AB-INITIO SPIN-ORBITRONICS

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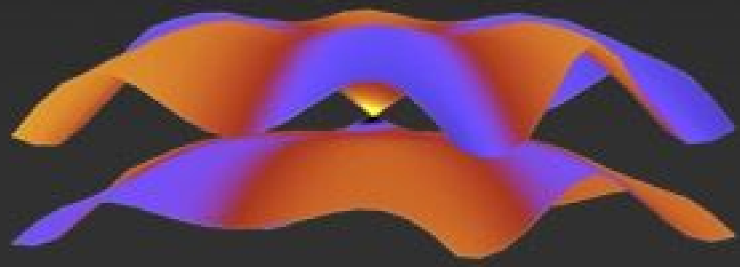


OUTLINE

MAIN CONCEPT

- Coupling spin and dipolar degrees of freedom in **FE** via **SOC**
- Control **spin texture** via **P** or **E**

INGRE-DIENTS

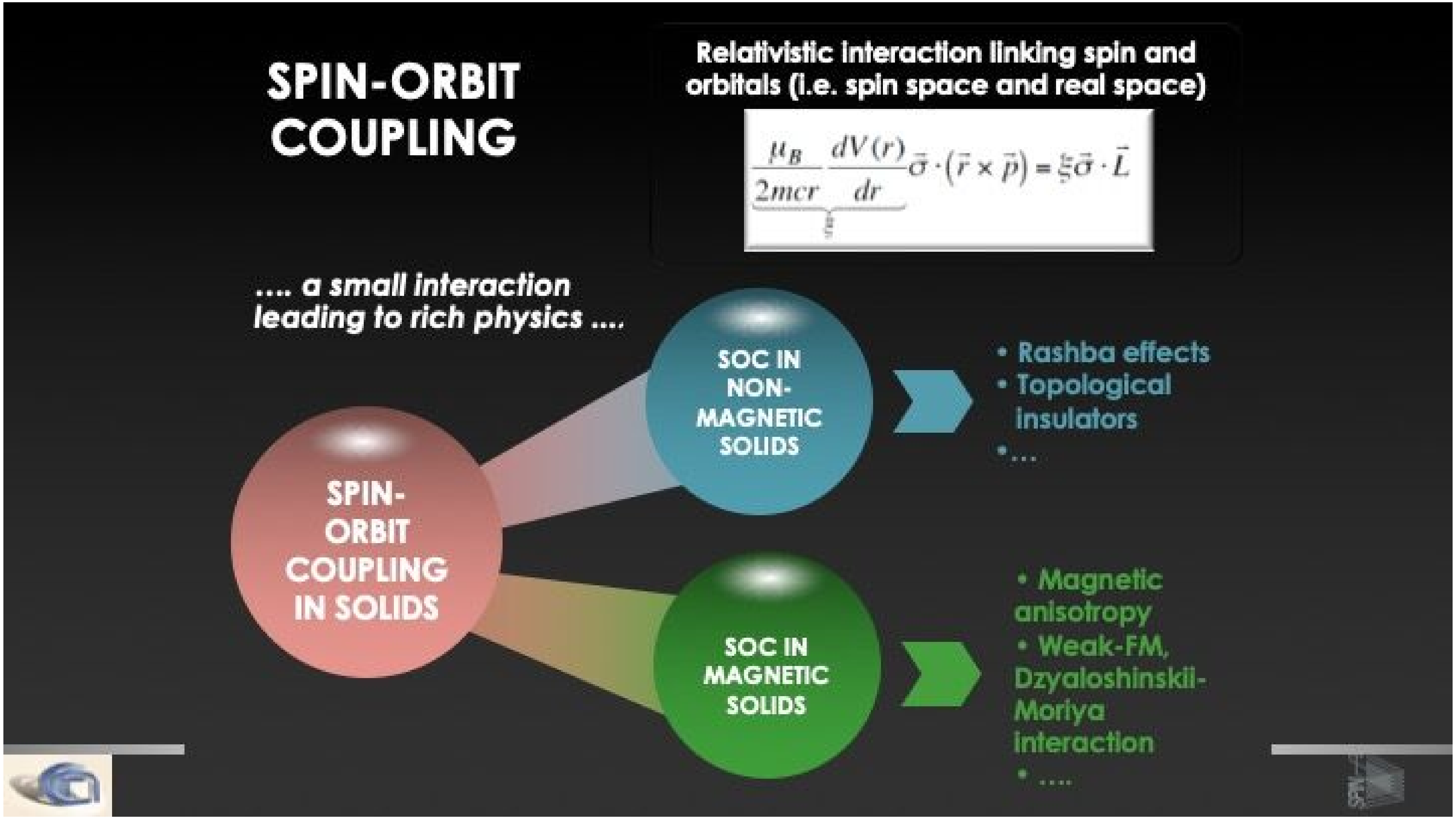
- **Spin-orbit coupling (from atoms to solids)**
- **Inversion-Symmetry Breaking & Ferroelec-tricity**

SOC EFFECTS

- **Rashba:**
  - **P out-of-plane**
  - **P In-plane**
- **Spin-valley Coupling**
- **Topology (?)**

MATE-RIALS

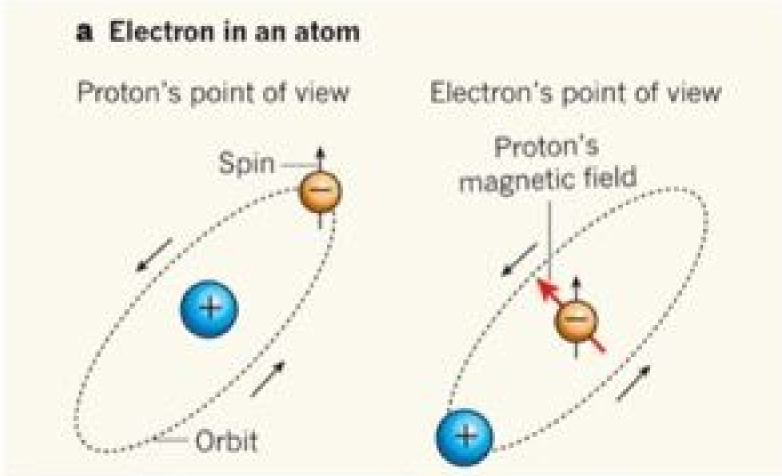
- GeTe (prototype)
- FE oxides
  - (WO_3,
  - Bi_2WO_6)
- Oxide-based Interfaces

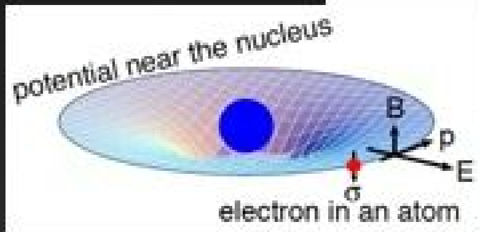

SPIN-ORBIT COUPLING
Relativistic interaction linking spin and orbitals (i.e. spin space and real space)
$\underbrace{\frac{\mu_B}{2mcr}\frac{dV(r)}{dr}}_{\xi}\vec{\sigma}\cdot(\vec{r}\times\vec{p}) = \xi\vec{\sigma}\cdot\vec{L}$
…. a small interaction leading to rich physics ….
SPIN-ORBIT COUPLING IN SOLIDS
SOC IN NON-MAGNETIC SOLIDS
• Rashba effects
• Topological insulators
• …
SOC IN MAGNETIC SOLIDS
• Magnetic anisotropy
• Weak-FM, Dzyaloshinskii-Moriya interaction
• ….

SPIN-ORBIT INTERACTION: A RELATIVISTIC EFFECT

Relativity:
Switch the coordinate frame
Moving E → $\mathbf{B} = \frac{1}{c^2}\mathbf{E} \times \mathbf{v}.$

Quantum spin:
Electron has a spin ***s*** → $h = -\mu_s \cdot B$





$$\mathbf{B} = \frac{1}{c^2}\mathbf{E} \times \mathbf{v}. \quad \sim Z^4$$

$$\mathbf{E} = -\frac{\mathbf{r}}{r}\phi' \qquad \mathbf{B} = -\frac{1}{rc^2}\phi' \mathbf{r} \times \mathbf{v}$$

As $\mathbf{l} = \mathbf{r} \times \mathbf{p}$, and hence $\mathbf{r} \times \mathbf{v} = \frac{1}{m_e}\mathbf{l}$, we get the Hamiltonian

$$h_{SO} = -\mu_{\mathbf{e}} \cdot \mathbf{B} = \frac{1}{m_e r c^2}\phi' \mu \cdot \mathbf{l} = \frac{e}{m_e^2 r c^2}\phi' \mathbf{s} \cdot \mathbf{l}.$$

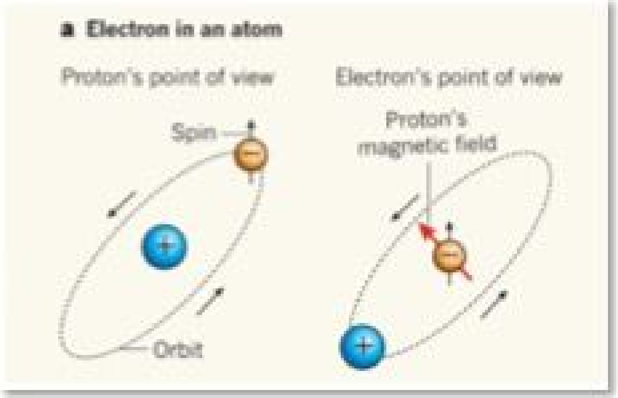
RELATIVISTIC EFFECTS

$$H_0 = \frac{\boldsymbol{p}^2}{2m} + V(r) = \frac{\boldsymbol{p}^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$$

Unperturbed Hamiltonian

$$H = H_0 + H_1 + H_2 + H_3$$

Three Relativistic corrections:



$$H_1 = -\frac{\boldsymbol{p}^4}{8m^3c^2}$$

H_1: Mass-velocity term (correction to Kinetic energy)

$$H_2 = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\boldsymbol{L}\cdot\boldsymbol{S}$$

H_2: Spin-orbit term

$$H_3 = \frac{\hbar^2}{8m^2c^2}\nabla^2 V(r) = \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\delta(r)$$

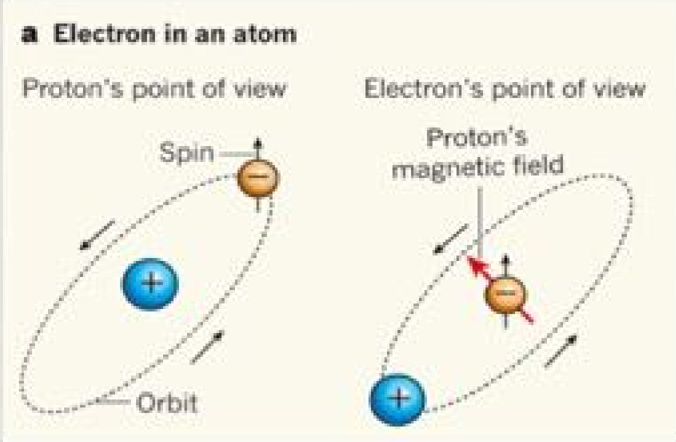
H_3: Darwin term

MAGNITUDE OF RELATIVISTIC CORRECTIONS

Tab. 1.1 Summary of relativistic and spin-dependent interaction terms.

Perturbation	Description	Magnitude
$\frac{\boldsymbol{p}^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$	The nonrelativistic motion,	$\gtrsim 10^5$ cm^{-1}
$H_1 = -\frac{\boldsymbol{p}^4}{8m^3c^2}$	Relativistic mass correction term.	≈ 0.1 cm^{-1}
$H_3 = \frac{\hbar^2}{8m^2c^2}\nabla^2 V(r)$	The "Darwin" term responsible for s-state shifts. It represents the relativistic nonlocalizability of the electron and is related to both the negative-energy sea and its rapid motion.	< 0.1 cm^{-1}
$H_2 = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\boldsymbol{L}\cdot\boldsymbol{S}$	Spin–orbit interaction. As shown in Problem 1.4, this term can be written as $\frac{e\hbar^2}{2m_e^2c^2}\frac{1}{r}\frac{d\phi}{dr}\left(\vec{l}\cdot\vec{s}\right)$, where $\vec{l}$ is the orbital angular momentum. In contrast to the previous term, this does not affect s states.	10–10^3 cm^{-1}

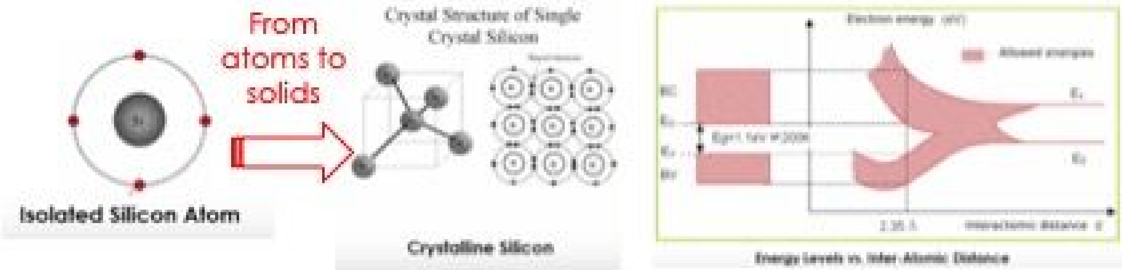
SPIN-ORBIT INTERACTION: FROM ATOMS TO SOLIDS



In an atom, an e^- (orange) orbits the nucleus (blue; here a single proton). *From the e^- point of view, the proton orbits the e^- and produces a magnetic field that couples with the e^- spin and alters its orbit.*

FROM ATOMS TO SOLIDS: SYMMETRY-INDEPENDENT SOC

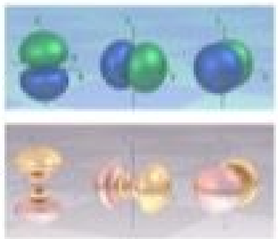
What SOC causes in the prototypical Semiconductors?

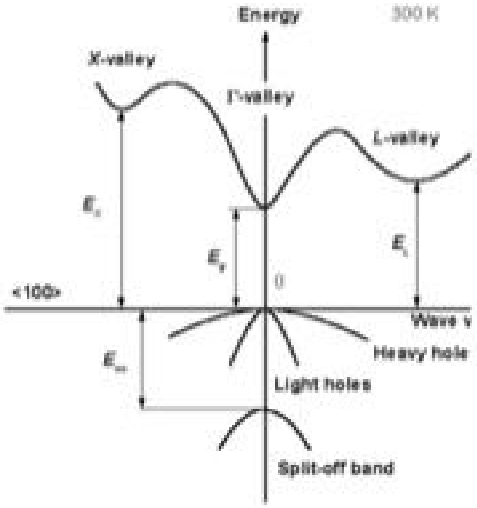


SYMMETRY-INDEPENDENT SOC

2p

4p





Δ ~ Z² (outer p shell)

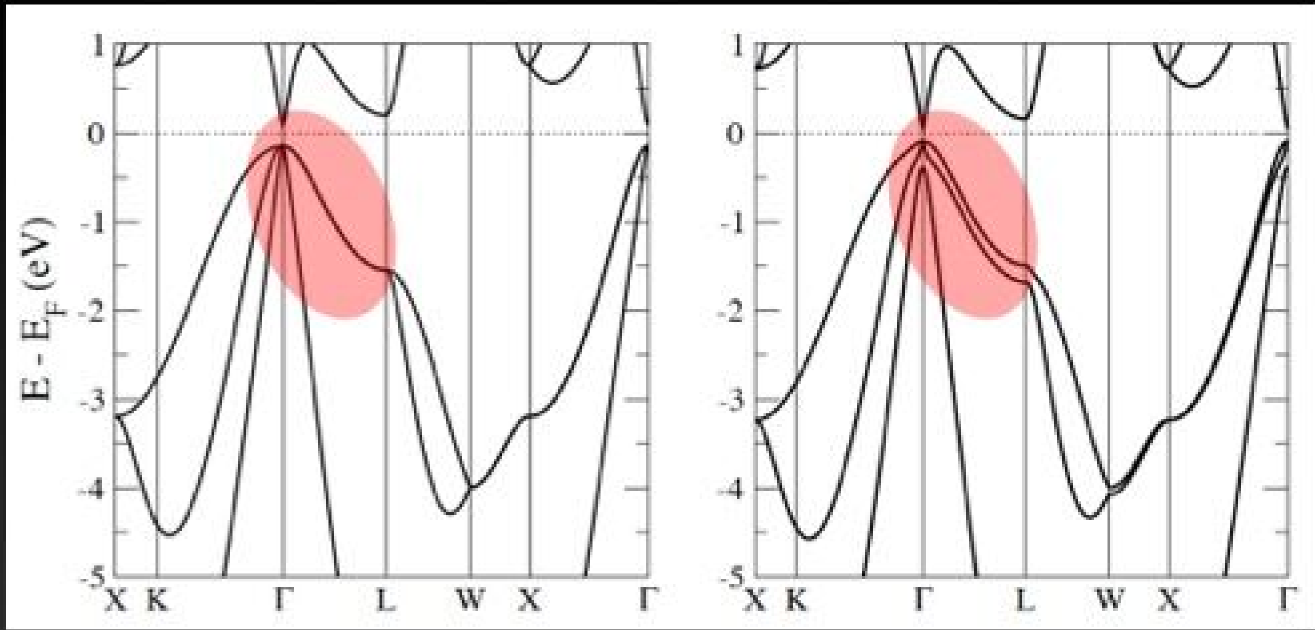
$$(\frac{Z_{Ge}}{Z_{Si}})^2 = (\frac{(Z_{Ga}+Z_{As})/2}{Z_{Si}})^2 = (\frac{32}{14})^2 = 5.2$$

$$\frac{\Delta_{Ge}}{\Delta_{Si}} = 6.6 \quad \frac{\Delta_{GaAs}}{\Delta_{Si}} = 7.7$$

SOC splits bands.

