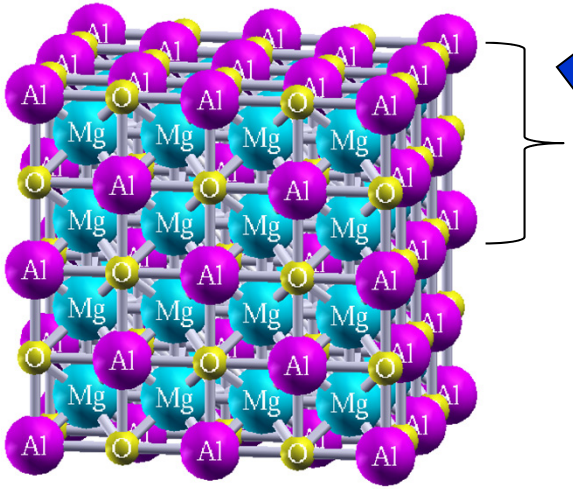
$Fd\bar{3}m$(No.227)

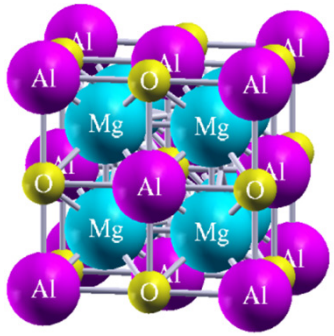
Normal Spinel $MgAl_2O_4$

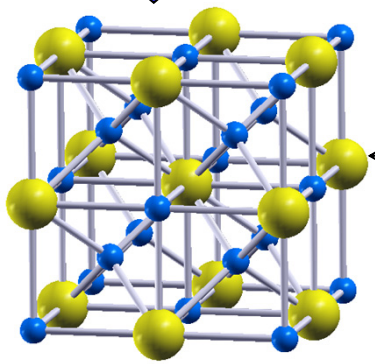


$a_{barrier}=a_{spinel}\approx 8.0$Å

All cation-sites are occupied by cation atoms







(Mg^{2+},Al^{3+})

O^{2-}

$a_{barrier}=a_{spinel}/2\approx 4.0$Å

$Fm\bar{3}m$(No.225)

$F\bar{4}3m$(No.216)

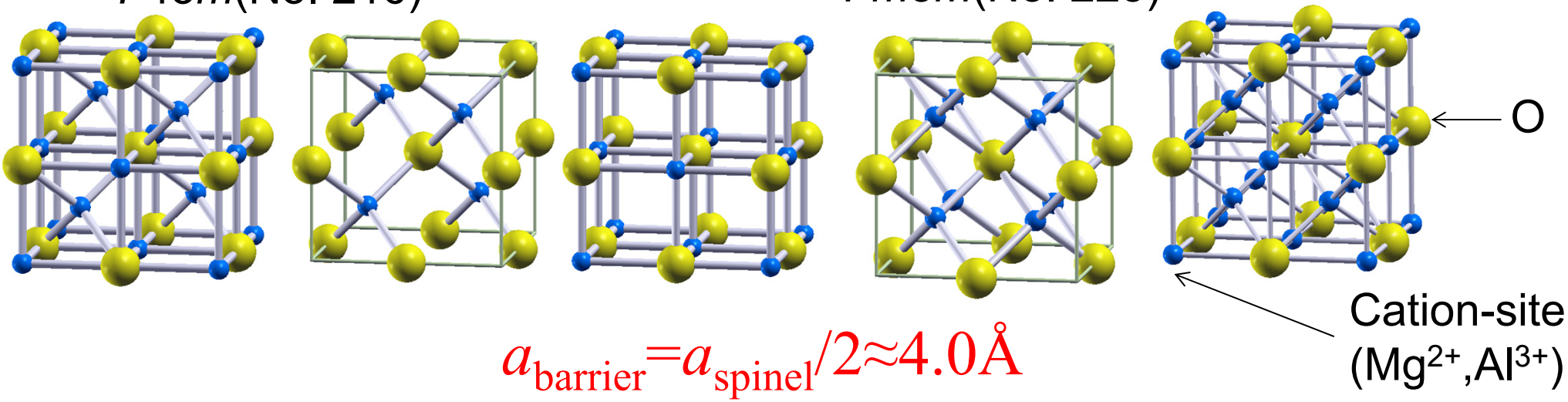
Cation-site disordered spinel

Cation-site disordered Mg-Al-O barrier

H. Sukegawa, *et al*., PRB **86**, 184401 (2012).

Possible structure of cation-site disordered structure

$F\bar{4}3m$(No. 216) $F\bar{m}3m$(No. 225)



$a_{barrier}=a_{spinel}/2\approx4.0$Å

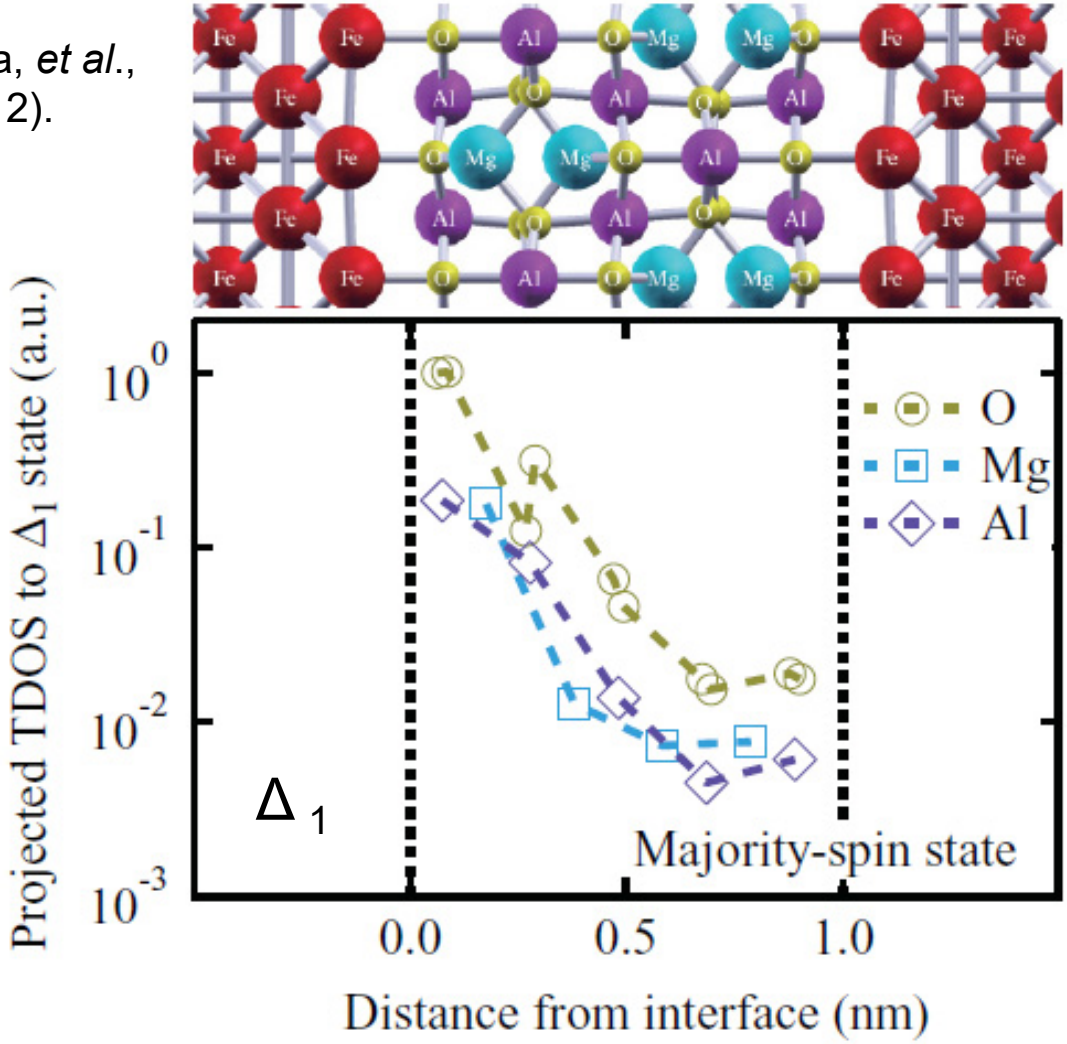
By H. Sukegawa and S. Mitani, *et al*., NIMS

Key

The anion-site does not changes from the spinel structure by the disordering, and it is always occupied by oxygen atoms making the fcc-sublattice.

Coherent tunneling in cation-site disordered spinel?

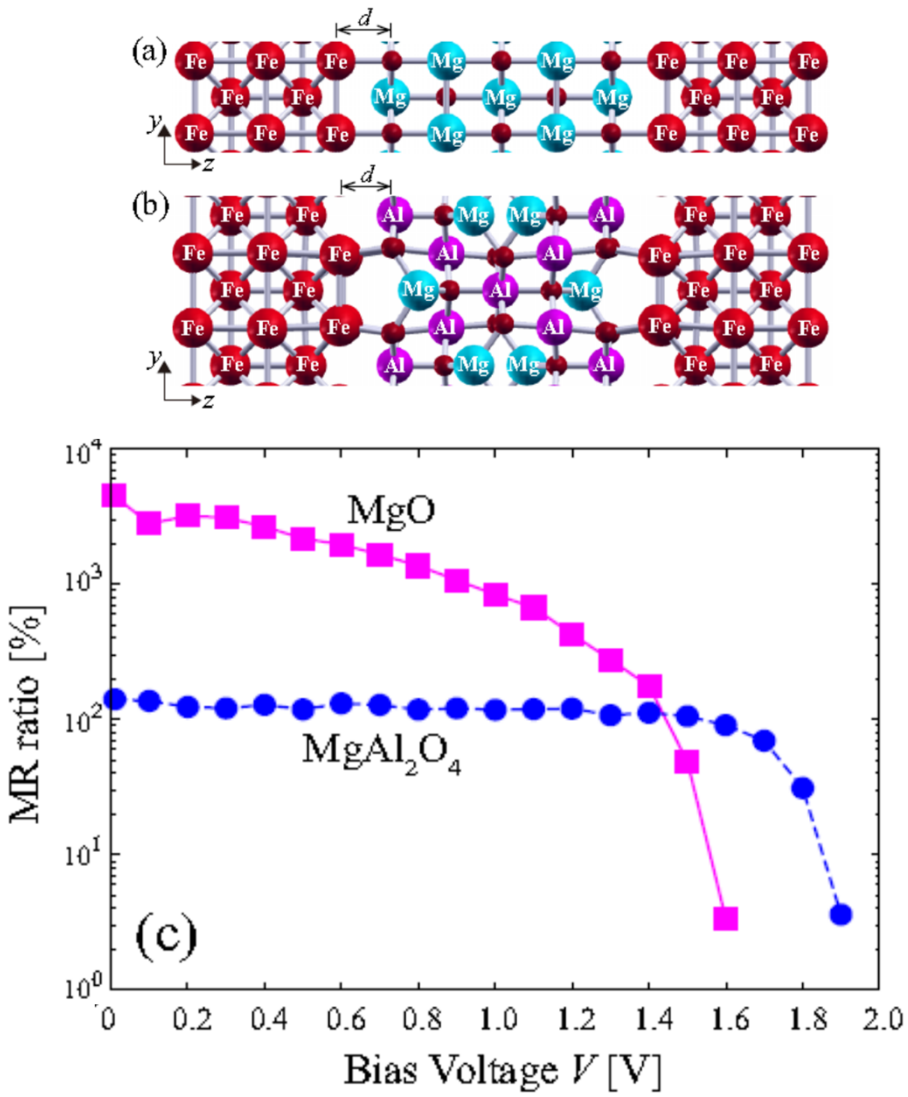
H. Sukegawa Y. Miura, *et al.*, PRB **86**, 184401 (2012).

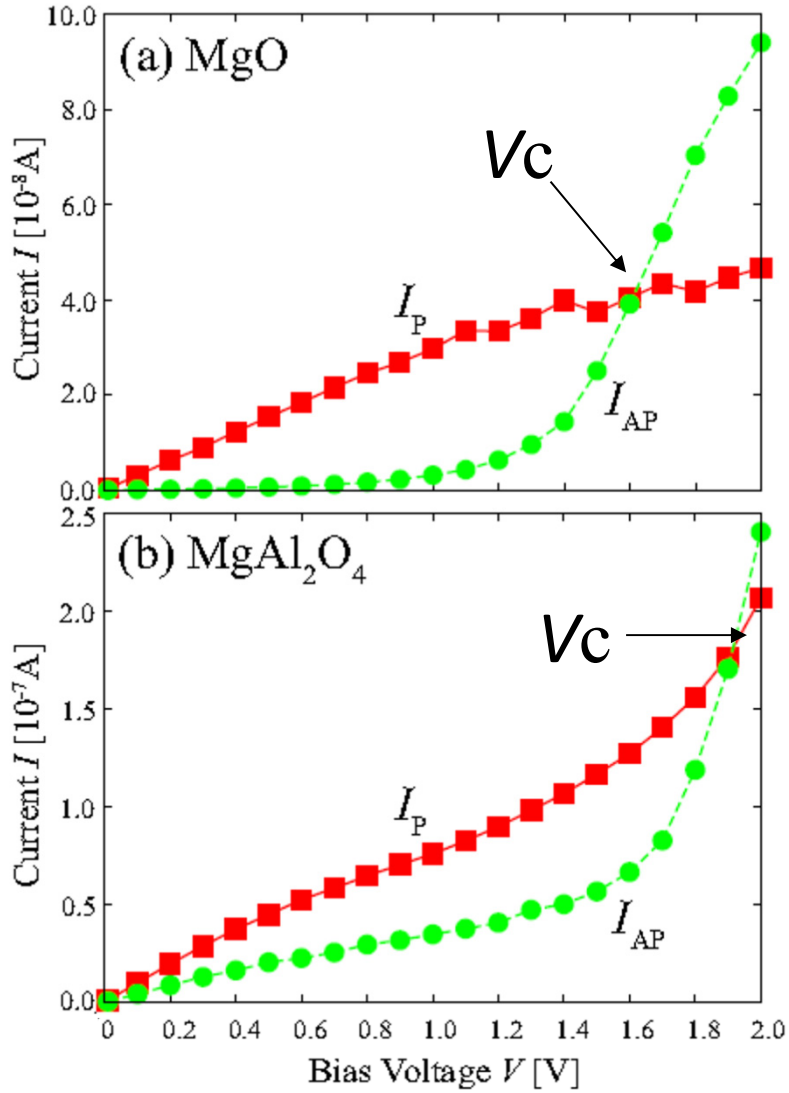


The projection of Δ_1 WF on O is one order magnitude larger than that of Mg and Al.

Coherent tunneling through Δ_1 state is dominated by Oxygen, cation-site disorder has little effect on coherent tunneling

Bias voltage dependence of TMR





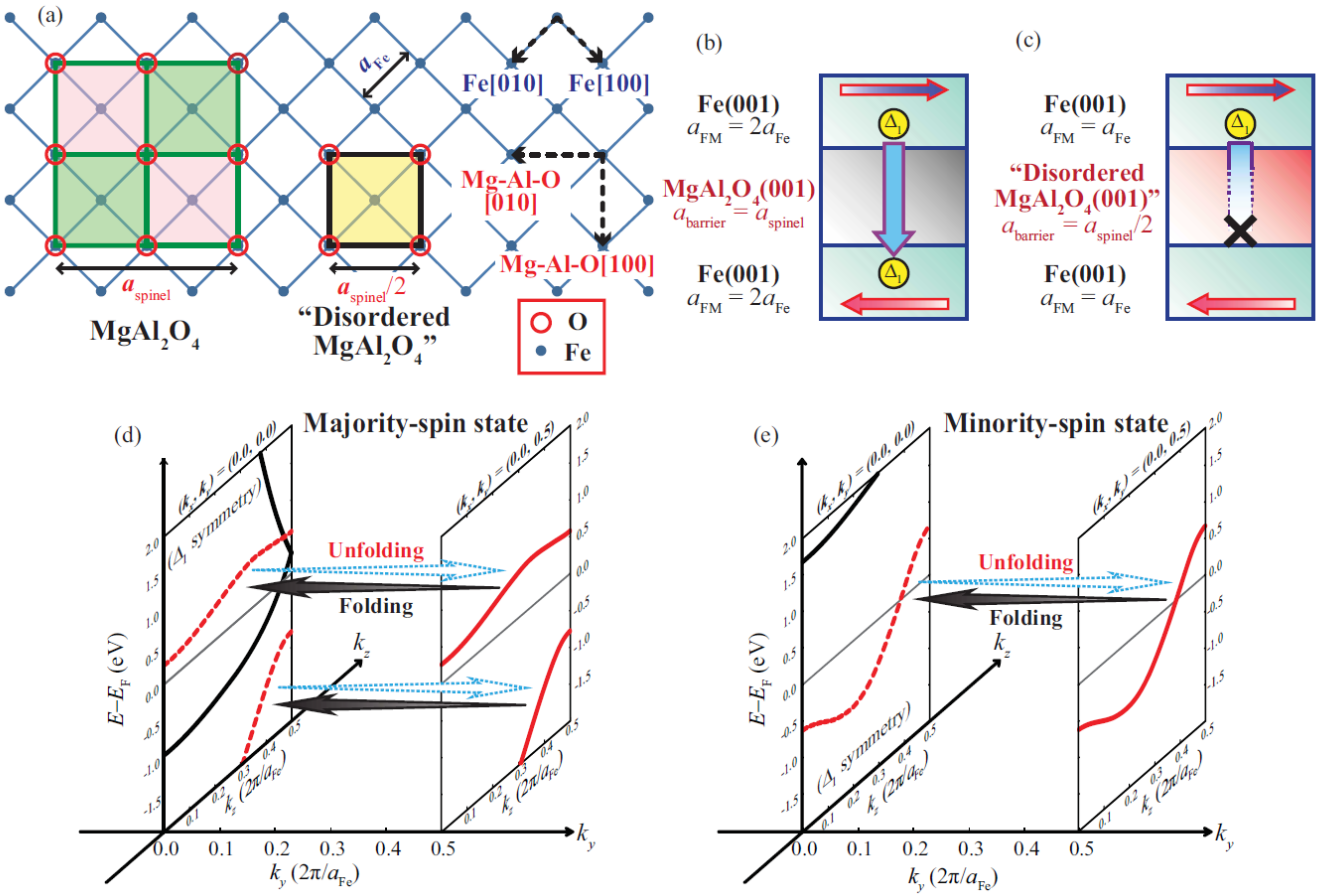
K. Masuda and Y. Miura, PRB **96**, 054428 (2017)

The critical bias voltage *V*c of the $MgAl_2O_4$-based MTJ is clearly larger than that of the MgO-based MTJ

Summary of the second topic

Band folding effects reduce TMR ratio of Fe/$MgAl_2O_4$/Fe(001) MTJs.

Suppression of band folding by cation-site disordered Mg-Al-O MTJs.



Giant TMR in Fe/MgAlO/Fe in experiments (479% at 15K)

Disorder-induced TMR enhancement in Fe/Mg-Al-O/Fe

H. Sukegawa and YM, *et al*., PRB **86**, 184401 (2012).

Contents

1. Spin-dependent transport in magnetic tunnel junctions with half-metallic Heusler alloys

Y. Miura, *et al*., Phys. Rev. B **83,** 214411 (2011).

2. Spin-dependent tunneling conductance in magnetic tunnel junctions with spinel-type $MgAl_2O_4$ barrier

Y. Miura, *et al*, PRB, **86**, 024426 (2012).
K. Masuda and Y. Miura, PRB **96**, 054428 (2017)

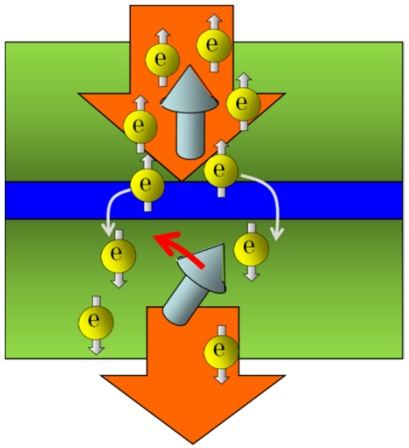
3. Electric field dependence of magnetic damping constant of Fe(001) surface

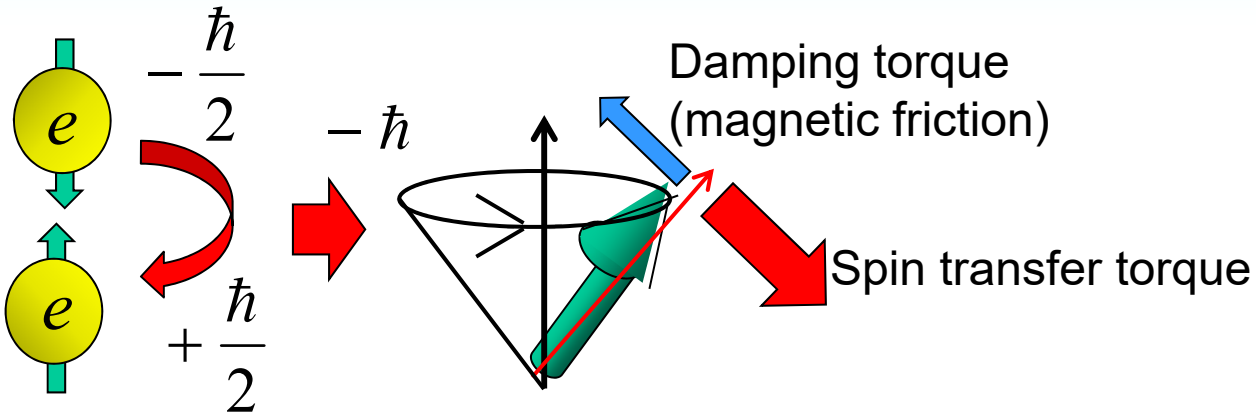
YM, M. Tsujikawa, M. Shirai, in preparation.

4. Magneto-crystalline anisotropy at interfaces of Fe(001) with various non-magnetic metals

Y. Miura, M. Tsujikawa, M. Shirai, J. Appl. Physics, **113**, 233908/1-6 (2013).

Magnetization reversal by spin transfer torque (STT)





Reduction of critical current density (J_{c0})

(10^7A/cm^2⇒10^5A/cm^2)

$$J_{c0} \propto \alpha M_S \left[H_{anti} \pm 2\pi M_S \right] t / P$$

J.C. Slonczewski, JMMM 159 (1996) L1.

α: Magnetic damping constant
M_S: Saturation Magnetization
$H_{anti} \pm 2\pi M_S$: Effective anisotropy field
P: Spin polarization
t: Thickness of FM layer

1. High spin polarization (P) with low resistance

2. Low damping constant(α) with perpendicular magnetic anisotropy(PMA)

   Usually strong perpendicular magnetic anisotropy (PMA) is originated to the large spin orbit interaction leading to large damping α

3. Small magnetization (M_s) with high Curie temperature

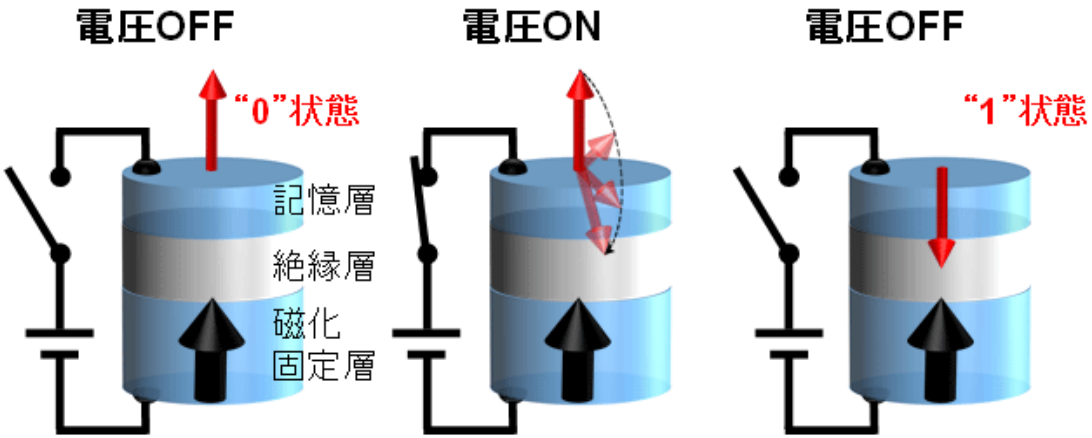
   Ferrimagnetic materials

Voltage-driven dynamic switching in MTJ

Applied Physics Express **9**, 013001 (2016)
http://doi.org/**10.7567/APEX.9.013001**

Evaluation of write error rate for voltage-driven dynamic magnetization switching in magnetic tunnel junctions with perpendicular magnetization

Yoichi Shiota*, Takayuki Nozaki, Shingo Tamaru, Kay Yakushiji, Hitoshi Kubota, Akio Fukushima, Shinji Yuasa, and Yoshishige Suzuki

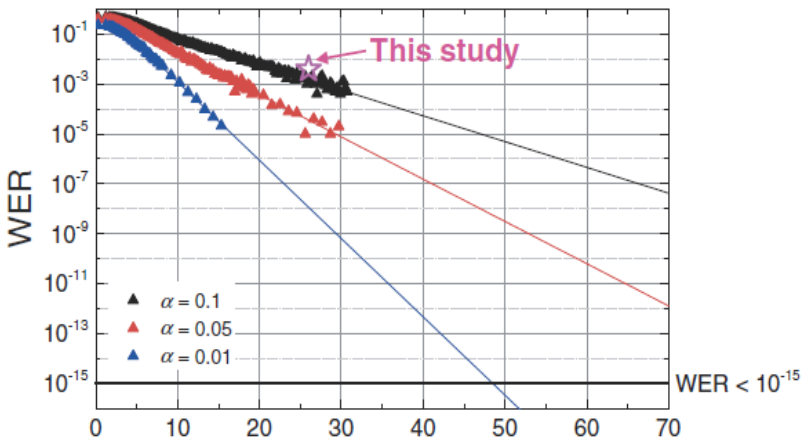


From website of Sahashi's ImPACT project in JST

Pulsed bias voltage changes PMA of interface of FM layer and promote the precession motion of the magnetization.

- By removing the voltage with a proper pulse duration, such as a half precession period, magnetization switching can be achieved.
- Basically, no current flow

Write Error Rate (WER)



Δ Thermal stability factor

Fig. 4. Calculated WER as a function of Δ for fixed tilted magnetization angle and half precession period τ_{pulse} for various damping constants.

