

Ideal nanocheckerboard BiFeO₃-BiMnO₃ from first principles

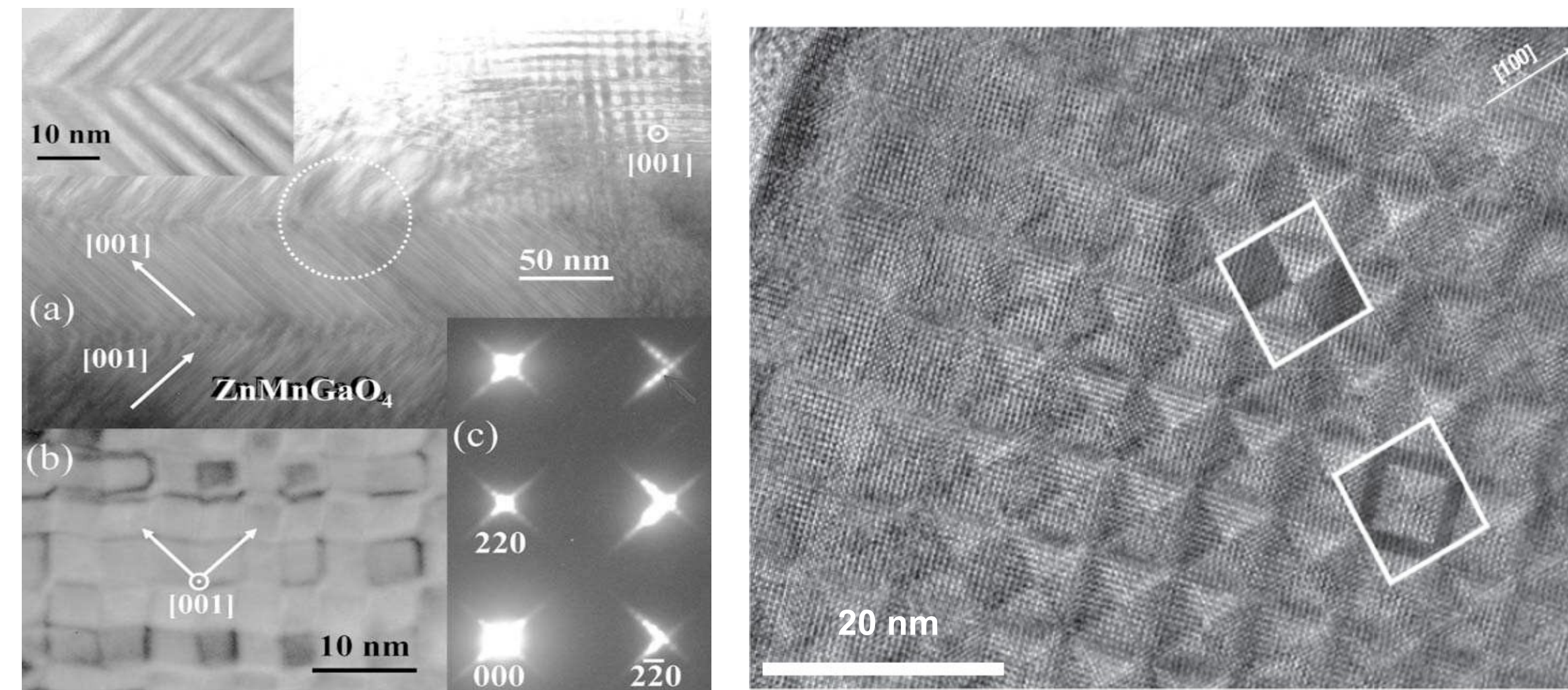
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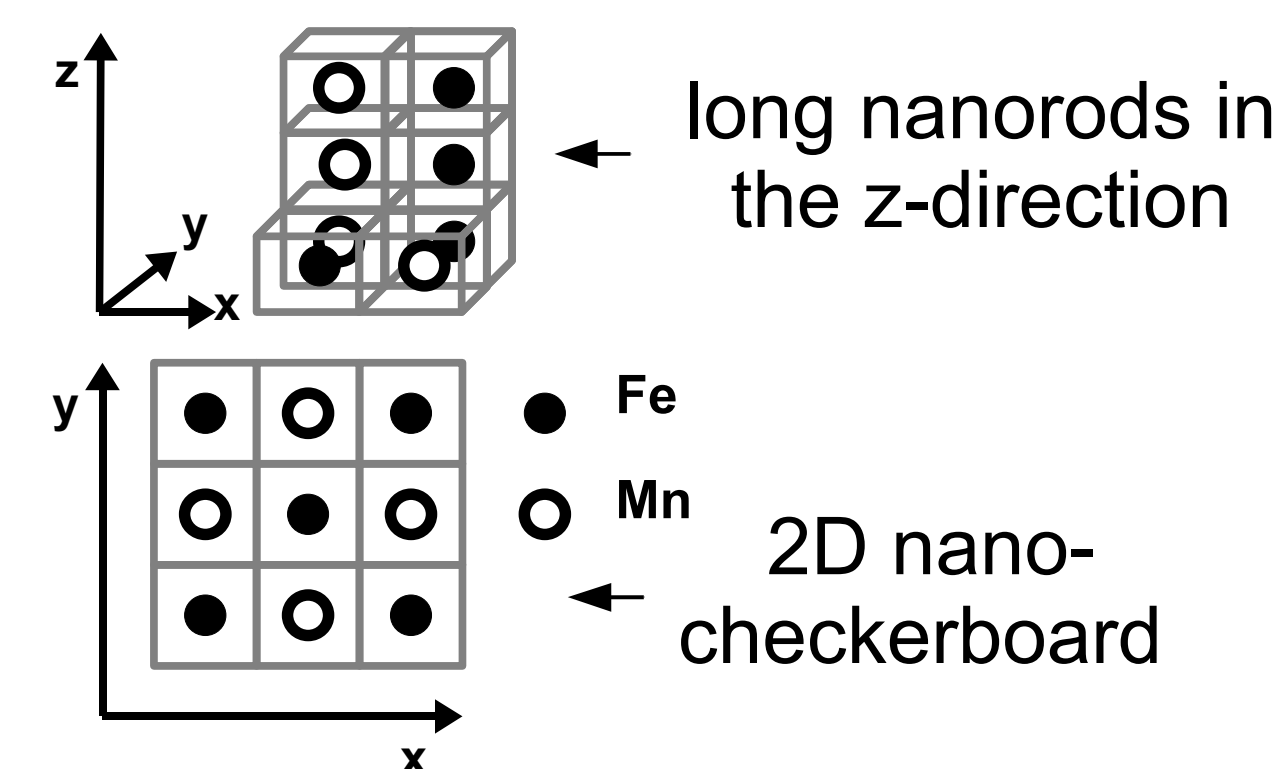
Motivation and Plan

