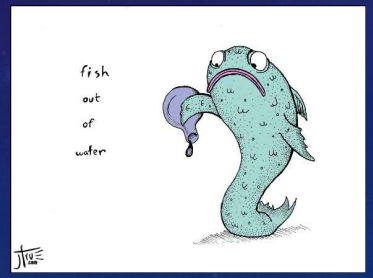
Magnetic properties as seen by X-ray based Electron Spectroscopies (the basics of the game: PART 1)

Giancarlo Panaccione
Istituto Officina dei Materiali (IOM)
Consiglio Nazionale delle Ricerche (CNR)
Trieste, Italy



- *Historical background and concepts*
- *X-ray electron spectroscopies and magnetism (PES and XAS)*
- *Why, what, where : examples*

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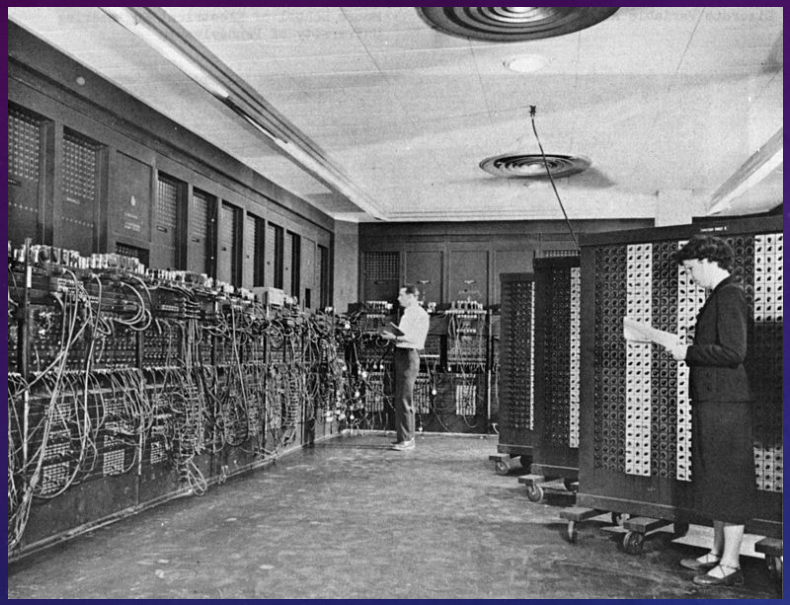
AIMagn - Associazione Italiana di Magnetismo

School on Magnetic Nanomaterials
Perugia
Oct 20th – 24th

Semiconductors Revolution

(1947 @ Bell labs: invention of bipolar transistor)

1945: First electronic general-purpose computer



It could add or subtract 5000 times a second

High speed memory was limited to 80 bytes

30 tons, 200 kilowatts, 18,000 vacuum tubes

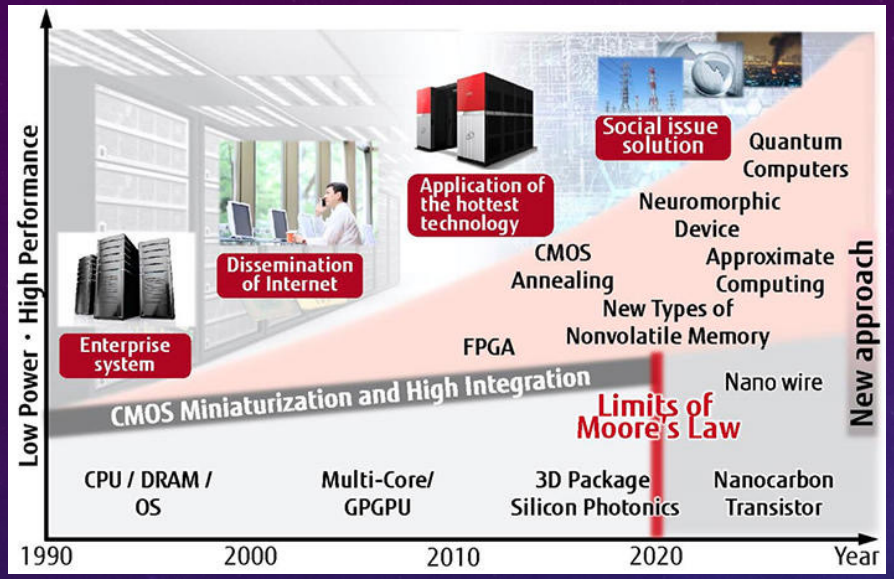


170 g, 512 GB, CPU 3.2 GHz RAM 4 GB

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Courtesy of A. Damascelli

Motivation: more on Moore or no more Moore's law ?



Gordon Moore, co-founder of Intel, predicted in 1965 that the cost of microchip transistors would continue to fall because the number that could be etched into a given surface area of silicon would double every two years.

Future Cost With Moore's Law		
Year	iPhone	Kindle
2010	$ 600.00	$ 139.00
2020	18.75	4.34
2030	Less than $1.00	Less than $1.00

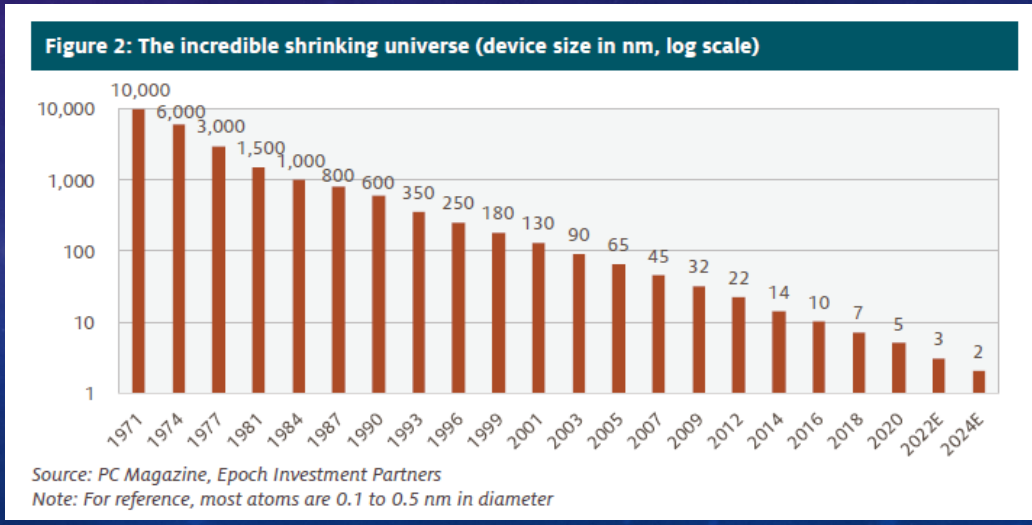
Expensive basket of technologies must be developed for each new generation of smaller transistors

BUT

So far no REAL (i.e. cost effective)

new technology is foreseen

CMOS technology will never die



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editorial

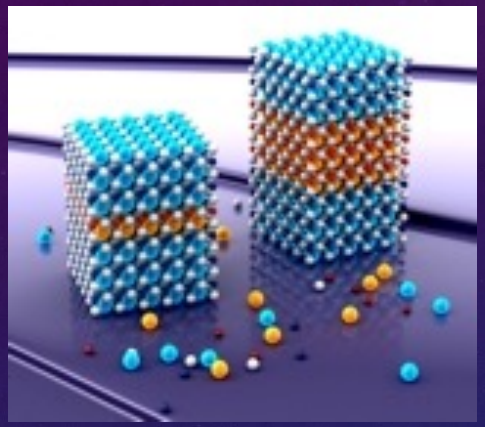
The rise of quantum materials

Emergent phenomena are common in condensed matter. Their study now extends beyond strongly correlated electron systems, giving rise to the broader concept of quantum materials.

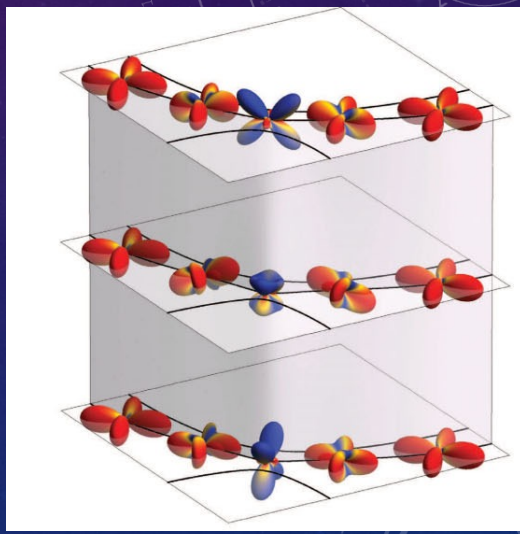
Quantum materials (R)Evolution (maybe…)

Quantum materials refers broadly to systems that cannot be adequately described by simple single-electron band-models. Such models and related theories provided foundational knowledge for the semiconductor revolution of the 20th century.

C. N. Veenstra, et al. PRL. **112**, 127002 (2014)







QuantumManifesto
A New Era of Technology Draft - March 2016

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CHALLENGES:
Understand complex collective behavior
Explore applicability
Control, at atomic level and/or at single layer
of magnetic and electronic, structural properties

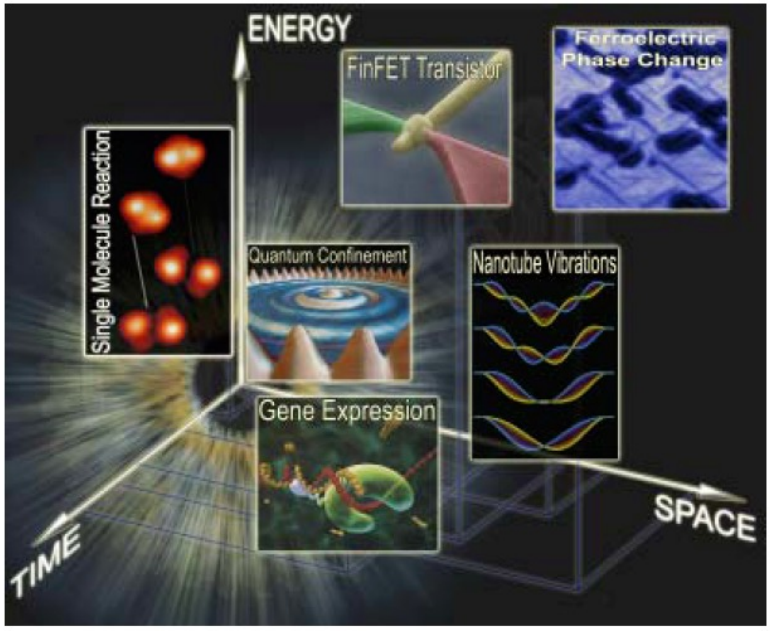
Quantum materials : from Observation to Control

Overall Challenge: *Making the Leap from Observation Science to Control Science*

BERKELEY LAB

Designing materials to have the properties we want require the ability to see functionality at the relevant *time, length & energy scales.*

We will need *to develop & disseminate new tools* capable of viewing the inner workings of matter — at the level of electrons, atoms or molecules



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Courtesy of : Z. Hussain, ALS, LBNL

Quantum materials (R)Evolution: New functionalities

Oxide Spintronics

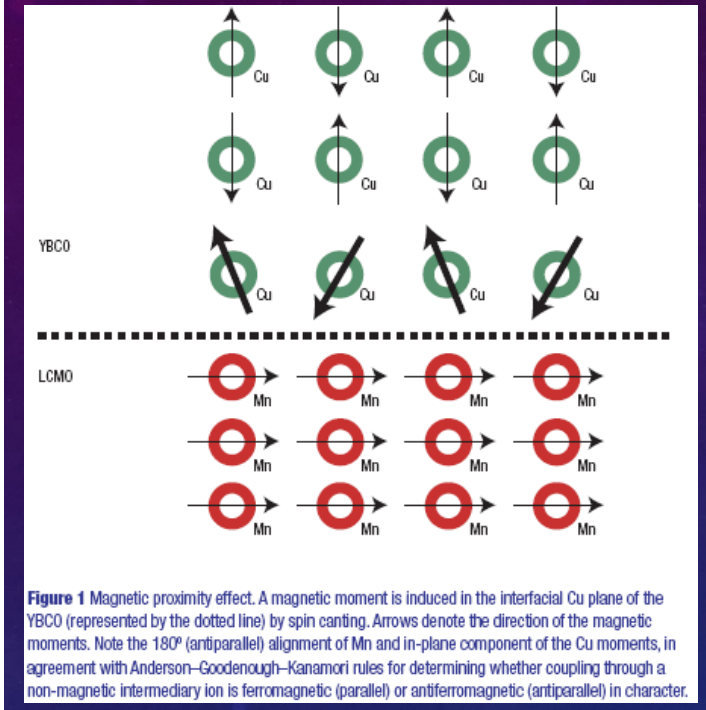


Figure 1 Magnetic proximity effect. A magnetic moment is induced in the interfacial Cu plane of the YBCO (represented by the dotted line) by spin canting. Arrows denote the direction of the magnetic moments. Note the 180° (antiparallel) alignment of Mn and in-plane component of the Cu moments, in agreement with Anderson–Goodenough–Kanamori rules for determining whether coupling through a non-magnetic intermediary ion is ferromagnetic (parallel) or antiferromagnetic (antiparallel) in character.