Compound	Δ_0^{exp} (eV)
C	0.006
Si	0.044
Ge	0.29
α-Sn	
AlN	
AlP	
AlAs	
AlSb	0.75
GaN	0.011
GaP	0.127
GaAs	0.34
GaSb	0.80
InN	
InP	0.11
InAs	0.38
InSb	0.82
ZnO	−0.005
ZnS	0.07
ZnSe	0.43
ZnTe	0.93
CdS	0.066
CdSe	
CdTe	0.92
HgS	
HgSe	
HgTe	1.08

SOC-DERIVED BAND SPLITTING



Bandstructure of Ge around the Fermi level without SOC (left) and with SOC (right). Three-fold degeneracy of the highest occupied state at the Γ point is split by SOC, as well as the doubly degenerate band along the lines Γ L and Γ X.

SYMMETRY PROPERTIES IN BAND STRUCTURE : SPACE/TIME INVERSION

What happens to spin-orbit coupling upon time-reversal symmetry?

$$
\begin{array}{ccc}
t & \rightarrow & -t \\
l & \rightarrow & -l \\
\sigma & \rightarrow & -\sigma
\end{array}
$$

↓

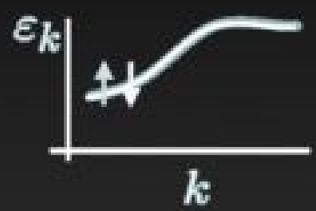
$$V_{so} \sim l \cdot \sigma \rightarrow V_{so}$$

SOC preserves time reversal symmetry!

SYMMETRY PROPERTIES IN BAND STRUCTURE : SPACE/TIME INVERSION

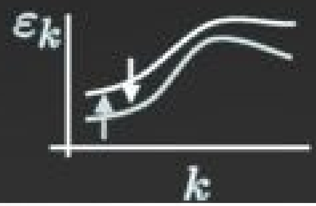
Two cases need to be distinguished:

- solids *with* space inversion symmetry



degeneracy

- solids *without* space inversion symmetry

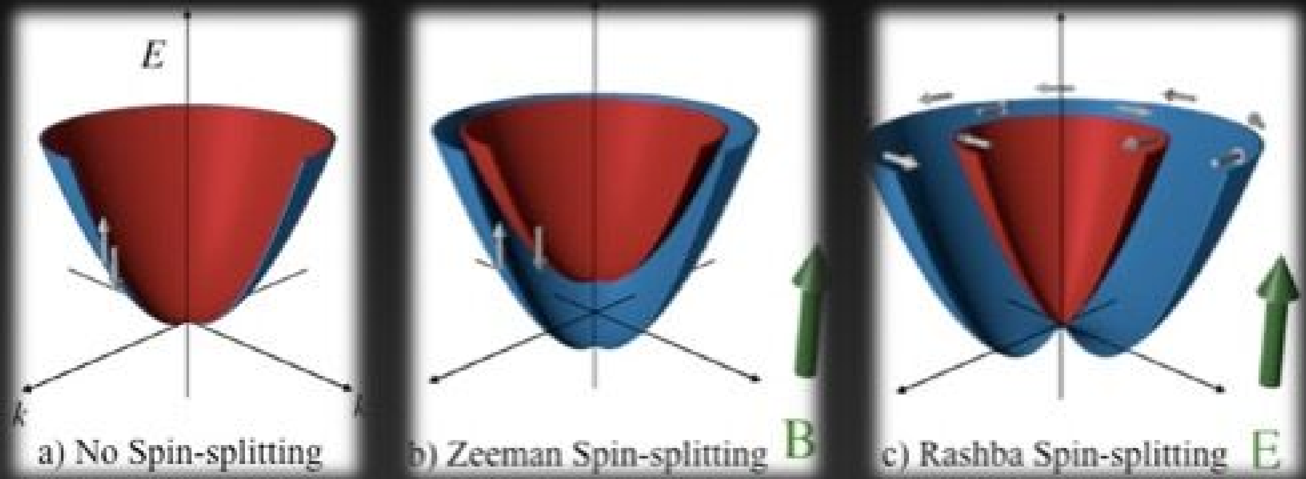


no degeneracy

SYMMETRY PROPERTIES IN BAND STRUCTURE : SPACE/TIME INVERSION

Time reversal symmetry: $\varepsilon_{k\uparrow} = \varepsilon_{-k\downarrow}$

(Space) inversion symmetry: $\varepsilon_{k\uparrow} = \varepsilon_{-k\uparrow}$



WITH time-reversal and **WITH inversion** symmetry

$\varepsilon_{k\uparrow} = \varepsilon_{-k\uparrow} = \varepsilon_{-k\downarrow}$

WITHOUT time-reversal symmetry

WITH inversion

$\varepsilon_{k\uparrow} = \varepsilon_{-k\uparrow} \neq \varepsilon_{k\downarrow}$

WITH time-reversal

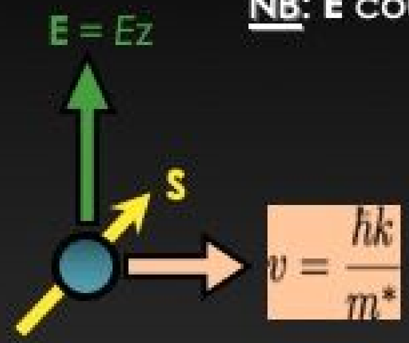
WITHOUT inversion symmetry:

$\varepsilon_{k\uparrow} = \varepsilon_{-k\downarrow} \neq \varepsilon_{k\downarrow}$

WHAT IS THE RASHBA EFFECT ?

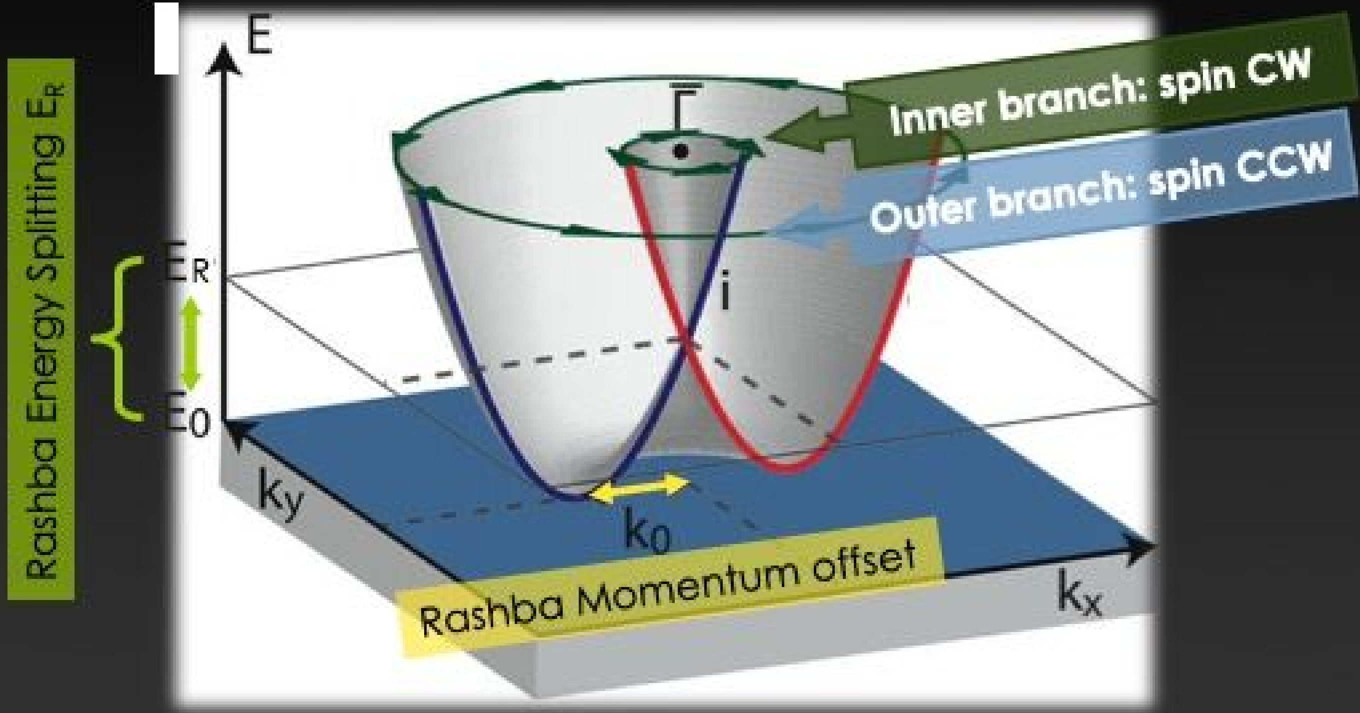
SOC effect: particle in **electric field E** experiences an internal **effective magnetic field $B_{eff} \propto v \times E$** in its moving frame

<u>NB</u>: **E** could be external (i.e. 2DEG), or "effective" (as in FE)



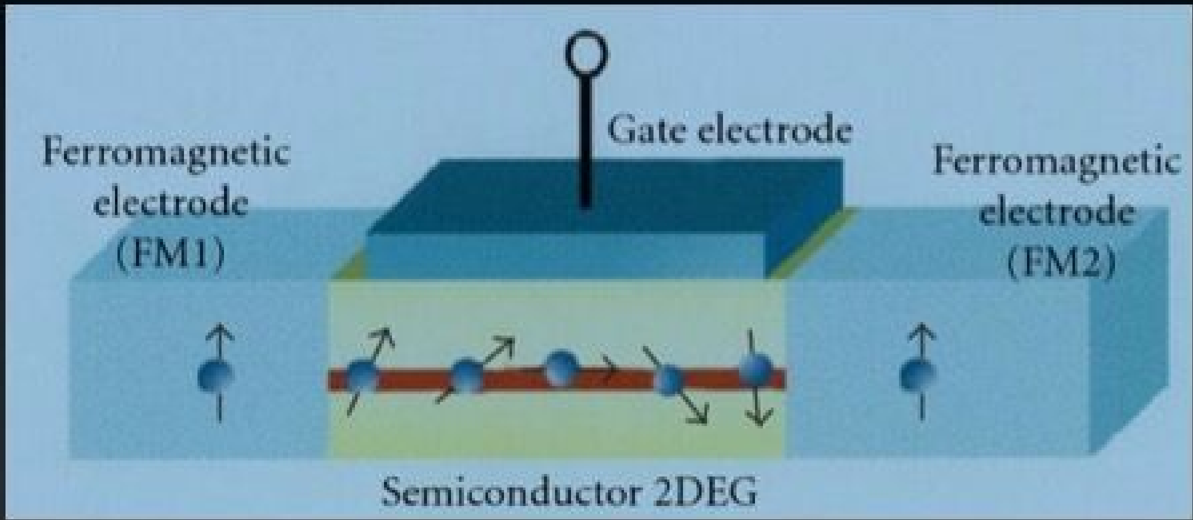
WHAT IS THE RASHBA EFFECT ?

Relevant properties/parameters:



Rashba coupling parameter (in eV Å): $\alpha_R = 2E_R/k_0$

USING RASHBA SPIN-ORBIT COUPLING: SEMICONDUCTOR-BASED SPIN-FET



- Das-Datta proposal *(Appl. Phys. Lett. 1990 , 56 , 665)*
- Animation by Bernevig and Sinova.

WHAT IS THE SPIN TEXTURE ?

Calculate the SPIN expectation value for each wavefunction

$$\langle \sigma_x \rangle_R = \langle \psi_n^*(k) | \sigma_x | \psi_n(k) \rangle / \langle \psi_n^*(k) || \psi_n(k) \rangle$$

$$\langle \sigma_y \rangle_R = \langle \psi_n^*(k) | \sigma_y | \psi_n(k) \rangle / \langle \psi_n^*(k) || \psi_n(k) \rangle$$

$$\langle \sigma_z \rangle_R = \langle \psi_n^*(k) | \sigma_z | \psi_n(k) \rangle / \langle \psi_n^*(k) || \psi_n(k) \rangle$$

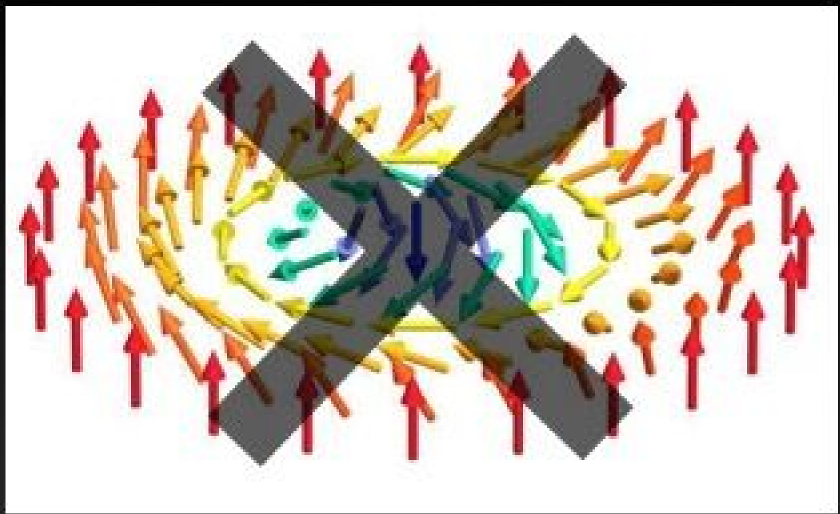
Pauli spin matrices

$$\sigma_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- ***Can one measure it?***
  Yes, with Spin-resolved ARPES
- ***What does it mean?***
  Intuitively: "spin" of an electron in a certain *(n,k)* state

Spin texture of Bi_2Se_3 Dirac cone

WHAT IS THE SPIN TEXTURE ?



Spin texture of Bi_2Se_3 Dirac cone

- **NB: we're in k-space** ***(not real space!)***

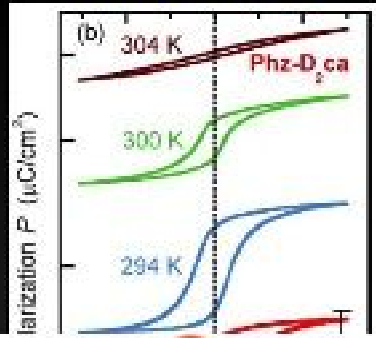
Arrows *do* ***not*** *represent* ***magnetic moments,***
Vortex-like spin textures *have nothing to*
do with ***Skyrmions, antiskyrmions, etc***

FERROELECTRICS: BASICS

- **Polar materials**, in which a **spontaneous electric polarization** can be **switched** via an **external electric field**

Ferroelectric Curie Temperature for PE-FE

P–E hysteresis

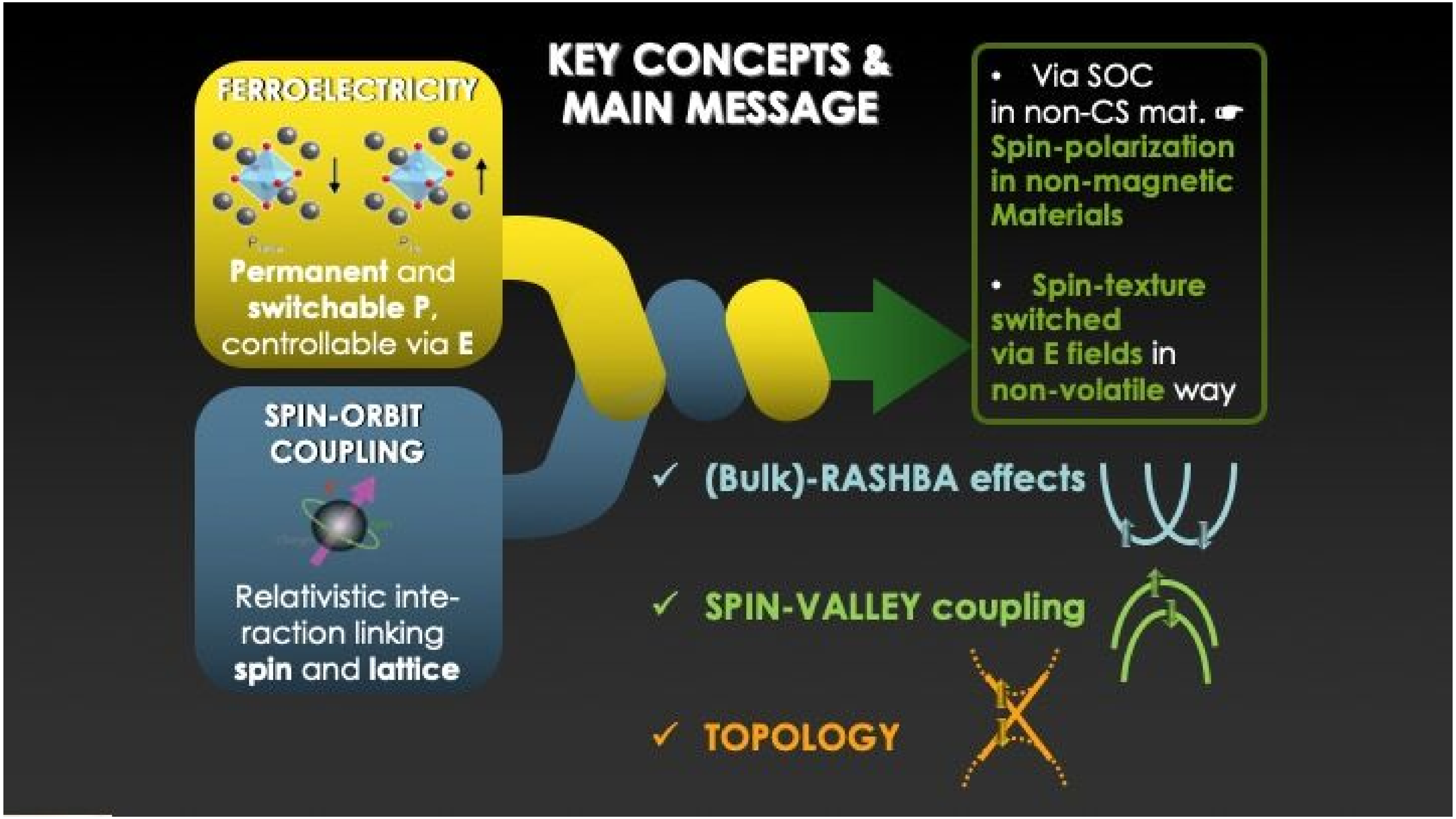


- Electric "bistability":
  ✓ for non-volatile memory elements

- By symmetry, all Ferroelectrics are non centro-symmetric (CS)