- Artificially structured oxides present intriguing opportunities for material design.
- Artificially structured oxides with checkerboard patterning at the nanoscale have been recently synthesized and show promise for novel properties.



(a) TEM images of ZnMnGaO₄, nanorods (a) and checkerboard (b) formation¹, (b) Lattice image (20nm bar) of a grain of (Nd_{0.53}Li_{0.43})TiO₃².

- We study BiFeO₃-BiMnO₃ nanocheckerboards.
- We relate the properties of the nanocheckerboards to those of the two bulk constituent materials.
- We study non-ground state bulk structures which may be energetically favored in the nanostructure.
- Our starting point : a BiFeO₃-BiMnO₃ nanocheckerboard with alternation of Fe and Mn at the atomic level.

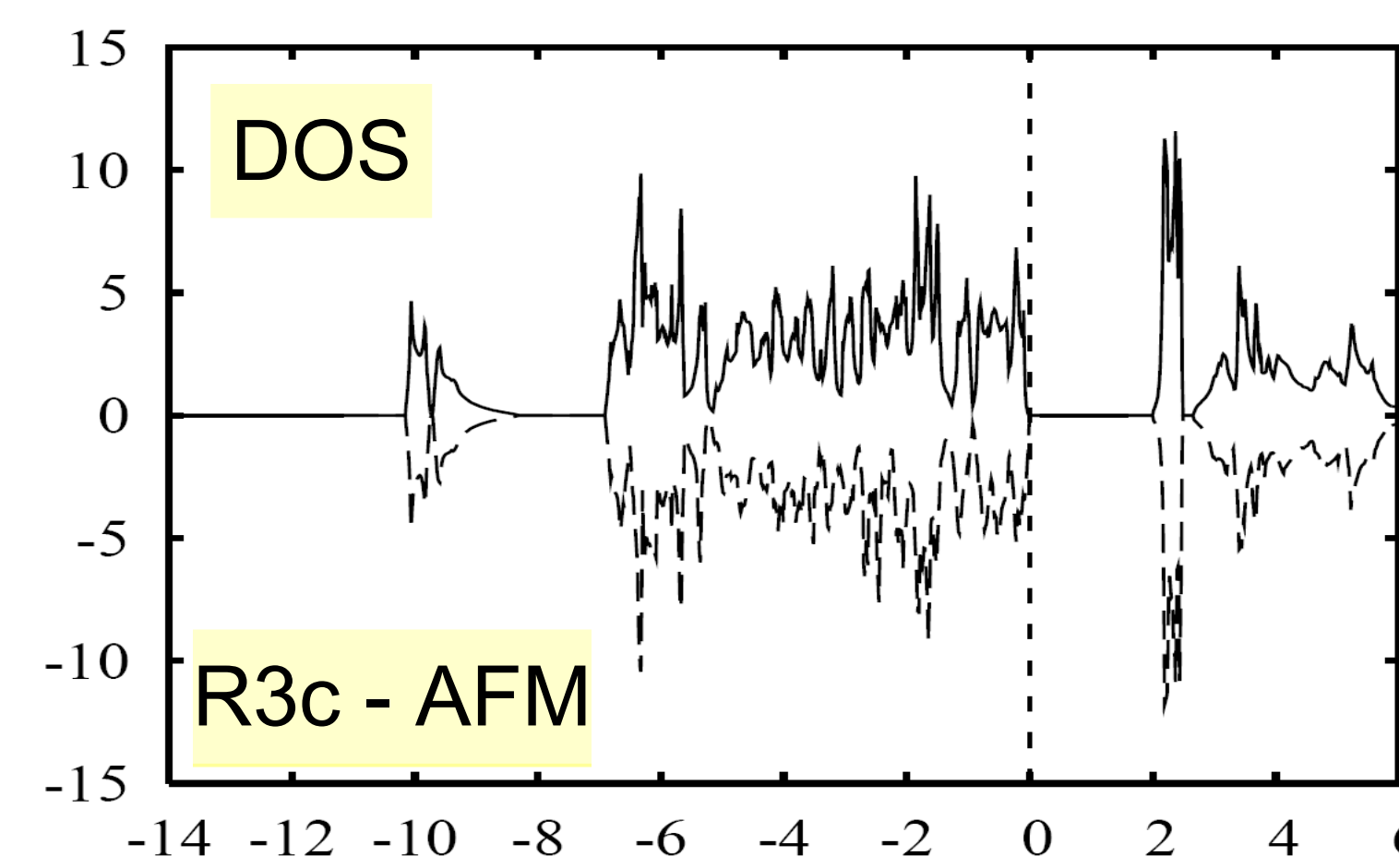
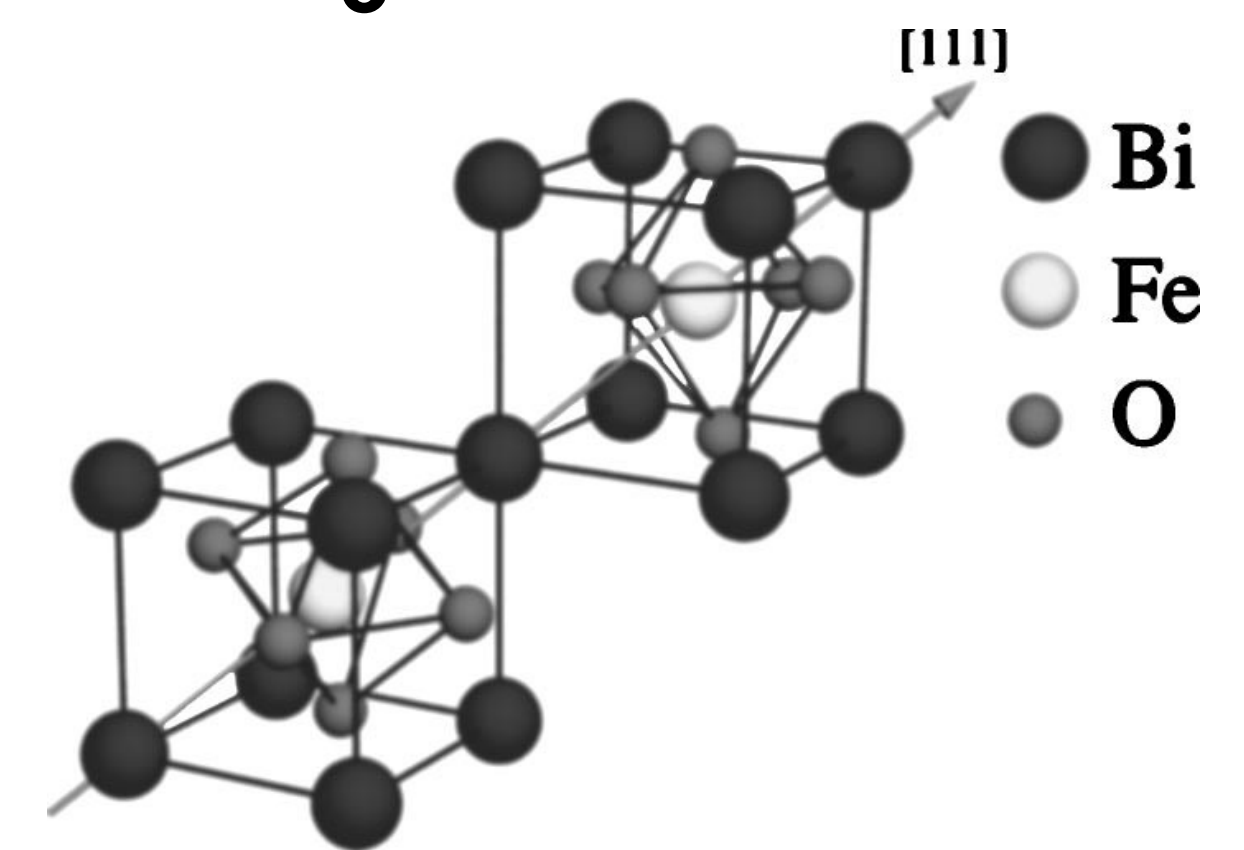


