Polar Half-Metal and Triferroic Insulator based on $PbMnO_3$: First-principles Theory

Arpita Paul[1] and *Umesh V. Waghmare*

Theoretical Sciences Unit

JNCASR, Bengaluru 560064 INDIA

[1]Department of Physics, IIT Jammu

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[1] Inspire Faculty Fellowship

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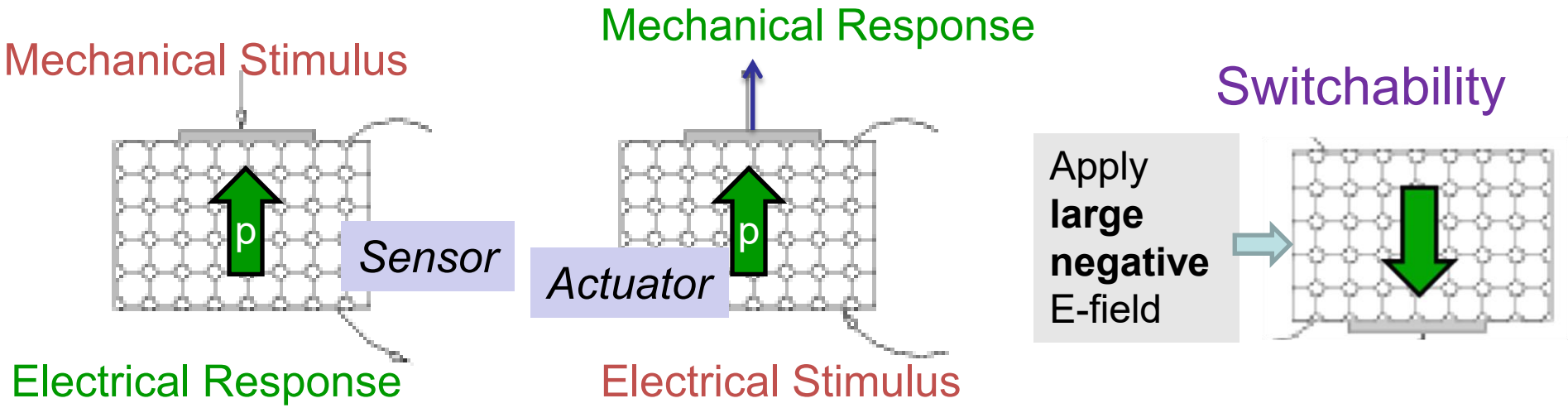
IIT Bombay

Polar Ferroic Materials: Ferroelectrics

Ferroelectrics: Smart Multifunctional Materials



Applications

Speakers, Heart Beat Monitors, Submarines,…

Non-volatile Memory

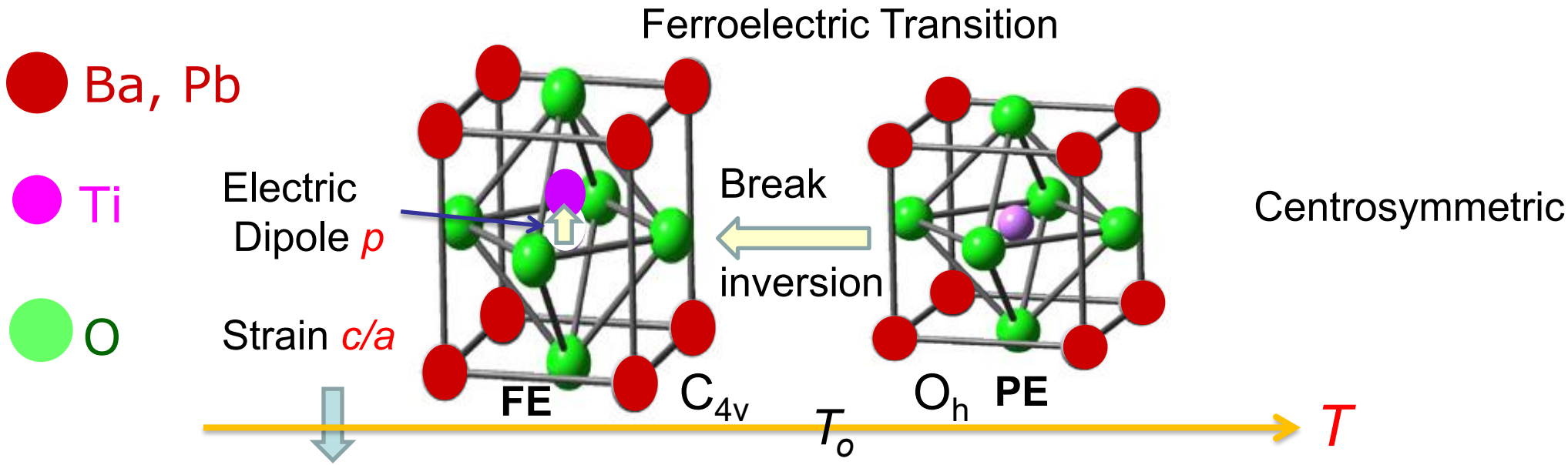
Interesting Science of Materials,

- Properties tunable by Electric Field and Stress
- Extreme Sensitivity to boundary conditions (surrounding)

- M. E. Lines and A. M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Oxford Univ Press (2001)
- M Dawber, K M Rabe and J F Scott, Rev Mod Phys 77, 20183 (2005).

Emergence of Properties across a Ferroic Transition

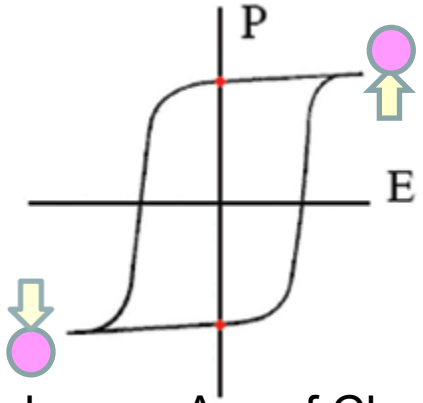
$BaTiO_3$, $PbTiO_3$



New Functional Properties ($T<T_o$): Applications

Linear Piezoelectric → Sensors, Actuators, MEMS, Speakers

Nonlinear Hysteresis → Memory

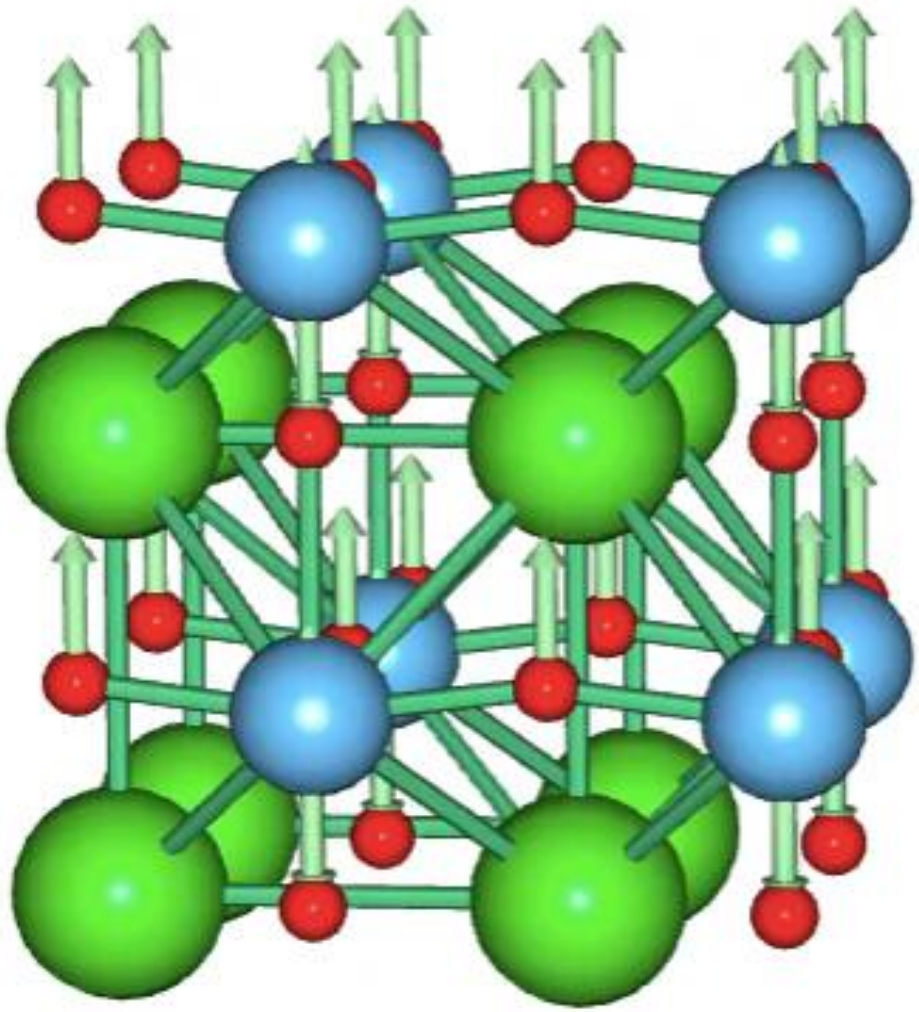


Near the Transition:

- Colossal piezo, dielectric properties
- Instability of Ti off-centering important!

U V Waghmare, Acc of Chem Res. 47, 3242 (2014)

TO Vibration (Phonon) Associated with ***Ferroelectric Lattice Instability***: $BaTiO_3$

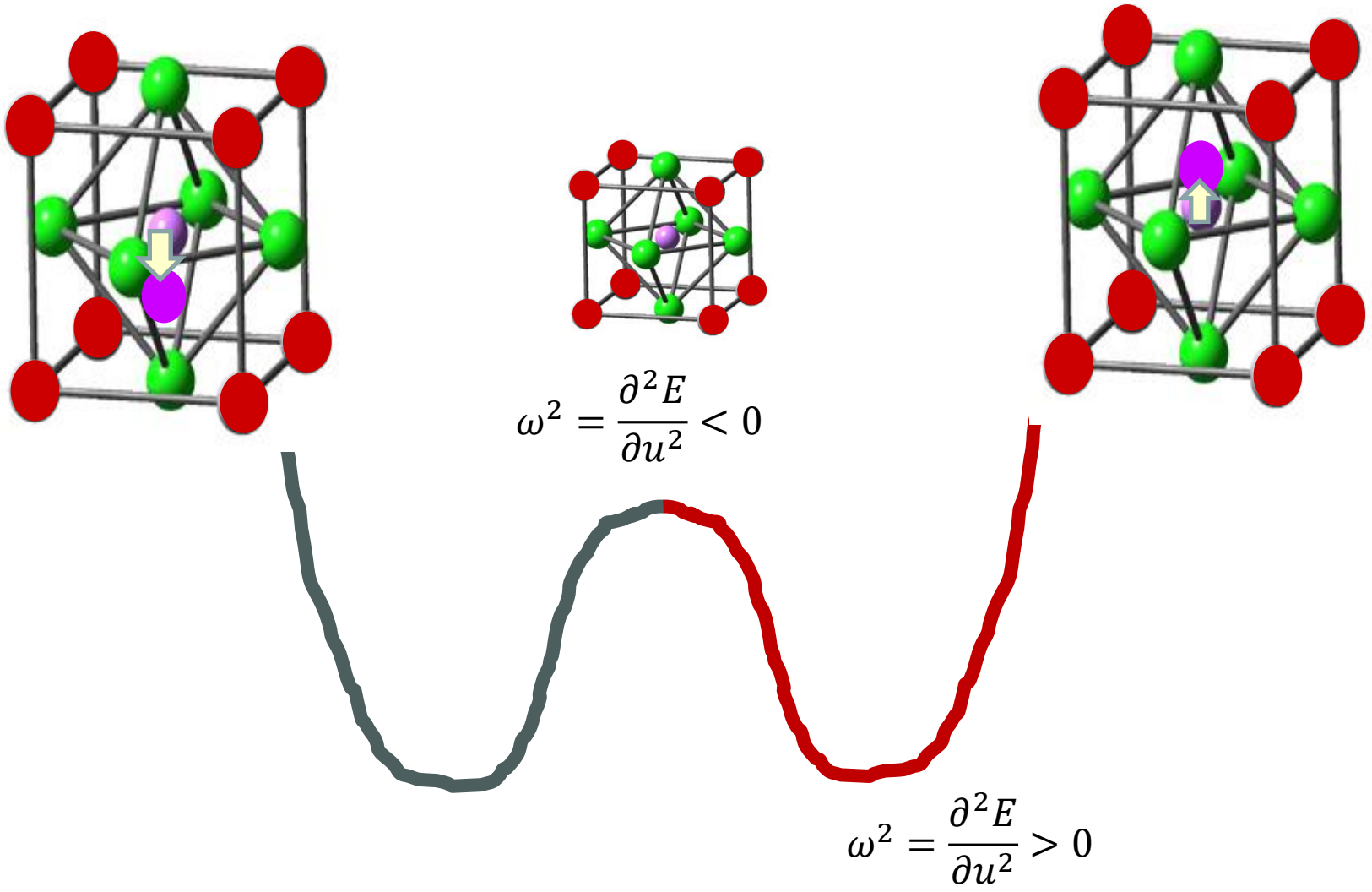


O

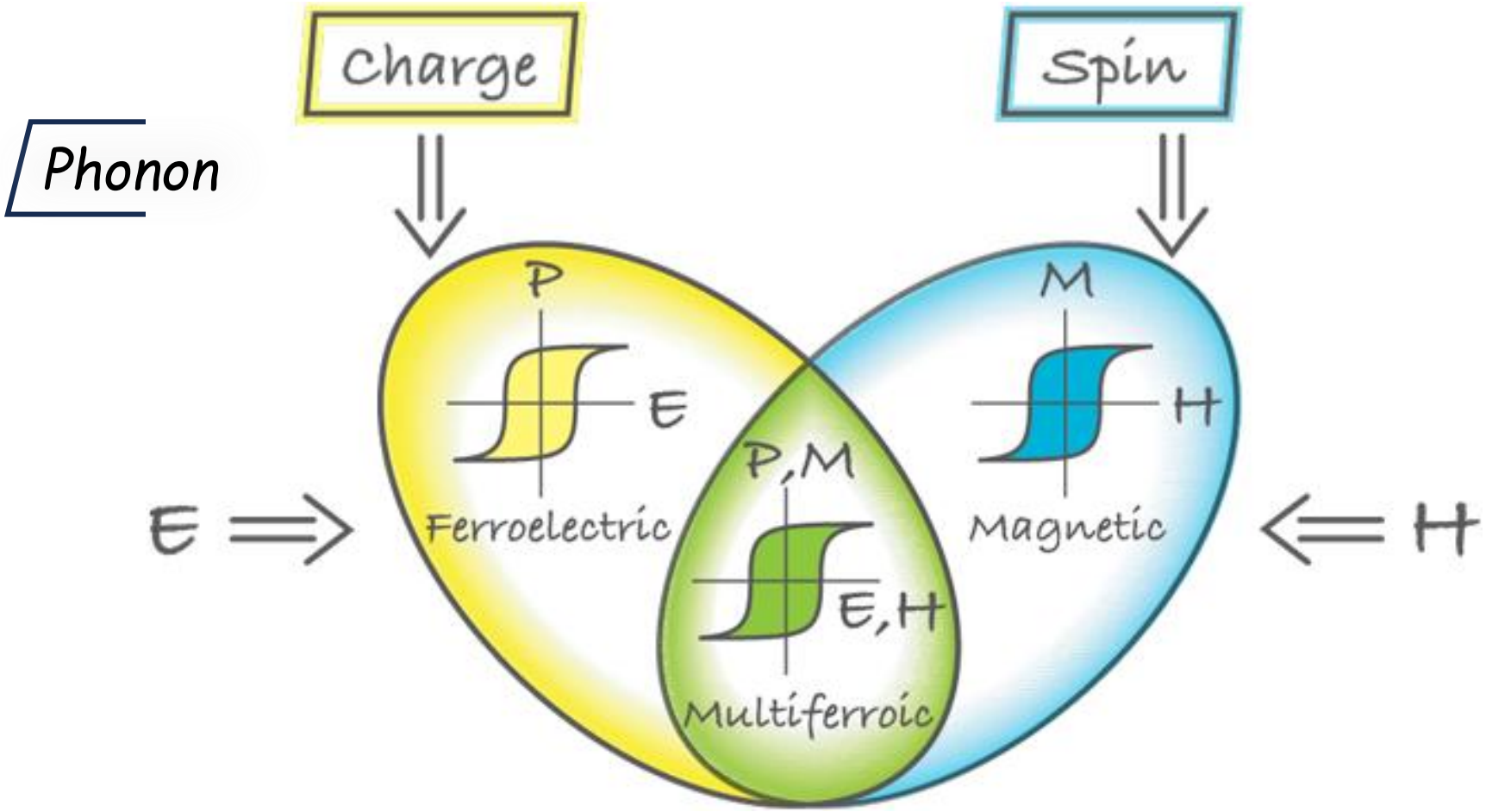
Ti

Ba

Lattice Instability



Interesting Science of Multi-ferroics

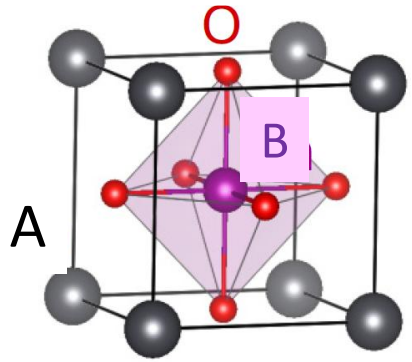


Khomskii, *Physics* 2, 20 (2009).