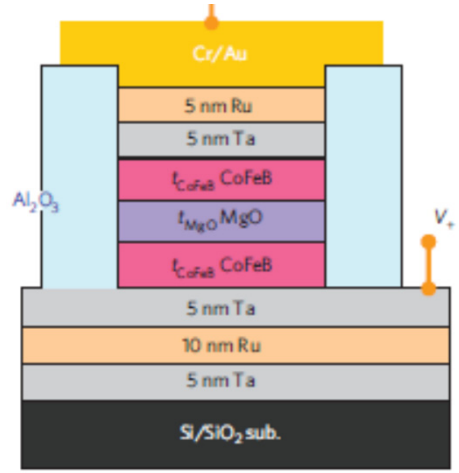
Large Ku and Small damping α can reduce the WER

Experiments electric field effects of PMA and magnetic damping

APPLIED PHYSICS LETTERS **105**, 052415 (2014)

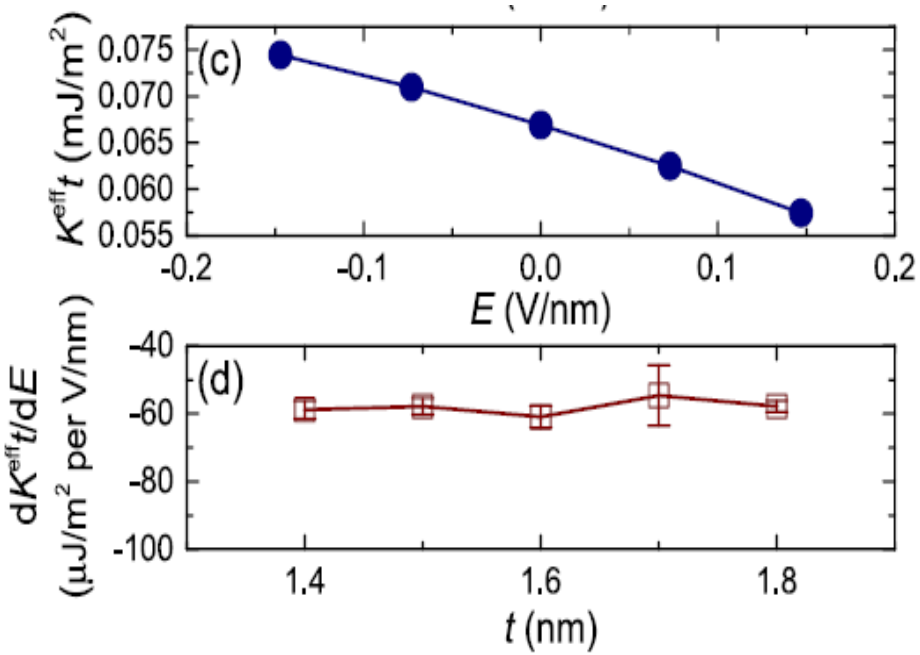
Electric-field effects on magnetic anisotropy and damping constant in Ta/CoFeB/MgO investigated by ferromagnetic resonance

A. Okada,[1] S. Kanai,[1] M. Yamanouchi,[1,2] S. Ikeda,[1,2] F. Matsukura,[3,2,a)] and H. Ohno[1,2,3]
[1]*Laboratory for Nanoelectronics and Spintronics, Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*
[2]*Center for Spintronics Integrated Systems, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*
[3]*WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*



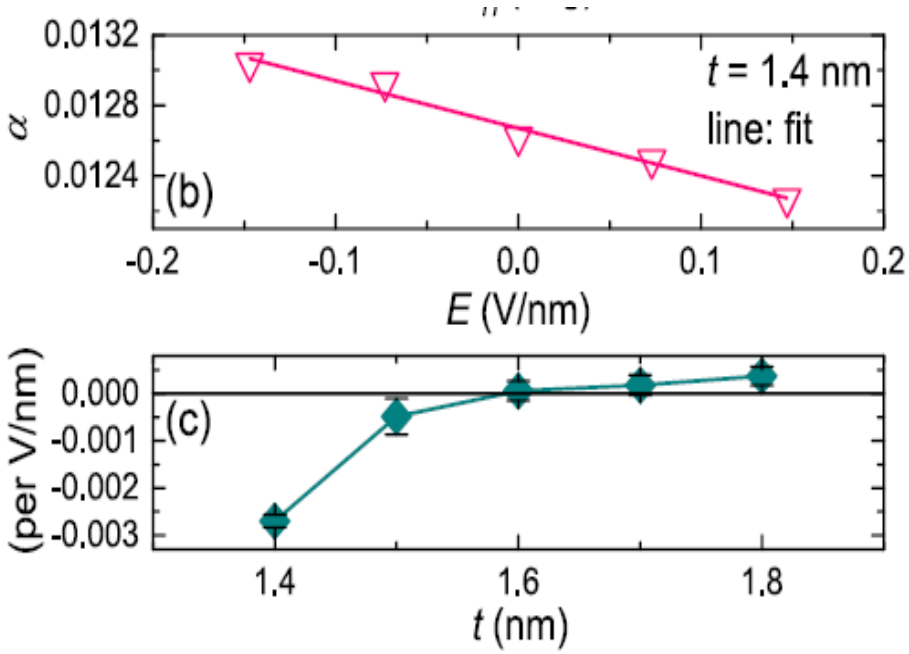
-21% of magnetic damping α is changed by 1V/nm EF for t=1.4nm

Magnetic anisotropy change by EF



EF dependence is insensitive to thickness of FM layer

Magnetic damping change by EF



Large thickness dependence of FM layer

Purpose of this work

Theoretical studies of electric field dependence of PMA

[Theory]

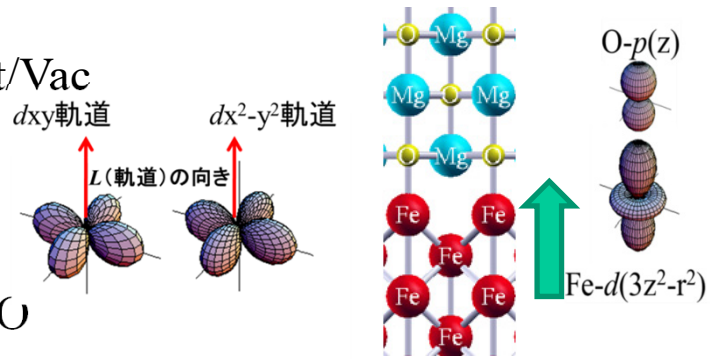
K. Nakamura, *et al*., PRL **102**, 187201 (2009). Vac/Fe/Vac

M. Tsujikawa, and T. Oda, PRL **102**, 247203 (2009). Vac/Pt/Fe/Pt/Vac

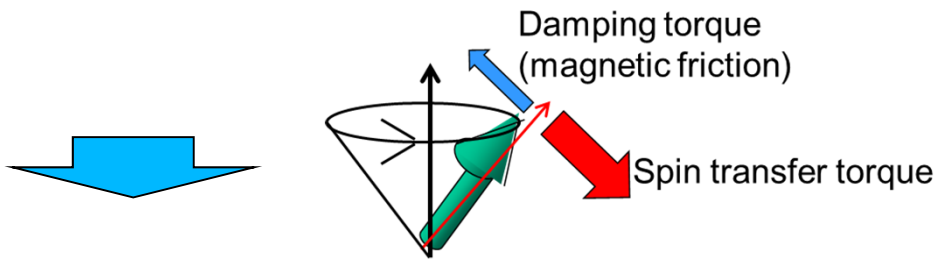
M. K. Niranjan, *et al*., APL **96**, 222504 (2010). Vac/Fe/Vac

D. Yoshikawa *et al*., APL **7**, 113005 (2014). MgO/Fe/MgO

M. Tsujikawa, *et al*., JAP **109**, 07C107 (2011). Vac/Pt/(Au)Fe/MgO



Electric field dependence of magnetic damping is hardly investigated.

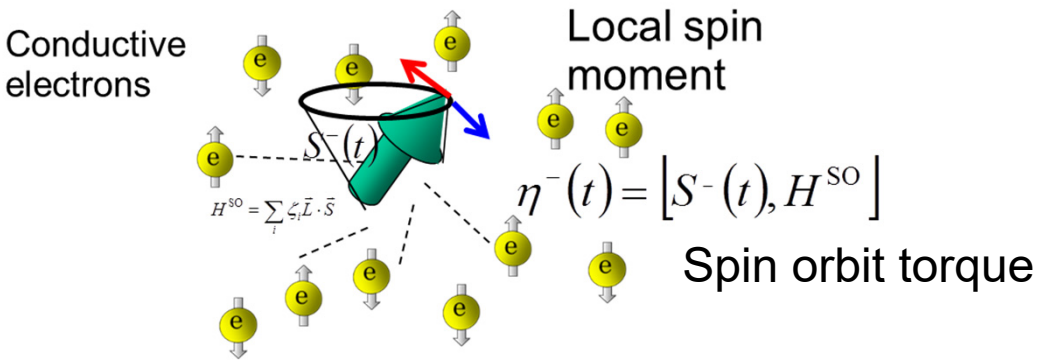


This work investigates the electric field effects of magnetic damping constant of FM layer on the basis of the first-principles calculation.

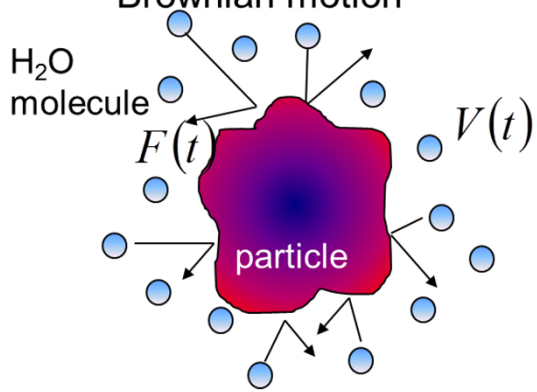
Kambersky's torque correlation model

V. Kambersky, Czechoslovak Journal of Physics B **26**, 1366 (1976).

Precession motion of local spin moment



Brownian motion



Generalized Langevin equation for magnetization dynamics

$$\frac{dS^-(t)}{dt} = -\underline{i\Omega S^-(t)} - \underline{i\eta^-(t)} - \underline{\int_0^t P^{-1}\left\langle\left[\eta^-(t'),\eta^+\right]\right\rangle_0 S^-(t)dt'}$$

Precession-tem

Spin-torque term from SOI

Damping-term

Magnetic susceptibility $\chi^+(\omega) = -\frac{\mu_0(g\mu_B)^2}{\hbar V}\frac{P}{\omega + i0 - (\Omega - \Delta) - P^{-1}F(\omega + i0)}$

Green function of Torque operator $F(\omega + i0) = -i\int_{-\infty}^{\infty}\left\langle\left[\eta^-(t),\eta^+\right]\right\rangle_0 \theta(t)e^{i(\omega+i0)t}dt$

Magnetic susceptibility from LLG equation $\chi^+(\omega) = -\frac{\gamma M_s}{\omega - \gamma H_{eff} + i\alpha\omega}$

Magnetic damping constant (comparing macroscopic formula) $\alpha = -\lim_{\omega\to 0}\frac{\gamma}{\hbar\mu_0 V M_S}\mathrm{Im}\left[\frac{1}{\omega}F(\omega + i0)\right]$

First-principles calculation of damping constant

V. Kambersky, Czechoslovak Journal of Physics B **26**, 1366 (1976).

$$\alpha = \frac{g^2 \mu_0 \mu_B^2}{\pi \hbar V \gamma M_S} \sum_{\vec{k}} \sum_{nm} \left| \Gamma_{nm}^{-}(\vec{k}) \right|^2 \frac{\delta}{\left(E_F - E_{n\vec{k}}\right)^2 + \delta^2} \frac{\delta}{\left(E_F - E_{m\vec{k}}\right)^2 + \delta^2}$$

Eigenstates at each k-point and band

$$\gamma = \mu_0 g \mu_B / \hbar$$

Matrix elements of torque operator

$$\Gamma_{nm}^{-}(\vec{k}) = \left\langle n, \vec{k} \middle| \zeta \left[S^{-}, H^{SO} \right] m, \vec{k} \right\rangle$$

$$H_{SO} = \xi \vec{L} \cdot \vec{S}$$

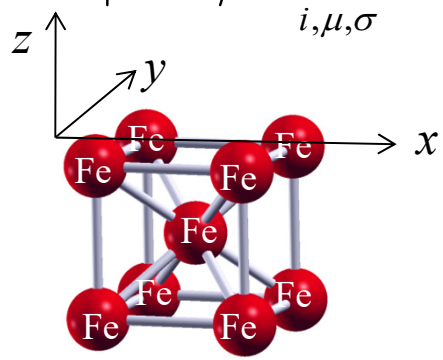
Spin-orbit interaction

$$\left| m, \vec{k} \right\rangle = \sum_{i,\mu,\sigma} c_{i\mu}^{\vec{k}m\sigma} \left| i\mu \right\rangle$$

Matrix elements of torque operator is calculated by the local atomic orbital.

VASP code

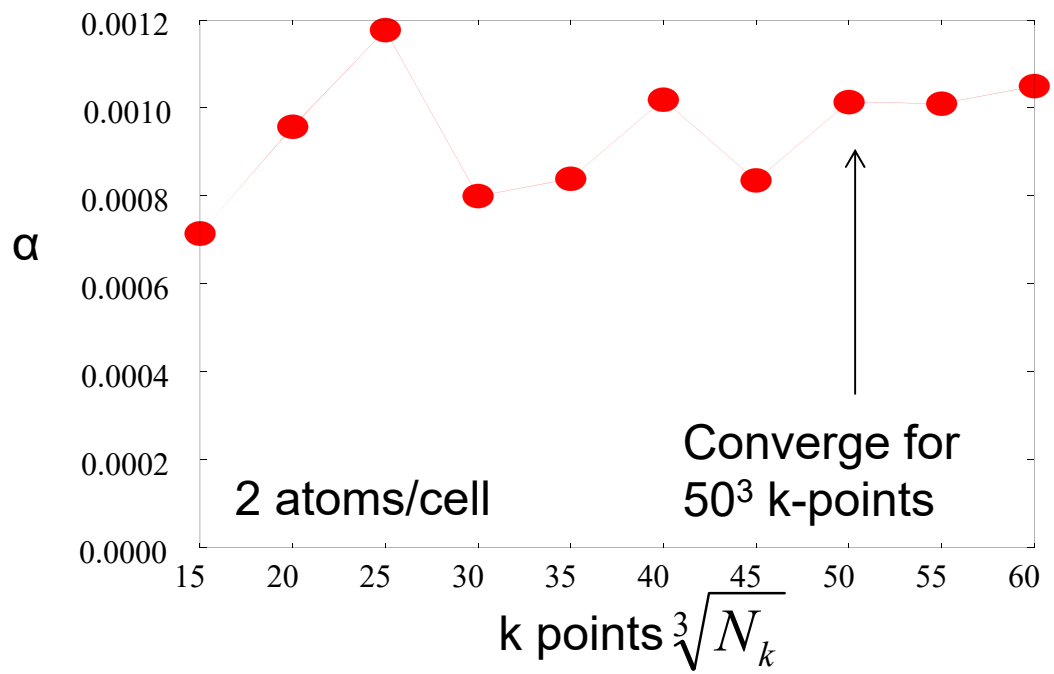
Bulk-Fe



α=0.0011 (this work)

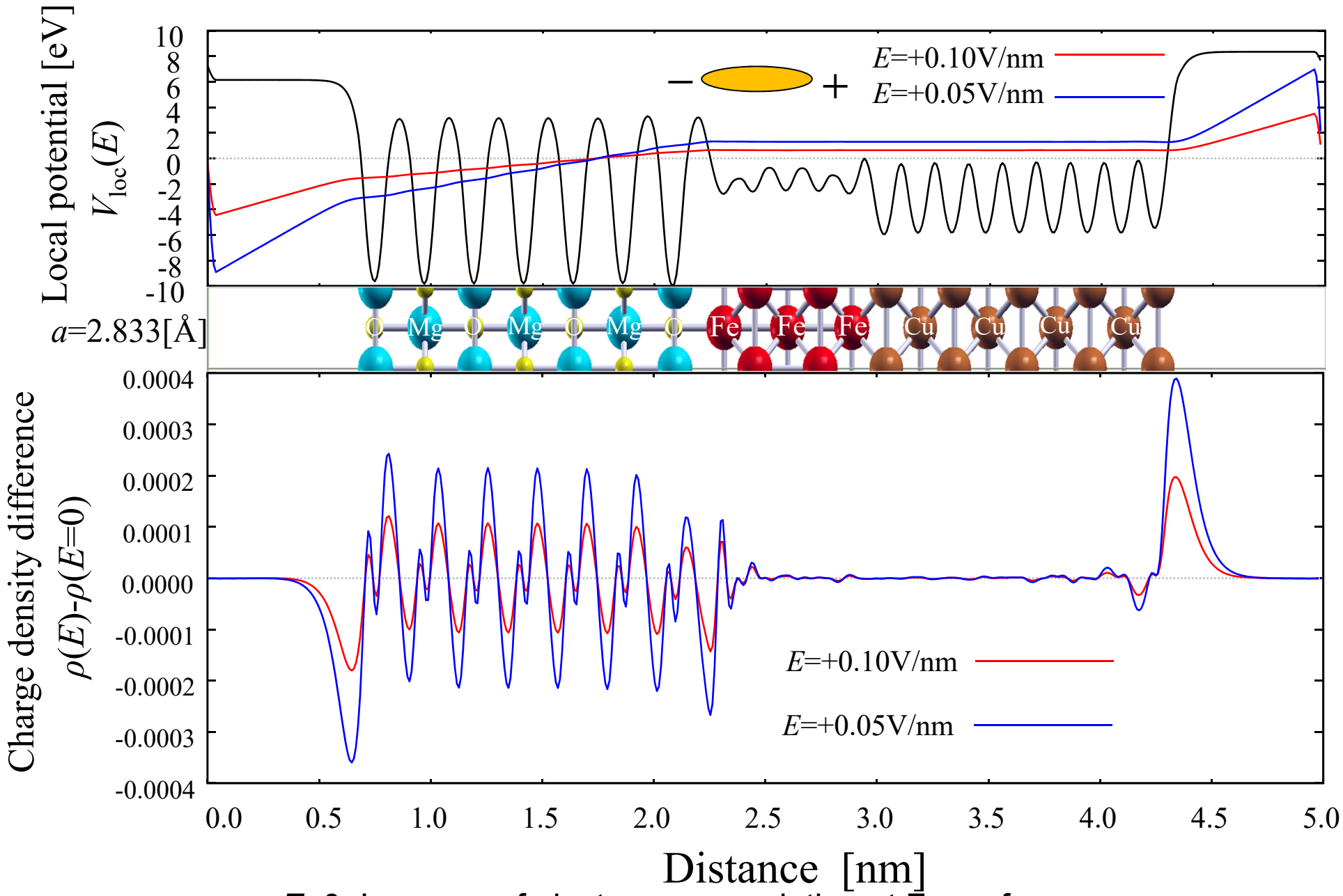
α=0.0013 (by Gilmore)

K. Gilmore, PRL **99,** 027204 (2007)



⇒For Fe surface, 50x50 is adopted.

Potential and Charge for model system

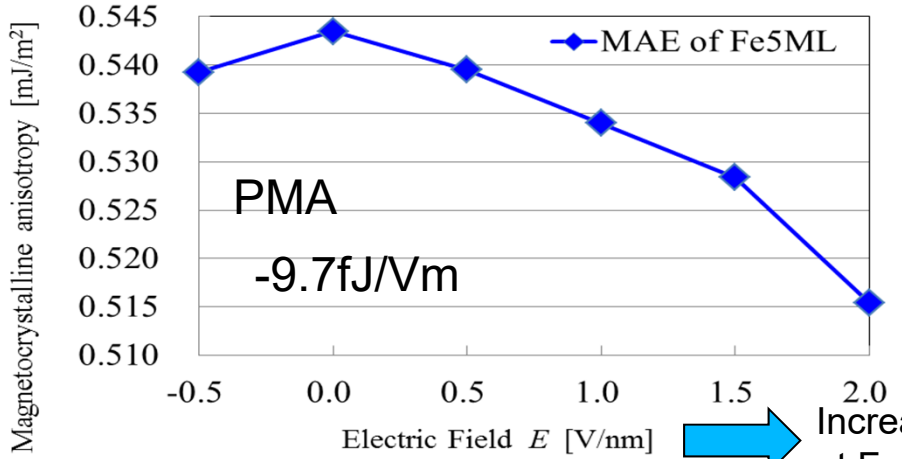


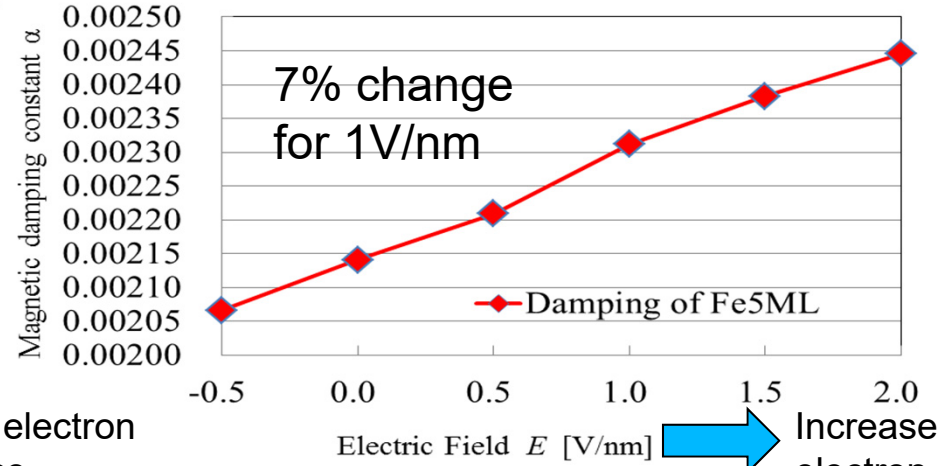
E>0 :Increase of electron accumulation at Fe surface

E<0 :Decrease of electron accumulation at Fe surface

Voltage dependence of PMA and damping α of Fe surface and Fe/MgO interface

Fe(001) surface



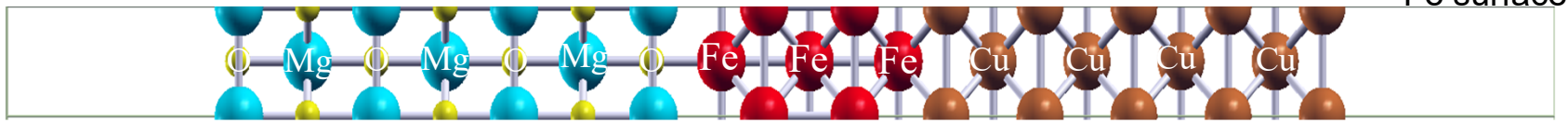


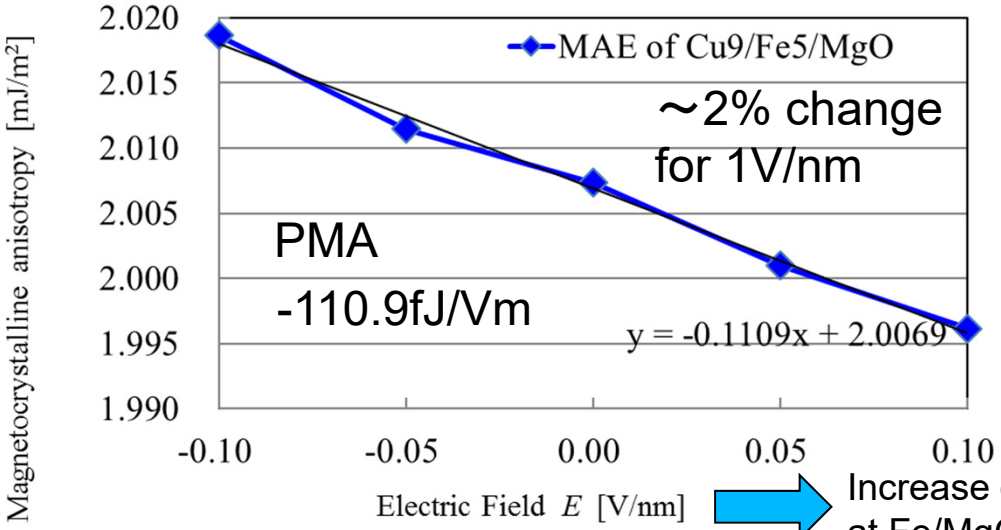
Increase of electron at Fe surface

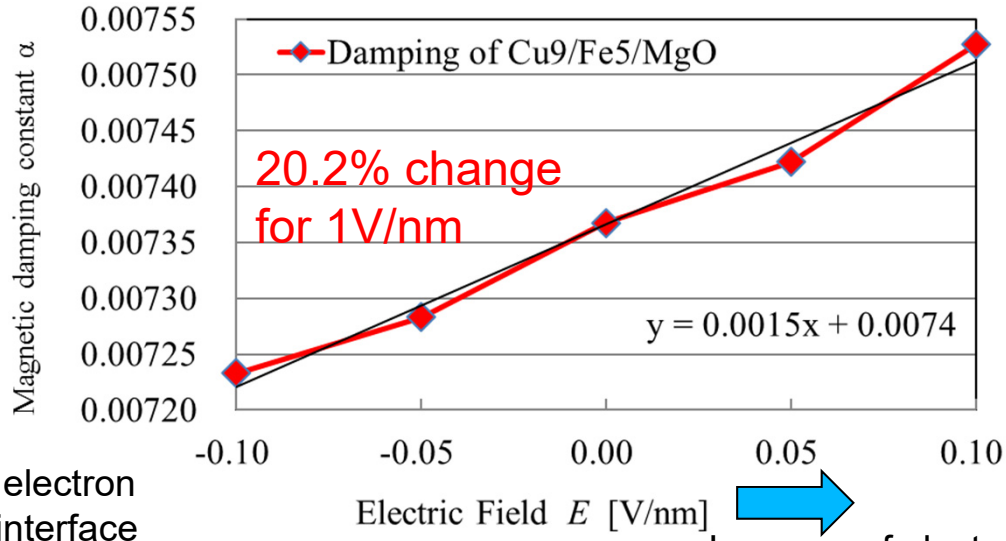
Increase of electron at Fe surface

C. G. Duan, *et al.*, PRL **101**, 137201 (2008).

Fe/MgO(001) interface







Increase of electron at Fe/MgO interface

Increase of electron at Fe/MgO interface

After T. Oda, et al., APEX **7**, 113005 (2014)

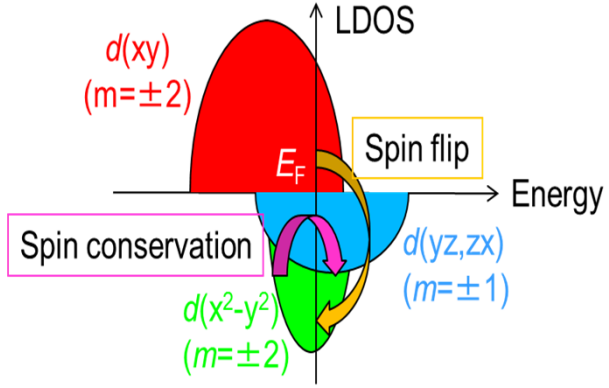
Decomposition of magnetic damping α

Torque operator $\Gamma^{-} = \left[S^{-}, H^{SO}\right] = \zeta\left(\underline{S^{z}L^{-}} - \underline{S^{-}L^{z}}\right)$

Spin conservation (Orbital deexcitation) term

$$\left\langle u^{\sigma} \middle| L^{-} \middle| o^{\sigma} \right\rangle$$

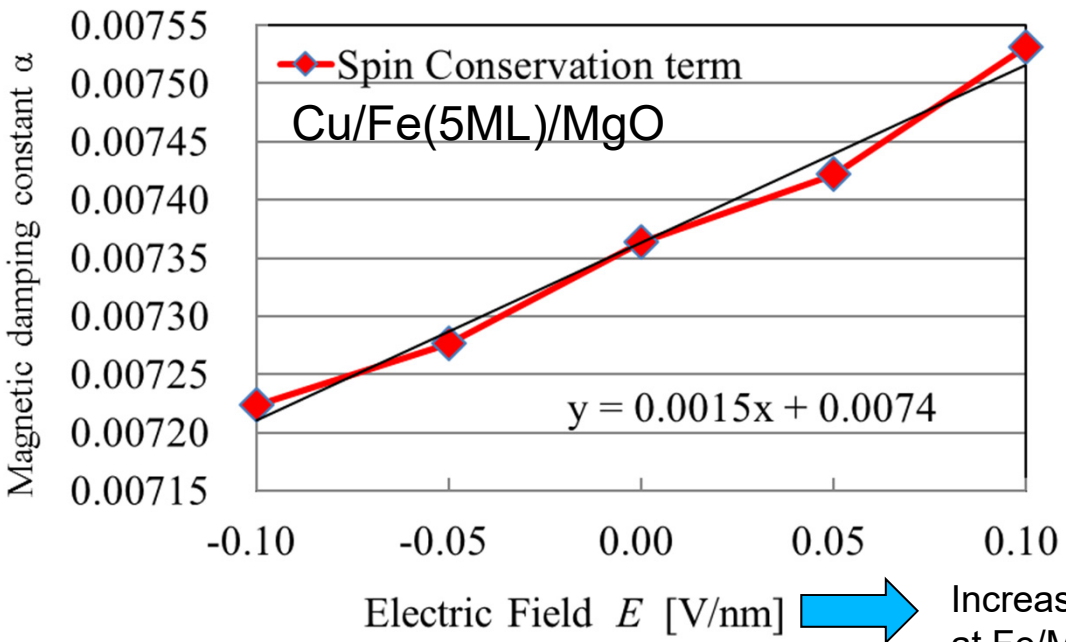
The matrix elements are non-zero for occupied and unoccupied atomic orbitals between different magnetic quantum number, such as *d*(yz,zx)-*d*(z^2), *d*(yz,zx)-*d*(x^2-y^2), *d*(yz,zx)-*d*(xy)



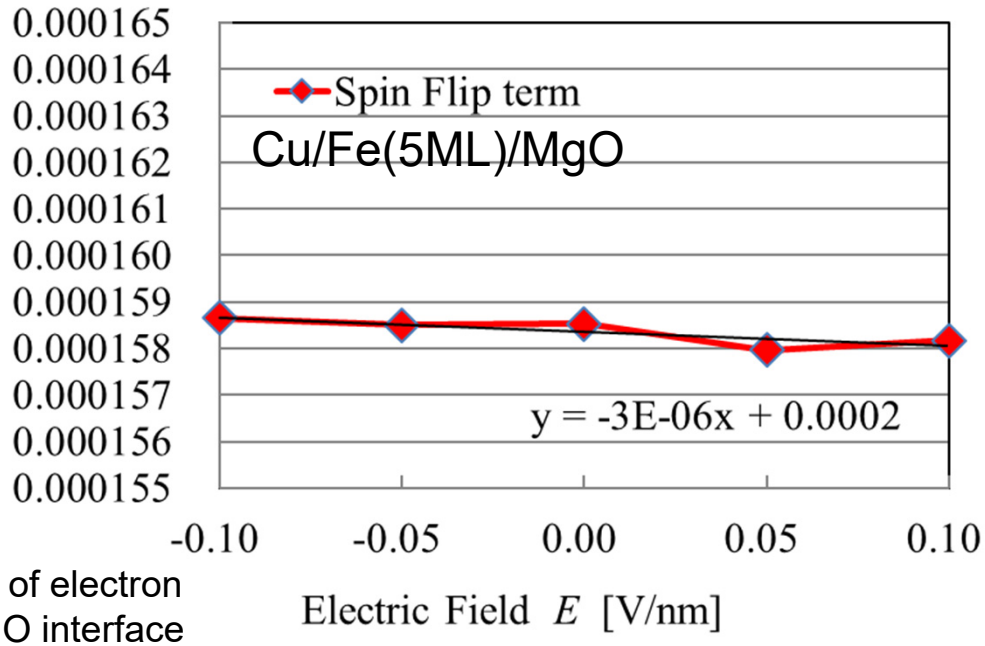
Spin flip (Orbital conservation) term

$$\left\langle u^{-\sigma} \middle| L_Z \middle| o^{\sigma} \right\rangle$$

The matrix elements are non-zero for occupied and unoccupied atomic orbitals between same magnetic quantum number, such as *d*(yz)-*d*(zx),*d*(x^2-y^2)-*d*(xy)