Method

- Density functional theory.
- Local spin-density approximation +U
U = 5eV
J = 1eV
- Vienna *ab initio* simulation package (VASP)
- Projector augmented-wave potentials (PAW)
- Plane wave basis set with cutoff energy 550eV
- Monkhorst-pack k-point mesh
4x4x4, 4x4x2 (doubled cell in the z-direction)
- Modern theory of polarization (Berry phase)³

¹ S. Yeo et al., Appl. Phys. Lett. **89**, 233120 (2006).
² B.S. Guiton, and P.K. Davies, Nature Mater. **6**, 586 (2007).
³ R. Resta and D. Vanderbilt, Physics of Ferroelectrics: a Modern Perspective, Springer-Verlag, 2007, Berlin, pp. 31-68.
⁴ J.B. Neaton et al., Phys. Rev. B **71**, 014113 (2005).
⁵ P. Baettig, R. Seshadri, and N.A. Spaldin, J. Am. Chem. Soc. **129**, 9854 (2007).

BiFeO₃ Structures



- Ground state (GS) structure is rhombohedrally distorted perovskite with space group R3c. The primitive unit cell contains two perovskite formula units with counter-rotations of oxygen octahedra along [111].
- Ferroelectric (FE) with T_c = 1100K and a ferroelectric polarization 90-100 μC/cm² along direction [111]⁴. Antiferromagnetic (AFM) with T_N = 640K.

