Novel (or at least remarkable) properties
(not only) of oxides

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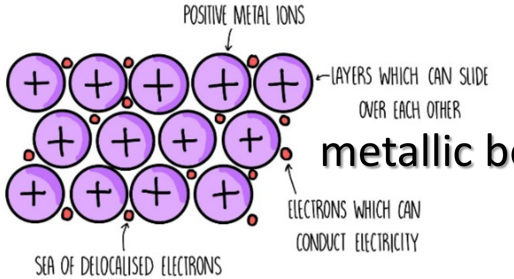
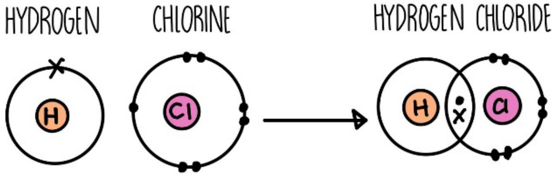
Laboratoire de Cristallographie et Sciences des Matériaux
Caen, France

What I will talk about

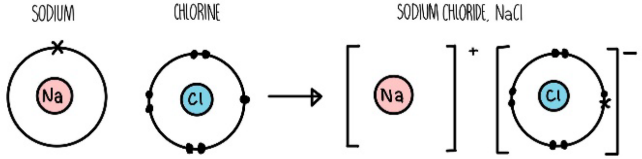


metallic bonding

covalent bonding

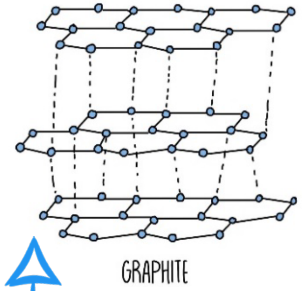


Ionic bonding



Images: the science sauce

electronic delocalization



Metals
Alloys
Intermetallics

2D

Semi-
conductors

Oxides

Valleytronics
(Topological Insulators)

Superconductors

Correlated Metals

Localised magnetism

Multiferroics

Ferroelectrics

What I won’t talk about

→ Ion – induced properties:

Electrochemical properties / Ionic conduction
Catalysis
Thermoelectrics / Magnetocalorics
Photo-induced properties

→ Proper introduction to the fundamentals of the properties

→ Proper introduction to materials: crystalline structure, critical temperatures, …

Topological Insulators

REVIEWS OF MODERN PHYSICS, VOLUME 82, OCTOBER–DECEMBER 2010

Colloquium: Topological insulators

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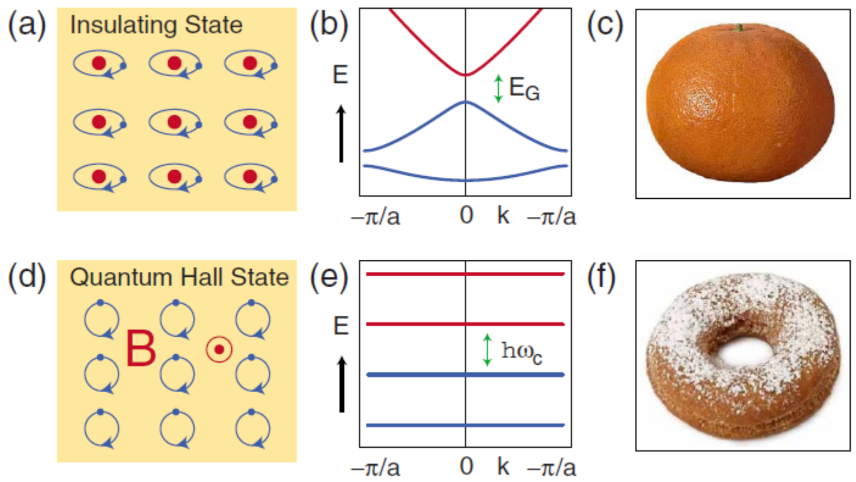
(Published 8 November 2010)

→ Normal insulators: topologically classified the same as vacuum
→ Other insulators have a different topology, called topological insulators
→ Quite a number of materials predicted now

n = 0

n = 1



Hall conductivity of electrons in a 2D system

$$\sigma_{xy} = Ne^2/h .$$

N: # Landau levels

Thouless, Kohmoto, Nightingale and den Nijs (TKKN):
N can be replaced by the Chern number n

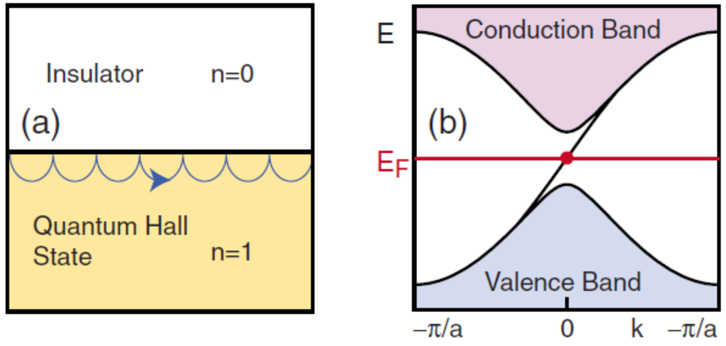
k → Bloch hamiltonian H(k), topologically classified with equivalence classes.
If k is transported around a closed loop, the associated Bloch state /u_m(k)> acquires a well defined Berry phase
→ Berry flux defines the Chern number, which is invariant for band degeneracies etc.

Graphene

REVIEWS OF MODERN PHYSICS, VOLUME 82, OCTOBER–DECEMBER 2010

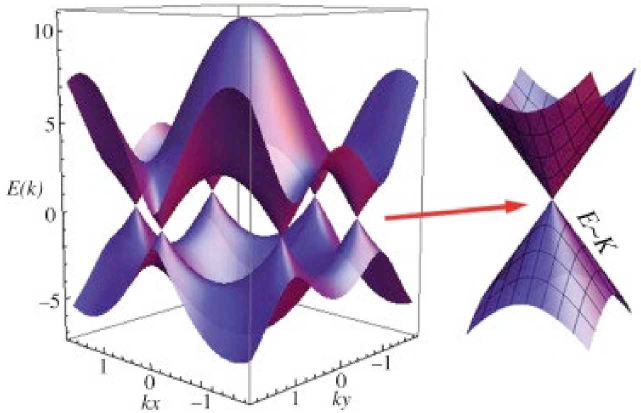
***Colloquium*: Topological insulators**

General



→ Generally: At interfaces of integer Quantum Hall states and vacuum (or other insulators with n= 0)
→ Lifting time-reversal symmetry (magnetic field): Quantum Hall state
→ Insensitive to disorder because there are no states available for backscattering (perfectly quantized electronic transport)

Graphene



Yotsarayuth Seekaew et al, in Carbon-Based Nanofillers and Their Rubber Nanocomposites, Elsevier, 2019, Pages 259-283,

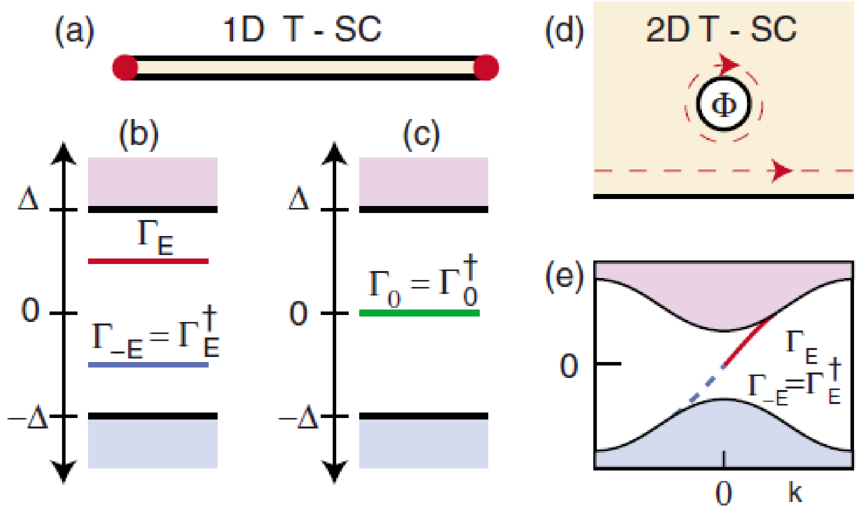
→ The conduction band and valence band touch each other at two distinct points in the Brillouin zone (K and K') due to Graphene's rotational symmetry
→ Linear dispersion of massless relativistic particles described by the Dirac equation ("Dirac cones", "Dirac semi-metal")
→ System keeping its inversion and time-reversal symmetry

Interesting features of 2D systems

REVIEWS OF MODERN PHYSICS, VOLUME 82, OCTOBER–DECEMBER 2010

Colloquium: Topological insulators

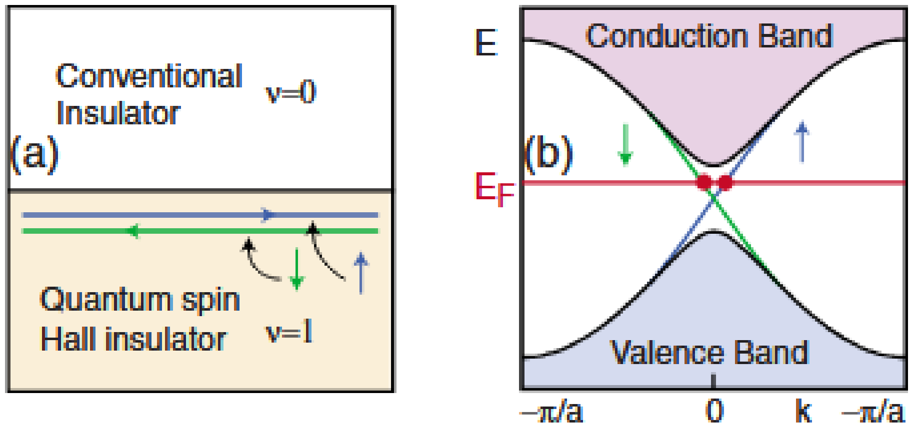
topological superconductors



→ edge-states related to half a Dirac fermion: Majorana fermion (quasiparticle being its own antiparticle)

→ Majorana zero modes must always come in pairs: non-locally stored quantum state

Spin currents

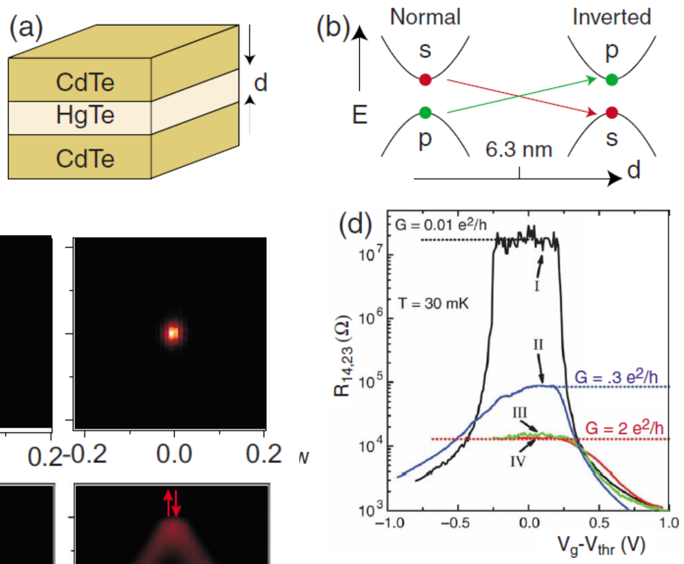


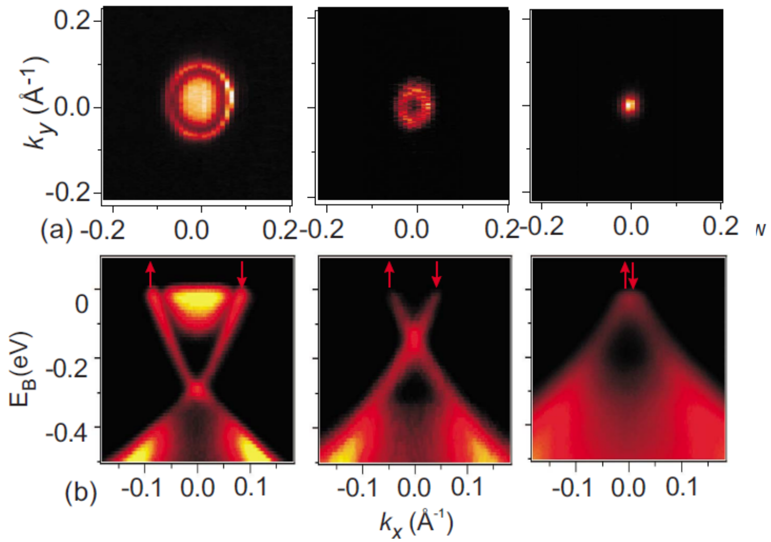
→ Spin currents are also protected topologically: no spin-decoherence by backscattering due to disorder

→ Up- and down Hall currents in opposite directions: no net Hall conductivity, but quantized spin Hall conductivity

Materials

HgTe/CdTe QW:
quantized conductance
due to edge states





Bi_2Se_3: Chemical gating to push chemical potential to the node

Oxides (typically spin-orbit coupling):

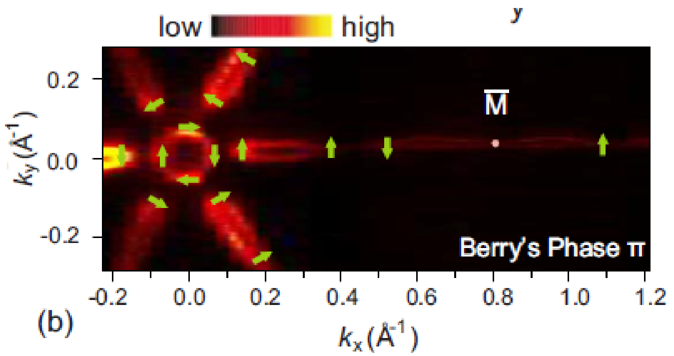
- Bi-based double perovskites
- $BaBiO_3$
- Oxide heterostructures and superlattices ($SrVO_3$/$SrTiO_3$)
- …

Intermetallics:

- Half-Heusler alloys
- …

Epitaxial thin films!