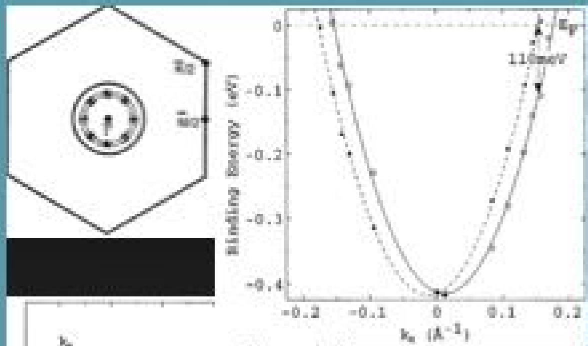
- «All insulator spin-orbitronics» (not based on spin-charge current conversion)

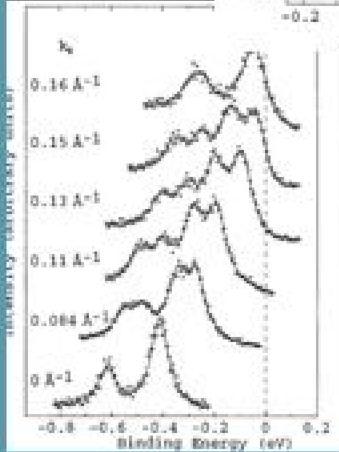
  ☛ Voltage-control (not current-control)
  ☛ no Joule heating



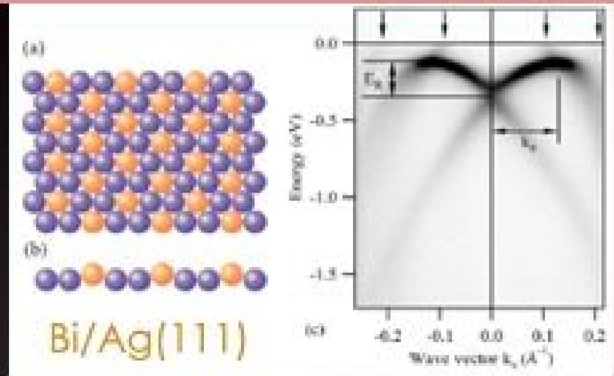
KEY CONCEPTS &
MAIN MESSAGE
FERROELECTRICITY
Permanent and
switchable P,
controllable via E
SPIN-ORBIT
COUPLING
Relativistic inte-
raction linking
spin and lattice
• Via SOC
in non-CS mat. ☛
Spin-polarization
in non-magnetic
Materials
• Spin-texture
switched
via E fields in
non-volatile way
✓ (Bulk)-RASHBA effects
✓ SPIN-VALLEY coupling
✓ TOPOLOGY

RASHBA EFFECT AT SURFACES

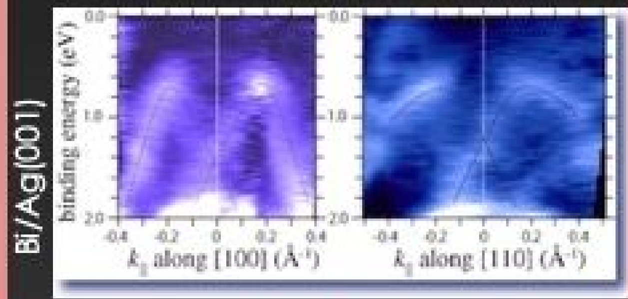




Au(111), La Shell et al., PRL 77, 3419 (1996)



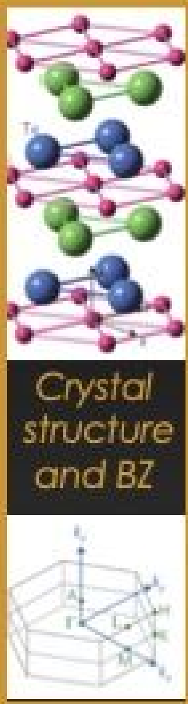
Ast et al., PRL 98, 186807 (2007)



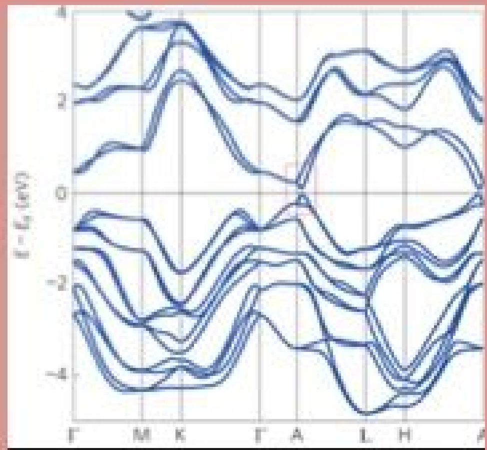
Nakagawa et al, PRB 75, 155409 (2007)

GIANT RASHBA EFFECT IN BULK BiTeI

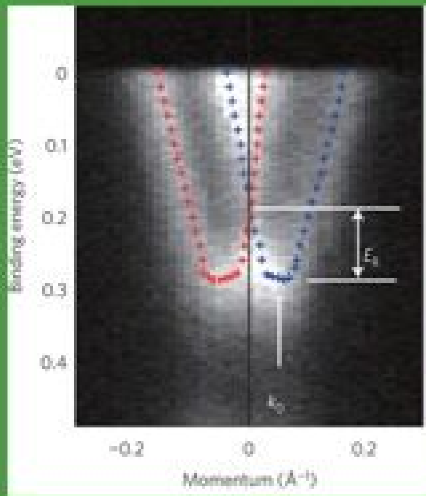
Tokura's group, Nature Materials 10, 521–526 (2011)



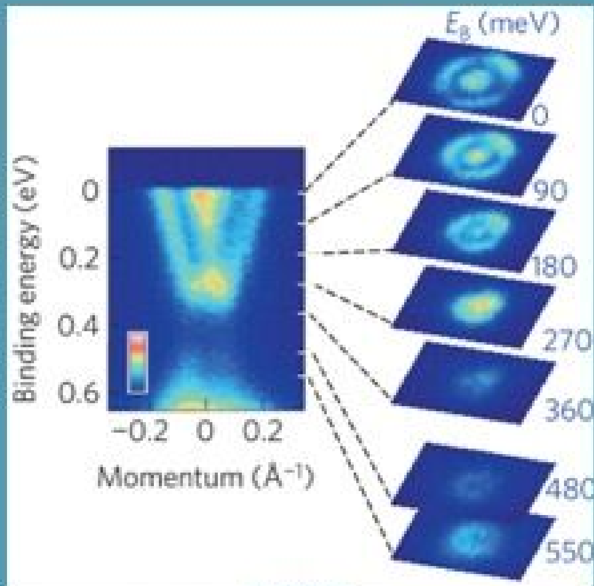
Crystal structure and BZ



DFT band structure



Spin-resolved ARPES

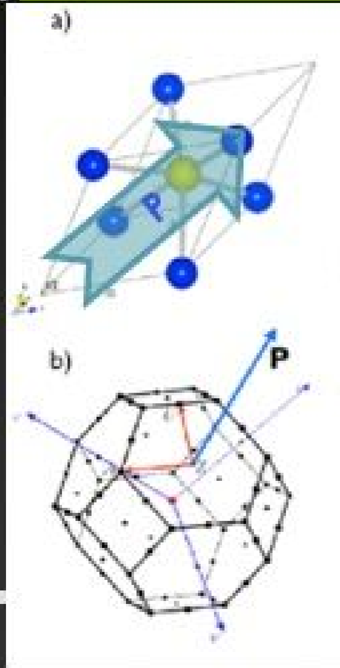


ARPES

FERROELECTRIC GeTe: "BULK" RASHBA SPIN-SPLITTING

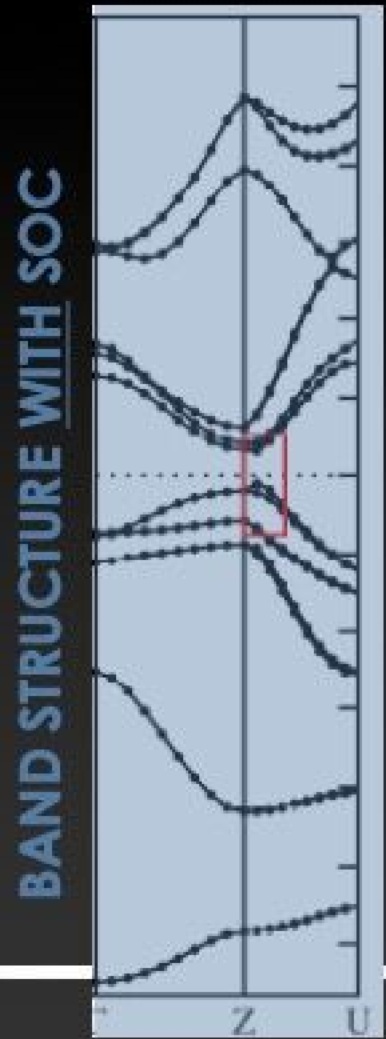
T_C^{FE} ~ 720 K
Space group: *R3m* (no. 160)
P along [111]

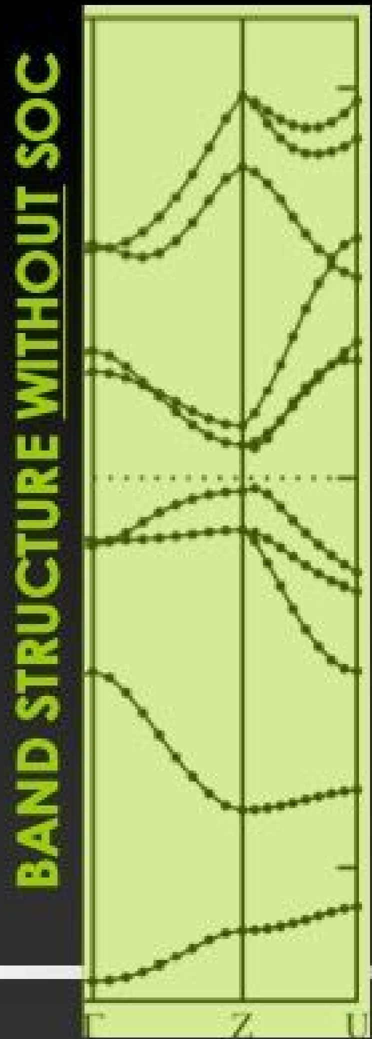
	Ω (Å^3)	a (Å)	a_0 (Å)	α (°)	ϑ (°)	τ	l (Å)	s (Å)	E_g (eV)	P ($\mu C/cm^2$)
PBE	56.08	4.373	6.080	57.76	88.02	0.0305	3.25	2.85	0.33	64.56
HSE	54.58	4.333	6.018	57.61	87.88	0.0331	3.24	2.81	0.65	70.27
Exp	53.31[a]		5.98[a]		88.35[a]	0.0248[a]	3.13[b]	2.80[b]	0.61[c,d]	



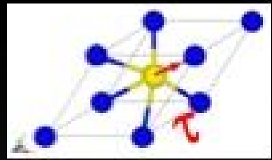
ORIGIN OF RASHBA SPIN SPLITTING

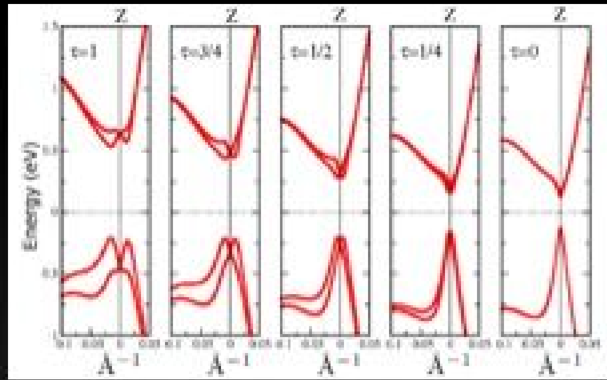
- ✓ Presence of **spin-orbit coupling**





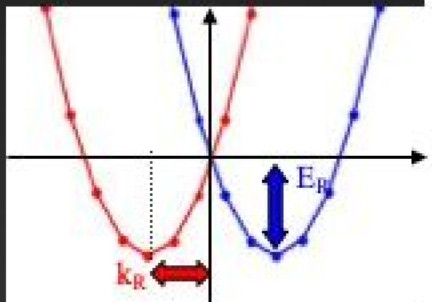
EVALUATION OF RASHBA PARAMETERS

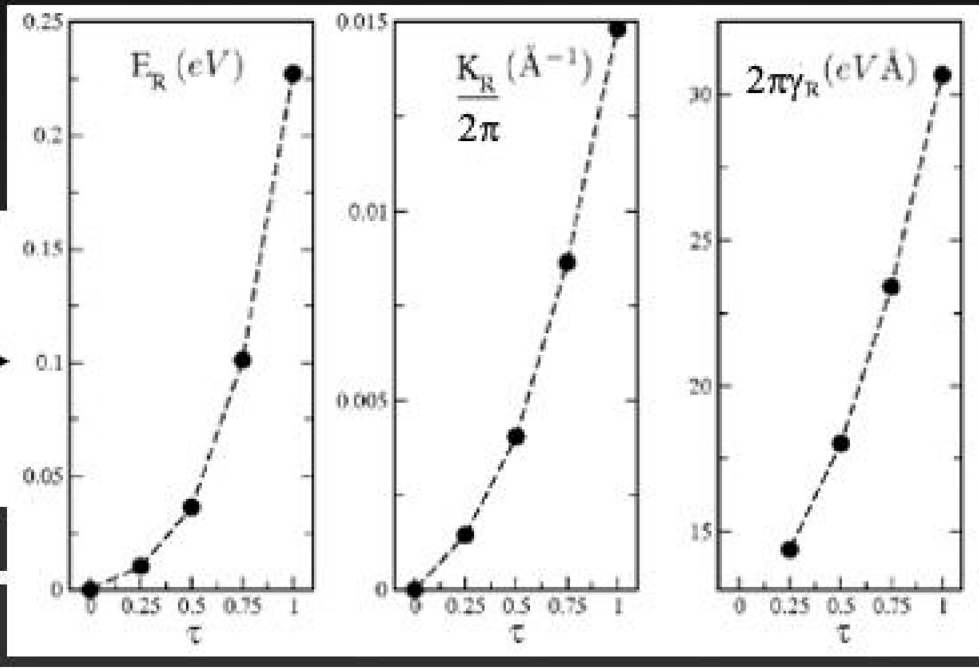




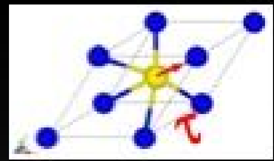
$$E_{\pm}(k_{\parallel}) = \frac{\hbar^2 k_{\parallel}^2}{2m^{\star}} \pm \gamma_R |k_{\parallel}| + E_0, \quad k_{\parallel} = (k_x, k_y)$$

$$k_R = |m^{\star}| \gamma_R / \hbar^2$$





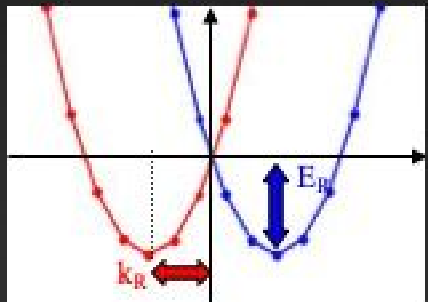
EVALUATION OF RASHBA PARAMETERS



The effect is "GIANT" in GeTe!