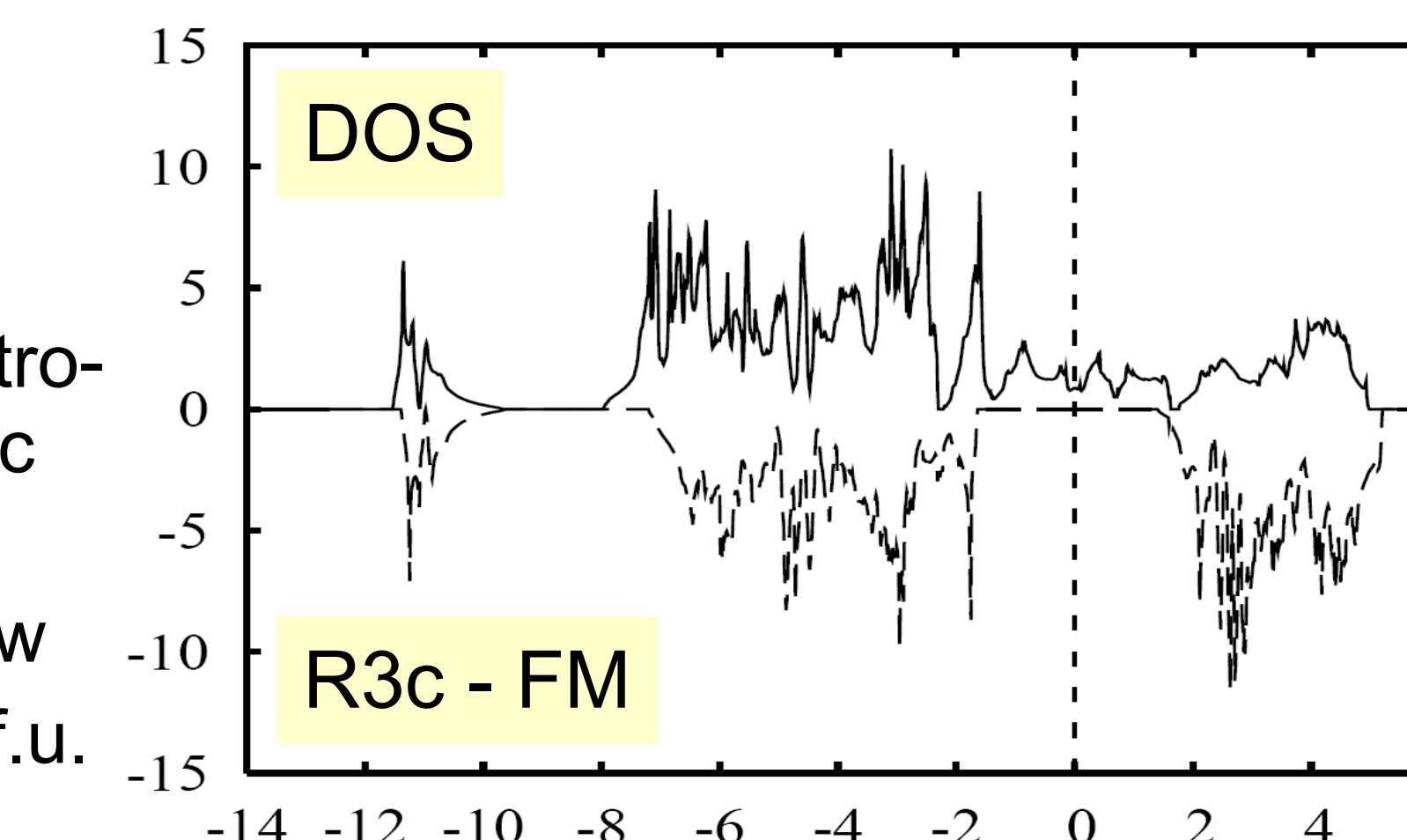
Other AFM ordered structures:

Structure	Ideal	Rotation and Distortion along z	Rotation and Distortion al. y	Rotation and Distortion al. [111]	
Magnetic order	G - AFM	G - AFM	G - AFM	G - AFM	Lowest in energy is R3c structure
Energy difference [eV]	-0.224	-1.626	-1.623	-1.945	Other structures: energetically close
Gap [eV]	0.67	1.76	2.01	1.99	All structures are insulating
Mag. Moment Fe [μ _B]	4.03	3.98	3.98	4.04	Magnetic moment 4.0μ _B per Fe
Magnetic order	C - AFM	C - AFM	C - AFM	(R3c structure)	Polarization (R3c) : 90 μC/cm ²
Energy difference [eV]	0.000	-1.636	-1.475		
Gap [eV]	0.78	2.23	2.06		
Mag. Moment Fe [μ _B]	4.08	3.98	4.01		

Energy diff. per double perovskite cell

BiMnO₃ Structures

- GS is distorted perovskite monoclinic centrosymmetric structure with space group C2/c and zero ferroelectric polarization⁵.
- Ferromagnetic (FM) with T_c = 105K and low temperature magnetic moment 3.2μ_B per f.u.