Bi_2Sb_3: spin-ARPES to measure the Berry phase



REVIEWS OF MODERN PHYSICS, VOL

***Colloquium*: Topological insulators**

Interesting properties of topological insulators

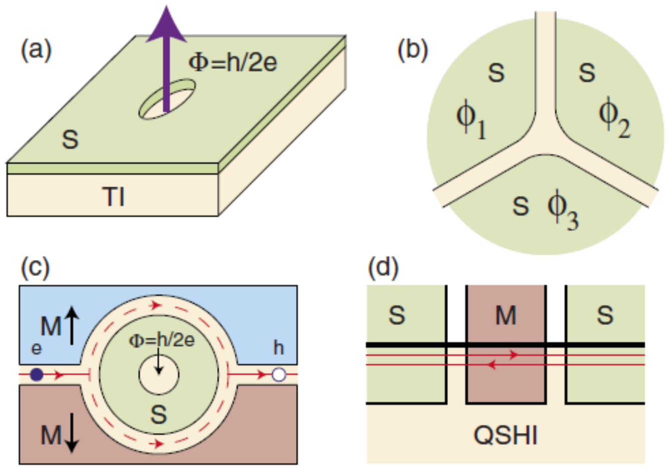
REVIEWS OF MODERN PHYSICS, VOLUME 82, OCTOBER–DECEMBER 2010

Colloquium: Topological insulators

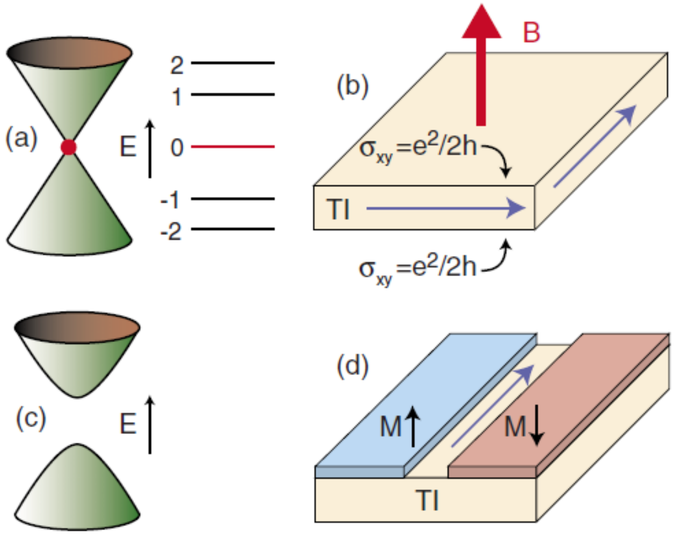
→ Induce a gap in the edge or surface states!

→ Breaking time-reversal symmetry with an external magnetic field or proximity to a magnetic material

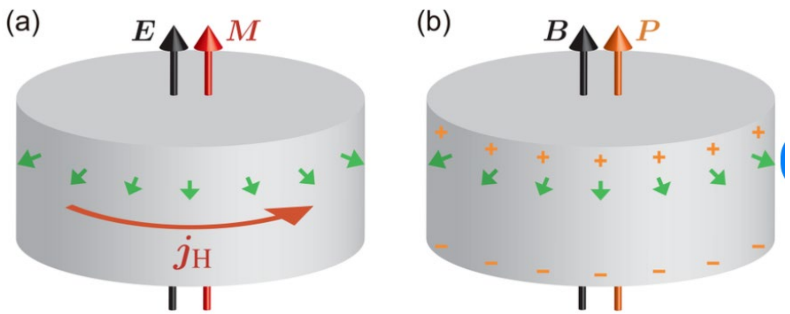
→ Breaking gauge symmetry due to proximity to a superconductor or by an excitonic instability of two coupled surfaces



A separated pair of Majorana bound states: a degenerate two-level system stored non-locally and with a topological protection of the quantum information



Chiral fermion modes: half integer quantized Hall conductivity

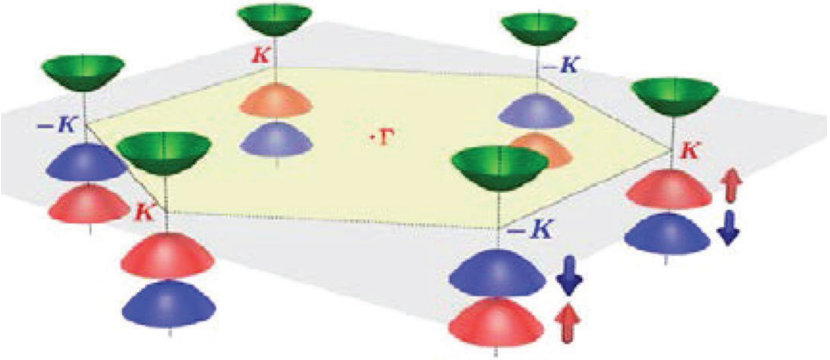


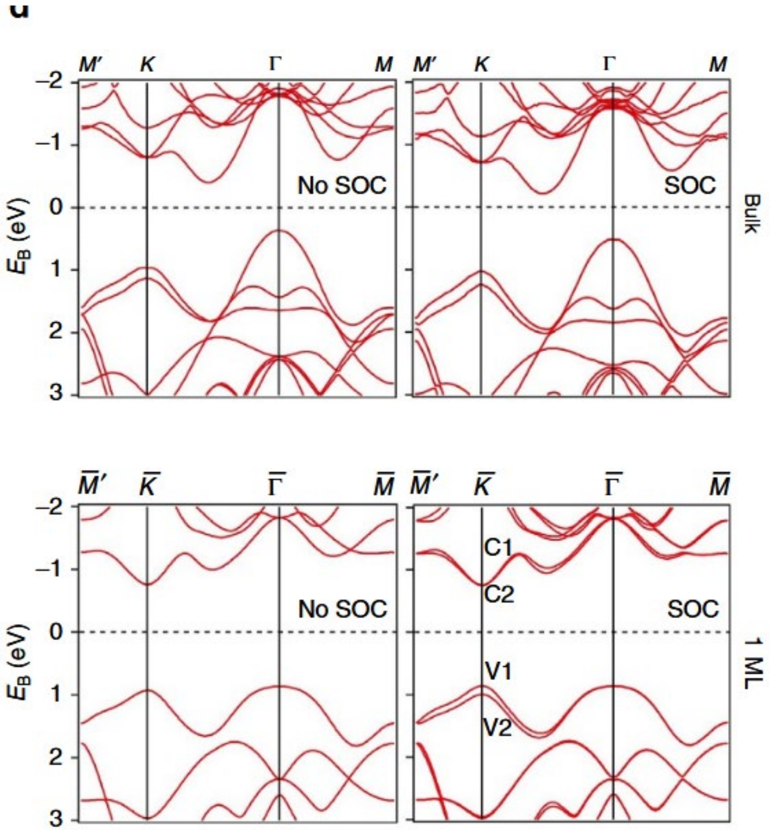
Topological magneto- electric effect: magnetic-dipole moment associated with an electric field with a quantized magnetoelectric polarizability

Valleytronics

→ Transition Metal Dichalogenides (MoS_2, …): 2D system without inversion symmetry, but with time-reversal symmetry: individually adressable valleys in momentum space

→ Selective population of one momentum distinguishable valley versus another: valley polarization





REVIEW

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Valleytronics

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Valleytronics: Opportunities, Challenges, and Paths Forward

Steven A. Vitale, Daniel Nezich, Joseph O. Varghese, Philip Kim, Nuh Gedik, Pablo Jarillo-Herrero, Di Xiao, and Mordechai Rothschild*

nature COMMUNICATIONS

ARTICLE

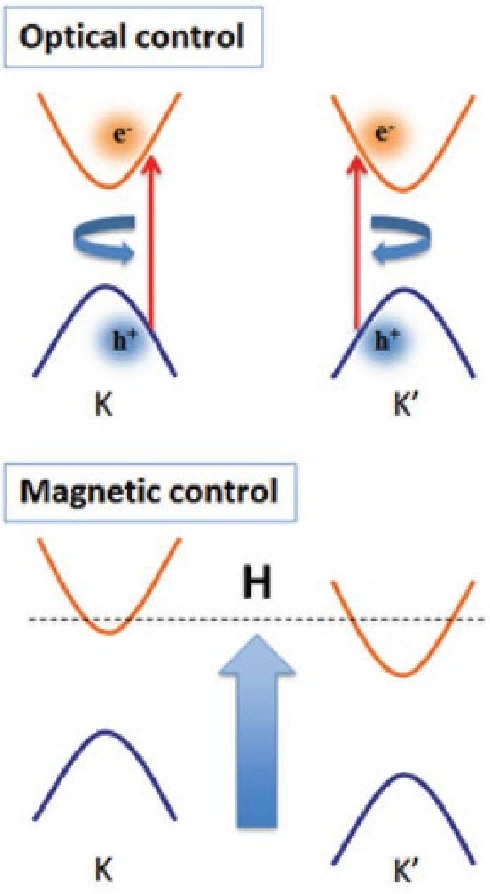
Received 30 Dec 2013 | Accepted 11 Jul 2014 | Published 22 Aug 2014 | Updated 13 Oct 2014 DOI: 10.1038/ncomms5673

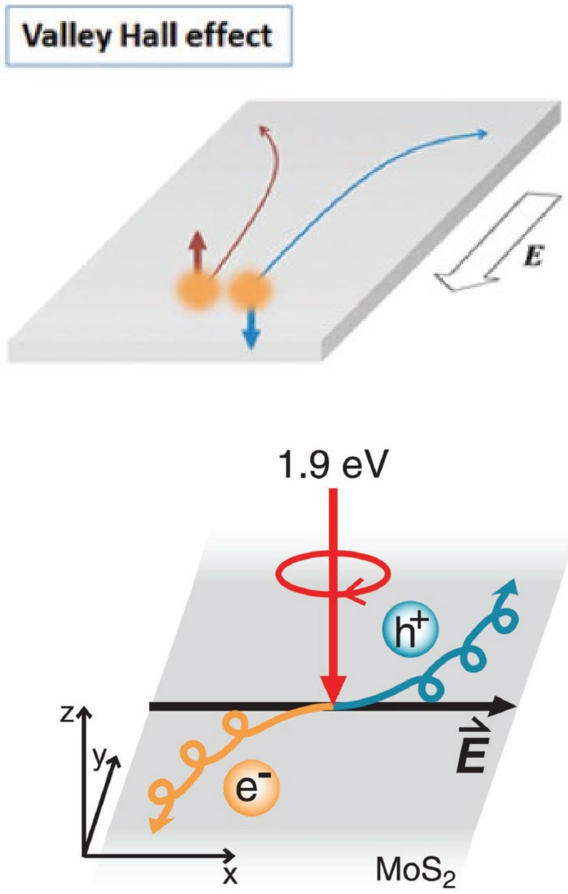
Observation of monolayer valence band spin-orbit effect and induced quantum well states in MoX_2

Nasser Alidoust[1], Guang Bian[1], Su-Yang Xu[1], Raman Sankar[2], Madhab Neupane[1], Chang Liu[1], Ilya Belopolski[1], Dong-Xia Qu[3], Jonathan D. Denlinger[4], Fang-Cheng Chou[2] & M. Zahid Hasan[1]

Control of the valley population

→ Finite orbital magnetic moment: circular dichroism for the optical control
→ Contrasting magnetic moments of the valleys: magnetic field control
→ Non-zero Berry curvature: Valley Hall effect under an in-plane electric field





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Valleytronics: Opportunities, Challenges, and Paths Forward

Possible applications

Quantum computing

→ Possibility of a simple planar architecture with high valley qubit density

→ Spin –orbit coupling: energy separation between spin states, valley index: momentum seperation between K and K'

→ Spin protection of valley or valley protection of spin may provide a more favorable gate to coherence time ratio than unprotected qubit candidates.