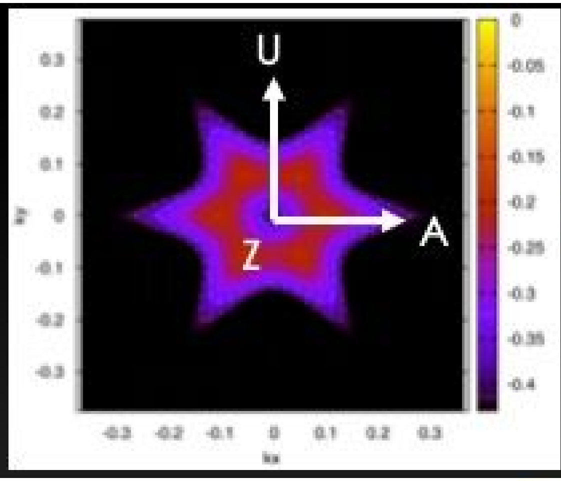
$$E_{\pm}(k_{\|}) = \frac{\hbar^2 k_{\|}^2}{2m^*} \pm \gamma_R |k_{\|}| + E_0, \quad k_{\|} = (k_x, k_y)$$

$$k_R = |m^*| \gamma_R / \hbar^2$$

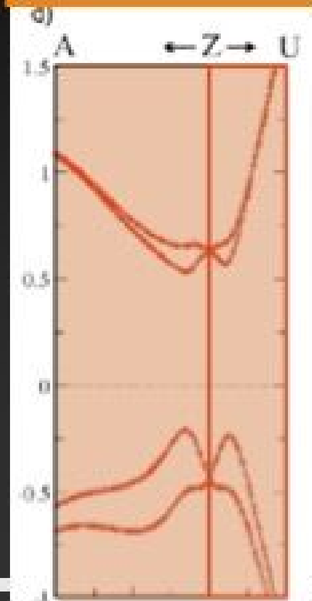


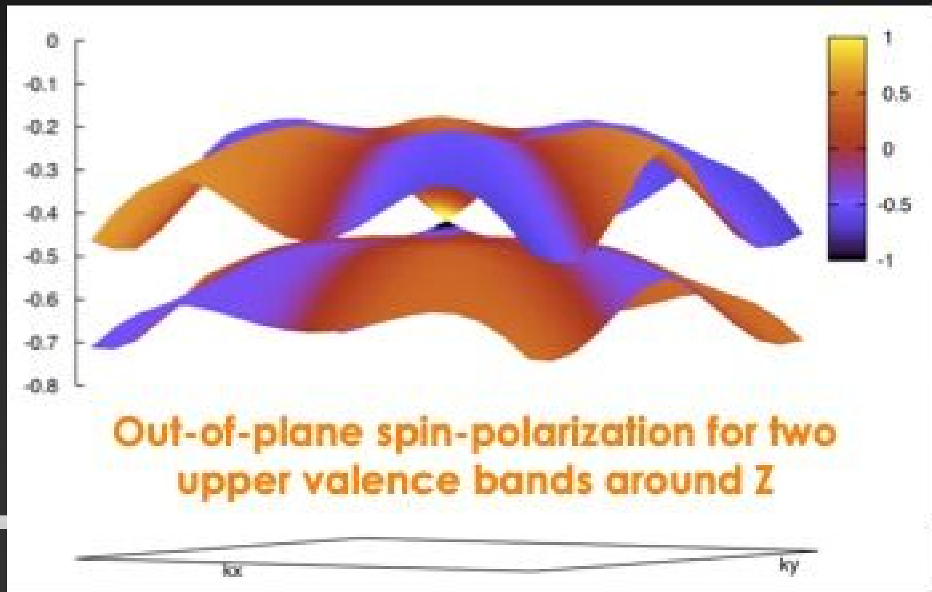
Sample	k_0 ($Å^{-1}$)	E_R (meV)	γ_R ($eVÅ$)
Surface state			
Au(111)	0.012	2.1	0.33
Bi(111)	0.05	14	0.55
1/3 ML Bi on Ag surface alloy	0.13	200	3.05
Interface			
InGaAs/InAlAs	0.028	<1	0.07
QW state			
Pb thin film (6-22 ML)	0.035	≲10	0.04
Bi thin film (7-40 BL)	-	-	-
1 ML Bi on Cu	N/A	N/A	2.5
Bulk			
BiTeI	0.052	100	3.8
Ferroelectric GeTe	*0.09*	*227*	*4.8*

RASHBA EFFECT AT TOP VALENCE BANDS



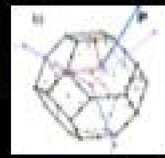
Isoenergy cuts off valence bands around Z

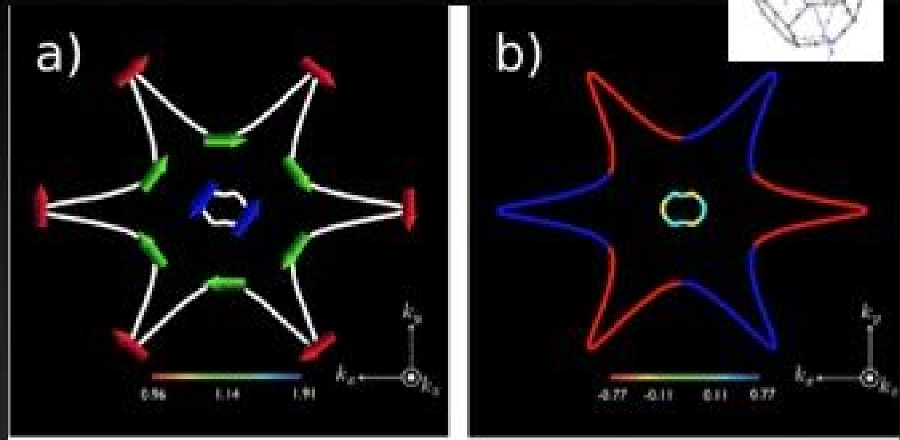




Out-of-plane spin-polarization for two upper valence bands around Z

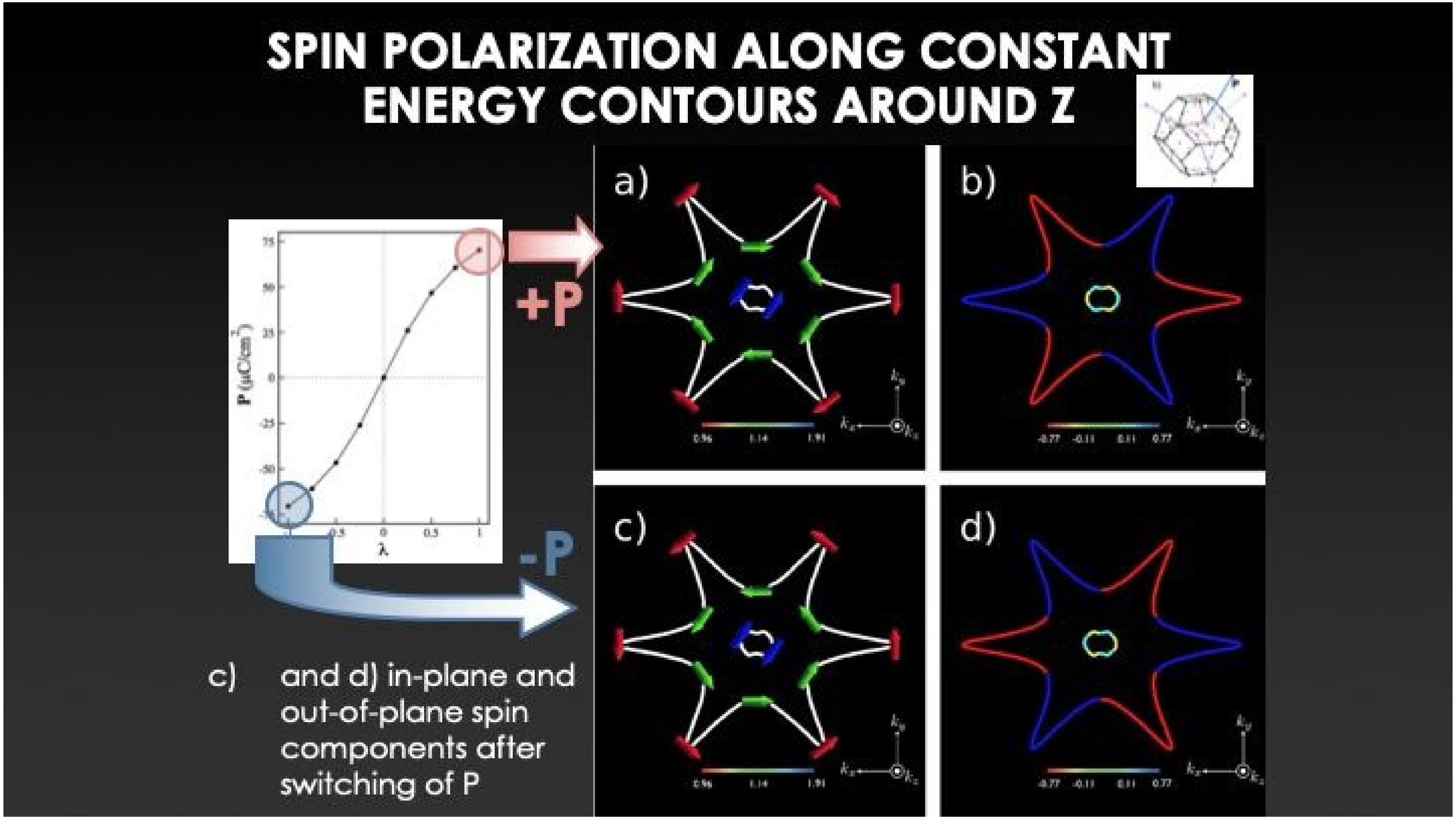
SPIN POLARIZATION ALONG CONSTANT ENERGY CONTOURS AROUND Z

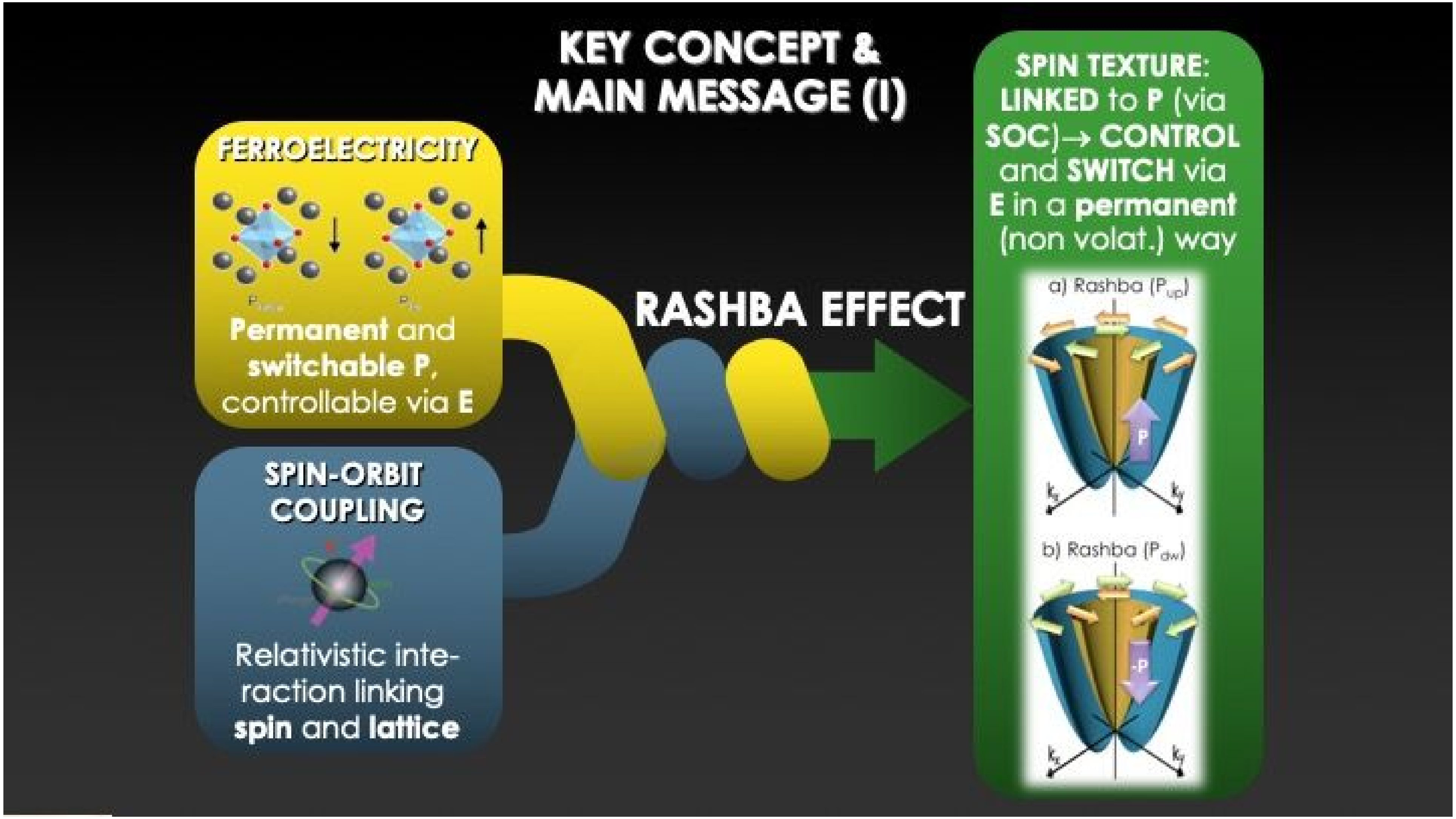




a) **In-plane spin texture** (constant-energy cut at -0.47 eV). Arrows refer to the in-plane orientation of spin (colors indicate the modulus of the spin polarization).

b) **Out-of-plane spin component** distribution

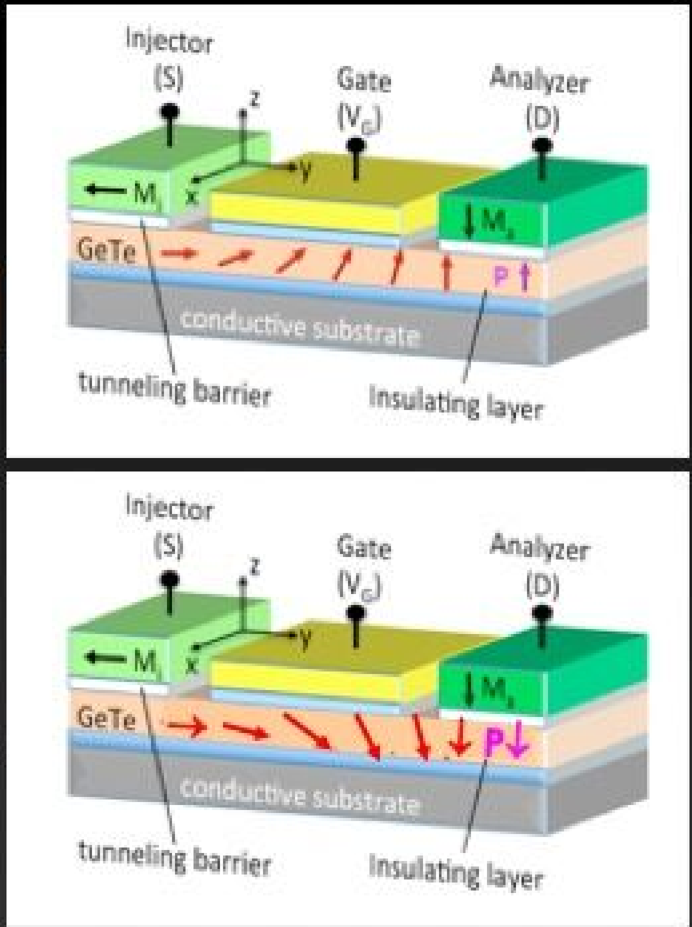

SPIN POLARIZATION ALONG CONSTANT ENERGY CONTOURS AROUND Z
a)
b)
c)
d)
+P
-P
λ
c) and d) in-plane and out-of-plane spin components after switching of P


KEY CONCEPT &
MAIN MESSAGE (I)
FERROELECTRICITY
Permanent and
switchable P,
controllable via E
SPIN-ORBIT
COUPLING
Relativistic inte-
raction linking
spin and lattice
RASHBA EFFECT
SPIN TEXTURE:
LINKED to P (via
SOC)→ CONTROL
and SWITCH via
E in a permanent
(non volat.) way
a) Rashba (P_up)
P
-P
b) Rashba (P_dw)

A POSSIBLE DEVICE ….

Datta-Das SPIN-FET

Polarization switching



RECONFIGURABLE LOGIC FUNCTIONS USING FERSC-BASED SPIN-FET

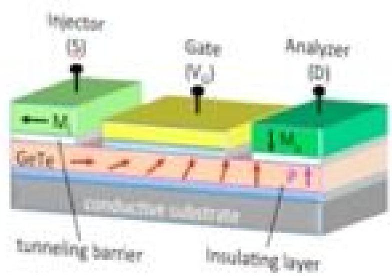


Table 1

M_i	M_a	P (V_G)	R_e (v_{out})	Spin rot.
←	↓ (0)	↑ (1)	L (0)	→ ↗ ↑
←	↓ (0)	↓ (0)	H (1)	→ ↘ ↓
←	↑ (1)	↑ (1)	H (1)	→ ↗ ↑
←	↑ (1)	↓ (0)	L (0)	→ ↘ ↓