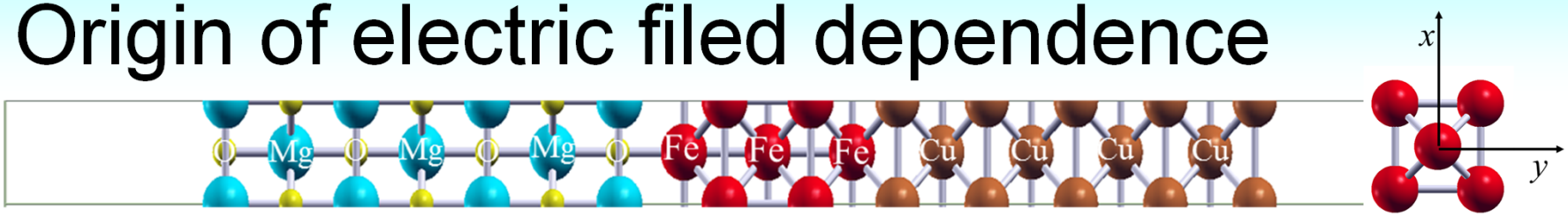


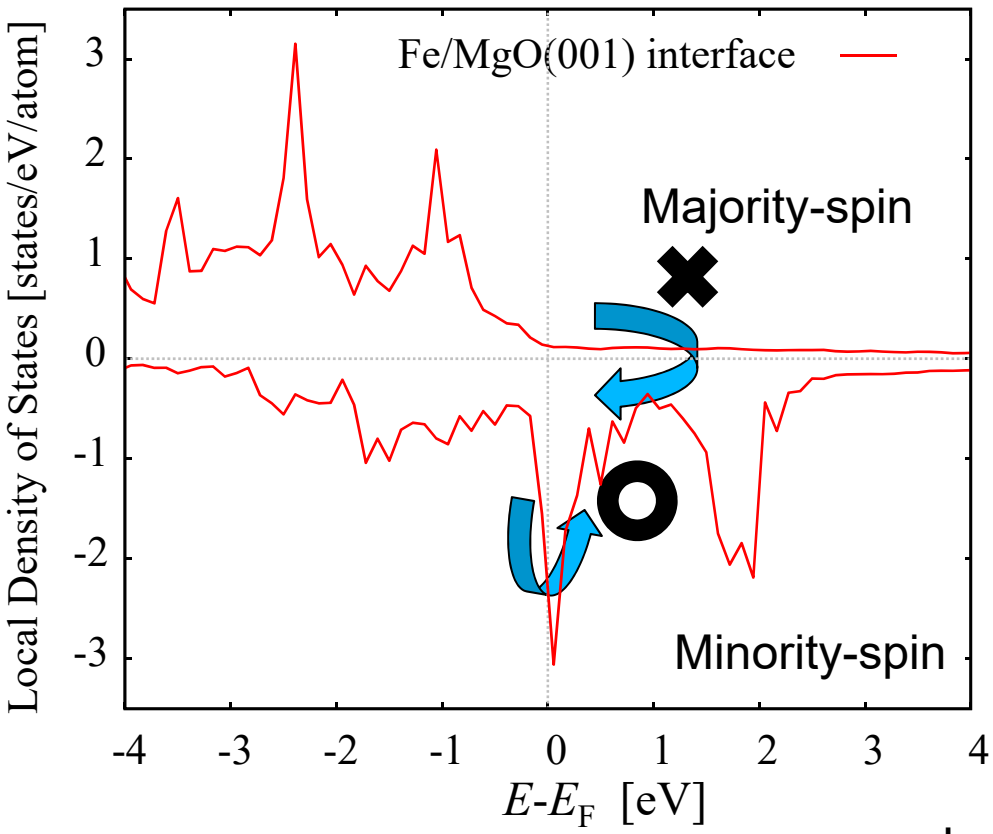
Increase of electron at Fe/MgO interface

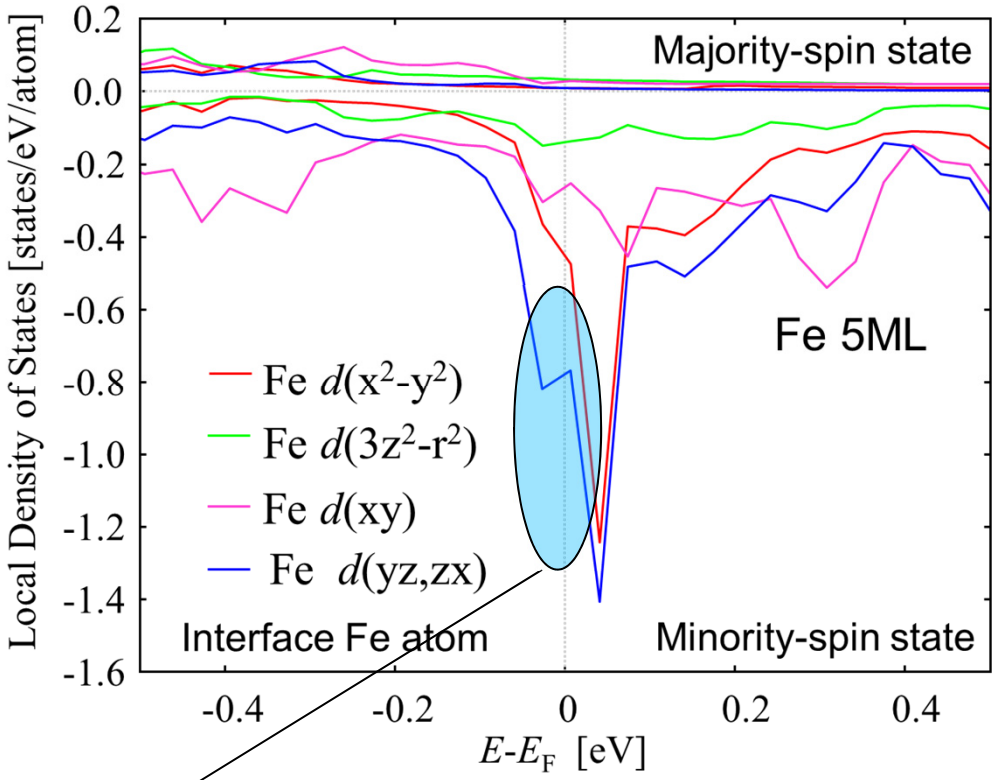


Origin of electric filed dependence

Fe/MgO(001) interface







Large matrix element of $\langle d(x^2-y^2)|L^-|d(yz,zx)\rangle$

Increase damping with increasing EF

Second order perturbation of SOI

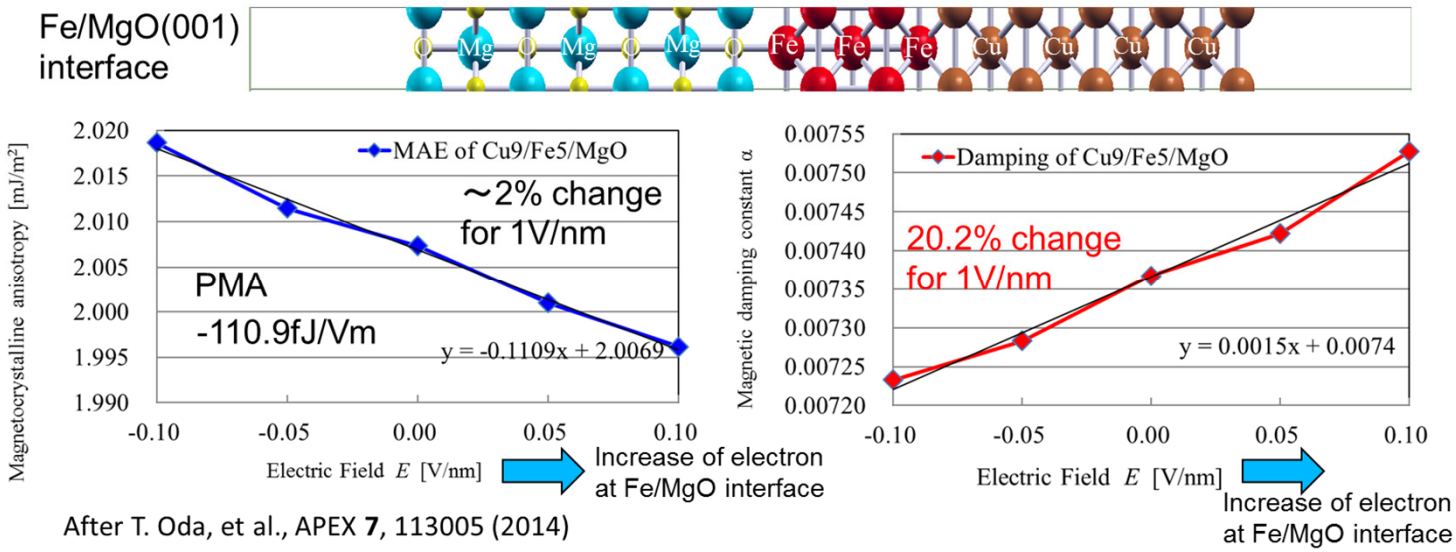
$$E_{\mathrm{PMA}} \propto (\xi)^2 \sum_{o,u,k} \frac{\left|\langle o,k,\downarrow|L_z|u,k,\downarrow\rangle\right|^2 - \left|\langle o,k,\downarrow|L_x|u,k,\downarrow\rangle\right|^2}{\varepsilon_{u,k}^{\downarrow} - \varepsilon_{o,k}^{\downarrow}}$$

$$L_x = \tfrac{1}{2}\left(L^- + L^+\right)$$

The $\langle d(x^2\text{-}y^2)|L^-|d(yz)\rangle$ increase the damping, but decrease the PMA.⇒opposite EF dependence

Summary of the third topic

Voltage dependence of PMA and magnetic damping constant of Fe(001) surface and Fe/MgO(001) interface



After T. Oda, et al., APEX **7**, 113005 (2014)

1. For Fe/MgO(001) surface, the magnetic damping increases with increasing the electron accumulation at interface (positive EF).

   (20% of damping constant α can be changed by EF=1[V/nm] for Fe/MgO(001))

2. It is opposite to that of PMA (perpendicular magnetic anisotropy).

3. Voltage dependence of magnetic damping can be attributed to spin conservation term between ***d*(yz,zx)** and ***d*(x^2-y^2)** of interfacial Fe atom .

Contents

1. Spin-dependent transport in magnetic tunnel junctions with half-metallic Heusler alloys

Y. Miura, *et al*., Phys. Rev. B **83,** 214411 (2011).

2. Spin-dependent tunneling conductance in magnetic tunnel junctions with spinel-type $MgAl_2O_4$ barrier

Y. Miura, *et al*, PRB, **86**, 024426 (2012).
K. Masuda and Y. Miura, PRB **96**, 054428 (2017)

3. Electric field dependence of magnetic damping constant of Fe(001) surface

YM, M. Tsujikawa, M. Shirai, in preparation.

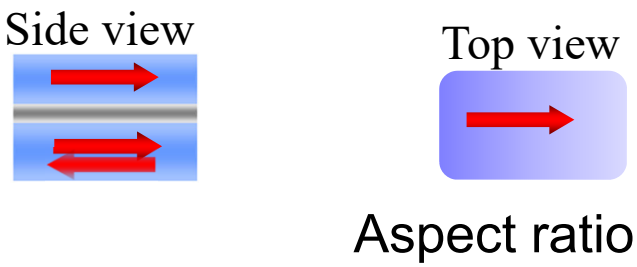
4. Magneto-crystalline anisotropy at interfaces of Fe(001) with various non-magnetic metals

Y. Miura, M. Tsujikawa, M. Shirai, J. Appl. Physics, **113**, 233908/1-6 (2013).

Thermal stability of magnetization in MTJs

To achieve ultra high density MRAM

In-plane MTJ



Perpendicular MTJ

For 10 year's write endurance

Thermal stability factor $\frac{K_u V}{k_B T} \geq 60$

K_u : uniaxial magnetic anisotropy

Large K_u is required with decreasing volume towards scaling down of device dimensions

MTJs with perpendicular magnetization

Using $L1_0$-type FePt, CoPt, CoFePd alloys and its multilayered structures

[1] M. Yoshikawa, *et al.*, IEEE Trans. Magn. vol.**44** 2573 (2008). (Toshiba)

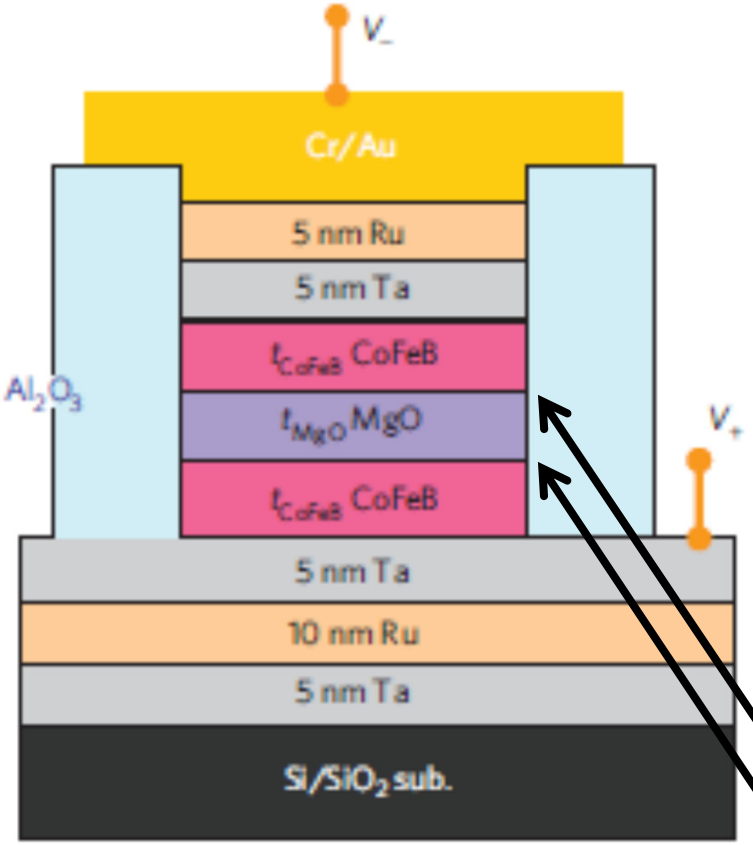
[2] K. Yakushiji, *et al.*, APEX vol. **3** 053003 (2010). (AIST)

[3] K. Mizunuma *et al.*, APEX vol. **4** 023002 (2011). (Tohoku)

MTJs with interfacial perpendicular MCA

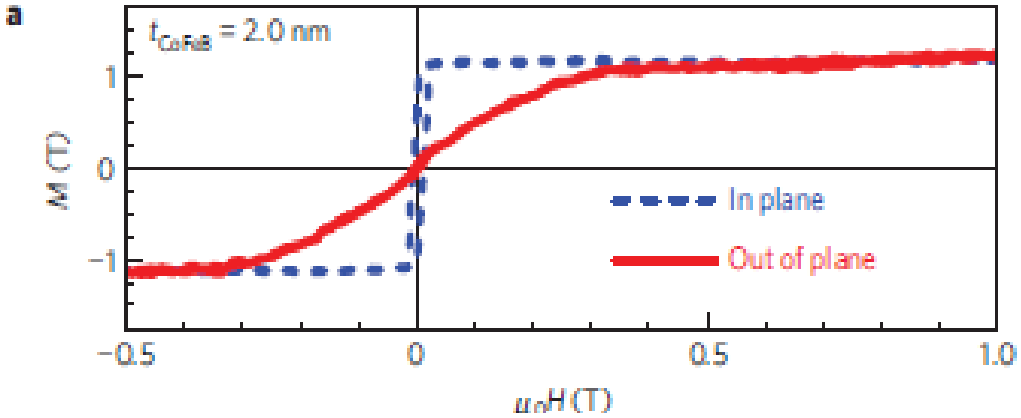
S. Ikeda, *et al*., Nature Materials **9**, 721 (2010).

- CoFeB/MgO/CoFeB(001)

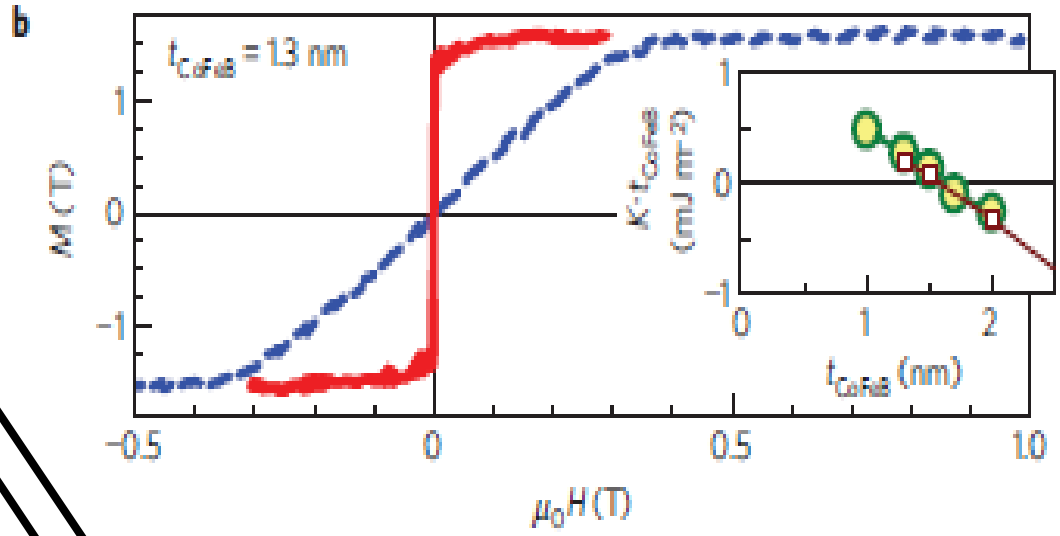


TMR ratio of 120% at 300K

In-plane magnetization (t_{CoFeB}=2.0nm)



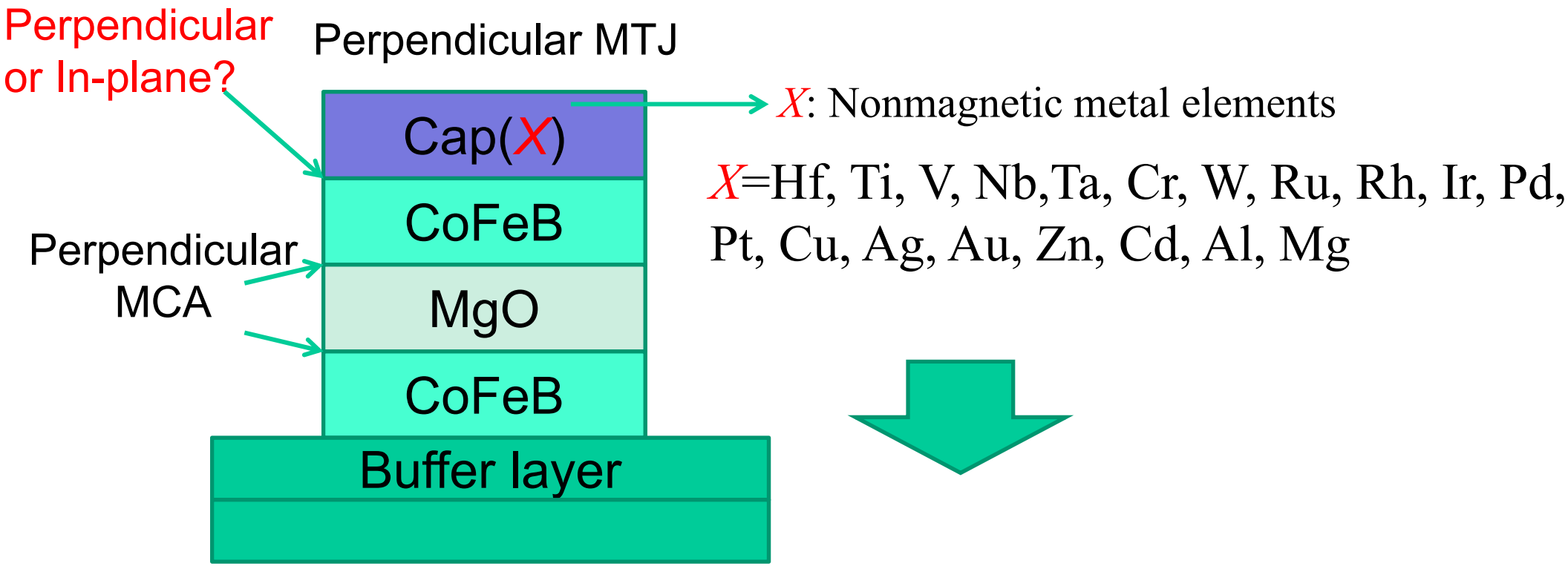
Perpendicular magnetization (t_{CoFeB}<1.3nm)



Interfacial perpendicular MCA of Fe/MgO(001), which is K_i=1.30 mJ/m^2

Purpose of this work

In order to achieve ultra high-density MRAM, we need further enhancement of the thermal stability of the ferromagnetic layer of MTJs.



We investigate MCA energy at the (001) interface between bcc-Fe and various non-magnetic metal elements (*X*) on the basis of the first principles calculations.

- To find nonmagnetic-metals showing the perpendicular MCA at interfaces with Fe
- To obtain the fundamental understanding of the interfacial MCA

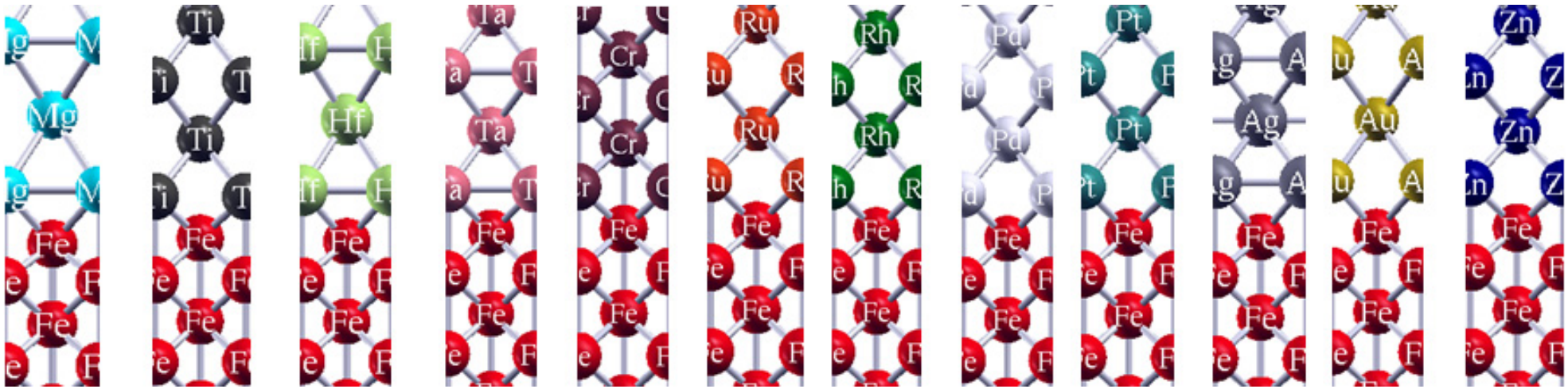
Calculation system

- VASP-PAW with plane wave basis set
- GGA for the exchange correlation term
- The Brillouin zone sampling with $24 \times 24 \times 2$.

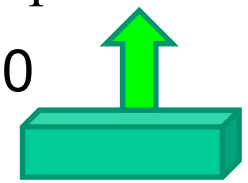
1) G. Kresse and J. Hafner, Phy. Rev. B **47**, RC558 (1993).

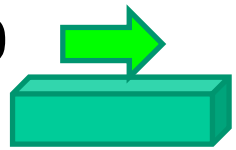
2) P. E. Blöchl, Phy. Rev. B **50**, 17953 (1994).

3) J. P. Perdew, *et al.*, Phy. Rev. Lett. **77**, 3865 (1996).

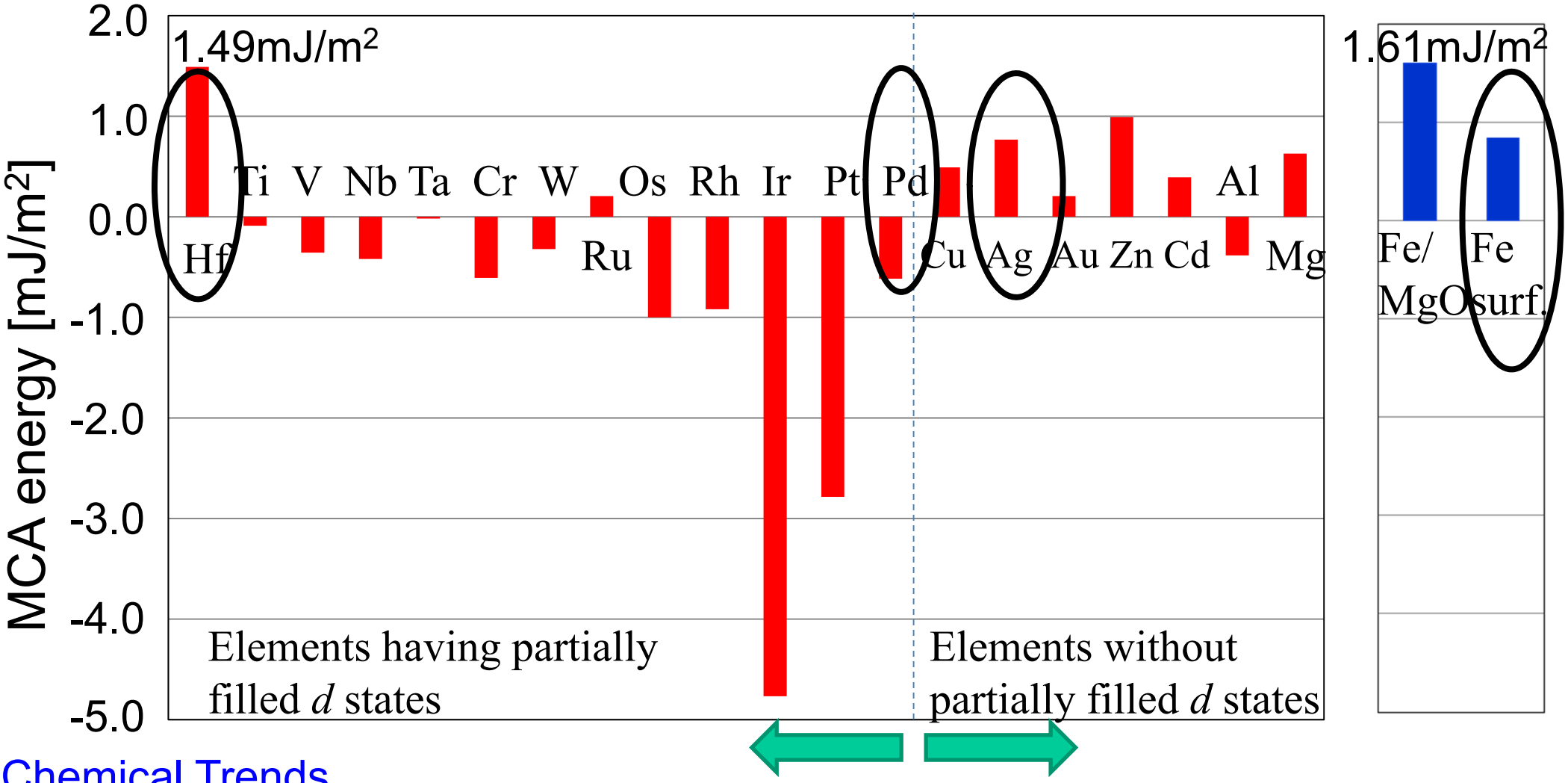


1. For non-magnetic metals elements (*X*), we assumed *fct* or *bct* structures
2. Construct super-cell of Fe/*X*(001) includimg 9 atomic layers of Fe and *X*.
3. The in-plane lattice constant is fixed to that of MgO.($a_{//}$=4.23/√2Å) $\boldsymbol{a_{Fe/X(001)}=a_{MgO}}$
4. *X*/Fe(001) interfacial structures are fully optimized along the perpendicular direction.
5. The MCA energy E_{MCA} is defined to be positive for out-of-plane easy axis.

$E_{MCA}>0$ 

$E_{MCA}<0$ 

MCA energy of Fe/*X*(001) interfaces ($a_{//}=a_{MgO}$)



Chemical Trends

Y. Miura, *et al.*, JAP **113**, 233908 (2013).

1. Fe(001) interfaces with noble metals or typical metal elements tends to show perpendicular MCA except for *X*=Al.

2. Fe(001) interfaces with transition elements having partially filled *d* bands tends to show in-plane MCA except for *X*=Hf.