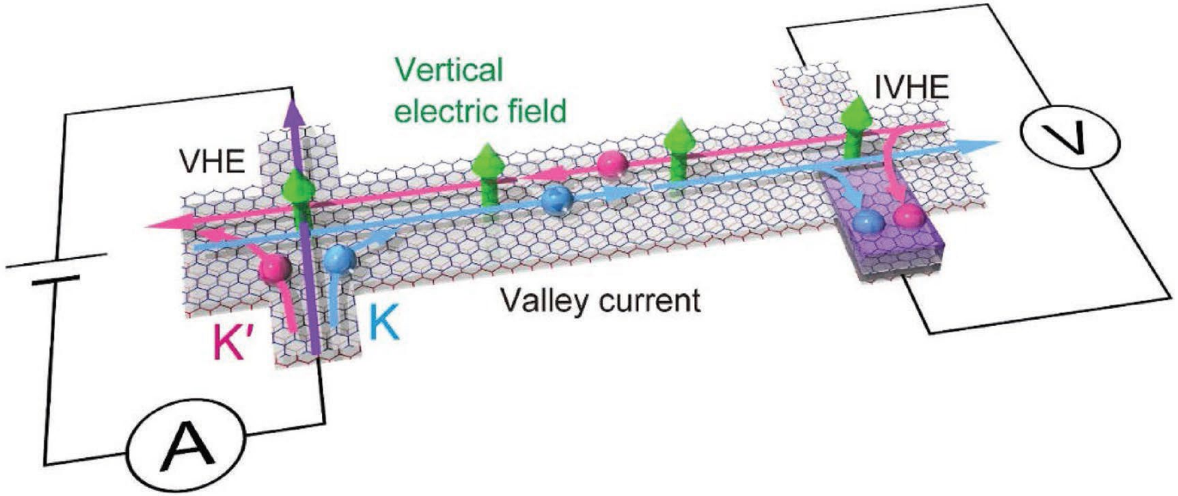
→ Optical reading

Integrated Optoelectronics

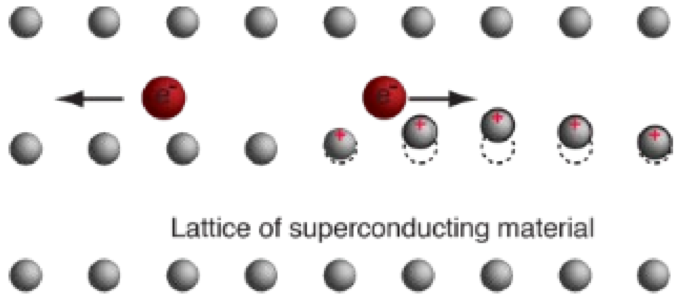
→ Generation of polarized photons and the remote detection for cryptographic protocols: need for integrated optoelectronics

→ Secure quantum channels between everyday personal devices

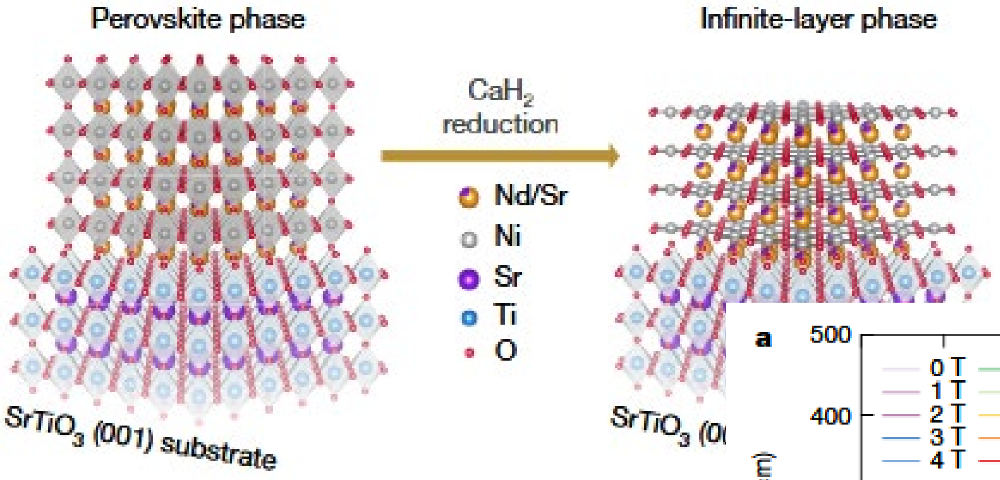
→ In TMCD, generation of circularly polarized light and its detection



Cooper Pairs



Thin film stabilized nickelates $(Nd,Sr)NiO_3$

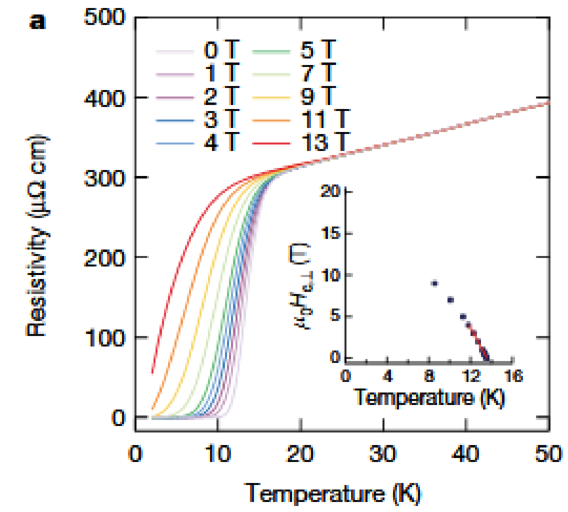


LETTER

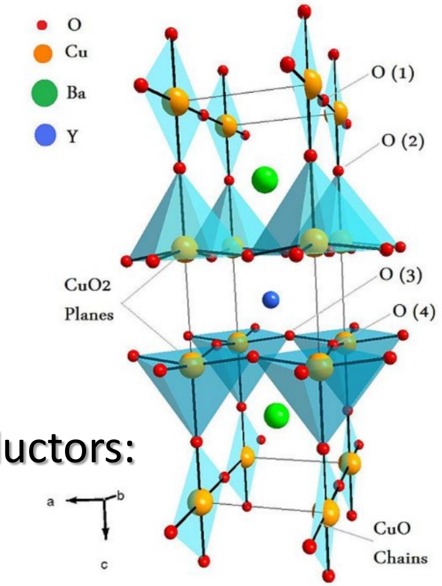
https://doi.org/10.1038/s41586-019-1496-5

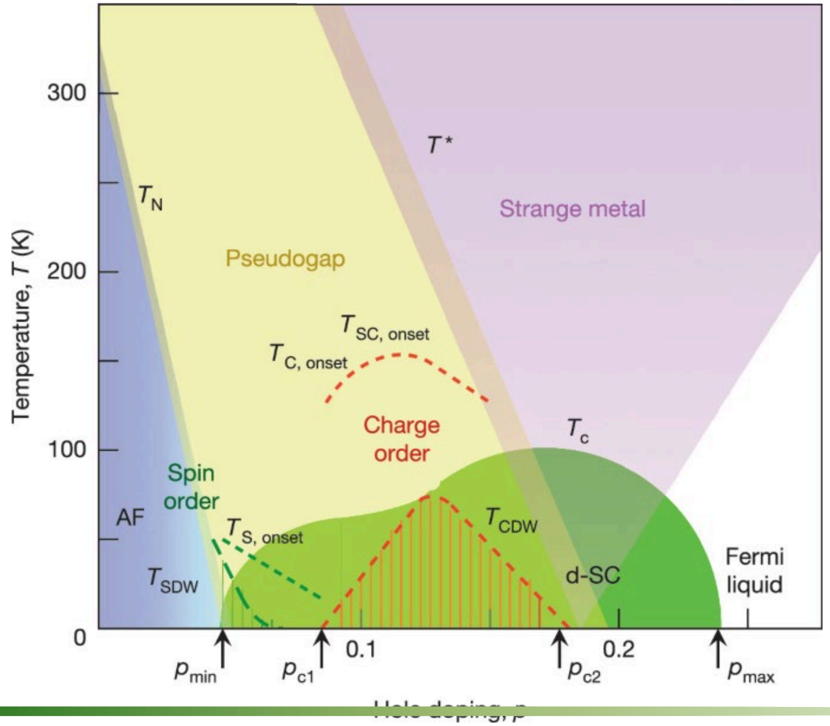
Superconductivity in an infinite-layer nickelate

Danfeng Li[1,2]*, Kyuho Lee[1,3], Bai Yang Wang[1,3], Motoki Osada[1,4], Samuel Crossley[1,2], Hye Ryoung Lee[1,4], Yi Cui[1,4], Yasuyuki Hikita[1] & Harold Y. Hwang[1,2]*



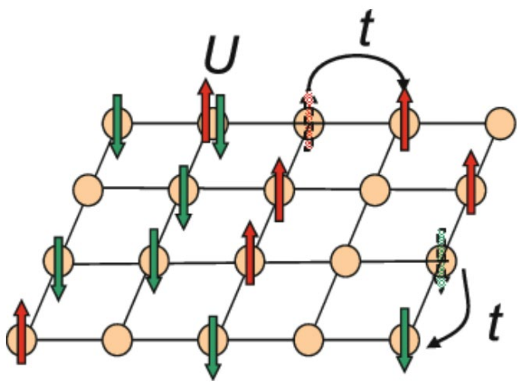
High Tc superconductors: the cuprates

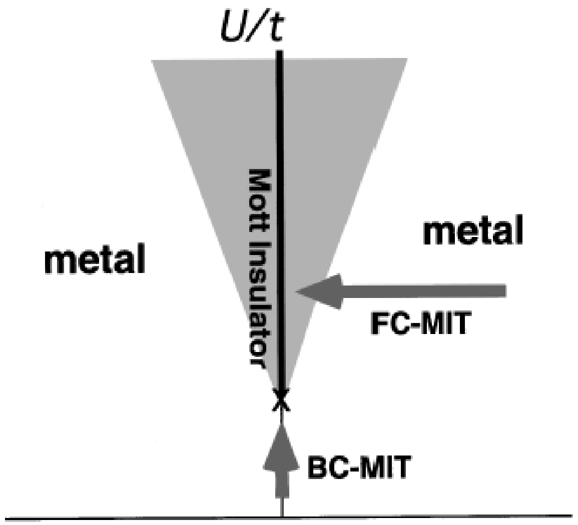




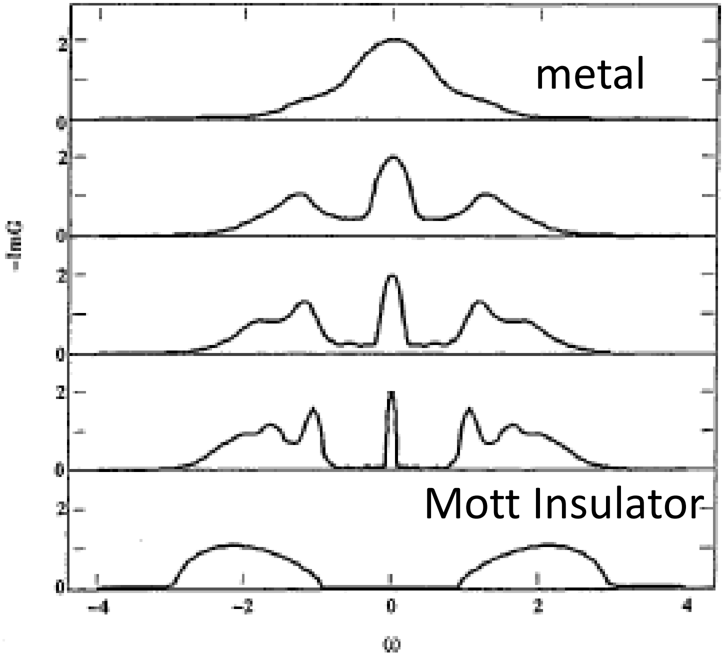
Strongly correlated oxides

Hubbard model

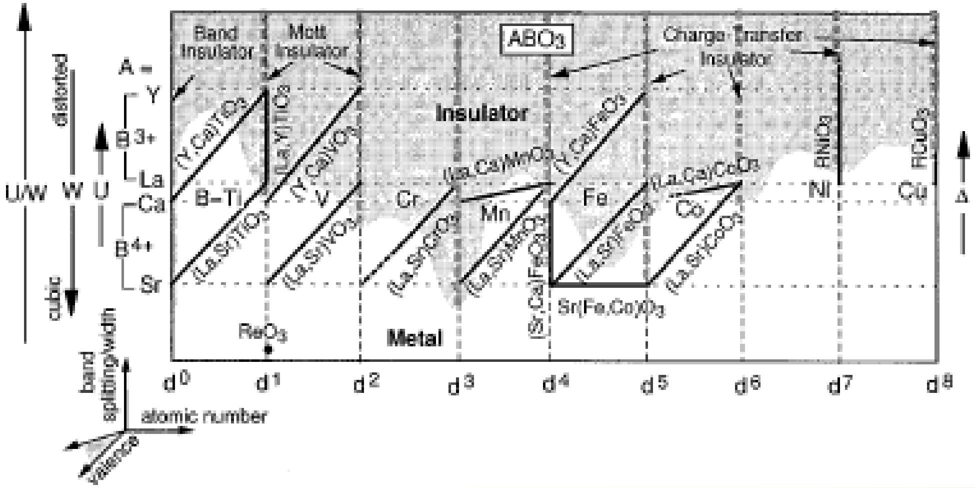




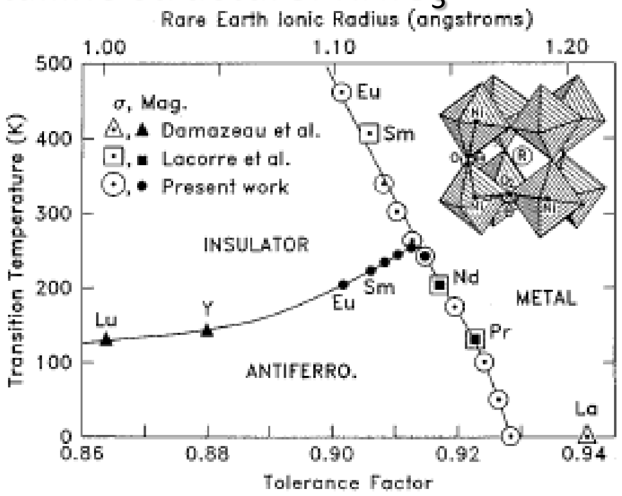
M. Imada et al,
Rev. Mod. Phys **70**, 1039 (1998)



