Perovskite Oxides: Spin Transport and Dynamics
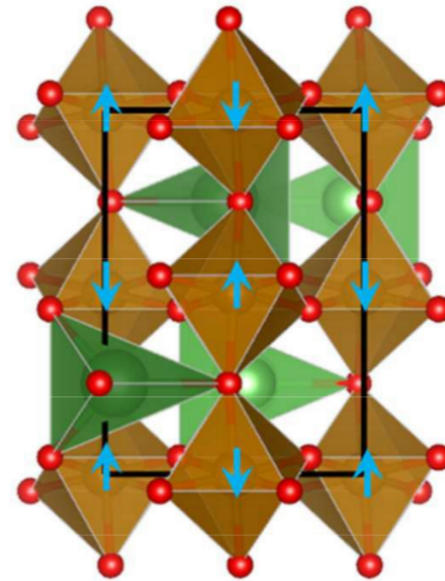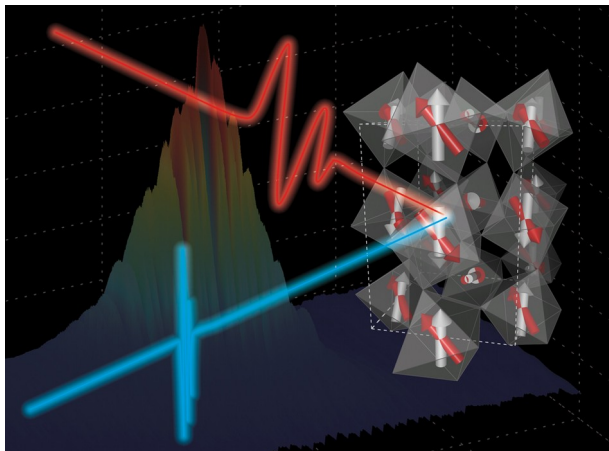
Jiwuer Jilili, Mousumi Upadhyay Kahaly
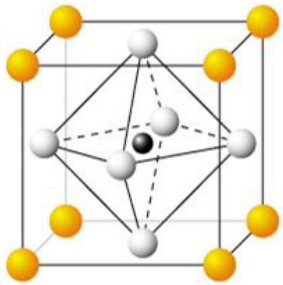
Computational and Applied Materials Science (CAMS)

2018.07.03.

► Introduction & Motivation

► Computational perspective

► $LaNiO_3/CaMnO_3$; $BiMnO_3/SrTiO_3$

► Electronic structure and spin transport

► Summary

http://pubs.rsc.org/en/content/articlelanding/2017/cp/c6cp08698e/unauth#!divAbstract
https://phys.org/news/2014-03-x-ray-laser-electricity-magnetism.html

Perovskite Oxides

ABO$_3$

A(yellow): rare-earth or alkali-metal cation
B(black): transition metal cation

Manganites: LaMnO$_3$, CaMnO$_3$
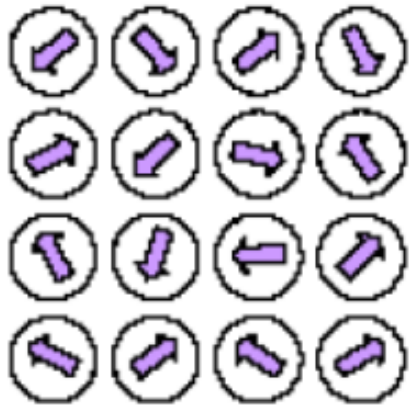Titantes: SrTiO$_3$, LaTiO$_3$, CaTiO$_3$
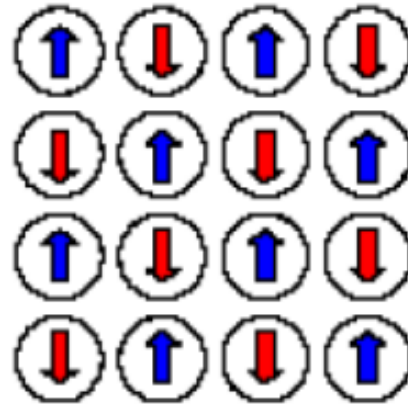Ferrites: BiFeO$_3$, LuFe$_2$O$_4$

Band gap tuning: optoelectronic application; Efficient solar cells; Transparent conducting oxides.

SrTiO$_3$: 3.2 eV; CaMnO$_3$: 3.1 eV; BiMnO$_3$: 0.9 eV; LaMnO$_3$: 1.7 eV

FM   AFM(A)   AFM(C)   AFM(G)

1998 review by Imada, Fujimori and Tokura (page 1122)

Paramagnetic

Antiferromagnetic

Ferromagnetic

Ferrimagnetic

NM: $SrTiO_3$, $PbTiO_3$...

FM: $La(Sr)MnO_3$, $BiMnO_3$, $SrRuO_3$

AFM: $LaMnO_3$, $CaMnO_3$...

http://magnetism.eu/esm/2013/slides/lacroix-slides.pdf

Motivation

2:8

$E-E_F$ (eV)

$LaMnO_3/SrTiO_3$

DOI: 10.1038/srep13762

LaAlO₃ — Thin film crystal

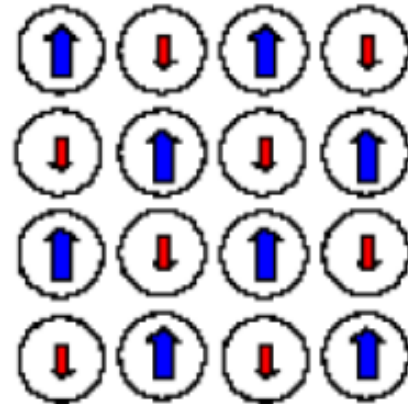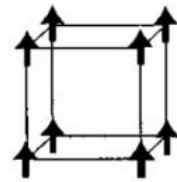2D electron gas

SrTiO₃ — Crystal substrate

https://en.wikipedia.org/wiki
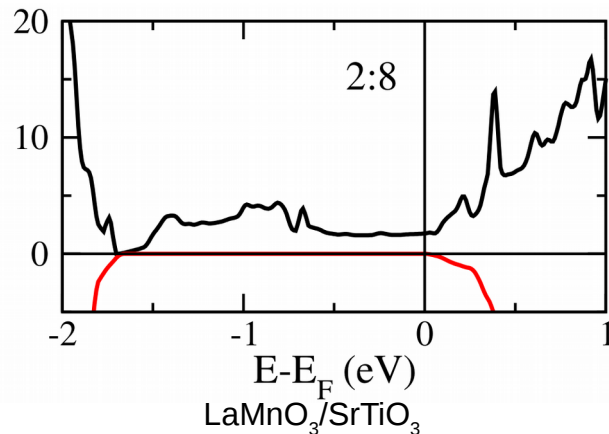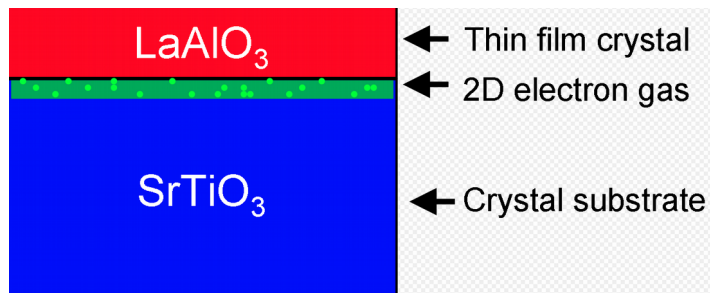
Variety of novel properties:
·Strongly correlated electron system
·High spin polarization
·2-dimensional electron gas
·Metal-insulator transition
·Interfacial ferromagnetism

Wide application range:
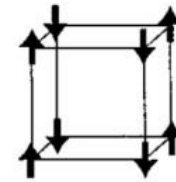Electronics, Spintronics(spin current in magnetic devices), Photonics, Optoelectronics, Photovoltaics...

Power conversion effeciency ~ 22% (2017)
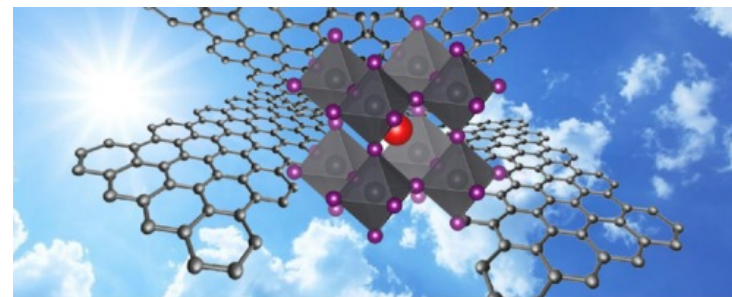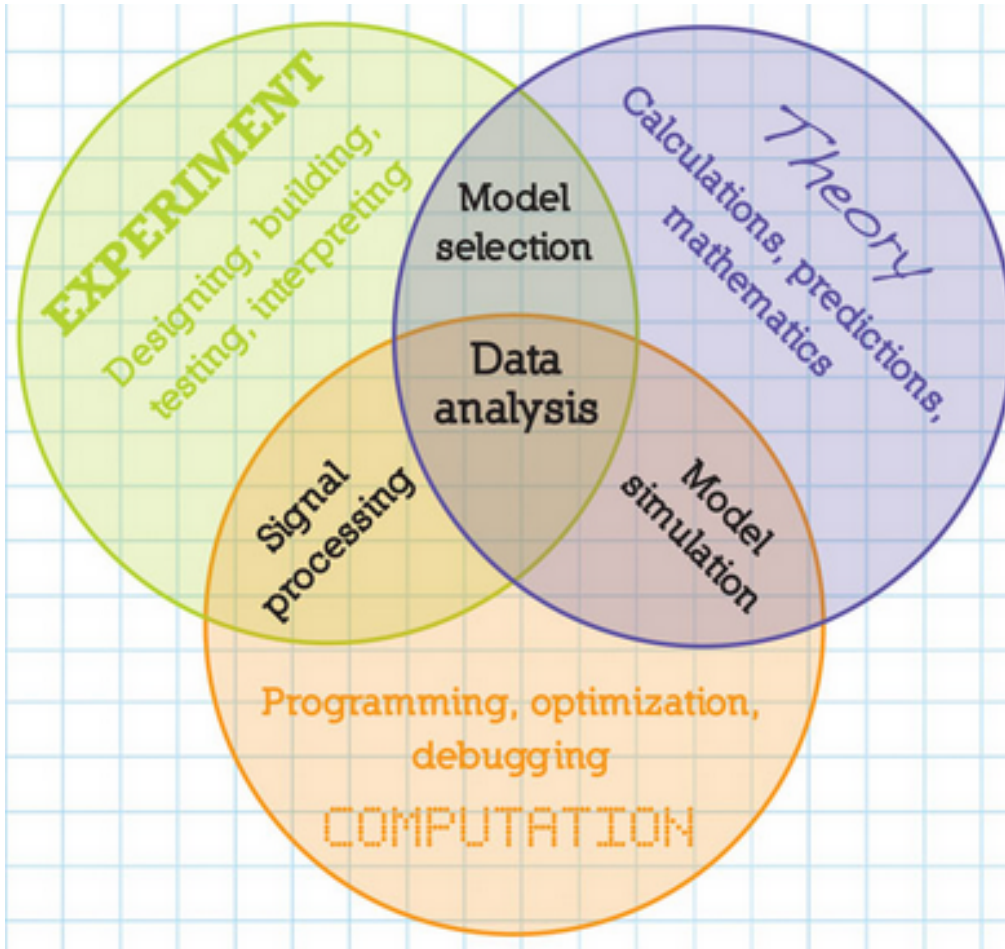
Density functional theory (DFT)
- Computational quantum mechanical modelling
- Compute the electronic structure of matter
- Ground state properties of a system

⟹ Electron density

$$n(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$$

⟹ Functionals:

Functions of another functions

Exchange interactions, magnetic moments, magnetic ground states...