Transition Metal Oxides

ABO_3 perovskites

Symmetry Lowering Orders: Multi Ferroics



B

Ferroelectrics

$d^{n=0}$

Insulators

Polarity

BiFerroics

Half-metals

Ferromagnets

$d^{n\neq0} \rightarrow S$

Metals

Inversion symmetry

Polar Half-metallic Ferromagnet?

Puggioni et al, Phys Rev Mat 2, 114403 (2018)

- Metallic in one spin channel: Ferromagnet
- Gapped in the states of other spin channel: Polarization

Valence State Crossover in PbT_MO_3

Not investigated properly

T_M	Titanium	Vanadium	Chromium	Manga-nese	Iron	Cobalt	Nickel
	22 **Ti** 47.867	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.845	27 **Co** 58.933	28 **Ni** 58.693

T_M^{4+}, Pb^{2+} ← → T_M^{2+}, Pb^{4+}

Ferroelectricity

Charge Glass / AFM

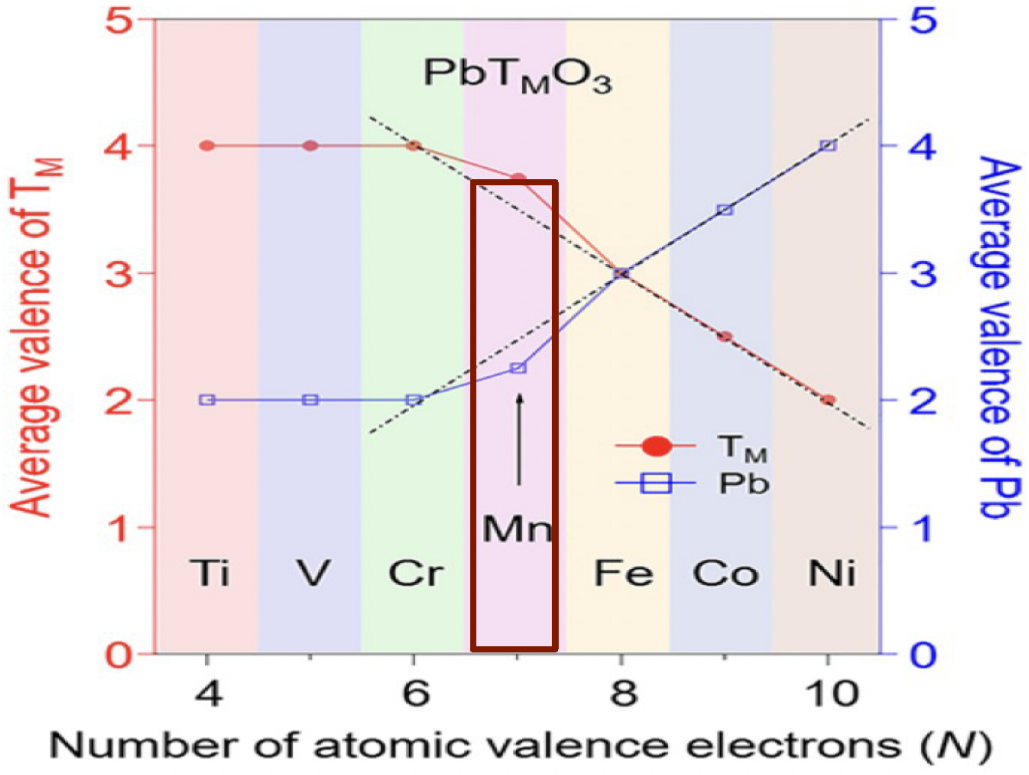
Antiferromagnetism

Charge ordering

Charge degree of freedom: Pb^{2+} ($6s^2$) and Pb^{4+} ($6s^0$)

Li et al, Chem Mater 33, 92 (2021)

Earlier studies on $PbMnO_3$



Nominal valence of Mn ≈ 4+ (d^3)

Goldschmidt tolerance factor

$$t = \frac{r_{Pb} + r_O}{\sqrt{2}(r_{T_M} + r_O)}$$

$PbTiO_3$: t=1.02

$PbMnO_3$: t=1.01

(structural distortion expected)

Li et. al., Chem. Mater 33, 92 (2021)

Ambient pressure

Hexagonal perovskite (6H)

AFM insulator (T_N=155 K)

15 GPa

Perovskite (3C)

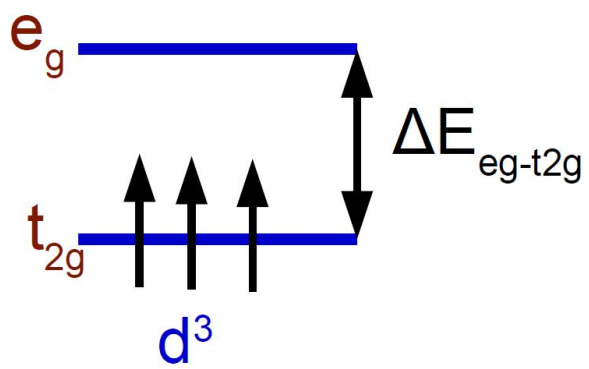
No consensus on crystal structure (polar/nonpolar), electronic (metal/insulator), Magnetic (FM/AFM) properties of 3C phase

Cubic $SrMnO_3$ and $PbMnO_3$

Lattice parameter:
$a(SrMnO_3) < a(PbMnO_3)$

$PbMnO_3$: Small $\Delta E_{eg\text{-}t2g}$

e_g-t_{2g} hopping increases
(FM interaction)

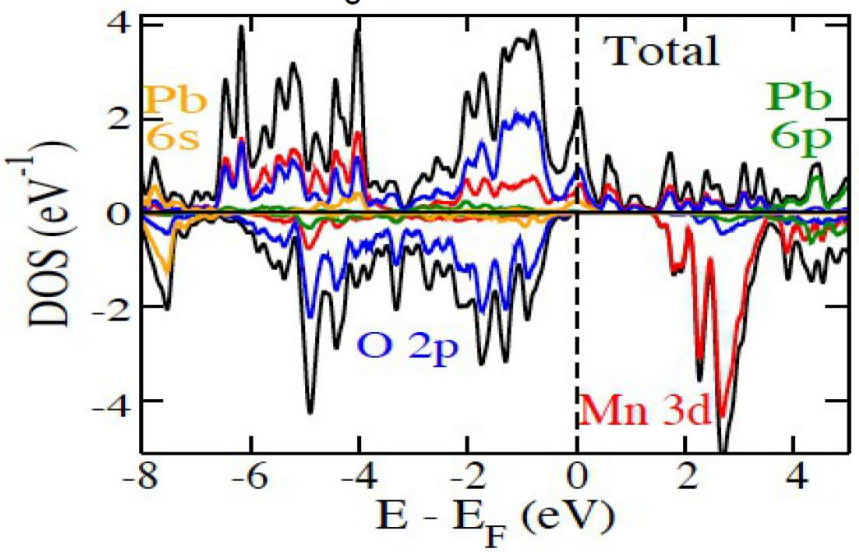


d^3 perovskite
(Half-filled)

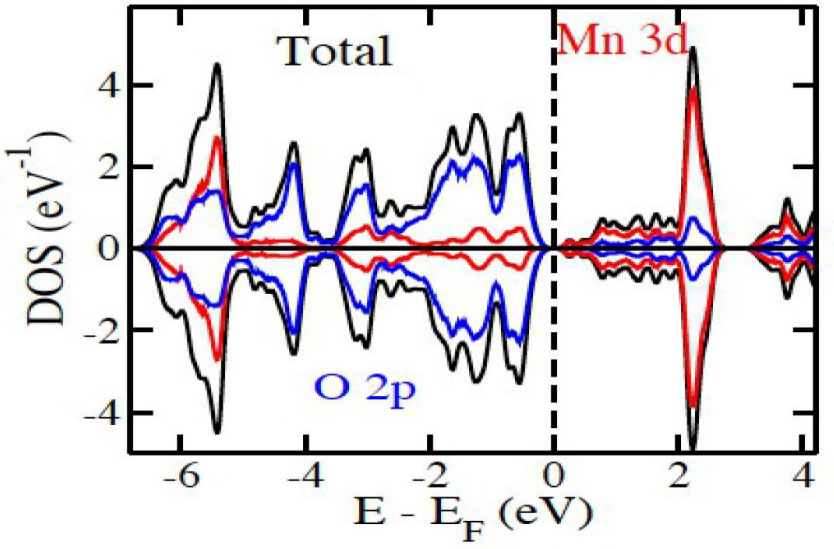
$SrMnO_3$: G-AFM

$PbMnO_3$: FM

$PbMnO_3$ (FM+Half-metal)



$SrMnO_3$ (AFM+Insulating)



Instabilities of the Cubic ($Pm\bar{3}m$) structure of $PbMnO_3$ and $SrMnO_3$

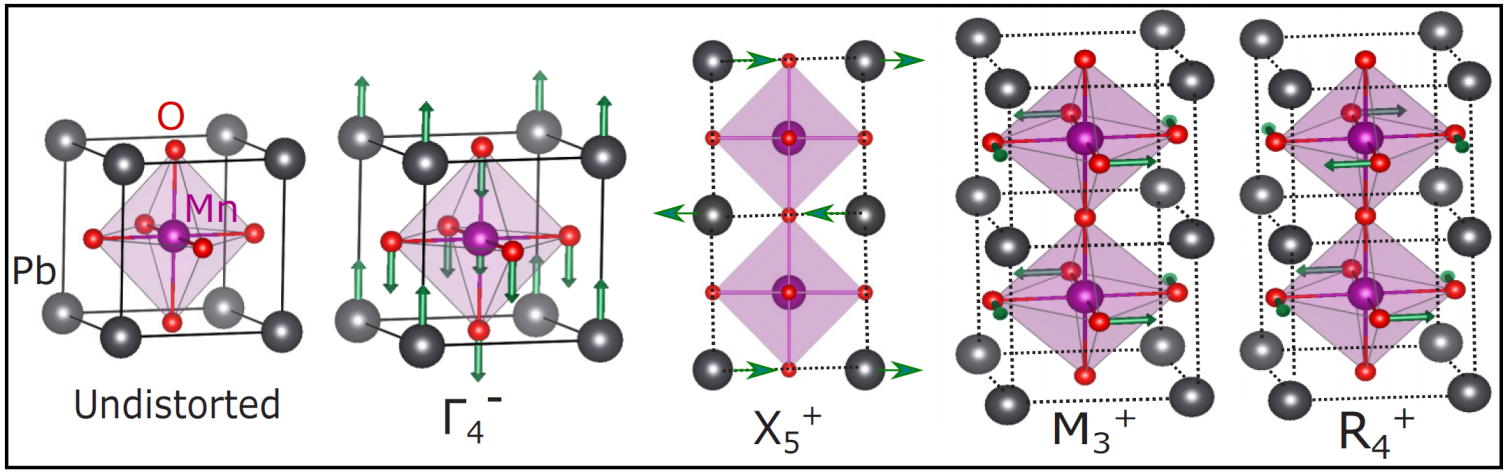
TABLE II. Our calculated phonon frequencies (in cm^{-1}) of polar (Γ_4^-), antipolar (X_5^+), and nonpolar (M_3^+ and R_4^+) phonon modes of cubic ($Pm\bar{3}m$) $PbMnO_3$ and $SrMnO_3$ in FM and G-AFM states, in comparison with earlier results [38]. Phonon frequencies of G-AFM $PbMnO_3$ (FM $SrMnO_3$) at the optimized lattice constant of cubic FM (G-AFM) structure are also computed.

Phase	Γ_4^- (cm^{-1})	X_5^+ (cm^{-1})	M_3^+ (cm^{-1})	R_4^+ (cm^{-1})
	$PbMnO_3$			
FM ($a = 3.84$ Å)	$i45$	28	$i163$	$i180$
G-AFM ($a = 3.84$ Å)	$i64$	43	$i104$	$i122$
G-AFM ($a = 3.82$ Å)	$i13$	51	$i93$	$i117$
	$SrMnO_3$			
FM ($a = 3.78$ Å)	$i90$	124	$i110$	$i136$
G-AFM ($a = 3.78$ Å)	164	123	51	$i88$
G-AFM ($a = 3.80$ Å, HSE [38])	177 [38]	–	–	64 [38]
G-AFM ($a = 3.80$ Å, $U = 2.8$ eV [38])	217 [38]	–	–	$i71$ [38]

Contrast: **PMO is unstable**; G-AFM SMO is weakly unstable

Lattice Instabilities

Of Cubic $PbMnO_3$



Polar Antipolar Antiferrodistortive

Structural Distortions of Cubic $PbMnO_3$

Low Symmetry structure

Mode

$Pm\bar{3}m$ (*cubic high symm*)

TABLE III. Energetics of polar and nonpolar phases of $PbMnO_3$ with FM and G-AFM orderings. The structural distortion is given with respect to the undistorted cubic structure ($Pm\bar{3}m$ symmetry group). $\Delta E = E_{\text{G-AFM}} - E_{\text{FM}}$, is the energy difference between FM and G-AFM states.