Filling: solid solutions

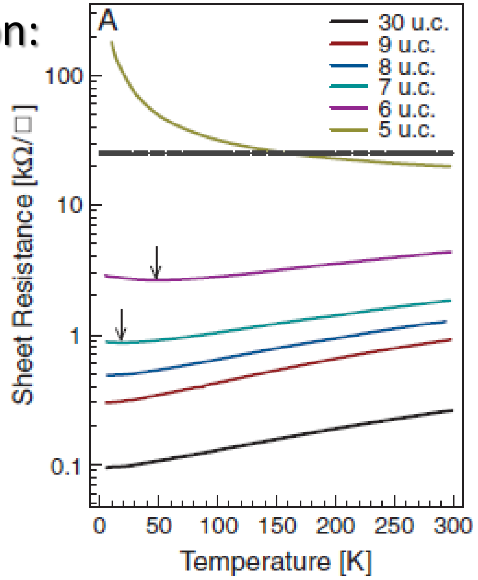


Crystalline structure: $RNiO_3$

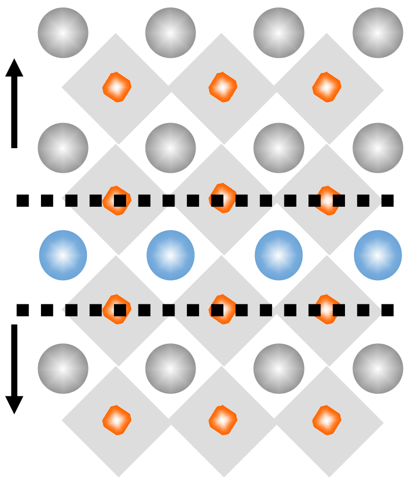


Dimension: films

R. Scherwitzl et al, PRL **106**, 243403 (2011)

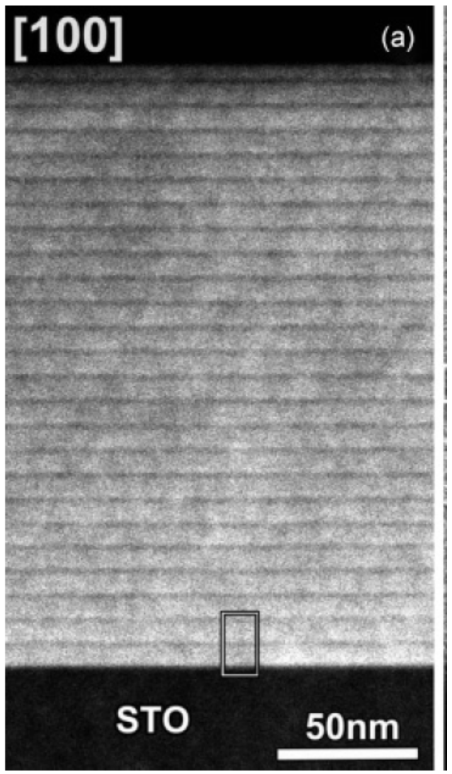


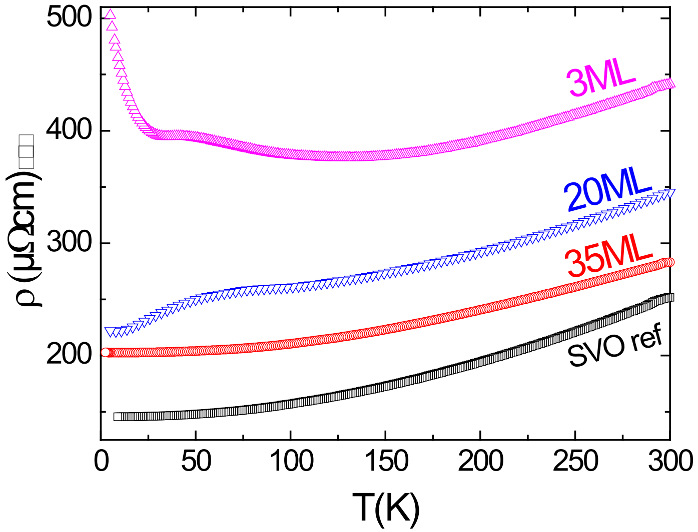
2D correlated conductor

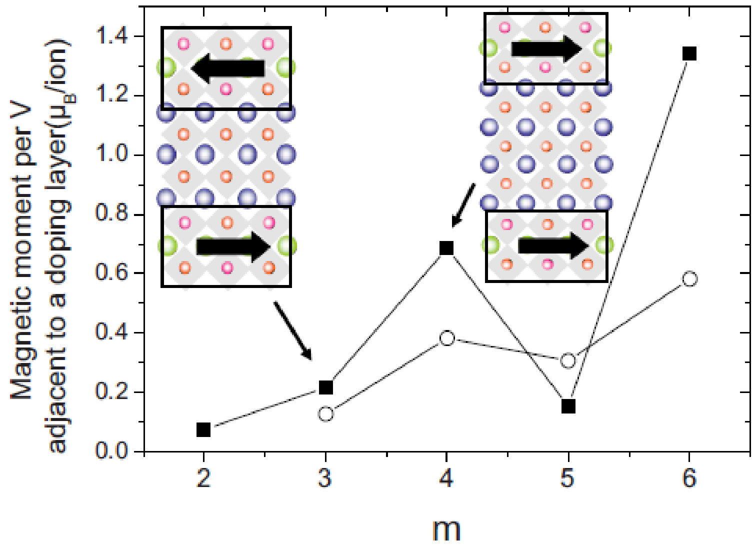


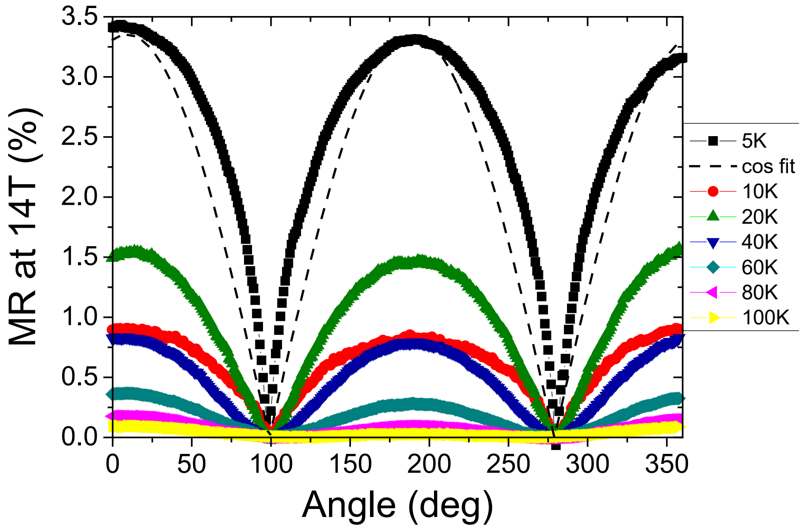
Geometrically confined doping: 2D character?

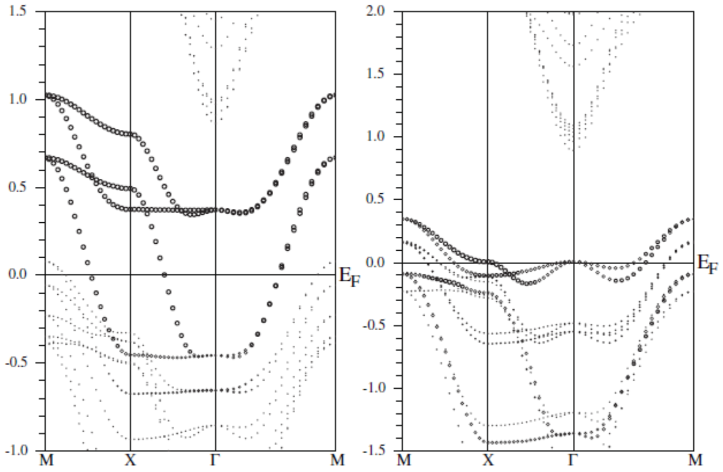
$LaVO_3$(18ML)/$SrVO_3$(3ML)





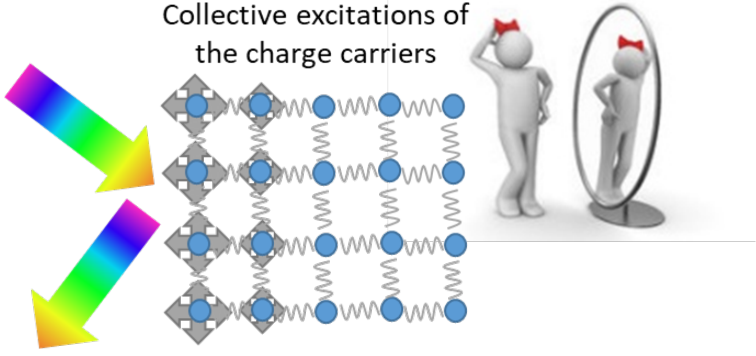






Transparent conducting oxides by correlations

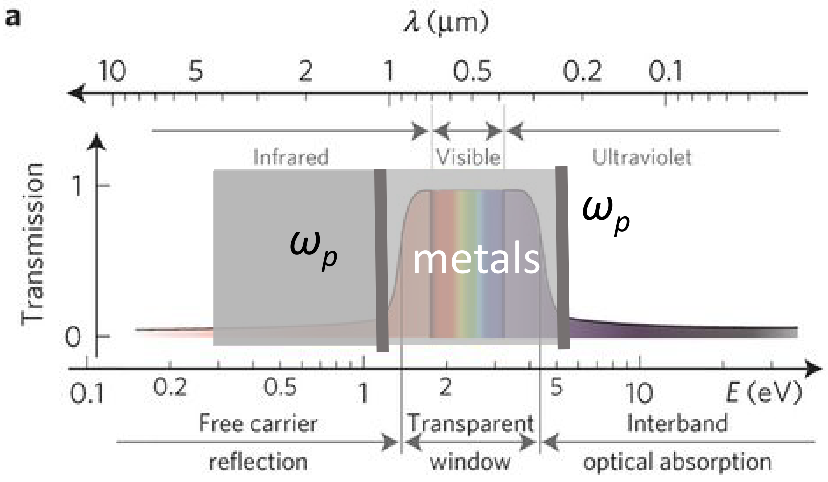
Metallic electrodes
Collective excitations of the charge carriers



$$\omega_p = \sqrt{\frac{e^2\, n}{\varepsilon_r \varepsilon_0\, m^*}}$$

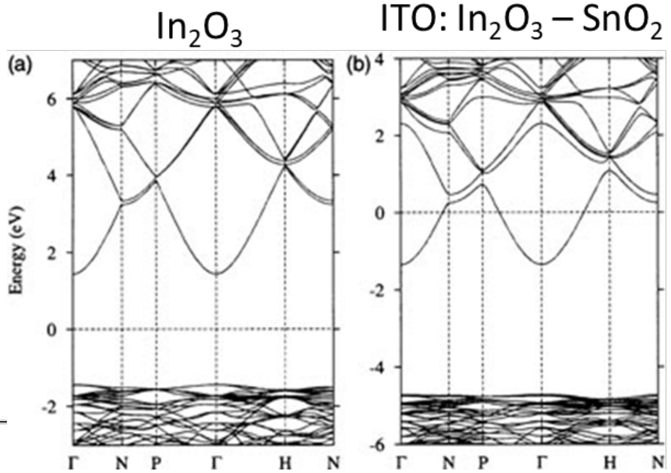
Charge density

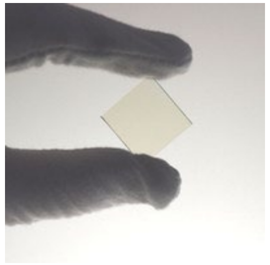
Effective mass



→ Decrease of the charge density (Doped semiconductors)

Charge density ≈ 10^{19} cm^{-3}
effective mass m* ≈ 1

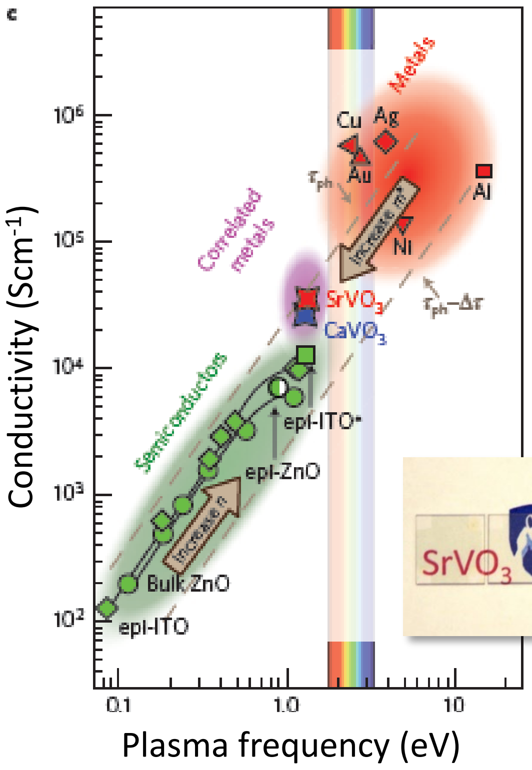




J.-J. Lin et al, J. Phys. Cond. Mat 2014

→ Enhancement of the effective mass m* (Strongly correlated metals)

Charge density ≈ 10^{22} cm^{-3}
Effective mass m* ≈ 4



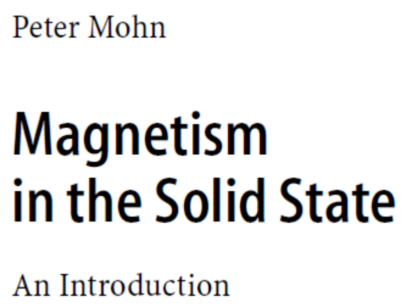
(Zhang et al, Nat. Mat. 2016)