S. Sanvito, Nature Phys.6, 562 (2010)
J. Chakhalian et al, Nature Phys.2, 244 (2006)
J. Santamaria , Nat. Physics 2, 229 (2006)

Role and importance of surfaces and interfaces

nm sized conduction channel at the interface of two **non-conducting** oxides.

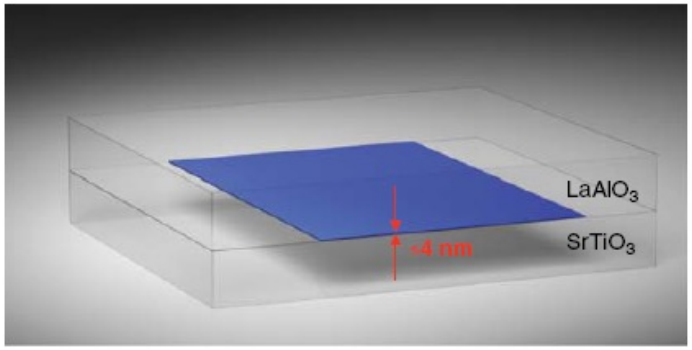


Figure 10. Sketch illustrating the generation of an ultrathin two-dimensional electron gas superconducting sheet at the $LaAlO_3/SrTiO_3$ interface. Based on the superconducting transition temperature and the carrier density, the thickness of the superconducting sheet is estimated to be less than ~4 nm.

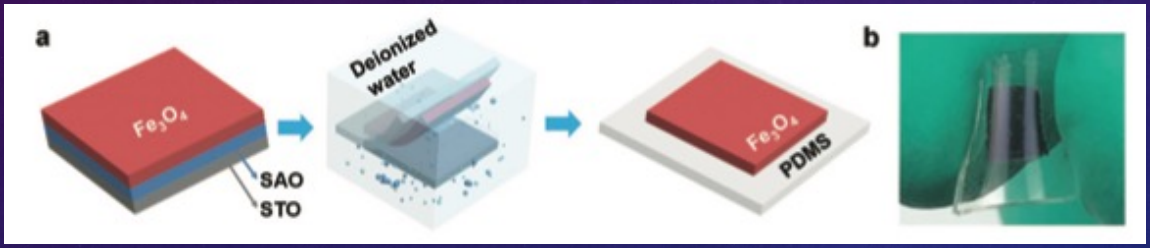
J. Mannhart, et al.,
MRS Bulletin **33**, 1027 (2008)

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Quantum materials (R)Evolution: New functionalities

Flexible spintronics and electronics

Self standing single/few layers.



FULL PAPER

ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.

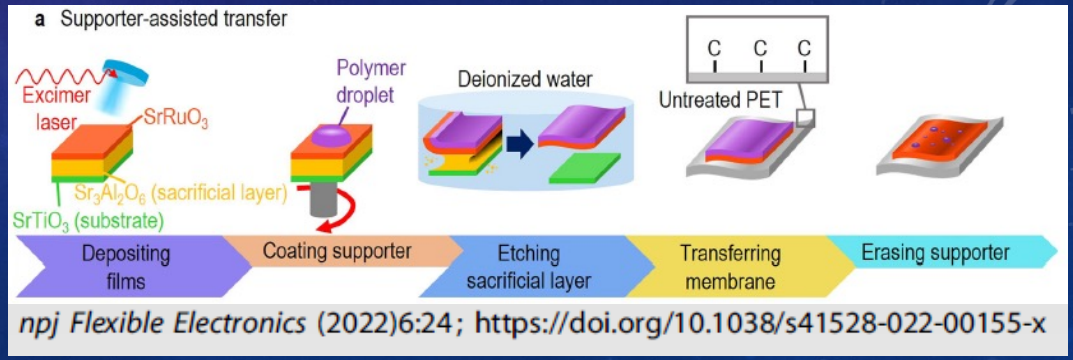
Highly Flexible and Twistable Freestanding Single Crystalline Magnetite Film with Robust Magnetism

Feng An, Ke Qu, Gaokuo Zhong, Yongqi Dong, Wenjie Ming, Mengfei Zi, Zhijie Liu, Yadong Wang, Biyun Qi, Zhen Ding, Jun Xu, Zhenlin Luo, Xingsen Gao, Shuhong Xie,* Peng Gao,* and Jiangyu Li**

Advanced capabilites in growth and synthesis

Assisted transfer

Microscopy tools needed



npj Flexible Electronics (2022)6:24; https://doi.org/10.1038/s41528-022-00155-x

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Low-dimensional magnetic phenomena

https://doi.org/10.1038/s41586-018-0631-z

Magnetism in two-dimensional van der Waals materials

Kenneth S. Burch[1], David Mandrus[2,3] & Je-Geun Park[4,5]*

RESEARCH REVIEW

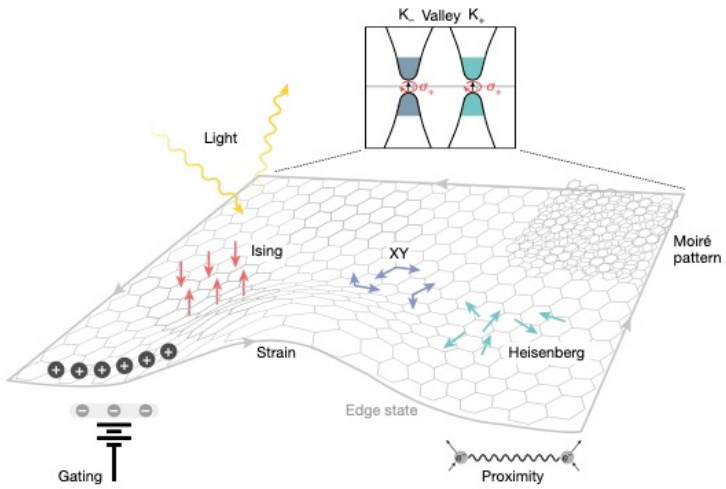


Fig. 1 | Physical phenomena that can be studied with magnetic vdW materials. 2D magnetic vdW materials are an ideal platform for investigating how the Hamiltonians of the fundamental magnetism models (the Ising, XY and Heisenberg models; magnetic moments indicated by the red, purple and cyan arrows, respectively) behave in the 2D limit. In addition, the magnetic ground states of these materials could be controlled by external perturbations, such as gating and strain, or via proximity effects and moiré patterns. Because of the intrinsic properties of their honeycomb lattice, there is also a possibility of light–matter interactions through valley coupling of K_- and K_+ points in the momentum space and the edge states (grey arrows).

Table 1 | List of potential research topics in four categories for magnetic van der Waals materials

Research directions	Specific topics
New materials	Room-temperature ferromagnetic and antiferromagnetic materials Multiferroic materials Magnetic vdW materials with quantum spin ($S = 1/2$) Magnetic vdW materials with 4*d*/5*d* elements and strong spin–orbit coupling Unconventional superconductors
Fundamental issues	Evolution of magnetic fluctuations as a function of layer number: Ising, XY and Heisenberg models XY model: BKT transition, vortex–antivortex pair fluctuations Effects of interface, including substrate and capping layer Proximity with other quantum phases: *s*-, *p*- and *d*-wave superconductors, ferroelectrics, FMs, AFMs Spin–valley coupling Magnetic excitons
Devices and applications	Controllability via strain and gating Heterostructures Magnetic sensors Terahertz magneto-optical devices Multiferroics Spintronics Topological quantum computing
Quantum and topological phases	Quantum spin liquids Quantum critical phenomena induced by external variables Unconventional superconductivity in two dimensions Kitaev interaction, spin-liquid physics and fractionalization Quantum spin Hall effect Skyrmions Landscaping quantum phases

Low-dimensional magnetic phenomena

generalized Heisenberg spin Hamiltonian

$$H = -\frac{1}{2}\sum_{i,j} J\boldsymbol{S}_i \cdot \boldsymbol{S}_j \quad +\Lambda S_i^z S_j^z - \sum_i A(S_i^z)^2$$

Exchange coupling

Exchange anisotropy

"On-site" anisotropy

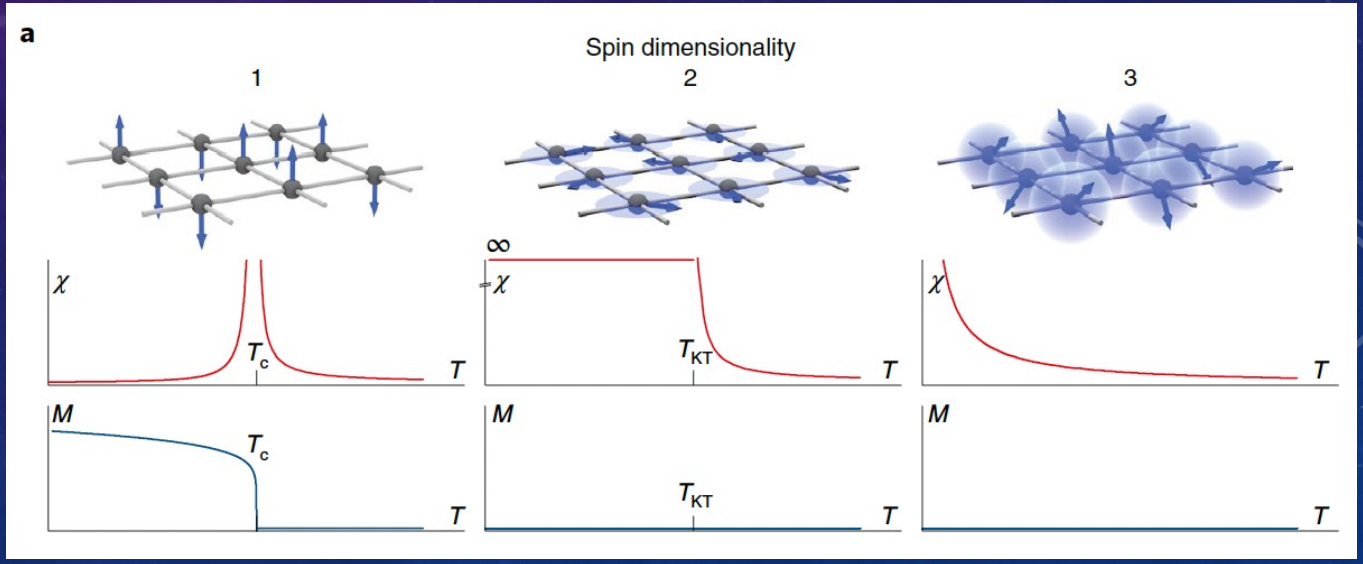
REVIEW ARTICLE
https://doi.org/10.1038/s41565-019-0438-6
nature nanotechnology