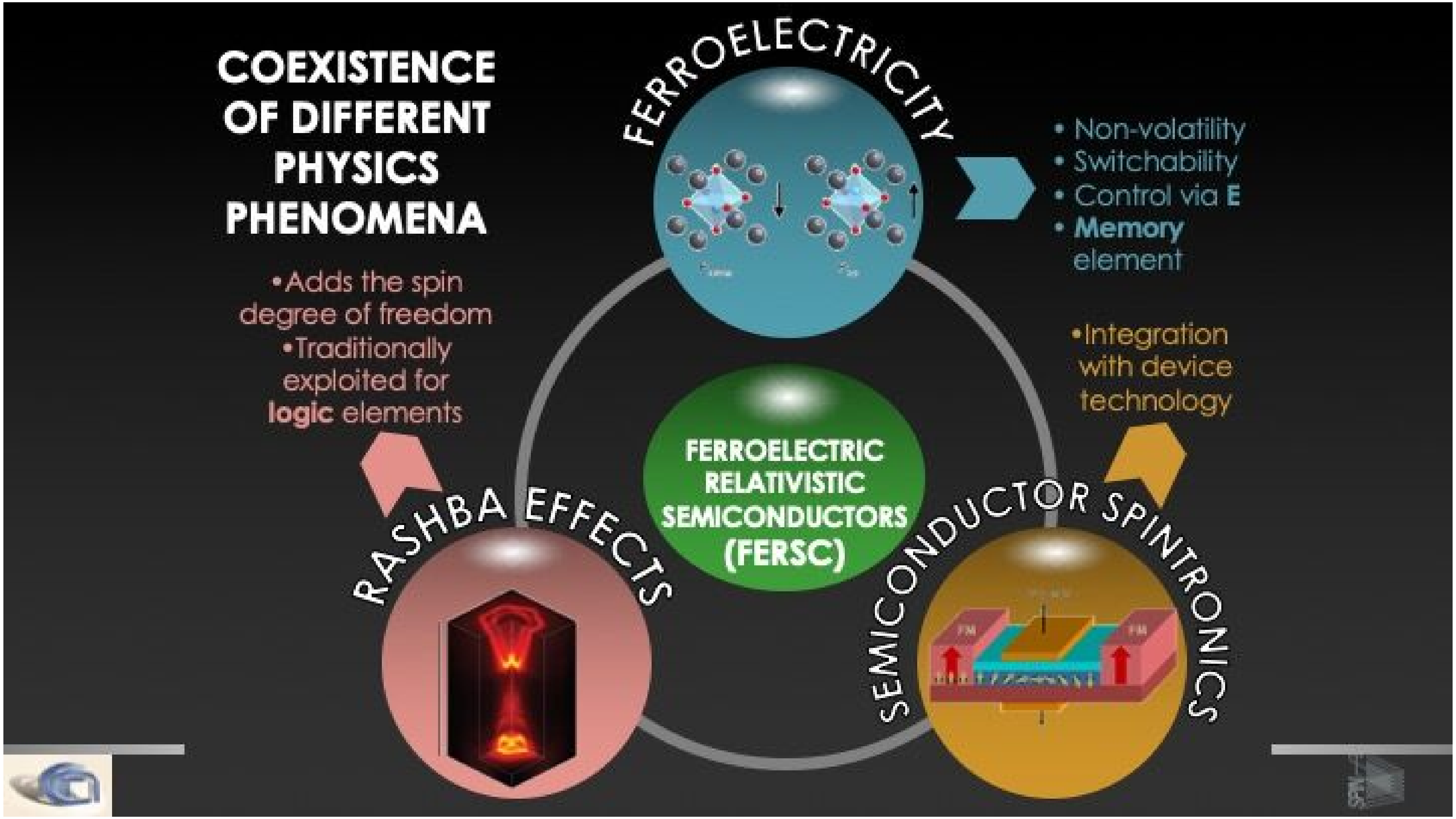
Table 2

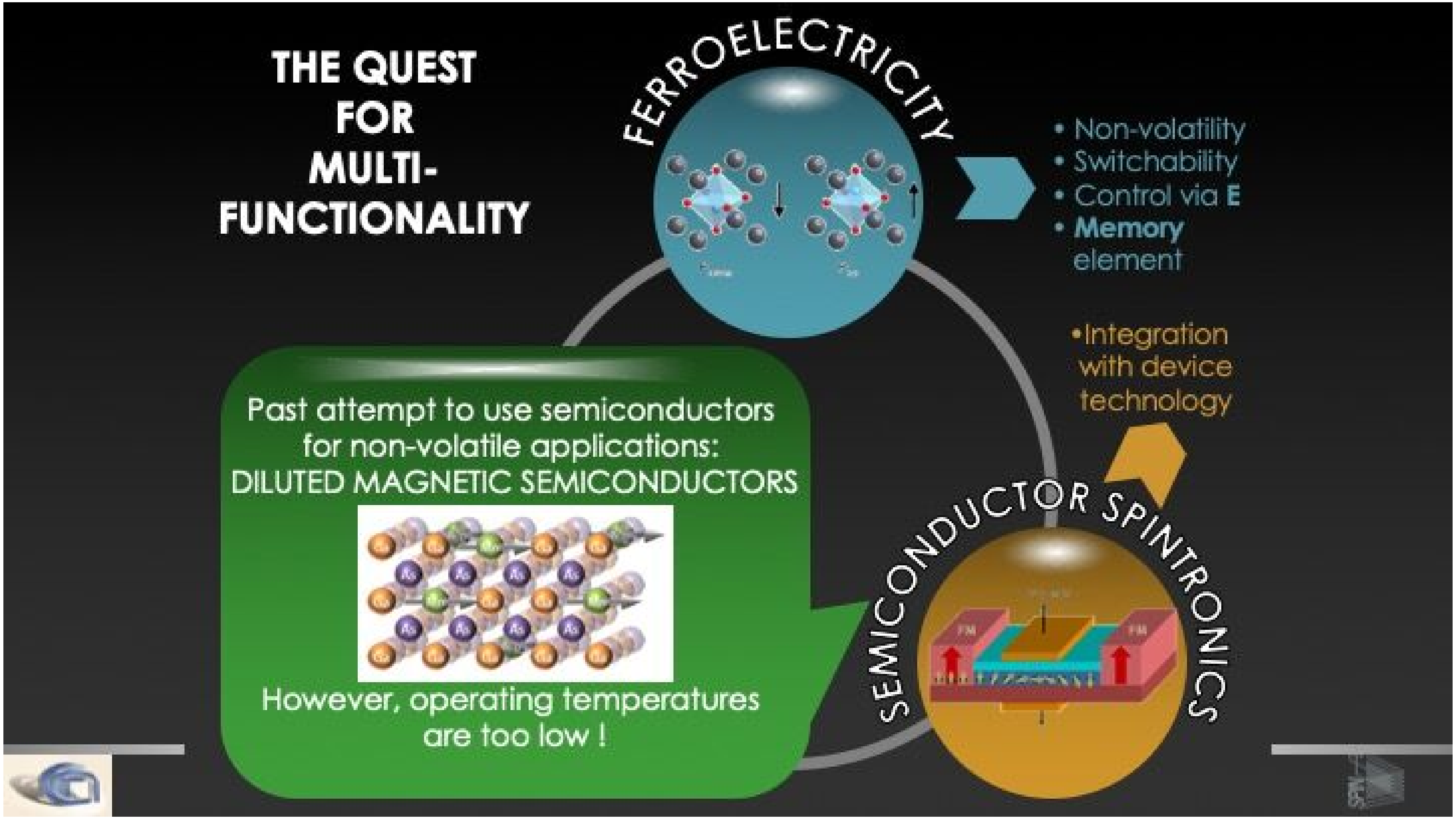
M_i	M_a	P (V_G)	R_e (v_{out})	Spin rot.
→	↓ (0)	↑ (1)	H (1)	← ↙ ↓
→	↓ (0)	↓ (0)	L (0)	← ↖ ↑
→	↑ (1)	↑ (1)	L (0)	← ↙ ↓
→	↑ (1)	↓ (0)	H (1)	← ↖ ↑

Reconfigurable logic gates:

- NOT
- BUFFER
- XNOR
- XOR

Table of truth for a spin-FET based on GeTe, operated in different configurations of the magnetization (M_i, M_a) in the two FM electrodes (injector, analyser) and of the dielectric polarization (P) in the GeTe channel. The high (low) device resistance (Re) state H (L) is associated to a logic state 1 (0)


COEXISTENCE OF DIFFERENT PHYSICS PHENOMENA
FERROELECTRICITY
• Non-volatility
• Switchability
• Control via **E**
• **Memory** element
•Adds the spin degree of freedom
•Traditionally exploited for **logic** elements
•Integration with device technology
FERROELECTRIC RELATIVISTIC SEMICONDUCTORS (FERSC)
RASHBA EFFECTS
SEMICONDUCTOR SPINTRONICS
FM
FM


THE QUEST
FOR
MULTI-
FUNCTIONALITY
FERROELECTRICITY
• Non-volatility
• Switchability
• Control via **E**
• **Memory** element
•Integration with device technology
Past attempt to use semiconductors for non-volatile applications:
DILUTED MAGNETIC SEMICONDUCTORS
However, operating temperatures are too low !
SEMICONDUCTOR SPINTRONICS
FM
FM

GeTe WORKS "IN THE COMPUTER", BUT ....

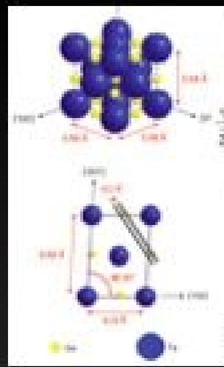
Shortcomings:

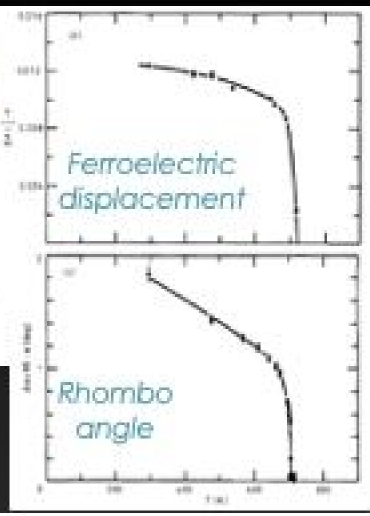
- low electrical resistivity (high density of Ge vacancies, leading to a density of free holes of up to ~ 10^{20} cm^{-3})

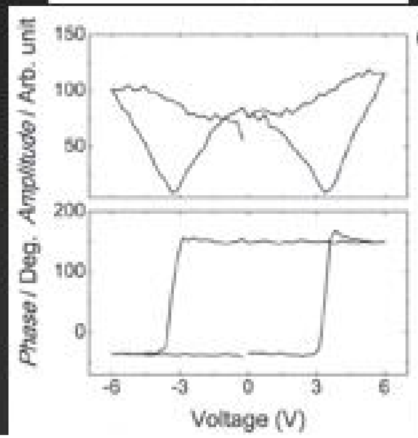
- a too small band gap (0.1 eV ? 0.6 eV ? indirect)
- structural ferroelectric distortions detected via neutron diffraction but no ferroelectric polarization ever measured

- recently, **FE switching via PFM** (*Gruverman et al, APL Mater (2014)* on MBE films grown on highly lattice-mismatched **Si(111)** substrates

- Rhombohedrally distorted rocksalt structure α-GeTe

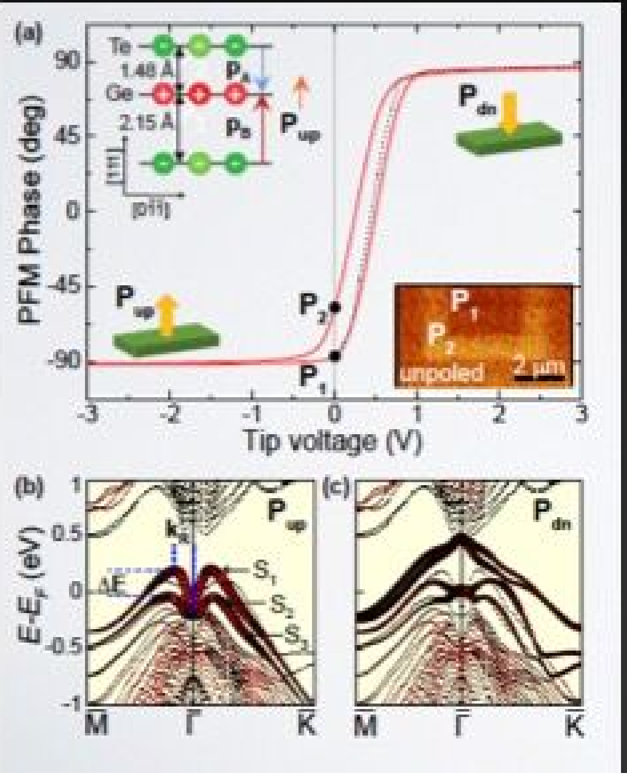




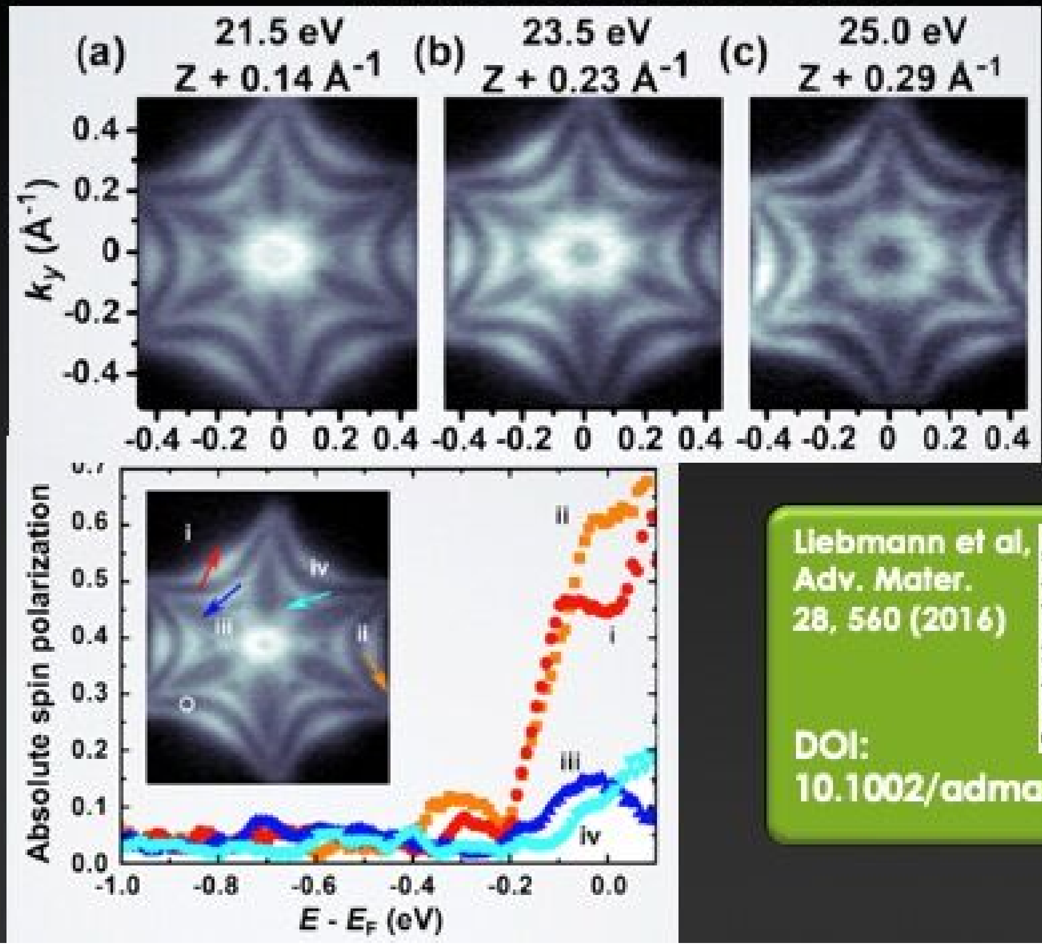


EXPERIMENTAL CONFIRMATION: SURFACE AND BULK RASHBA BANDS IN FE GeTe

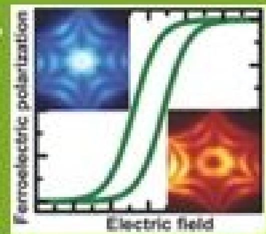
M. Liebmann, C. Rinaldi, D. Di Sante, A. Giussani, R. Wang, S. Bertoli, M. Cantoni, L. Baldrati, I. Vobornik, G.Panaccione, R. Calarco, S. Picozzi, R. Bertacco and M. Morgenstern



SURFACE AND BULK RASHBA BANDS IN FERROELECTRIC GeTe



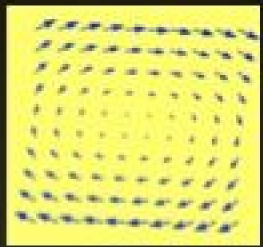
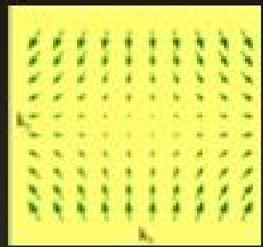
Liebmann et al, Adv. Mater. 28, 560 (2016)



DOI: 10.1002/adma.201503459

SPIN SPLITTING: RASHBA VS DRESSELHAUS

Historically, two kind of SOC-induced spin-splitting effects:

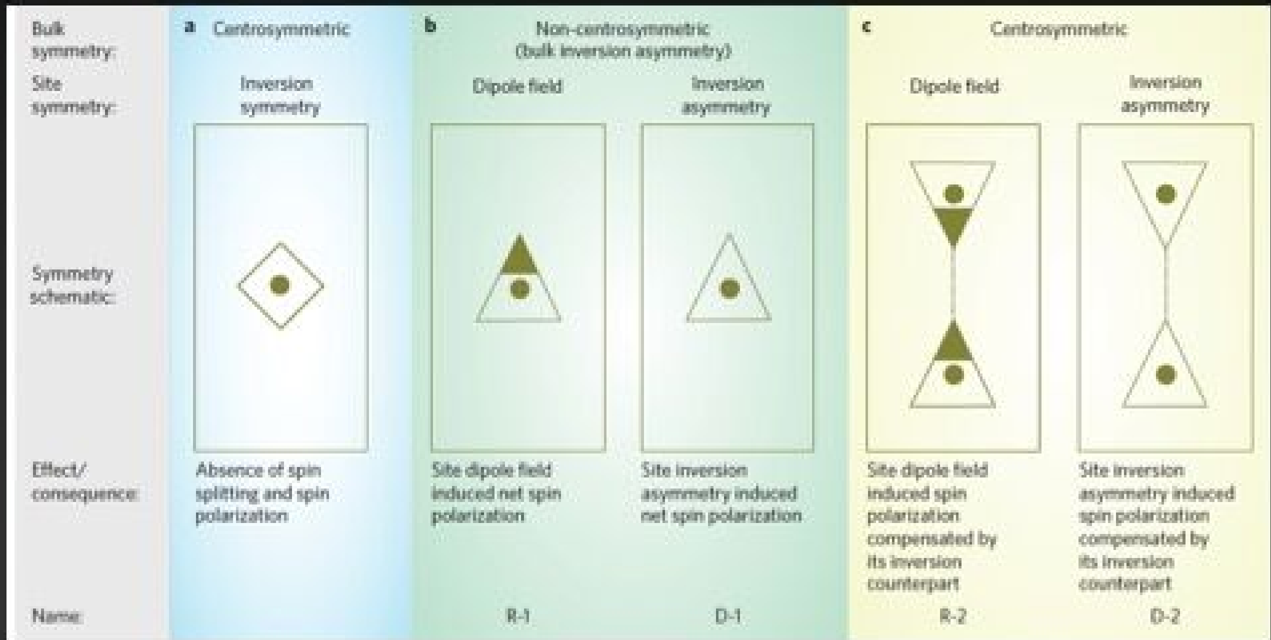
Rashba Effect	**Dresselhaus effect**
E. I. Rashba, Sov. Phys. Solid State 2, 1109 (1960). 	*G. Dresselhaus, Phys. Rev. B 100, 580 (1955)* 
Structural inversion Asymmetry (SIA) *i.e. Interfaces, surfaces, 2DEG*	Bulk Inversion Asymmetry (BIA) *i.e. Zincblende, wurtzite crystal*

… but Rashba-like spin-textures in bulk 3D crystals have been reported….