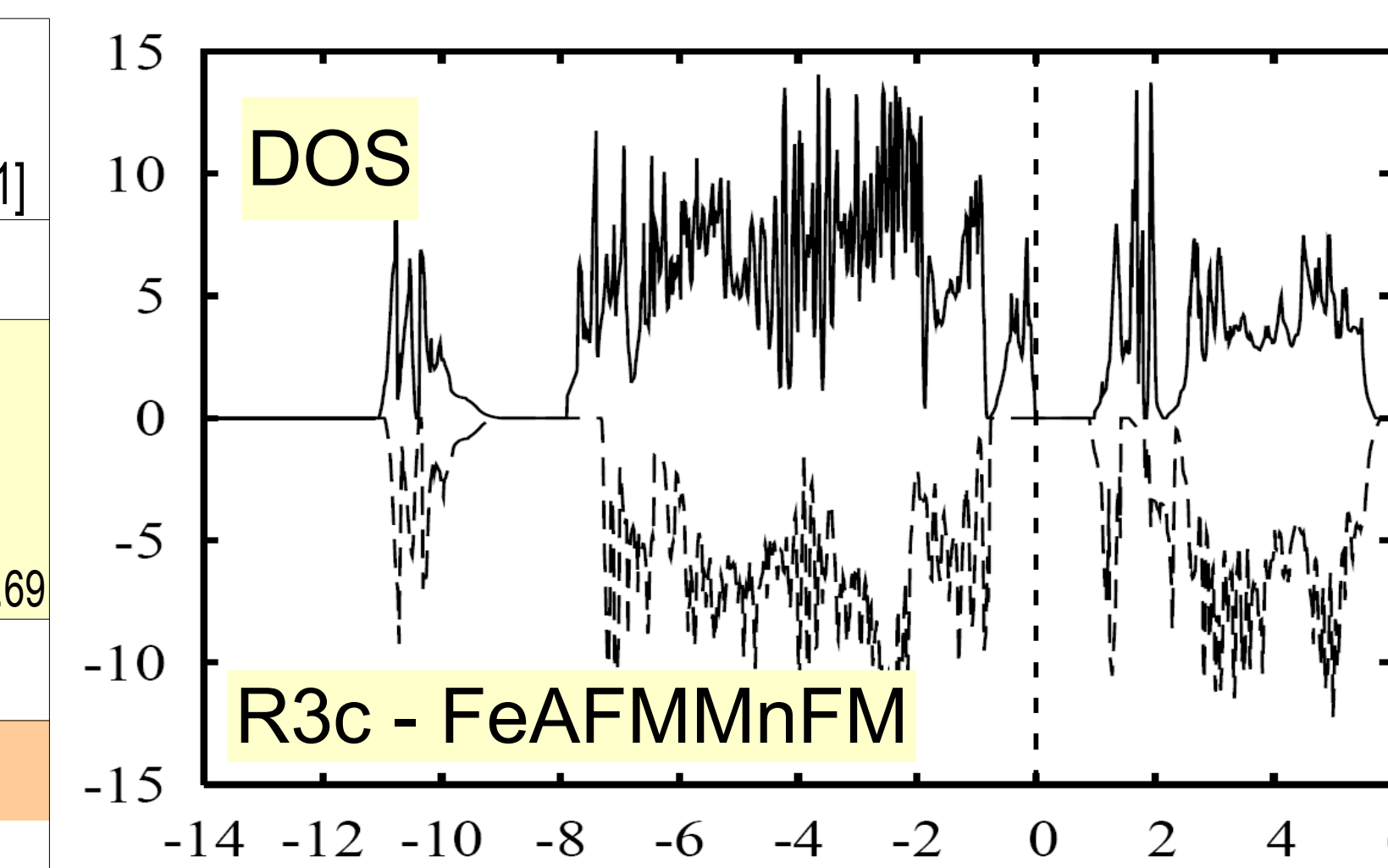
Structure	Ideal	Rotation and Distortion al. z	Rotation and Distortion al. y	Rotation and Distortion al. [111]	
Magnetic order	G - AFM	G - AFM	G - AFM	G - AFM	Insulating gap opens at rotations of oxygen octahedra around, and ionic distortions along z and y direction
Energy difference [eV]	0.000	-0.936	-1.289	-0.939	
Gap [eV]	Metallic	0.74	1.32	Metallic	
Mag. Moment Mn [μ _B]	3.48	3.54	3.54	3.65	
Magnetic order	C - AFM	C - AFM	C - AFM		
Energy difference [eV]	-0.044	-1.191	-1.289		
Gap [eV]	Metallic	0.93	1.18		
Mag. Moment Mn [μ _B]	3.37	3.57	3.58		
Magnetic order	FM	FM	FM	FM	Ferromagnetic order (FM) is most energetically favored among different structures
Energy difference [eV]	-0.527	-1.432	-1.447	-1.826	Half-metallic lowest energy state
Gap [eV]	Metallic	Half-metallic	Half-metallic	Half-metallic	Magnetic moment 3.8μ _B per Mn
Mag. Moment Mn [μ _B]	3.74	3.81	3.81	3.84	