⟹ Excited state properties (DFPT)

⟹ Time-dependent DFT (TDDFT)

(Quantum Espresso, VASP, Wien2K...)

https://www.spsnational.org/the-sps-observer/spring/2015/theory-experiment

Spin: an intrinsic angular momentum of the electron

spin-down

s = − ½

spin-up

s = + ½
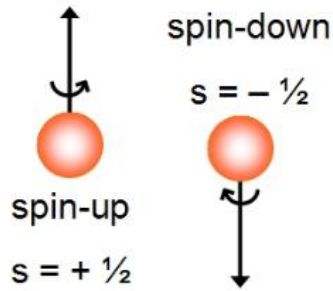
The two possible spin polarisations of the electron

http://cronodon.com/Atomic/quantum_angular_momentum.html

ferromagnetic spin-chain

ground state

exchange

excited state

wavelength, λ
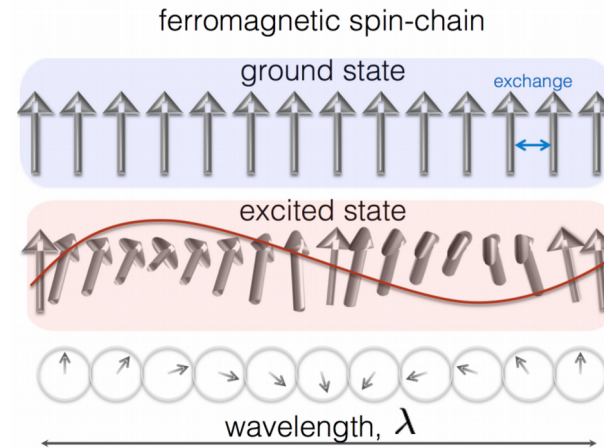
Springer Verlag (2005)
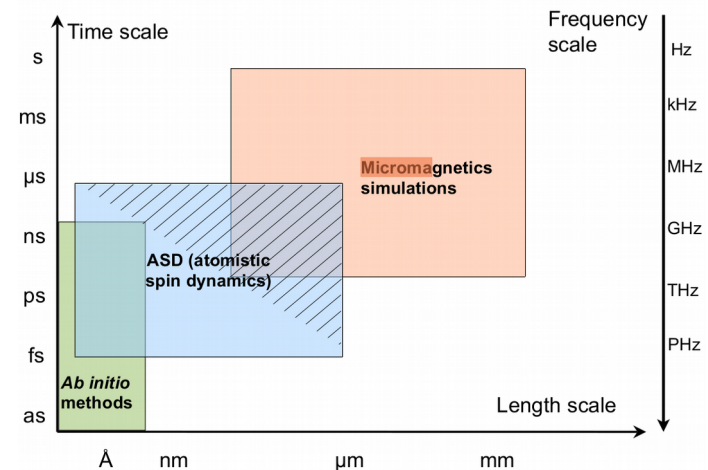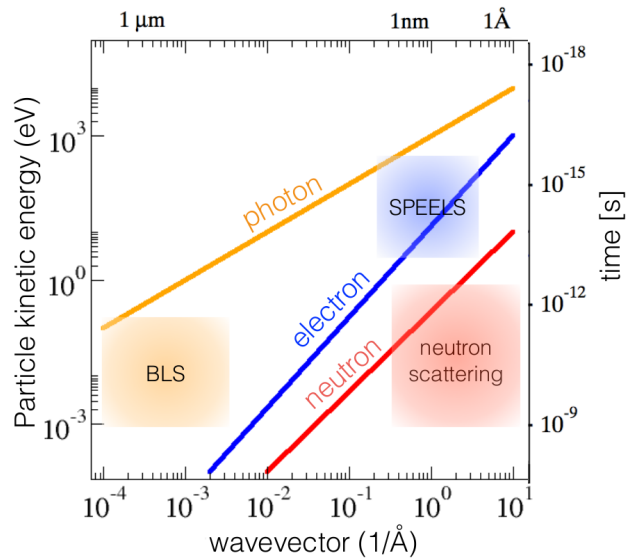
Experimental techniques:
neutrons, electrons, photons scattering experiment

Theoretical methods:
Ab initio calculations:(DFT,time-dependent DFT, Frozen magnon approach…)
Atomistic spin dynamics;
Micromagnetics simulations;

Large-amplitude spin dynamics driven by a THz pulse in resonance with an electromagnon[1]

Magnetic structure of $TbMnO_3$

- Time-resolved resonant soft x-ray diffraction
- Intense THz pulses (1.8)
- Using electric field of light on a sub pico-second time scale
- Control the spin dynamics of the multiferroic $TbMnO_3$

[1] T. Kubacka, Science, **343**, 1333, 2014
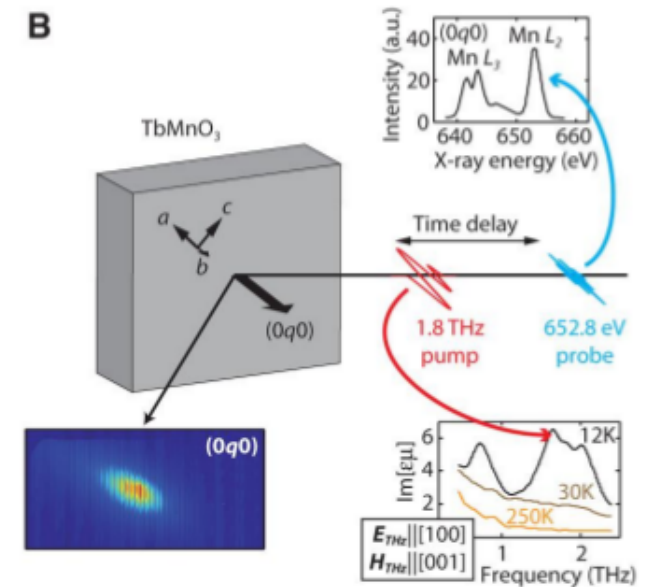
Schematic of the experiment

A high-mobility electron gas at the LaAlO$_3$/SrTiO$_3$ heterointerface[2]

https://www.slideshare.net/nirupam12/
charge-spin-and-orbitals-in-oxides

3.789 Å (LAO), 3.905 Å (STO)
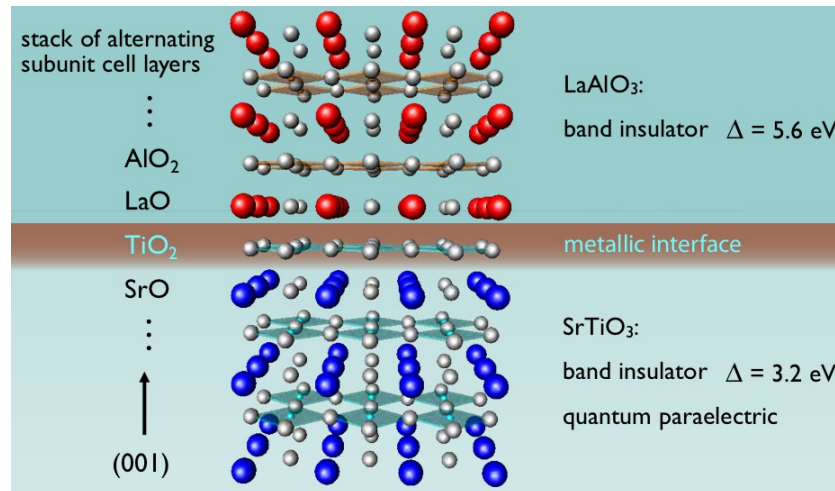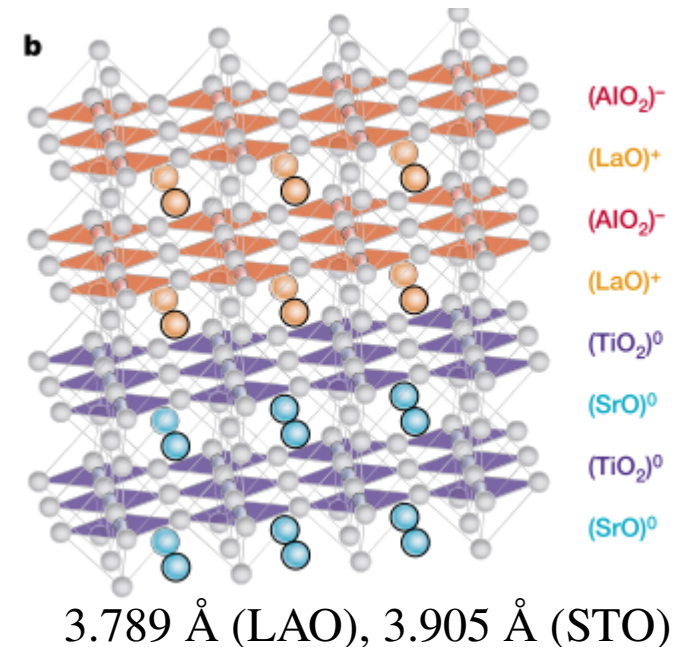
- Pulsed laser deposition
- Polarity discontinuity
- Hole-doped interface $(SrO)^0/(AlO_2)^-$ is insulating
- Electron-doped interface $(LaO)^+/(TiO_2)^0$ is conducting
- High-mobility electron gas >10000cm^2/v.s