Phase	Rotation pattern	Distortion	Phase	E_{FM} (meV/f.u.)	ΔE (meV/f.u.)
$Pm\bar{3}m$	$a^0a^0a^0$	undistorted	Nonpolar	146	88
$P4mm$	$a^0a^0a^0$	$\Gamma_4^-[001]$	Polar	139	95
$Amm2$	$a^0a^0a^0$	$\Gamma_4^-[110]$	Polar	142	93
$I4/mcm$	$a^0a^0c^-$	$R_4^+[001]$	Nonpolar	35	180
$R\bar{3}c$	$a^-a^-a^-$	$R_4^+[111]$	Nonpolar	10	207
$Imma$	$a^-a^-c^0$	$R_4^+[110]$	Nonpolar	12	200
$Pnma$	$a^-a^-c^+$	$R_4^+[110] + M_3^+[001] + X_5^+[110]$	Nonpolar	0	209

$PbMnO_3$: *FM state* remains lower in energy than the AFM

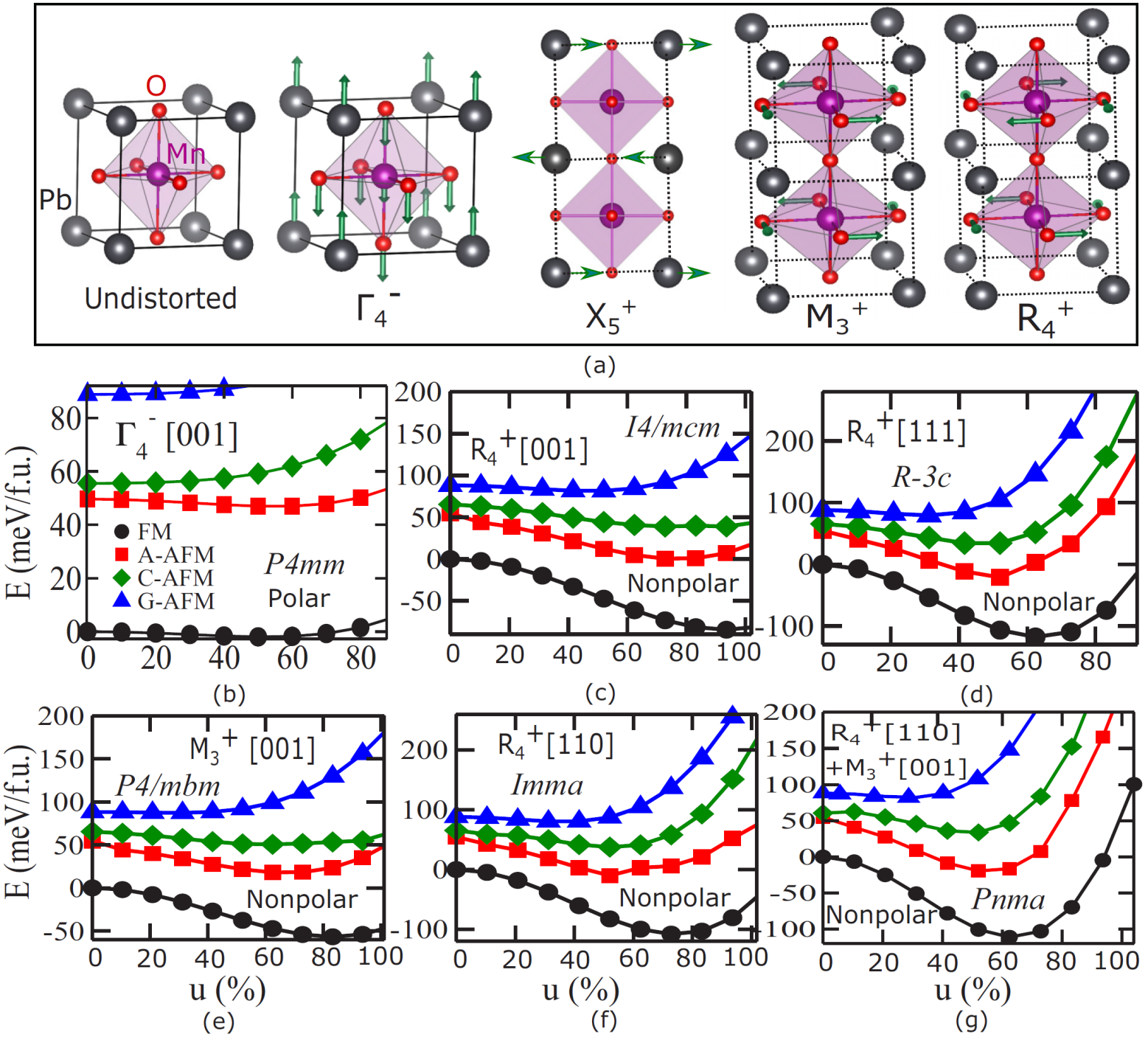
Pnma is the lowest energy structure

Lattice Instabilities

Of Cubic $PbMnO_3$

Strong Instabilities of *MnO_6 octahedral Rotations*

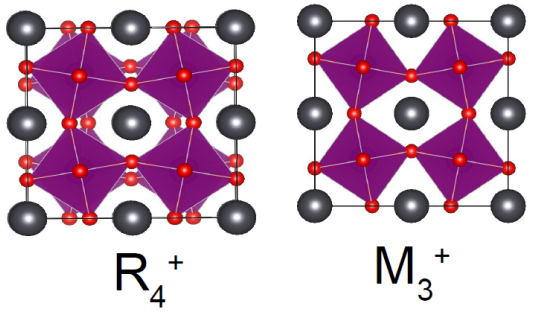
FE instability is weak

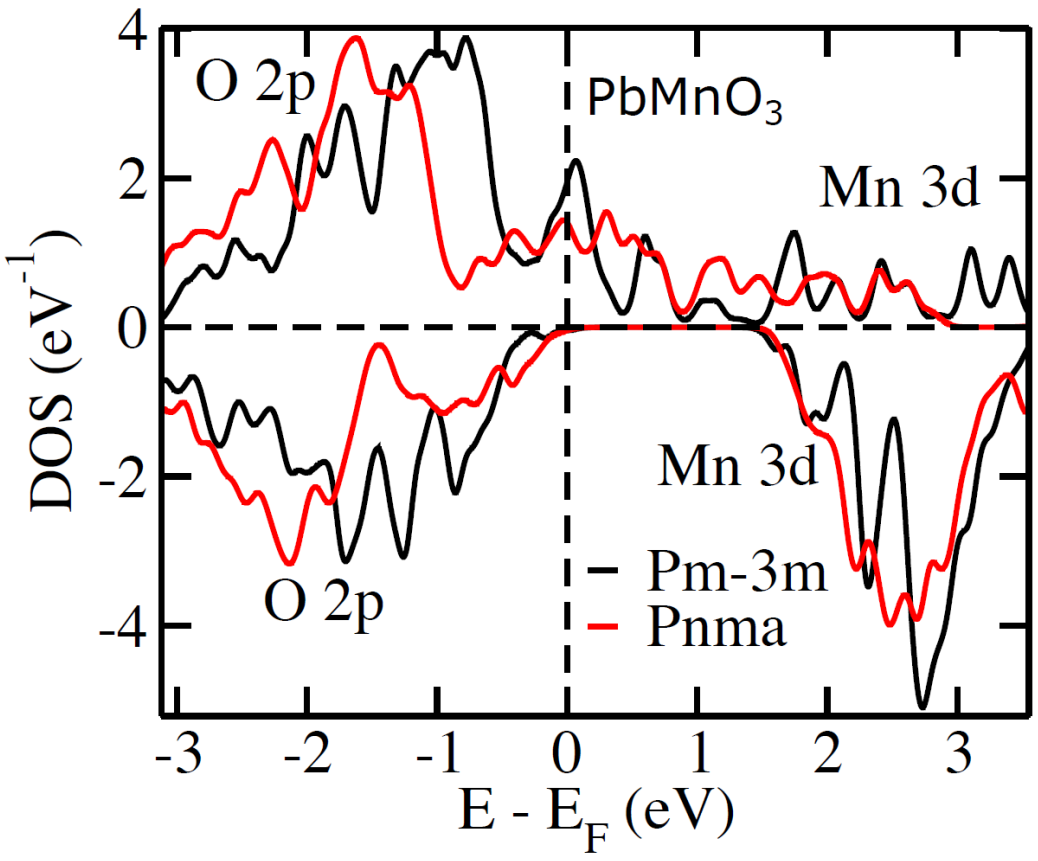


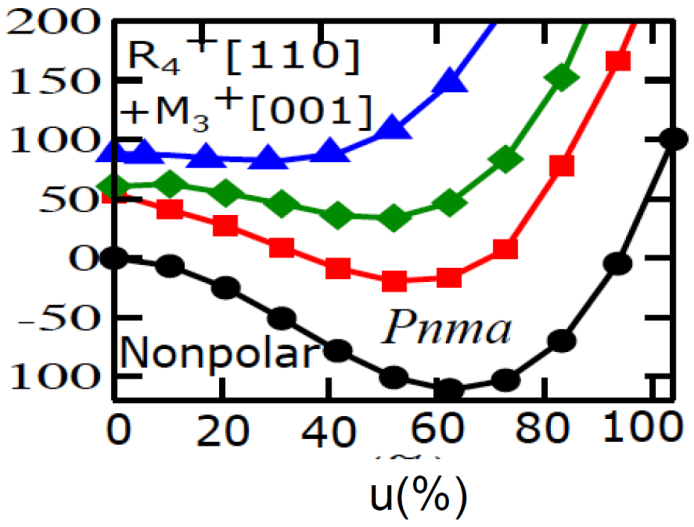
Crystal & Electronic Structure of $PbMnO_3$

ω (cm^{-1})	Γ_4^-	M_3^+	R_4^+
FM	i45	i163	i180

Strong antiferro-distortive/ rotational instabilities







Lowest energy structure: Nonpolar Pnma phase ($a^-a^-c^+$)
FM Half-metal

2nd order phonon-spin coupling

How to make $PbMnO_3$ multiferroic?

Engineering polar phases in $PbMnO_3$

Mn^{4+}: d^3 (Half-filled)

Cubic $PbMnO_3$

Ferromagnetic Half-metal

Unstable modes: R_4^+ and M_3^+
Rotation of MnO_6 octahedra

Unstable polar phonon mode: Γ_4^-

Competition

Nonpolar orthorhombic phase

Ferromagnetic Half-metal

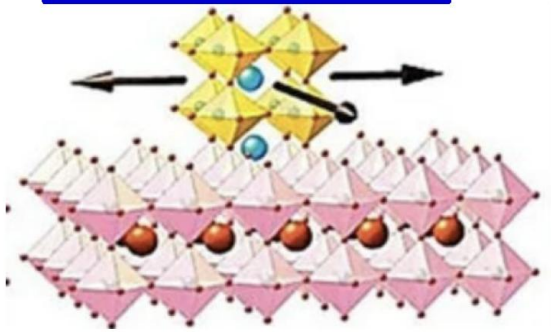
Stabilizing polar phases

X

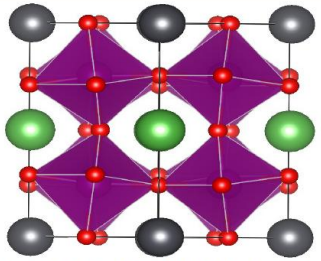
V

X

Epitaxial strain

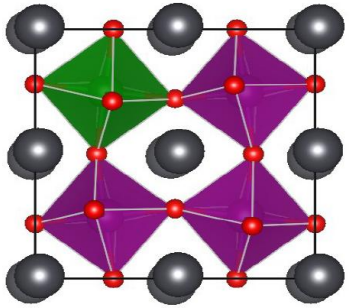


Hetero-structuring

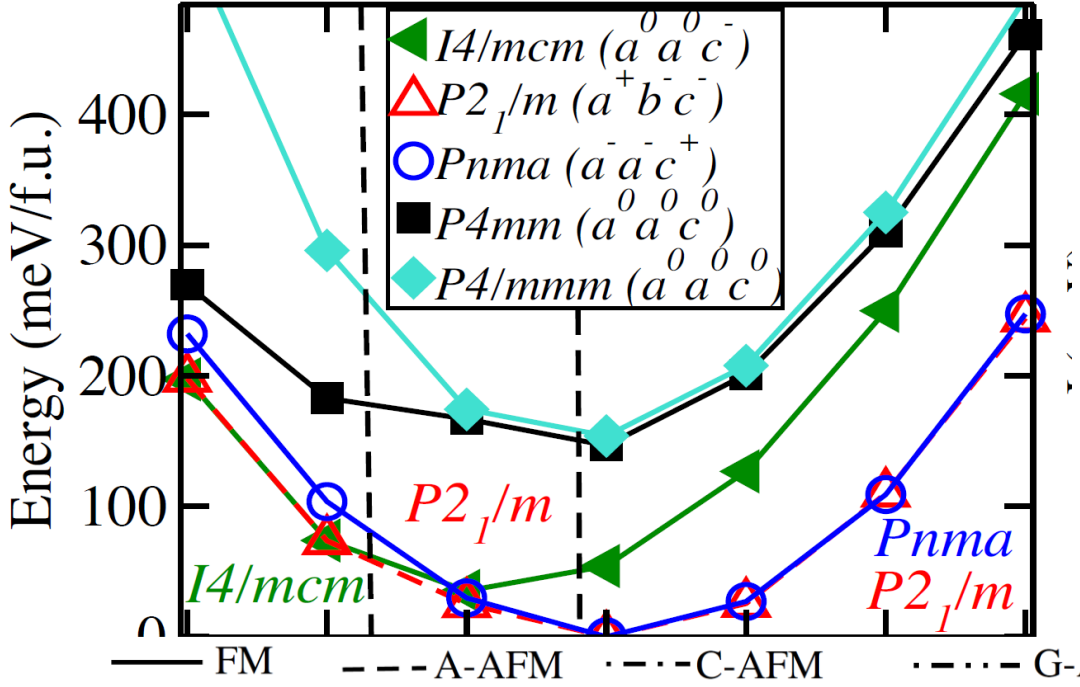


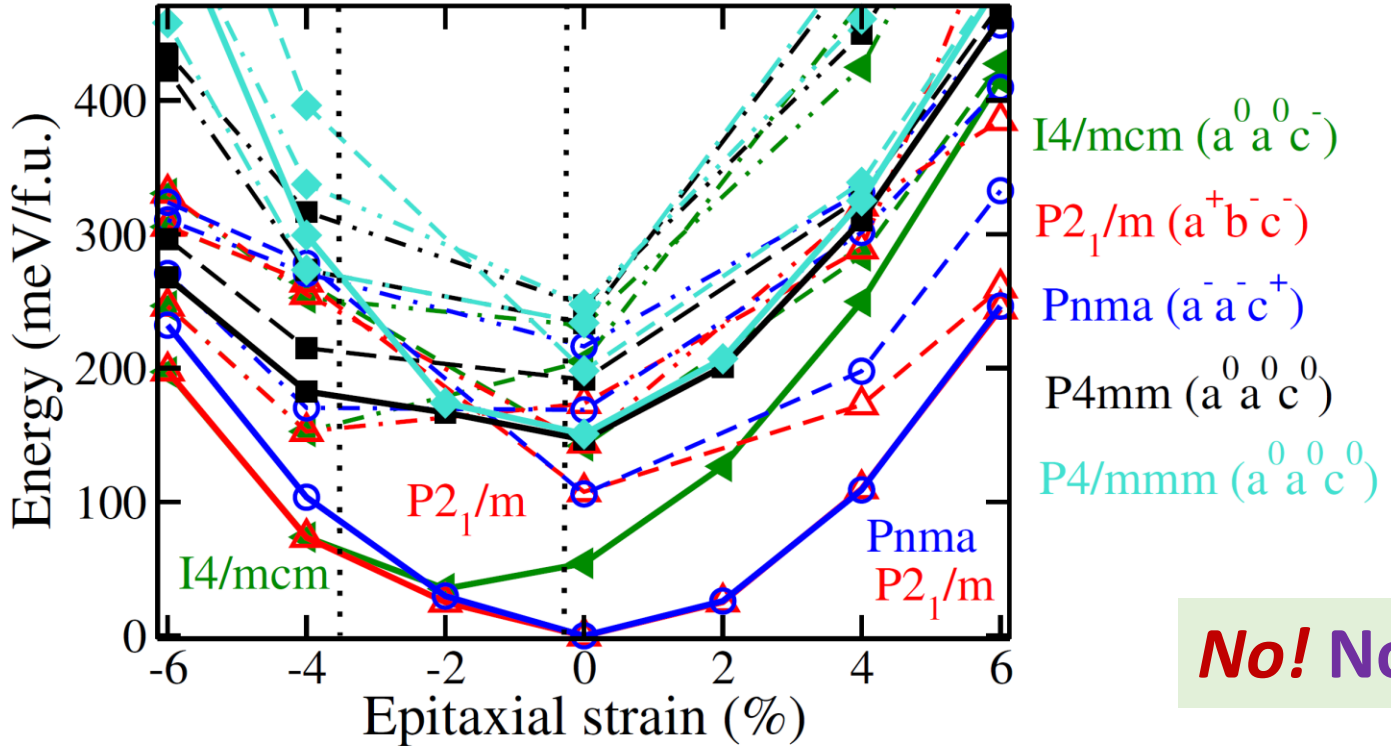
$(ABO_3)_1/(A'BO_3)_1$

Cation substitution



Mn site





C_{2h}

D_{4h}

Can Epitaxial Strain Make $PbMnO_3$ ***Polar***?