Second order perturbation of spin-orbit interaction

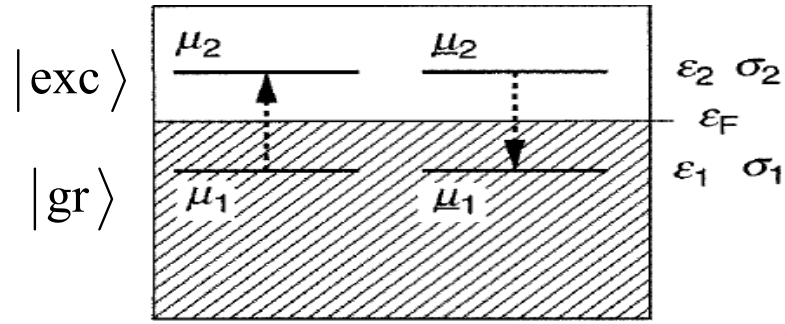
P. Bruno, PRB **39**, 865 (1989). G. Laan, JPCM **10**, 3239 (1998).

$$E_\eta^{(2)} = -\sum_{\text{exc}} \frac{\left|\langle \text{exc}\,|H_{\text{SO}}|\,\text{gr}\rangle\right|^2}{\varepsilon_{\text{exc}} - \varepsilon_{\text{gr}}}$$

$$H_{\text{SO}} = \xi \vec{L}\cdot\vec{S}$$

$$|\text{gr}\,(\text{exc})\rangle = \sum_{\mu,\sigma} c_{i,\mu,\sigma}|i,\mu\rangle$$

η:direction of spin (x or z)



μ: local atomic orbital index

i,j: index of atomic position

$$E_\eta^{(2)}(i) = \xi_i \sum_{\mu_1,\mu_2,\underline{\mu_1},\underline{\mu_2}} \langle \underline{\mu_1}\uparrow|\vec{L}\cdot\vec{S}|\underline{\mu_2}\uparrow\rangle_\eta \langle \mu_2\uparrow|\vec{L}\cdot\vec{S}|\mu_1\uparrow\rangle_\eta$$

$$\times \sum_j \xi_j \left[G_{\mu_1,\underline{\mu_1}}^{\mu_2,\underline{\mu_2}}(\uparrow,\uparrow;i,j) + G_{\mu_1,\underline{\mu_1}}^{\mu_2,\underline{\mu_2}}(\downarrow,\downarrow;i,j) - G_{\mu_1,\underline{\mu_1}}^{\mu_2,\underline{\mu_2}}(\uparrow,\downarrow;i,j) - G_{\mu_1,\underline{\mu_1}}^{\mu_2,\underline{\mu_2}}(\downarrow,\uparrow;i,j)\right]$$

Joint LDOS

$$G_{\mu_1,\underline{\mu_1}}^{\mu_2,\underline{\mu_2}}(\sigma_1,\sigma_2;i,j) = \int_{\varepsilon_1<E_F<\varepsilon_2} \frac{d\varepsilon_1 d\varepsilon_2}{\varepsilon_2-\varepsilon_1} \sum_{\text{k}} n_{\mu_1,\underline{\mu_1},\sigma_1}^{i,j}(\text{k},\varepsilon_1)\, n_{\mu_2,\underline{\mu_2},\sigma_2}^{i,j}(\text{k},\varepsilon_2)$$

$$\Delta E_{\text{MCA}}^{(2)}(i) = E_{\text{z}}^{(2)}(i) - E_{\text{x}}^{(2)}(i)$$

$$\sum_n^{occ} c_{i\mu\sigma}^{kn*} c_{j\lambda\sigma}^{kn} \delta(\epsilon - \epsilon_{kn\sigma}^{(0)}) \qquad \sum_{n'}^{unocc} c_{i\mu'\sigma'}^{kn'*} c_{j\lambda'\sigma'}^{kn'} \delta(\epsilon' - \epsilon_{kn'\sigma'}^{(0)})$$

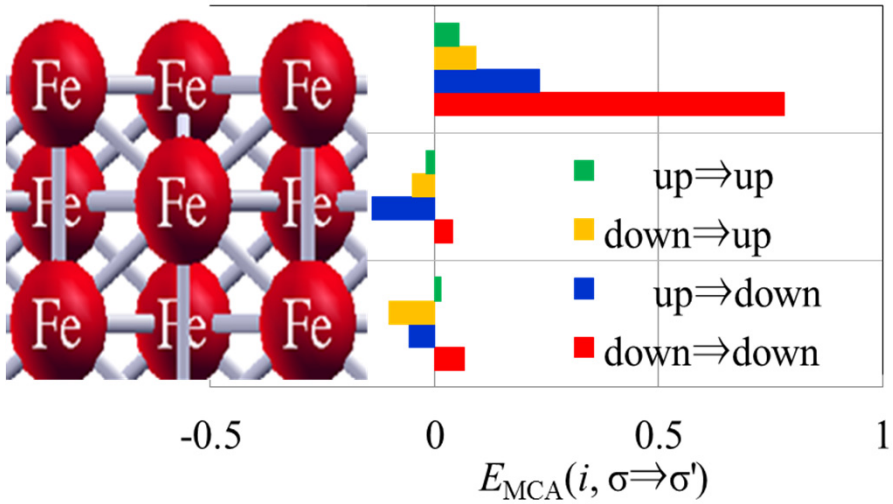
We directly estimated the second-order perturbative contribution of MCA energy depending on each atomic site and spin-transition process.

ξ_{Fe}=50meV ξ_{Ag}=200meV ξ_{Pd}=200meV ξ_{Hf}=350meV

MCA energy of Fe(001) surface($a_{//}=a_{MgO}$)

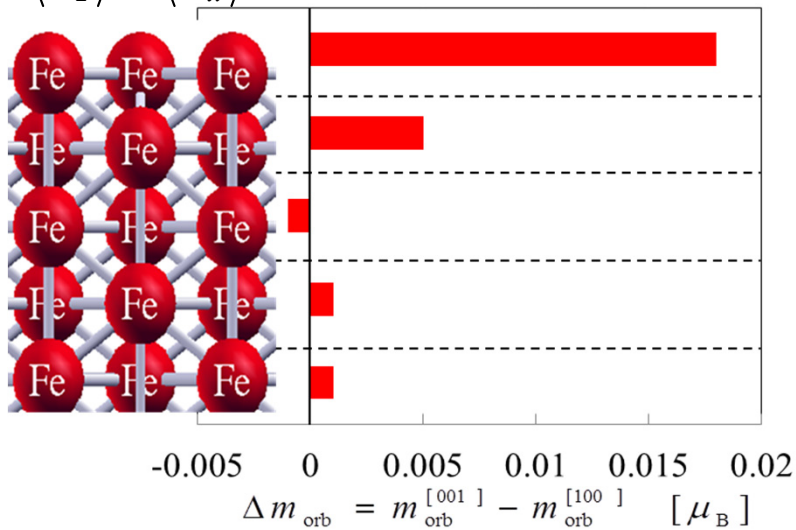
Second-order contribution to MCA energy

Fe(001) surface: 0.851[mJ/m²]



Y. Miura, *et al.*, JAP, **113**, 233908 (2013)

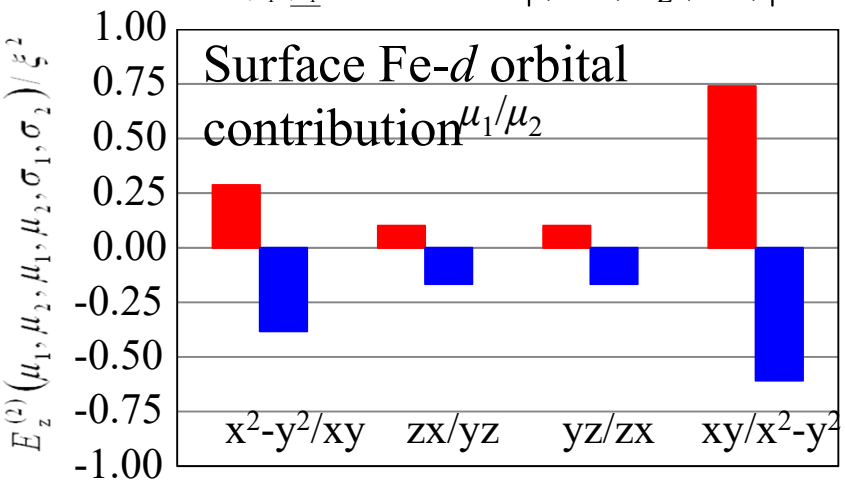
$\langle L_z \rangle - \langle L_x \rangle$ Orbital moment difference

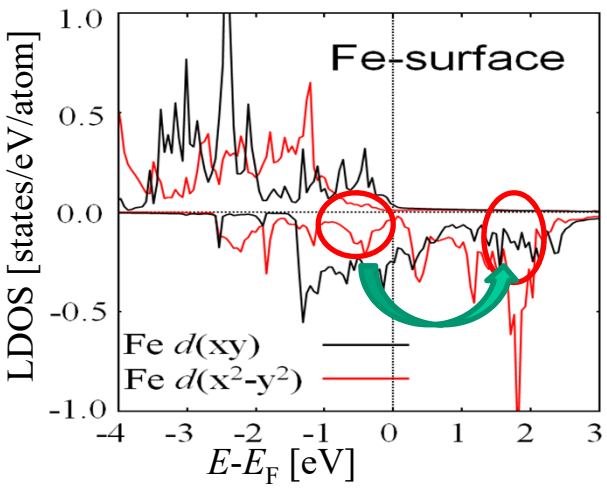


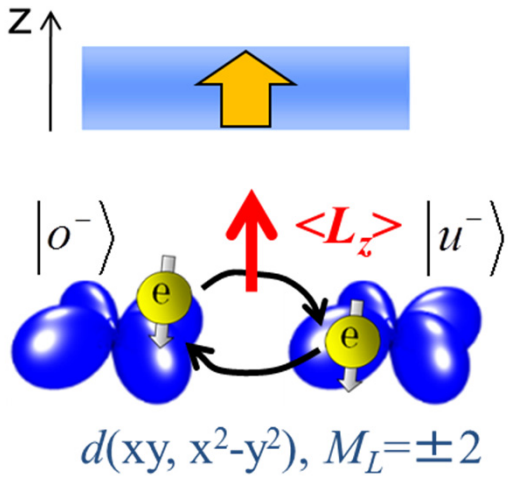
Bruno's relation PRB **39**, 865 (1989).

$$\Delta E_{MCA} \approx \frac{\xi}{4}\left[\langle L_z \rangle - \langle L_x \rangle\right]$$

$$G_{\mu_1,\underline{\mu_1}}^{\mu_2,\underline{\mu_2}}(\downarrow,\downarrow;i,i)\left|\langle \mu_2 | L_Z | \mu_1 \rangle\right|^2$$





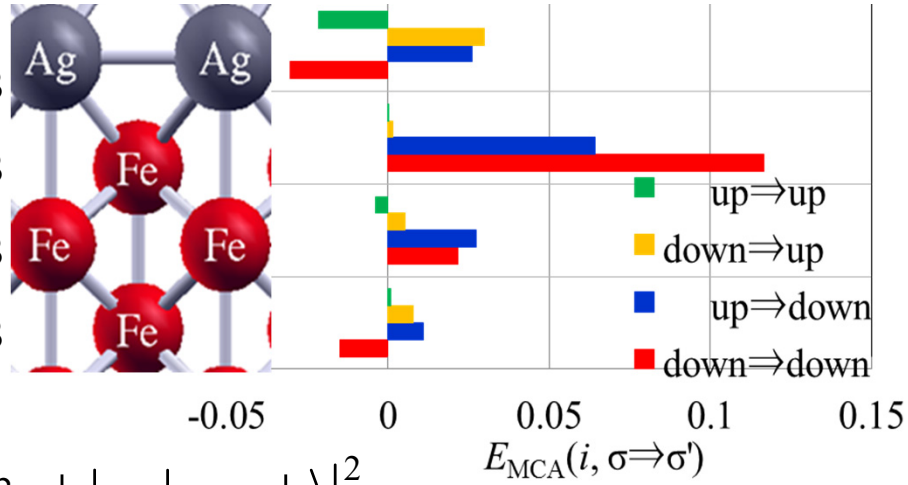


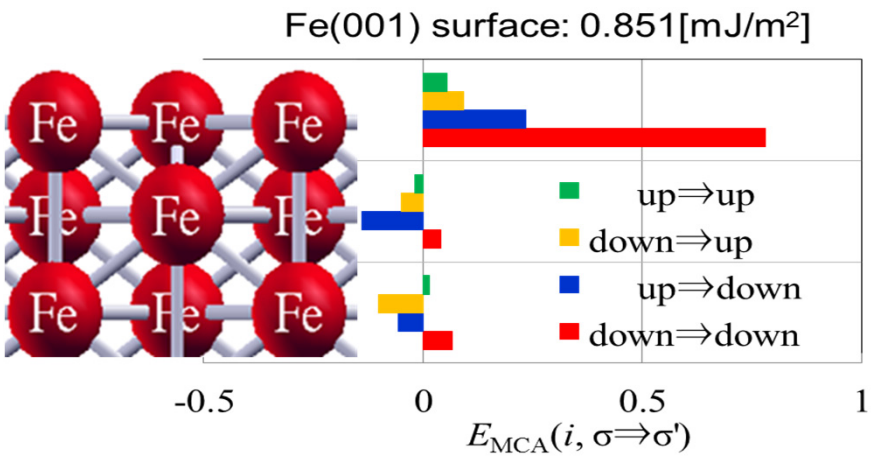
Ag/Fe(001) interfaces (E_{MCA}=+0.768 [mJ/m^2])

Second-order contribution to MCA energy

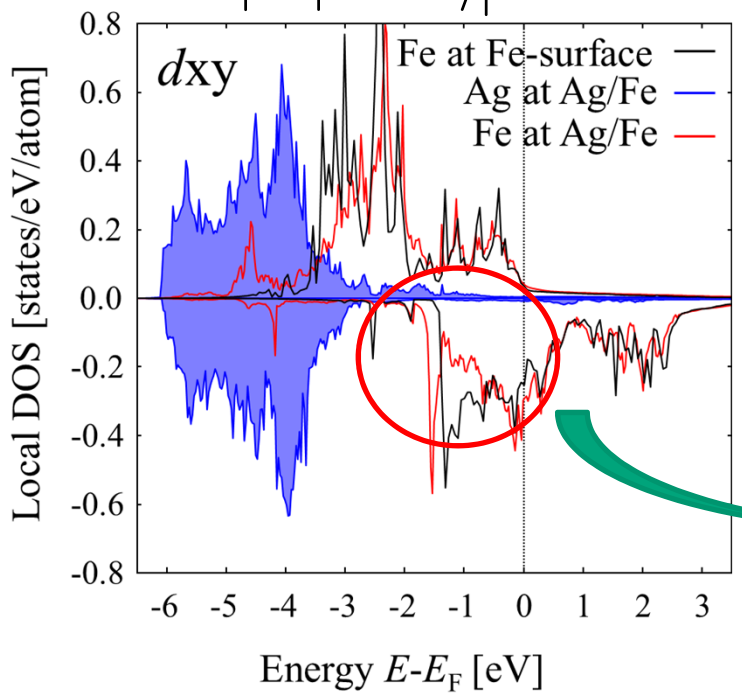
Y. Miura, *et al.*, JAP **113**, 233908 (2013).

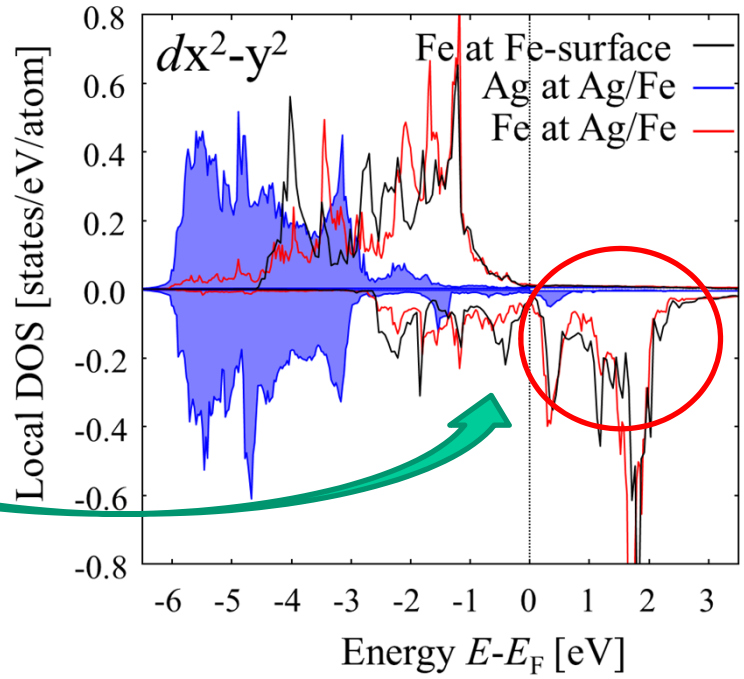
$0.022\mu_B$
$2.774\mu_B$
$2.461\mu_B$
$2.541\mu_B$

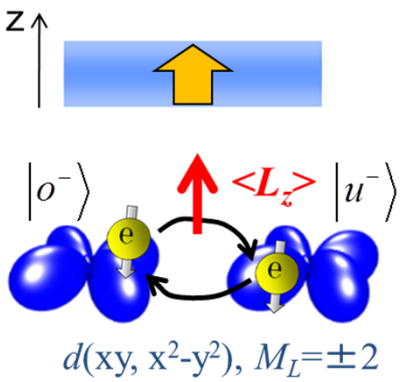




$$\left|\left\langle x^2-y^2,\downarrow\left|L_z\right|xy,\downarrow\right\rangle\right|^2$$







LDOS of Fe *d* states at Ag/Fe(001) interfaces is very similar to LDOS of Fe(001) surface around Fermi level because of the absence of Ag *d* states around the Fermi level.

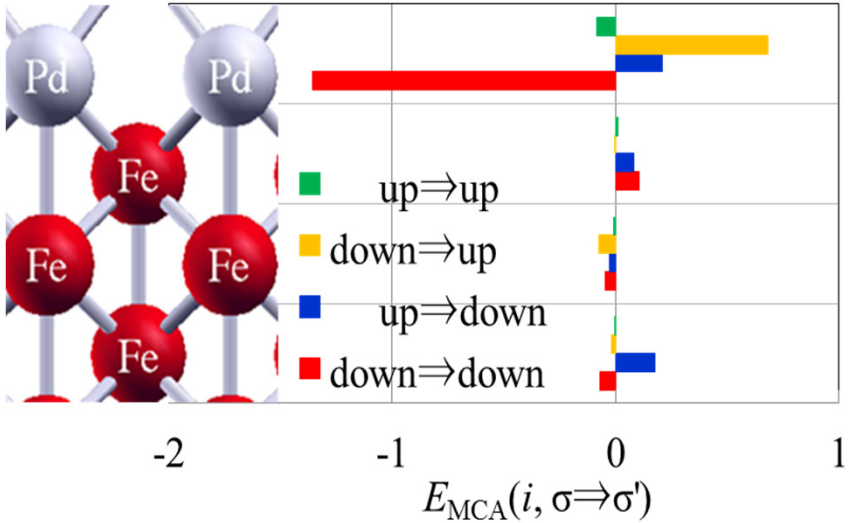
Pd/Fe(001) interfaces (E_{MCA}=−0.616[mJ/m^2])

Second-order contribution to MCA energy

Interfacial Pd atom mainly contribute to the in-plane MCA

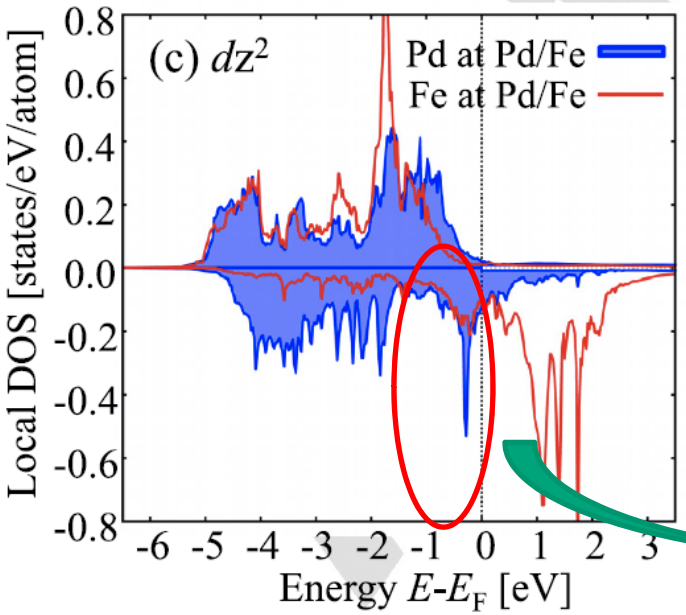
Relatively large induced spin moment of interfacial Pd

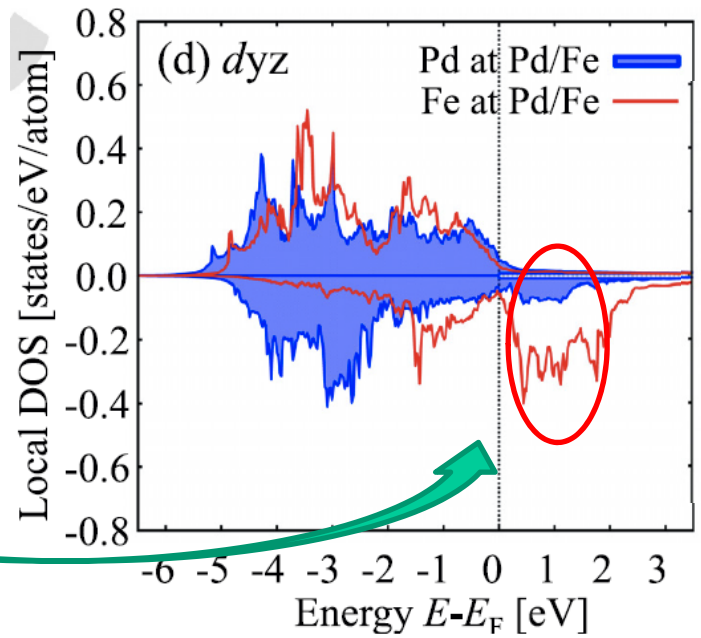
0.309μ_B
2.915μ_B
2.537μ_B
2.513μ_B

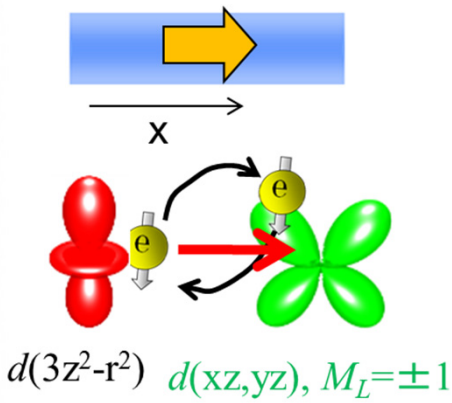


Y. Miura, *et al.*, JAP **113**, 233908 (2013).

$$\left|\left\langle yz,\downarrow\left|L_z\right|z^2,\downarrow\right\rangle\right|^2$$







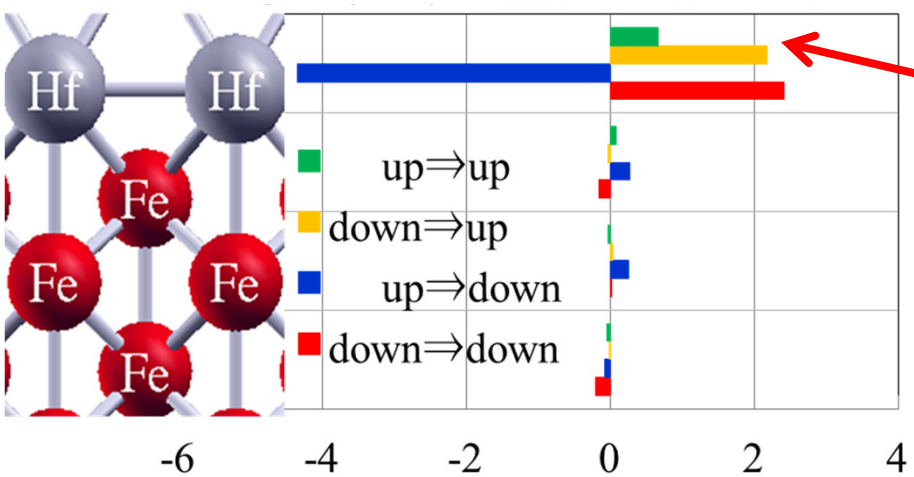
Pd *d* orbital strongly hybridize with the Fe *d* orbital at the Pd/Fe(001) interface, leading to the significant change of the LDOS of Fe *d* orbital around E_F.

Hf/Fe(001) interfaces (E_{MCA}=+1.49[mJ/m^2])

Second-order contribution to MCA energy

Y. Miura, *et al.*, JAP **113**, 233908 (2013).

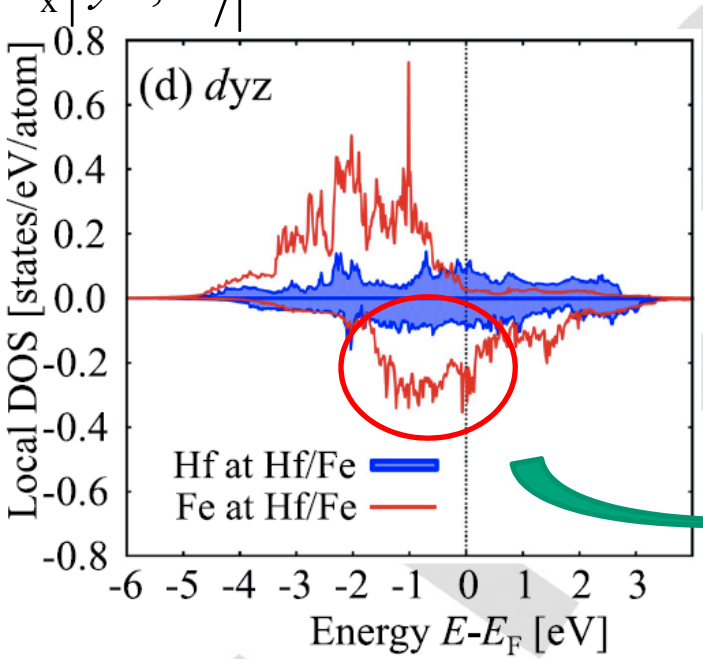
-0.186μ_B
2.484μ_B
2.450μ_B
2.476μ_B

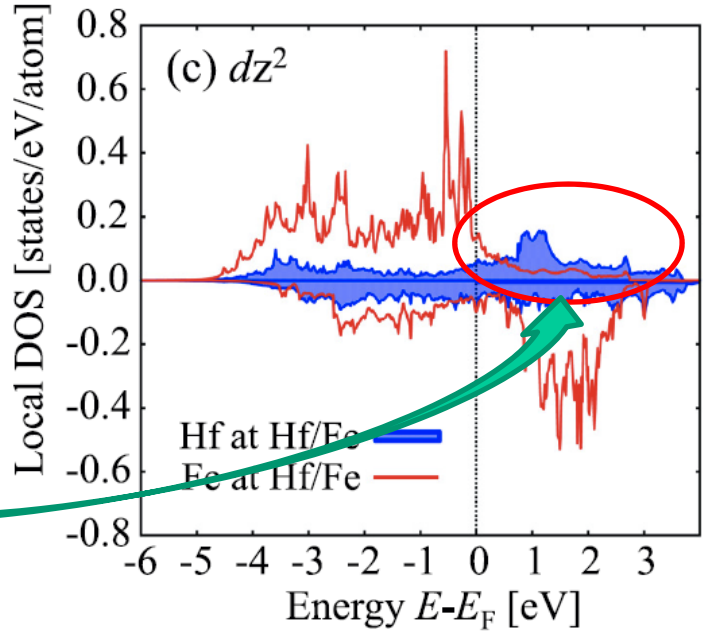


Spin down-up term of interfacial Hf shown by yellow bar has large positive contribution to MCA

Hf is transition metal element with less than half *d* orbital, and it has large unoccupied *d* states.

$$\left|\left\langle z^2, \uparrow \middle| L_x \middle| yz, \downarrow \right\rangle\right|^2$$





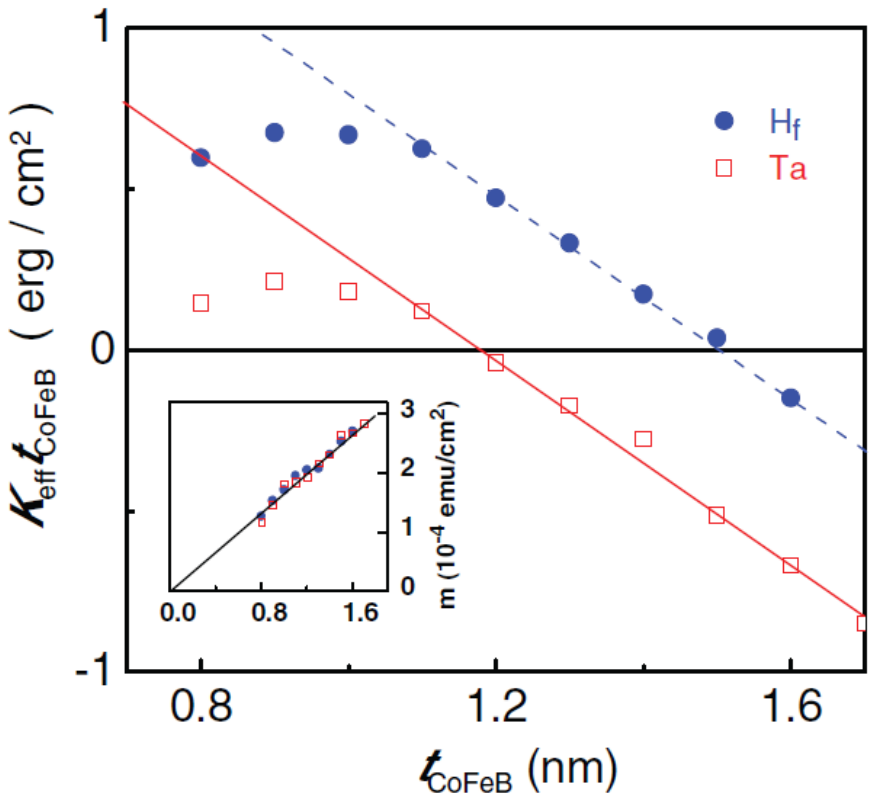
The unoccupied states significantly contribute to the perpendicular MCA thorough the second perturbation from occupied spin-down states to unoccupied spin-up states.