Magnetic 2D materials and heterostructures

M. Gibertini[1,2], M. Koperski[3,4], A. F. Morpurgo[1,5] and K. S. Novoselov[3,4]*

Table 1 | Critical behaviour from 2D to 3D

Model	β	γ
	$M(T<T_c) \propto \lvert t\rvert^{\beta}$	$\chi \propto \lvert t\rvert^{-\gamma}$
2D Ising	1/8	7/4
3D Ising	0.3265	1.237
3D XY	0.348	1.318
3D Heisenberg	0.369	1.396
Mean field	0.5	1



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Low-dimensional magnetic phenomena

generalized Heisenberg spin Hamiltonian

$$H = -\frac{1}{2}\sum_{i,j} J\boldsymbol{S}_i \cdot \boldsymbol{S}_j \quad +\Lambda S_i^z S_j^z - \sum_i A(S_i^z)^2$$

Exchange coupling

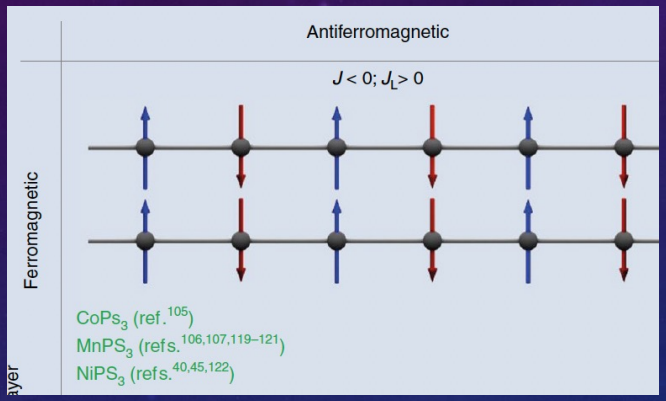
Exchange anisotropy

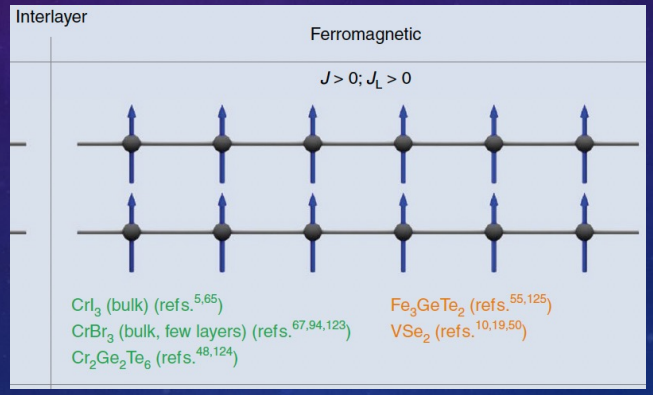
"On-site" anisotropy

https://doi.org/10.1038/s41586-018-0631-z

Magnetism in two-dimensional van der Waals materials

Kenneth S. Burch[1], David Mandrus[2,3] & Je-Geun Park[4,5]*





Green: semiconductor materials
Orange: metallic

Long range magnetic order

Anisotropy

Antiferromagnetic, $J < 0$ - Ferromagnetic, $J > 0$

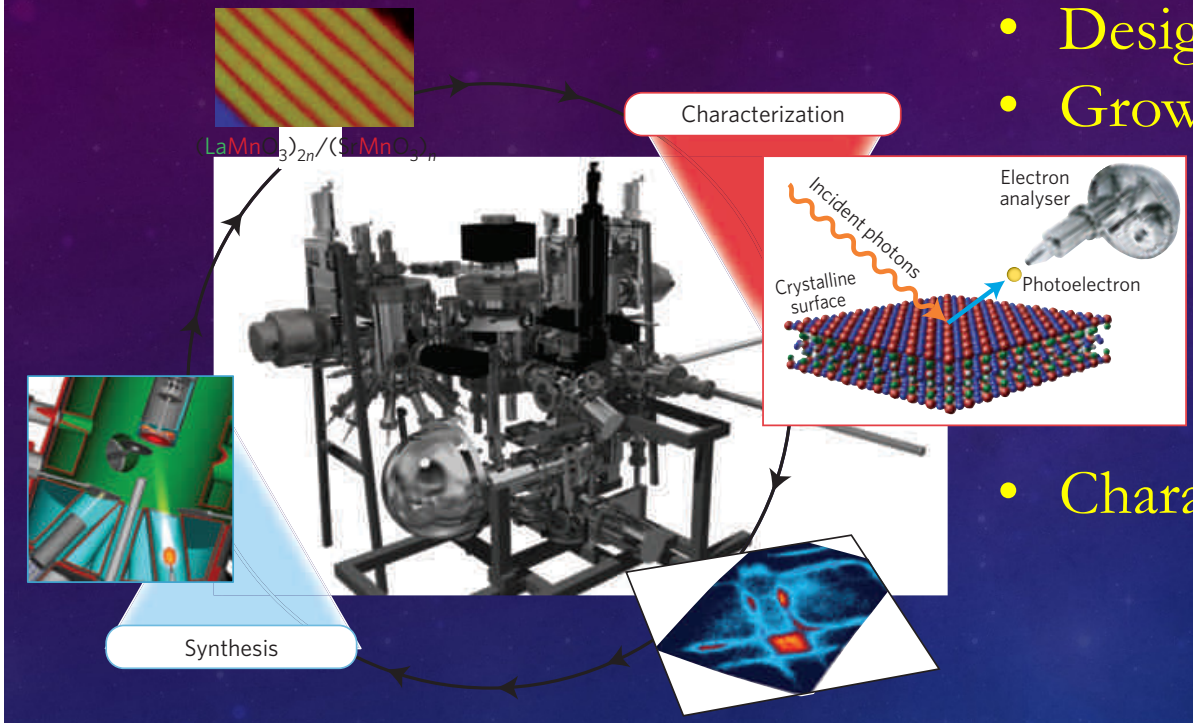
Importance of Interlayer vs Intralayer coupling

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See M. Gilbertini et al *Nat.. Nanotechnol.* **14**, 408–419 (2019).

Quantum materials (R)Evolution: Methodology and Needs

- Design (theory and chemistry)
- Growth (reliable/reproducible protocols)



- Characterization (lab and @synchrotron)

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J. Rondinelli NATURE MATERIALS, news and views | VOL 11 | OCTOBER 2012 |

Importance of X-rays

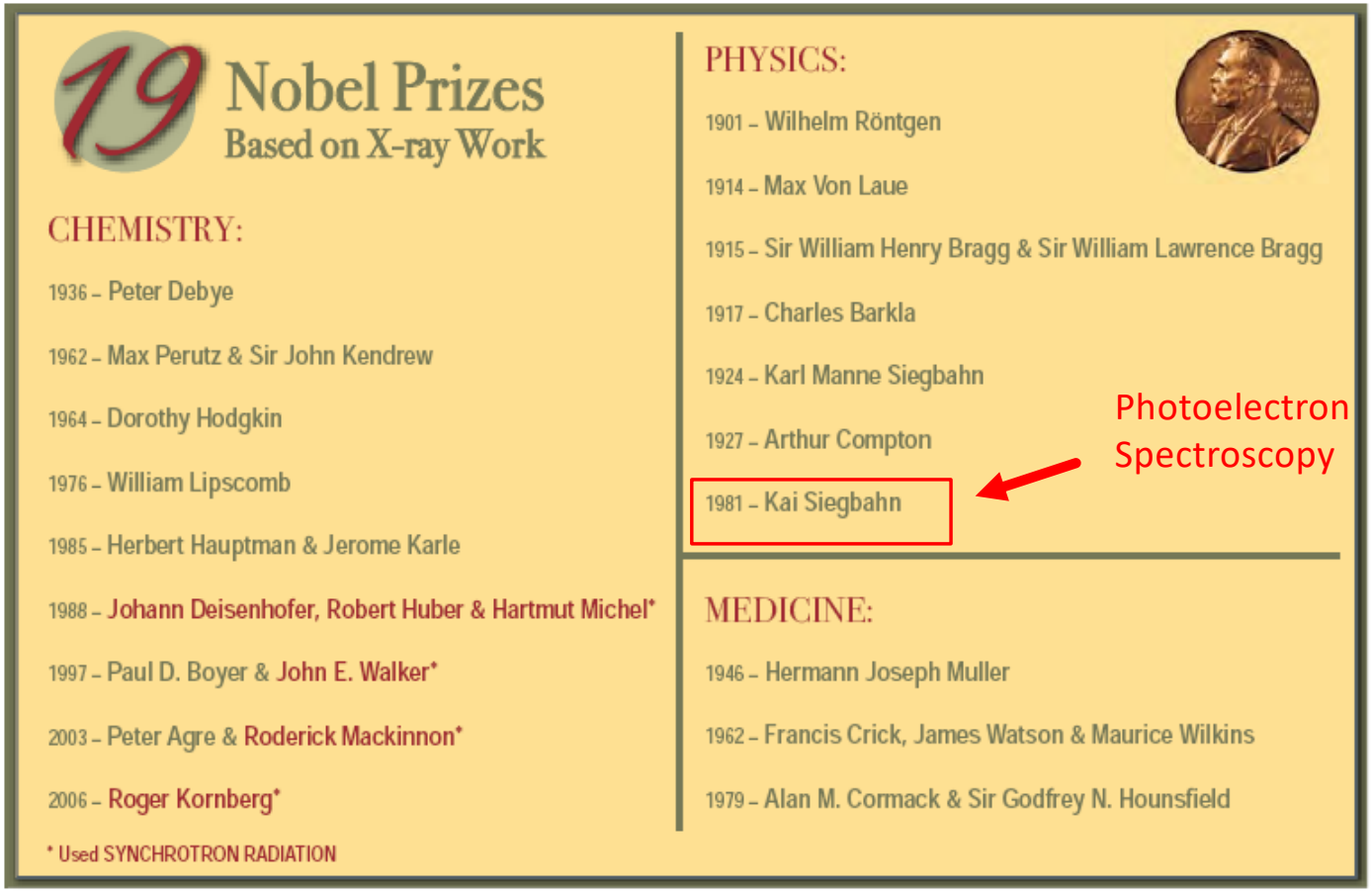
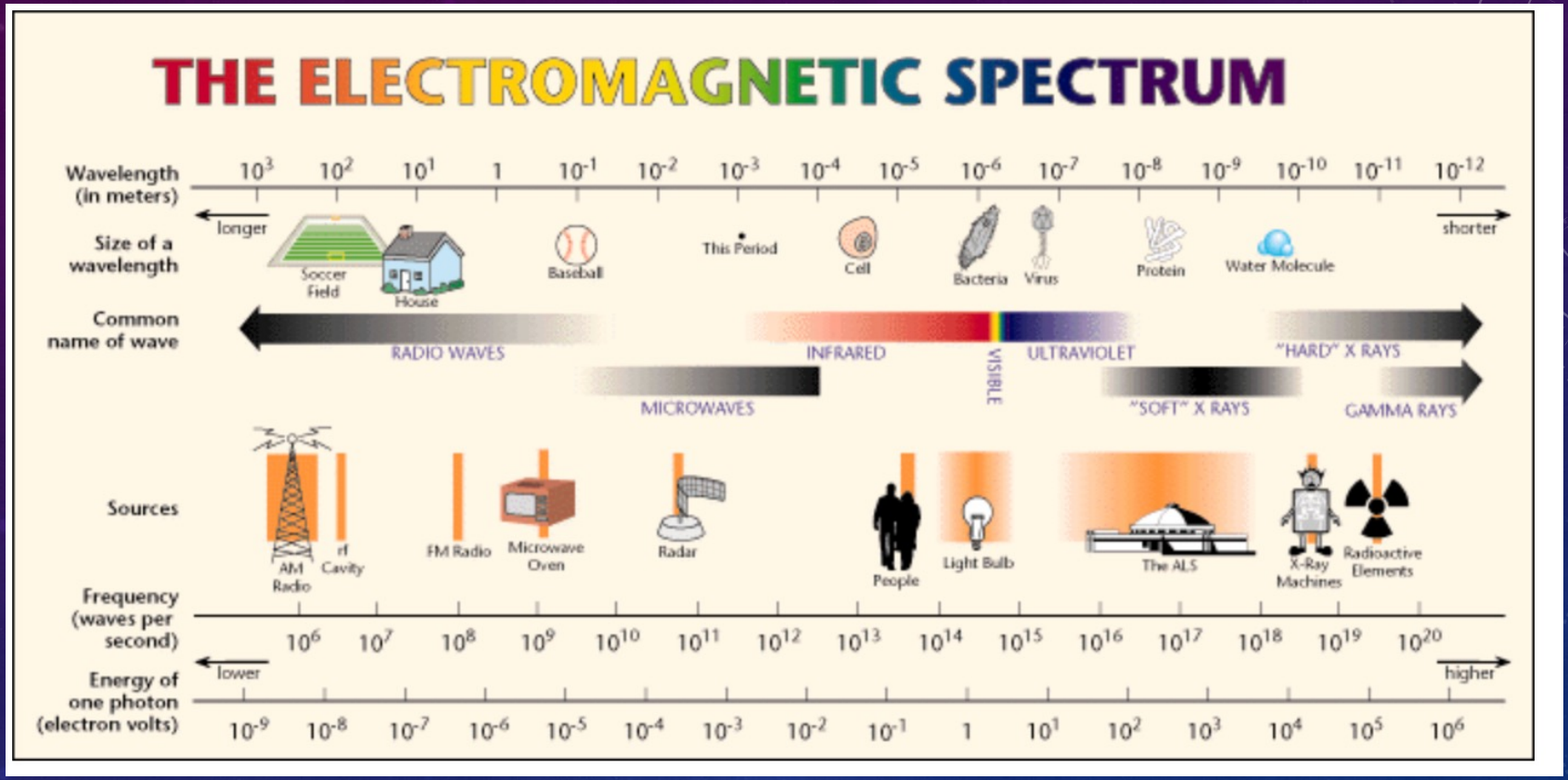