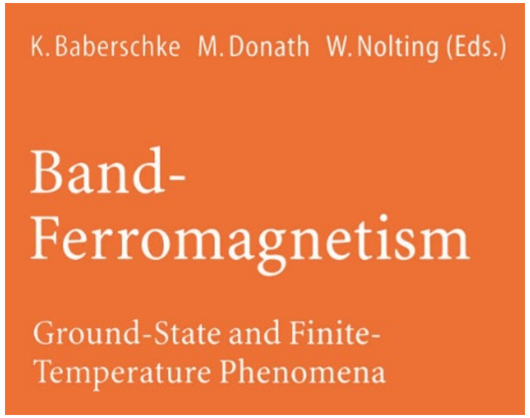
- $SrVO_3$, $SrMoO_3$, $SrNbO_3$
- $CaVO_3$
- p-type $(La,Sr)CrO_3$

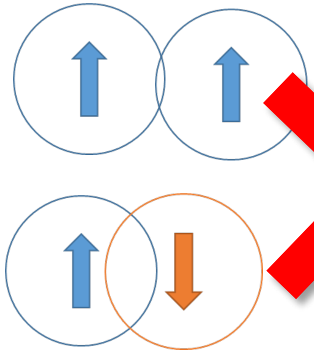
Magnetism

→ Ferromagnetic metals (Ni, Co, Fe, + alloys, …)
→ Ferromagnetic oxides (Fe_3O_4, $(La,Sr)MnO_3$, …)
→ Antiferromagnetic oxides + funny spin structures
→ Antiferromagnetic metals (Cr, IrMn, …)

Serious Information:







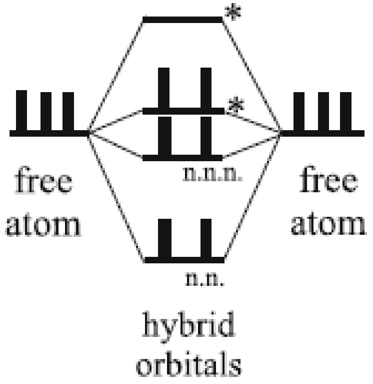
~~Dipole interactions: ferromagnetic alignment~~

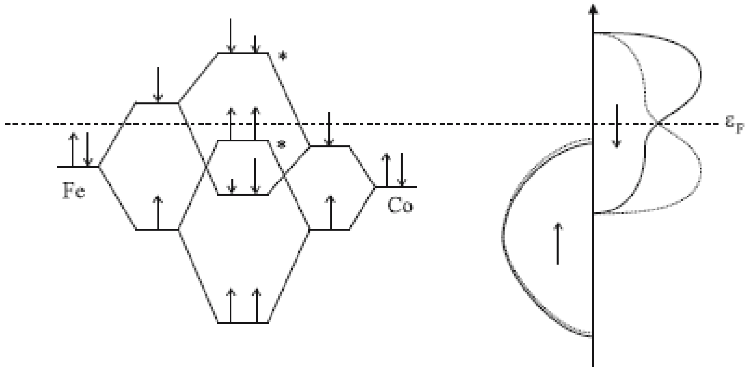
Pauli exclusion principle: antiferromagnetic alignment

Hartree-Fock

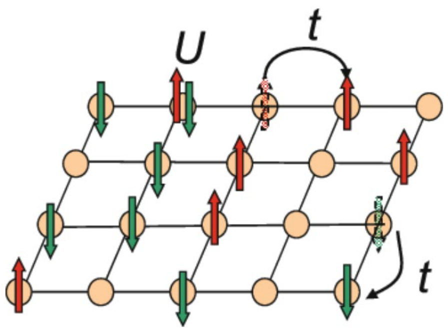
$$\hat{F}_i = -\frac{\hbar^2}{2m}\nabla^2_{\xi_i} + \cancel{V(\xi_i)} + \sum_j \hat{J}_j - \hat{K}_j$$

⇨ Ab-initio, DFT with electron-electron interactions





Hubbard



⇨ Exactly solvable for some few special cases, Slave-boson approach, Numerical solutions

Special cases: superexchange

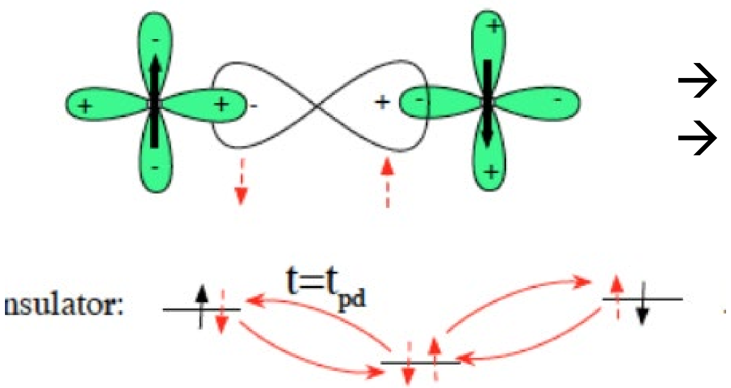
Goodenough-Kanamori-Anderson rules:

RULE 1: Half-filled orbitals: 180° superexchange

RULE 2: Half-filled 90° exchange

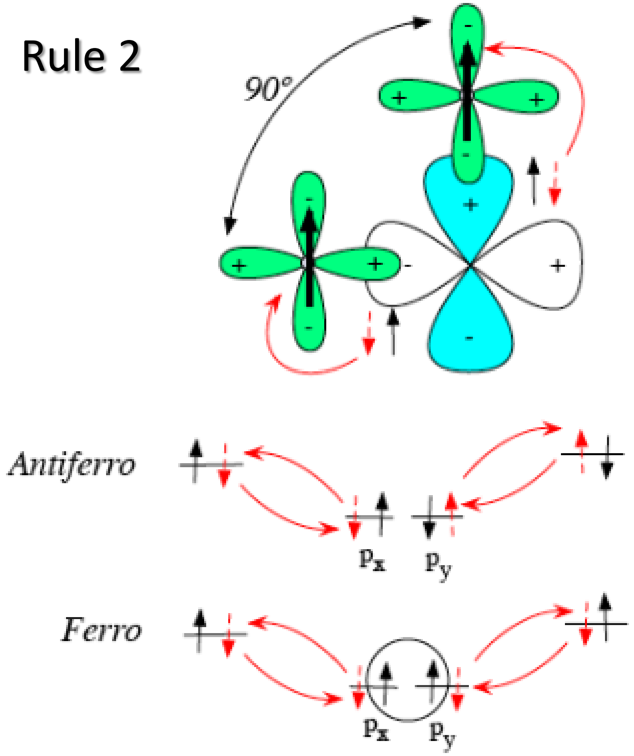
RULE 3: Overlap half-filled and empty 180° exchange

Rule 1



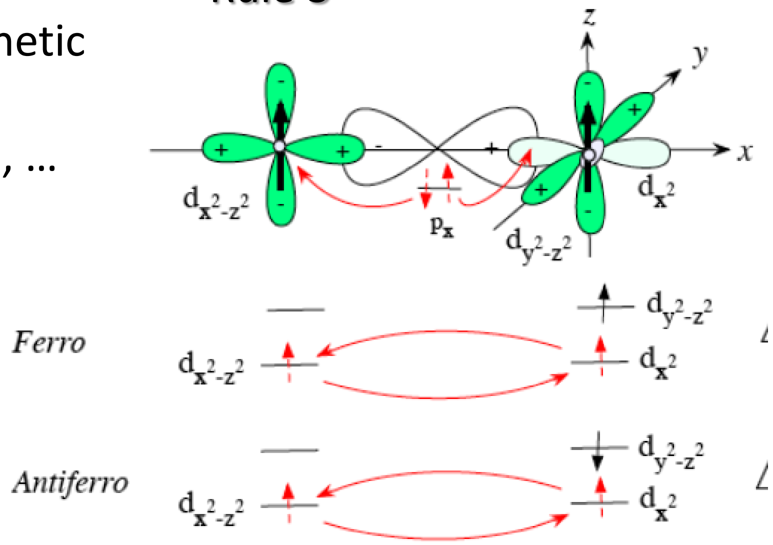
→ Works also without the bridging anion
→ Strong interaction
→ Most oxide antiferromagnetics

Rule 2



→ Rather weak interaction
→ Both antiferromagnetic and ferromagnetic
→ Spin ladder, zig-zag, …

Rule 3

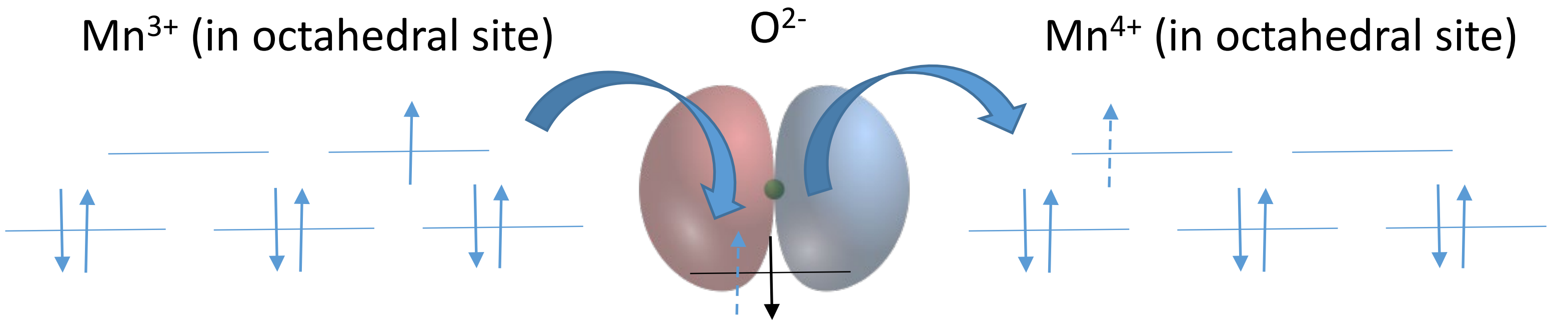


→ Even weaker interaction
→ 1D or 2D structures

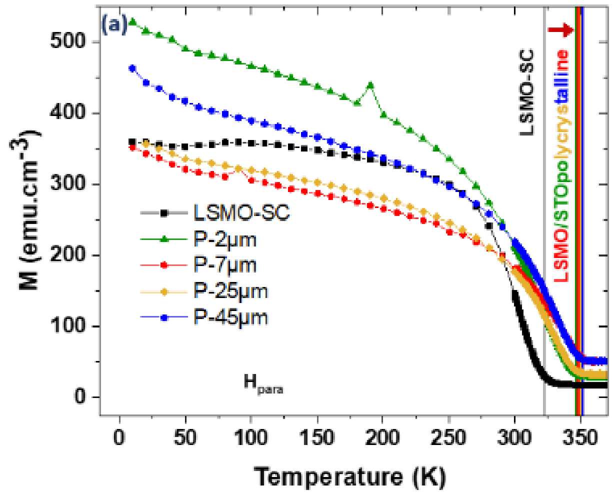
Lecture 4
"Magnetic interactions"

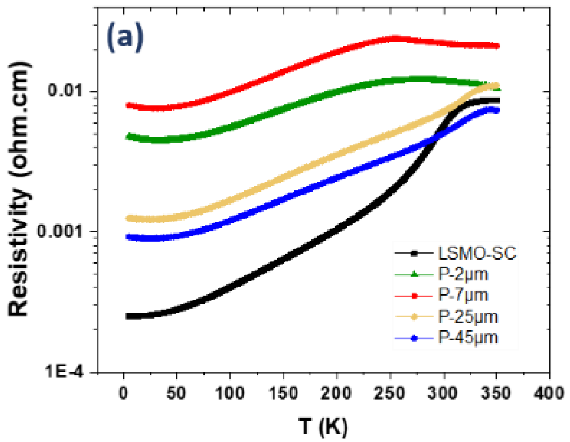
Luigi Paolasini
paolasini@esrf.fr

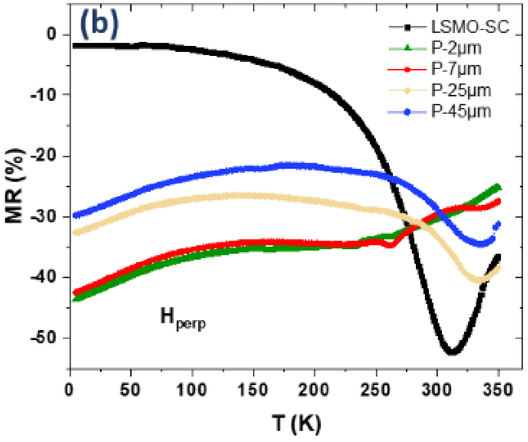
Special cases: double exchange



- → Strong ferroelectric ordering with high ordering temperatures (Fe_3O_4 and other ferrites, (La,Sr)MnO_3)
- → Relation with transport: higher scattering if spins are disordered – magnetoresistive effects





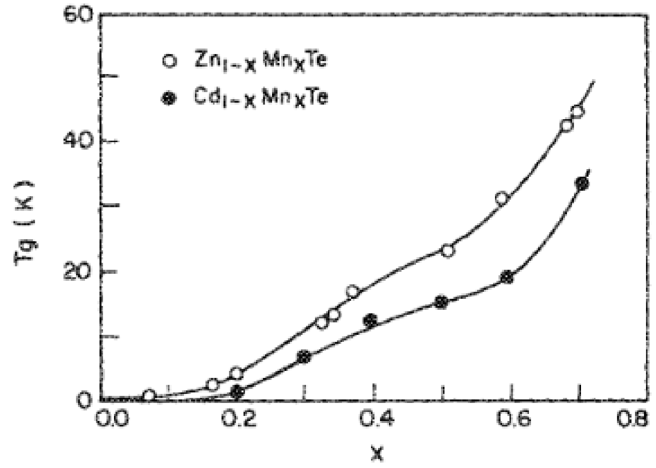


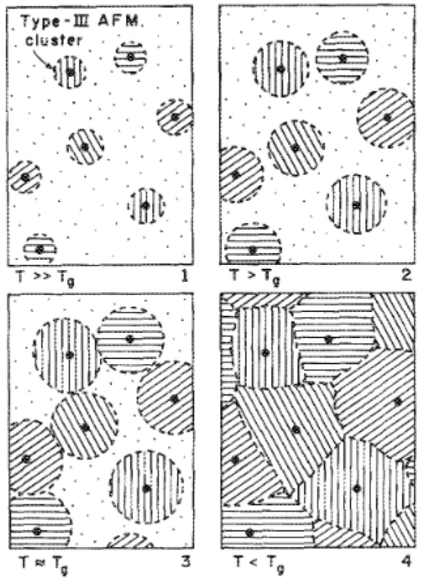
- → Low temperature bolometers
- → Low noise, high sensitivity magnetic sensors