Energy diff. per double perovskite cell

Nanocheckerboard BiFeO₃-BiMnO₃

Structure	Ideal	Distortion along z	Distortion al. y	Rotation and Distortion al. [111]
Magnetic order	FeAFMMnFM (+ - + +)*	FeAFMMnFM*	FeAFMMnFM*	FeAFMMnFM
Energy difference [eV]	-0.519	-1.485	-1.623	-2.567
Gap [eV]	Metallic	Metallic	0.59	0.88
Mag. Moment Fe/Mn [μ _B]	1.24 / 3.52	4.08, 1.22 / 3.65, 3.72	4.06, 0.06 / 3.06, 3.57	4.07, -4.04 / 3.71, 3.69
Magnetic order	FeFMMnAFM (+ + + +)**	FeFMMnAFM	FeFMMnAFM	FeFMMnAFM
Energy difference [eV]	-0.432	-1.263	-1.642	-2.466
Gap [eV]	Metallic	Half-metallic	0.58	0.95
Mag. Moment Fe/Mn [μ _B]	1.18, -1.20 / 3.68, -3.19	4.08, 0.22 / 3.69, -2.90	4.08, 0.87 / 3.72, -3.52	4.11 / -3.50, 3.75
Magnetic order	G-AFM (+ - +)	G - AFM	G - AFM	G - AFM
Energy difference [eV]	-0.303	-1.202	-2.364	-2.463
Gap [eV]	Metallic	1.12	1.55	0.94
Mag. Moment Fe/Mn [μ _B]	0.51 / 3.38	0.99 / 3.52	3.98 / 3.54	4.04 / 3.54
Magnetic order	C - FIM (+ + -)	C - FIM	C - FIM	C - FIM
Energy difference [eV]	0.000	-2.045	-2.128	-2.418
Gap [eV]	Half-metallic	0.56	0.84	0.39
Mag. Moment Fe/Mn [μ _B]	0.39 / -3.18	4.01 / 3.49	4.03 / 3.55	4.08 / 3.58
Magnetic order	FeAFMMnAFM (+ - + -)	FeAFMMnAFM	FeAFMMnAFM	FeAFMMnAFM
Energy difference [eV]	-0.355	-0.785	-2.178	-2.377
Gap [eV]	Metallic	Metallic	1.31	0.85
Mag. Moment Fe/Mn [μ _B]	1.18 / 3.50	1.14 / 3.57	4.02 / 3.65	4.07 / 3.71
Magnetic order	FM (+ + + +)	FM	FM	FM
Energy difference [eV]	-0.519	-1.763	-1.937	-2.261
Gap [eV]	Metallic	Metallic	Metallic	0.13
Mag. Moment Fe/Mn [μ _B]	1.24 / 3.52	3.86 / 3.41	3.83 / 3.40	4.11 / 3.79