Figure 1.2. The impact of x-rays is proven by 19 Nobel Prizes that have been awarded for related work.



Duality Particle-waves

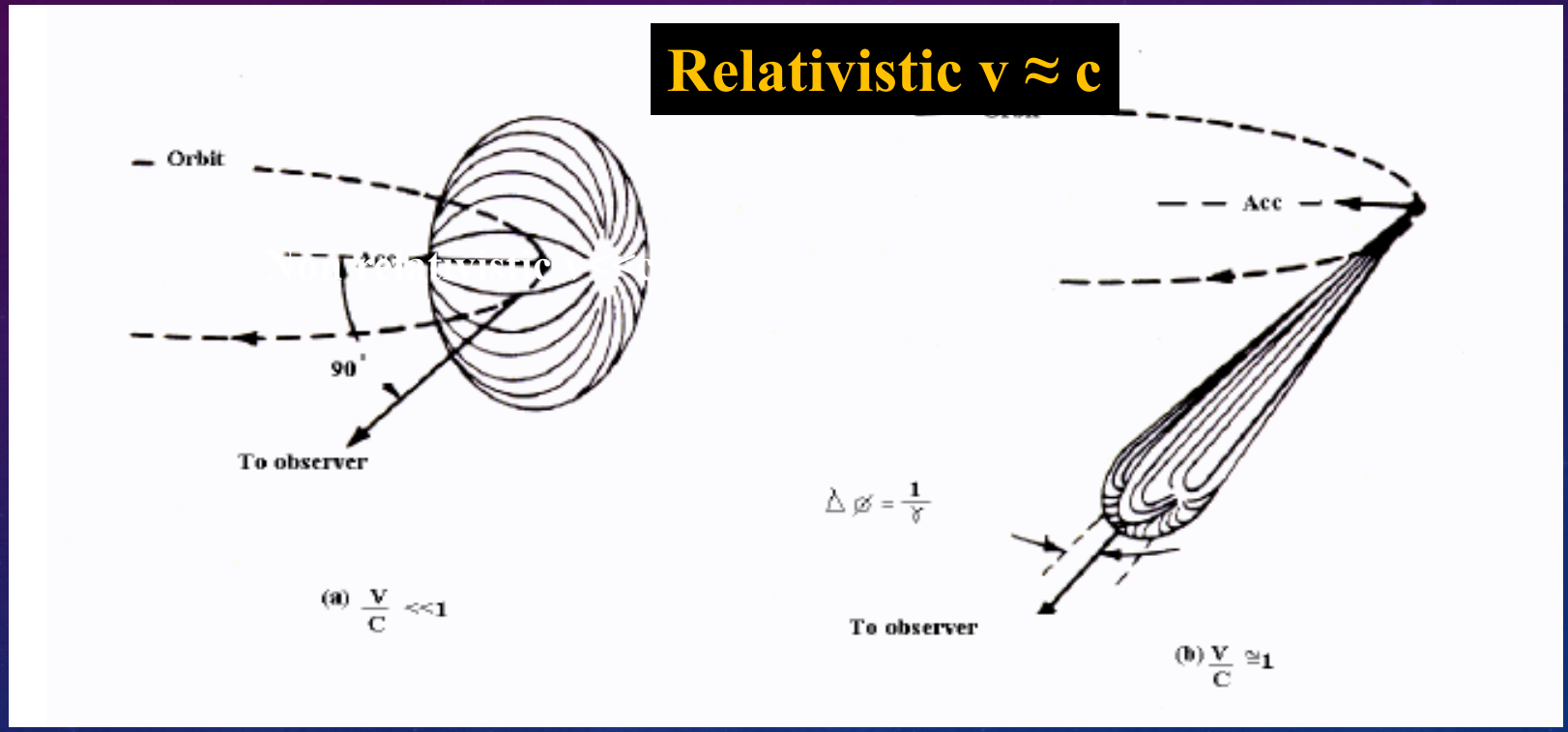
Extremely broad spectral range

Vision of the ‘invisible’

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Production of Synchrotron Radiation: relativistic electrons

A charged particle constrained to move in curved path experiences a centripetal acceleration.
Due to this acceleration, the particle radiates energy according to Maxwell equations

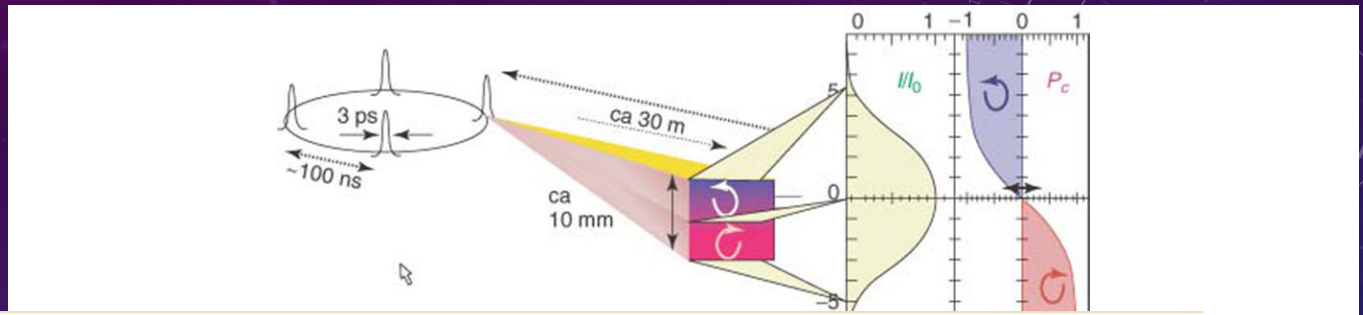


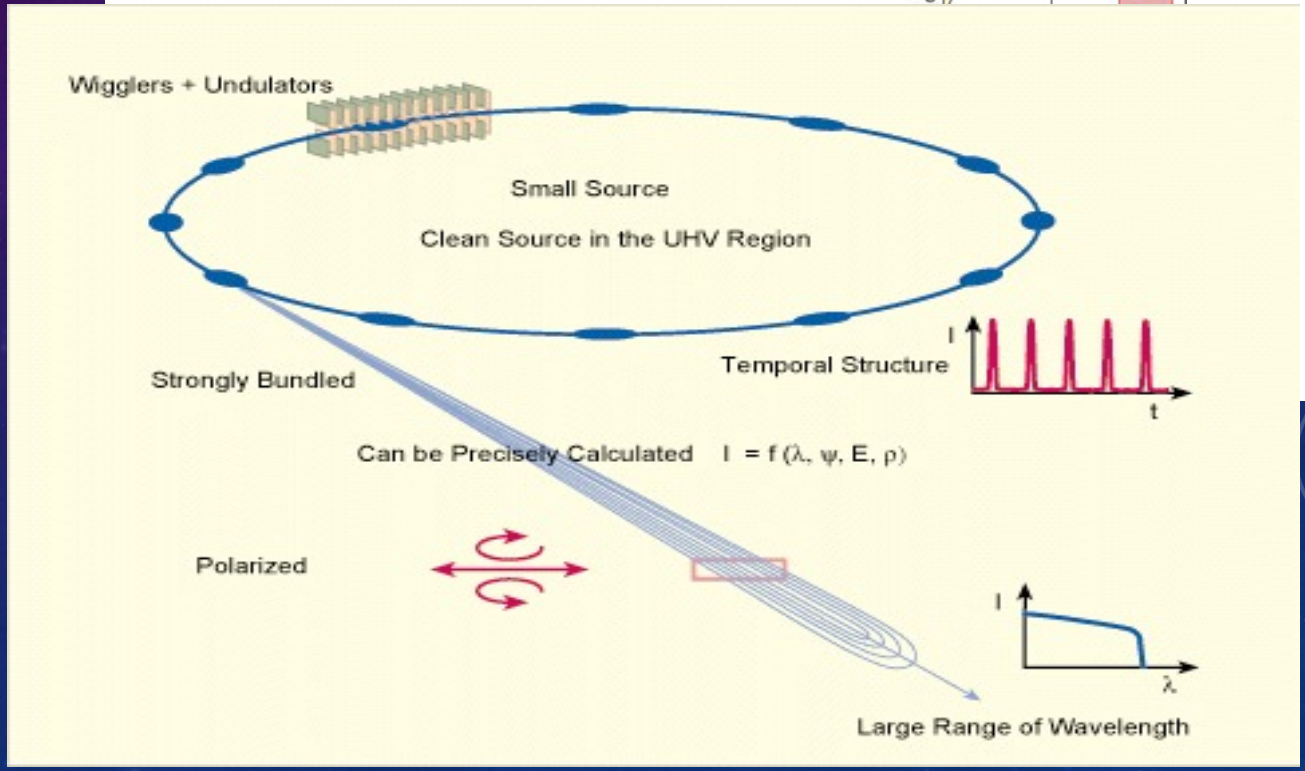
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Versatile tool for X-ray production