Marie Dallocchio, Alexis Boileau, Bernard Mercey, Adrian David, Ulrike Lüders, et al.. Tunable magnetic and magnetotransport properties in locally epitaxial La 0.67 Sr 0.33 MnO 3 thin films on polycrystalline SrTiO 3 , by control of grain size. Journal of Physics D: Applied Physics, 2022, 55 (23), pp.1-11. 10.1088/1361-6463/ac5a1f . hal-03608785

Special cases: Diluted Magnetic Semiconductors

II-IV semiconductors doped with Mn: CdSe, HgTe





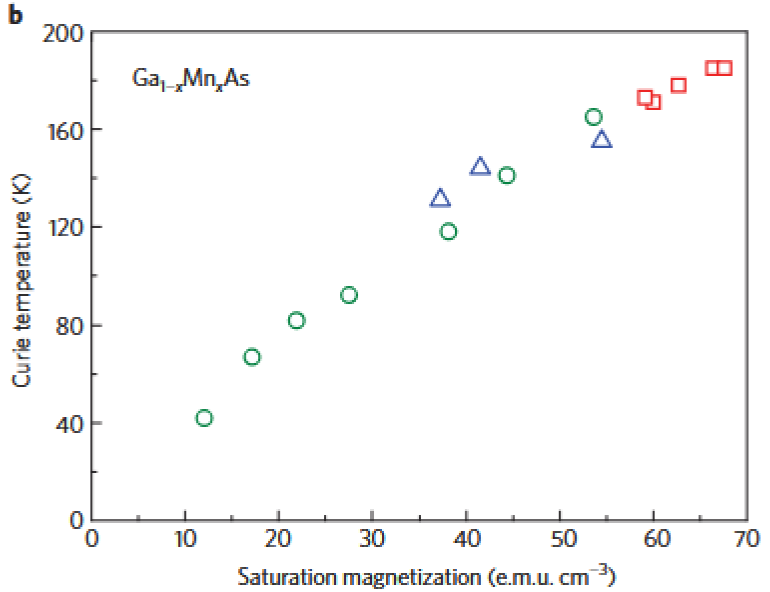
Diluted magnetic semiconductors

J. K. Furdyna

Check for updates

J. Appl. Phys. 64, R29–R64 (1988)
https://doi.org/10.1063/1.341700

III-V semiconductors doped with Mn: InMnAs, GaMnAs

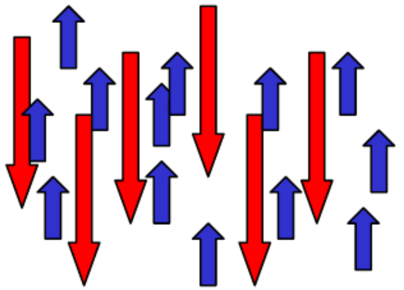


nature materials
REVIEW ARTICLE
PUBLISHED ONLINE: 23 NOVEMBER 2010 | DOI: 10.1038/NMAT2898

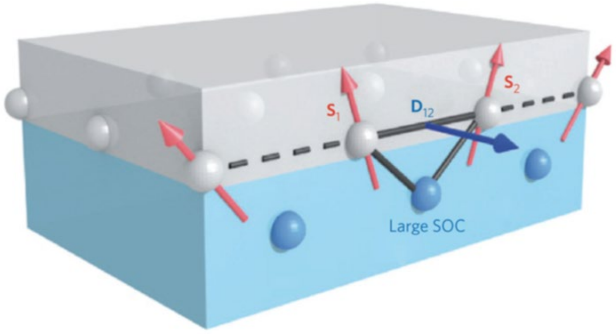
A ten-year perspective on dilute magnetic semiconductors and oxides

Tomasz Dietl[1,2]*

Zener s-d exchange

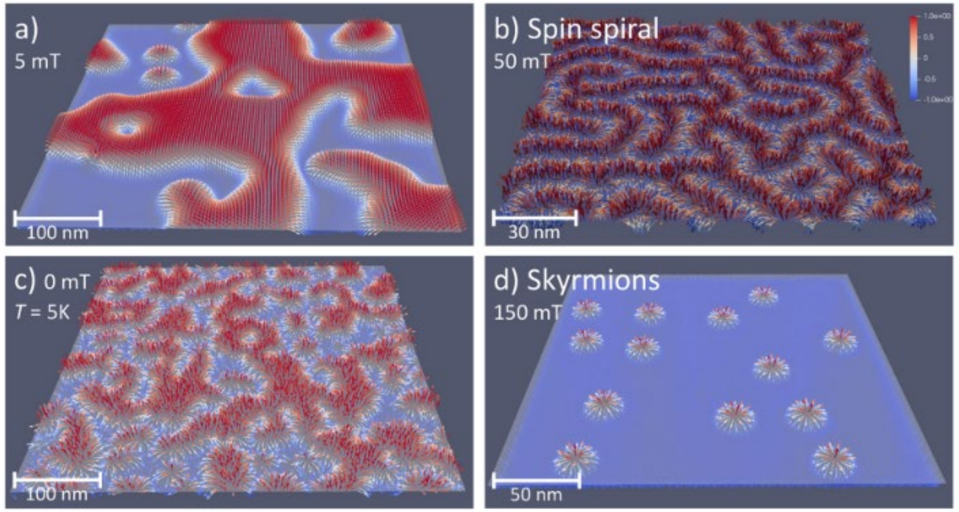


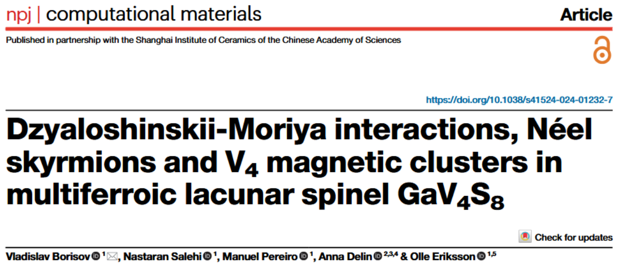
Special cases: Dzyaloshinskii-Moriya interaction



→ Spin-orbit coupling in a material with antiferromagnetic tendencies: spin canting through DM interaction (asymmetric exchange)

Skyrmions: topologically protected, moveable spin structures




npj | computational materials

Article

Published in partnership with the Shanghai Institute of Ceramics of the Chinese Academy of Sciences

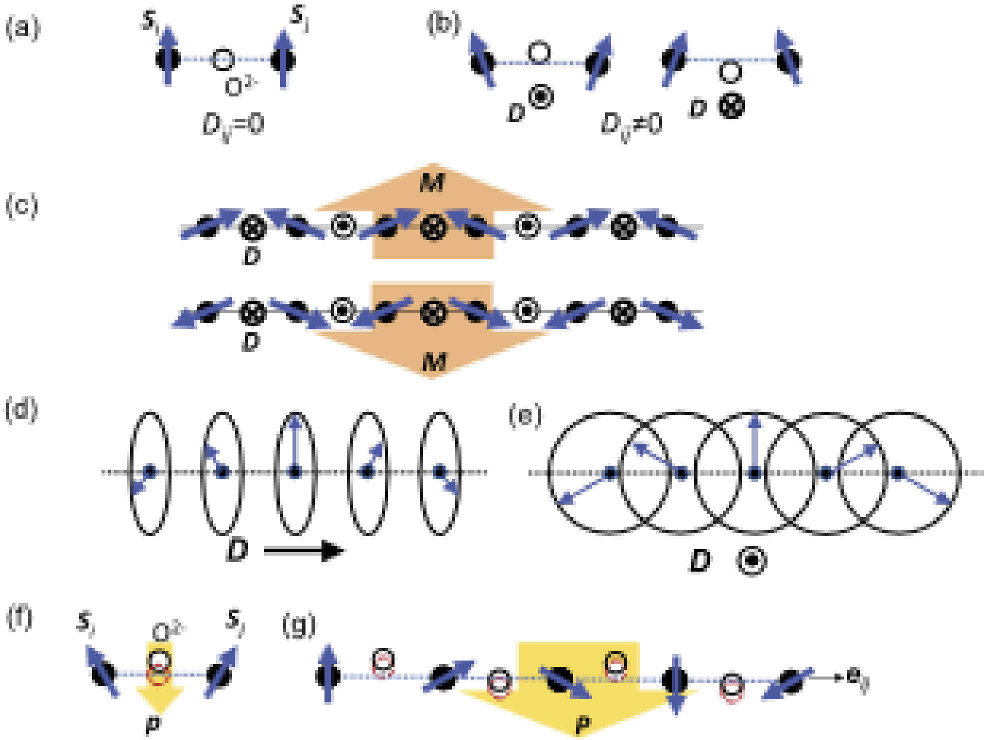
https://doi.org/10.1038/s41524-024-01232-7

Dzyaloshinskii-Moriya interactions, Néel skyrmions and V_4 magnetic clusters in multiferroic lacunar spinel GaV_4S_8

Check for updates

Vladislav Borisov, Nastaran Salehi, Manuel Pereiro, Anna Delin & Olle Eriksson

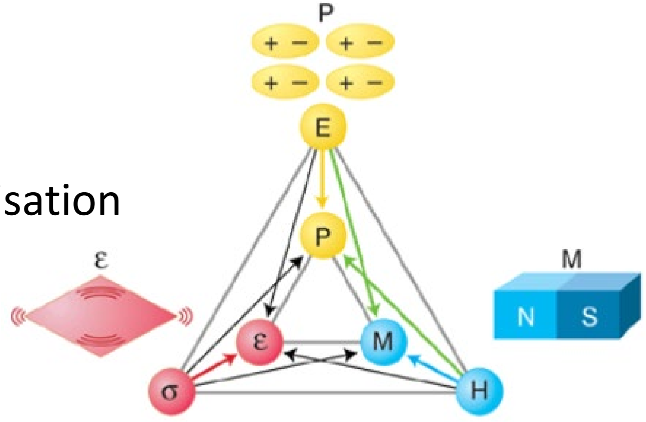
Inverse DM interaction: cycloidal spin orders lead to a electric polarisation, with a strong coupling to the magnetism



Dzyaloshinskii–Moriya Interaction in Multiferroics and Noncentrosymmetric Skyrmion Hosts

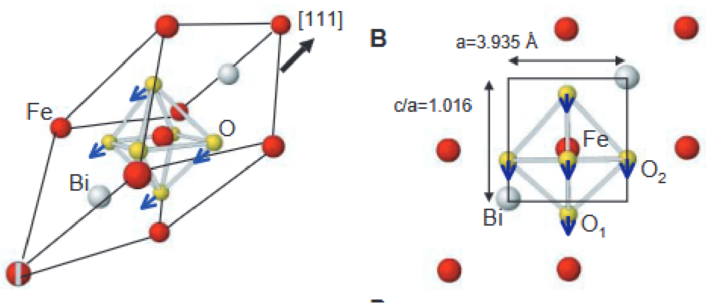
Yusuke Tokunaga[1*], Tsuyoshi Kimura[1,2], and Taka-hisa Arima[1,3]

Multiferroics



→ Possibility to couple magnetization and polarisation
→ Control polarisation by a magnetic field and magnetization by an electric field

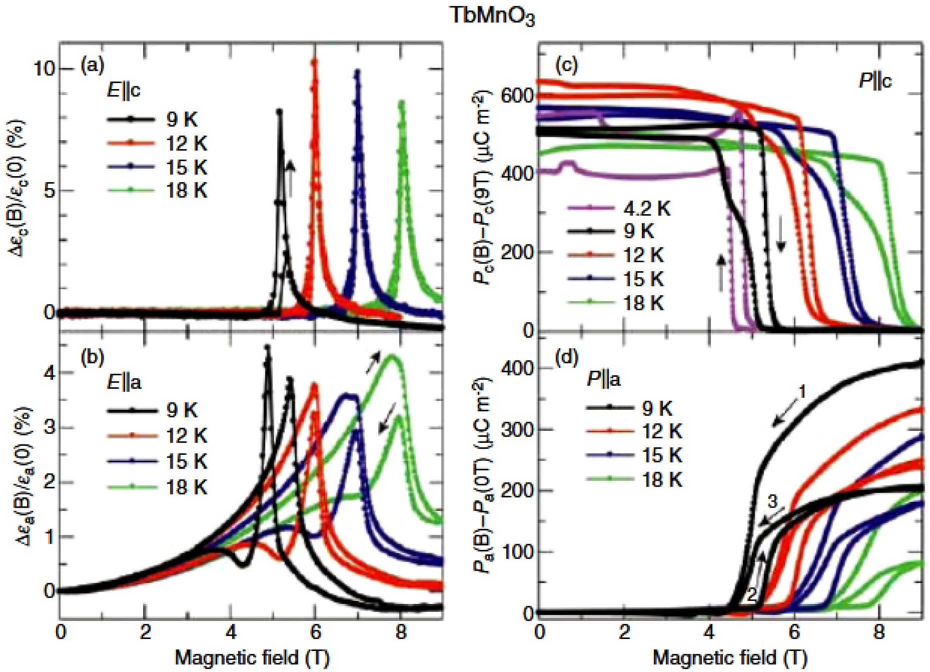
Type 1: ferroelectrics which happen to have a magnetic order