SPIN SPLITTING: RASHBA VS DRESSELHAUS

Unified description of spin-polarization effects:

"Because SOC is a relativistic effect, anchored on particular nuclear sites in the solid, it is the <u>symmetry of such individual atomic sites</u> in the solid that forms a good starting point to describe the SOC-induced spin polarization effect, <u>rather than the global symmetry of the unit cell</u> (as in SIA or BIA) "

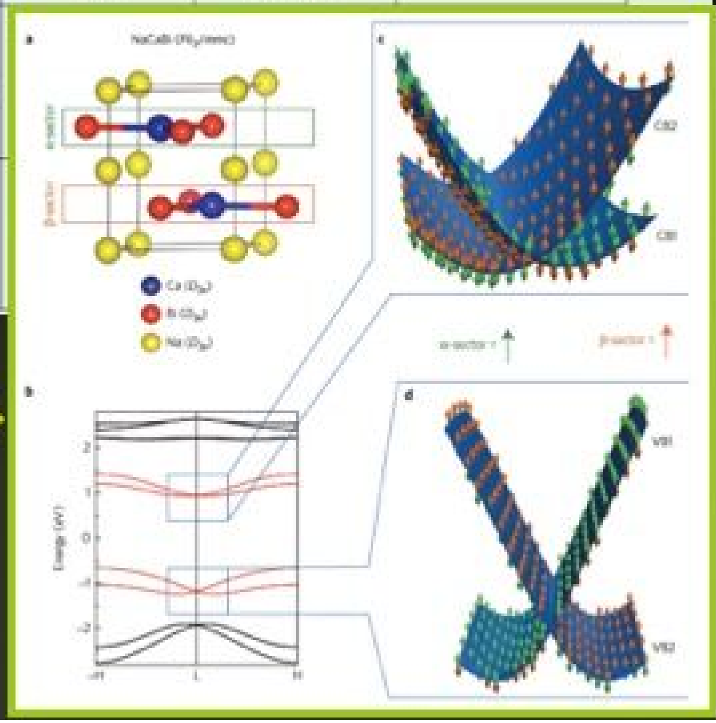


Zhang et al, Nature Physics 10, 387 (2014)

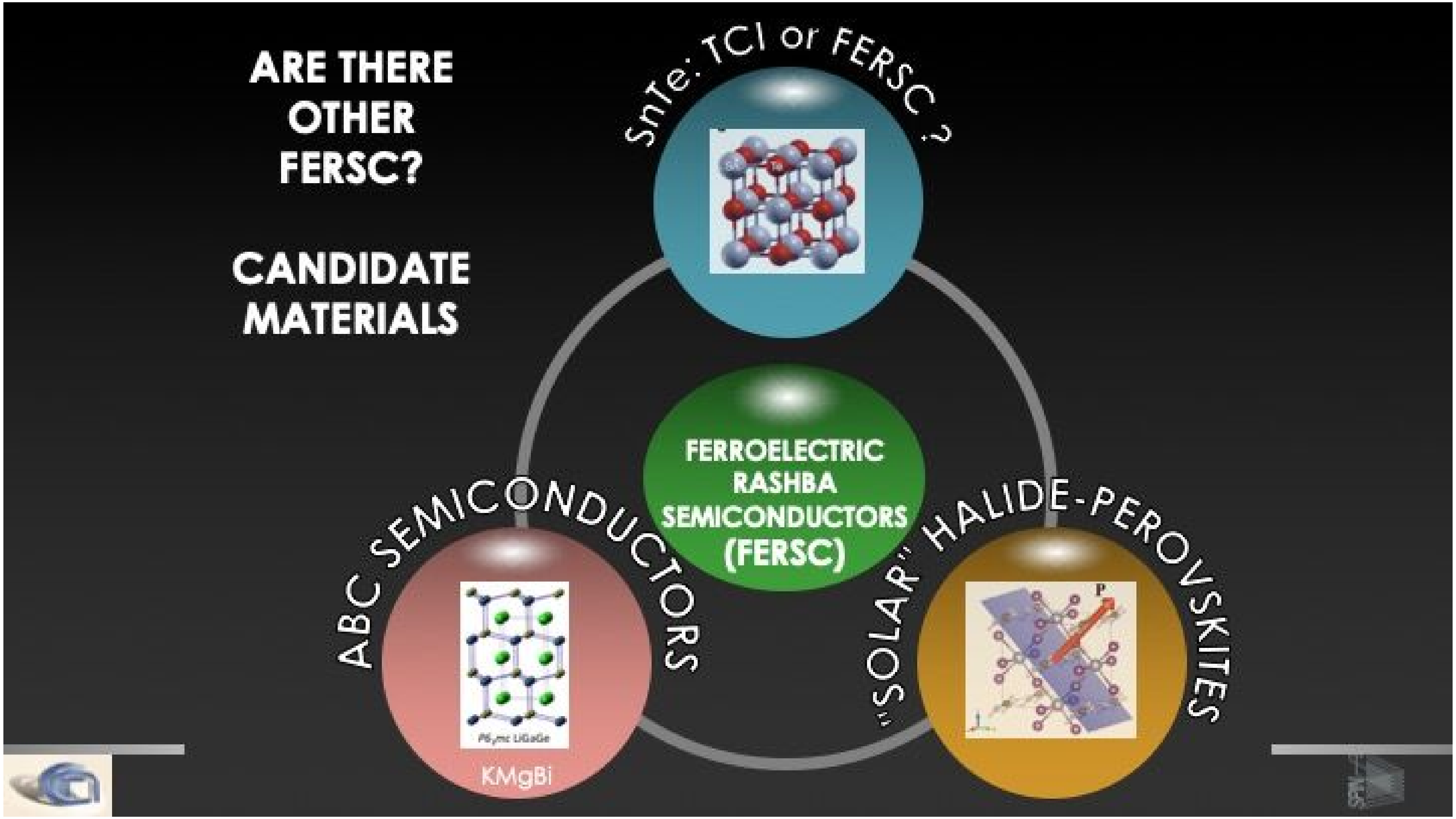
SPIN SPLITTING: RASHBA VS DRESSELHAUS

Table 1 | Classification of spin polarization in nonmagnetic bulk materials on the basis of bulk space group and site point group.

Bulk space group \ Site point group	Non-centrosymmetric (at least one site)			Centrosymmetric (all sites)
	Non-polar (all sites) (D_2, D_3, D_4, D_6, S_4, D_{2d}, C_{3h}, D_{3h}, T, T_d, O)	Polar (at least one site) (C_1, C_2, C_3, C_4, C_6, C_{1v}, C_{2v}, C_{3v}, C_{4v}, C_{6v})		(C_i, C_{2h}, D_{2h}, C_{4h}, D_{4h}, S_6, D_{3d}, C_{6h}, D_{6h}, T_h, O_h)
		Dipoles add up to zero	Dipoles add up to non-zero	
Non-centrosymmetric (for example, $F\bar{4}3m$)	a D-1 Example: GaAs, ZrCoBi			
Centrosymmetric (for example, $R\bar{3}m$)	d D-2 Example: Si, NaCaBi			

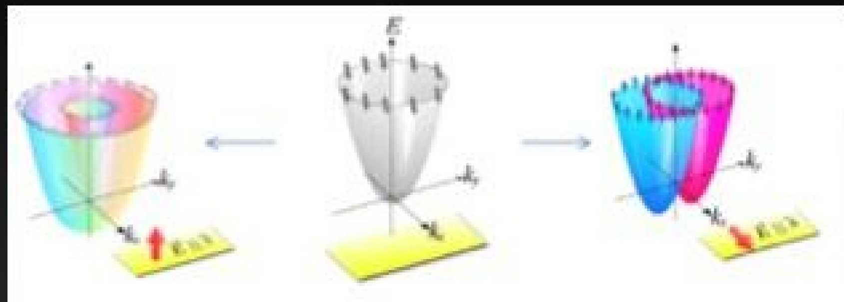


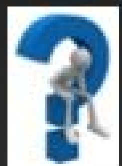
Zhang et al, Nature Physics 10, 387 (2014)


ARE THERE OTHER FERSC?
CANDIDATE MATERIALS
SnTe: TCI or FERSC ?
FERROELECTRIC RASHBA SEMICONDUCTORS (FERSC)
ABC SEMICONDUCTORS
KMgBi
"SOLAR" HALIDE-PEROVSKITES
P

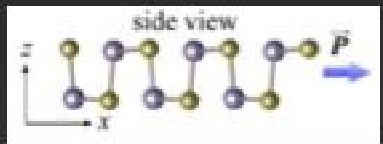
CAN WE USE OXIDES ?

- **Motivations:**
  - Better **insulators** (*i.e. ferroelectrics*) wrt GeTe (quite "leaky" semicond.)
  - **Different directions for polarization** (… P is often in-plane for thin-films due to depolarization fields)





What happens if P is in-plane?



H. Lee et al., arxiv:1712.06112v3 on FE SnTe thin-films

CAN WE USE OXIDES ?

- **Motivations:**
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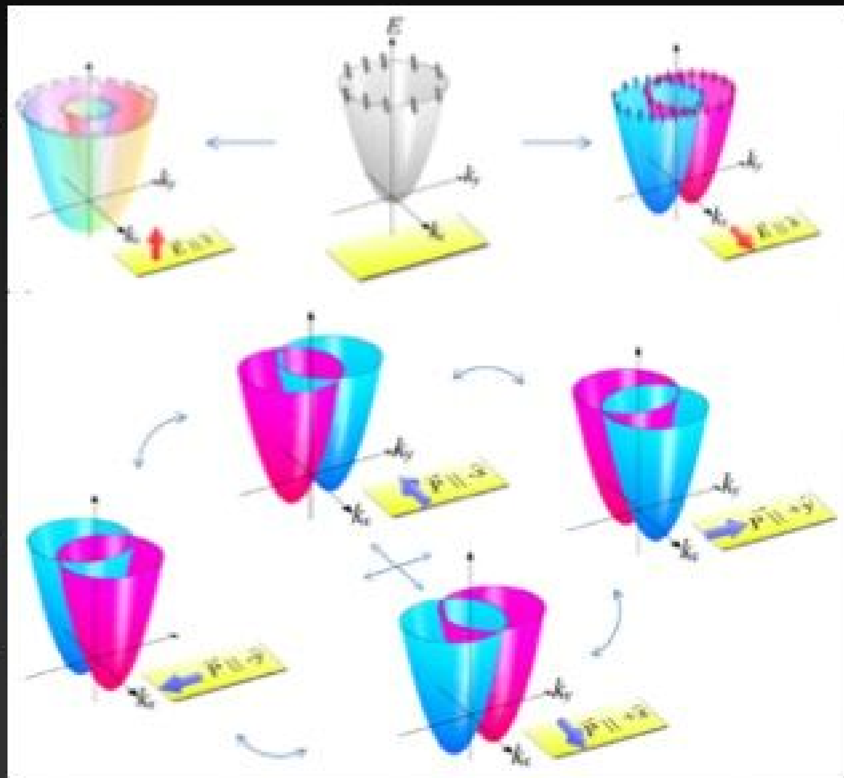
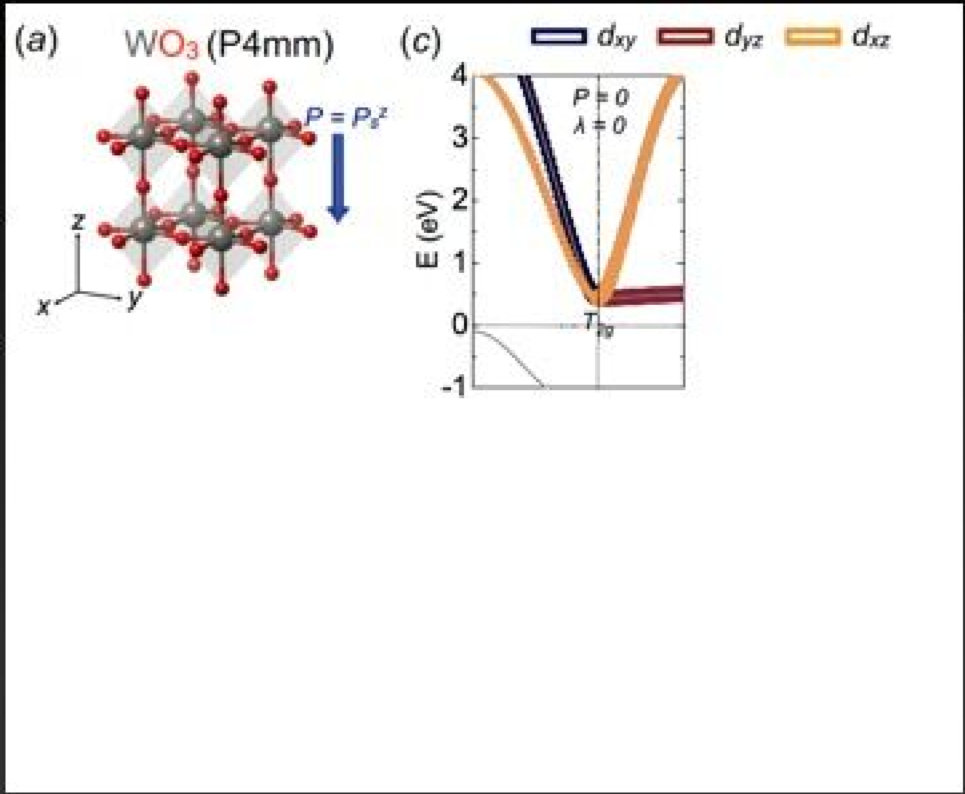
  - **Different directions for polarization** (… P is often in-plane for thin-films due to depolarization fields)



TUNGSTEN-BASED OXIDES (I)

- **WO_3 :** ground state (non-polar) *$P2_1/c$*, but (polar) orthorhombic *Amm2* only 20 meV/f.u. higher in energy.
- (Simpler) tetragonal polar *P4mm* also close (74 meV/f.u.)

✓ **P=0, no SOC:**
Triply degenerate t_{2g}



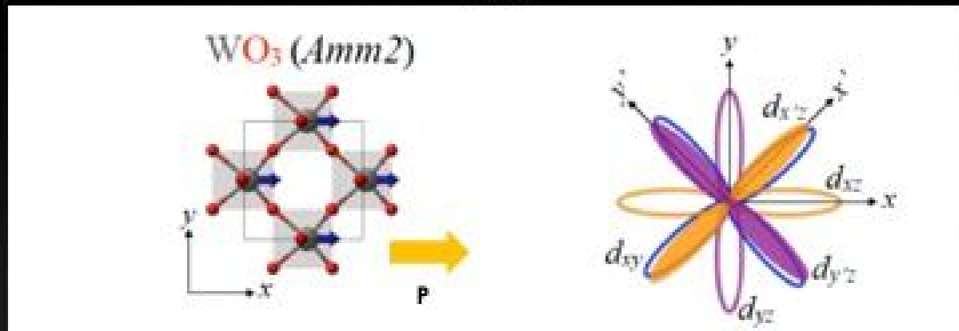
TUNGSTEN-BASED OXIDES (II)

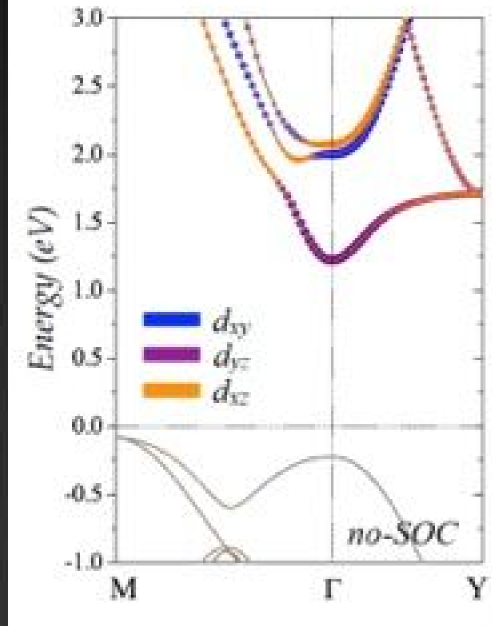
- **WO_3 :** ground state (non-polar) $P2_1/c$, but (polar) orthorhombic *Amm2* only 20 meV/f.u. higher in energy.
- (Simpler) tetragonal polar *P4mm* also close (74 meV/f.u.)