SYNCHROTRON RADIATION

- **Tunable Energy** (Element Selective)
- **High Intensity** (High energy resolution)
- Time Structure
- **Polarization** (Symmetry control)
- Coherence
- Focalisation





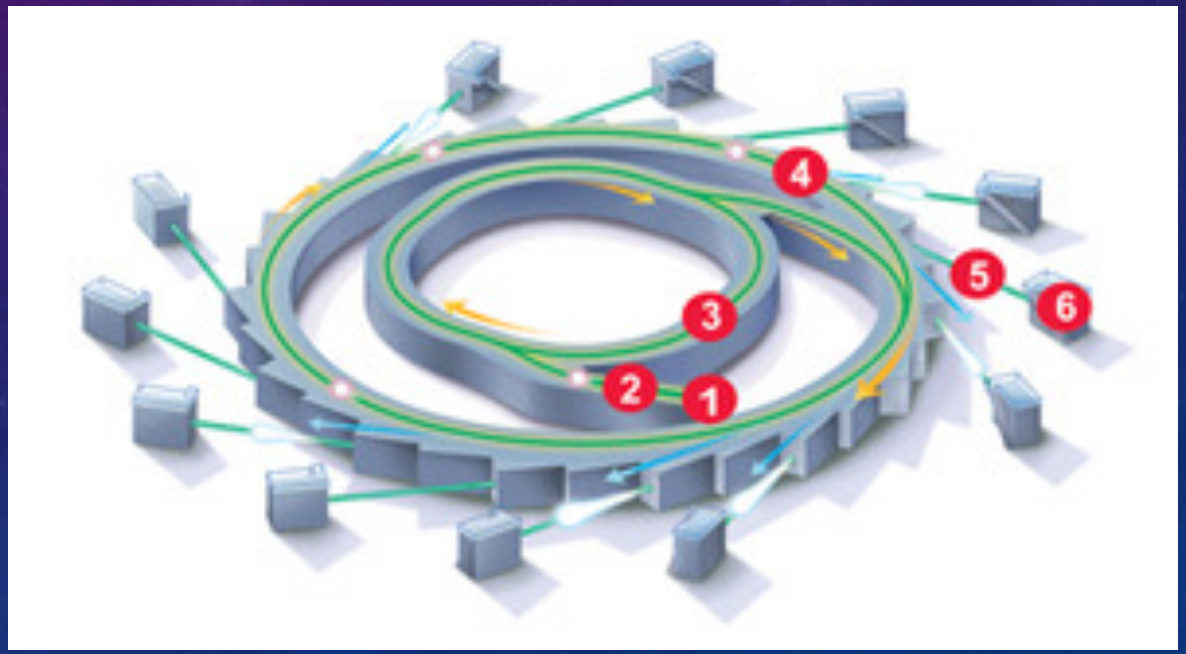
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Why Synchrotron Radiation: Facility for users

Costs, average 1000/4000 euro/hour
Experiments have time limit, fixed time window

- 70% beamtime open to external users
- Program committee, external members
- Annual Budget: 30/200 M€
- 700/2000 users/yrs
- 50% users from abroad
- Staff: 400 persons
- 24/24 h, >5000 hrs/yr

1. electron gun
2. linac
3. booster ring
4. storage ring
5. beamline
6. end station



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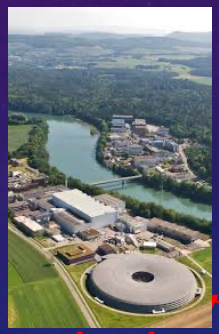
The playground(s)

SYNCHROTRON RADIATION FACILITIES



Exploiting and Exploring
the relevant
Time, Length, Energy scale





SLS
Switzerland



SPring8 - Japan



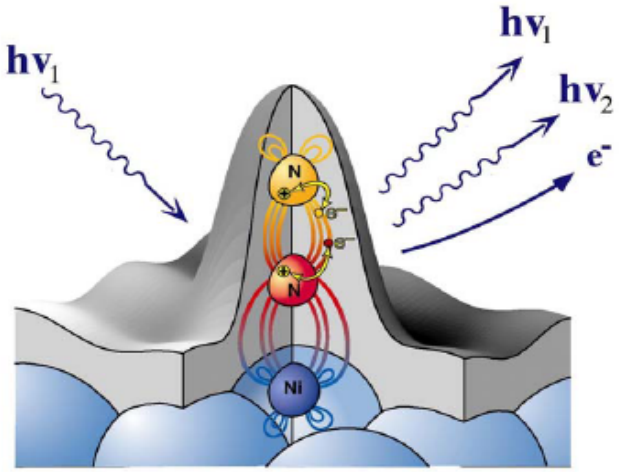
ELETTRA- Italy



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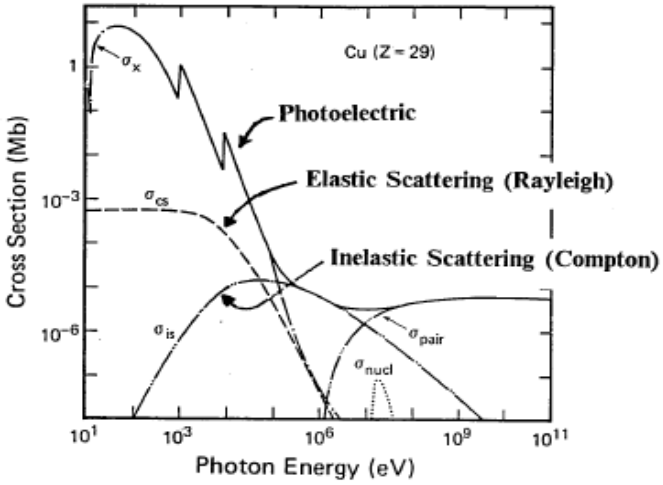
Photon Interaction

Incident photon interacts with electrons
Core and Valence



- Photon is
  - Adsorbed
  - Elastic Scattered
  - Inelastic Scattered
- Electron is
  - Emitted
  - Excited
  - Dexcitated