A-AFM: (001)

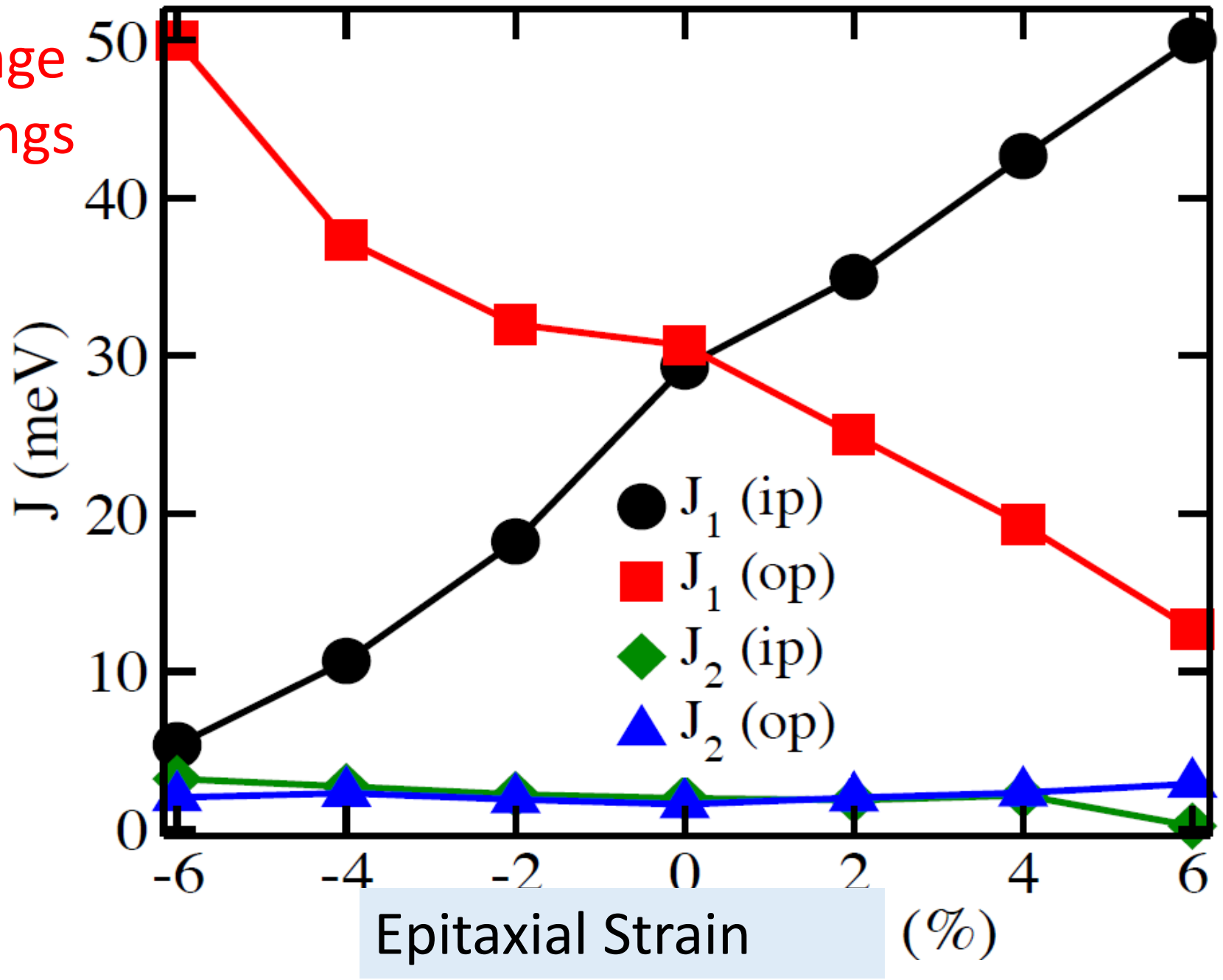
C-AFM: (110)

G-AFM: (111)

FM: (000)

No! **Nonpolar** HMFM is robust

Exchange Couplings



Epitaxial Strain

$PbMnO_3$: Strong Magneto Striction!

Can Substitution at B-site make $PbMnO_3$ ***Polar***?

TABLE S2: Our estimates of phonon frequencies (in cm^{-1}) of polar (Γ_4^-) and nonpolar antiferrodistortive (M_3^+ and R_4^+) phonon modes of ferromagnetic $PbMn_{0.875}TM_{0.125}O_3$ (TM=Ti and Nb) in the $Pm\bar{3}m$ structure (undistorted phase).

Compound	Γ_4^- (cm^{-1})	M_3^+ (cm^{-1})	R_4^+ (cm^{-1})
$PbMnO_3$	$i45$	$i163$	$i180$
$PbMn_{0.875}Nb_{0.125}O_3$	$i46$	$i128$	$i147$
$PbMn_{0.875}Ti_{0.125}O_3$	$i50$	$i145$	$i168$

Ti & Nb: Strengthen polar, weaken T_MO_6 rotational instabilities

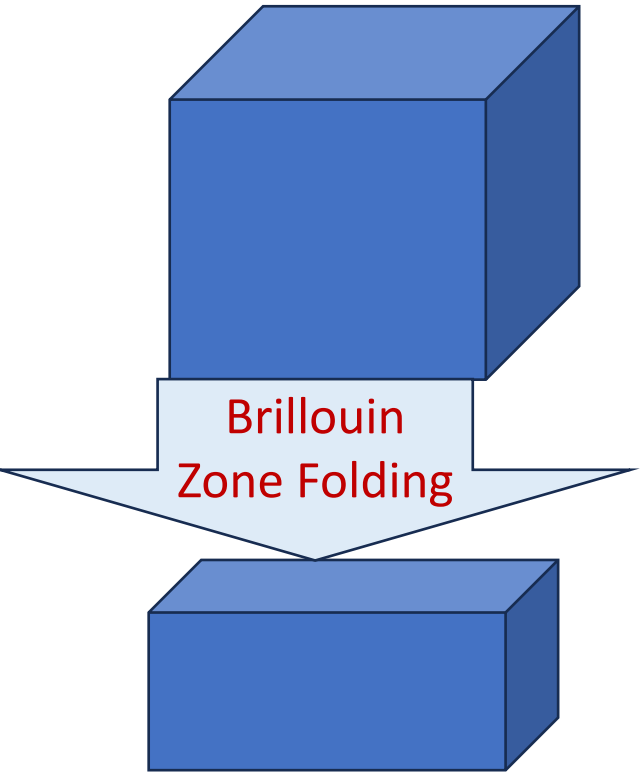
Can Substitution at B-site make $PbMnO_3$ ***Polar***?

No!

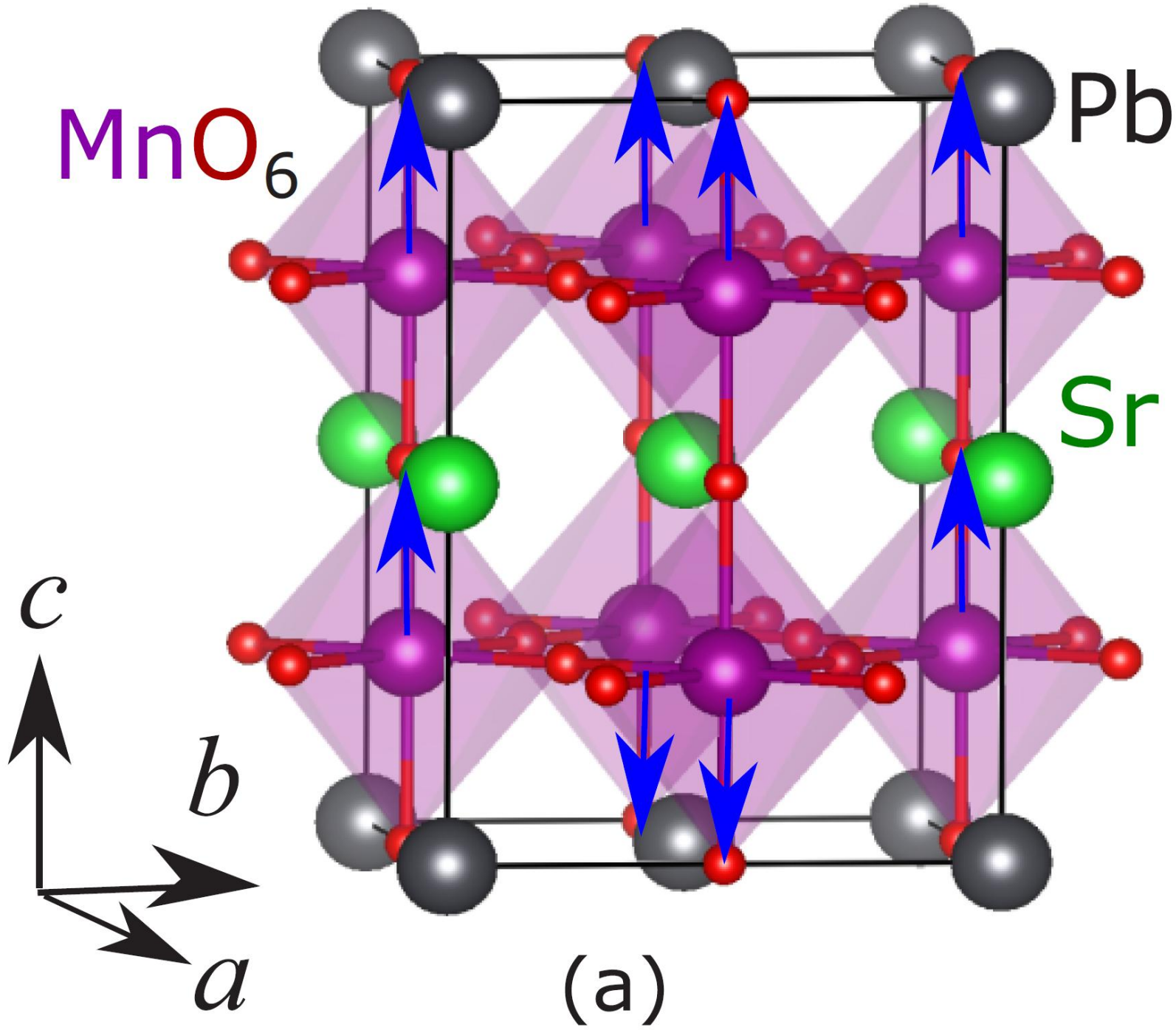
TABLE S1: Structural distortion (Δ_d), bond angle Mn-O-Mn, energy difference between FM and G-AFM states, and unit cell ($2 \times 2 \times 2$ supercell of five atomic perovskite unit cell) volume of $PbMn_{0.875}M_{0.125}O_3$ (M=V, Ti and Nb) with ferromagnetic ordering.

Compound	Mn-O-Mn (°)	Δ_d (10^{-5})	E_{G-AFM} - E_{FM} (meV/f.u.)	V (Å^3)
$PbMnO_3$	159	0.2	209	461
$PbMn_{0.875}V_{0.125}O_3$	161	0.3 (away from V)	127	461
	168 (V-O-Mn)	9.0		
$PbMn_{0.875}Nb_{0.125}O_3$	162	8.1	132	468
	172 (Nb-O-Mn)	0.5 (away from Nb)		
$PbMn_{0.875}Ti_{0.125}O_3$	161	7.8	129	462
	167 (Ti-O-Mn)	0.2 (away from Ti)		

Heterostructure
$PbMnO_3$: $SrMnO_3$

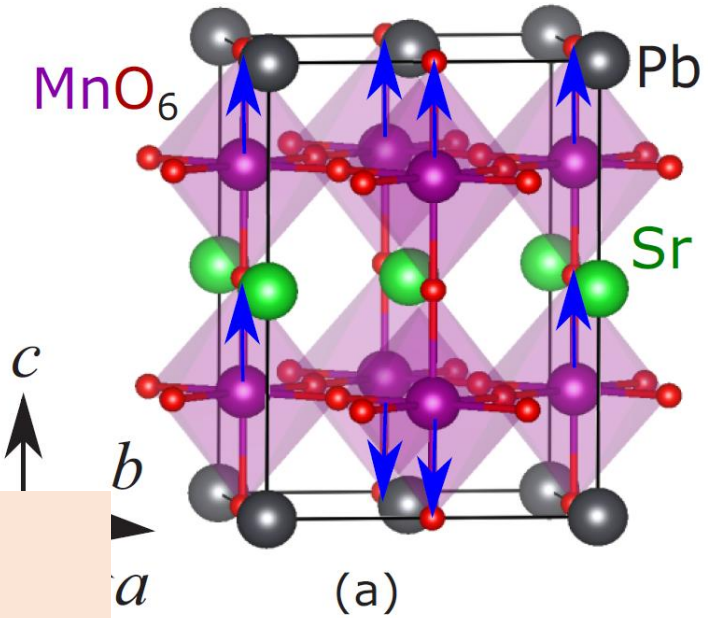


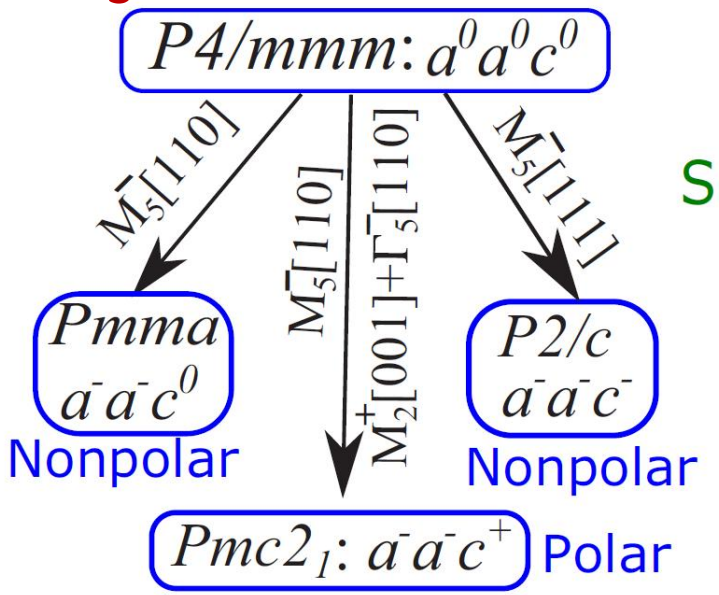
Z(cubic) to Γ(H/S)
R(cubic) to M(H/S)