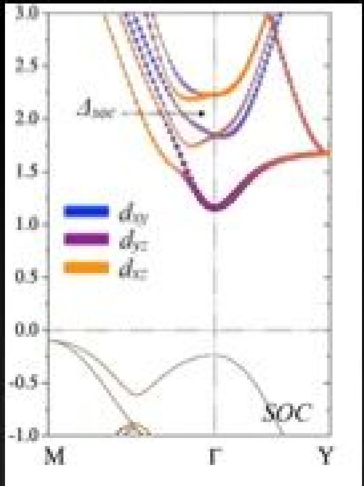
d_{xz}: *Highest energy band, points towards P*

d_{xy}: *medium energy band, in the plane (also containing P)*

d_{yz}: *lowest energy band, perpendic. to P*

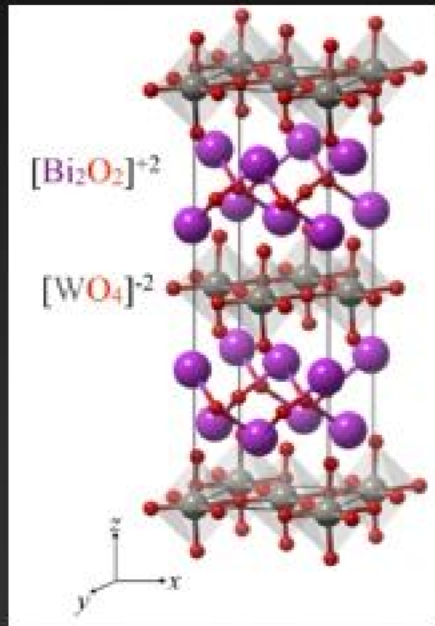






TUNGSTEN-BASED OXIDES (III)

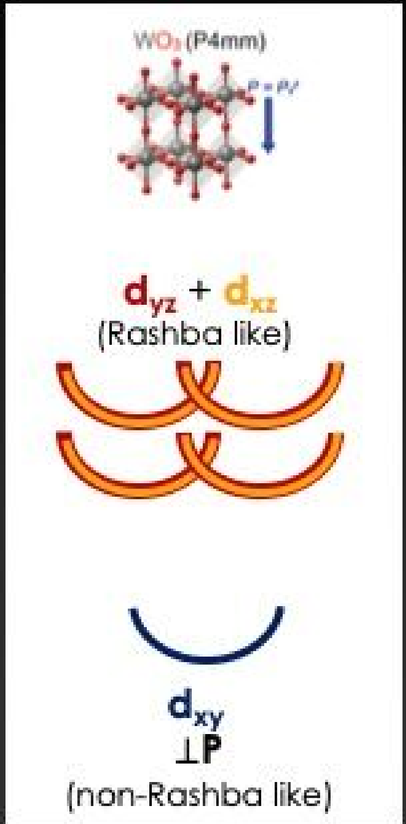
- **STRATEGY:** raise the energy of (non-Rashba-like) d_{yz} *(perpendic. to P)*
- **HOW?** Destabilize out-of-plane orbitals by changing the W-O-W out-of-plane coordination and keep d_{xy} as lowest (Rashba-like) state



- **POSSIBLE SOLUTION:** Aurivillius phase Bi_2WO_6
- **Layered structure:** $(Bi_2O_2)^{+2}$ $(A_{m-1}B_mO_{3m+1})^{-2}$
  - Bi_2O_2 = fluorite layer
  - $A_{m-1}B_mO_{3m+1}$ = perovsite blocks
- Here **m=1** (smallest member of Aurivillius phases, A-site deficient)
- Space group *F2mm*
- **P** along **x** ~ 50 μC/cm²
- Quite wide gap (about 2.7 eV)

TUNGSTEN-BASED OXIDES (IV)

"t_{2g} Band engineering" in Ferroelectric oxides

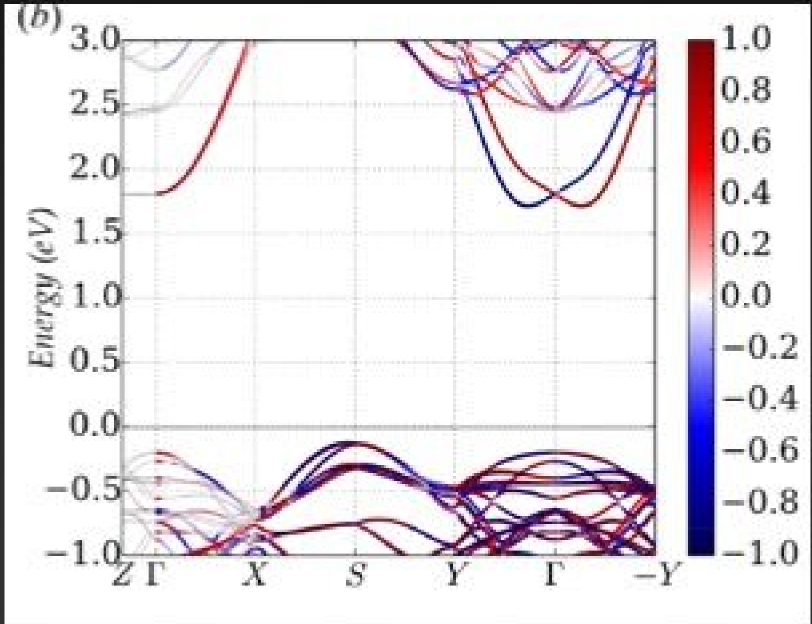


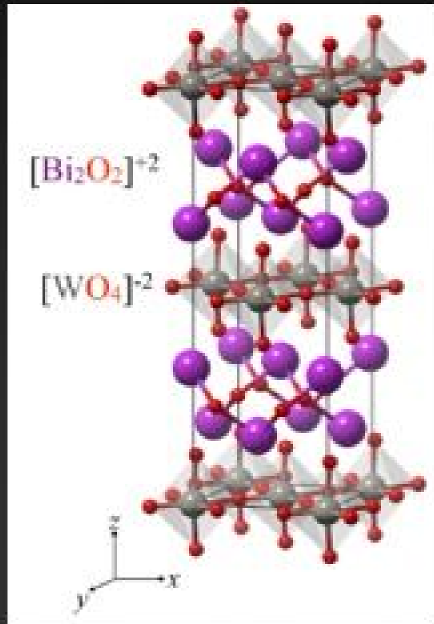
TUNGSTEN-BASED OXIDES (V)

- ***F2mm*** ***Bi_2WO_6***(Γ_5^- from tetragonal ***I4/mmm*** PE)
- Small dispersion along Γ-Z: roughly "2D"

- Lowest band Rashba-like: ΔE = 104 meV, Δ**k** = 0.14 $Å^{-1}$, **α_R = 1.45 eVÅ**
  - Mainly d_{xy} , whereas d_{xz} and d_{yz} upper in energy

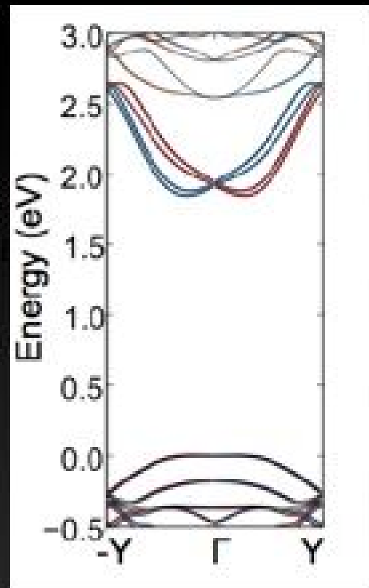
Spin-polarization s_z: red/blue color

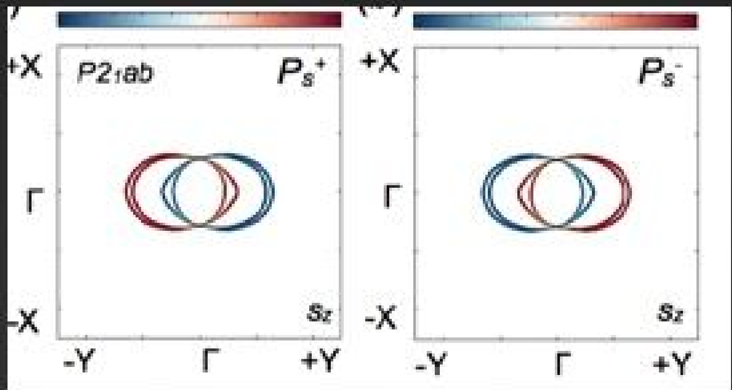




TUNGSTEN-BASED OXIDES (VI)

- Complex distortions/tilting in ground-state structure of $\mathbf{Bi_2WO_6}$:
  - X_2^+: rotation of O octahedra around z
  - X_3^+: tilt of O octahedra around x
  - Γ_5^-: polar zone center along x
- ***F2mm*** (Γ_5^- from tetragonal ***I4/mmm*** PE)
- ***P2₁ab*** ($X_2^+ + X_3^+ + \Gamma_5^-$)

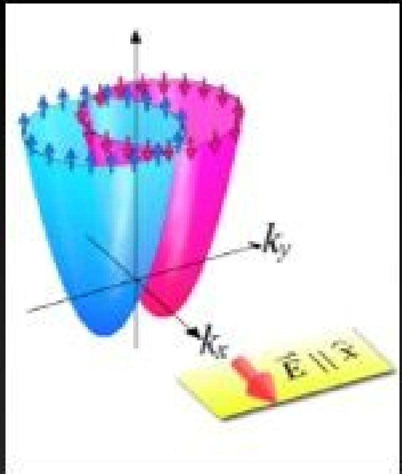


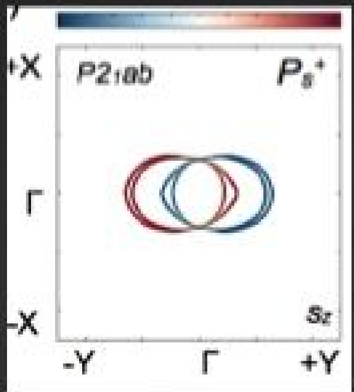


Polarization switching implies $\mathbf{s_z}$ switching:

Electric control of spin-texture !

TUNGSTEN-BASED OXIDES (VI)



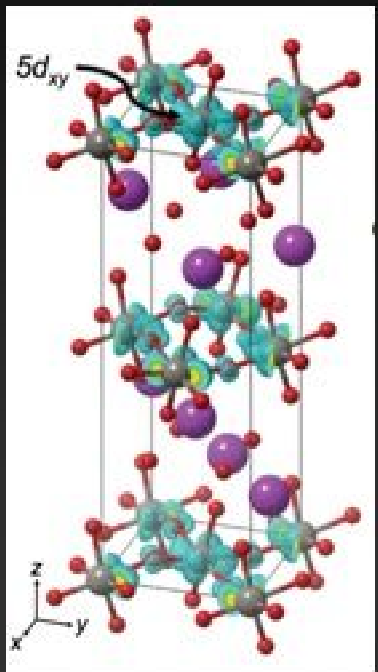


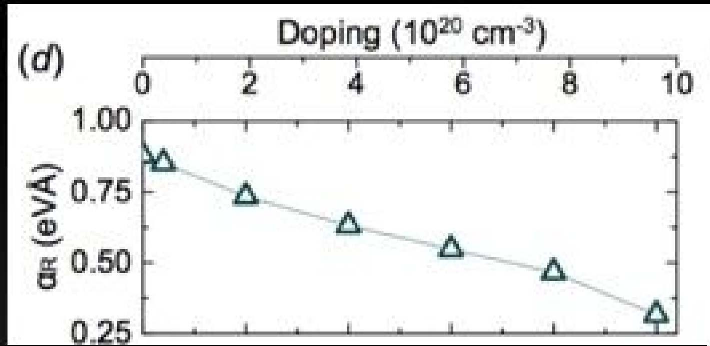
PERSISTENT SPIN HELIX
(well known in Semiconducting Quantum wells)

- ✓ **Protection against spin scattering**
- ✓ **Long spin lifetime !**

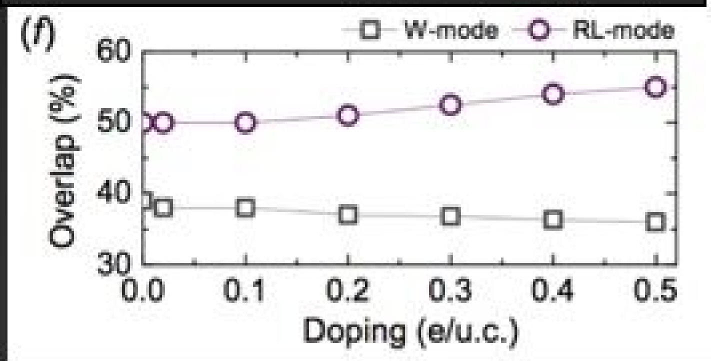
TUNGSTEN-BASED OXIDES (V)

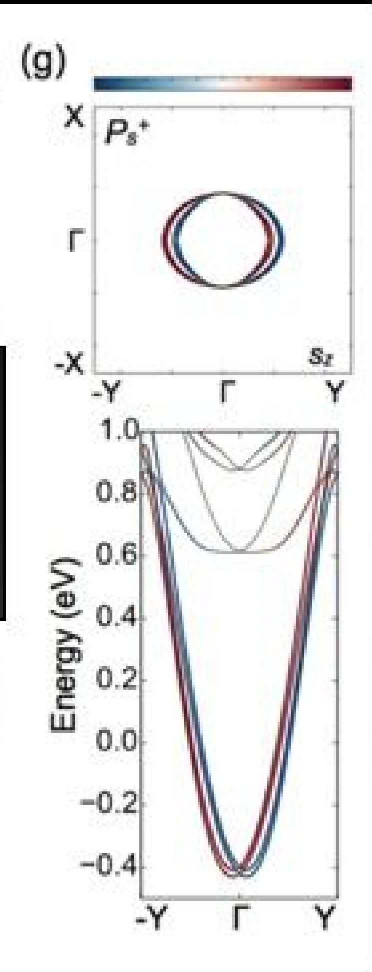
- What happens upon electron doping?





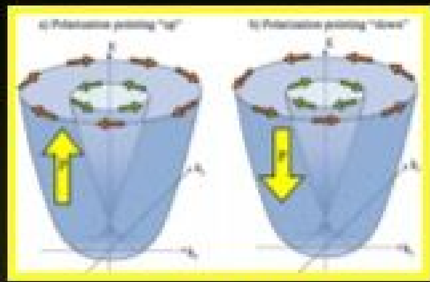
- Doping of 0.5 e/unit cell
- Spin-texture into $k_x k_y$ plane at E = 2.0 eV

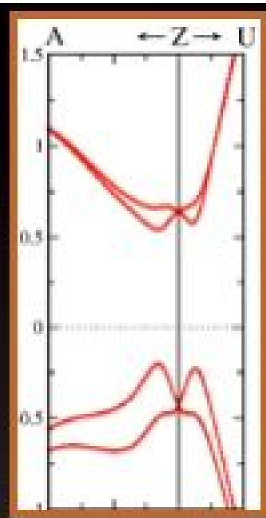




TAKE HOME MESSAGES (I)

- **GeTe**: first example of **FERSC** (**FErroelectric Rashba SemiConductor**)

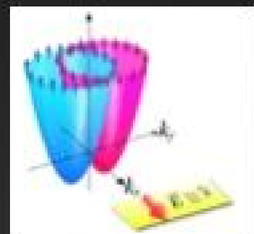


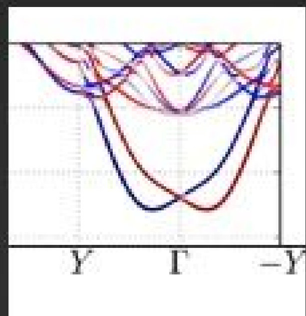


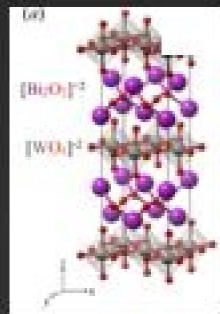
- Sense of spin-rotation: **opposite when P is switched**

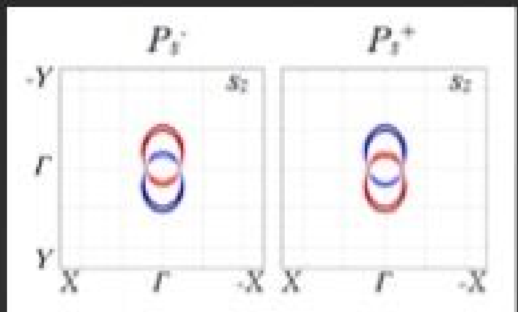
- **Large Bulk Rashba** effect in **oxides:** Aurivillius-phase **Bi_2WO_6: PSH**

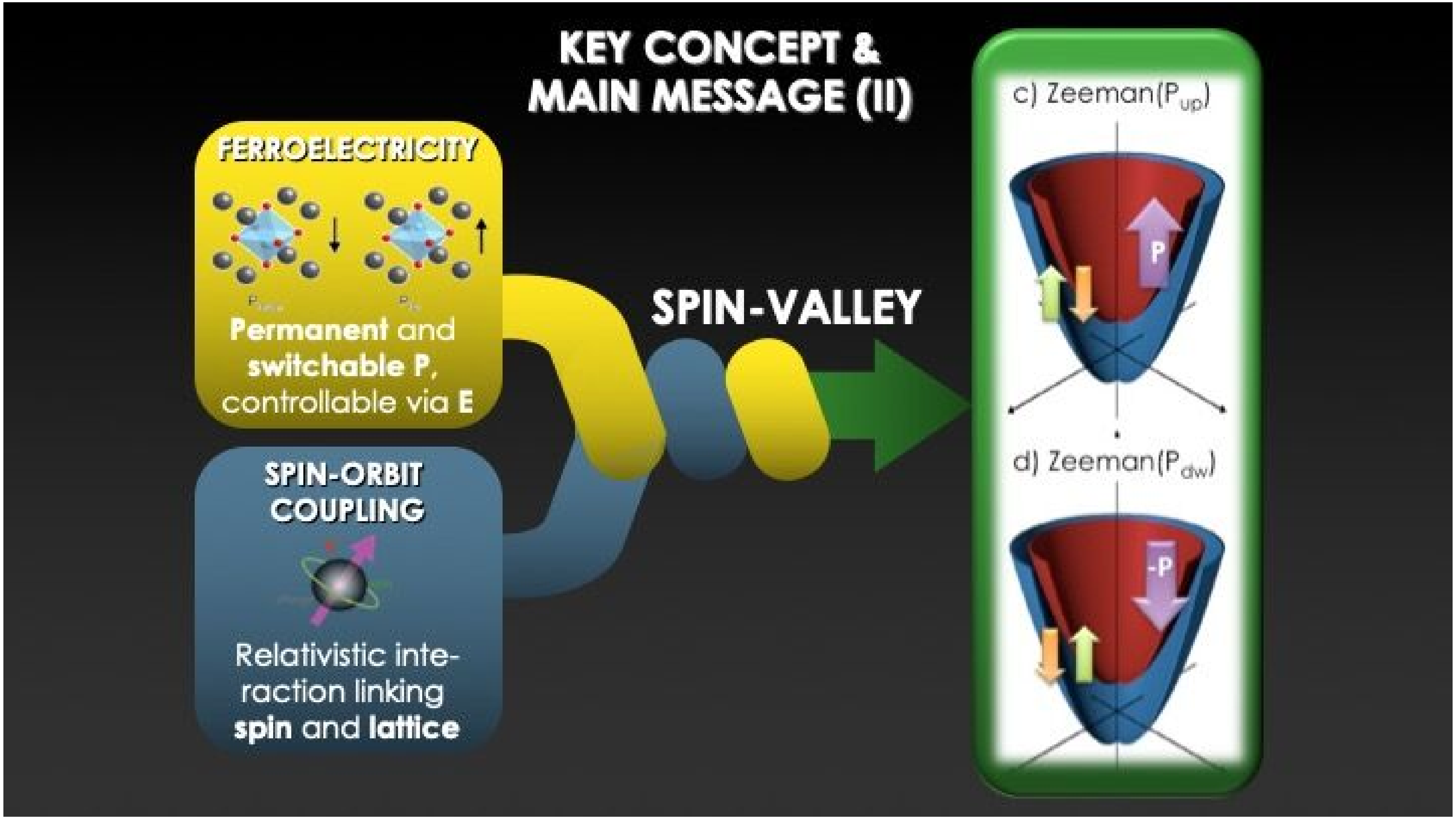
- Oxides (strong Ferroelectrics) offer possibilities to "***engineer***" SOC effects in band structures