Cross Sections



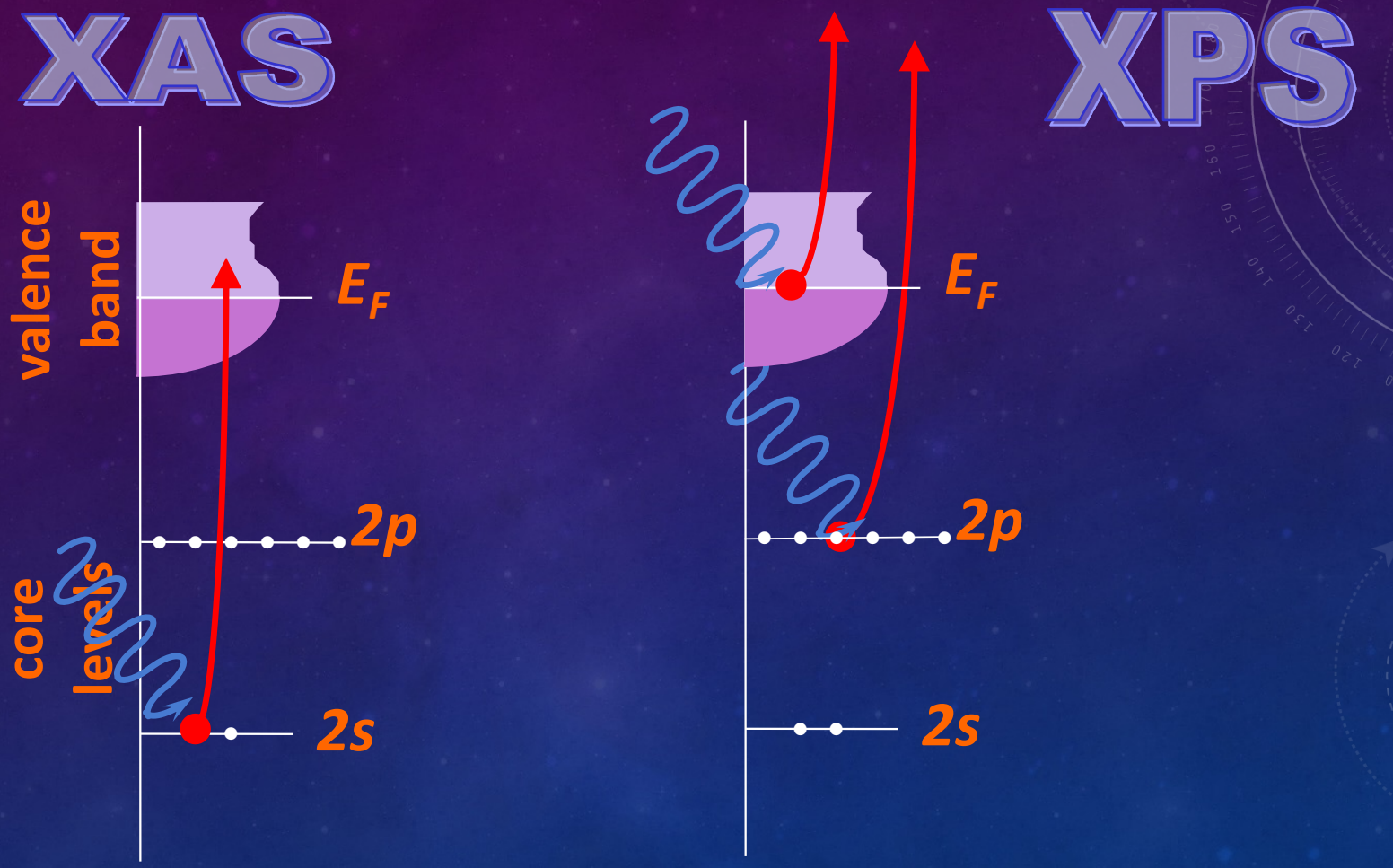
Stöhr, NEXAPS spectroscopy

Below 100 keV

Photoelectric cross section dominates

Spectroscopy

Electron spectroscopies with Synchrotron Radiation

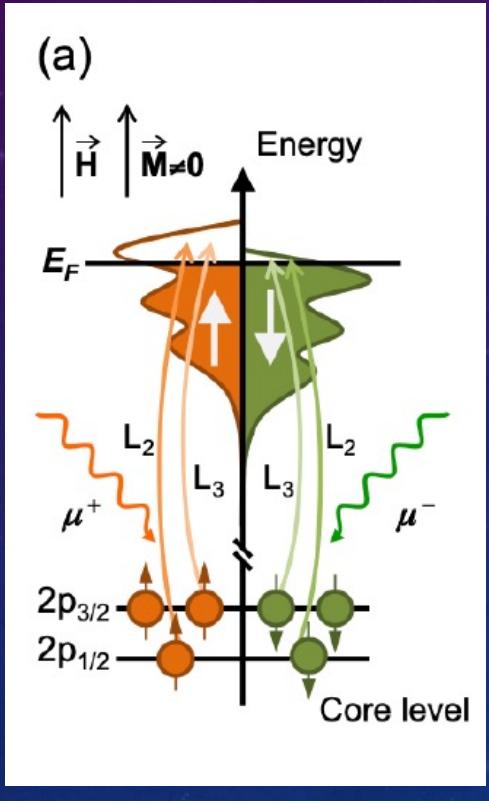


Courtesy of J. Vogel, CNRS, Grenoble, France

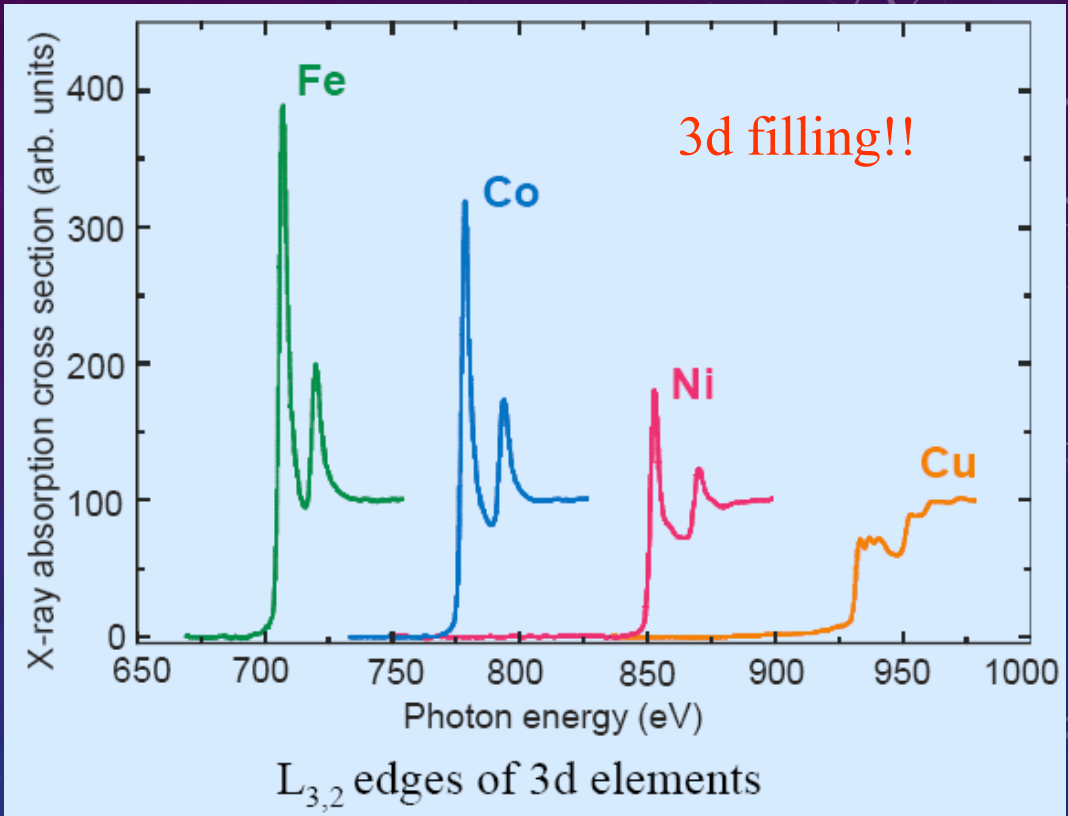
X-ray Absorption Spectroscopy

Dipole selection rules: $\Delta l = \pm 1$

K-edge: 1s → empty *p*-states
$L_{2,3}$-edges: $2p_{1/2,\,3/2}$ → empty *d (s)* -states
$M_{4,5}$ -edges: $3d_{3/2,\,5/2}$ → empty *f (p)* -states



Transition Metal $L_{2,3}$-edges: the white lines



$L_{3,2}$ edges of 3d elements

Absorption process: an electron is promoted from the core shell to the empty states of the valence band

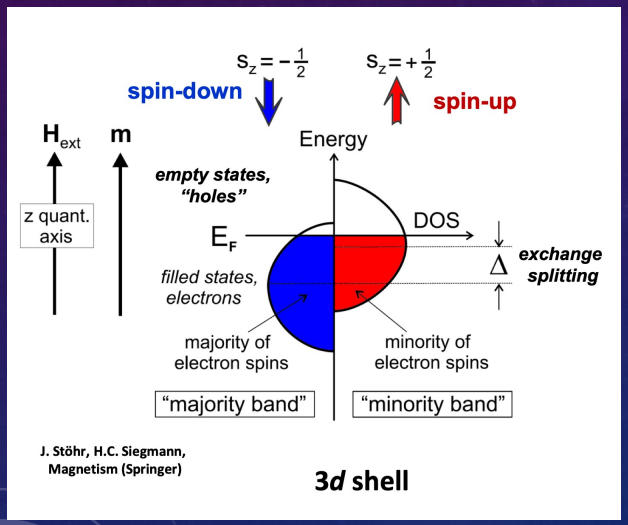
Courtesy of J. Vogel, CNRS, Grenoble, France

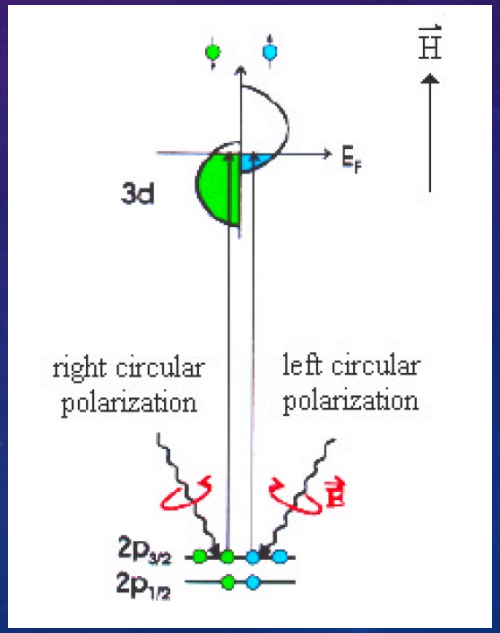
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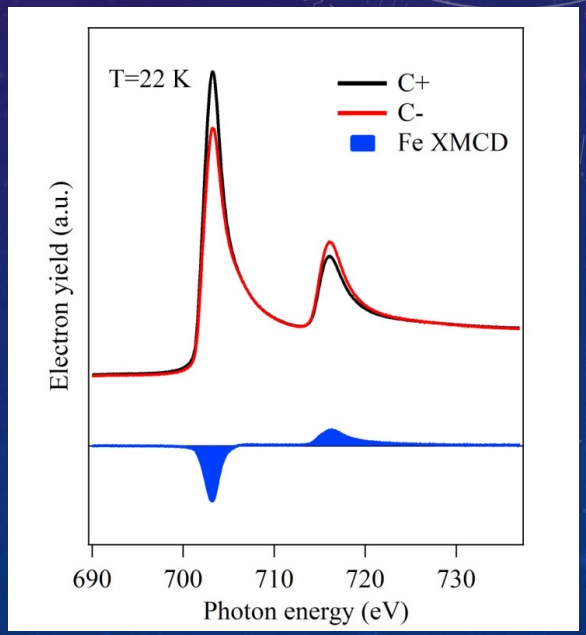
Magnetism and XAS: ingredients

J. Stöhr, S. Anders, IBM J. RES. DEVELOP.VOL. 44 N. 4 (2000)

- The **d shell has a spin moment** which is given by the imbalance of spin-up and spin-down electrons
- The photon helicity couples to electron spin via spin-orbit
(helicity defines a symmetry = mirror experiment / dichroism)
- Spin-up/down photoelectrons from the p core shell can only be excited into spin-up/down d hole states



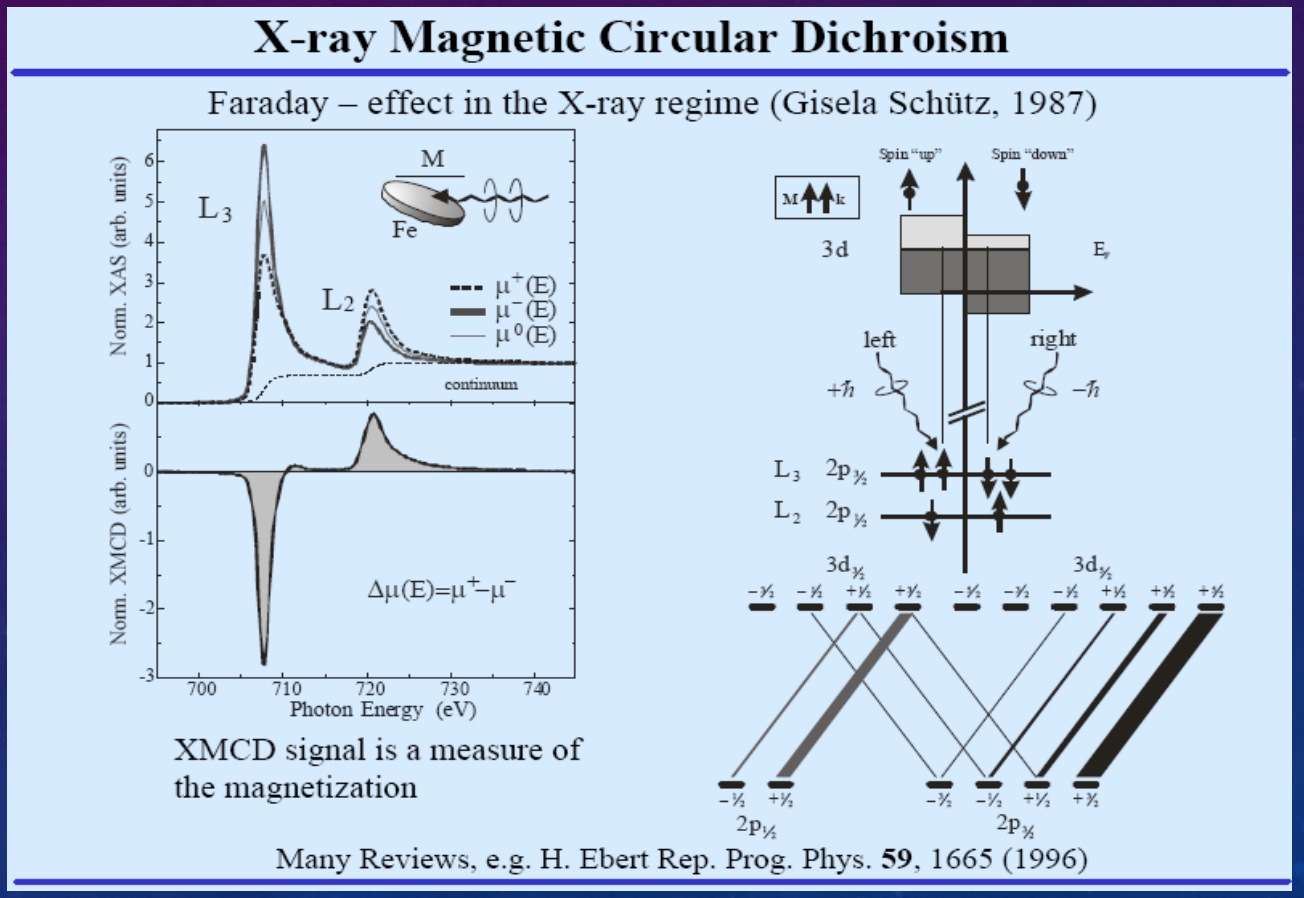




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XMCD- X-ray Magnetic Circular Dichroism

Direct measure
of local moments
(spin and orbital)
+
Measure of
Long range magnetization



Gisela Schütz et al. in 1987
P.T. Thole, et al.. Rev. Lett. 68, 1943 (1992)
P.Carra, et al. Phys.Rev.Lett. 70, 694 (1993).
C.T.Chen,et al. , Phys.Rev.B 42, 7262 (1990).
G. van der Laan, Phys.Rev.B 55, 8086 (1997).
B.T.Thole et al., Phys.Rev.Lett. 68, 1943 (1992)
M.Altarelli, Phys.Rev.B 47, 597 (1993)