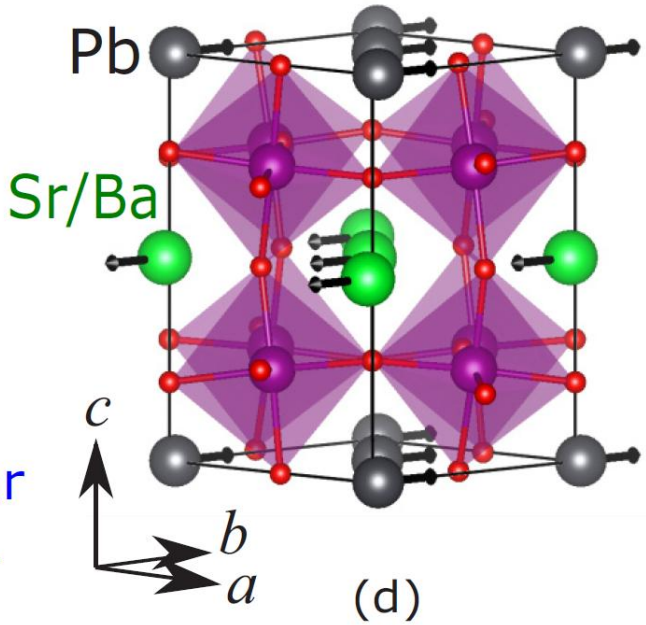


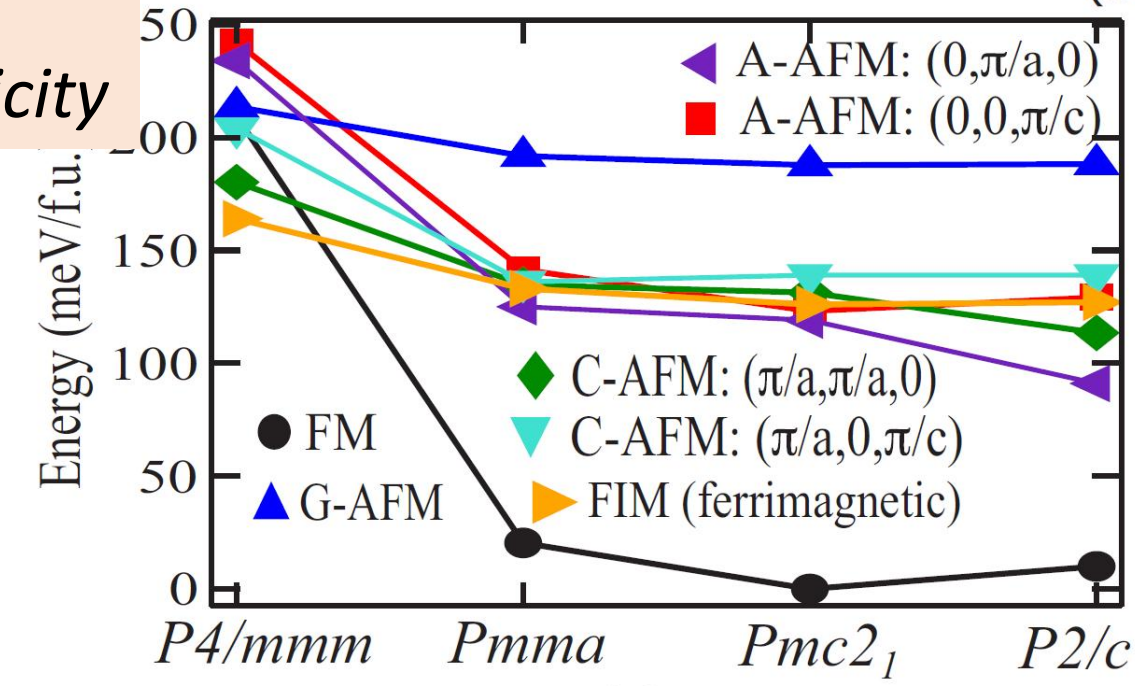
Heterostructure: $PbMnO_3$: $SrMnO_3$

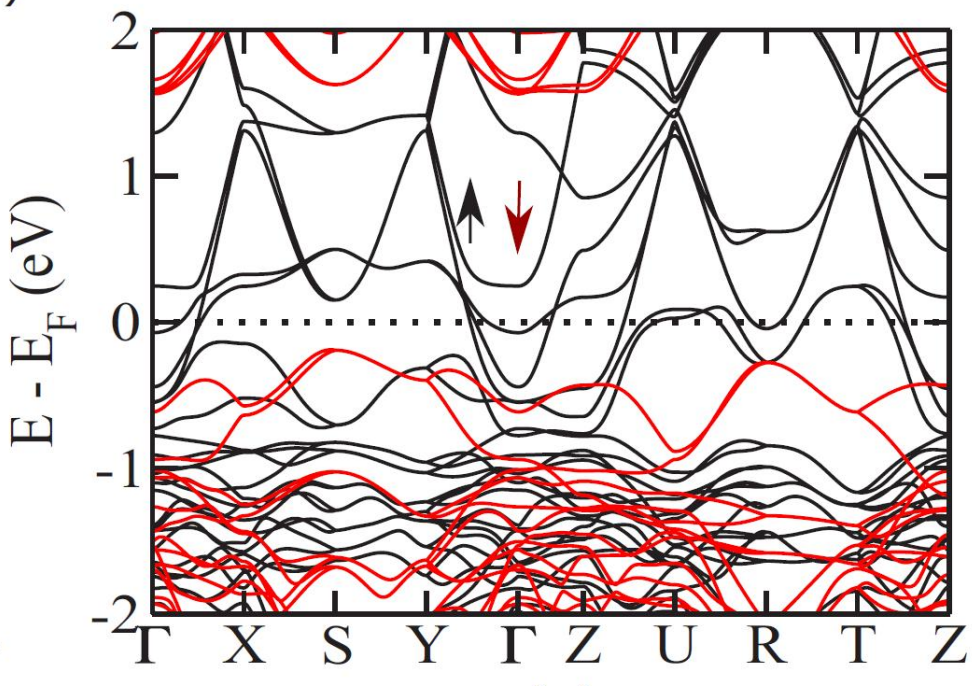
Hybrid Improper *Ferroelectricity*

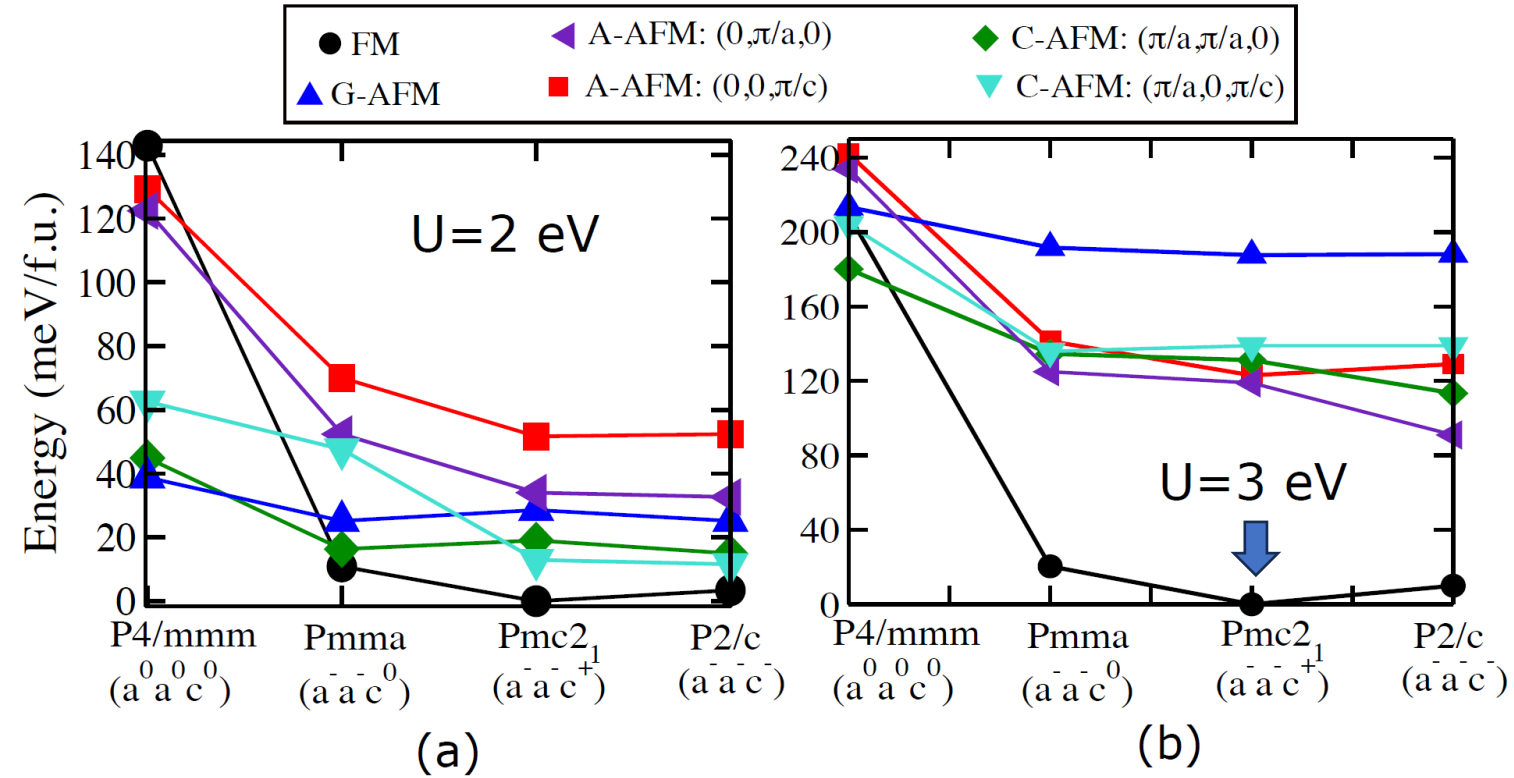


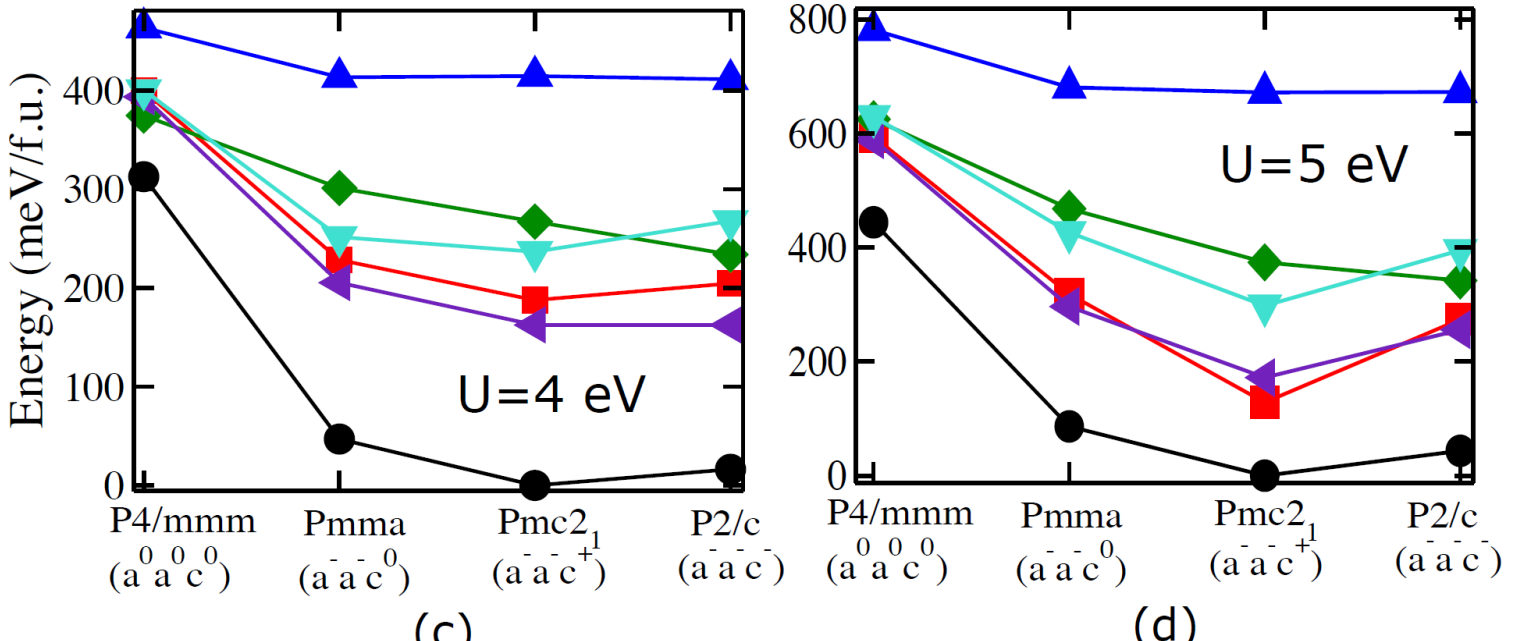












0.3 Γ_5^-+0.6 M_2^++0.6 M_5^-

Heterostructure

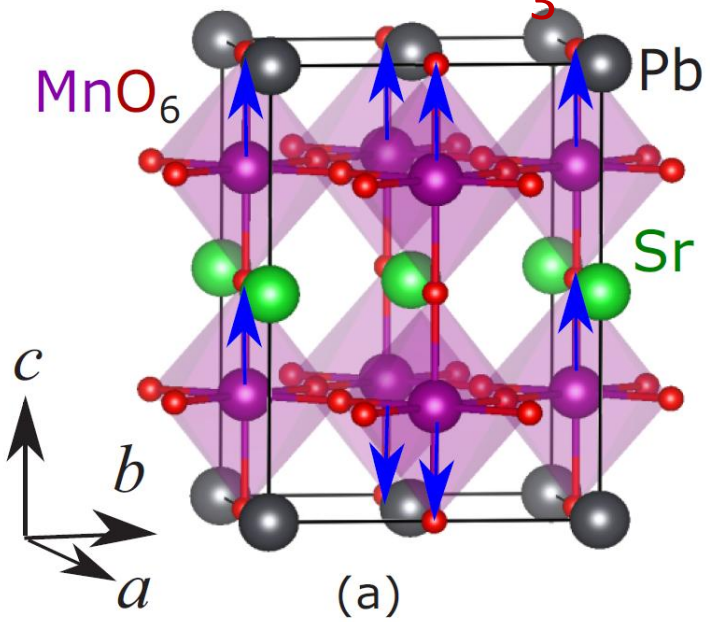
$PbMnO_3$: $SrMnO_3$

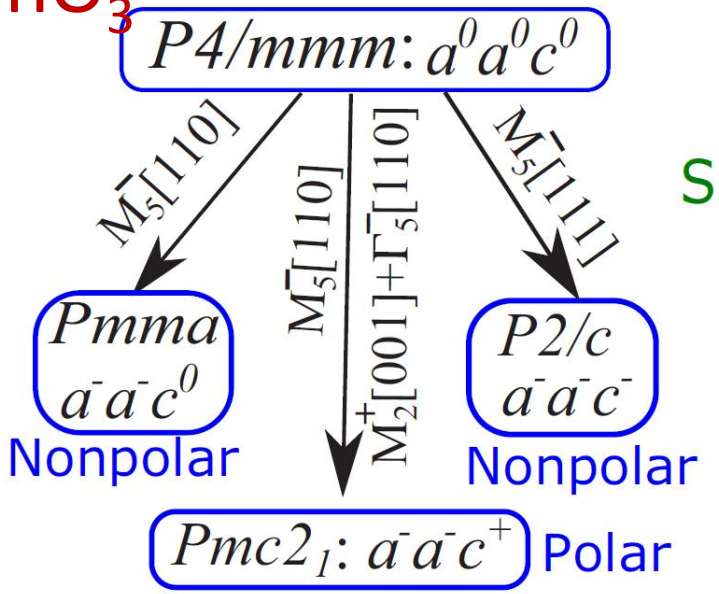
A robust **POLAR** HM FM

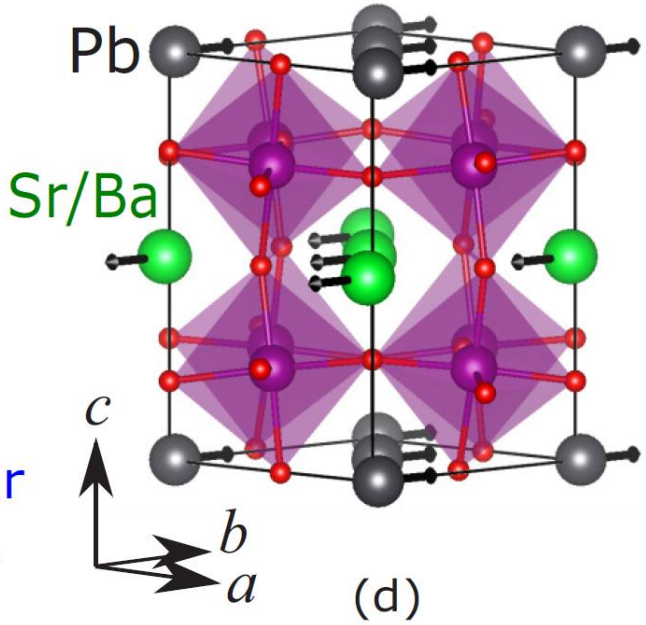
0.5 Γ_5^-+0.4 M_2^++0.7 M_5^-

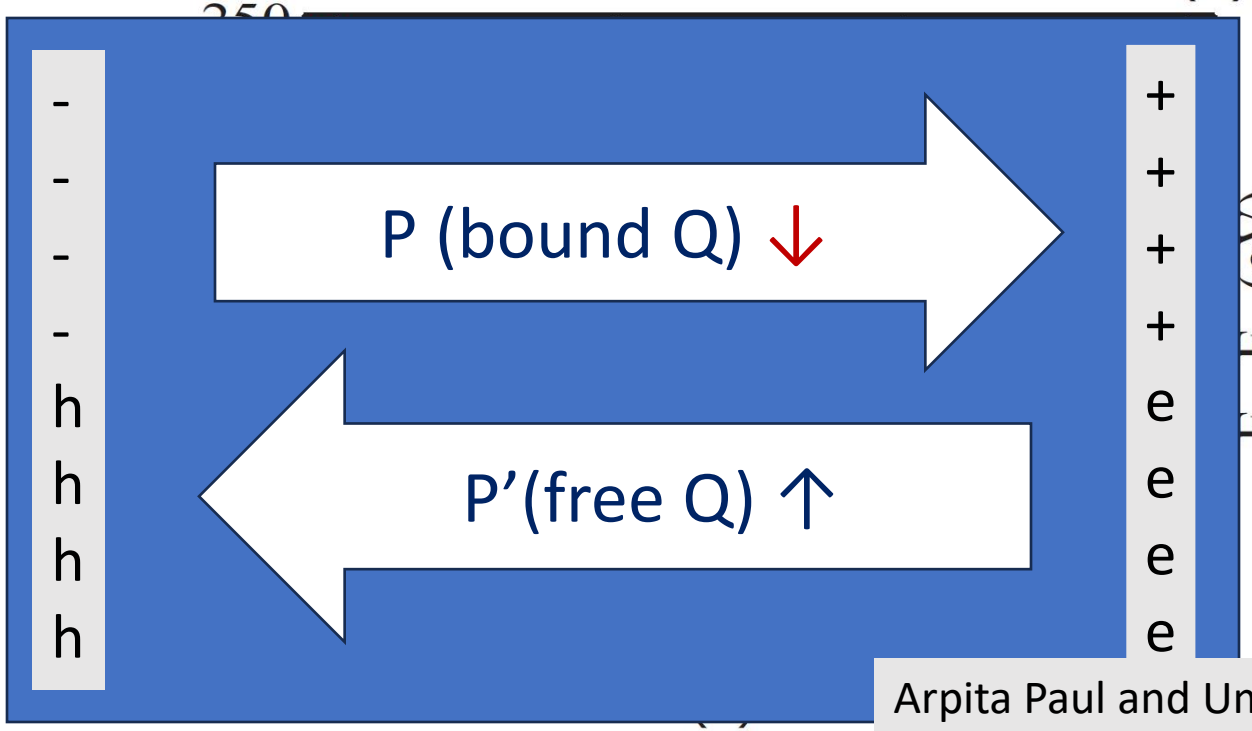
For $PbMnO_3$:$BaMnO_3$

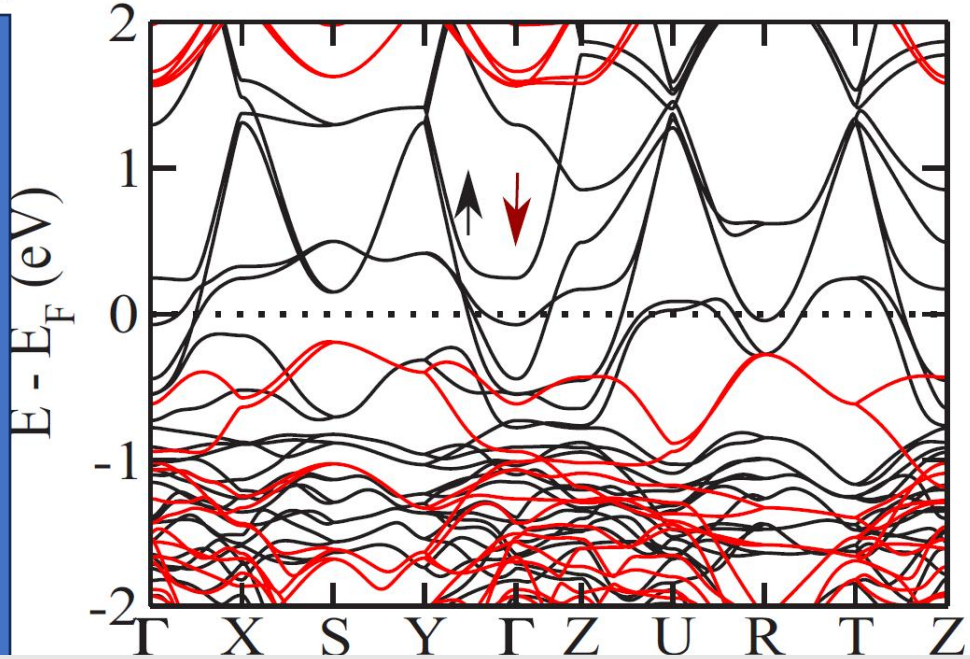
Heterostructure: $PbMnO_3$: $SrMnO_3$











Arpita Paul and Umesh V Waghmare, Phys Rev B 110, 184110 (2024)

Summary *<Polar Half-Metal>*

- $PbMnO_3$: HM FM in ***Pnma*** structure (nonpolar R_4^+, M_3^+, X_5^+)
- Nonpolar structure robust against epitaxial strain or substitution
- $PbMnO_3$:$SrMnO_3$ An excellent Polar Ferromagnetic *Half-Metal*

  Polarity: *Hybrid Improper Ferroelectricity (*R_4^+, M_3^+, $\mathbf{X_5^+ \rightarrow \Gamma_5^-}$)

  *uncompensated in-plane off-centering of **Pb** and Sr*