[2] A. Ohtomo et al, Nature **427**, 423, 2004

Interfacial Ferromagnetism in LaNiO$_3$/CaMnO$_3$ Superlattices[3]
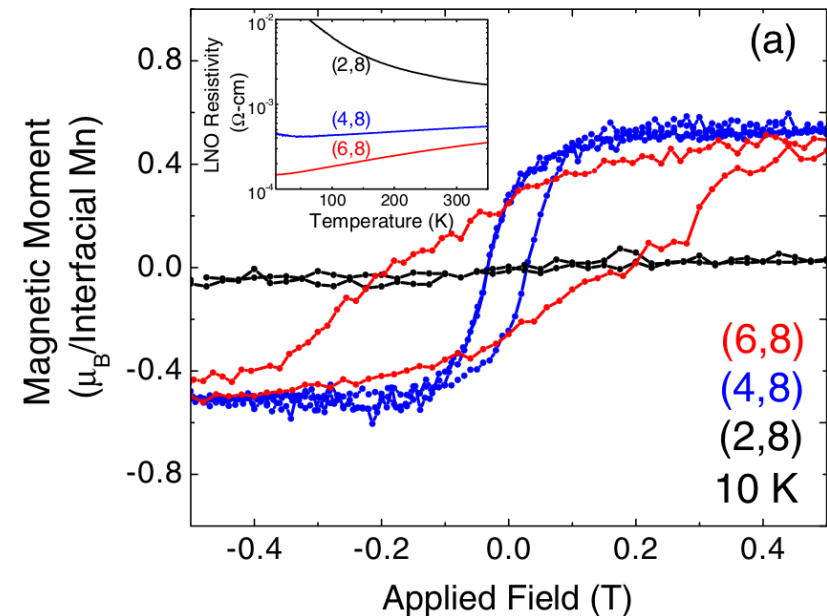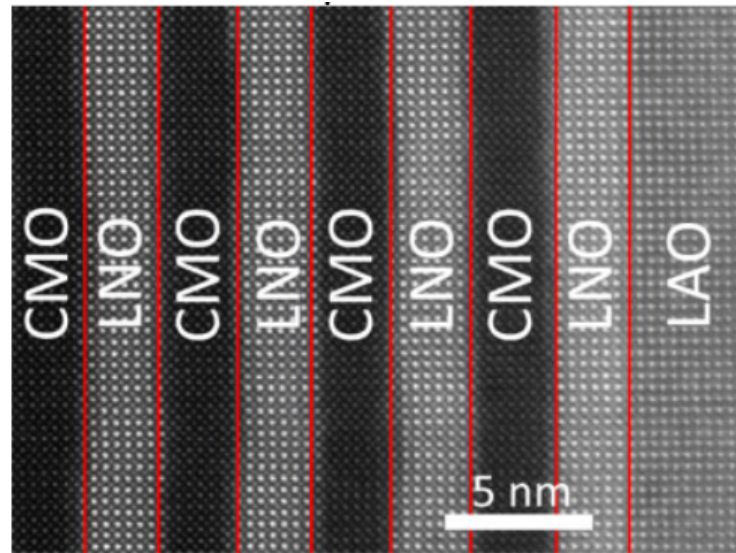
- Pulsed laser deposition
- CaMnO$_3$: AFM insulator, LaNiO$_3$: paramagnetic metal
- Thickness dependent metal-insulator transition
- Ferromagnetism at interface

[3] A. J. Grutter et al, PRL **111**, 087202 (2013)

Role of polar compensation in interfacial ferromagnetism of $LaNiO_3/CaMnO_3$ superlattices[4]
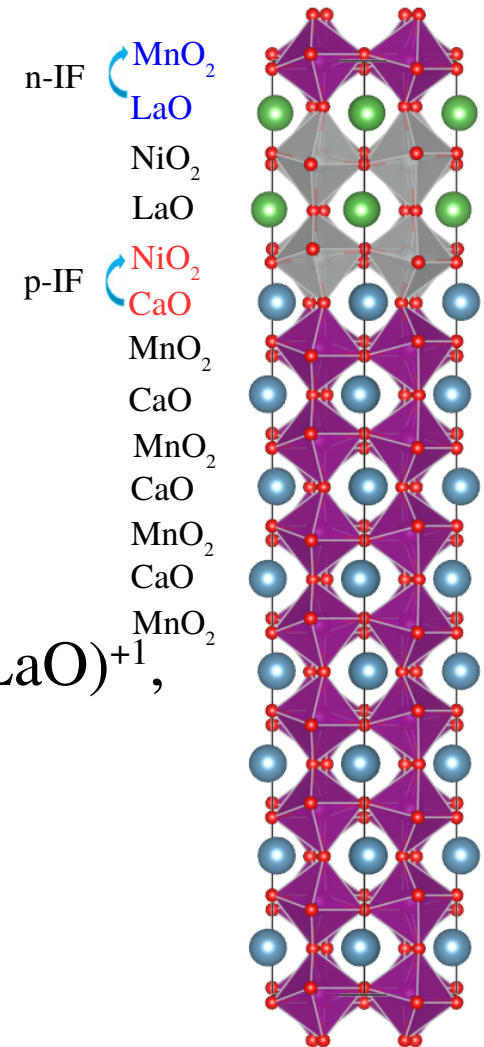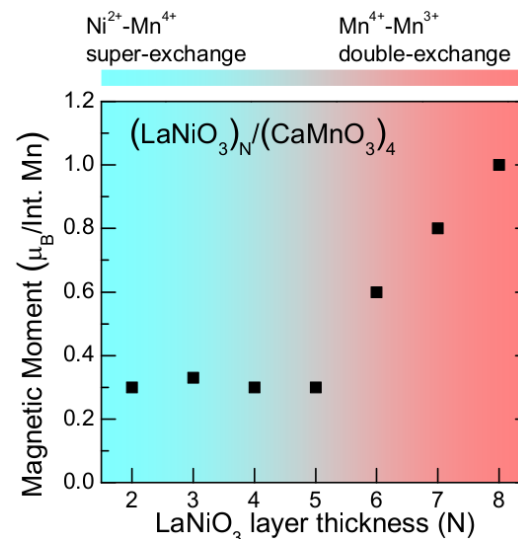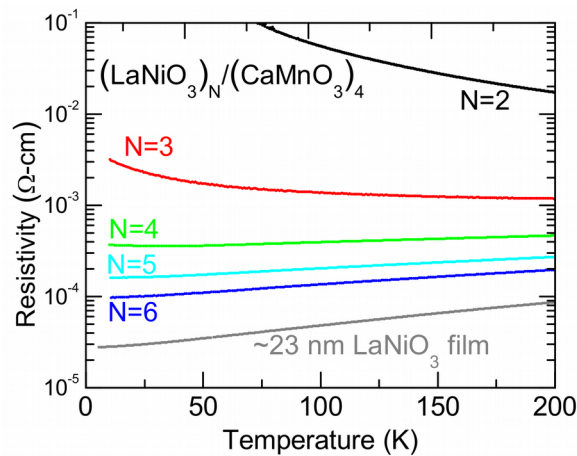
- Polar compensation due to polar mismatch: $(MnO_2)^0$, $(LaO)^{+1}$, $(CaO)^0$, $(NiO_2)^{-1}$
- Magnetic exchange interaction: spin flip process
- Ferromagnetic signal for all superlattices
- Ni magnetism

[4] C. L. Flint et al,, Phys. Rev. Materials **1**, 024404 (2017)
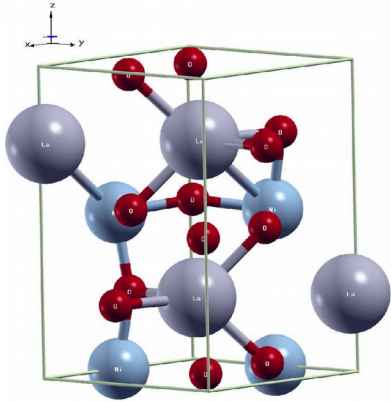
LaNiO$_3$: Paramagnetic metal
CaMnO$_3$: Antiferromagnetic insulator
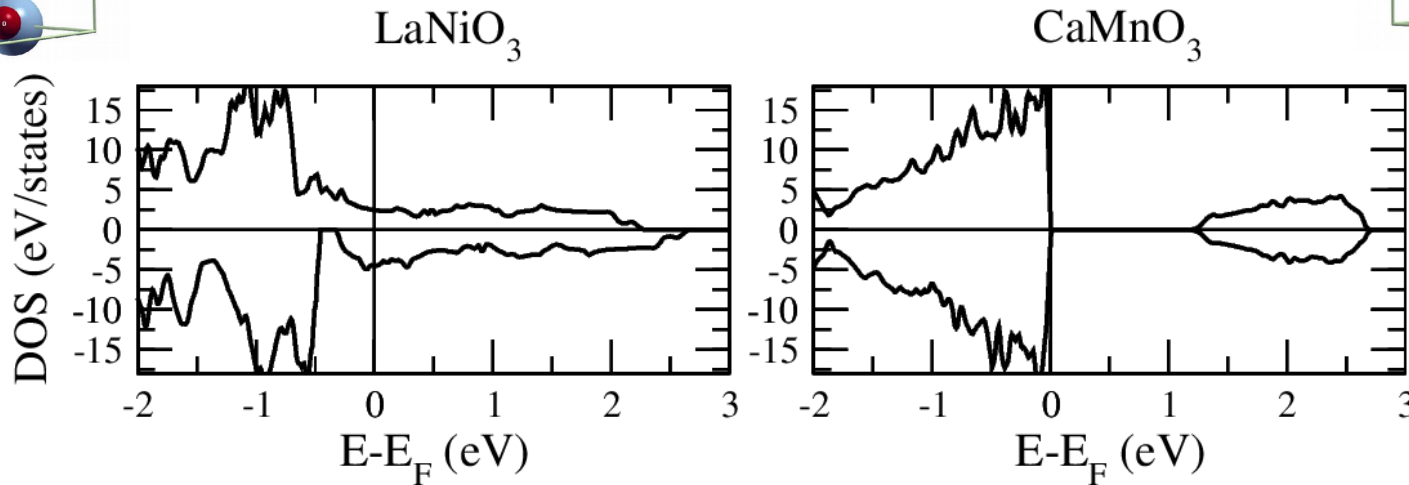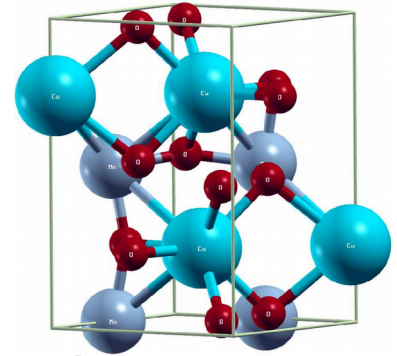
- Coulomb interaction term U: correlated nature of the localized d-orbitals
- Ferromagnetism is favorable when U> 0 eV for LaNiO$_3$
- Antiferromagnetism is favorable U≤3 eV for CaMnO$_3$
- Bulk electronic structure is well reproduced