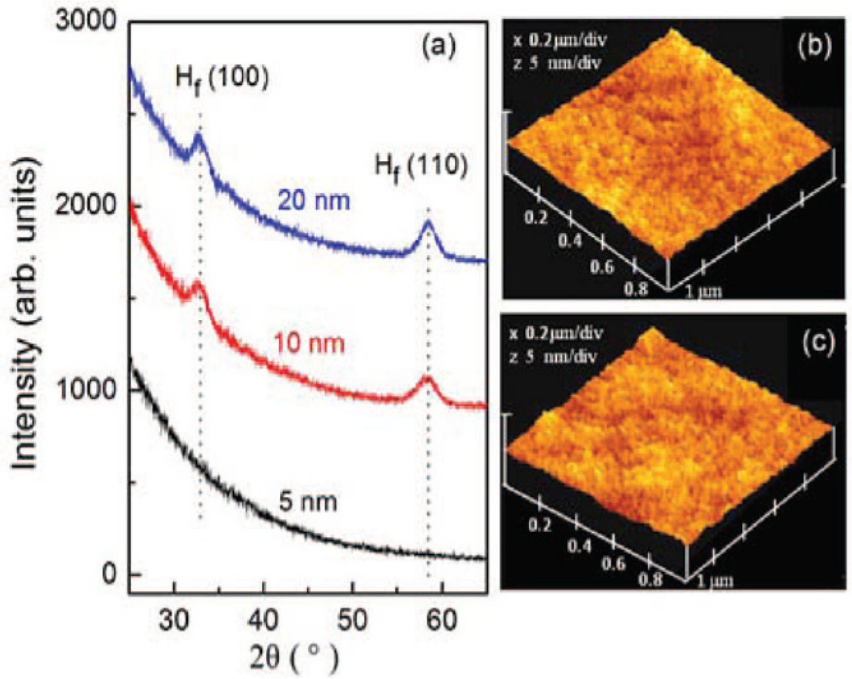
Experiments

AIP ADVANCES 2, 032151 (2012)

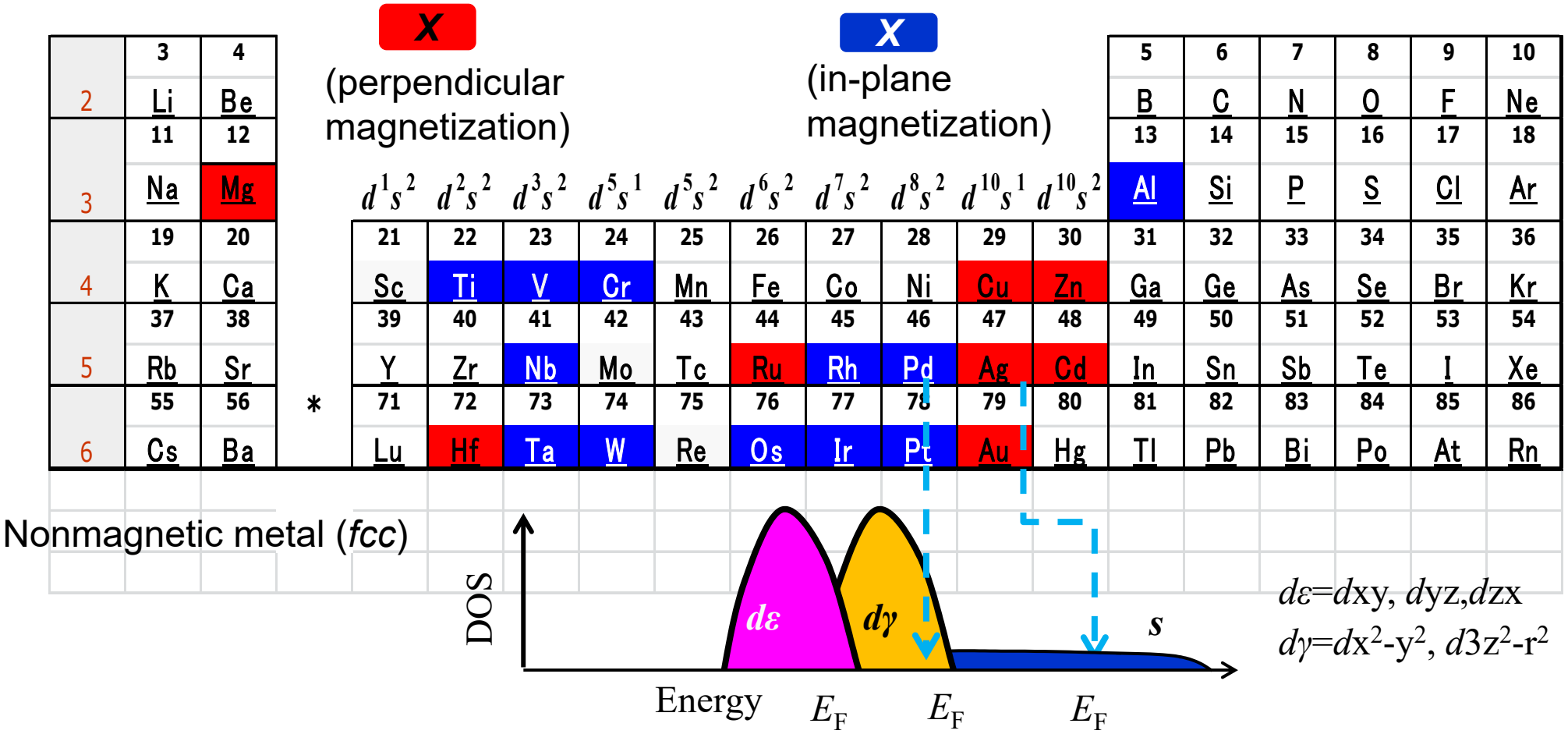
Large enhanced perpendicular magnetic anisotropy in CoFeB/MgO system with the typical Ta buffer replaced by an Hf layer

T. Liu,[1] J. W. Cai,[1,a] and Li Sun[2]





Summary of the fourth topic



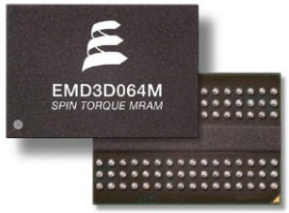
1. Fe(001) interfaces with noble metals (Cu,Ag,Au) or typical metal elements (Zn,Cd,Mg) without *d* orbital around E_F tends to show perpendicular MCA.

2. Fe(001) interfaces with elements having partially filled *d* orbitals (Pd, Pt, Rh, Ir, Os, Cr, Nb, Ta, V, W, Ti) tends to show in-plane MCA except for Hf.

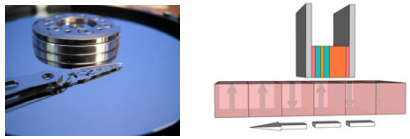
3. Hf/Fe(001) show the strong perpendicular MCA corresponding to Fe/MgO(001).

Summary of this talk

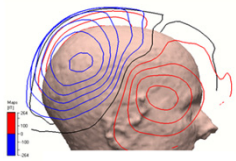
MRAM



Magnetic censer



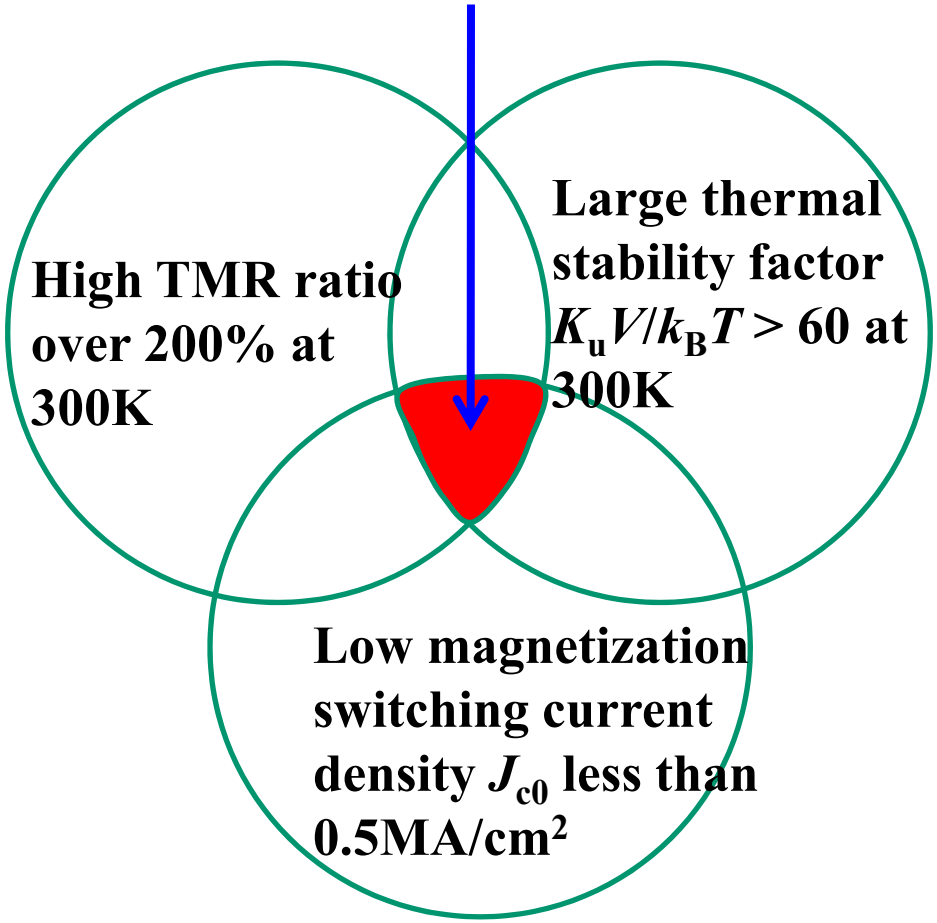
HDD read-out-head



Earth's magnetic field censer・current censer for car・biomagnetic censer

Corresponding to SQUID

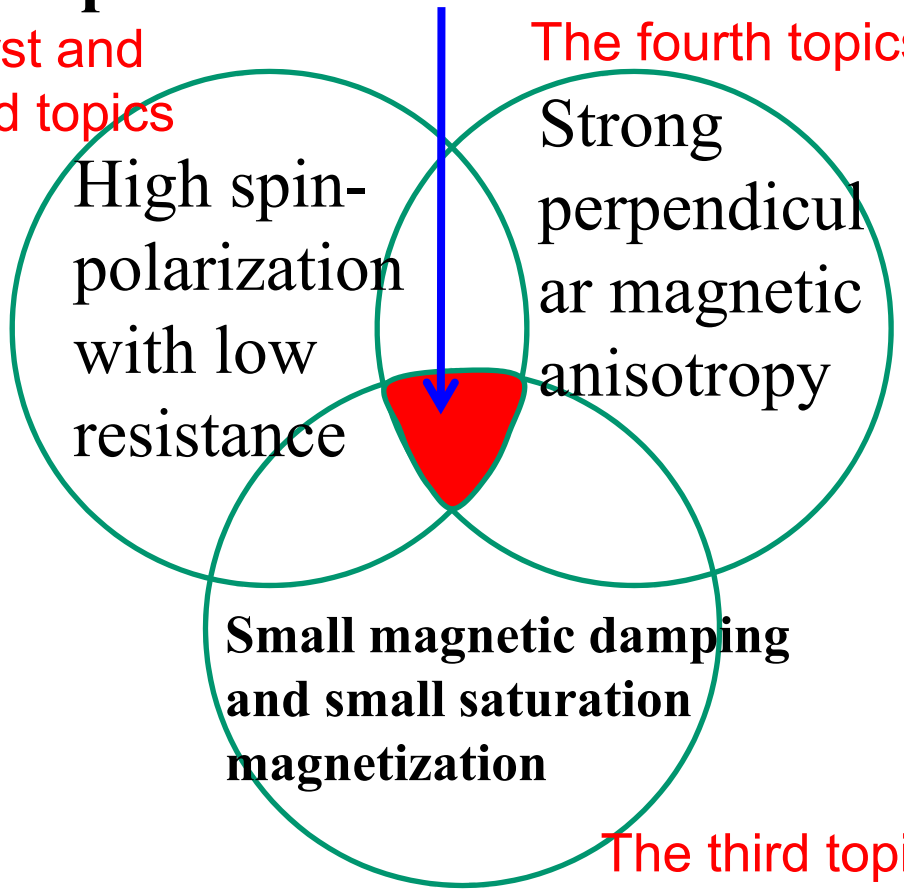
Required performance for pMTJs



Required properties for spintronic materials

The first and second topics

The fourth topics



The third topics

END

摂動論

既に解けている系からわずかにずれた系のエネルギーや波動関数を求める手法

無摂動系のシュレディンガー方程式　$H_0\psi_n^{(0)} = \varepsilon_n^{(0)}\psi_n^{(0)}$(すべて既知)

全系のシュレディンガー方程式　$\boxed{H\psi_n = \varepsilon_n\psi_n}$

全ハミルトニアン　$\boxed{H = H_0 + H'}$

摂動ハミルトニアン　H'

全系のエネルギー固有値　$\varepsilon_n = \varepsilon_n^{(0)} + \varepsilon_n^{(1)} + \varepsilon_n^{(2)} + \cdots$

摂動の1次のエネルギー

$$\boxed{\varepsilon_n^{(1)} = \langle n|H'|n\rangle}$$

摂動の2次のエネルギー

$$\boxed{\varepsilon_n^{(2)} = -\sum_{m\neq n}\frac{\langle n|H'|m\rangle^*\langle m|H'|n\rangle}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}}}$$

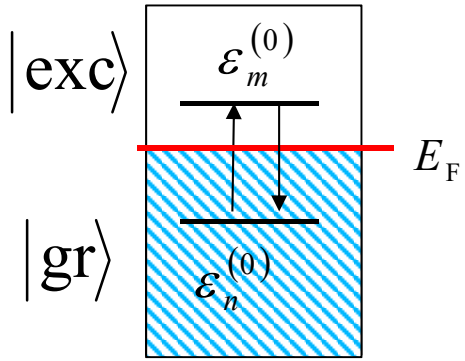
1次摂動の全エネルギーへの寄与　$E^{(1)} = \sum_n^{\text{占有}}\varepsilon_n^{(1)} = \sum_n^{\text{occ}}\langle n|H'|n\rangle$

2次摂動の全エネルギーへの寄与　$E^{(2)} = \sum_n^{\text{占有}}\varepsilon_n^{(2)} = -\sum_n^{\text{occ}}\sum_{m\neq n}\frac{\langle n|H'|m\rangle^*\langle m|H'|n\rangle}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}}$

⇒フェルミ準位を挟んだ占有状態(ground states)と非占有状態(excited states)の間の行列要素のみ寄与（H'がエルミート演算子の場合）

例）$\frac{|\langle 3|H'|2\rangle|^2}{\varepsilon_3^{(0)} - \varepsilon_2^{(0)}} f\left(\varepsilon_2^{(0)}\right) + \frac{|\langle 2|H'|3\rangle|^2}{\varepsilon_2^{(0)} - \varepsilon_3^{(0)}} f\left(\varepsilon_3^{(0)}\right)$　占有数$f(\varepsilon)$がともに1 or 0の場合は消える

⇒フェルミ準位から遠い状態間の摂動エネルギーは分母が大きくなり、全エネルギーへの寄与は小さくなる(フェルミ準位付近の状態のみ寄与)



結晶磁気異方性の摂動論

スピン軌道相互作用ハミルトニアン:
（摂動ハミルトニアン）

$$H_\eta^{\mathrm{SO}} = \sum_I \zeta_I \vec{L}_\eta \cdot \vec{S}$$

η:スピンの向き ([001] or [100])

$\vec{k}$: k点ベクトル

σ: スピン

n: バンド

$I(i)$: 原子位置

μ: 局在原子軌道

無摂動系のシュレディンガー方程式:

$$H_0 \left| \vec{k} n \sigma \right\rangle = E_{\vec{k} n \sigma} \left| \vec{k} n \sigma \right\rangle$$

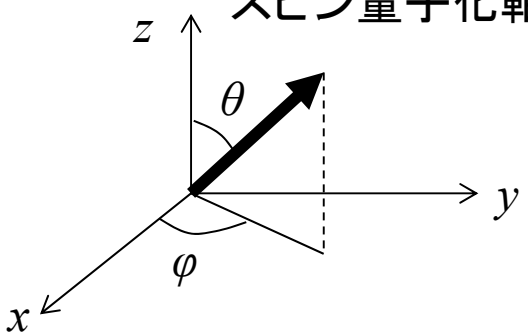
ブロッホ状態の局在原子基底による展開:

$$\boxed{\left| \vec{k} n \sigma \right\rangle = \sum_{i,\mu} c_{i\mu\sigma}^{kn} \left| i \mu \sigma \right\rangle}$$

1次摂動エネルギー

$$\boxed{E_1 = \left\langle kn\sigma \middle| H_\eta^{\mathrm{SO}} \middle| kn\sigma \right\rangle = \sum_{\mu\mu'} \left\langle \mu'\sigma \middle| \vec{L}_\eta \cdot \vec{S} \middle| \mu\sigma \right\rangle \sum_I \zeta_I \sum_{kn\sigma} c_{I\mu'\sigma}^{kn*} c_{I\mu\sigma}^{kn} = 0}$$

スピン量子化軸の向き



$$\left[\left\langle \lambda \uparrow \middle| \vec{L}_\eta \cdot \vec{S} \middle| \mu \uparrow \right\rangle \right] = \begin{array}{c} \begin{array}{ccccc} d_{xy} & d_{yz} & d_{zx} & d_{x^2-y^2} & d_{3z^2-r^2} \end{array} \\ \begin{pmatrix} 0 & \frac{\mathrm{i}}{2}\sin\varphi\sin\theta & \frac{-\mathrm{i}}{2}\cos\varphi\sin\theta & \mathrm{i}\cos\theta & 0 \\ \frac{-\mathrm{i}}{2}\sin\varphi\sin\theta & 0 & \frac{\mathrm{i}}{2}\cos\theta & \frac{-\mathrm{i}}{2}\cos\varphi\sin\theta & \frac{-\mathrm{i}\sqrt{3}}{2}\cos\varphi\sin\theta \\ \frac{\mathrm{i}}{2}\cos\varphi\sin\theta & \frac{-\mathrm{i}}{2}\cos\theta & 0 & \frac{-\mathrm{i}}{2}\sin\varphi\sin\theta & \frac{\mathrm{i}\sqrt{3}}{2}\sin\varphi\sin\theta \\ -\mathrm{i}\cos\theta & \frac{\mathrm{i}}{2}\cos\varphi\sin\theta & \frac{\mathrm{i}}{2}\sin\varphi\sin\theta & 0 & 0 \\ 0 & \frac{\mathrm{i}\sqrt{3}}{2}\cos\varphi\sin\theta & \frac{-\mathrm{i}\sqrt{3}}{2}\sin\varphi\sin\theta & 0 & 0 \end{pmatrix} \end{array}$$

スピン軌道演算子の
対角要素はゼロ

$$\left[\left\langle \lambda \uparrow \middle| \vec{L}_\eta \cdot \vec{S} \middle| \mu \downarrow \right\rangle \right] = \begin{pmatrix} 0 & \frac{1}{2}f(\varphi,\theta) & \frac{1}{2}g(\varphi,\theta) & -\mathrm{i}\sin\theta & 0 \\ -\frac{1}{2}f(\varphi,\theta) & 0 & \frac{-\mathrm{i}}{2}\sin\theta & \frac{1}{2}g(\varphi,\theta) & \frac{\sqrt{3}}{2}g(\varphi,\theta) \\ -\frac{1}{2}g(\varphi,\theta) & \frac{\mathrm{i}}{2}\sin\theta & 0 & -\frac{1}{2}f(\varphi,\theta) & \frac{\sqrt{3}}{2}f(\varphi,\theta) \\ \mathrm{i}\sin\theta & -\frac{1}{2}g(\varphi,\theta) & \frac{1}{2}f(\varphi,\theta) & 0 & 0 \\ 0 & -\frac{\sqrt{3}}{2}g(\varphi,\theta) & -\frac{\sqrt{3}}{2}f(\varphi,\theta) & 0 & 0 \end{pmatrix}$$

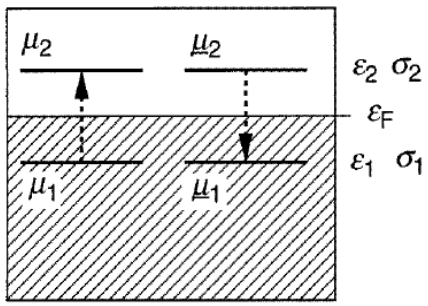
スピン軌道相互作用の2次摂動によるエネルギー補正式の導出

$$E_\eta^{(2)} = -\sum_{\mathrm{gr,exc}} \frac{\left|\left\langle \mathrm{exc}\left|H_\eta^{\mathrm{SO}}\right|\mathrm{gr}\right\rangle\right|^2}{\varepsilon_{\mathrm{exc}} - \varepsilon_{\mathrm{gr}}}$$

η:スピンの向き ([001] or [100])

$\left|\mathrm{exc}\right\rangle$

$\left|\mathrm{gr}\right\rangle$



σ:スピン

n:バンド

$I(j)$:原子位置

μ:局在原子軌道

$$H_\eta^{\mathrm{SO}} = \sum_I \zeta_I \vec{L}_\eta \cdot \vec{S}$$

$$\left|\mathrm{gr}\right\rangle = \left|k,n,\sigma\right\rangle = \sum_{j,\mu} c_{j\mu\sigma}^{kn} \left|j\mu\sigma\right\rangle$$

$$\left|\mathrm{exc}\right\rangle = \left|k,n',\sigma'\right\rangle = \sum_{i',\lambda'} c_{i'\lambda'\sigma'}^{kn'} \left|i'\lambda'\sigma'\right\rangle$$

$$E_\eta^{(2)} = -\sum_k \sum_{\substack{n\sigma \\ (\mathrm{occ})}} \sum_{\substack{n'\sigma' \\ (\mathrm{unocc})}} \frac{\left|\left\langle kn'\sigma'\left|H_\eta^{\mathrm{SO}}\right|kn\sigma\right\rangle\right|^2}{\varepsilon_{kn'\sigma'} - \varepsilon_{kn\sigma}} = -\sum_k \sum_{\substack{n\sigma \\ (\mathrm{occ})}} \sum_{\substack{n'\sigma' \\ (\mathrm{unocc})}} \frac{\left\langle kn\sigma\left|H_\eta^{\mathrm{SO}*}\right|kn'\sigma'\right\rangle\left\langle kn'\sigma'\left|H_\eta^{\mathrm{SO}}\right|kn\sigma\right\rangle}{\varepsilon_{kn'\sigma'} - \varepsilon_{kn\sigma}}$$

$$= -\sum_k \sum_{\substack{n\sigma \\ (\mathrm{occ})}} \sum_{\substack{n'\sigma' \\ (\mathrm{unocc})}} \frac{\sum_{i\lambda}\left\langle i\lambda\sigma\left|C_{i\lambda\sigma}^{kn*}\left(\sum_I \varsigma_I \vec{L}_\eta \cdot \vec{S}\right)^*\right.\sum_{j'\mu'} C_{j'\mu'\sigma'}^{kn'}\left|j'\mu'\sigma'\right\rangle\sum_{i'\lambda'}\left\langle i'\lambda'\sigma'\left|C_{i'\lambda'\sigma'}^{kn'*}\left(\sum_{I'} \varsigma_{I'} \vec{L}_\eta \cdot \vec{S}\right)\right.\sum_{j\mu} C_{j\mu\sigma}^{kn}\left|j\mu\sigma\right\rangle}{\varepsilon_{kn'\sigma'} - \varepsilon_{kn\sigma}}$$

スピン軌道相互作用は1電子相互作用で同一原子内のみ働くため

$$= -\sum_k \sum_{\substack{n\sigma \\ (\mathrm{occ})}} \sum_{\substack{n'\sigma' \\ (\mathrm{unocc})}} \frac{\sum_I \sum_{i\lambda} \sum_{j'\mu'}\left\langle i\lambda\sigma\left|\delta_{iI}\delta_{Ij'}\left(\varsigma_I \vec{L}_\eta \cdot \vec{S}\right)^*\right|j'\mu'\sigma'\right\rangle C_{i\lambda\sigma}^{kn*} C_{j'\mu'\sigma'}^{kn'} \sum_{I'} \sum_{i'\lambda'} \sum_{j\mu}\left\langle i'\lambda'\sigma'\left|\delta_{i'I'}\delta_{I'j}\left(\varsigma_{I'} \vec{L}_\eta \cdot \vec{S}\right)\right|j\mu\sigma\right\rangle C_{i'\lambda'\sigma'}^{kn'*} C_{j\mu\sigma}^{kn}}{\varepsilon_{kn'\sigma'} - \varepsilon_{kn\sigma}}$$

$$= -\sum_k \sum_{\substack{n\sigma \\ (\mathrm{occ})}} \sum_{\substack{n'\sigma' \\ (\mathrm{unocc})}} \frac{\sum_I \sum_{\lambda\mu'}\left\langle I\lambda\sigma\left|\varsigma_I \vec{L}_\eta \cdot \vec{S}\right|I\mu'\sigma'\right\rangle C_{I\lambda\sigma}^{kn*} C_{I\mu'\sigma'}^{kn'} \sum_{I'} \sum_{\lambda'\mu}\left\langle I'\lambda'\sigma'\left|\varsigma_{I'} \vec{L}_\eta \cdot \vec{S}\right|I'\mu\sigma\right\rangle C_{I'\lambda'\sigma'}^{kn'*} C_{I'\mu\sigma}^{kn}}{\varepsilon_{kn'\sigma'} - \varepsilon_{kn\sigma}}$$

$$\left|i\mu\sigma\right\rangle \Rightarrow \left|\mu\sigma\right\rangle$$

各原子位置を中心とした球面調和関数で与えるので、基底のindexから原子位置I,I'を消去

$$= -\sum_{k}\sum_{\substack{n\sigma \\ (\mathrm{occ})}}\sum_{\substack{n'\sigma' \\ (\mathrm{unocc})}} \frac{\sum_{I}\varsigma_{I}\sum_{\lambda\mu'}\left\langle\lambda\sigma\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu'\sigma'\right\rangle C^{kn*}_{I\lambda\sigma}C^{kn'}_{I\mu'\sigma'}\sum_{I'}\varsigma_{I'}\sum_{\lambda'\mu}\left\langle\lambda'\sigma'\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\sigma\right\rangle C^{kn'*}_{I'\lambda'\sigma'}C^{kn}_{I'\mu\sigma}}{\varepsilon_{kn'\sigma'}-\varepsilon_{kn\sigma}}$$

$$= -\sum_{\lambda\mu'\lambda'\mu}\sum_{II'}\sum_{\sigma\sigma'}\varsigma_{I}\varsigma_{I'}\left\langle\lambda\sigma\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu'\sigma'\right\rangle\left\langle\lambda'\sigma'\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\sigma\right\rangle \underbrace{\sum_{k}\sum_{\substack{n \\ (\mathrm{occ})}}\sum_{\substack{n' \\ (\mathrm{unocc})}} C^{kn*}_{I\lambda\sigma}C^{kn'}_{I\mu'\sigma'}\frac{1}{\varepsilon_{kn'\sigma'}-\varepsilon_{kn\sigma}}C^{kn'*}_{I'\lambda'\sigma'}C^{kn}_{I'\mu\sigma}}_{G^{\sigma,\sigma'}_{I,I'}(\lambda\mu',\lambda'\mu)}$$

$$= -\sum_{\lambda\mu'\lambda'\mu}\sum_{I,I'}\sum_{\sigma\sigma'}\varsigma_{I}\varsigma_{I'}\left\langle\lambda\sigma\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu'\sigma'\right\rangle\left\langle\lambda'\sigma'\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\sigma\right\rangle \underbrace{\sum_{k}\sum_{n}\int_{-\infty}^{\varepsilon_{\mathrm{F}}}d\varepsilon\,\delta(\varepsilon-\varepsilon_{kn\sigma})\sum_{n'}\int_{\varepsilon_{\mathrm{F}}}^{+\infty}d\varepsilon'\,\delta(\varepsilon-\varepsilon_{kn'\sigma'})C^{kn*}_{I\lambda\sigma}C^{kn'}_{I\mu'\sigma'}\frac{1}{\varepsilon'-\varepsilon}C^{kn'*}_{I'\lambda'\sigma'}C^{kn}_{I'\mu\sigma}}_{G^{\sigma,\sigma'}_{I,I'}(\lambda\mu',\lambda'\mu)}$$

$$= -\sum_{\lambda\mu'\lambda'\mu}\sum_{I,I'}\sum_{\sigma\sigma'}\varsigma_{I}\varsigma_{I'}\left\langle\lambda\sigma\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu'\sigma'\right\rangle\left\langle\lambda'\sigma'\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\sigma\right\rangle G^{\sigma,\sigma'}_{I,I'}(\lambda\mu',\lambda'\mu)$$

ゆえに

$$\begin{aligned}E^{(2)}_{\eta} = -\sum_{\lambda\mu'\lambda'\mu}\sum_{I,I'}\sum_{\sigma\sigma'}\varsigma_{I}\varsigma_{I'}\Big[&\left\langle\lambda\uparrow\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu'\uparrow\right\rangle\left\langle\lambda'\uparrow\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\uparrow\right\rangle G^{\uparrow,\uparrow}_{I,I'}(\lambda\mu',\lambda'\mu) \\ &+\left\langle\lambda\downarrow\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu'\downarrow\right\rangle\left\langle\lambda'\downarrow\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\uparrow\right\rangle G^{\downarrow,\downarrow}_{I,I'}(\lambda\mu',\lambda'\mu) \\ &+\left\langle\lambda\uparrow\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu'\downarrow\right\rangle\left\langle\lambda'\downarrow\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\uparrow\right\rangle G^{\uparrow,\downarrow}_{I,I'}(\lambda\mu',\lambda'\mu) \\ &+\left\langle\lambda\downarrow\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu'\uparrow\right\rangle\left\langle\lambda'\uparrow\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\downarrow\right\rangle G^{\downarrow,\downarrow}_{I,I'}(\lambda\mu',\lambda'\mu)\Big]\end{aligned}$$

LDOS

$$D_{I\lambda\sigma}(\varepsilon) = \sum_{\vec{k}}\sum_{\substack{n \\ (\mathrm{occ})}} C^{\vec{k}n*}_{I\lambda\sigma}C^{\vec{k}n}_{I\lambda\sigma}\delta\left(\varepsilon-\varepsilon_{\vec{k}n\sigma}\right)$$

$$
\begin{aligned}
= -\sum_{\lambda\mu'\lambda'\mu}\sum_{I,I'}\sum_{\sigma\sigma'}\varsigma_I\varsigma_{I'}\Big[&\left\langle\lambda\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu'\uparrow\right\rangle\left\langle\lambda'\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\uparrow\right\rangle G_{I,I'}^{\uparrow,\uparrow}(\lambda\mu',\lambda'\mu)\\
&+\left\langle\lambda\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu'\downarrow\right\rangle\left\langle\lambda'\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\uparrow\right\rangle G_{I,I'}^{\uparrow,\downarrow}(\lambda\mu',\lambda'\mu)\\
&+\left\langle\lambda\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu'\uparrow\right\rangle\left\langle\lambda'\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\downarrow\right\rangle G_{I,I'}^{\downarrow,\uparrow}(\lambda\mu',\lambda'\mu)\\
&+\left\langle\lambda\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu'\downarrow\right\rangle\left\langle\lambda'\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\downarrow\right\rangle G_{I,I'}^{\downarrow,\downarrow}(\lambda\mu',\lambda'\mu)\Big]
\end{aligned}
$$