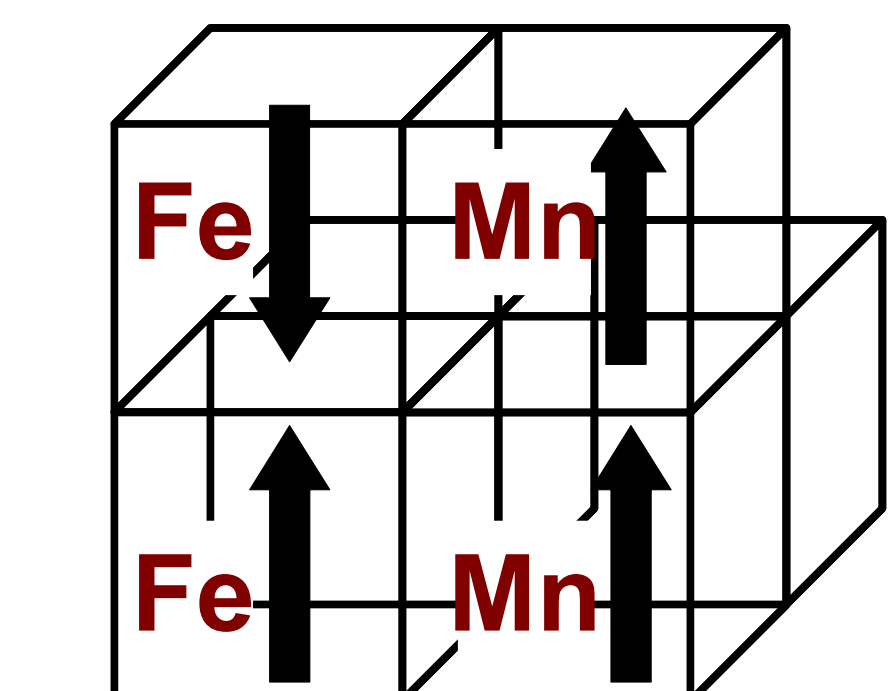
* converges to (+ + + +) : FM order
 ** converges to (+ - + -) : FeAFMMnAFM order
 Energy diff. per double perovskite cell



Lowest in energy is R3c structure with rotation of oxygen octahedra and distortion of ions along [111] direction; this structure is lowest in energy among all magnetic orders

Rotation of oxygen octahedra is preferable; it lowers energy and opens insulating gap

Magnetic order FeAFMMnFM: Fe_↑ Fe_↓ Mn_↑ Mn_↑ (+ - + +)



Summary and Open Questions

Nanocheckerboard BiFeO₃-BiMnO₃ as combination of AFM polar (FE) BiFeO₃ and FM non-polar BiMnO₃:

- Magnetic order** : FeAFMMnFM has Fe-AFM and Mn-FM order along nanopillars with alternating FM and AFM planes in the checkerboard xy-direction reflecting the "AFM" and "FM" nature of parent compounds.
- Structure** has oxygen octahedra rotations and ionic distortions along [111] : same as GS of bulk BiFeO₃ and most energetically favored of bulk BiMnO₃ structures studied. Structures that are not energetically favorable in the bulk are important for the nanocheckerboard.
- Multiferroic** :
 - nonzero ferroelectric polarization: P = 62 μC/cm² roughly along [111] direction. BiMnO₃ polarized by interaction with strongly polar BiFeO₃
 - nonzero net magnetic moment: M = 1.85μ_B per perovskite cell due to Mn mag. moments
- Energy [R3c - AFM BiFeO₃] + Energy [R3c - FM BiMnO₃] → Energy [R3c - FeAFMMnFM BiFeO₃-BiMnO₃] - 0.061 eV

- What are the precise roles of oxygen-octahedron rotations and strain in the ferroelectric and magnetic ordering of the 2D nanocheckerboard?
- Can we predict the nanocheckerboard magnetic transition temperature by modeling the exchange couplings?
- How do the structural and magnetic degrees of freedom interact to produce magnetoelectric coupling?
- How would the nanocheckerboard structure and properties change with epitaxial strain?
- How will the ferroelectric and magnetic ordering change with an increase in the nanocheckerboard length scale?