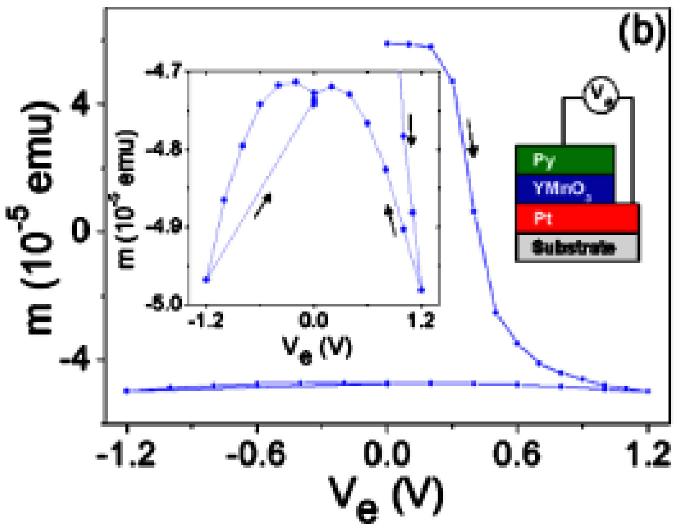


Epitaxial $BiFeO_3$ Multiferroic Thin Film Heterostructures

J. Wang,[1] J. B. Neaton,[2]† H. Zheng,[1]† V. Nagarajan,[1] S. B. Ogale,[3] B. Liu,[1] D. Viehland,[4] V. Vaithyanathan, [5] D. G. Schlom,[5] U. V. Waghmare,[6] N. A. Spaldin,[7] K. M. Rabe,[2] M. Wuttig,[1] R. Ramesh[3]*

Type 2: one order is induced by the other one





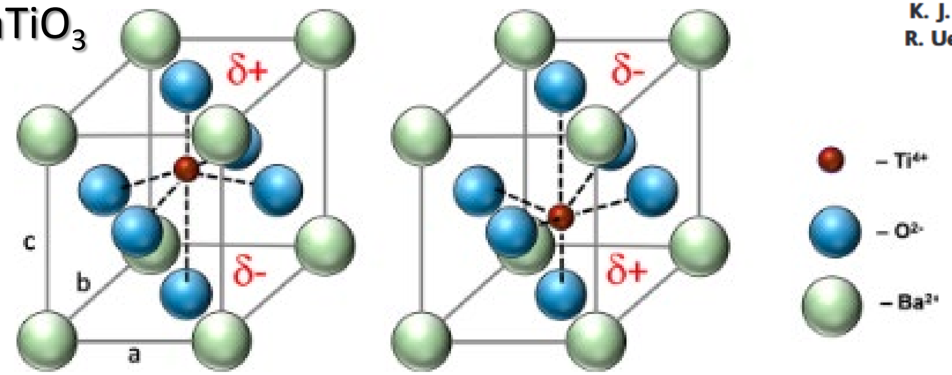
RL 97, 227201 (2006) PHYSICAL REVIEW LETTERS week ending 1 DECEMBER 2006

Electric-Field Control of Exchange Bias in Multiferroic Epitaxial Heterostructures

. Laukhin,[1,2] V. Skumryev,[2,3] X. Martí,[1] D. Hrabovsky,[1] F. Sánchez,[1] M. V. García-Cuenca,[4] C. Ferrater,[4] M. Varela,[4] U. Lüders,[5] J. F. Bobo,[5] and J. Fontcuberta[1]

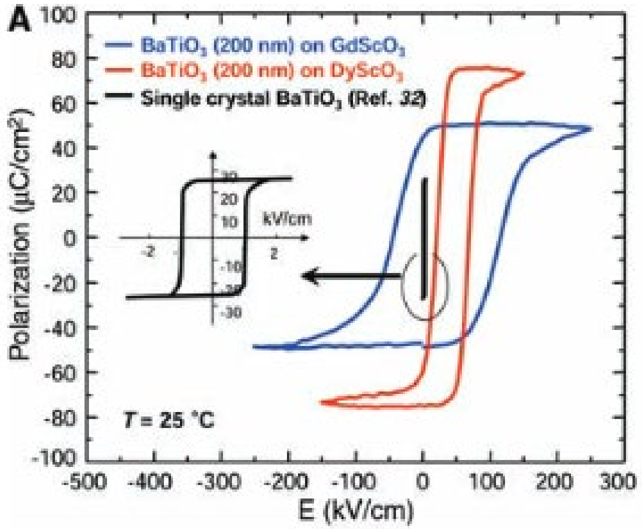
Ferroelectrics

BaTiO$_3$



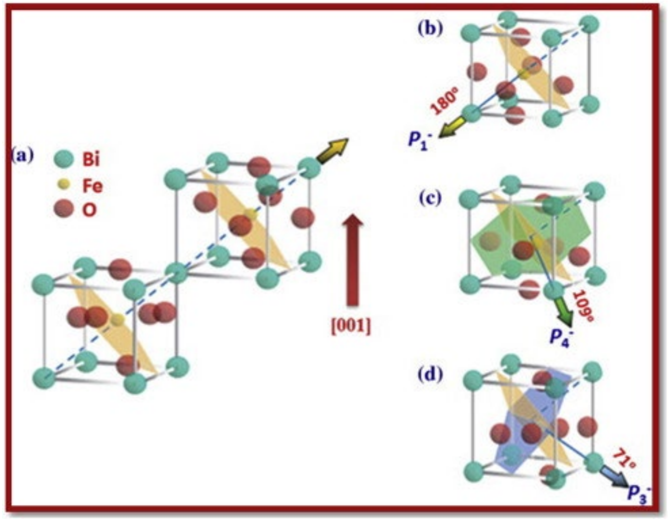
Enhancement of Ferroelectricity in Strained BaTiO$_3$ Thin Films

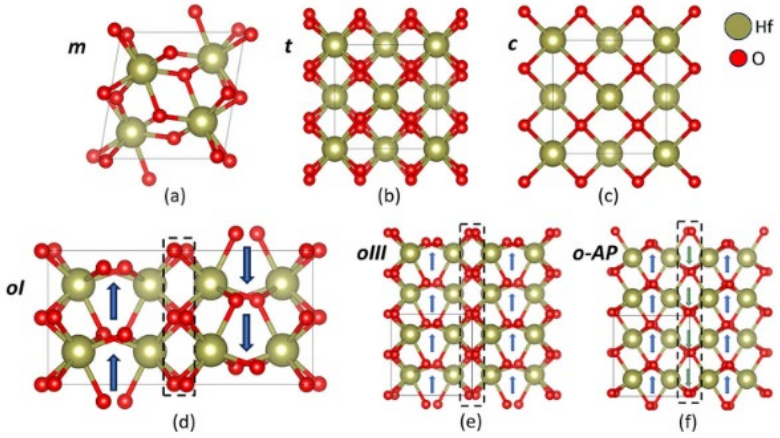
K. J. Choi,[1] M. Biegalski,[2] Y. L. Li,[2] A. Sharan,[2] J. Schubert,[3] R. Uecker,[4] P. Reiche,[4] Y. B. Chen,[5] X. Q. Pan,[5] V. Gopalan,[2] L.-Q. Chen,[2] D. G. Schlom,[2] C. B. Eom[1*]



HfO$_2$: epitaxial stabilisation of metastable phases

BiFeO$_3$: lone-pair mediated





npj | computational materials — Article

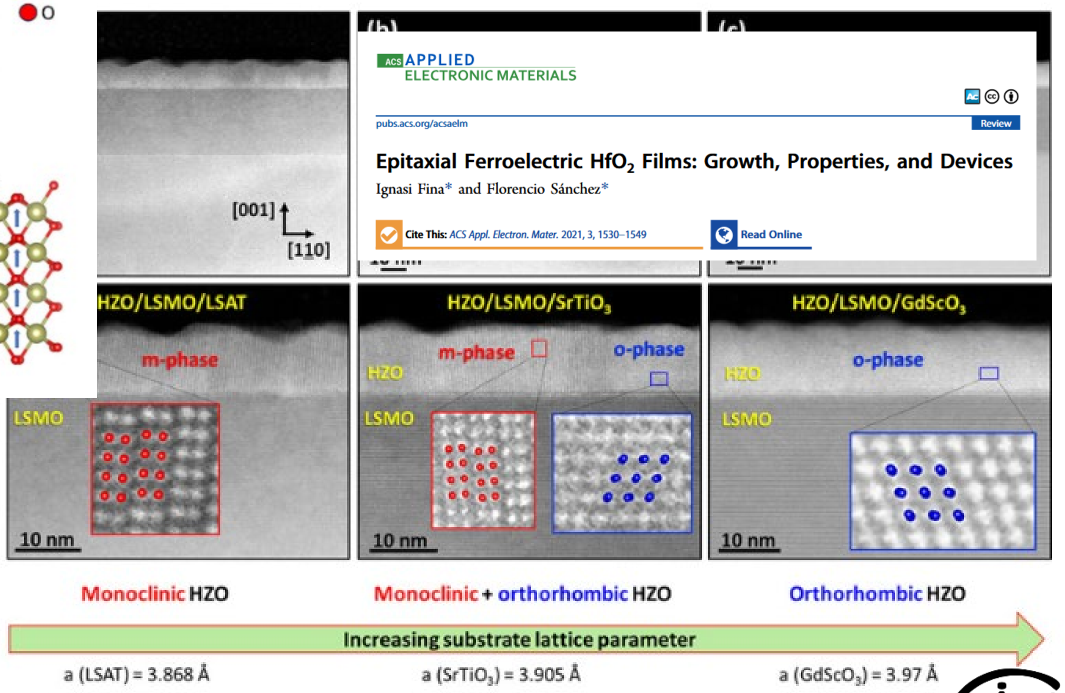
Published in partnership with the Shanghai Institute of Ceramics of the Chinese Academy of Sciences

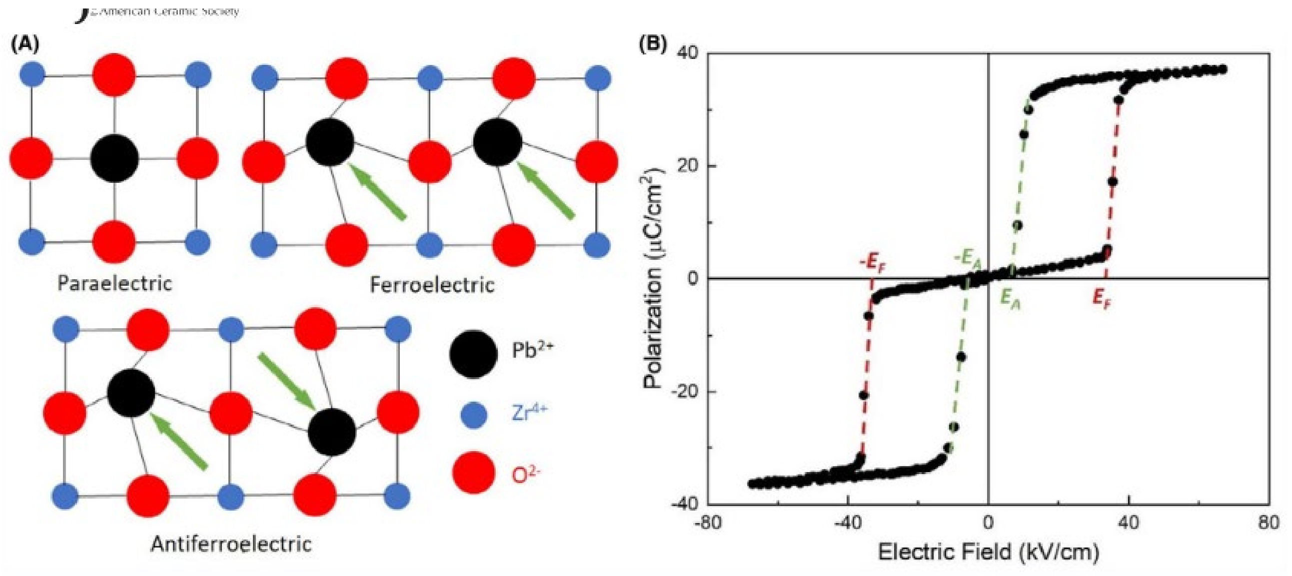
https://doi.org/10.1038/s41524-024-01344-0