ここで　$\left\langle\lambda,\sigma\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\sigma\right\rangle=\left\langle\lambda,-\sigma\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,-\sigma\right\rangle^*=-\left\langle\lambda,-\sigma\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,-\sigma\right\rangle$　より

$$
\left\langle\lambda\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu'\downarrow\right\rangle\left\langle\lambda'\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\downarrow\right\rangle=\left(-\left\langle\lambda\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu'\uparrow\right\rangle\right)\left(-\left\langle\lambda'\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\uparrow\right\rangle\right)
$$

ゆえに

$$
\left\langle\lambda\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu'\downarrow\right\rangle\left\langle\lambda'\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\downarrow\right\rangle=\left\langle\lambda\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu'\uparrow\right\rangle\left\langle\lambda'\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\uparrow\right\rangle \quad \cdots⓪
$$

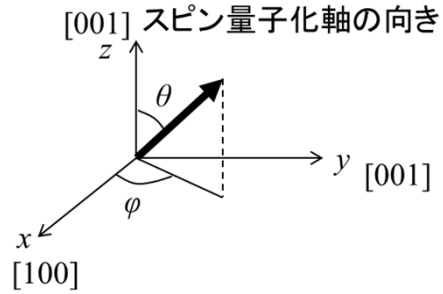
また

$$
\mathrm{Re}\left[\left\langle\lambda\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu'\downarrow\right\rangle\left\langle\lambda'\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\uparrow\right\rangle\right]+\left\langle\lambda\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu'\uparrow\right\rangle\left\langle\lambda'\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\uparrow\right\rangle=C(\text{一定}) \quad \cdots①
$$

が成立する。

①式の証明　　J. Phys.: Condens. Matter 18 (2006) 6785–6813　のAppendix Aより

スピンの量子化軸をz軸にとり、スピンSの角度をθ、φで表すと



$$\left[\left\langle \lambda\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\uparrow\right\rangle\right]=\frac{1}{2}\begin{array}{c} \begin{array}{ccccc}1&2&3&4&5\end{array}\\ \begin{pmatrix} 0 & i\sin\theta\sin\varphi & -i\sin\theta\sin\varphi & 2i\cos\theta & 0\\ -i\sin\theta\sin\varphi & 0 & i\cos\theta & -i\sin\theta\sin\varphi & -i\sqrt{3}\sin\theta\cos\varphi\\ i\sin\theta\sin\varphi & -i\cos\theta & 0 & -i\sin\theta\sin\varphi & i\sqrt{3}\sin\theta\sin\varphi\\ -2i\cos\theta & i\sin\theta\cos\varphi & i\sin\theta\sin\varphi & 0 & 0\\ 0 & i\sqrt{3}\sin\theta\cos\varphi & -i\sqrt{3}\sin\theta\sin\varphi & 0 & 0 \end{pmatrix}\end{array}\begin{array}{c}1\\2\\3\\4\\5\end{array}\quad\cdots②$$

(1,2,3,4,5)=
(dxy , dyz, dzx , dx^2-y^2 , $d3z^2-r^2$)

$$\left[\left\langle \lambda\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\downarrow\right\rangle\right]=-\frac{1}{2}\begin{array}{c} \begin{array}{ccccc}1&2&3&4&5\end{array}\\ \begin{pmatrix} 0 & i\sin\theta\sin\varphi & -i\sin\theta\sin\varphi & 2i\cos\theta & 0\\ -i\sin\theta\sin\varphi & 0 & i\cos\theta & -i\sin\theta\sin\varphi & -i\sqrt{3}\sin\theta\cos\varphi\\ i\sin\theta\sin\varphi & -i\cos\theta & 0 & -i\sin\theta\sin\varphi & i\sqrt{3}\sin\theta\sin\varphi\\ -2i\cos\theta & i\sin\theta\cos\varphi & i\sin\theta\sin\varphi & 0 & 0\\ 0 & i\sqrt{3}\sin\theta\cos\varphi & -i\sqrt{3}\sin\theta\sin\varphi & 0 & 0 \end{pmatrix}\end{array}\begin{array}{c}1\\2\\3\\4\\5\end{array}\quad\cdots③$$

VASP-Codeでは、
(1,2,3,4,5,6,7,8,9)=
(s, py, pz, px, dxy , dyz, $d3z^2-r^2$, dxz , dx^2-y^2)

$$\left[\left\langle \lambda\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\downarrow\right\rangle\right]=\frac{1}{2}\begin{array}{c} \begin{array}{ccccc}1&2&3&4&5\end{array}\\ \begin{pmatrix} 0 & (\cos\varphi+i\cos\theta\sin\varphi) & (\sin\varphi-i\cos\theta\cos\varphi) & -2i\sin\theta & 0\\ -(\cos\varphi+i\cos\theta\sin\varphi) & 0 & -i\sin\theta & (\sin\varphi-i\cos\theta\cos\varphi) & \sqrt{3}(\sin\varphi-i\cos\theta\cos\varphi)\\ -(\sin\varphi-i\cos\theta\cos\varphi) & i\sin\theta & 0 & -(\cos\varphi+i\cos\theta\sin\varphi) & \sqrt{3}(\cos\varphi+i\cos\theta\sin\varphi)\\ 2i\sin\theta & -(\sin\varphi-i\cos\theta\cos\varphi) & (\cos\varphi+i\cos\theta\sin\varphi) & 0 & 0\\ 0 & -\sqrt{3}(\sin\varphi-i\cos\theta\cos\varphi) & -\sqrt{3}(\cos\varphi+i\cos\theta\sin\varphi) & 0 & 0 \end{pmatrix}\end{array}\begin{array}{c}1\\2\\3\\4\\5\end{array}$$

・・・④

$$\left[\left\langle \lambda\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu\uparrow\right\rangle\right]=\frac{1}{2}\begin{array}{c} \begin{array}{ccccc}1&2&3&4&5\end{array}\\ \begin{pmatrix} 0 & -(\cos\varphi-i\cos\theta\sin\varphi) & -(\sin\varphi+i\cos\theta\cos\varphi) & -2i\sin\theta & 0\\ (\cos\varphi-i\cos\theta\sin\varphi) & 0 & -i\sin\theta & -(\sin\varphi+i\cos\theta\cos\varphi) & -\sqrt{3}(\sin\varphi+i\cos\theta\cos\varphi)\\ (\sin\varphi+i\cos\theta\cos\varphi) & i\sin\theta & 0 & (\cos\varphi-i\cos\theta\sin\varphi) & -\sqrt{3}(\cos\varphi-i\cos\theta\sin\varphi)\\ 2i\sin\theta & (\sin\varphi+i\cos\theta\cos\varphi) & -(\cos\varphi-i\cos\theta\sin\varphi) & 0 & 0\\ 0 & \sqrt{3}(\sin\varphi+i\cos\theta\cos\varphi) & \sqrt{3}(\cos\varphi-i\cos\theta\sin\varphi) & 0 & 0 \end{pmatrix}\end{array}\begin{array}{c}1\\2\\3\\4\\5\end{array}$$

となる。　このとき、　・・・⑤

$\lambda=\mu,\mu'=\lambda'$のとき

$$\mathrm{Re}\left[\langle\lambda\uparrow|\vec{L}\cdot\vec{S}|\mu'\downarrow\rangle\langle\lambda'\downarrow|\vec{L}\cdot\vec{S}|\mu\uparrow\rangle\right]=\begin{cases}\mathrm{Re}\left[\langle 1\uparrow|\vec{L}\cdot\vec{S}|2\downarrow\rangle\langle 2\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=\frac{1}{4}\left(\cos^2\varphi+\cos^2\theta\sin^2\varphi\right)\\ \mathrm{Re}\left[\langle 1\uparrow|\vec{L}\cdot\vec{S}|3\downarrow\rangle\langle 3\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=\frac{1}{4}\left(\sin^2\varphi+\cos^2\theta\cos^2\varphi\right)\\ \mathrm{Re}\left[\langle 2\uparrow|\vec{L}\cdot\vec{S}|5\downarrow\rangle\langle 5\downarrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle\right]=\frac{3}{4}\left(\sin^2\varphi+\cos^2\theta\cos^2\varphi\right)\\ \mathrm{Re}\left[\langle 3\uparrow|\vec{L}\cdot\vec{S}|5\downarrow\rangle\langle 5\downarrow|\vec{L}\cdot\vec{S}|3\uparrow\rangle\right]=\frac{3}{4}\left(\cos^2\varphi+\cos^2\theta\sin^2\varphi\right)\\ \mathrm{Re}\left[\langle 2\uparrow|\vec{L}\cdot\vec{S}|3\downarrow\rangle\langle 3\downarrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle\right]=\frac{1}{4}\sin^2\theta\\ \mathrm{Re}\left[\langle 1\uparrow|\vec{L}\cdot\vec{S}|4\downarrow\rangle\langle 4\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=\sin^2\theta\end{cases}$$

$$\langle\lambda\uparrow|\vec{L}\cdot\vec{S}|\mu'\uparrow\rangle\langle\lambda'\uparrow|\vec{L}\cdot\vec{S}|\mu\uparrow\rangle=\begin{cases}\langle 1\uparrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle\langle 2\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=\frac{1}{4}\sin^2\theta\sin^2\varphi\\ \langle 1\uparrow|\vec{L}\cdot\vec{S}|3\uparrow\rangle\langle 3\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=\frac{1}{4}\sin^2\theta\cos^2\varphi\\ \langle 2\uparrow|\vec{L}\cdot\vec{S}|5\uparrow\rangle\langle 5\uparrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle=\frac{3}{4}\sin^2\theta\cos^2\varphi\\ \langle 3\uparrow|\vec{L}\cdot\vec{S}|5\uparrow\rangle\langle 5\uparrow|\vec{L}\cdot\vec{S}|3\uparrow\rangle=\frac{3}{4}\sin^2\theta\sin^2\varphi\\ \langle 2\uparrow|\vec{L}\cdot\vec{S}|3\uparrow\rangle\langle 3\uparrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle=\frac{1}{4}\cos^2\theta\\ \langle 1\uparrow|\vec{L}\cdot\vec{S}|4\uparrow\rangle\langle 4\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=\cos^2\theta\end{cases}$$

$\lambda\neq\mu,\mu'\neq\lambda'$のとき

$$\mathrm{Re}\left[\langle\lambda\uparrow|\vec{L}\cdot\vec{S}|\mu'\downarrow\rangle\langle\lambda'\downarrow|\vec{L}\cdot\vec{S}|\mu\uparrow\rangle\right]\begin{cases}\mathrm{Re}\left[\langle 1\uparrow|\vec{L}\cdot\vec{S}|3\downarrow\rangle\langle 2\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=\frac{1}{4}\left(\sin\varphi\cos\varphi-\cos^2\theta\sin\varphi\cos\varphi\right)\\ \mathrm{Re}\left[\langle 2\uparrow|\vec{L}\cdot\vec{S}|4\downarrow\rangle\langle 2\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=\frac{1}{4}\left(\sin\varphi\cos\varphi-\cos^2\theta\sin\varphi\cos\varphi\right)\\ \mathrm{Re}\left[\langle 3\uparrow|\vec{L}\cdot\vec{S}|4\downarrow\rangle\langle 2\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=-\frac{1}{4}\left(\cos^2\varphi+\cos^2\theta\sin^2\varphi\right)\\ \mathrm{Re}\left[\langle 2\uparrow|\vec{L}\cdot\vec{S}|3\downarrow\rangle\langle 2\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=-\frac{1}{4}\sin\theta\cos\theta\sin\varphi\\ \mathrm{Re}\left[\langle 1\uparrow|\vec{L}\cdot\vec{S}|4\downarrow\rangle\langle 2\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=-\frac{1}{2}\sin\theta\cos\theta\sin\varphi\\ \mathrm{Re}\left[\langle 2\uparrow|\vec{L}\cdot\vec{S}|5\downarrow\rangle\langle 2\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=\frac{\sqrt{3}}{4}\left(\sin\varphi\cos\varphi-\cos^2\theta\sin\varphi\cos\varphi\right)\\ \mathrm{Re}\left[\langle 3\uparrow|\vec{L}\cdot\vec{S}|5\downarrow\rangle\langle 2\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=\frac{\sqrt{3}}{4}\left(\cos^2\varphi+\cos^2\theta\sin^2\varphi\right)\\ \mathrm{Re}\left[\langle 1\uparrow|\vec{L}\cdot\vec{S}|3\downarrow\rangle\langle 3\downarrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle\right]=\frac{1}{4}\sin\theta\cos\theta\cos\varphi\\ \mathrm{Re}\left[\langle 1\uparrow|\vec{L}\cdot\vec{S}|4\downarrow\rangle\langle 3\downarrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle\right]=\frac{1}{2}\sin^2\theta\\ \mathrm{Re}\left[\langle 2\uparrow|\vec{L}\cdot\vec{S}|5\downarrow\rangle\langle 3\downarrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle\right]=\frac{\sqrt{3}}{4}\sin\theta\cos\theta\cos\varphi\\ \mathrm{Re}\left[\langle 3\uparrow|\vec{L}\cdot\vec{S}|5\downarrow\rangle\langle 3\downarrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle\right]=-\frac{\sqrt{3}}{4}\sin\theta\cos\theta\sin\varphi\\ \mathrm{Re}\left[\langle 1\uparrow|\vec{L}\cdot\vec{S}|4\downarrow\rangle\langle 3\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=\frac{1}{2}\sin\theta\cos\theta\cos\varphi\\ \mathrm{Re}\left[\langle 2\uparrow|\vec{L}\cdot\vec{S}|4\downarrow\rangle\langle 3\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=\frac{1}{4}\left(\sin^2\theta+\cos^2\theta\cos^2\varphi\right)\\ \mathrm{Re}\left[\langle 2\uparrow|\vec{L}\cdot\vec{S}|5\downarrow\rangle\langle 3\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=\frac{\sqrt{3}}{4}\left(\sin^2\theta+\cos^2\theta\cos^2\varphi\right)\\ \mathrm{Re}\left[\langle 3\uparrow|\vec{L}\cdot\vec{S}|5\downarrow\rangle\langle 3\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle\right]=\frac{\sqrt{3}}{4}\left(\sin\varphi\cos\varphi-\cos^2\theta\sin\varphi\cos\varphi\right)\end{cases}$$

$$\langle\lambda\uparrow|\vec{L}\cdot\vec{S}|\mu'\uparrow\rangle\langle\lambda'\uparrow|\vec{L}\cdot\vec{S}|\mu\uparrow\rangle\begin{cases}\langle 1\uparrow|\vec{L}\cdot\vec{S}|3\uparrow\rangle\langle 2\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=-\frac{1}{4}\sin^2\theta\sin\varphi\cos\varphi\\ \langle 2\uparrow|\vec{L}\cdot\vec{S}|4\uparrow\rangle\langle 2\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=-\frac{1}{4}\sin^2\theta\sin\varphi\cos\varphi\\ \langle 3\uparrow|\vec{L}\cdot\vec{S}|4\uparrow\rangle\langle 2\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=-\frac{1}{4}\sin^2\theta\sin^2\varphi\\ \langle 2\uparrow|\vec{L}\cdot\vec{S}|3\uparrow\rangle\langle 2\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=\frac{1}{4}\sin\theta\cos\theta\sin\varphi\\ \langle 1\uparrow|\vec{L}\cdot\vec{S}|4\uparrow\rangle\langle 2\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=\frac{1}{2}\sin\theta\cos\theta\sin\varphi\\ \langle 2\uparrow|\vec{L}\cdot\vec{S}|5\uparrow\rangle\langle 2\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=-\frac{\sqrt{3}}{4}\sin^2\theta\sin\varphi\cos\varphi\\ \langle 3\uparrow|\vec{L}\cdot\vec{S}|5\uparrow\rangle\langle 2\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=\frac{\sqrt{3}}{4}\sin^2\theta\sin^2\varphi\\ \langle 1\uparrow|\vec{L}\cdot\vec{S}|3\uparrow\rangle\langle 3\uparrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle=\frac{1}{4}\sin\theta\cos\theta\cos\varphi\\ \langle 1\uparrow|\vec{L}\cdot\vec{S}|4\uparrow\rangle\langle 3\uparrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle=\frac{1}{2}\cos^2\theta\\ \langle 2\uparrow|\vec{L}\cdot\vec{S}|5\uparrow\rangle\langle 3\uparrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle=-\frac{\sqrt{3}}{4}\sin\theta\cos\theta\cos\varphi\\ \langle 3\uparrow|\vec{L}\cdot\vec{S}|5\uparrow\rangle\langle 3\uparrow|\vec{L}\cdot\vec{S}|2\uparrow\rangle=\frac{\sqrt{3}}{4}\sin\theta\cos\theta\sin\varphi\\ \langle 1\uparrow|\vec{L}\cdot\vec{S}|4\uparrow\rangle\langle 3\downarrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=-\frac{1}{2}\sin\theta\cos\theta\cos\varphi\\ \langle 2\uparrow|\vec{L}\cdot\vec{S}|4\uparrow\rangle\langle 3\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=\frac{1}{4}\sin^2\theta\cos^2\varphi\\ \langle 2\uparrow|\vec{L}\cdot\vec{S}|5\uparrow\rangle\langle 3\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=\frac{\sqrt{3}}{4}\sin^2\theta\cos^2\varphi\\ \langle 3\uparrow|\vec{L}\cdot\vec{S}|5\uparrow\rangle\langle 3\uparrow|\vec{L}\cdot\vec{S}|1\uparrow\rangle=-\frac{\sqrt{3}}{4}\sin^2\theta\sin\varphi\cos\varphi\end{cases}$$

よって $\mathrm{Re}\left[\langle\lambda\uparrow|\vec{L}\cdot\vec{S}|\mu'\downarrow\rangle\langle\lambda'\downarrow|\vec{L}\cdot\vec{S}|\mu\uparrow\rangle\right]+\langle\lambda\uparrow|\vec{L}\cdot\vec{S}|\mu'\uparrow\rangle\langle\lambda'\uparrow|\vec{L}\cdot\vec{S}|\mu\uparrow\rangle=C(\text{一定})$ **が成立**

ここで、

$$\sum_{\lambda\mu'\lambda'\mu}\left\{\left\langle\lambda,\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\downarrow\right\rangle\left\langle\lambda',\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\uparrow\right\rangle G_{I,I'}^{\uparrow\downarrow}(\lambda\mu',\lambda'\mu)+\left\langle\lambda,\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\uparrow\right\rangle\left\langle\lambda',\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\downarrow\right\rangle G_{I,I'}^{\downarrow\uparrow}(\lambda\mu',\lambda'\mu)\right\} \quad \cdots ⑥$$

を考える。④式と⑤式より $\left\langle\lambda,\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\uparrow\right\rangle=-\left\langle\lambda,\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\downarrow\right\rangle^*$ であるため、

$$⑥式=\frac{1}{2}\left\langle\lambda,\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\downarrow\right\rangle\left\langle\lambda',\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\uparrow\right\rangle G_{I,I'}^{\uparrow\downarrow}(\lambda\mu',\lambda'\mu)+\frac{1}{2}\left\langle\lambda,\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\downarrow\right\rangle\left\langle\lambda',\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\uparrow\right\rangle G_{I,I'}^{\uparrow\downarrow}(\lambda\mu',\lambda'\mu)$$

$$+\frac{1}{2}\left\langle\lambda,\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\uparrow\right\rangle\left\langle\lambda',\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\downarrow\right\rangle G_{I,I'}^{\downarrow\uparrow}(\lambda\mu',\lambda'\mu)+\frac{1}{2}\left\langle\lambda,\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\uparrow\right\rangle\left\langle\lambda',\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\downarrow\right\rangle G_{I,I'}^{\downarrow\uparrow}(\lambda\mu',\lambda'\mu)$$

$$=\left\{\frac{1}{2}\left\langle\lambda,\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\uparrow\right\rangle^*\left\langle\lambda',\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\downarrow\right\rangle^*+\frac{1}{2}\left\langle\lambda,\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\downarrow\right\rangle\left\langle\lambda',\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\uparrow\right\rangle\right\}G_{I,I'}^{\uparrow\downarrow}(\lambda\mu',\lambda'\mu)$$

$$+\left\{\frac{1}{2}\left\langle\lambda,\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\downarrow\right\rangle^*\left\langle\lambda',\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\uparrow\right\rangle^*+\frac{1}{2}\left\langle\lambda,\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\uparrow\right\rangle\left\langle\lambda',\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\downarrow\right\rangle\right\}G_{I,I'}^{\downarrow\uparrow}(\lambda\mu',\lambda'\mu)$$

$$=\left\{\frac{1}{2}\left\langle\lambda',\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\downarrow\right\rangle^*\left\langle\lambda,\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\uparrow\right\rangle^*+\frac{1}{2}\left\langle\lambda,\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\downarrow\right\rangle\left\langle\lambda',\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\uparrow\right\rangle\right\}G_{I,I'}^{\uparrow\downarrow}(\lambda\mu',\lambda'\mu)$$

$$+\left\{\frac{1}{2}\left\langle\lambda',\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\uparrow\right\rangle^*\left\langle\lambda,\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\downarrow\right\rangle^*+\frac{1}{2}\left\langle\lambda,\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\uparrow\right\rangle\left\langle\lambda',\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\downarrow\right\rangle\right\}G_{I,I'}^{\downarrow\uparrow}(\lambda\mu',\lambda'\mu)$$

上記の式は軌道 $\lambda'\lambda\mu'\mu$ に対して和をとれば、同じ項が出てくるので、虚部は消え
実部のみが残る（$z^*+z=(a-ib)+(a+ib)=2a=2\mathrm{Re}[z]$）。ゆえに

$$\sum_{\lambda\mu'\lambda'\mu}\left\{\left\langle\lambda,\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\downarrow\right\rangle\left\langle\lambda',\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\uparrow\right\rangle G_{I,I'}^{\uparrow\downarrow}(\lambda\mu',\lambda'\mu)+\left\langle\lambda,\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\uparrow\right\rangle\left\langle\lambda',\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\downarrow\right\rangle G_{I,I'}^{\downarrow\uparrow}(\lambda\mu',\lambda'\mu)\right\}$$

$$=\sum_{\lambda\mu,\lambda'\mu'}\left\{\mathrm{Re}\left[\left\langle\lambda,\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\downarrow\right\rangle\left\langle\lambda',\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\uparrow\right\rangle\right]G_{I,I'}^{\uparrow\downarrow}(\lambda\mu',\lambda'\mu)+\mathrm{Re}\left[\left\langle\lambda,\downarrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu',\uparrow\right\rangle\left\langle\lambda',\uparrow\left|\vec{L}_\eta\cdot\vec{S}\right|\mu,\downarrow\right\rangle\right]G_{I,I'}^{\downarrow\uparrow}(\lambda\mu',\lambda'\mu)\right\}$$

よって

$$E_\eta^{(2)} = -\sum_{I,I'} \varsigma_I \varsigma_{I'} \sum_{\lambda\mu'\lambda'\mu} \Big[\langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle G_{I,I'}^{\uparrow,\uparrow}(\lambda\mu',\lambda'\mu)$$
$$+ \langle \lambda\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu'\downarrow \rangle \langle \lambda'\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle G_{I,I'}^{\downarrow,\downarrow}(\lambda\mu',\lambda'\mu)$$
$$+ \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\downarrow \rangle \langle \lambda'\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle G_{I,I'}^{\uparrow,\downarrow}(\lambda\mu',\lambda'\mu)$$
$$+ \langle \lambda\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\downarrow \rangle G_{I,I'}^{\downarrow,\downarrow}(\lambda\mu',\lambda'\mu) \Big]$$

$$= -\sum_{I,I'} \varsigma_I \varsigma_{I'} \sum_{\lambda\mu'\lambda'\mu} \Big\{ \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle G_{I,I'}^{\uparrow,\uparrow}(\lambda\mu',\lambda'\mu)$$
$$+ \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle G_{I,I'}^{\downarrow,\downarrow}(\lambda\mu',\lambda'\mu)$$
$$+ \mathrm{Re}\Big[\langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\downarrow \rangle \langle \lambda'\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle \Big] G_{I,I'}^{\uparrow,\downarrow}(\lambda\mu',\lambda'\mu)$$
$$+ \mathrm{Re}\Big[\langle \lambda\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\downarrow \rangle \Big] G_{I,I'}^{\downarrow,\uparrow}(\lambda\mu',\lambda'\mu) \Big\}$$

①より

$$\mathrm{Re}\Big[\langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\downarrow \rangle \langle \lambda'\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle \Big] = C - \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle$$

同様に

$$\mathrm{Re}\Big[\langle \lambda\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\downarrow \rangle \Big] = C - \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle$$

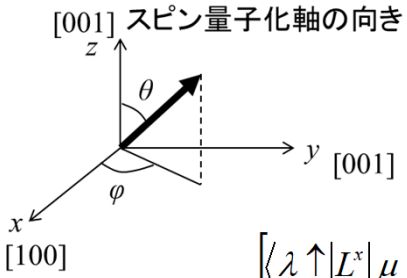
$$E_\eta^{(2)} = -\sum_{I,I'} \varsigma_I \varsigma_{I'} \sum_{\lambda\mu'\lambda'\mu} \Big\{ \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle G_{I,I'}^{\uparrow,\uparrow}(\lambda\mu',\lambda'\mu)$$
$$+ \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle G_{I,I'}^{\downarrow,\downarrow}(\lambda\mu',\lambda'\mu)$$
$$- \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle G_{I,I'}^{\uparrow,\downarrow}(\lambda\mu',\lambda'\mu)$$
$$- \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle G_{I,I'}^{\downarrow,\uparrow}(\lambda\mu',\lambda'\mu) \Big\}$$
$$- C \sum_{I,I'} \varsigma_I \varsigma_{I'} \sum_{\lambda\mu'\lambda'\mu} \Big[G_{I,I'}^{\uparrow\downarrow}(\lambda\mu,\lambda'\mu') + G_{I,I'}^{\downarrow\uparrow}(\lambda\mu',\lambda'\mu) \Big]$$

スピン反転項の符号がマイナスとなることが重要

$-C\sum_{I,I'}\varsigma_I\varsigma_{I'}\sum_{\lambda\mu,\lambda'\mu'}\left[G^{\uparrow\downarrow}_{I,I'}(\lambda\mu',\lambda'\mu)+G^{\downarrow\uparrow}_{I,I'}(\lambda\mu',\lambda'\mu)\right]$ は、磁化方向η(=[001],[100])を変えても変化しないので、結晶磁気異方性の計算で差分をとると消える

ゆえに、スピン軌道相互作用の2次摂動によるエネルギー補正の表式は、

$$
\begin{aligned}
E^{(2)}_{\eta} = -\sum_{I,I'}\varsigma_I\varsigma_{I'}\sum_{\lambda\mu'\lambda'\mu}\Big\{&\langle\lambda\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu'\uparrow\rangle\langle\lambda'\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu\uparrow\rangle G^{\uparrow,\uparrow}_{I,I'}(\lambda\mu',\lambda'\mu)\\
&+\langle\lambda\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu'\uparrow\rangle\langle\lambda'\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu\uparrow\rangle G^{\downarrow,\downarrow}_{I,I'}(\lambda\mu',\lambda'\mu)\\
&-\langle\lambda\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu'\uparrow\rangle\langle\lambda'\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu\uparrow\rangle G^{\uparrow,\downarrow}_{I,I'}(\lambda\mu',\lambda'\mu)\\
&-\langle\lambda\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu'\uparrow\rangle\langle\lambda'\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu\uparrow\rangle G^{\downarrow,\uparrow}_{I,I'}(\lambda\mu',\lambda'\mu)\Big\}
\end{aligned}
$$



また、②式より

$$
\left[\langle\lambda\uparrow|L^x|\mu\uparrow\rangle\right]=\begin{pmatrix}0&0&-i&0&0\\0&0&0&-i&-i\sqrt{3}\\i&0&0&0&0\\0&i&0&0&0\\0&i\sqrt{3}&0&0&0\end{pmatrix}
\quad
\left[\langle\lambda\uparrow|L^y|\mu\uparrow\rangle\right]=\begin{pmatrix}0&i&0&0&0\\-i&0&0&0&0\\0&0&0&-i&i\sqrt{3}\\0&0&i&0&0\\0&0&-i\sqrt{3}&0&0\end{pmatrix}
\quad
\left[\langle\lambda\uparrow|L^z|\mu\uparrow\rangle\right]=\begin{pmatrix}0&0&0&2i&0\\0&0&i&0&0\\0&-i&0&0&0\\-2i&0&0&0&0\\0&0&0&0&0\end{pmatrix}
$$

とすると

$$
\langle\lambda\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu'\uparrow\rangle=\frac{1}{2}\sin\theta\cos\varphi\langle\lambda|L_x|\mu'\rangle+\frac{1}{2}\sin\theta\sin\varphi\langle\lambda|L_y|\mu'\rangle+\frac{1}{2}\cos\theta\langle\lambda|L_z|\mu'\rangle
$$

であるため

①スピンが垂直[001]方向のとき（θ=0°　,φ=0°　のとき）　$\langle\lambda\uparrow|\vec{L}_{[001]}\cdot\vec{S}|\mu'\uparrow\rangle=\frac{1}{2}\langle\lambda|L_z|\mu'\rangle$

②スピンが面内[100]方向のとき（θ=90°　,φ=0°　のとき）　$\langle\lambda\uparrow|\vec{L}_{[100]}\cdot\vec{S}|\mu'\uparrow\rangle=\frac{1}{2}\langle\lambda|L_x|\mu'\rangle$

$-C\sum_{I,I'}\varsigma_I\varsigma_{I'}\sum_{\lambda\mu,\lambda'\mu'}\left[G^{\uparrow\downarrow}_{I,I'}(\lambda\mu',\lambda'\mu)+G^{\downarrow\uparrow}_{I,I'}(\lambda\mu',\lambda'\mu)\right]$ は、磁化方向η(=[001],[100])を変えても変化しないので、結晶磁気異方性の計算で差分をとると消える