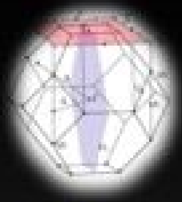


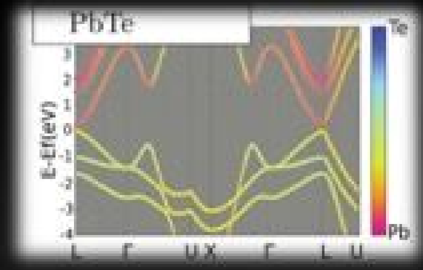



KEY CONCEPT &
MAIN MESSAGE (II)
FERROELECTRICITY
Permanent and
switchable P,
controllable via E
SPIN-ORBIT
COUPLING
Relativistic inte-
raction linking
spin and lattice
SPIN-VALLEY
c) Zeeman(P_up)
P
d) Zeeman(P_dw)
-P

INTRODUCING THE VALLEY CONCEPT

- **Valleys**: energy extrema in momentum space





Band structure of Rock-salt Chalcogenides - Valleys at TRIM L points

- Valley two-valued **pseudospin** : defined when valleys occur at points which are not time-reversal invariant momenta (TRIM)

ALL-OXIDE VALLEYTRONICS

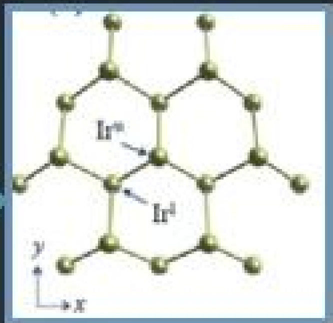
Starting point: $(ABO_3)_2(AB'O_3)_n$ [111] heterostructure

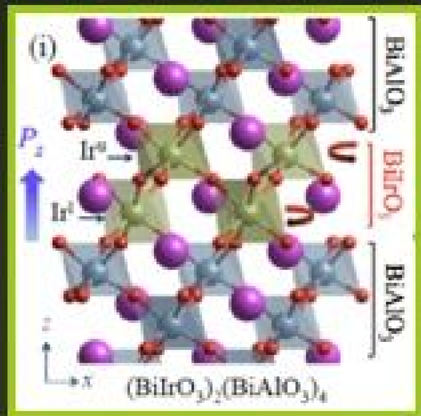
- ✓ (111) TM bilayer with honeycomb lattice
- ✓ 2 trigonal sublattices on different layers
- ✓ Lattice geometry supports Dirac points*

** Nagaosa, Okamoto, Nat. Comms (2011)*

- Our **Receipt:** Embed **5d-oxide bilayer*** (large SOC) in a **(111) FE host**
- **FE $BiAlO_3$** (**P**//[111], *R3c*)
- **Materials design**: $BiIrO_3$ in $BiAlO_3$

Top view: Honeycomb lattice

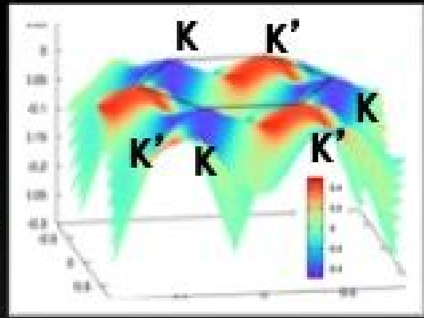




Side view: Unit cell: $Bi_6Ir_2Al_4O_{18}$

$BiIrO_3/BiAlO_3$ BAND STRUCTURE

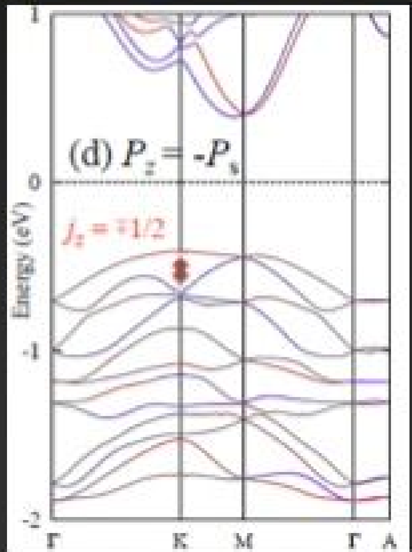
☛ Exactly as in MoS_2: **spin-polarized valleys!**

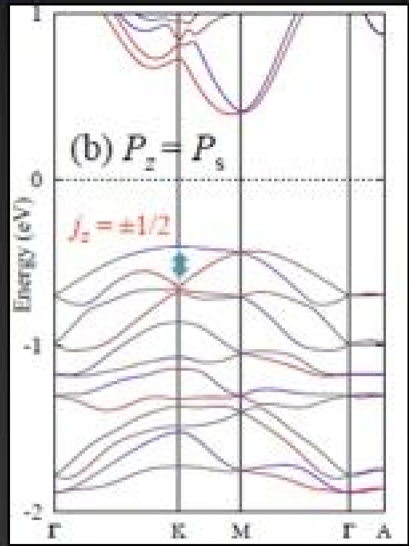


Valence Band Maximum at K/K ' with opposite spin-polarization

WHAT HAPPENS UPON POLARIZATION SWITCHING?

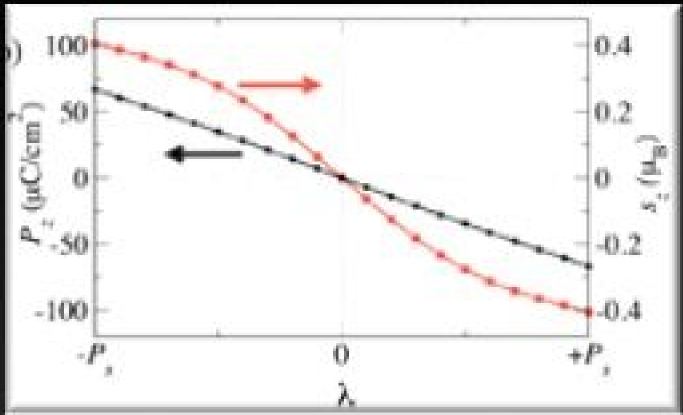
-Ps (w SOC)
∗ Spin-polarization switching





Ps (w SOC)
∗ VBM @K (hybridization A1g and Eg')

COUPLING BETWEEN P AND SPIN-SPLITTING



polar ionic distortion

Electric polarization P_z and s_z polarization are strongly coupled i.e. one can tune s_z by applying electric field !

☛ **Layer** degree of freedom related to FE polarization

☛ **Spin-valley-layer coupling** :

Sort of "**magnetoelectric**" coupling

(Gong et al Nat Commun 4, 2053 (2013))

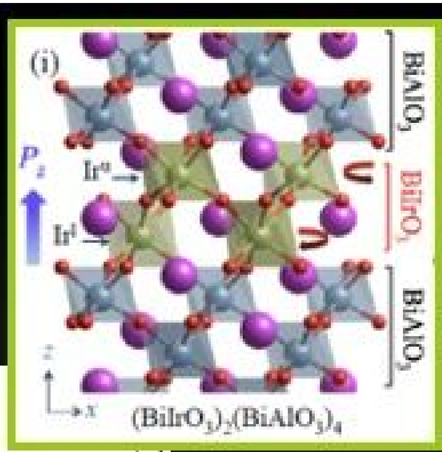
TAKE HOME MESSAGES (II)

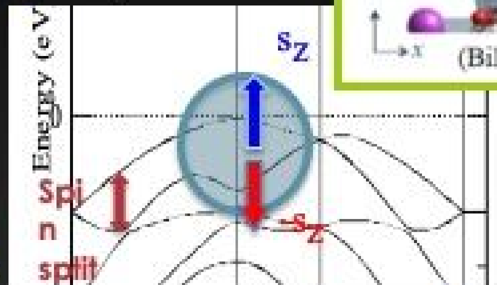
- Combination of **Ferroelectricity** with **SOC** leads to **Zeeman-like spin-splitting**

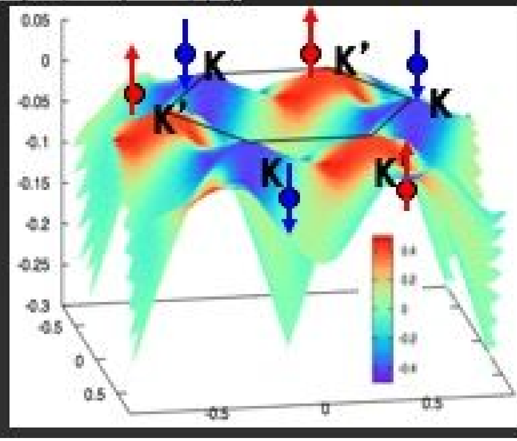
- **Receipt:** Embed a **5d-oxide bilayer** (lar-ge SOC) in **ferroelectric host**

- **$BiIrO_3$ bilayer in $BiAlO_3$:**
  - **Spin-polarized valley at K** (useful for **valleytronics**)
  - **S_z spin-polarization** can be **switched** by flipping **P**

✓ **ALL-OXIDE VALLEYTRONICS IN FERROELECTRIC HETEROSTRUCTURE**

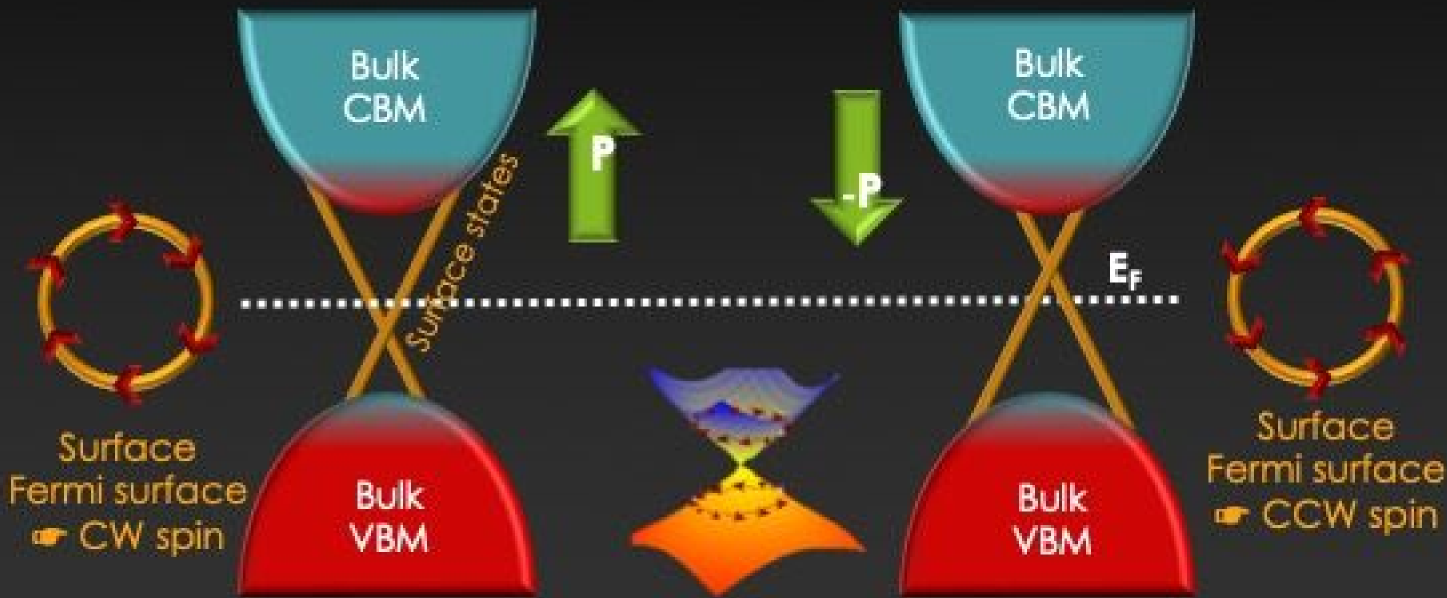




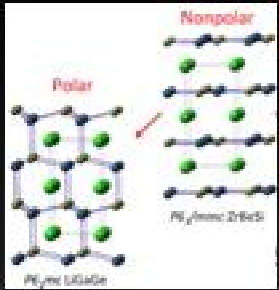


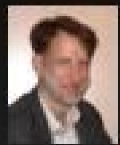
KEY CONCEPT & MAIN MESSAGE (III)

Topological Ferroelectric Semiconductor
(SOC-induced band inversion)



"ABC" HYPER-FERROELECTRICS



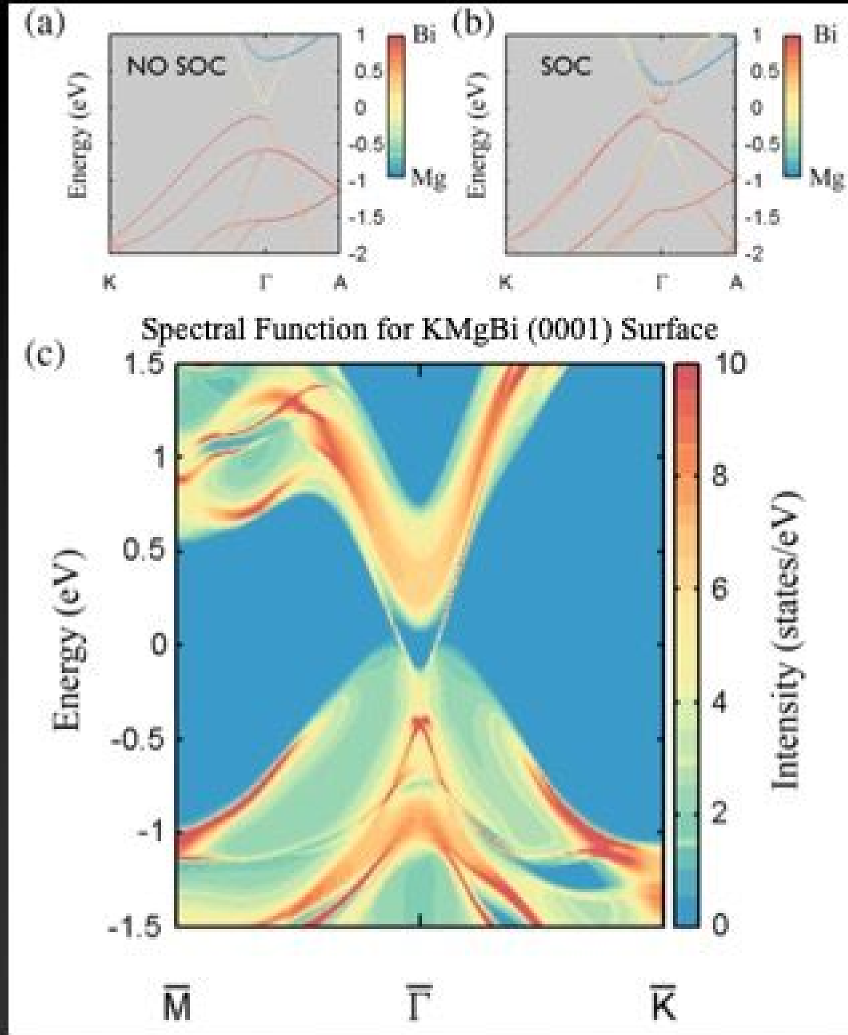


- FE that should maintain their **P** even in thin film limit

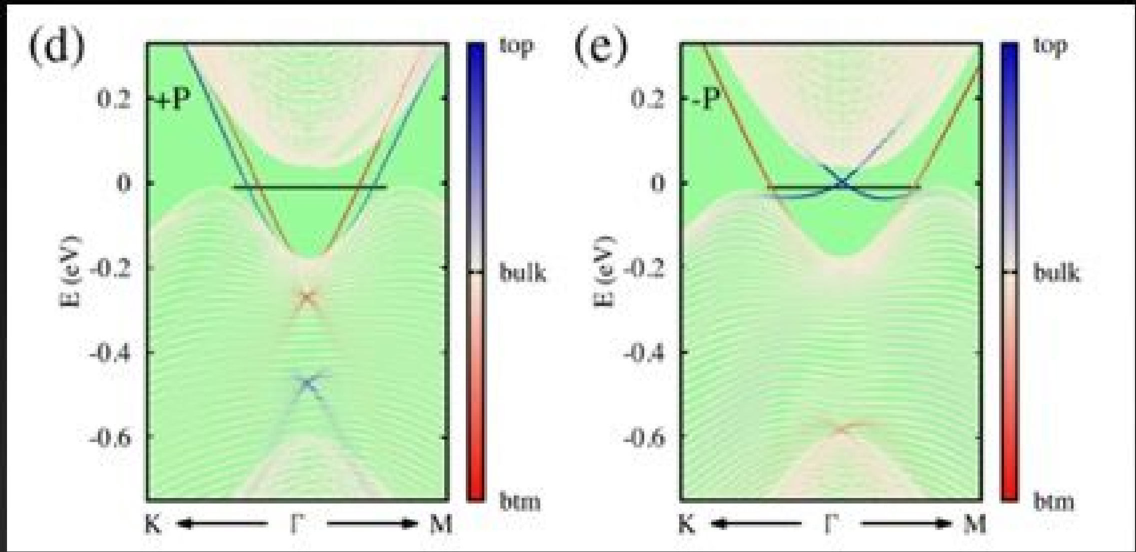
  *J. Bennett et al., PRL **109**, 167602 (2012)*

- **Some of these** (i.e. **KMgBi) are (FE) Top. Ins.!**

  *D. Di Sante et al., PRL **117**, 076401 (2014)*



"ABC" HYPER-FERROELECTRICS



4 term:

- K & MgBi;
- P_{in} & P_{out}

Summary:
WHY ARE RELATIVISTIC FERROELECTRICS USEFUL AND INTERESTING?

- From the **Fundamental Research** point of view:
  New mechanism for **cross-coupled spin-electric effect** =>
  interplay between ferroelectric order and spin degrees of freedom

- From the **Materials Science** point of view
  New class of **Multifunctional Materials** (... and, as such, open to **understanding** and **optimization** from theory, synthesis, characterization, ...)

- From the **Device/Technology** point of view
  New class of **electrically controlled spintronic devices** combining logic functions and storage

THANK YOU FOR YOUR ATTENTION !!