LaNiO$_3$/CaMnO$_3$ superlattice
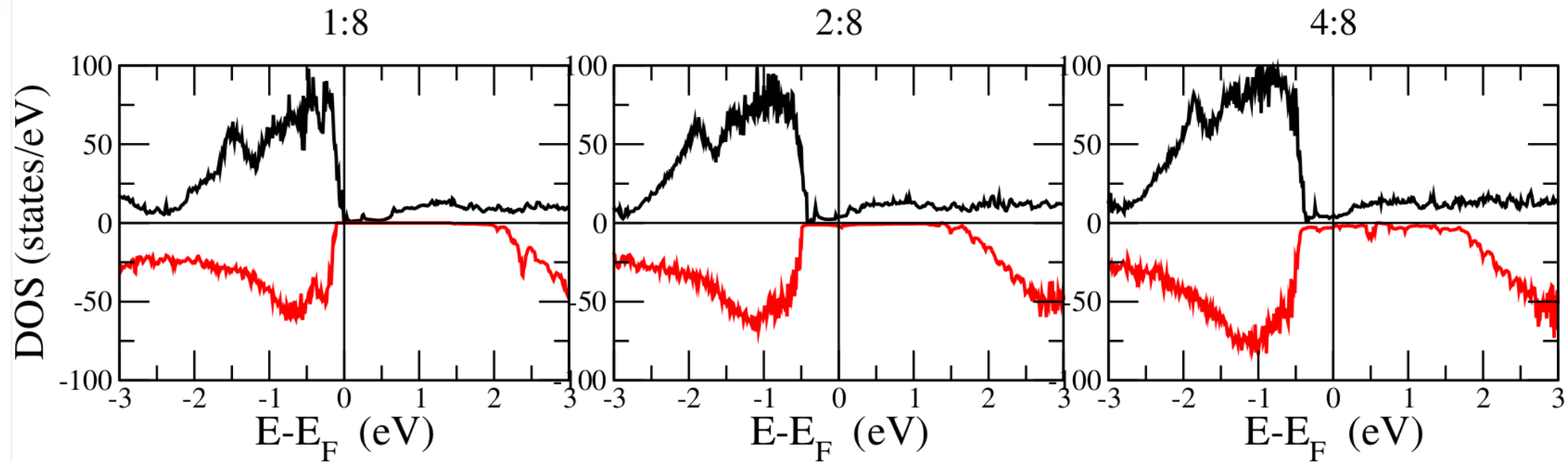
- O-Mn-O off-centering along z axis toward p-IF up by up to 0.05Å
- More tilted MnO$_6$ octahedra than NiO$_6$ octahedra
- Orthorhombic ($a^-a^-c^+$) tilt pattern[5]
- Insulator to metallic phase transition
- Charge transfer and polar discontinuity

[5] Glazer, A. M. Acta Cryst. B **28**, 3384 (1972)
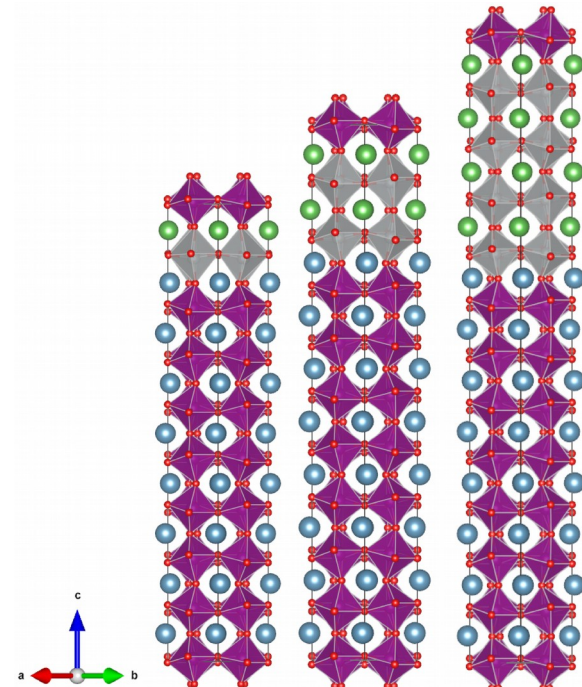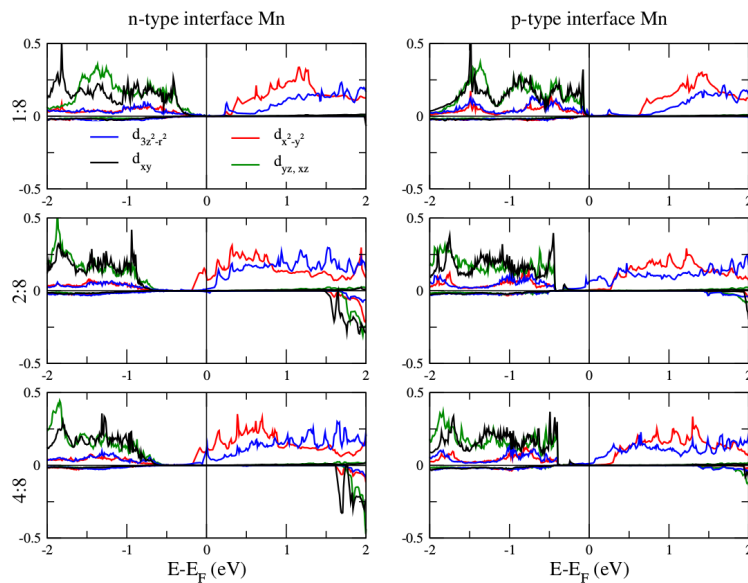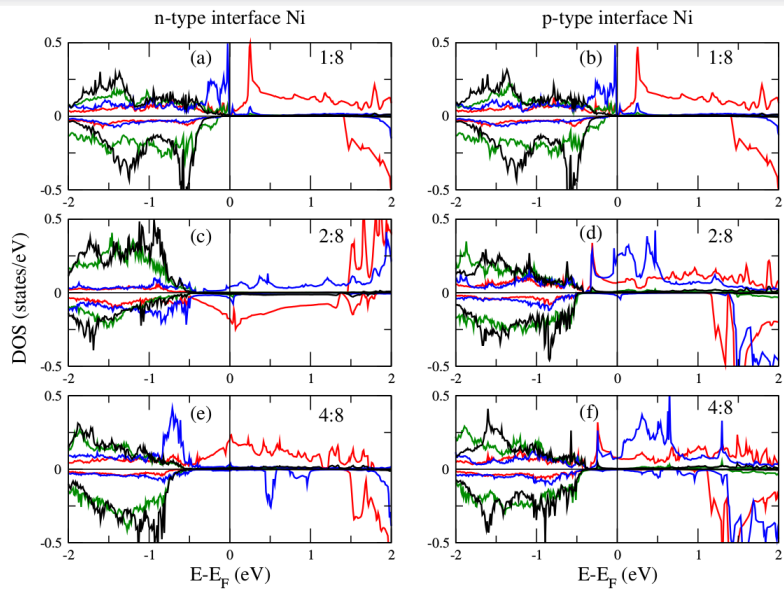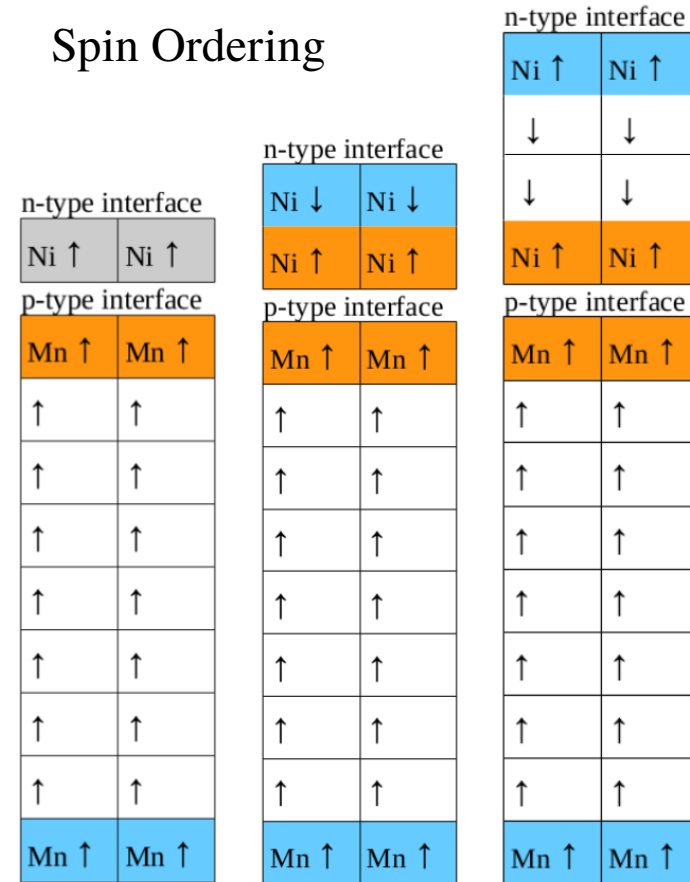
Spin Ordering

- Charge transfer from LaNiO$_3$ to CaMnO$_3$
- Spin exchange in LaNiO$_3$ layers: AFM ordering
- Magnetic moments: Ni: 0.81~1.19 u_B; Mn: 3.02~3.07 u_B
- Interplay between exchange interactions due to mixed valence states at interface

BiMnO$_3$/SrTiO$_3$ Heterointerface

(another interesting candidate)

Origin of Interface Magnetism in BiMnO$_3$/SrTiO$_3$ and LaAlO$_3$/SrTiO$_3$ Heterostructures[6]