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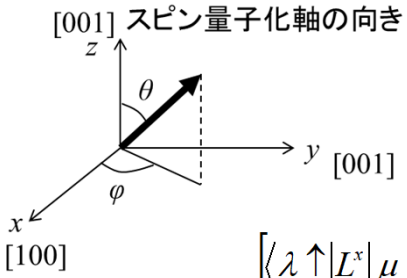
&+\langle\lambda\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu'\uparrow\rangle\langle\lambda'\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu\uparrow\rangle G^{\downarrow,\downarrow}_{I,I'}(\lambda\mu',\lambda'\mu)\\
&-\langle\lambda\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu'\uparrow\rangle\langle\lambda'\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu\uparrow\rangle G^{\uparrow,\downarrow}_{I,I'}(\lambda\mu',\lambda'\mu)\\
&-\langle\lambda\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu'\uparrow\rangle\langle\lambda'\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu\uparrow\rangle G^{\downarrow,\uparrow}_{I,I'}(\lambda\mu',\lambda'\mu)\Big\}
\end{aligned}
$$



また、②式より

$$
[\langle\lambda\uparrow|L^x|\mu\uparrow\rangle]=\begin{pmatrix}0&0&-i&0&0\\0&0&0&-i&-i\sqrt{3}\\i&0&0&0&0\\0&i&0&0&0\\0&i\sqrt{3}&0&0&0\end{pmatrix}
\quad
[\langle\lambda\uparrow|L^y|\mu\uparrow\rangle]=\begin{pmatrix}0&i&0&0&0\\-i&0&0&0&0\\0&0&0&-i&i\sqrt{3}\\0&0&i&0&0\\0&0&-i\sqrt{3}&0&0\end{pmatrix}
\quad
[\langle\lambda\uparrow|L^z|\mu\uparrow\rangle]=\begin{pmatrix}0&0&0&2i&0\\0&0&i&0&0\\0&-i&0&0&0\\-2i&0&0&0&0\\0&0&0&0&0\end{pmatrix}
$$

とすると

$$
\langle\lambda\uparrow|\vec{L}_\eta\cdot\vec{S}|\mu'\uparrow\rangle=\frac{1}{2}\sin\theta\cos\varphi\langle\lambda|L_x|\mu'\rangle+\frac{1}{2}\sin\theta\sin\varphi\langle\lambda|L_y|\mu'\rangle+\frac{1}{2}\cos\theta\langle\lambda|L_z|\mu'\rangle
$$

であるため

①スピンが垂直[001]方向のとき（θ=0°　,φ=0°　のとき）　$\langle\lambda\uparrow|\vec{L}_{[001]}\cdot\vec{S}|\mu'\uparrow\rangle=\frac{1}{2}\langle\lambda|L_z|\mu'\rangle$

②スピンが面内[100]方向のとき（θ=90°　,φ=0°　のとき）　$\langle\lambda\uparrow|\vec{L}_{[100]}\cdot\vec{S}|\mu'\uparrow\rangle=\frac{1}{2}\langle\lambda|L_x|\mu'\rangle$

結晶磁気異方性の2次摂動の表式

$$
\begin{aligned}
\Delta E^{(2)} &= E^{(2)}_{[100]} - E^{(2)}_{[001]} \\
&= \sum_{I,I'} \varsigma_I \varsigma_{I'} \sum_{\lambda\mu'\lambda'\mu} \frac{1}{4} \Big\{ \Big(\langle \lambda \uparrow | L_z | \mu' \uparrow \rangle \langle \lambda' \uparrow | L_z | \mu \uparrow \rangle - \langle \lambda \uparrow | L_x | \mu' \uparrow \rangle \langle \lambda' \uparrow | L_x | \mu \uparrow \rangle \Big) G^{\uparrow,\uparrow}_{I,I'}(\lambda\mu', \lambda'\mu) \\
&\qquad + \Big(\langle \lambda \uparrow | L_z | \mu' \uparrow \rangle \langle \lambda' \uparrow | L_z | \mu \uparrow \rangle - \langle \lambda \uparrow | L_x | \mu' \uparrow \rangle \langle \lambda' \uparrow | L_x | \mu \uparrow \rangle \Big) G^{\downarrow,\downarrow}_{I,I'}(\lambda\mu', \lambda'\mu) \\
&\qquad - \Big(\langle \lambda \uparrow | L_z | \mu' \uparrow \rangle \langle \lambda' \uparrow | L_z | \mu \uparrow \rangle - \langle \lambda \uparrow | L_x | \mu' \uparrow \rangle \langle \lambda' \uparrow | L_x | \mu \uparrow \rangle \Big) G^{\uparrow,\downarrow}_{I,I'}(\lambda\mu', \lambda'\mu) \\
&\qquad - \Big(\langle \lambda \uparrow | L_z | \mu' \uparrow \rangle \langle \lambda' \uparrow | L_z | \mu \uparrow \rangle - \langle \lambda \uparrow | L_x | \mu' \uparrow \rangle \langle \lambda' \uparrow | L_x | \mu \uparrow \rangle \Big) G^{\downarrow,\uparrow}_{I,I'}(\lambda\mu', \lambda'\mu) \Big\}
\end{aligned}
$$

joint LDOS $G_{I,I'}^{\sigma,\sigma'}(\lambda\mu',\lambda'\mu)$を使わない表式

$\mathrm{sgn}(\uparrow)=+1,\quad \mathrm{sgn}(\downarrow)=-1$

$$\begin{cases} E_{[001]}^{(2)} = -\dfrac{1}{4}\displaystyle\sum_{\sigma,\sigma'}\mathrm{sgn}(\sigma)\mathrm{sgn}(\sigma')\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I\left(\sum_{\lambda\mu'} C_{I\lambda\sigma}^{kn*}C_{I\mu'\sigma'}^{kn'}\langle\lambda\uparrow|L_z|\mu'\uparrow\rangle\right)\sum_{I'}\varsigma_{I'}\left(\sum_{\lambda'\mu} C_{I'\lambda'\sigma'}^{kn'*}C_{I'\mu\sigma}^{kn}\langle\lambda'\uparrow|L_z|\mu\uparrow\rangle\right)\dfrac{1}{\varepsilon_{kn'\sigma'}-\varepsilon_{kn\sigma}} \\ E_{[100]}^{(2)} = -\dfrac{1}{4}\displaystyle\sum_{\sigma,\sigma'}\mathrm{sgn}(\sigma)\mathrm{sgn}(\sigma')\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I\left(\sum_{\lambda\mu'} C_{I\lambda\sigma}^{kn*}C_{I\mu'\sigma'}^{kn'}\langle\lambda\uparrow|L_x|\mu'\uparrow\rangle\right)\sum_{I'}\varsigma_{I'}\left(\sum_{\lambda'\mu} C_{I'\lambda'\sigma'}^{kn'*}C_{I'\mu\sigma}^{kn}\langle\lambda'\uparrow|L_x|\mu\uparrow\rangle\right)\dfrac{1}{\varepsilon_{kn'\sigma'}-\varepsilon_{kn\sigma}} \end{cases}$$

$$\begin{cases} E_{[001]}^{(2)} = -\dfrac{1}{4}\displaystyle\sum_{\sigma,\sigma'}\mathrm{sgn}(\sigma)\mathrm{sgn}(\sigma')\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \underbrace{\left(\sum_{\mu'\lambda} C_{I\mu'\sigma}^{kn'*}C_{I\lambda\sigma'}^{kn}\langle\mu'\uparrow|L_z|\lambda\uparrow\rangle\right)^*}_{p_z^{\sigma\sigma'}(I,k,n',n)^*}\sum_{I'}\varsigma_{I'}\underbrace{\left(\sum_{\lambda'\mu} C_{I'\lambda'\sigma'}^{kn'*}C_{I'\mu\sigma}^{kn}\langle\lambda'\uparrow|L_z|\mu\uparrow\rangle\right)}_{p_z^{\sigma\sigma'}(I',k,n',n)}\dfrac{1}{\varepsilon_{kn'\sigma'}-\varepsilon_{kn\sigma}} \\ E_{[100]}^{(2)} = -\dfrac{1}{4}\displaystyle\sum_{\sigma,\sigma'}\mathrm{sgn}(\sigma)\mathrm{sgn}(\sigma')\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \underbrace{\left(\sum_{\mu'\lambda} C_{I\mu'\sigma}^{kn'*}C_{I\lambda\sigma'}^{kn}\langle\mu'\uparrow|L_x|\lambda\uparrow\rangle\right)^*}_{p_x^{\sigma\sigma'}(I,k,n',n)^*}\sum_{I'}\varsigma_{I'}\underbrace{\left(\sum_{\lambda'\mu} C_{I'\lambda'\sigma'}^{kn'*}C_{I'\mu\sigma}^{kn}\langle\lambda'\uparrow|L_x|\mu\uparrow\rangle\right)}_{p_x^{\sigma\sigma'}(I',k,n',n)}\dfrac{1}{\varepsilon_{kn'\sigma'}-\varepsilon_{kn\sigma}} \end{cases}$$

$$\begin{cases} E_{[001]}^{(2)} = -\dfrac{1}{4}\displaystyle\sum_{\sigma,\sigma'}\mathrm{sgn}(\sigma)\mathrm{sgn}(\sigma')\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \left\{p_z^{\sigma\sigma'}(I,k,n',n)\right\}^*\sum_{I'}\varsigma_{I'}p_z^{\sigma\sigma'}(I',k,n',n)\dfrac{1}{\varepsilon_{kn'\sigma'}-\varepsilon_{kn\sigma}} \\ E_{[100]}^{(2)} = -\dfrac{1}{4}\displaystyle\sum_{\sigma,\sigma'}\mathrm{sgn}(\sigma)\mathrm{sgn}(\sigma')\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \left\{p_x^{\sigma\sigma'}(I,k,n',n)\right\}^*\sum_{I'}\varsigma_{I'}p_x^{\sigma\sigma'}(I',k,n',n)\dfrac{1}{\varepsilon_{kn'\sigma'}-\varepsilon_{kn\sigma}} \end{cases}$$

結晶磁気異方性の2次摂動の表式

$$\Delta E^{(2)} = E_{[100]}^{(2)} - E_{[001]}^{(2)} = \Delta E_{\uparrow\uparrow}^{(2)} + \Delta E_{\downarrow\downarrow}^{(2)} + \Delta E_{\uparrow\downarrow}^{(2)} + \Delta E_{\downarrow\uparrow}^{(2)}$$

$$\Delta E_{\uparrow\uparrow}^{(2)} = \frac{1}{4}\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \left\{p_z^{\uparrow\uparrow}(I,k,n',n,I)\right\}^*\sum_{I'}\varsigma_{I'}p_z^{\uparrow\uparrow}(I',k,n',n)\frac{1}{\varepsilon_{kn'\uparrow}-\varepsilon_{kn\uparrow}} - \frac{1}{4}\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \left\{p_x^{\uparrow\uparrow}(I,k,n',n)\right\}^*\sum_{I'}\varsigma_{I'}p_x^{\uparrow\uparrow}(I',k,n',n)\frac{1}{\varepsilon_{kn'\uparrow}-\varepsilon_{kn\uparrow}}$$

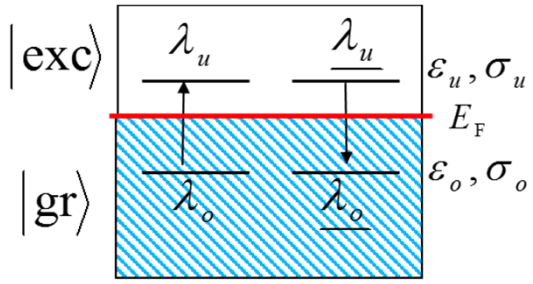
$$\Delta E_{\downarrow\downarrow}^{(2)} = \frac{1}{4}\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \left\{p_z^{\downarrow\downarrow}(I,k,n',n)\right\}^*\sum_{I'}\varsigma_{I'}p_z^{\downarrow\downarrow}(I',k,n',n)\frac{1}{\varepsilon_{kn'\downarrow}-\varepsilon_{kn\downarrow}} - \frac{1}{4}\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \left\{p_x^{\downarrow\downarrow}(I,k,n',n)\right\}^*\sum_{I'}\varsigma_{I'}p_x^{\downarrow\downarrow}(I',k,n',n)\frac{1}{\varepsilon_{kn'\downarrow}-\varepsilon_{kn\downarrow}}$$

$$\Delta E_{\uparrow\downarrow}^{(2)} = -\frac{1}{4}\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \left\{p_z^{\uparrow\downarrow}(I,k,n',n)\right\}^*\sum_{I'}\varsigma_{I'}p_z^{\uparrow\downarrow}(I',k,n',n)\frac{1}{\varepsilon_{kn'\downarrow}-\varepsilon_{kn\uparrow}} + \frac{1}{4}\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \left\{p_x^{\uparrow\downarrow}(I,k,n',n)\right\}^*\sum_{I'}\varsigma_{I'}p_x^{\uparrow\downarrow}(I',k,n',n)\frac{1}{\varepsilon_{kn'\downarrow}-\varepsilon_{kn\uparrow}}$$

$$\Delta E_{\downarrow\uparrow}^{(2)} = -\frac{1}{4}\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \left\{p_z^{\downarrow\uparrow}(I,k,n',n)\right\}^*\sum_{I'}\varsigma_{I'}p_z^{\downarrow\uparrow}(I',k,n',n)\frac{1}{\varepsilon_{kn'\uparrow}-\varepsilon_{kn\downarrow}} + \frac{1}{4}\sum_k \sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_I \varsigma_I \left\{p_x^{\downarrow\uparrow}(I,k,n',n)\right\}^*\sum_{I'}\varsigma_{I'}p_x^{\downarrow\uparrow}(I',k,n',n)\frac{1}{\varepsilon_{kn'\uparrow}-\varepsilon_{kn\downarrow}}$$

スピン軌道相互作用の2次摂動による軌道モーメントの導出

スピン軌道相互作用の1次摂動による波動関数の補正



$$\left|\delta\mathrm{gr}^{(1)}\right\rangle = -\sum_{\mathrm{exc}} \frac{\left\langle \mathrm{exc}\left|H_\eta^{\mathrm{SO}}\right|\mathrm{gr}\right\rangle}{\varepsilon_{\mathrm{exc}} - \varepsilon_{\mathrm{gr}}}\left|\mathrm{exc}\right\rangle$$

原子iの軌道モーメント　（1次摂動の波動関数による軌道角運動量演算子L_ηの期待値）

$$\left\langle \vec{L}_\eta \right\rangle_i = \sum_{\mathrm{gr}} \left\langle \mathrm{gr} + \delta\mathrm{gr}^{(1)}\left|\vec{L}_\eta\right|\mathrm{gr} + \delta\mathrm{gr}^{(1)}\right\rangle = \sum_{\mathrm{gr}} \left\{\left\langle \mathrm{gr}\left|\vec{L}_\eta\right|\mathrm{gr}\right\rangle + \left\langle \mathrm{gr}\left|\vec{L}_\eta\right|\mathrm{gr} + \delta\mathrm{gr}^{(1)}\right\rangle + \left\langle \mathrm{gr} + \delta\mathrm{gr}^{(1)}\left|\vec{L}_\eta\right|\mathrm{gr}\right\rangle + \left\langle \delta\mathrm{gr}^{(1)}\left|\vec{L}_\eta\right|\delta\mathrm{gr}^{(1)}\right\rangle\right\}$$

スピン軌道相互作用がないと軌道モーメントはゼロ

補正$|\delta\mathrm{gr}^{(1)}\rangle$の2次なので無視

$$\approx \sum_{\mathrm{gr}} \left\langle \mathrm{gr}\left|\vec{L}_\eta\cdot\delta\right|\mathrm{gr}^{(1)}\right\rangle + \sum_{\mathrm{gr}} \left\langle \delta\mathrm{gr}^{(1)}\left|\vec{L}_\eta\cdot\delta\right|\mathrm{gr}\right\rangle = -\sum_{\mathrm{gr,exc}} \left\langle \mathrm{gr}\left|\vec{L}_\eta\right|\mathrm{exc}\right\rangle \frac{\left\langle \mathrm{exc}\left|H_\eta^{\mathrm{SO}}\right|\mathrm{gr}\right\rangle}{\varepsilon_{\mathrm{exc}} - \varepsilon_{\mathrm{gr}}} - \sum_{\mathrm{gr,exc}} \frac{\left\langle \mathrm{gr}\left|H_\eta^{\mathrm{SO}}\right|\mathrm{exc}\right\rangle}{\varepsilon_{\mathrm{exc}} - \varepsilon_{\mathrm{gr}}} \left\langle \mathrm{exc}\left|\vec{L}_\eta\right|\mathrm{gr}\right\rangle$$

$$H_\eta^{\mathrm{SO}} = \sum_I \zeta_I \vec{L}_\eta \cdot \vec{S} \qquad \left|\mathrm{gr}\right\rangle = \left|k, n, \sigma\right\rangle = \sum_{j,\mu} c_{j\mu\sigma}^{kn} \left|j\mu\sigma\right\rangle$$

を代入

$$\left|\mathrm{exc}\right\rangle = \left|k, n', \sigma'\right\rangle = \sum_{i',\lambda'} c_{i'\lambda'\sigma'}^{kn'} \left|i'\lambda'\sigma'\right\rangle$$

$$-\sum_k \sum_{\substack{n\sigma \\ (\mathrm{occ})}} \sum_{\substack{n'\sigma' \\ (\mathrm{unocc})}} \left\langle kn\sigma\left|\vec{L}_\eta\right|kn'\sigma'\right\rangle \frac{\left\langle kn'\sigma'\left|H_\eta^{\mathrm{SO}}\right|kn\sigma\right\rangle}{\varepsilon_{kn'\sigma'} - \varepsilon_{kn\sigma}} =$$

$$= -\sum_k \sum_{\substack{n\sigma \\ (\mathrm{occ})}} \sum_{\substack{n'\sigma' \\ (\mathrm{unocc})}} \sum_{i\lambda} \left\langle i\lambda\sigma\left|C_{i\lambda\sigma}^{kn*} \vec{L}_\eta \sum_{j'\mu'} C_{j'\mu'\sigma'}^{kn'}\right| j'\mu'\sigma'\right\rangle \frac{\sum_{i'\lambda'} \left\langle i'\lambda'\sigma'\left|C_{i'\lambda'\sigma'}^{kn'*}\left(\sum_I \varsigma_I \vec{L}_\eta \cdot \vec{S}\right)\right.\right. \sum_{j\mu} C_{j\mu\sigma}^{kn} \left|j\mu\sigma\right\rangle}{\varepsilon_{kn'\sigma'} - \varepsilon_{kn\sigma}}$$

$$= -\sum_{k}\sum_{\substack{n\sigma\\(\mathrm{occ})}}\sum_{\substack{n'\sigma'\\(\mathrm{unocc})}}\sum_{i\lambda}\left\langle i\lambda\sigma\left|C^{kn*}_{i\lambda\sigma}\vec{L}_{\eta}\sum_{j'\mu'}C^{kn'}_{j'\mu'\sigma'}\right|j'\mu'\sigma'\right\rangle\frac{\sum_{i'\lambda'}\left\langle i'\lambda'\sigma'\left|C^{kn'*}_{i'\lambda'\sigma'}\left(\sum_{I}\varsigma_{I}\vec{L}_{\eta}\cdot\vec{S}\right)\sum_{j\mu}C^{kn}_{j\mu\sigma}\right|j\mu\sigma\right\rangle}{\varepsilon_{kn'\sigma'}-\varepsilon_{kn\sigma}}$$

軌道角運動量演算子は同一原子内で定義されかつスピンを含まないため

スピン軌道相互作用は1電子相互作用で同一原子内のみ働くため

$$= -\sum_{k}\sum_{\substack{n\sigma\\(\mathrm{occ})}}\sum_{\substack{n'\sigma'\\(\mathrm{unocc})}}\sum_{i\lambda}\sum_{j'\mu'}\left\langle i\lambda\sigma\left|\delta_{ij'}\delta_{\sigma\sigma'}\vec{L}_{\eta}\right|j'\mu'\sigma'\right\rangle C^{kn*}_{i\lambda\sigma}C^{kn'}_{j'\mu'\sigma'}\frac{\sum_{I}\sum_{i'\lambda'}\sum_{j\mu}\left\langle i'\lambda'\sigma\left|\delta_{i'I}\delta_{Ij}\left(\varsigma_{I}\vec{L}_{\eta}\cdot\vec{S}\right)\right|j\mu\sigma\right\rangle C^{kn'*}_{i'\lambda'\sigma'}C^{kn}_{j\mu\sigma}}{\varepsilon_{kn'\sigma'}-\varepsilon_{kn\sigma}}$$

$$= -\sum_{k}\sum_{\sigma}\sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}\sum_{\lambda\mu'}\left\langle i\lambda\sigma\left|\vec{L}_{\eta}\right|i\mu'\sigma\right\rangle C^{kn*}_{i\lambda\sigma}C^{kn'}_{i\mu'\sigma}\frac{\sum_{I}\sum_{\lambda'\mu}\left\langle I\lambda'\sigma\left|\varsigma_{I}\vec{L}_{\eta}\cdot\vec{S}\right|I\mu\sigma\right\rangle C^{kn'*}_{I\lambda'\sigma}C^{kn}_{I\mu\sigma}}{\varepsilon_{kn'\sigma}-\varepsilon_{kn\sigma}}$$

$$= -\sum_{\sigma}\sum_{\lambda\mu'\lambda'\mu}\left\langle\lambda\sigma\left|\vec{L}_{\eta}\right|\mu'\sigma\right\rangle\sum_{I}\varsigma_{I}\left\langle I\lambda'\sigma\left|\vec{L}_{\eta}\cdot\vec{S}\right|I\mu\sigma\right\rangle\sum_{k}\sum_{\substack{n\\(\mathrm{occ})}}\sum_{\substack{n'\\(\mathrm{unocc})}}C^{kn*}_{i\lambda\sigma}C^{kn'}_{i\mu'\sigma}\frac{1}{\varepsilon_{kn'\sigma}-\varepsilon_{kn\sigma}}C^{kn'*}_{I\lambda'\sigma}C^{kn}_{I\mu\sigma}$$

$$= -\sum_{\sigma}\sum_{\lambda\mu'\lambda'\mu}\left\langle\lambda\sigma\left|\vec{L}_{\eta}\right|\mu'\sigma\right\rangle\left\langle\lambda'\sigma\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\sigma\right\rangle\sum_{I}\varsigma_{I}\underbrace{\sum_{k}\sum_{n}\int_{-\infty}^{\varepsilon_{\mathrm{F}}}d\varepsilon\,\delta\left(\varepsilon-\varepsilon_{kn\sigma}\right)\sum_{n'}\int_{\varepsilon_{\mathrm{F}}}^{+\infty}d\varepsilon'\,\delta\left(\varepsilon'-\varepsilon_{kn'\sigma}\right)C^{kn*}_{i\lambda\sigma}C^{kn'}_{i\mu'\sigma}\frac{1}{\varepsilon'-\varepsilon}C^{kn'*}_{I\lambda'\sigma}C^{kn}_{I\mu\sigma}}_{G^{\sigma,\sigma}_{i,I}\left(\lambda\mu',\lambda'\mu\right)}$$

$$= -\sum_{\sigma}\sum_{\lambda\mu'\lambda'\mu}\left\langle\lambda\sigma\left|\vec{L}_{\eta}\right|\mu'\sigma\right\rangle\left\langle\lambda'\sigma\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\sigma\right\rangle\sum_{I}\varsigma_{I}G^{\sigma\sigma}_{i,I}\left(\lambda\mu',\lambda'\mu\right)$$

$$= -\sum_{\lambda\mu'\lambda'\mu}\left[\left\langle\lambda\uparrow\left|\vec{L}_{\eta}\right|\mu'\uparrow\right\rangle\left\langle\lambda'\uparrow\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\uparrow\right\rangle\sum_{I}\varsigma_{I}G^{\uparrow\uparrow}_{i,I}\left(\lambda\mu',\lambda'\mu\right)+\left\langle\lambda\downarrow\left|\vec{L}_{\eta}\right|\mu'\downarrow\right\rangle\left\langle\lambda'\downarrow\left|\vec{L}_{\eta}\cdot\vec{S}\right|\mu\downarrow\right\rangle\sum_{I}\varsigma_{I}G^{\downarrow\downarrow}_{i,I}\left(\lambda\mu',\lambda'\mu\right)\right]$$

ここで、②,③式より $\langle \lambda\sigma | \vec{L}_\eta | \mu\sigma \rangle = 2\,\mathrm{sgn}(\sigma) \langle \lambda\sigma | \vec{L}_\eta \cdot \vec{S} | \mu\sigma \rangle \vec{e}_\eta$ $\quad \mathrm{sgn}(\sigma) = \begin{cases} +1 & (\sigma = \uparrow) \\ -1 & (\sigma = \downarrow) \end{cases}$

$\vec{e}_\eta$ はスピンの方向の単位ベクトル

（軌道モーメントはスピンの方向にしか成分をもたないので）

スピンによって符号が変わることがポイント

よって、

$$-\sum_k \sum_{\substack{n\sigma \\ (\mathrm{occ})}} \sum_{\substack{n'\sigma' \\ (\mathrm{unocc})}} \langle kn\sigma | \vec{L}_\eta | kn'\sigma' \rangle \frac{\langle kn'\sigma' | H_\eta^{\mathrm{SO}} | kn\sigma \rangle}{\varepsilon_{kn'\sigma'} - \varepsilon_{kn\sigma}}$$

$$= -\sum_{\lambda\mu'\lambda'\mu} \left[2\langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle \sum_I \varsigma_I G_{i,I}^{\uparrow\uparrow}(\lambda\mu', \lambda'\mu) - 2\langle \lambda\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu'\downarrow \rangle \langle \lambda'\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu\downarrow \rangle \sum_I \varsigma_I G_{i,I}^{\downarrow\downarrow}(\lambda\mu', \lambda'\mu) \right] \vec{e}_\eta$$

また、⓪式より $\langle \lambda\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu'\downarrow \rangle \langle \lambda'\downarrow | \vec{L}_\eta \cdot \vec{S} | \mu\downarrow \rangle = \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle$

$$-\sum_k \sum_{\substack{n\sigma \\ (\mathrm{occ})}} \sum_{\substack{n'\sigma' \\ (\mathrm{unocc})}} \langle kn\sigma | \vec{L}_\eta | kn'\sigma' \rangle \frac{\langle kn'\sigma' | H_\eta^{\mathrm{SO}} | kn\sigma \rangle}{\varepsilon_{kn'\sigma'} - \varepsilon_{kn\sigma}}$$

$$= +2 \sum_{\lambda\mu'\lambda'\mu} \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle \sum_I \varsigma_I \left[G_{i,I}^{\downarrow\downarrow}(\lambda\mu', \lambda'\mu) - G_{i,I}^{\uparrow\uparrow}(\lambda\mu', \lambda'\mu) \right] \vec{e}_\eta$$

全く、同様に

$$-\sum_{\mathrm{gr,exc}} \frac{\langle \mathrm{gr} | H_\eta^{\mathrm{SO}} | \mathrm{exc} \rangle}{\varepsilon_{\mathrm{exc}} - \varepsilon_{\mathrm{gr}}} \langle \mathrm{exc} | \vec{L}_\eta | \mathrm{gr} \rangle$$

$$= +2 \sum_{\lambda\mu'\lambda'\mu} \langle \lambda\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu'\uparrow \rangle \langle \lambda'\uparrow | \vec{L}_\eta \cdot \vec{S} | \mu\uparrow \rangle \sum_I \varsigma_I \left[G_{i,I}^{\downarrow\downarrow}(\lambda\mu', \lambda'\mu) - G_{i,I}^{\uparrow\uparrow}(\lambda\mu', \lambda'\mu) \right] \vec{e}_\eta$$

$$\left\langle \vec{L}_\eta \right\rangle_i \approx \sum_{\mathrm{gr}} \left\langle \mathrm{gr} \middle| \vec{L}_\eta \cdot \delta \middle| \mathrm{gr}^{(1)} \right\rangle + \sum_{\mathrm{gr}} \left\langle \delta \mathrm{gr}^{(1)} \middle| \vec{L}_\eta \cdot \delta \middle| \mathrm{gr} \right\rangle = -\sum_{\mathrm{gr,exc}} \left\langle \mathrm{gr} \middle| \vec{L}_\eta \middle| \mathrm{exc} \right\rangle \frac{\left\langle \mathrm{exc} \middle| H_\eta^{\mathrm{SO}} \middle| \mathrm{gr} \right\rangle}{\varepsilon_{\mathrm{exc}} - \varepsilon_{\mathrm{gr}}} - \sum_{\mathrm{gr,exc}} \frac{\left\langle \mathrm{gr} \middle| H_\eta^{\mathrm{SO}} \middle| \mathrm{exc} \right\rangle}{\varepsilon_{\mathrm{exc}} - \varepsilon_{\mathrm{gr}}} \left\langle \mathrm{exc} \middle| \vec{L}_\eta \middle| \mathrm{gr} \right\rangle$$

$$= +4 \sum_{\lambda\mu'\lambda'\mu} \left\langle \lambda \uparrow \middle| \vec{L}_\eta \cdot \vec{S} \middle| \mu' \uparrow \right\rangle \left\langle \lambda' \uparrow \middle| \vec{L}_\eta \cdot \vec{S} \middle| \mu \uparrow \right\rangle \sum_I \varsigma_I \left[G_{i,I}^{\downarrow\downarrow}(\lambda\mu', \lambda'\mu) - G_{i,I}^{\uparrow\uparrow}(\lambda\mu', \lambda'\mu) \right] \vec{e}_\eta$$

$$\boxed{\left\langle \vec{L}_\eta \right\rangle_i = +4 \sum_{\lambda\mu'\lambda'\mu} \left\langle \lambda \uparrow \middle| \vec{L}_\eta \cdot \vec{S} \middle| \mu' \uparrow \right\rangle \left\langle \lambda' \uparrow \middle| \vec{L}_\eta \cdot \vec{S} \middle| \mu \uparrow \right\rangle \sum_I \varsigma_I \left[G_{i,I}^{\downarrow\downarrow}(\lambda\mu', \lambda'\mu) - G_{i,I}^{\uparrow\uparrow}(\lambda\mu', \lambda'\mu) \right] \vec{e}_\eta}$$