Arpita Paul and Umesh V Waghmare, Phys Rev B 110, 184110 (2024)

Can we integrate

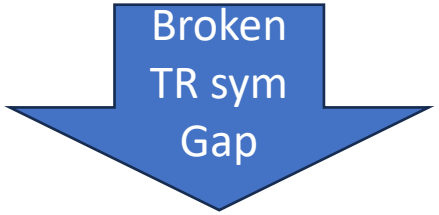
Quantum Geometric Features into Multi-Ferroics?

Superlattices based on $PbMnO_3$ and $PbVO_3$

Strengthen Ferroelectricity through A (*6s* lone pair of Pb) and B (d^0)sites

- Mn^{4+}: d^3 versus V^{4+}: d^1
- Mn^{3+}: d^4 versus V^{5+}: d^0

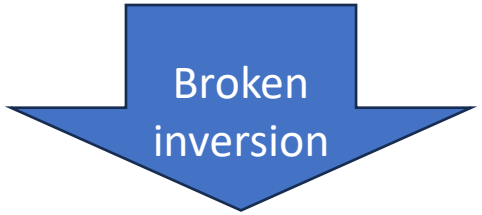
Jahn-Teller, Magnetism



Berry Curvature Dipole

Quantum Geometry

Ferroelectricity



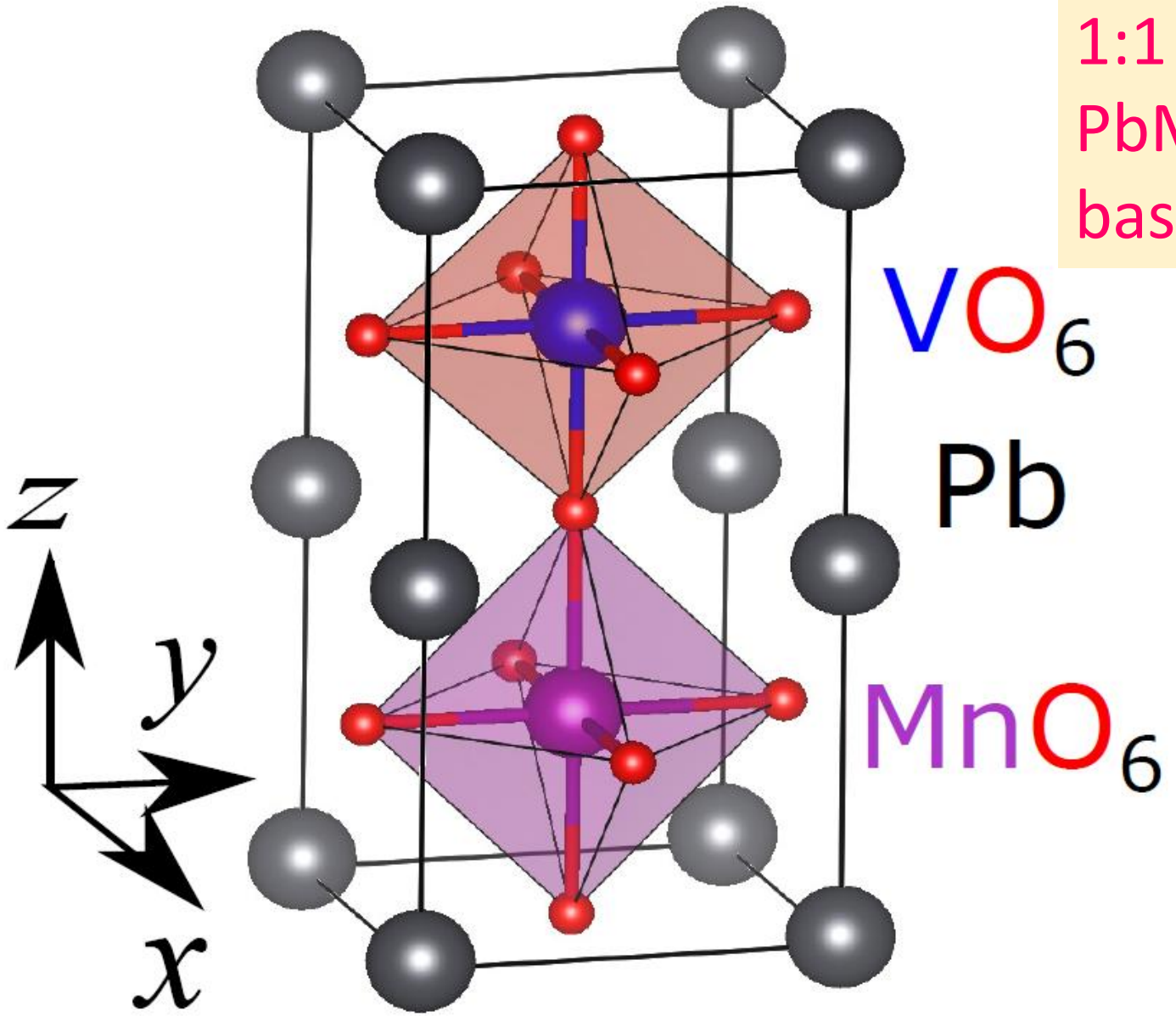
Electric Polarization

Polarity

Possibility of a Tri-ferroic

Magnetization
Polarization
Berry Curvature Dipole

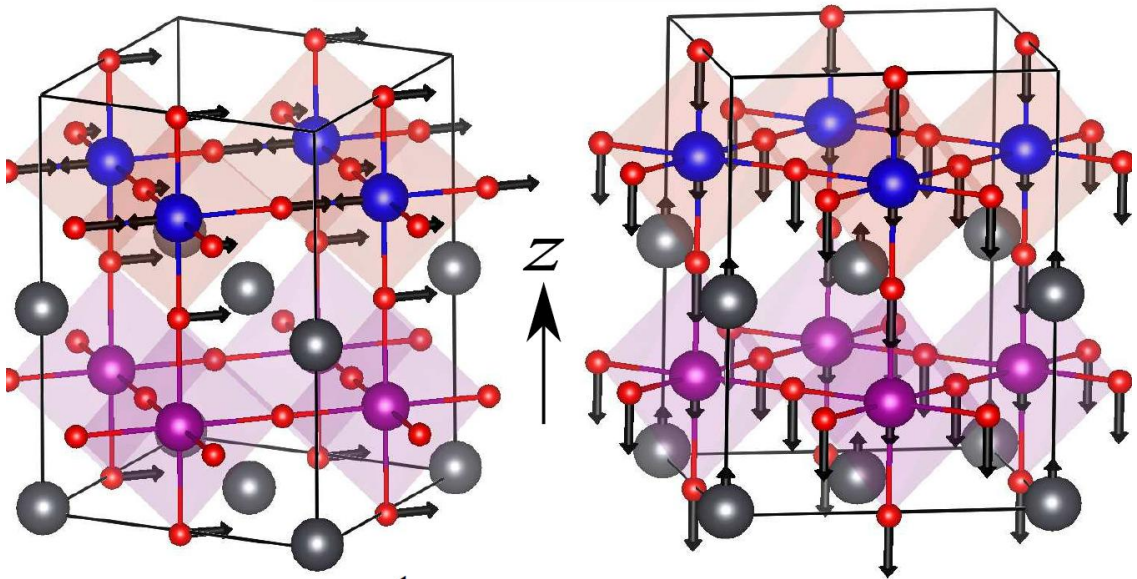
P4/mmm



High Symmetry Structure of 1:1 Superlattice of $PbMnO_3$ and $PbVO_3$ based on (001) Orientation

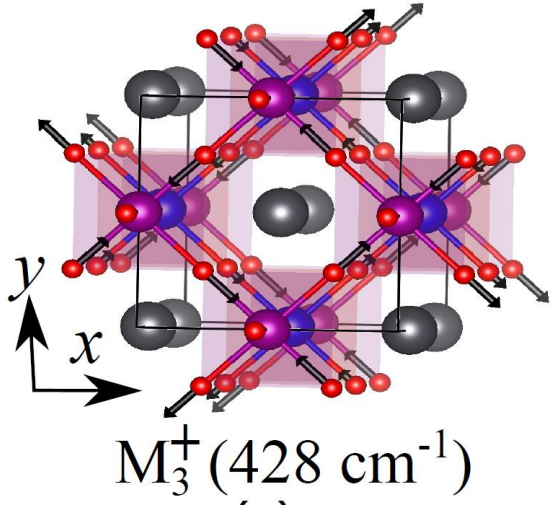
Structural Instabilities of the High Symmetry Structure of 1:1 Superlattice of $PbMnO_3$ and $PbVO_3$

Polar modes

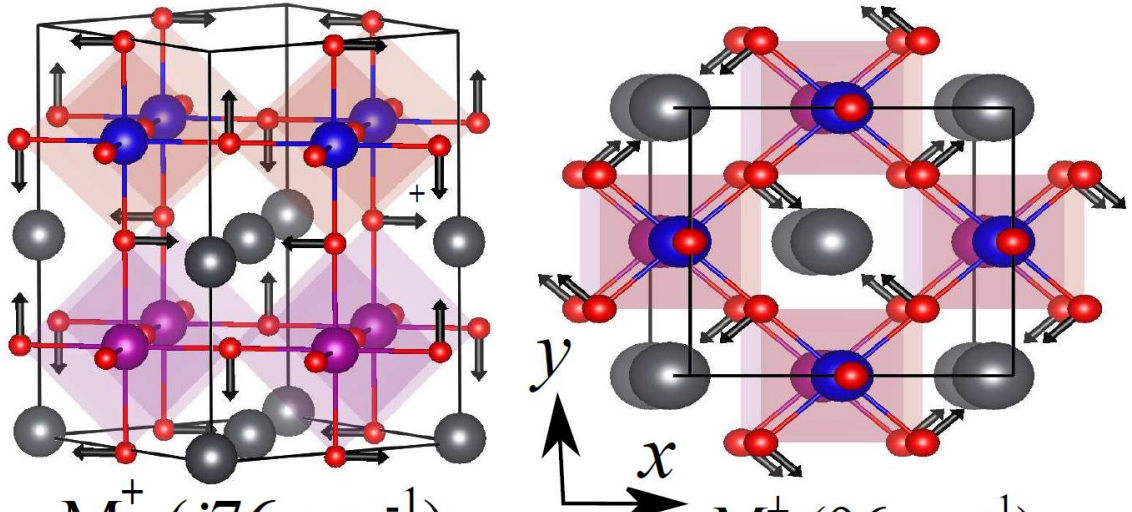


(b)

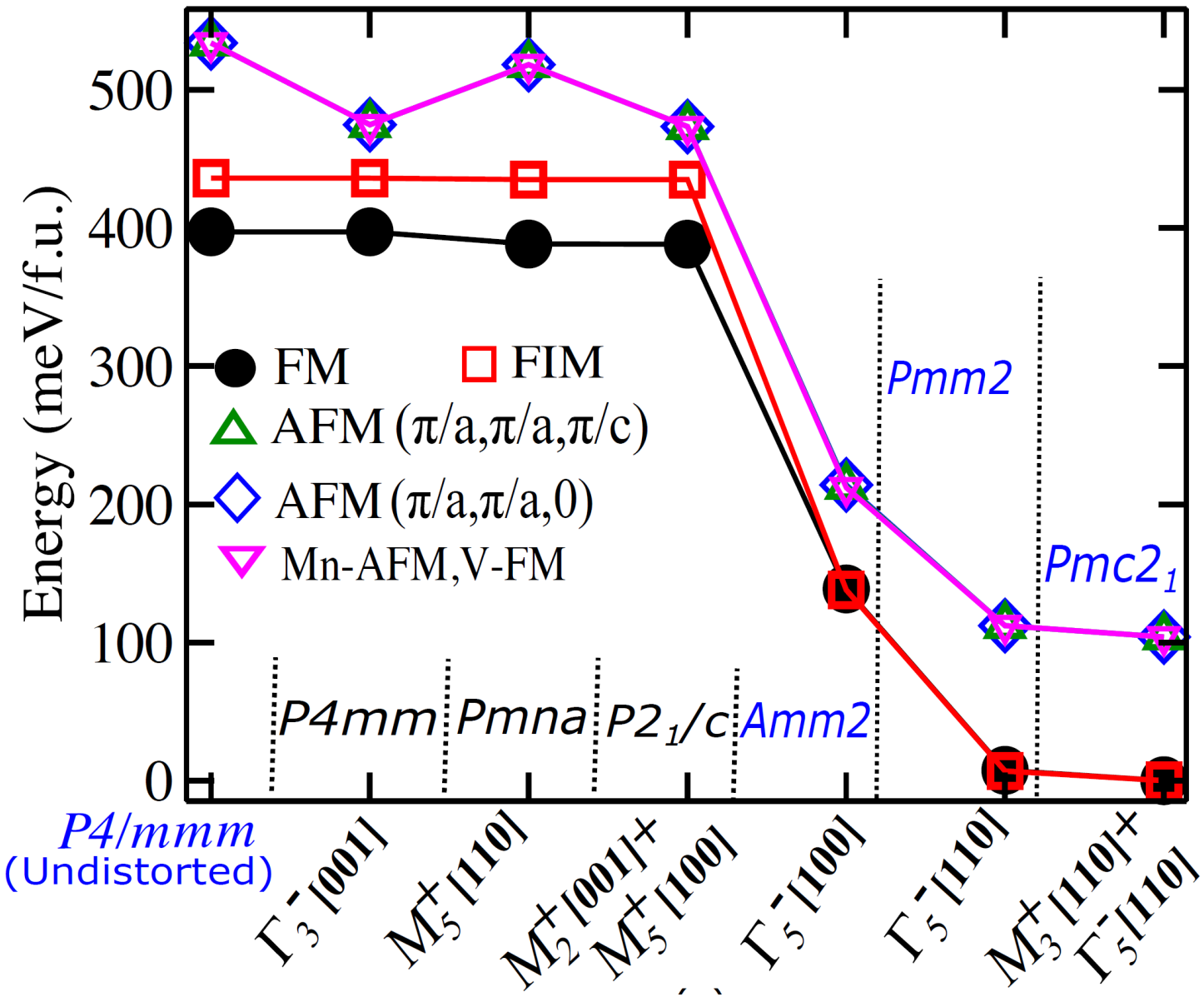
JT distortion



Antiferrodistortive modes



Low Symmetry & Low Energy Structures of 1:1 Superlattice of $PbMnO_3$ and $PbVO_3$