- LaAlO$_3$, BiMnO$_3$, SrTiO$_3$ - non-magnetic insulators
- Interfacial magnetism at both systems
- O vacancy induced magnetism
- Exchange interaction between interface states and localized moments of Mn^{3+}
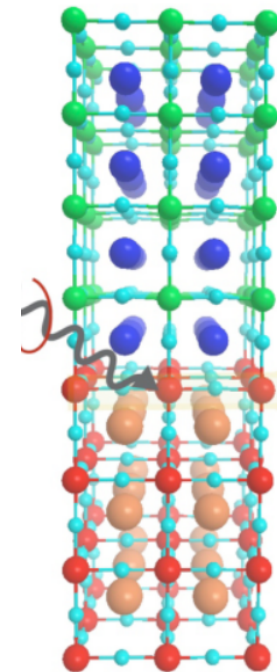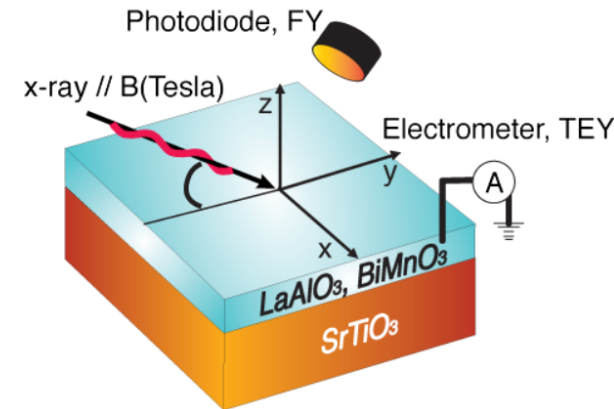
[6] M. Salluzzo, Phys Rev Lett. **111**,087204, 2013
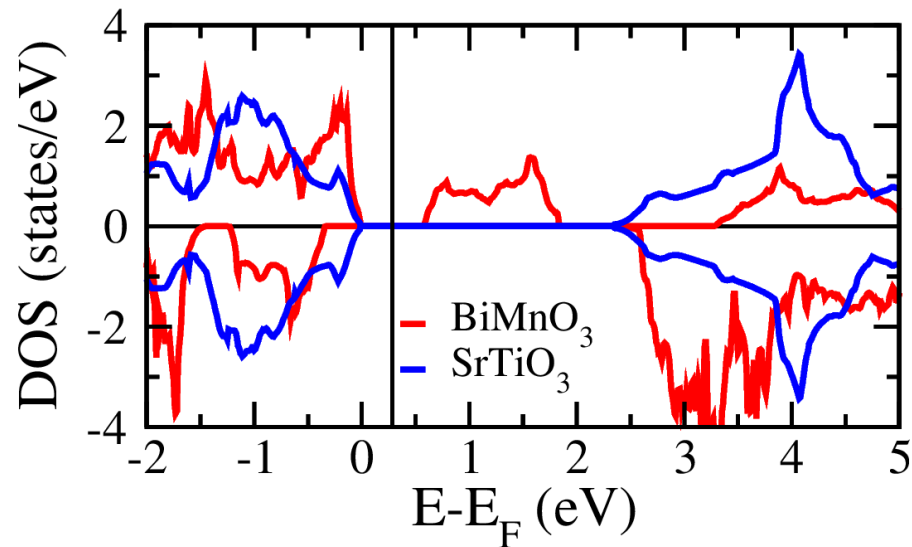
- ► SrTiO$_3$: Cubic perovskite, non-magnetic insulator
- ► BiMnO$_3$: Highly distorted, ferromagnetic insulator
- ► BiMnO$_3$: Low temperature monoclinic phase
- ► Small BiMnO$_3$ band gap
- ► Mn magnetic moments: $3.8 u_B$
- ► Ferromagnetic VS Antiferromagnetic

Thermoelectricity: direct conversion of heat into electricity or vice vesra

Seebeck coefficient   electrical conductivity

Figure of merit $\rightarrow$ $ZT = \dfrac{S^2 \sigma T}{\kappa}$ $\leftarrow$ thermal conductivity

what makes a good thermoelectric $\rightarrow$ $\uparrow ZT$ --- $\uparrow S, \uparrow \sigma, \downarrow \kappa$

Optimal Doping, nanostructuring, spin injection, heterostructure formation…

ZT: << 1 usually,

Goal : stable material with high ZT

Spin-dependent TE properties—higher ZT

Thermoelectric properties and ZT versus doping concentration at 300 K for n-type $Si_{80}Ge_{20}$

DOI: 10.1039/b822664b

Distorted SrTiO$_3$

► Different behavior of two spin channels
► Sharp DOS near the Fermi level indicates promising thermoelectricity
► O vacancy at different layers, spin flip when O vac at BiO layer
► Strong hybridization of Mn and Ti

Thermoelectricity: direct conversion of heat into electricity or vice vesra

Seebeck coefficient   electrical conductivity

Figure of merit $\rightarrow$ $ZT = \dfrac{S^2 \sigma T}{\kappa}$ $\leftarrow$ thermal conductivity

what makes a good thermoelectric $\rightarrow$ $\uparrow ZT$ --- $\uparrow S$, $\uparrow \sigma$, $\downarrow \kappa$

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Thermoelectric properties and ZT versus doping concentration at 300 K for n-type $Si_{80}Ge_{20}$

DOI: 10.1039/b822664b

Effect of two spin channels

- The contributions in DOS from different orbitals from spin-up and spin-dn channel are different, so different transport behavior is also expected from both the channels.

- Metallic state for one channel corresponds to higher electrical conductivity.

- Semiconducting state corresponds to lower electrical conductivity.

- Thermal excitation of spin moments can alter the magnetic state of materials.

- Corresponding transport properties can alter with different spin channel

https://doi.org/10.1016/j.physleta.2017.07.034
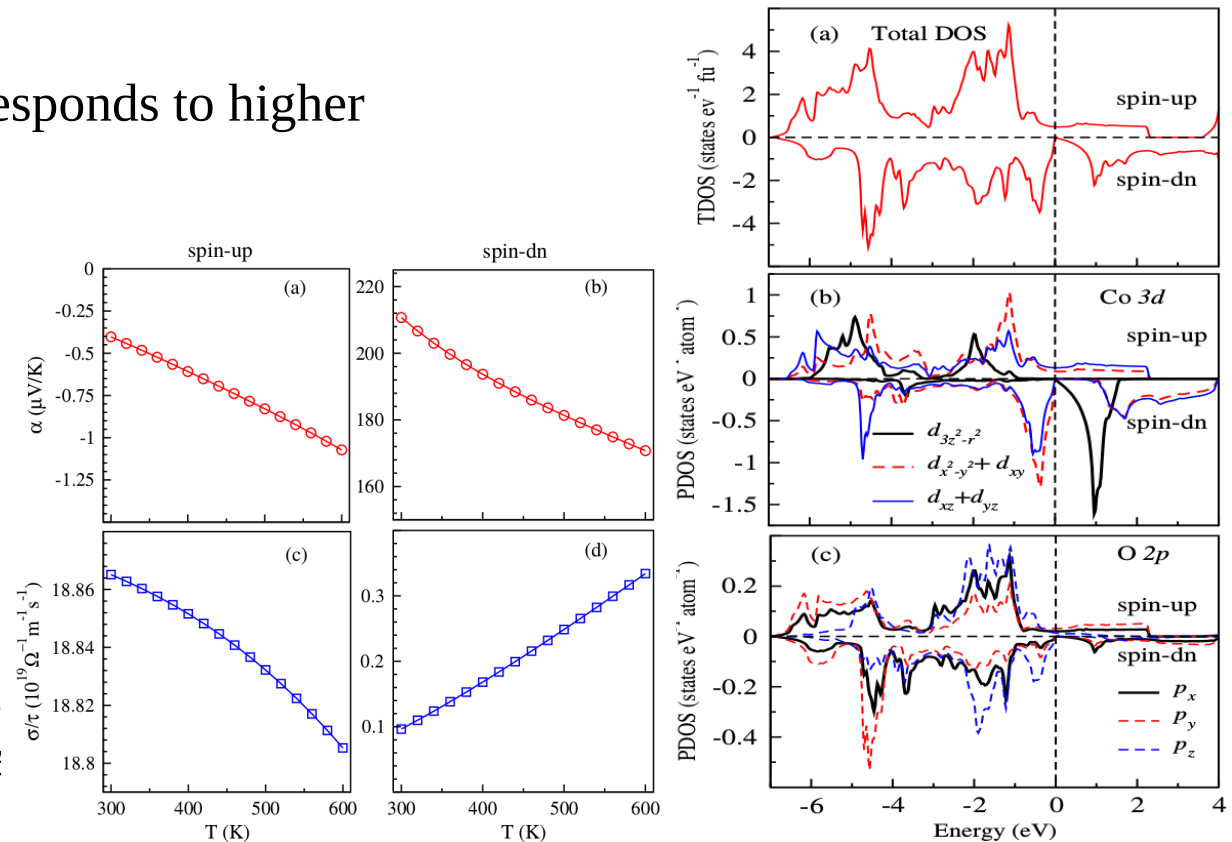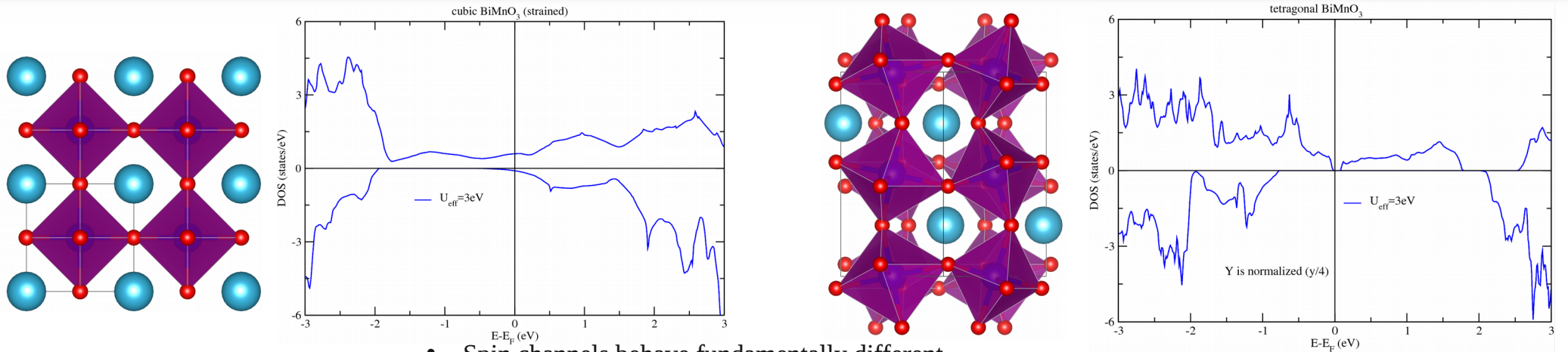
- Spin channels behave fundamentally different.
- Thermoelectric properties mainly governed by spin up channel.
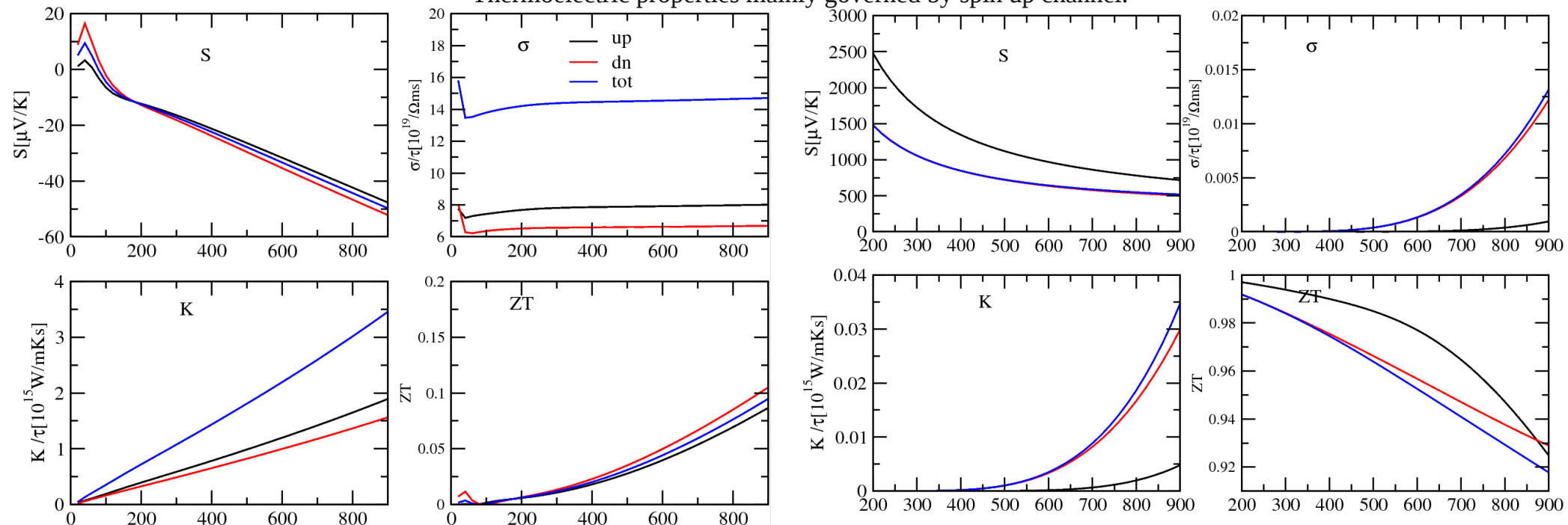
- Reasonable performance when compared to existing 'good thermoelectrics'.
- Ferromagnetic spin exchange plays dominant roles in these perovskite IFs.