First-principles predictions of HfO$_2$-based ferroelectric superlattices

Check for updates

Binayak Mukherjee, Natalya S. Fedorova & Jorge Íñiguez-González





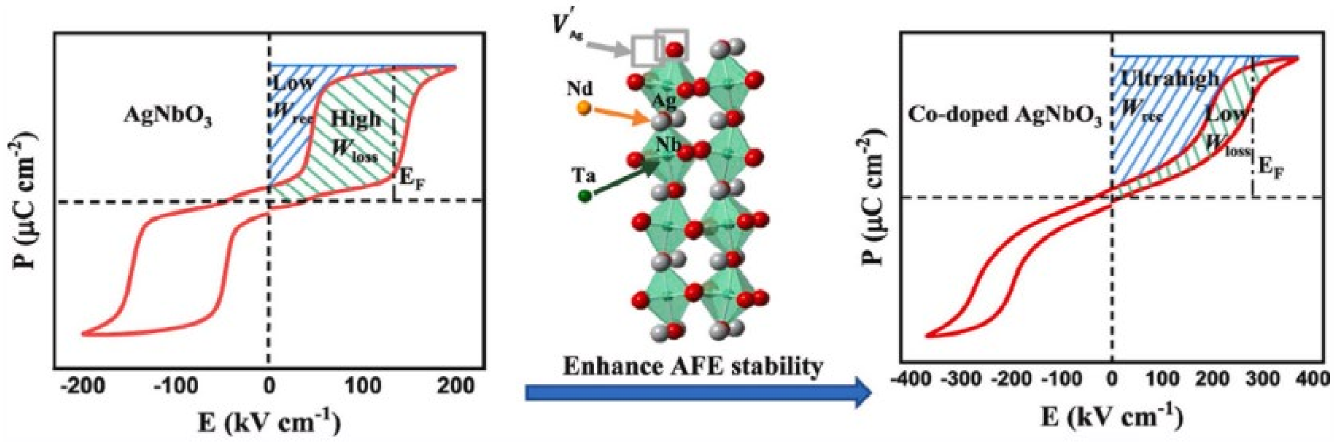
DOI: 10.1111/jace.17834

INVITED FEATURE ARTICLE

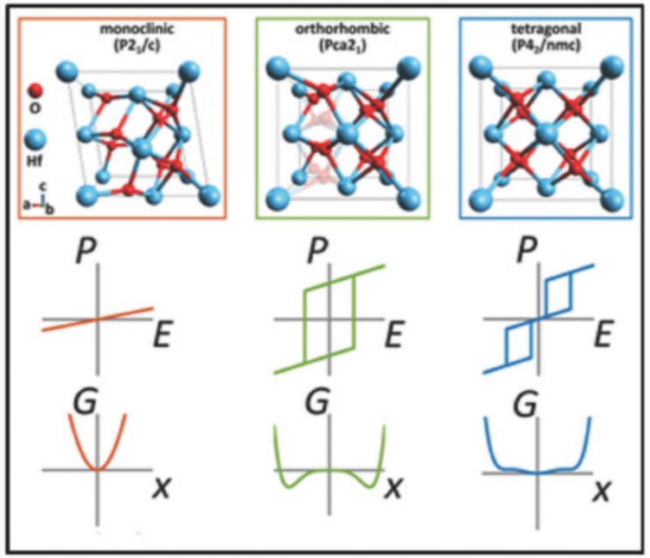
Journal of the American Ceramic Society

Antiferroelectrics: History, fundamentals, crystal chemistry, crystal structures, size effects, and applications

Clive A. Randall[1] | Zhongming Fan[1] | Ian Reaney[2] | Long-Qing Chen[1] | Susan Trolier-McKinstry[1]



HfO_2: antiferromagnetic phase

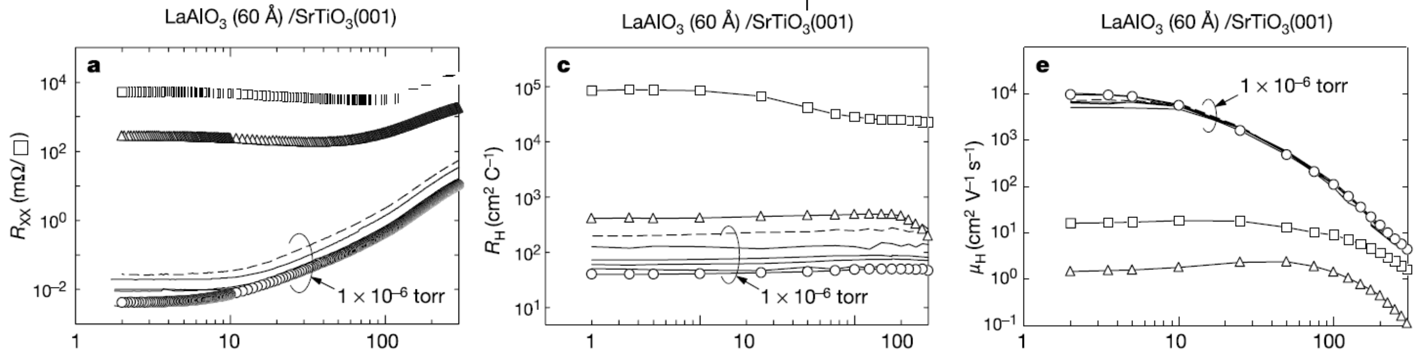


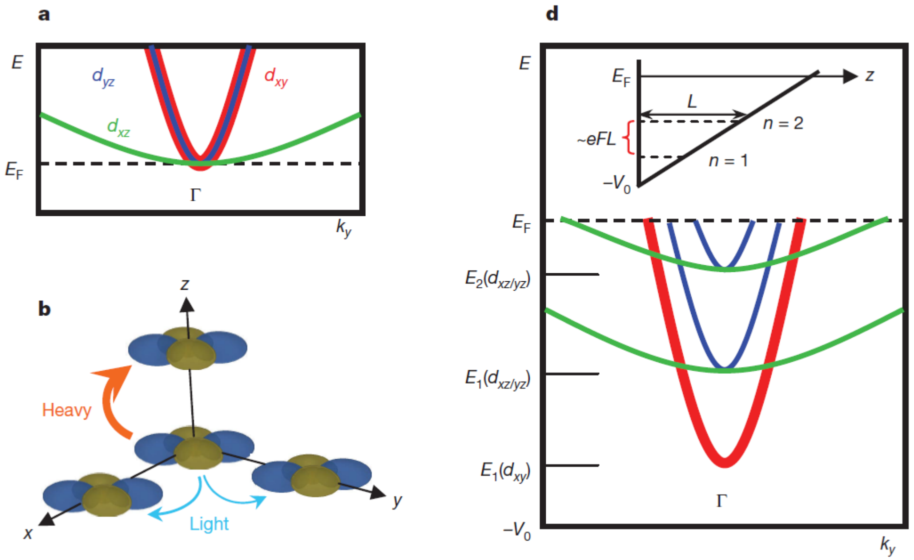
n-type $SrTiO_3$

→ A highly mobile 2D electron gas can be creatred at the interface between two band insulators
→ Comparable effects for oxygen-deficient $SrTiO_3$
→ Many interesting effects: record mobility values for oxides, tuneable superconductors, magnetic puddles

A high-mobility electron gas at the $LaAlO_3/SrTiO_3$ heterointerface

A. Ohtomo[1,2,3] & H. Y. Hwang[1,3,4]





LETTER

doi:10.1038/nature09720

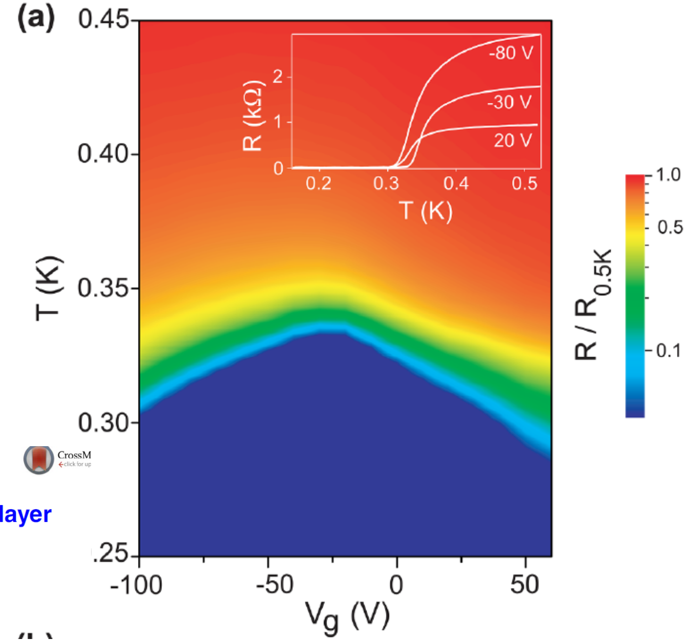
Two-dimensional electron gas with universal subbands at the surface of $SrTiO_3$

A. F. Santander-Syro[1,2], O. Copie[3,4,5], T. Kondo[6], F. Fortuna[1], S. Pailhès[7], R. Weht[8,9], X. G. Qiu[10], F. Bertran[11], A. Nicolaou[11], A. Taleb-Ibrahimi[11], P. Le Fèvre[11], G. Herranz[12], M. Bibes[3,4], N. Reyren[3,4], Y. Apertet[13], P. Lecoeur[13], A. Barthélémy[3,4] & M. J. Rozenberg[14,15]

JOURNAL OF APPLIED PHYSICS **124**, 213902 (2018)

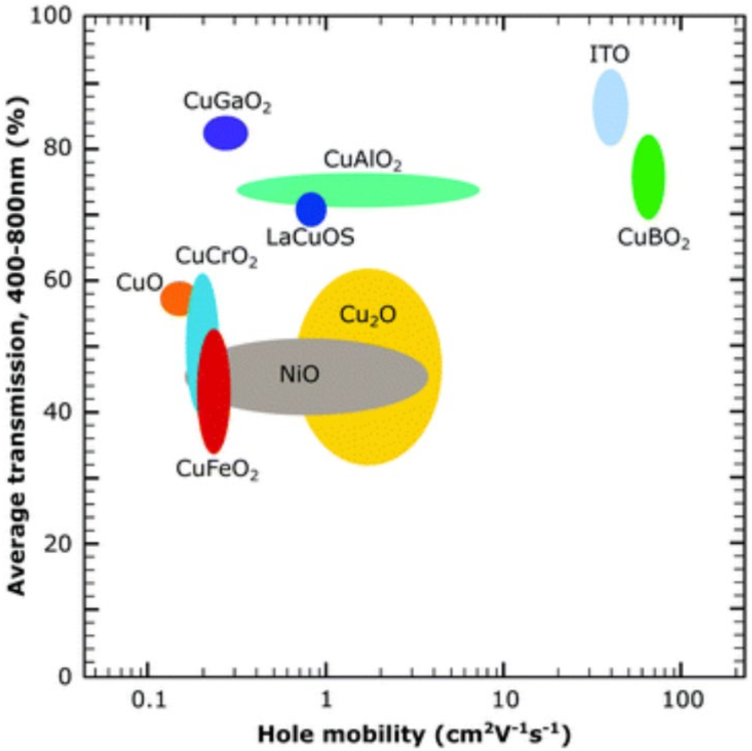
Gate-tunable superconductivity at $SrTiO_3$ surface realized by Al layer evaporation

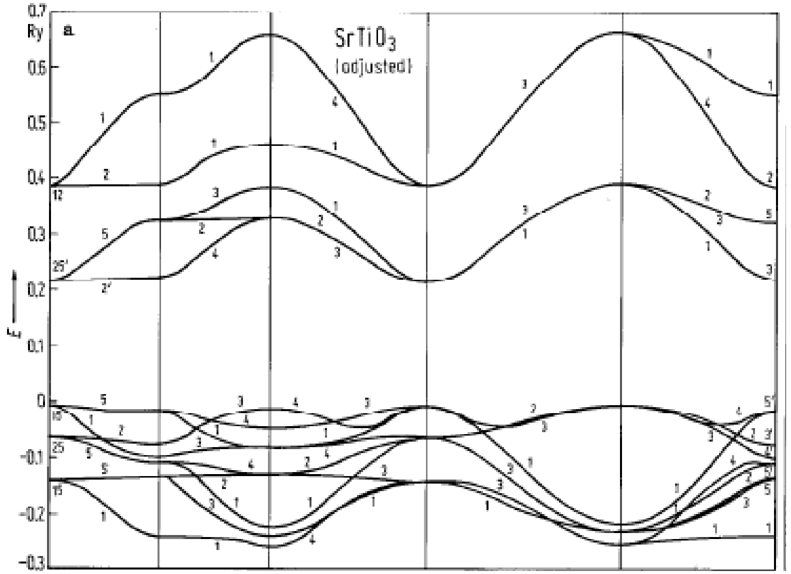
Shamashis Sengupta,[1,a)] Emilie Tisserond,[2,b)] Florence Linez,[3,b)] Miguel Monteverde,[2] Anil Murani,[2] Tobias Rödel,[1] Philippe Lecoeur,[3] Thomas Maroutian,[3] Claire Marrache-Kikuchi,[1] Andrés F. Santander-Syro,[1] and Franck Fortuna[1]



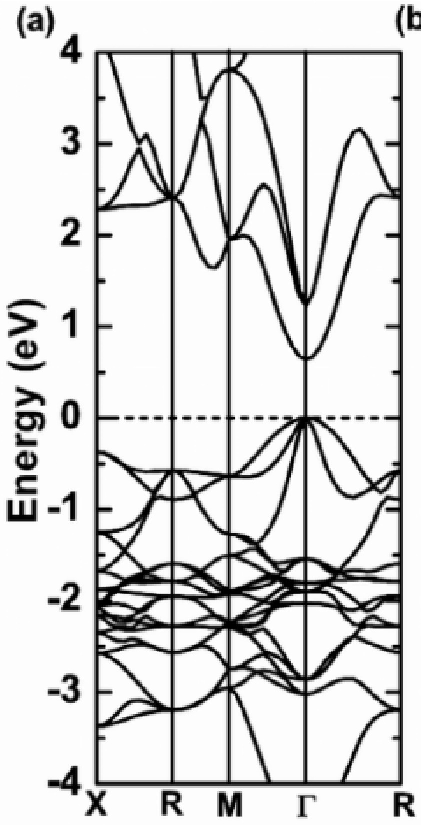
p-type conduction

→ Flat oxygen bands: use heavy transition metals to use charge transfer insulators
→ Self compensations with oxygen vacancies
→ Rather low mobilities in p-type oxides





Charge transfer insulators:
Cu_2O



Conclusions

→ It is all about interactions

→ Order is a fundamental ingredient

→ There is a universe out there. Have fun!

Questions?
ulrike.luders@ensicaen.fr