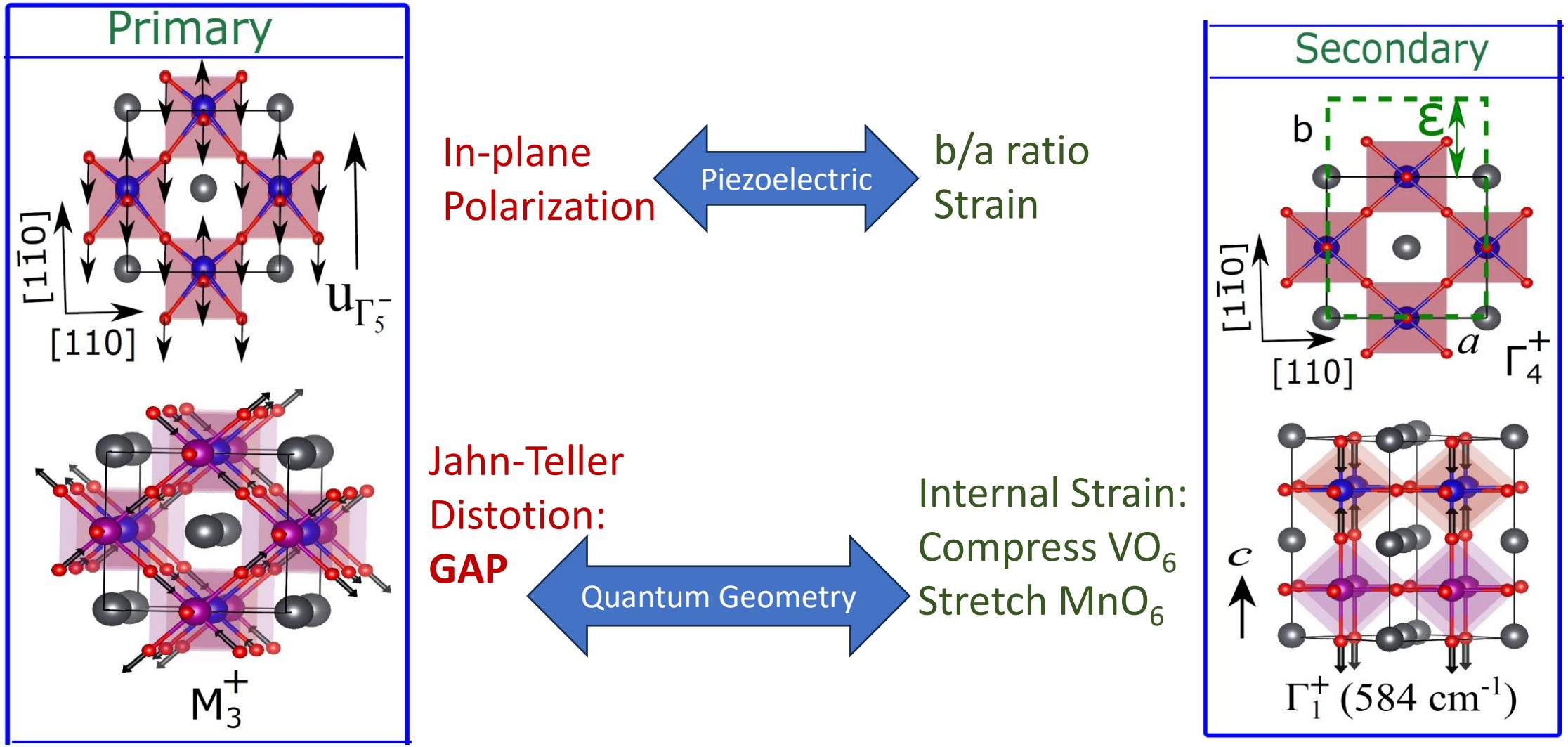


$Pmc2_1$ Structure is

- Polar
- Lowest Energy

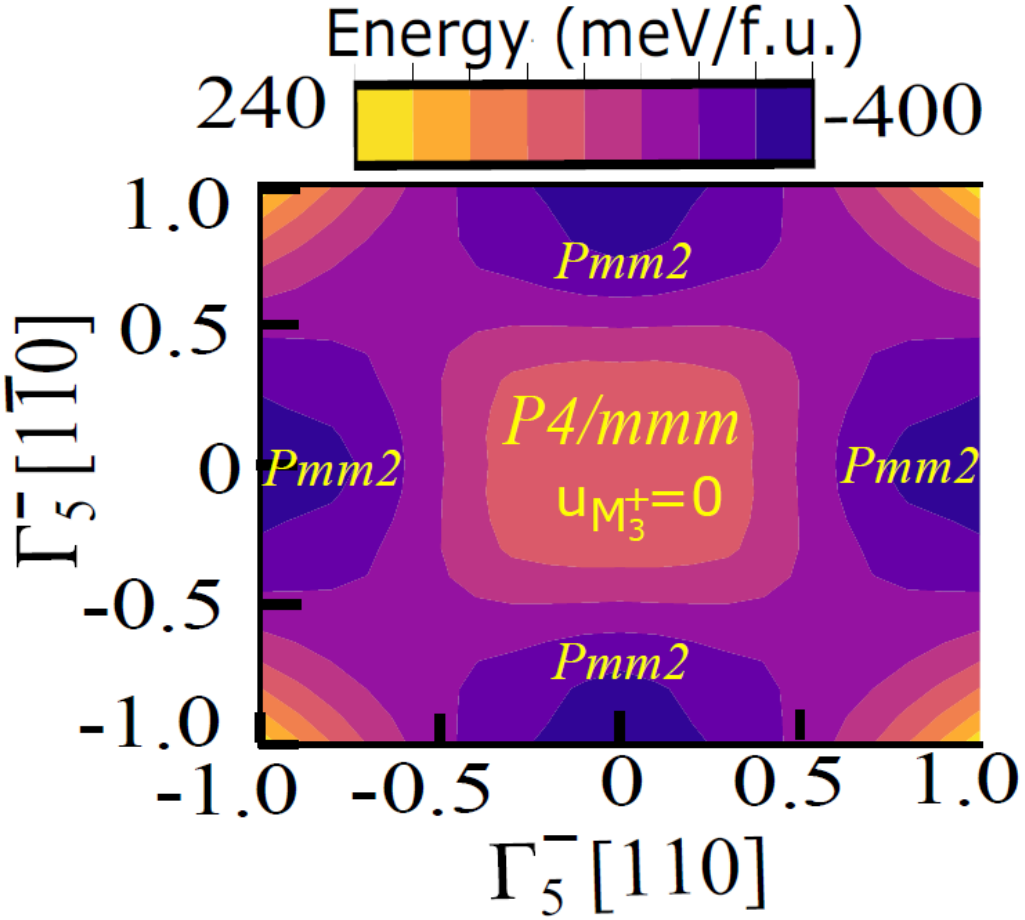
Order Parameters of P4/mmm to $Pmc2_1$ Structural Transition

Superlattice of $PbMnO_3$ and $PbVO_3$

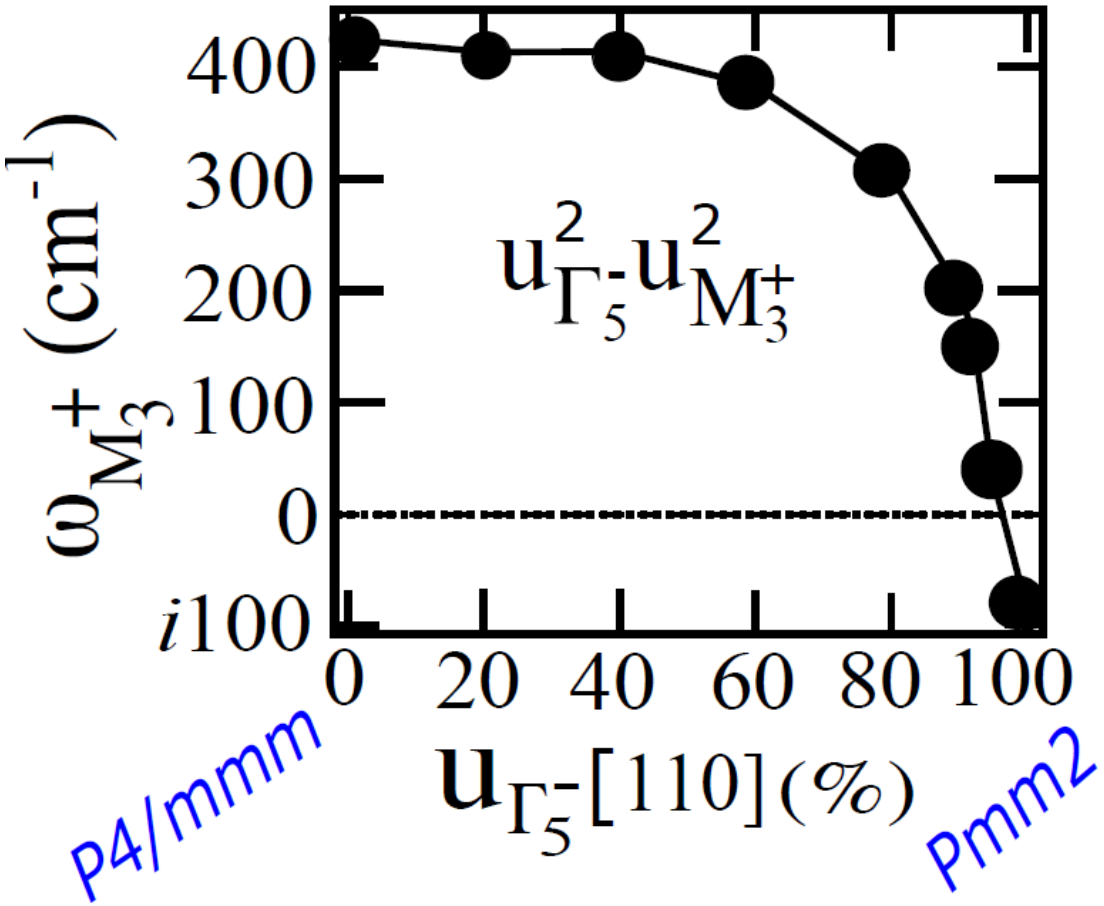


Energy Landscape:

Polar distortion of P4/mmm to Pmm2

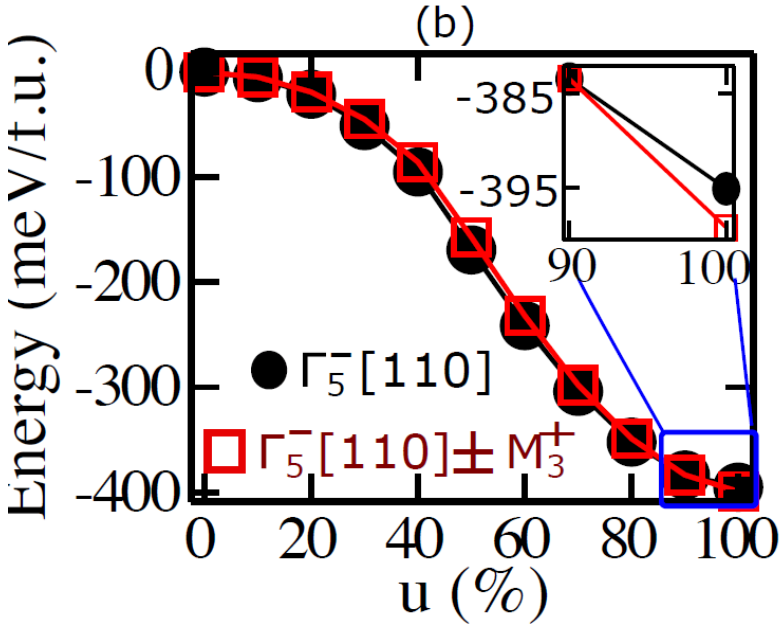


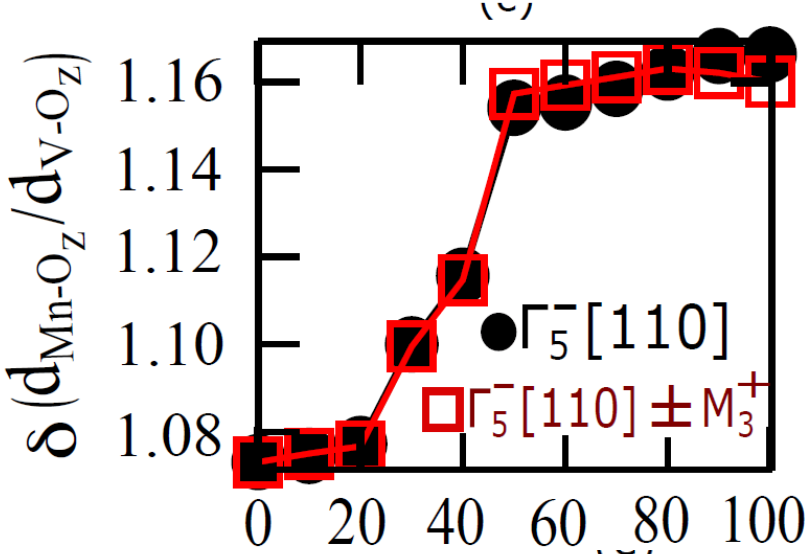
Jahn-Teller Instability



Weak coupling between P [V] and JT [Mn]; *sharp change* ↔ *nonlinear coupling*

Sharp Changes during *P4/mmm to Pmc2$_1$* Structural Transition: Internal Strain and Magnetic Moments

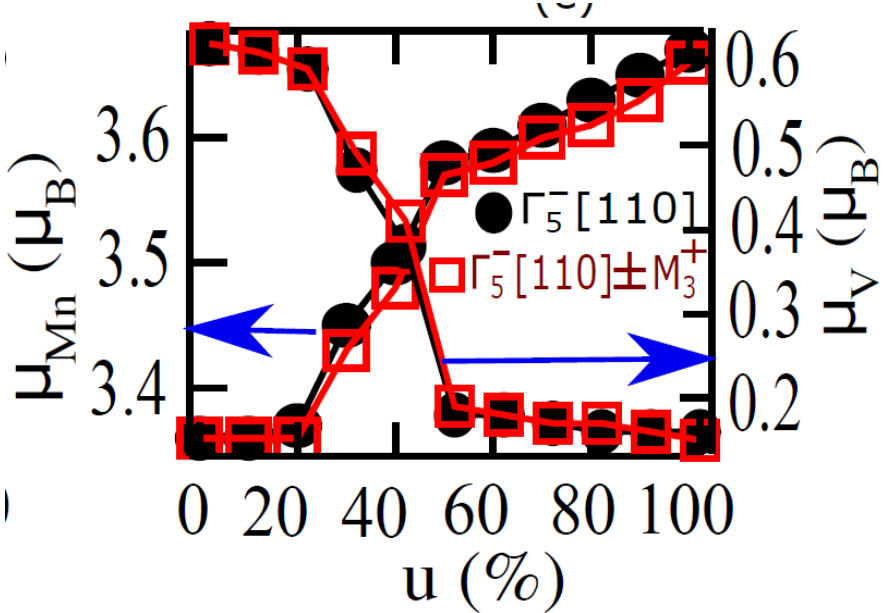




Internal Strain:
Elongation of MnO_6
Compression of VO_6

Favor in-plane *polar* distortions

V: d^0



Magnetic Moments:
e charge transfer from V to Mn

Electronic Mechanism:

Polar distortion of P4/mmm **(NP)** to Pmm2 **(P)**

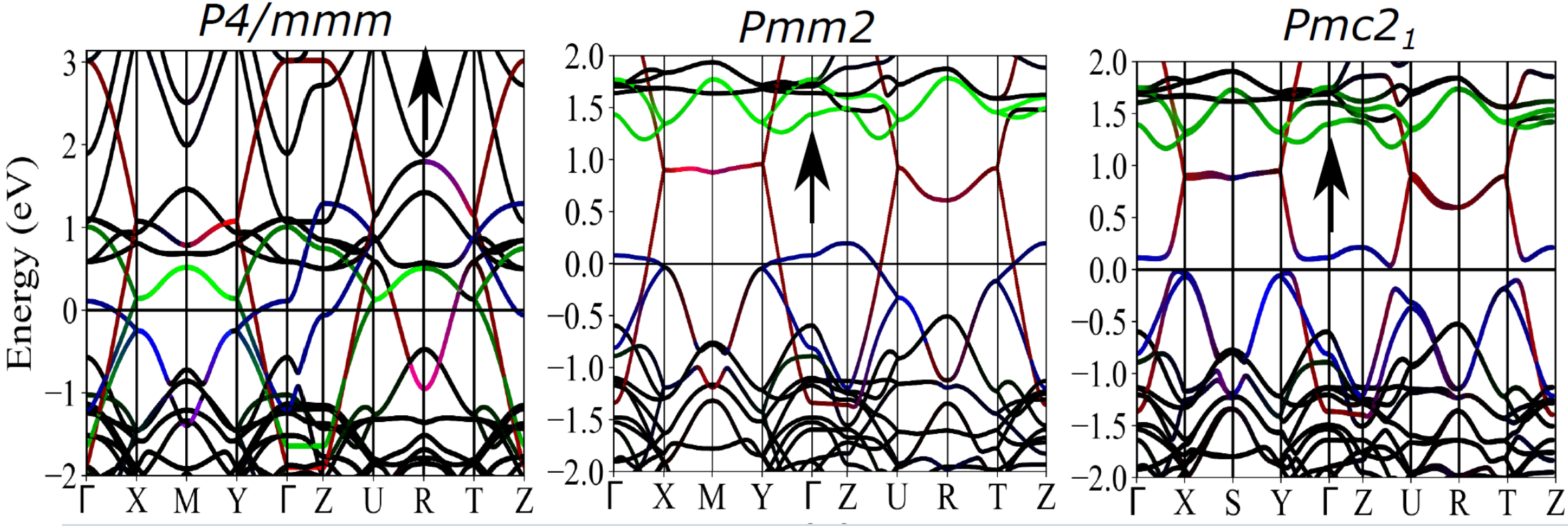
$$\int_{-\infty}^{E_F}{}_{P}\rho^{\uparrow}(E)dE - \int_{-\infty}^{E_F}{}_{NP}\rho^{\uparrow}(E)dE$$

Atom	xy	yz	xz	x^2-y^2	z^2
V	-0.3	0	0	0	0
Mn	0	0	0	0	0.2

- e^- transfer from V to Mn
- Consequent d^0 ness of V: polar distortion
- Augmentation of magnetic moment at Mn

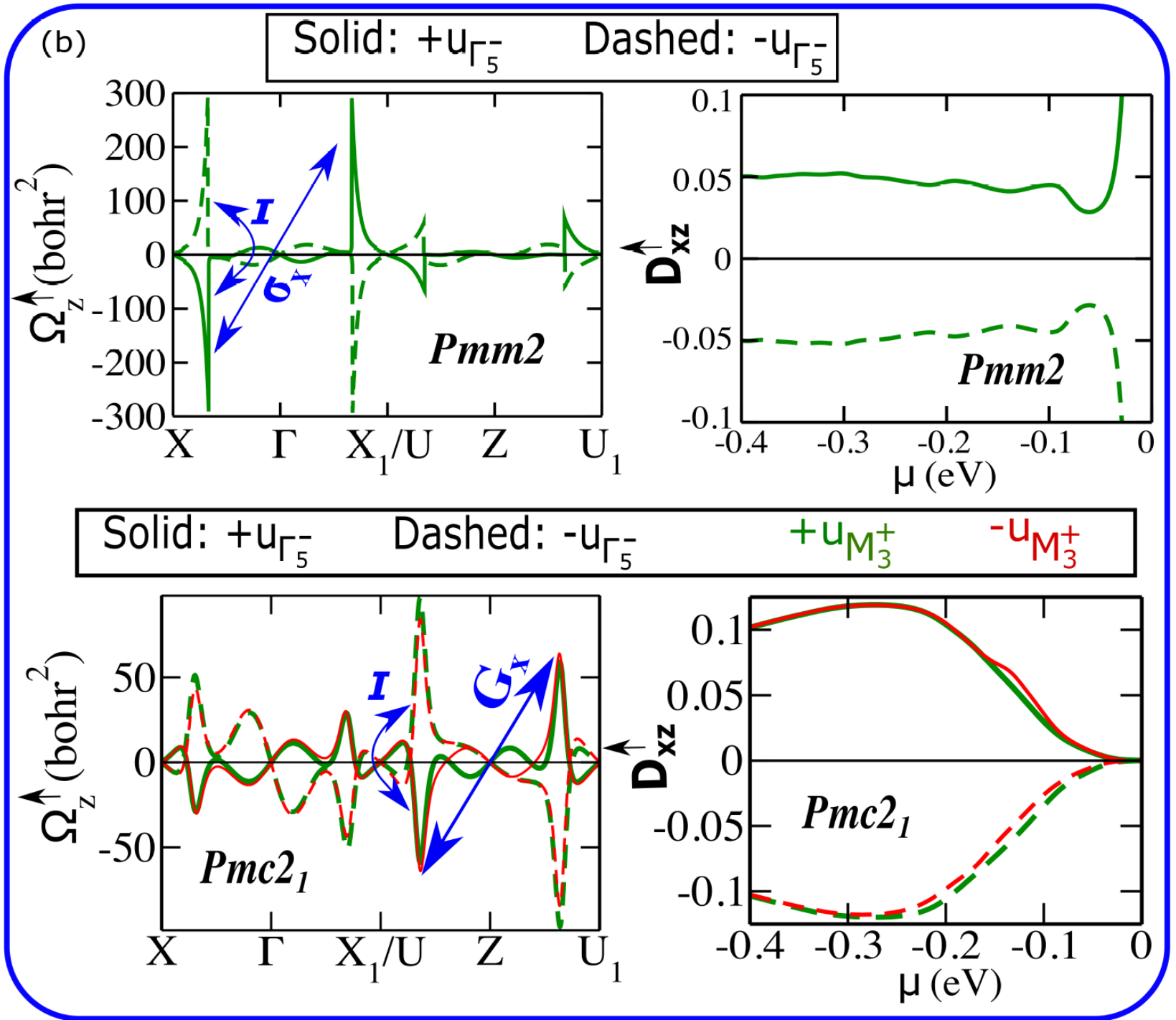
- c-compression of $PbVO_3$ layer: in-plane polar distortion
- Jahn-Teller distortion M_3^+ mode: *Gap*?

Gap opening: Jahn-Teller distortion



Paraelectric Half-metal | Ferroelectric Half-Metal | Ferroelectric Semiconductor

Peierls-like mechanism: Emerging Magnetic Field?



Quantum Geometry

Berry potential:

$$\mathbf{A}(\mathbf{k}) = -\mathrm{Im}\,\langle u_\mathbf{k}|\nabla_\mathbf{k}|u_\mathbf{k}\rangle$$

Berry phase:

$$\phi = \oint \mathbf{A}(\mathbf{k})\cdot d\mathbf{k}$$

Polarization

Berry curvature:

$$\Omega(\mathbf{k}) = \nabla \times \mathbf{A}$$

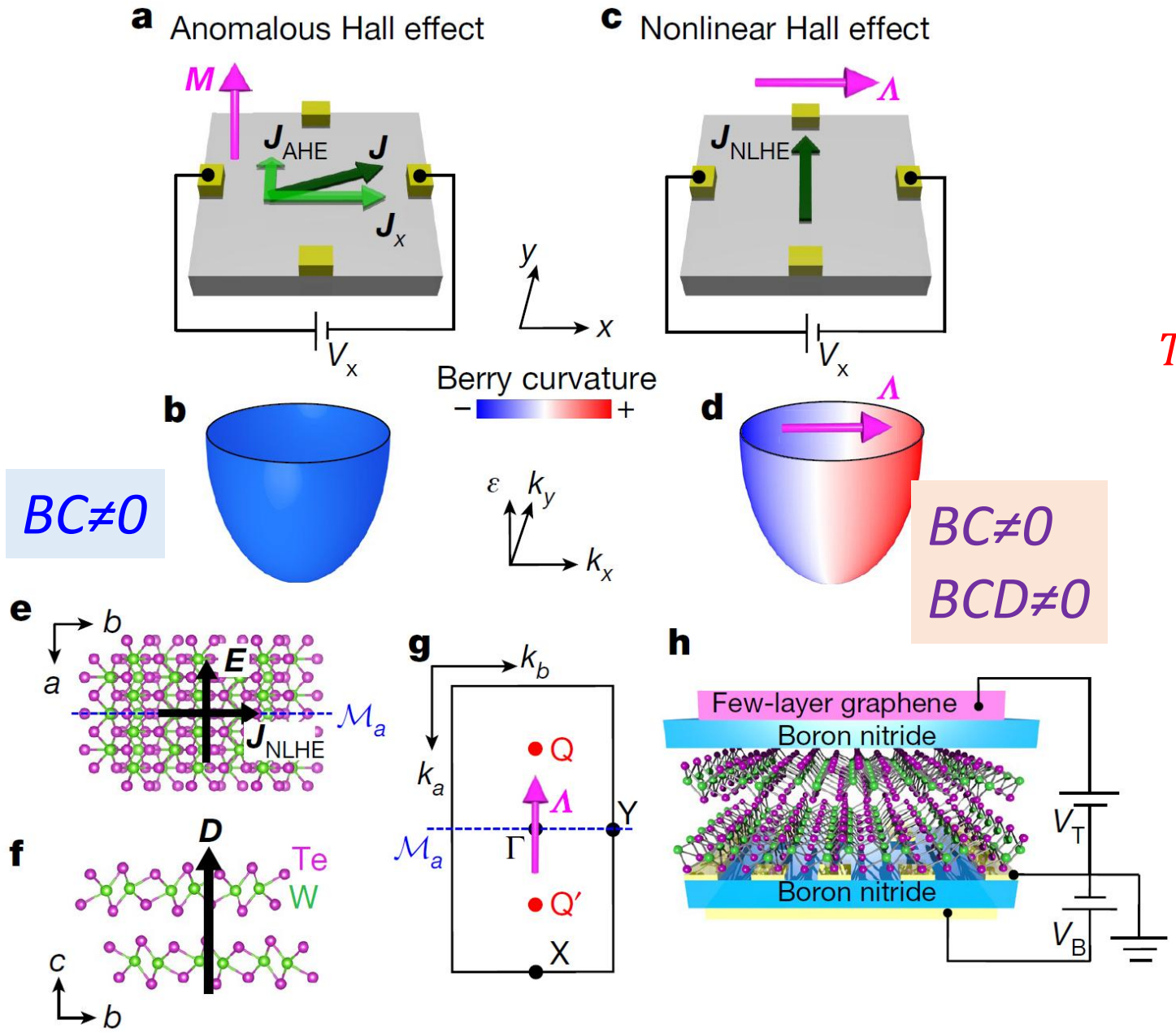
Emerging magnetic field

Spin-polarized Switchable

Berry Curvature Dipole:

1. Nonlinear Hall Effect with B=0 (anomalous)
2. Coupling with B_{ext} enables E and B control of NLHE

Consequences of Berry Curvature Dipole: *Nonlinear Hall Effect*



Demonstrated experimentally in noncentrosymmetric T_d-WTe_2 type-II Weyl semimetal

$\Lambda = BCD \neq 0$

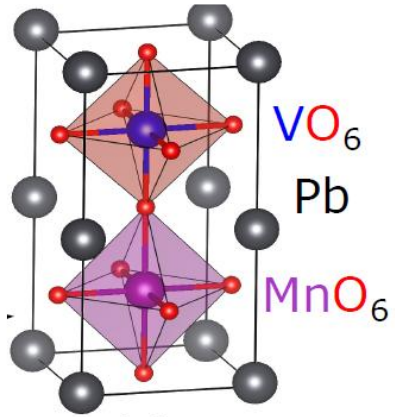
Q Ma et al, Nature 565, 337 (2019)

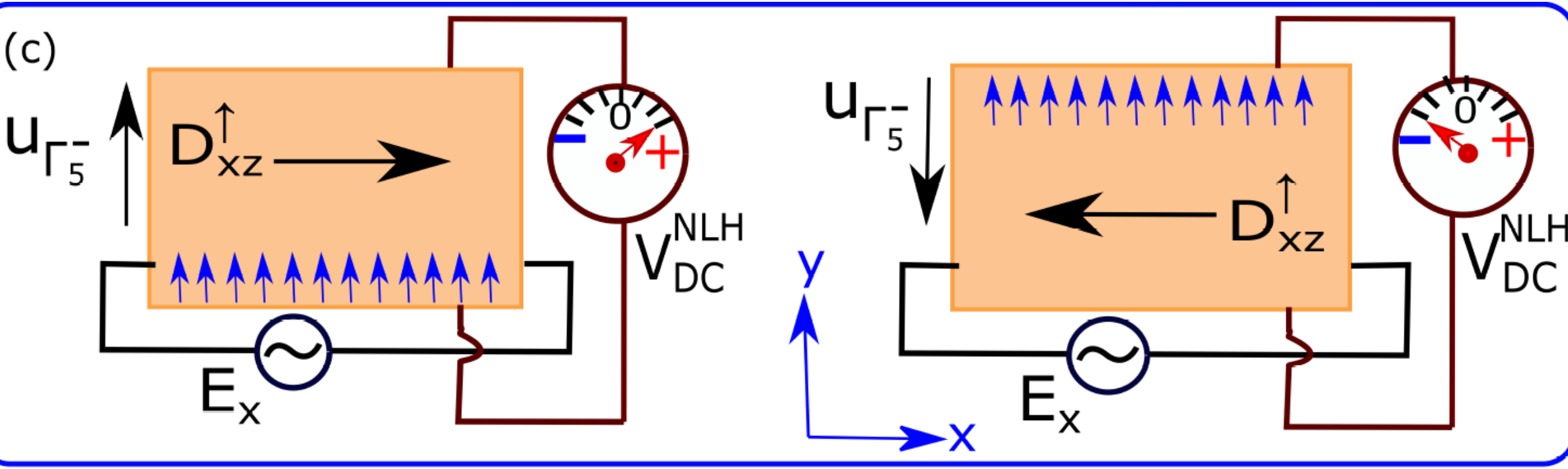
B=0

For driving Frequency ω, Hall signals at frequencies 0 and 2ω

A Multi-ferroic with Switchable

1. **Magnetization *M***
2. **Electric Polarization *P***
3. **Spin-polarized Berry Curvature Dipole *D***





Innovative Device, Exciting Applications Possible!

Nonvolatile Hall Memory

Summary

$PbMnO_3$:
Half-Metal Ferromagnet
Nonpolar (Pnma)

$PbMnO_3$: $SrMnO_3$
Half-Metal Ferromagnet
Polar Half-Metal

$Pmc2_1$

$PbMnO_3$: $PbVO_3$
Magnetic Ferroelectric
Switchable BCD

Hybrid Improper Ferroelectricity

Strong T_MO_6 rotational instability

Proper FE

Jahn-Teller Instability

Quantum Geometry

Arpita Paul and Umesh V Waghmare, Phys Rev B 110, 184110 (2024);

Paul and UVW, under review (2026)

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