- Figure of merit of approximately 1.5 (600 K) can be achieved in current 'good thermoelectric' systems

- $BiMnO_3/SrTiO_3 \sim 1$ (200-400 K)

- With modification in induced spin channels, perovskite IF can be very efficient 'thermoelectric material'

- Spin exchange and dynamics play important role

- Thermoelectric materials based on perovskite oxides, spin caloritronics
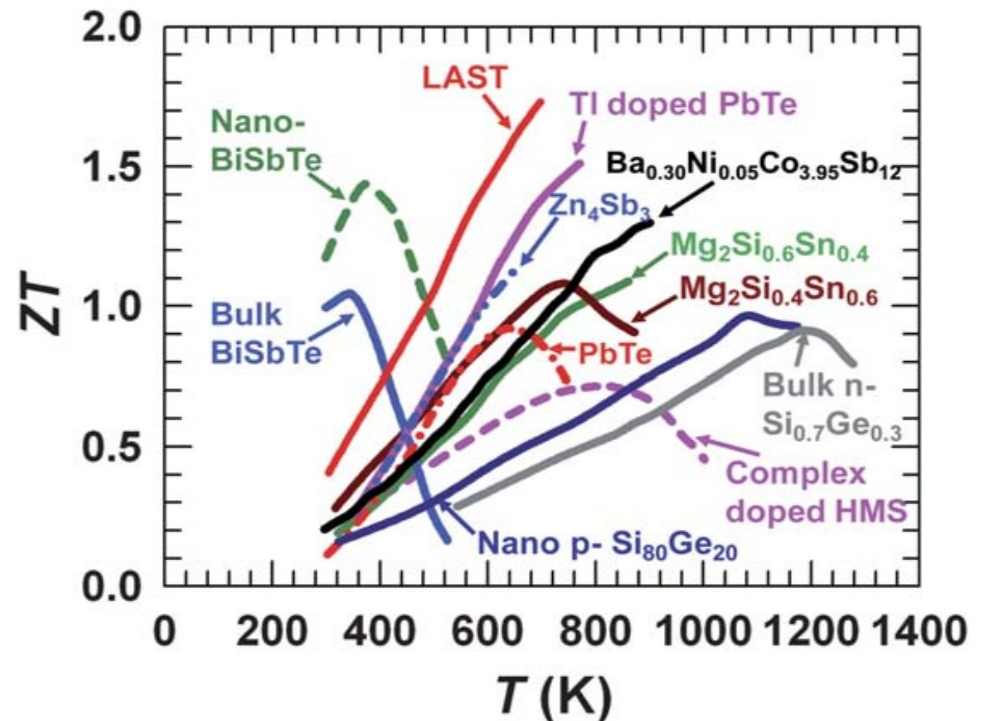
J. Mater. Chem. **21**, 4037 (2013)

Conclusion

- Perovskite materials are good candidates for electronic structural, spin transport and dynamical application

- The interfacial magnetism and metal-insulator transition were achieved in $LaNiO_3$/$CaMnO_3$; Role of spin dynamics

- Good thermoelectric property of $BiMnO_3$, tunability via different spin channels, doping concentration.

- Manipulation of TE of superlattice via strain, defect engineering

- Spin dependent heat transport, spin caloritronics.
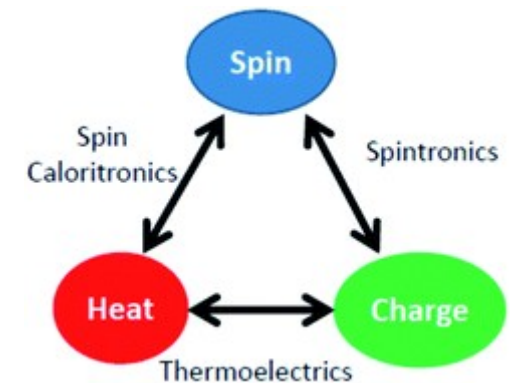
Thank you

Investigate: Excited states, optical, charge, spin dynam

Package:Octopus, MD, Qprob etc

https://www.sciencedirect.com/science/article/pii/S03759601163
693

It has been shown also that a spin current can be induced by
heating with ultrafast laser pulses [101], [102].

heat-driven spin currents

BoltzTraP code is based on the Semi-classical Boltzmann transport theory
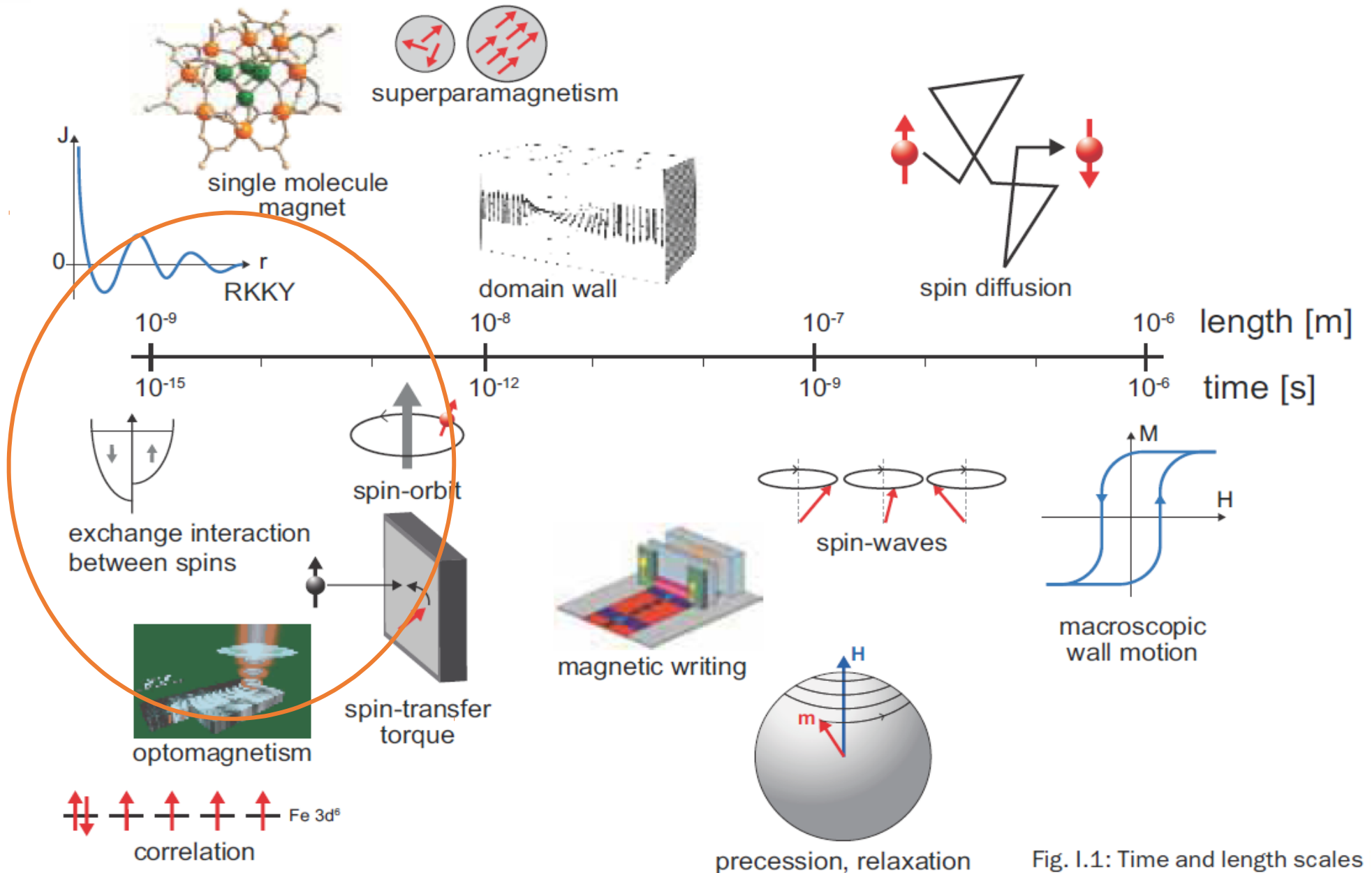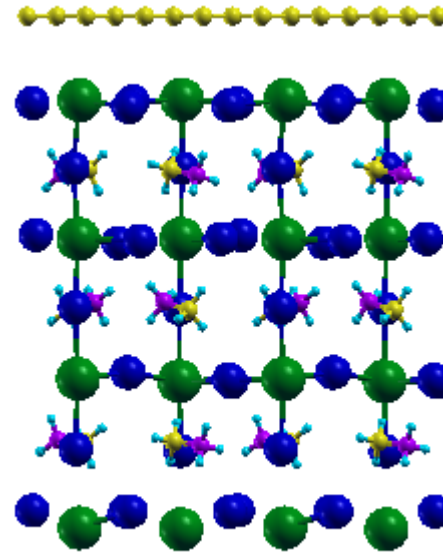
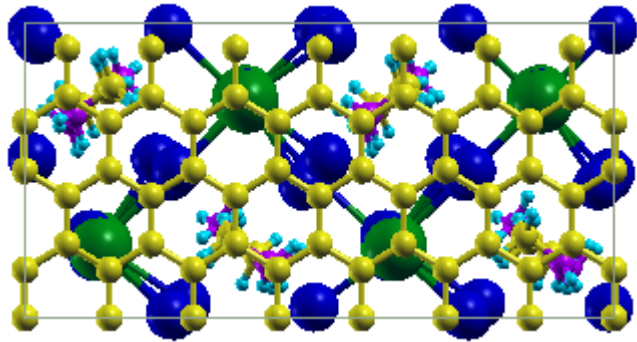Fig. I.1: Time and length scales