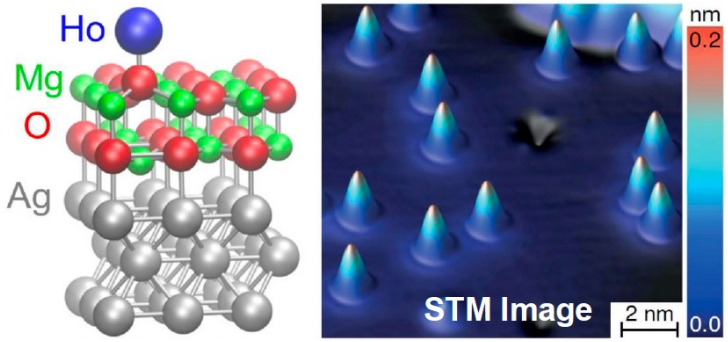
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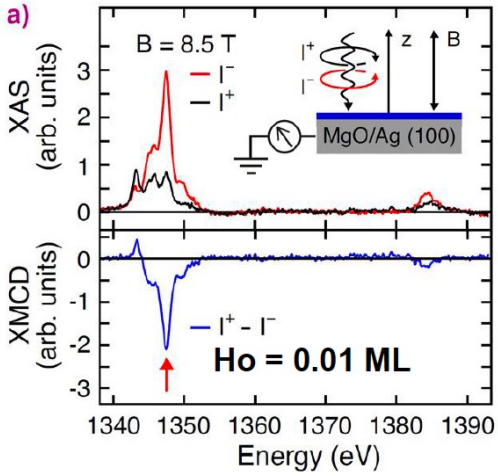
Courtesy of K.Baberschke, Freie Univ. Berlin

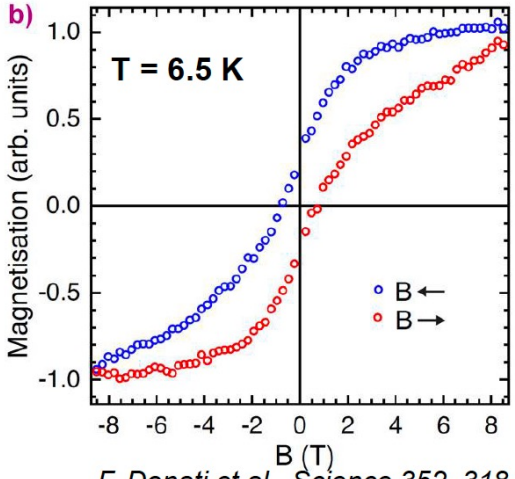
XMCD- X-ray Magnetic Circular Dichroism

SENSITIVITY OF XMCD: A SINGLE SURFACE-ADSORBED ATOM

Ho atoms on a two-monolayer-thick MgO film deposited on Ag(100)







ESRF ID32

F. Donati et al., Science 352, 318-321 (2016)

XMCD- **X-ray Magnetic Circular Dichroism**

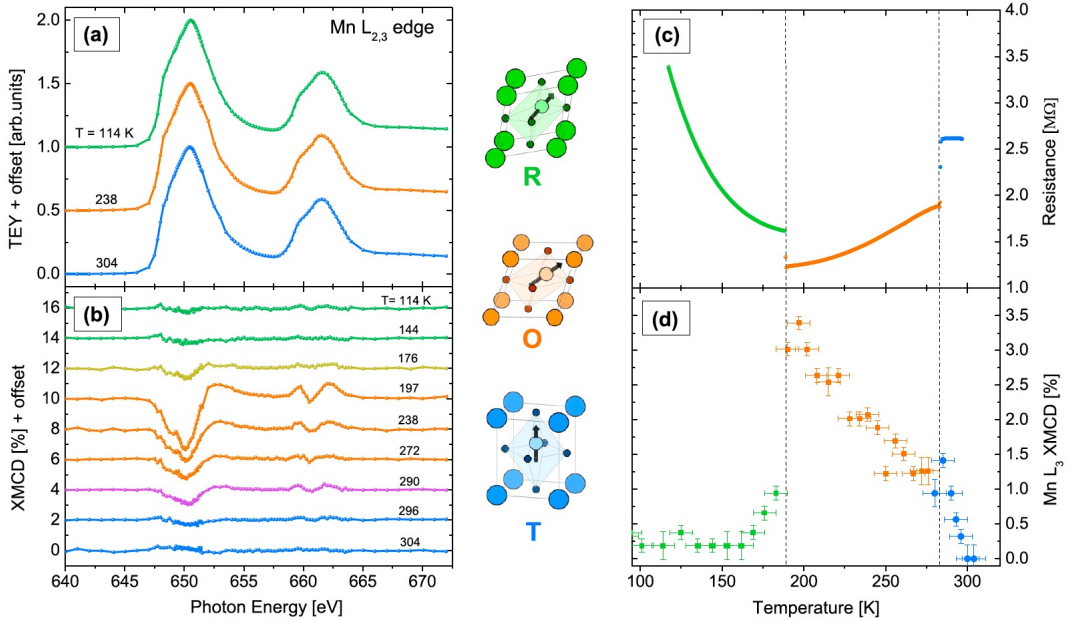
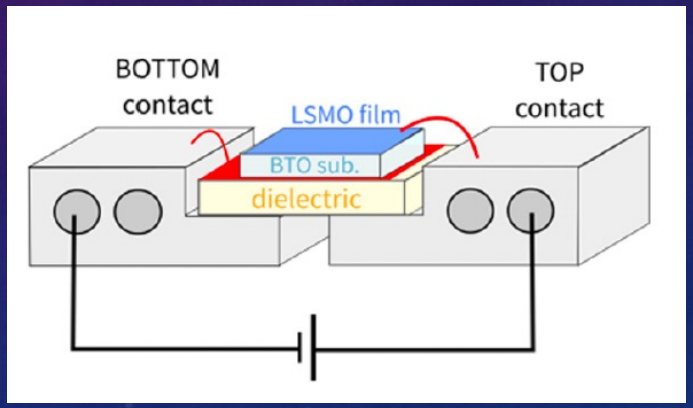


FIG. 2. Mn $L_{2,3}$ XAS (a) and XMCD (b) spectra acquired for various temperatures corresponding to different BTO structural phases, for the pristine case. The XAS curves shown are the sum of the two absorption spectra measured after magnetic field saturation with opposite field directions. Temperature dependence of LSMO/BTO resistance (c) and XMCD signal on the Mn L_3 edge (d) with BTO in the pristine state. Dashed lines correspond to BTO structural transitions.

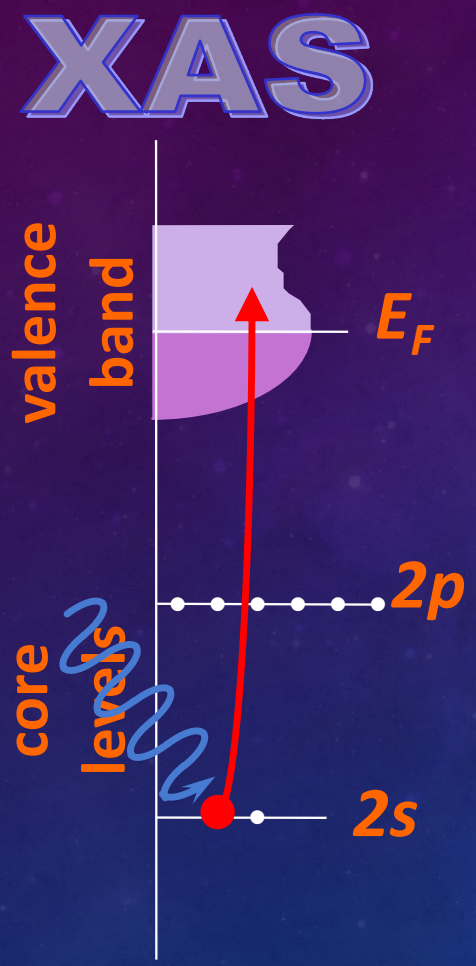
Strain-induced FM properties in LSMO film

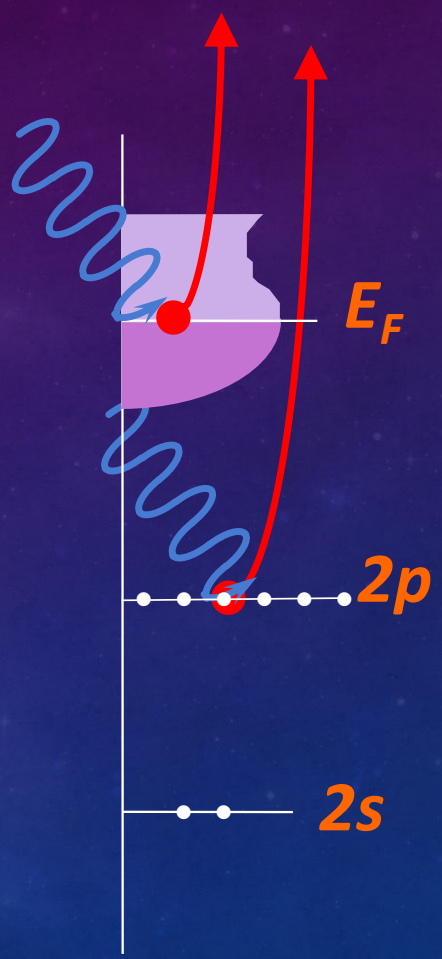


ISTITUTO OFFICINA DEI MATERIALI

F. Motti et al. Phys. Rev. 97, 094423 (2018)

Electron spectroscopies with Synchrotron Radiation





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Courtesy of J. Vogel, CNRS, Grenoble, France

1950: Birth of PhotoElectron Spectroscopy (PES-ESCA-XPS)

PHYSICAL REVIEW VOLUME 105, NUMBER 5 MARCH 1, 1957

Precision Method for Obtaining Absolute Values of Atomic Binding Energies

CARL NORDLING, EVELYN SOKOLOWSKI, AND KAI SIEGBAHN
Department of Physics, University of Uppsala, Uppsala, Sweden
(Received January 10, 1957)

WE have recently developed a precision method of investigating atomic binding energies, which we believe will find application in a variety of problems in atomic and solid state physics. In principle, the method is an old one: a magnetic analysis of electrons expelled from a substance exposed to x-radiation. Previous attempts in this direction have, however, given considerably less information about atomic structure than ordinary x-ray spectroscopic experiments, and some twenty years ago the method seems to have been definitely abandoned. We have introduced a number of improvements, both regarding the intensity and, in particular, the accuracy (a factor 100), which now enables us to measure atomic binding energies with an accuracy of one single electron volt from microgram quantities. The definition of the lines is essentially limited by the natural line widths of the atomic levels themselves. There is no shift of the lines due to electron scattering or similar causes, which could introduce systematic errors.

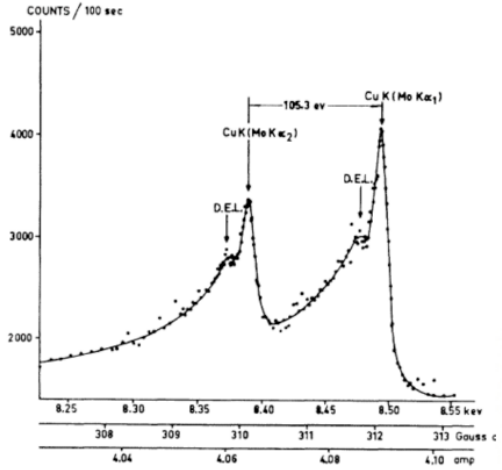


FIG. 1. Lines resulting from photoelectrons expelled from Cu by Mo $K\alpha_1$ and Mo $K\alpha_2$ x-radiation. The satellites marked D.E.L. are interpreted as due to electrons which have suffered a discrete energy loss when scattered in the source.