①スピンが垂直[001]方向のとき（θ=0°　,φ=0°　のとき）

$$\left\langle \lambda \uparrow \middle| \vec{L}_{[001]} \cdot \vec{S} \middle| \mu' \uparrow \right\rangle = \frac{1}{2} \left\langle \lambda \middle| L_z \middle| \mu' \right\rangle$$

②スピンが面内[100]方向のとき（θ=90°　,φ=0°　のとき）

$$\left\langle \lambda \uparrow \middle| \vec{L}_{[100]} \cdot \vec{S} \middle| \mu' \uparrow \right\rangle = \frac{1}{2} \left\langle \lambda \middle| L_x \middle| \mu' \right\rangle$$

$$\left\langle \vec{L}_{[001]} \right\rangle_i = + \sum_{\lambda\mu'\lambda'\mu} \left\langle \lambda \uparrow \middle| L_z \middle| \mu' \uparrow \right\rangle \left\langle \lambda' \uparrow \middle| L_z \middle| \mu \uparrow \right\rangle \sum_I \varsigma_I \left[G_{i,I}^{\downarrow\downarrow}(\lambda\mu', \lambda'\mu) - G_{i,I}^{\uparrow\uparrow}(\lambda\mu', \lambda'\mu) \right] \vec{e}_{[001]}$$

$$\left\langle \vec{L}_{[100]} \right\rangle_i = + \sum_{\lambda\mu'\lambda'\mu} \left\langle \lambda \uparrow \middle| L_x \middle| \mu' \uparrow \right\rangle \left\langle \lambda' \uparrow \middle| L_x \middle| \mu \uparrow \right\rangle \sum_I \varsigma_I \left[G_{i,I}^{\downarrow\downarrow}(\lambda\mu', \lambda'\mu) - G_{i,I}^{\uparrow\uparrow}(\lambda\mu', \lambda'\mu) \right] \vec{e}_{[100]}$$

Gilbert磁気ダンピング項の導出

系のハミルトニアン $H = H^0 + H^1$

$$H^1 = \frac{\Delta}{\langle S^z \rangle}\left(\langle S^+ \rangle S^- + \langle S- \rangle S^+\right)$$ 摂動項

$$H^0 = H_{\mathrm{Kin}} + H_{\mathrm{SO}} + H_{\mathrm{F}}^0$$ 非摂動項

$$H^{\mathrm{Kin}} = \sum_{ij} t_{ij} c_i^+ c_j$$ 運動項

$$H^{\mathrm{SO}} = \zeta \vec{L} \cdot \vec{S}$$ スピン軌道相互作用項

$$H_{\mathrm{F}}^0 = \Delta S_{\mathrm{z}}$$ 強磁性項

$$S^-(t) = e^{iH^0 t/\hbar} S^- e^{-iH^0 t/\hbar}$$ 相互作用表示

$$\frac{dS^-(t)}{dt} = \frac{d}{dt}\left\{e^{iH^0 t/\hbar} S^- e^{-iH^0 t/\hbar}\right\} = \frac{i}{\hbar} H^0 e^{iH^0 t/\hbar} S^- e^{-iH^0 t/\hbar} + e^{iH^0 t/\hbar} S^- e^{-iH^0 t/\hbar}\left(-\frac{i}{\hbar} H^0\right) = \frac{i}{\hbar}\left\{H^0 S^-(t) - S^-(t) H^0\right\} = \frac{i}{\hbar}\left[H^0, S^-(t)\right]$$

$$\boxed{\frac{dS^-(t)}{dt} = \frac{i}{\hbar}\left[H^0, S^-(t)\right]} \Rightarrow \boxed{\frac{dS^-(t)}{dt} = \mathcal{L} S^-(t)}$$

$\mathcal{L}$:リュービル演算子

$$\Rightarrow \frac{1}{S^-(t)} dS^-(t) = \mathcal{L}\, dt \Rightarrow \int \frac{1}{S^-(t)} dS^-(t) = \int \mathcal{L}\, dt \Rightarrow \log S^-(t) = \mathcal{L} t + C \Rightarrow S^-(t) = e^{\mathcal{L} t} e^C \Rightarrow S^-(0) = e^C$$

$$\Rightarrow \boxed{S^-(t) = e^{\mathcal{L} t} S^-(0)}$$ 形式解

$e^{\mathcal{L} t}$:時間発展演算子

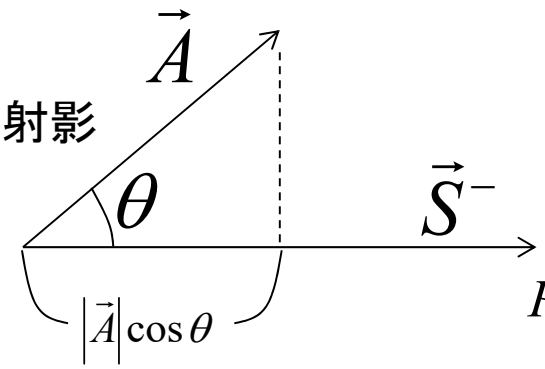
$$\boxed{\mathcal{L} S^-(0) = \mathcal{L} S^- = \dot{S}^-}$$

射影演算子の導入

演算子AのS^-成分（遅い運動）への射影

$$\boxed{PA = \frac{(A, S^+)}{(S^-, S^+)} S^-}$$

$$\boxed{\text{演算子}A\text{と}S^-\text{の内積} \equiv (A, S^+)}$$



射影の大きさ $|P\vec{A}| = |\vec{A}|\cos\theta$

内積 $(\vec{A}, \vec{S}^-) = |\vec{S}^-||\vec{A}|\cos\theta = |\vec{S}^-||P\vec{A}|$

$$P\vec{A} = |P\vec{A}|\frac{\vec{S}^-}{|\vec{S}^-|} = \frac{(\vec{A}, \vec{S}^-)}{|\vec{S}^-|}\frac{\vec{S}^-}{|\vec{S}^-|} = \frac{(\vec{A}, \vec{S}^-)}{|\vec{S}^-|^2}\vec{S}^-$$

$(1-P)A$：演算子AのS^-を含まない成分への射影 ⇒ 定義より：$(1-P)\{PA\}=0$

次に、射影演算子を使って、$S^-(t)$の運動方程式をS^-を含む成分と含まない成分に分ける。

$$\frac{dS^-(t)}{dt}=\mathcal{L}S^-(t)=P\{\mathcal{L}S^-(t)\}+(1-P)\{\mathcal{L}S^-(t)\}$$

（$\mathcal{L}$：とPは可換）

⇒ $$\frac{dS^-(t)}{dt}=P\mathcal{L}S^-(t)+(1-P)\mathcal{L}S^-(t)$$

⇒ $$\frac{dS^-(t)}{dt}-(1-P)\mathcal{L}S^-(t)=P\mathcal{L}S^-(t)$$

非同次方程式 $\frac{dy}{dx}+f(x)y=g(x)$

の一般解 $y=e^{-\int f(x)dx}\left\{\int_0^x e^{\int f(x')dx'}g(x')dx'+y_0\right\}$

$y\Rightarrow S^-(t)$

$f(x)\Rightarrow -(1-P)\mathcal{L}$ $\quad g(x)\Rightarrow P\mathcal{L}S^-(t)$

⇒ $$S^-(t)=e^{\int(1-P)\mathcal{L}dt}\left\{\int_0^t e^{-\int(1-P)\mathcal{L}dt'}\mathcal{L}PS^-(t')dt'+S^-(0)\right\}$$ ⇒ $$S^-(t)=e^{t(1-P)\mathcal{L}}\left\{\int_0^t e^{-t'(1-P)\mathcal{L}}\mathcal{L}PS^-(t')dt'+S^-\right\}$$

⇒ $$S^-(t)=\int_0^t e^{(t-t')(1-P)\mathcal{L}}\mathcal{L}PS^-(t')dt'+e^{t(1-P)\mathcal{L}}S^-$$

これを、 $S^-(t)=PS^-(t)+(1-P)S^-(t)$

の右辺第２項に代入。 $$S^-(t)=PS^-(t)+(1-P)\int_0^t e^{(t-t')(1-P)\mathcal{L}}P\mathcal{L}\underline{\underline{S^-(t')}}dt'+(1-P)e^{t(1-P)\mathcal{L}}S^-$$

（$\mathcal{L}$：とPは可換）

$$S^-(t)=PS^-(t)+\int_0^t e^{(t-t')(1-P)\mathcal{L}}P\mathcal{L}(1-P)\underline{\underline{e^{t'\mathcal{L}}S^-}}dt'+e^{t(1-P)\mathcal{L}}(1-P)S^-$$

これを、更に

このS⁻(t)の形式解を　$\dfrac{dS^-(t)}{dt} = \mathcal{L}\, S^-(t)$ に代入。

$$\frac{dS^-(t)}{dt} = \mathcal{L}\, PS^-(t) + \int_0^t dt' e^{(t-t')(1-P)\mathcal{L}} P\mathcal{L}(1-P) e^{t'\mathcal{L}} \underline{\underline{\mathcal{L}\, S^-}} + e^{t(1-P)\mathcal{L}}(1-P)\underline{\underline{\mathcal{L}\, S^-}}$$

$$\frac{dS^-(t)}{dt} = \mathcal{L}\, PS^-(t) + \left\{ \int_0^t dt' e^{t'\mathcal{L}} P\mathcal{L}\, e^{(t-t')(1-P)\mathcal{L}} \right\}(1-P)\dot{S}^- + e^{t(1-P)\mathcal{L}}(1-P)\dot{S}^-$$

積分の中を変数変換　$t - t' = s$ ⇨ $t' = t - s$　　$t' : 0 \to t$

⇨ $dt' = -ds$　　$s : t \to 0$

$$\frac{dS^-(t)}{dt} = \mathcal{L}\, PS^-(t) - \left\{ \int_s^0 ds e^{(t-s)\mathcal{L}} P\mathcal{L}\, e^{s(1-P)\mathcal{L}} \right\}(1-P)\dot{S}^- + e^{t(1-P)\mathcal{L}}(1-P)\dot{S}^-$$

$s \Rightarrow t'$

$$\Rightarrow \boxed{\frac{dS^-(t)}{dt} = \mathcal{L}\, PS^-(t) + \left\{ \int_0^{t'} dt' e^{(t-t')\mathcal{L}} P\mathcal{L}\, e^{t'(1-P)\mathcal{L}} \right\}(1-P)\dot{S}^- + e^{t(1-P)\mathcal{L}}(1-P)\dot{S}^-}$$

また、逆に、$\dfrac{dS^-(t)}{dt} = \mathcal{L}\, S^-(t)$　より、

$$\frac{dS^-(t)}{dt} = P\mathcal{L}\, S^-(t) + (1-P)\mathcal{L}\, S^-(t) = \mathcal{L}\, PS^-(t) + (1-P)\mathcal{L}\, e^{t\mathcal{L}} S^- = \mathcal{L}\, PS^-(t) + e^{t\mathcal{L}}(1-P)\mathcal{L}\, S^-$$

$$\frac{dS^-(t)}{dt} = \mathcal{L}\, PS^-(t) + e^{tP\mathcal{L} + t(1-P)\mathcal{L}}(1-P)\dot{S}^-$$

比べると、　$e^{t\mathcal{L}} = e^{tP\mathcal{L} + t(1-P)\mathcal{L}} = \displaystyle\int_0^{t'} dt' e^{(t-t')\mathcal{L}} P\mathcal{L}\, e^{t'(1-P)\mathcal{L}} + e^{t(1-P)\mathcal{L}}$　　森公式

$$\boxed{\frac{dS^-(t)}{dt} = \underline{\mathcal{L}PS^-(t)} + \underline{\left\{\int_0^{t'} dt' e^{(t-t')\mathcal{L}} P\mathcal{L} e^{t'(1-P)\mathcal{L}}\right\}(1-P)\dot{S}^-} + \underline{e^{t(1-P)\mathcal{L}}(1-P)\dot{S}^-}}$$

S^-を含む成分の時間発展
⇒遅い運動
⇒磁化の歳差運動

S^-を含まない成分（ランダムなスピントルク）の過去から現在までの相関⇒摩擦

S^-を含まない成分の時間発展
⇒速い運動
（ランダム力⇒　スピントルク）
（スピンを反転させる力）

$$\mathcal{L}PS^-(t) = \mathcal{L}Pe^{t\mathcal{L}}S^- = e^{t\mathcal{L}}P\mathcal{L}S^- = e^{t\mathcal{L}}P\dot{S}^- = e^{t\mathcal{L}}\frac{(\dot{S}^-,S^+)}{(S^-,S^+)}S^- = \frac{\left(\frac{i}{\hbar}[H^0,S^-],S^+\right)}{(S^-,S^+)}e^{t\mathcal{L}}S^- = -i\frac{([S^-,H^0],S^+)}{\hbar(S^-,S^+)}S^-(t)$$

$$\Omega \equiv \frac{([S^-,H^0],S^+)}{\hbar(S^-,S^+)}$$

Ωを固有周波数と定義すると、

$$\boxed{\mathcal{L}PS^-(t) = -i\Omega S^-(t)}$$

$$(1-P)\dot{S}^- = \dot{S}^- - P\dot{S}^- = \frac{i}{\hbar}[H^0,S^-] - \frac{(\dot{S}^-,S^+)}{(S^-,S^+)}S^- = -\frac{i}{\hbar}[S^-,H^0] - \frac{\left(\frac{i}{\hbar}[H^0,S^-],S^+\right)}{(S^-,S^+)}S^- = -\frac{i}{\hbar}[S^-,H^0] + i\frac{([S^-,H^0],S^+)}{\hbar(S^-,S^+)}S^-$$

$$(1-P)\dot{S}^- = -i\left\{\frac{1}{\hbar}[S^-,H^0] - \Omega S^-\right\}$$

トルク演算子 $\phi^- \equiv \frac{1}{\hbar}[S^-,H^0] - \Omega S^-$ を定義すると、

$$\boxed{(1-P)\dot{S}^- = -i\phi^-}$$

また、トルク演算子の時間発展は、

$$\boxed{e^{t(1-P)\mathcal{L}}(1-P)\dot{S}^- = -ie^{t(1-P)\mathcal{L}}\phi^- = -i\phi^-(t)}$$

よって、

$$\boxed{\frac{dS^-(t)}{dt} = -i\Omega S^-(t) - i\left\{\int_0^{t'} dt' e^{(t-t')\mathcal{L}} \underline{\underline{P\mathcal{L}\phi^-(t')}}\right\} - i\phi^-(t)}$$

$$P\mathcal{L}\phi^-(t') = \frac{(\mathcal{L}\phi^-(t'),S^+)}{(S^-,S^+)}S^-$$

$$P\mathcal{L}\phi^-(t') = \frac{\left(\mathcal{L}\phi^-(t'), S^+\right)}{\left(S^-, S^+\right)} S^- = -\frac{\left(\phi^-(t'), \mathcal{L}S^+\right)}{\left(S^-, S^+\right)} S^- = -\frac{\left(\phi^-(t'), \dot{S}^+\right)}{\left(S^-, S^+\right)} S^-$$

内積の性質

$$\left(\mathcal{L}\phi^-(t'), S^+\right) \equiv \int d\Gamma \mathcal{L}\phi^-(t') S^+ = \int d\Gamma \frac{d\phi^-(t')}{dt'} S^+ = \int d\Gamma \frac{d\phi^-(t')}{d\Gamma}\frac{d\Gamma}{dt} S^+ = \int d\Gamma \frac{d\phi^-(t')}{d\Gamma}\left(\dot{\Gamma} S^+\right)$$

部分積分すると、 $= \phi^-(t')\left(\dot{\Gamma} S^+\right) - \int d\Gamma \phi^-(t') \frac{d}{d\Gamma}\left(\dot{\Gamma} S^+\right) = -\int d\Gamma \phi^-(t') \frac{d}{d\Gamma}\frac{d\Gamma}{dt} S^+ = -\int d\Gamma \phi^-(t') \frac{dS^+}{dt} = -\int d\Gamma \phi^-(t') \mathcal{L} S^+$

$$\left(\mathcal{L}\phi^-(t'), S^+\right) = \left(\phi^-(t'), \mathcal{L}S^+\right) = \left(\phi^-(t'), \dot{S}^+\right)$$

ここで、 $\phi^- = \frac{1}{\hbar}\left[S^-, H^0\right] - \Omega S^- = -\frac{1}{\hbar}\left[H^0, S^-\right] - \Omega S^- = i\frac{i}{\hbar}\left[H^0, S^-\right] - \Omega S^- = i\dot{S}^- - \Omega S^-$

$\Rightarrow$ $\dot{S}^- = -i\phi^- - i\Omega S^-$ $\Rightarrow$ $\dot{S}^+ = i\phi^+ + i\Omega S^+$

$$P\mathcal{L}\phi^-(t') = -\frac{\left(\phi^-(t'), i\phi^+ + i\Omega S^+\right)}{\left(S^-, S^+\right)} S^- \Rightarrow P\mathcal{L}\phi^-(t') = -i\frac{\left(\phi^-(t'), \phi^+\right)}{\left(S^-, S^+\right)} S^- - i\Omega \underline{\frac{\left(\phi^-(t'), S^+\right)}{\left(S^-, S^+\right)} S^-}$$

$$\frac{\left(\phi^-(t'), S^+\right)}{\left(S^-, S^+\right)} S^- = P\phi^-(t') = Pe^{t'(1-P)\mathcal{L}}(1-P)\dot{S}^- = e^{t'(1-P)\mathcal{L}} P(1-P)\dot{S}^- = 0$$

射影演算子の定義より、任意の演算子Aに対して、$P(1\text{-}P)A=0$

よって、 $$\boxed{P\mathcal{L}\phi^-(t') = -i\frac{\left(\phi^-(t'), \phi^+\right)}{\left(S^-, S^+\right)} S^-}$$

ゆえに、 $$\frac{dS^-(t)}{dt} = -i\Omega S^-(t) - i\left\{\int_0^{t'} dt' e^{(t-t')\mathcal{L}}\left(-i\frac{(\phi(t'),\phi^+)}{(S^-,S^+)}\right)S^-\right\} - i\phi^-(t)$$

$$\boxed{\frac{dS^-(t)}{dt} = -i\Omega S^-(t) - \left\{\int_0^{t'} dt' \frac{(\phi(t'),\phi^+)}{(S^-,S^+)} S^-(t-t')\right\} - i\phi^-(t)}$$

ここでは、演算子の内積を、演算子の交換関係のカノニカル相関？として定義する。 $\boxed{(\phi(t'),\phi^+) \equiv \langle[\phi(t'),\phi^+]\rangle_0}$

$$(S^-,S^+) = \langle[S^-,S^+]\rangle_0 = \langle S^-S^+ - S^+S^-\rangle_0 = \langle(S^x - iS^y)(S^x + iS^y) - (S^x + iS^y)(S^x - iS^y)\rangle_0$$

$$= 2i\langle S^xS^y - S^yS^x\rangle_0 = 2i\langle[S^x,S^y]\rangle_0 = 2i\langle i\hbar S^z\rangle_0 = -2\hbar\langle S^z\rangle_0 = \hbar M$$ M:磁化

$$\boxed{\frac{dS^-(t)}{dt} = -i\Omega S^-(t) - \left\{\int_0^{t'} dt' \frac{\langle[\phi(t'),\phi^+]\rangle_0}{\hbar M} S^-(t-t')\right\} - i\phi^-(t)}$$

ここで、両辺に対して、Pの射影をとる。 $P\phi^-(t) = 0$ より、

$$\frac{dPS^-(t)}{dt} = -i\Omega PS^-(t) - \left\{\int_0^{t'} dt' \frac{\langle[\phi(t'),\phi^+]\rangle_0}{\hbar M} PS^-(t-t')\right\}$$

$$\Rightarrow \frac{d}{dt}\frac{\langle[S^-(t),S^+]\rangle_0}{\hbar M}S^- = -i\Omega\frac{\langle[S^-(t),S^+]\rangle_0}{\hbar M}S^- - \left\{\int_0^{t'} dt' \frac{\langle[\phi(t'),\phi^+]\rangle_0}{\hbar M}\frac{\langle[S^-(t-t'),S^+]\rangle_0}{\hbar M}S^-\right\}$$

トルク応答関数として、 $f(t') \equiv \langle [\phi^-(t'), \phi^+] \rangle_0$ と定義する。

応答関数として、 $\chi_0(t) \equiv \dfrac{\langle [S^-(t), S^+] \rangle_0}{\hbar M}$ として定義すると、S^-に対して、

$$\Rightarrow \quad \frac{d\chi(t)}{dt} = -i\Omega\chi(t) - (\hbar M)^{-1}\left\{\int_0^{t'} dt' f(t')\chi(t-t')\right\}$$

両辺をラプラス変換する。 $\tilde{\chi}_0(z) \equiv \int_0^\infty \chi_0(t) e^{-zt} dt$ $\tilde{f}(z) \equiv \int_0^\infty f(t) e^{-zt} dt$ と定義すると、

微分のFFT $\int_0^\infty \dfrac{d\chi_0(t)}{dt} e^{-zt} dt = z\tilde{\chi}_0(z) - \tilde{\chi}_0(0)$ 畳込み積分のFFT $\int_0^\infty dt e^{-zt}\left\{\int_0^{t'} dt' f(t')\chi_0(t-t')\right\} = \tilde{f}(z)\tilde{\chi}_0(z)$

$$z\tilde{\chi}_0(z) - 1 = -i\Omega\tilde{\chi}_0(z) - (\hbar M)^{-1}\tilde{f}(z)\tilde{\chi}_0(z) \quad \Rightarrow \quad \left[z + i\Omega + (\hbar M)^{-1}\tilde{f}(z)\right]\tilde{\chi}_0(z) = 1$$

$$\tilde{\chi}_0(z) = \frac{1}{z + i\Omega + (\hbar M)^{-1}\tilde{f}(z)} \qquad z = \varepsilon - i\omega$$

（εは微小量）

$$\Rightarrow \quad -i\hbar M\tilde{\chi}_0(z) \equiv \chi_0^+(\omega + i\varepsilon) = -i\int_{-\infty}^{+\infty} \theta(t)\langle [S^-(t), S^+] \rangle_0 e^{i(\omega+i\varepsilon)t} dt$$

スピン相関の２時間グリーン関数のフーリエ変換

（$\theta(t)$は階段関数）

$$\boxed{\chi_0^+(\omega + i\varepsilon) = \frac{\hbar M}{\omega + i\varepsilon - \Omega - (\hbar M)^{-1} F(\omega + i\varepsilon)}}$$

$$\boxed{F(\omega + i\varepsilon) \equiv -i\tilde{f}(z) = -i\int_{-\infty}^{+\infty} \theta(t)\langle [\phi^-(t), \phi^+] \rangle_0 e^{i(\omega+i\varepsilon)t} dt}$$

トルク相関の２時間グリーン関数のフーリエ変換

電子論おける帯磁率

線形応答の理論よる横帯磁率の表式

$$\chi^{+}(\omega) = -i\frac{\mu_0 (g\mu_B)^2}{\hbar V}\int_0^{\infty}\left\langle\left[S^{-}(t), S^{+}\right]\right\rangle e^{i\omega t}dt$$

系のハミルトニアン

$$H = H^{\mathrm{Kin}} + H^{\mathrm{SO}} + H^{\mathrm{F}}$$

$$H^{\mathrm{Kin}} = \sum_{ij} t_{ij} c_i^{+} c_j \quad H^{\mathrm{F}} = -2\frac{\Delta}{\hbar M}\left\langle\vec{S}\right\rangle\cdot\vec{S}$$

$$H^{\mathrm{SO}} = \zeta\vec{L}\cdot\vec{S}$$

遅延Green関数のフーリエ変換

$$G_r(t) = -i\left\langle\left[S^{-}(t), S^{+}\right]\right\rangle\theta(t)$$

Green関数の運動方程式

$$\frac{dG_r(t)}{dt} = \left\langle\left[\left[H, S^{-}\right], S^{+}\right]\right\rangle\theta(t) - i\left\langle\left[S^{-}(t), S^{+}\right]\right\rangle\delta(t)$$

乱雑位相近似（RPA)によるGreen関数の切断

$$\boxed{\chi^{+}(\omega) = -\frac{\mu_0 (g\mu_B)^2}{\hbar V}\frac{\chi_0^{+}(\omega + i\varepsilon)}{1 + \Delta(\hbar M)^{-1}\chi_0^{+}(\omega + i\varepsilon)}}$$

（εは微小量）

$H^{\mathrm{F}} = H_0^{\mathrm{F}} = \Delta S^z$のときの帯磁率

$$\chi_0^{+}(\omega + i\varepsilon) = -i\int_{-\infty}^{\infty}\left\langle\left[S^{-}(t), S^{+}\right]\right\rangle_0\theta(t)e^{i(\omega + i\varepsilon)t}dt$$

磁気緩和の電子論

電子論的に導出した横帯磁率の表式

$$\chi^{+}(\omega) = -\frac{\mu_0 (g\mu_B)^2}{\hbar V} \frac{\hbar M}{\omega + i\varepsilon - (\Omega - \Delta) - (\hbar M)^{-1} F(\omega + i\varepsilon)}$$

現象論的に導出した横帯磁率の表式

$$\chi^{+}(\omega) = -\frac{\gamma M_s}{\omega - \gamma H_{eff} + i\alpha\omega}$$

磁気緩和振動数

$$\lambda = -\lim_{\omega \to 0} \frac{\gamma^2}{\hbar \mu_0 V} \mathrm{Im}\left[\frac{1}{\omega} F(\omega + i\varepsilon)\right]$$

（Green関数の計算）

$$\lambda = \frac{g^2 \mu_0 \mu_B^2}{\pi \hbar V} \sum_{\vec{k}} \sum_{nm} \left|\Gamma^{-}_{nm}(\vec{k})\right|^2 \frac{\delta}{(E_F - E_{n\vec{k}})^2 + \delta^2} \frac{\delta}{(E_F - E_{n\vec{k}})^2 + \delta^2}$$

トルク演算子の行列要素

$$\Gamma^{-}_{nm}(\vec{k}) = \langle n, \vec{k} | [S^{-}, H^{SO}] | m, \vec{k} \rangle$$

トルク演算子

$$[S^{-}, H^{SO}] = \zeta (S^{-} L^{z} - S^{z} L^{-})$$

スピン反転項　軌道励起項

$$\lambda \approx \zeta \frac{\mu_B^2}{\pi \hbar} \int D(E_F) \frac{\delta}{\varepsilon^2 + \delta^2} d\varepsilon$$

スピン軌道相互作用の強さとフェルミ準位での状態密度に強く依存

磁化緩和定数の第一原理計算

$$\lambda = \frac{g^2 \mu_0 \mu_B^2}{\pi \hbar V} \sum_{\vec{k}} \sum_{nm} \left| \Gamma_{nm}^{-}\left(\vec{k}\right) \right|^2 \frac{\delta}{\left(E_F - E_{n\vec{k}}\right)^2 + \delta^2} \frac{\delta}{\left(E_F - E_{n\vec{k}}\right)^2 + \delta^2}$$

$$\alpha = \frac{\gamma M_s}{\lambda}$$

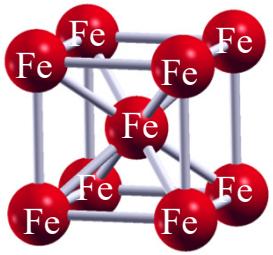
$$\gamma = \mu_0 g \mu_B / \hbar$$

各k点,バンドに対する
エネルギー固有値

$$\Gamma_{nm}^{-}\left(\vec{k}\right) = \left\langle n, \vec{k} \middle| \zeta \left(S^{-} L^{z} - S^{z} L^{-} \right) \middle| m, \vec{k} \right\rangle$$

第一原理計算から得られた波動関数を用いて、トルク演算子行列要素を計算

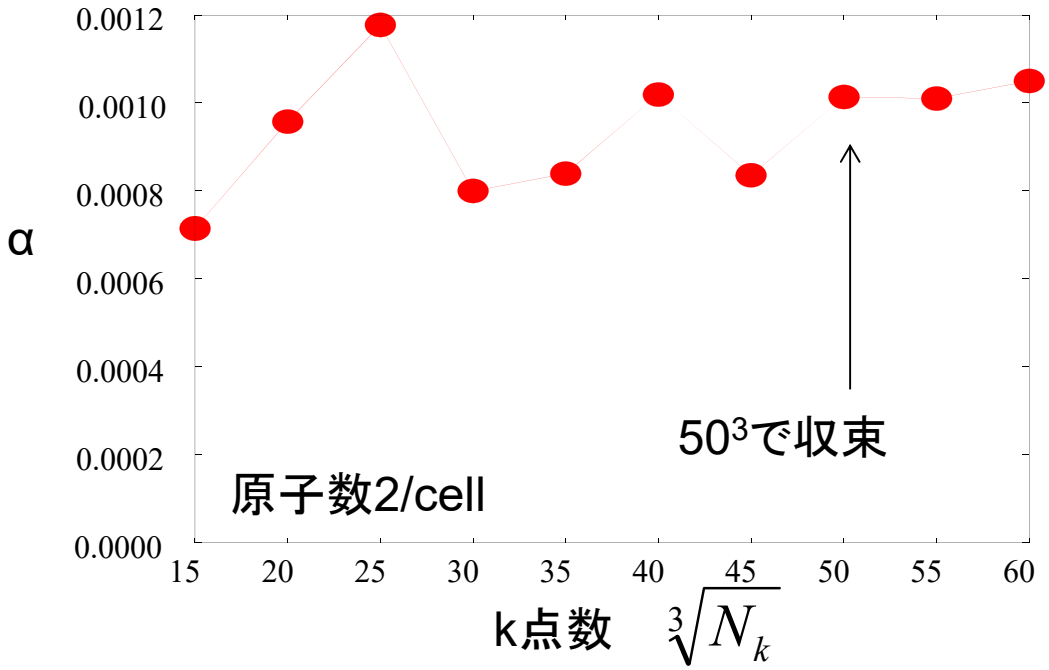
Bulk-Fe



μ_s=2.207μ_B

μ_l=0.049μ_B

α=0.00105



⇒界面の計算では50x50点を採用