A. Melnikov et al, Phys. Rev. Lett. **91**, 227403 (2003)

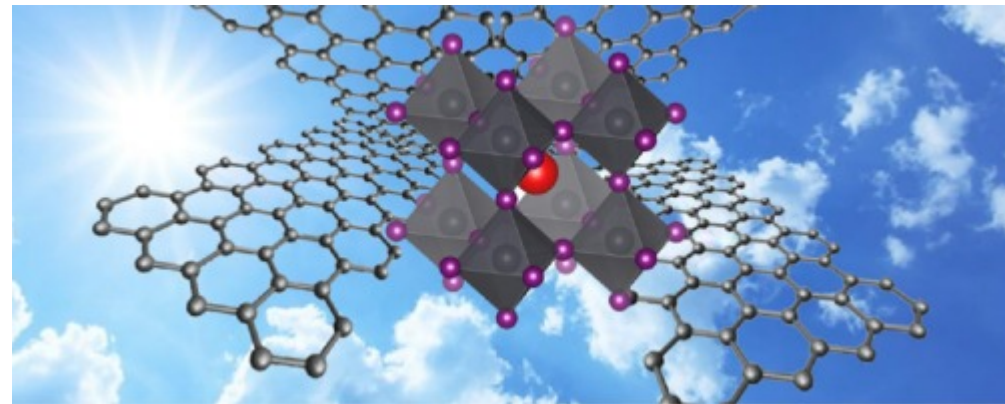# Future Plan

Hybrid Perovskites with 2D materials

*Photo-induced electron–hole pairs in the pristine
  perovskite recombine within a few picoseconds[1].

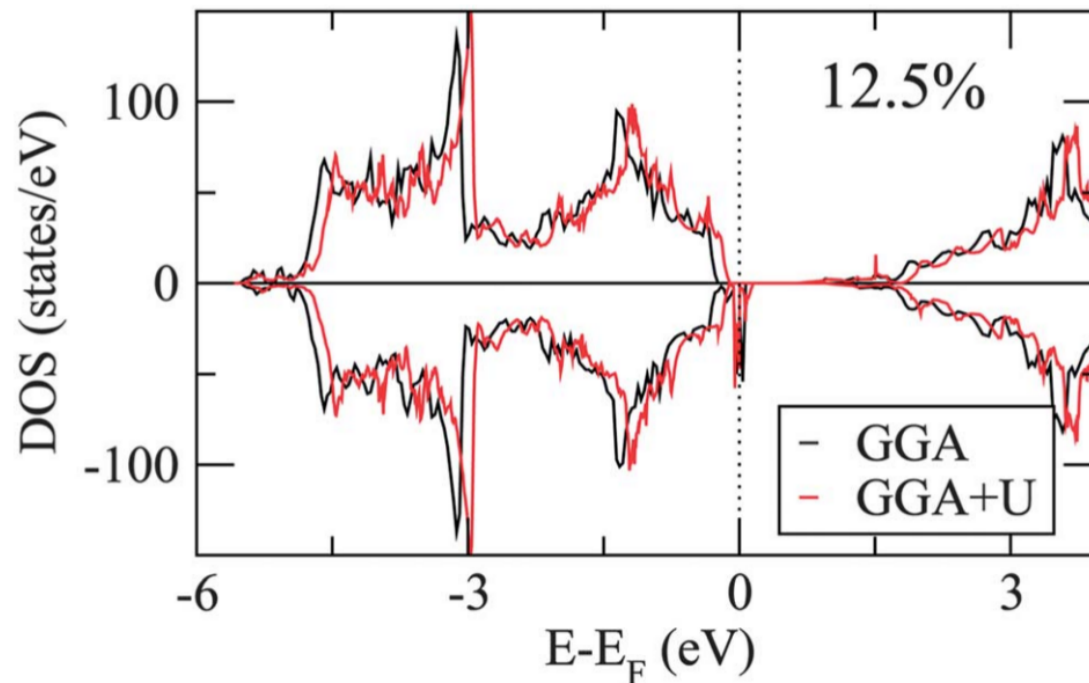*Photoelectronic applications

*Optoelectronic applications

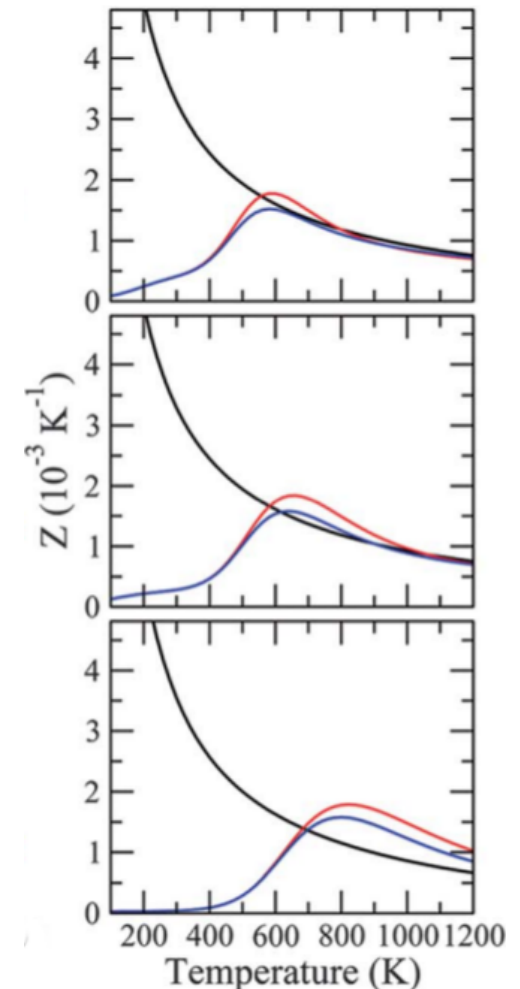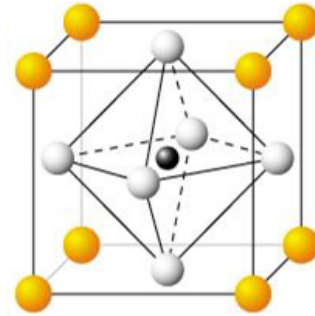[1] Adv. Mater. 27, 41–46 (2015)

Half-metallic perovskite superlattices with colossal thermoelectric figure of merit[7]

►Insulator to a half-metallic transition via Co doping
►High value of the spin Seebeck coefficient
►Colossal figure of merit of $0.45*10^{-3}K^{-1}$
►Spin-caloritronics

[7] J. Mater. Chem. A, **1**, 8406, 2013

CaTiO$_3$ oxide mineral, 1839, Russia

A: Rare-earth or alkali-metal cation
B: 3d, 4d, 5d transition metal cations

ABO$_3$ pervoskite structure

bulk ABO3, layered perovskites, double perovskite, thin films, superlattices, organo-halide perovskites...

Manganites: LaMnO$_3$, CaMnO$_3$, BiMnO$_3$, La$_{1-x}$Sr$_x$MnO$_3$, SrMnO$_3$ etc
Titantes: SrTiO$_3$, LaTiO$_3$, CaTiO$_3$, BaTiO$_3$ etc
Ferrites: BiFeO$_3$, LuFe$_2$O$_4$ etc
Nicklates: LaNiO$_3$ etc

Enhanced photovoltaic performance of perovskite $CH_3NH_3PbI_3$ solar cells with freestanding TiO_2 nanotube array films[3]

- •>90% of light absorption
- •Reduced charge recombination rate
- •Improved conversion efficiency
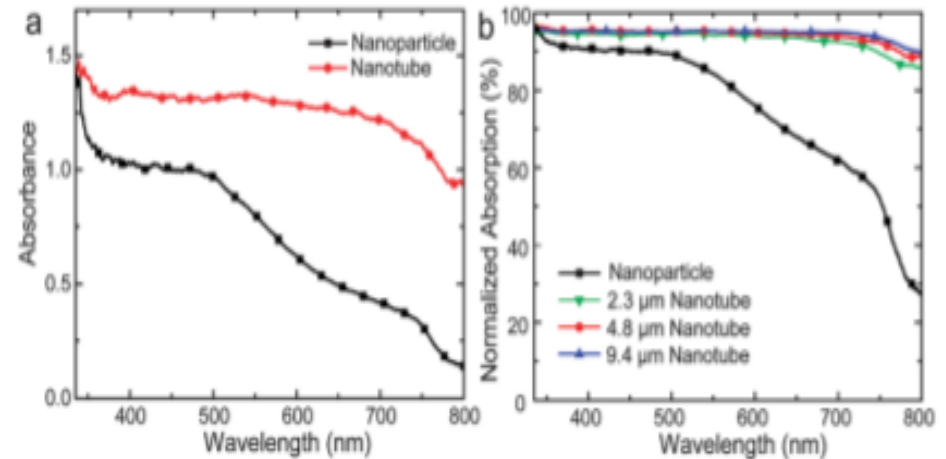- •Enhanced photovoltaic performance
- •Solar cell device

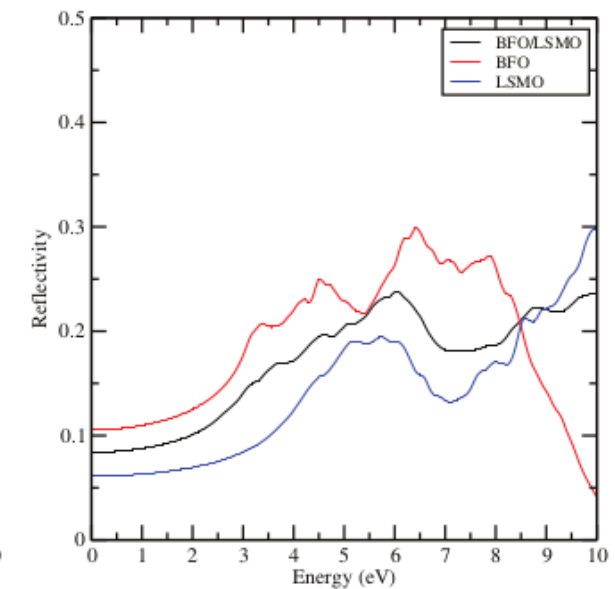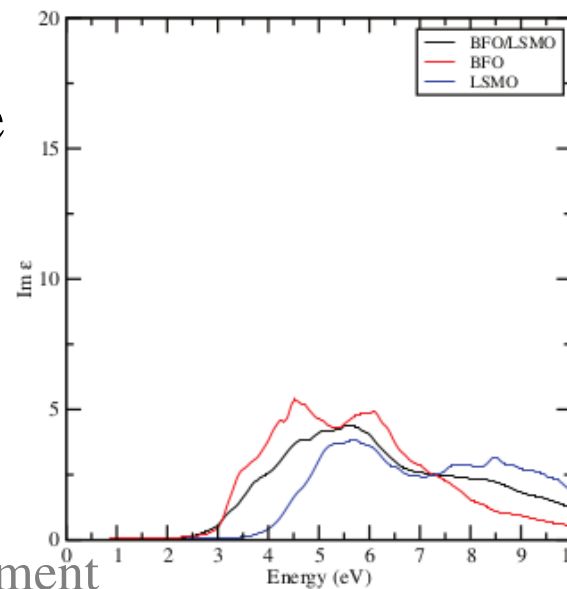Fig. 3 (a) UV-Vis absorption of $CH_3NH_3PbI_3$ sensitized TiO_2 nanoparticle and TiO_2 nanotube electrode. (b) Normalized adsorption spectra as a function of TiO_2 nanotube thickness compared with TiO_2 nanoparticle electrodes.

[3]Chem. Commun., 50, 6368, 2014
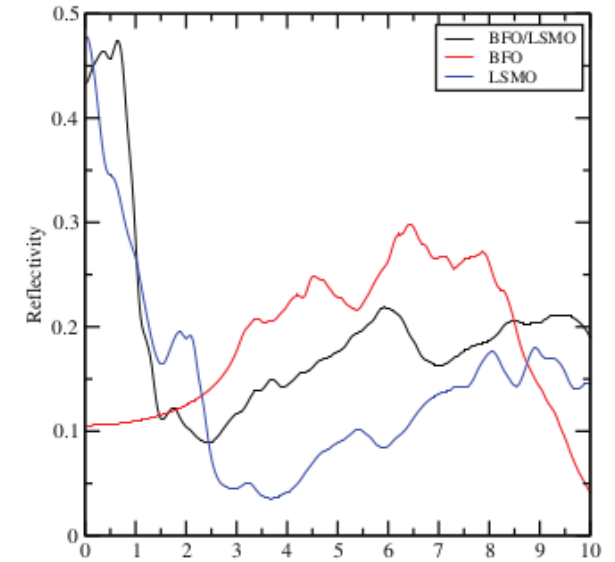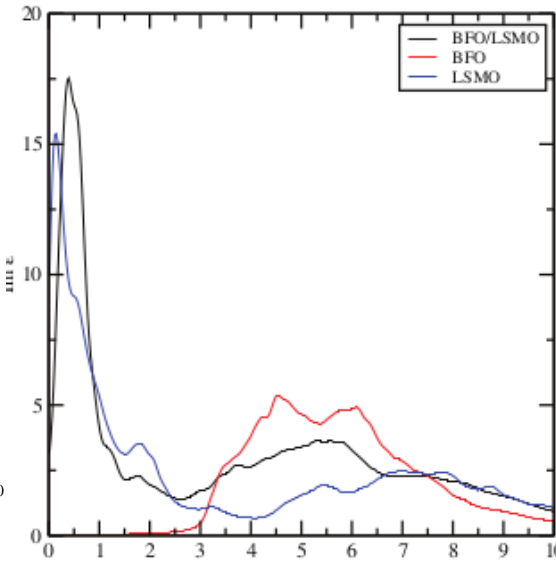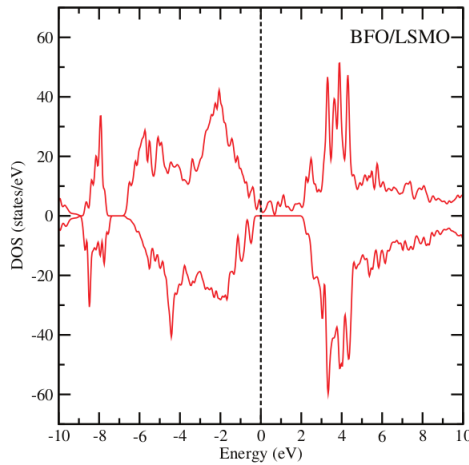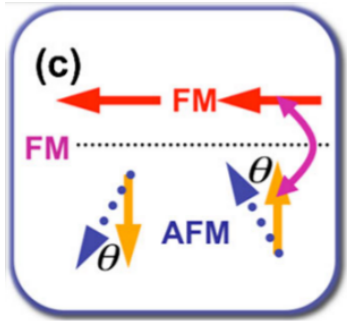
- Half-metallic character
- Optical properties resemble the DOS
- Combined property
- Spintronics

[6]PRL **105**, 027201 (2010)--experiment
[7]EPL, **102** (2013) 67009--DFT

Ising model: In order to map out the energetic interactions between the magnetic and rotational degrees of freedom, we utilizea modified Ising model. The Ising Model was orginally developed to study properties of interacting lattice systems,such as ferromagnetic materials.19In the model, an arbi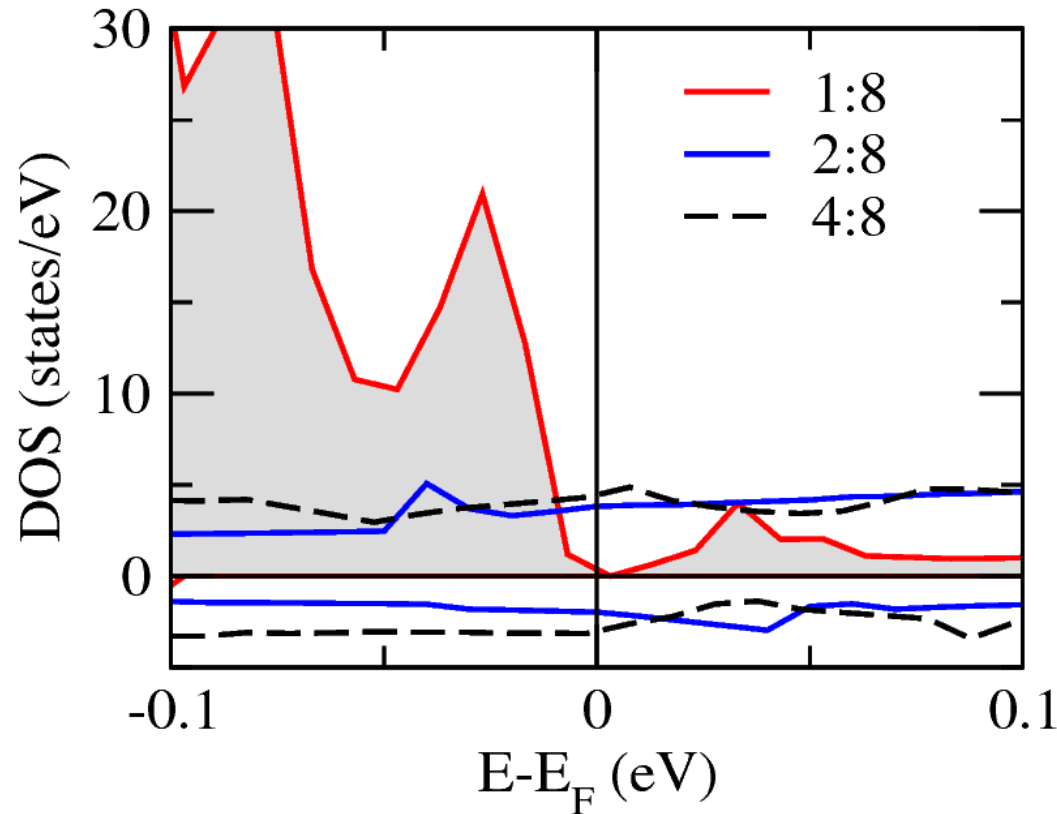trary lattice ofNsites is set up. A given siteican be filledwith a particle with some relevant property specified, such as spin, and is assigned an occupation term,σi, whereσi= 0 if siteiis empty, andσi= 1 if siteiis occupied. The energy contribution due to the presence of a particlein siteiis designated as the field term,hi. Energy contributions due to particle interactions in neighboring sites arecaptured by the nearest-neighbor interaction term,ji,kwhereiandkare two distinct sites. These nearest-neighborinteractions can be attractive or repulsive. Further interactions can also be accounted for, such as next-nearest-neighbor interactions. These would be assigned a different set of interaction termsji,k. The total energy of theN-sitelattice is then calculated as:

The Ising Model allows derivation of a reduced-order Hamiltonian for the system under consideration. Simulatedformation enthapies are used to calculate relevant Ising Model coefficients for the system. Through the use ofcoefficients derived with the Ising Model, the new Hamiltonian can be implemented in a Monte Carlo simulationof larger bulk structures. These simulations introduce and allow the quantification of the effect of thermal disorderon the system.Coefficients derived from the Ising Model were then used to simulate larger bulk cells with higher degree of