The Nobel Prize in Physics 1981
Nicolaas Bloembergen, Arthur L. Schawlow, Kai M. Siegbahn

Share this: 18

The Nobel Prize in Physics 1981


Nicolaas Bloembergen
Prize share: 1/4


Arthur Leonard Schawlow
Prize share: 1/4


Kai M. Siegbahn
Prize share: 1/2

The Nobel Prize in Physics 1981 was divided, one half jointly to Nicolaas Bloembergen and Arthur Leonard Schawlow *"for their contribution to the development of laser spectroscopy"* and the other half to Kai M. Siegbahn *"for his contribution to the development of high-resolution electron spectroscopy"*.

Ideal tool for the chemical investigation of materials, expressed in the famous acronym created by Siegbahn: **ESCA** (Electron Spectroscopy for Chemical Analysis)

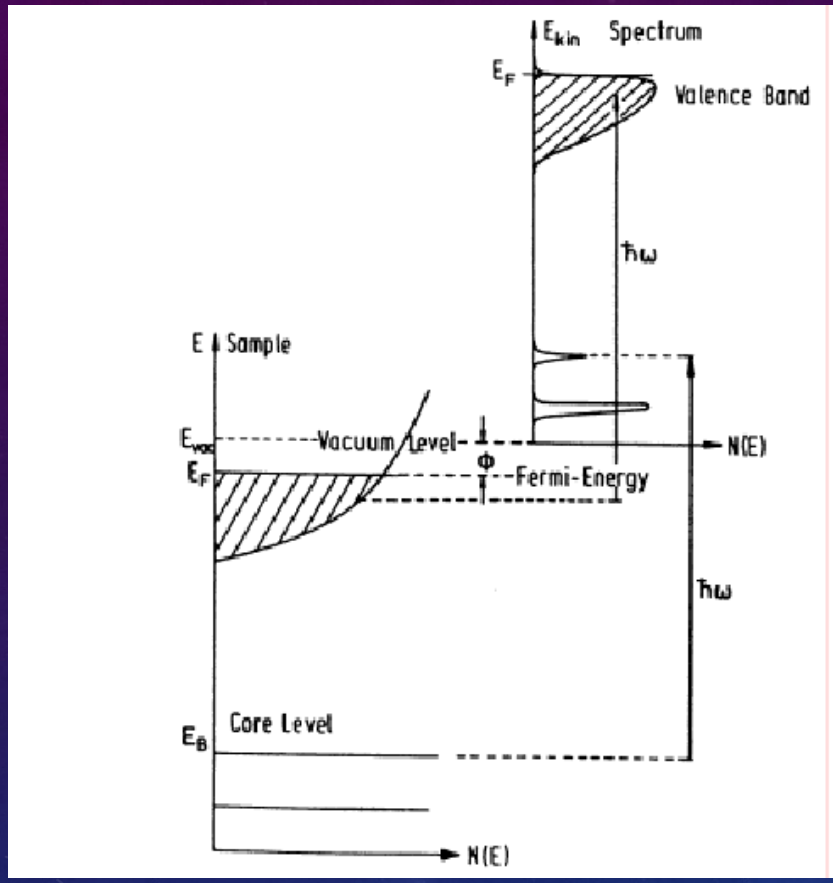
or

XPS – X-ray Photoelectron/Photoemission Spectroscopy

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Courtesy of I. Vobornik, CNR-IOM

ESCA: Electron Spectroscopy for chemical analysis



$$E_{kin} = \hbar\omega - \Phi - |E_B|$$

Measured Kinetic Energy

Measureed Photon Energy

Measured Work Function

Electron Binding Energy

Electron binding energy in a solid is ELEMENT SPECIFIC

Identification of element

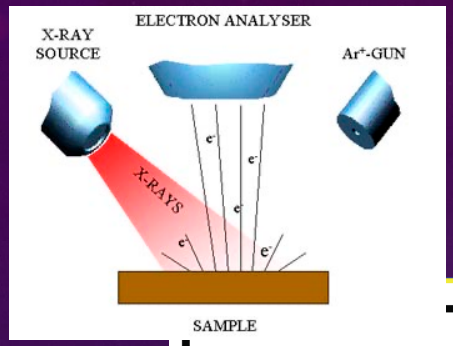
=

chemical sensitivity

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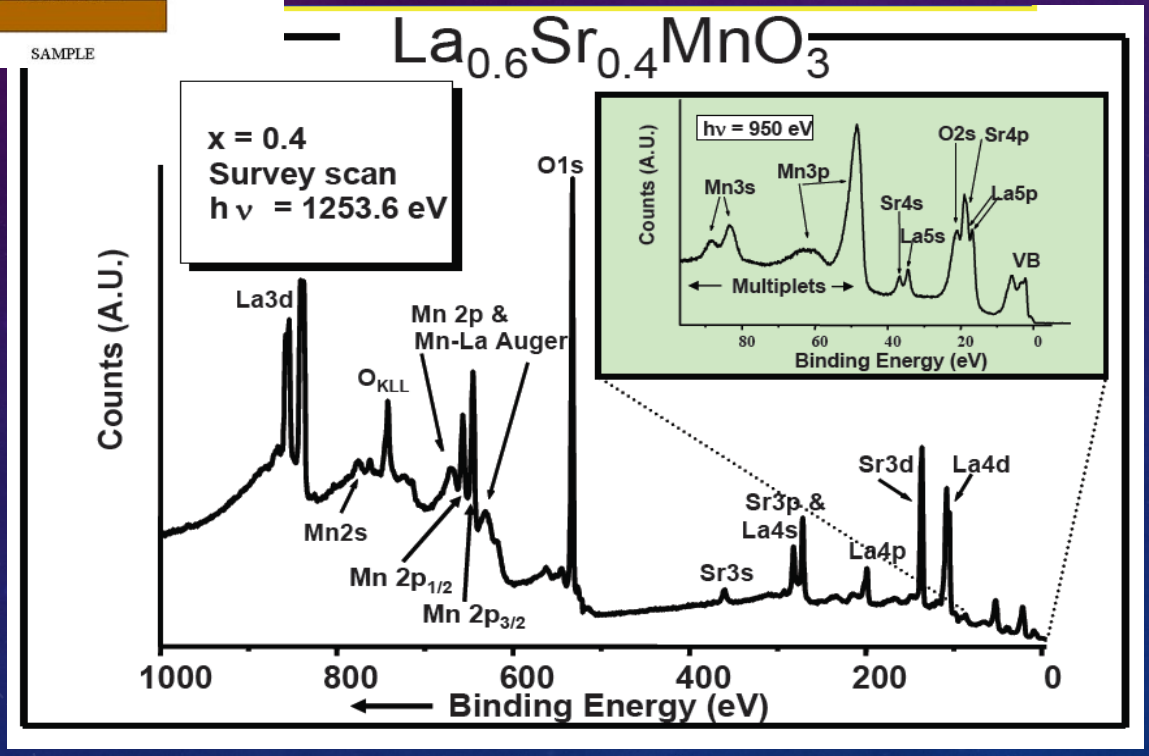
http://www-bl7.lbl.gov/BL7/who/eli/SRSchoolER.pdf

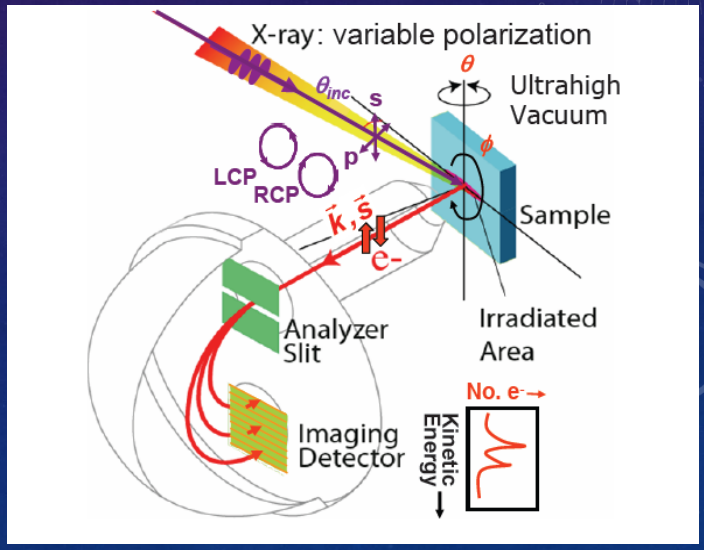
PhotoElectron Spectroscopy (PES) in a 'nutslide'



$$E_{kin} = h\nu - \phi - |E_B|$$

- Magnetic sensitivity (circular polarization or spin detection)
- Chemical sensitive (**Surface AND bulk**)



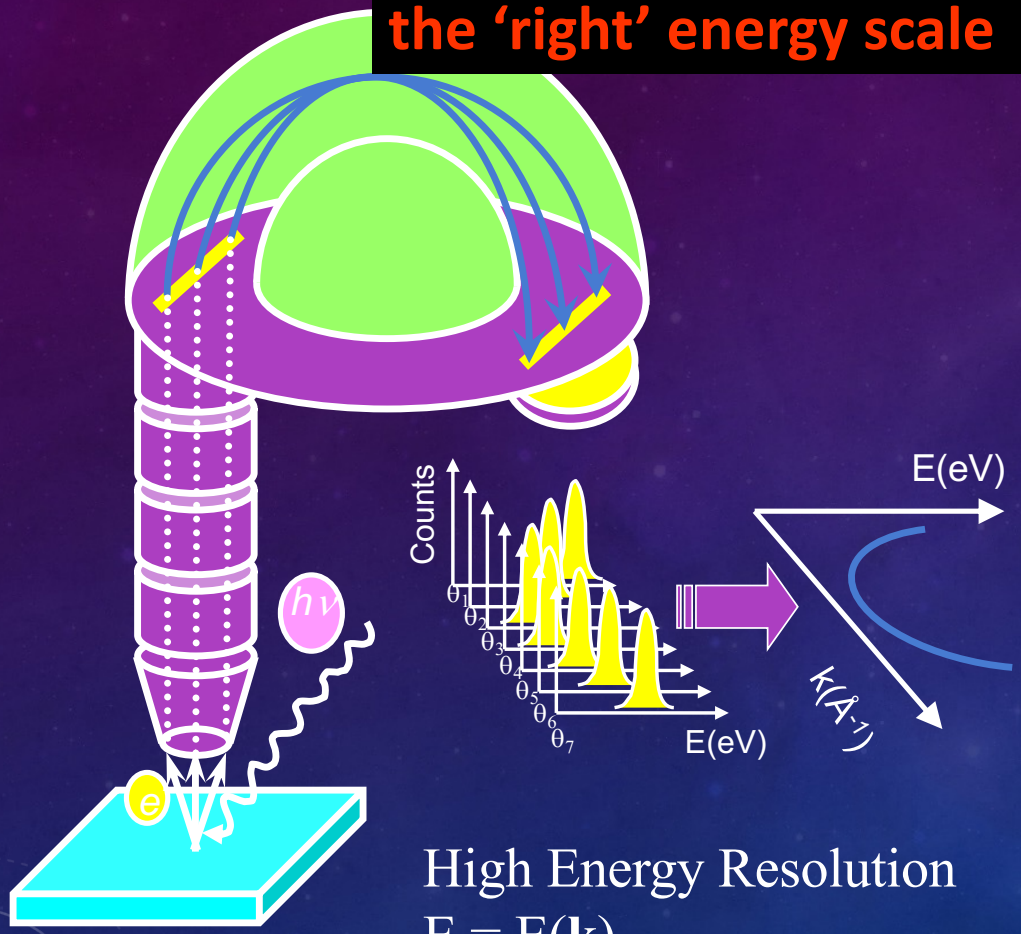


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For a review, see e.g. P.D.C. King et al , Chem. Reviews 2021, 121, 2816 (2021)

OK….in two ‘nutslides’

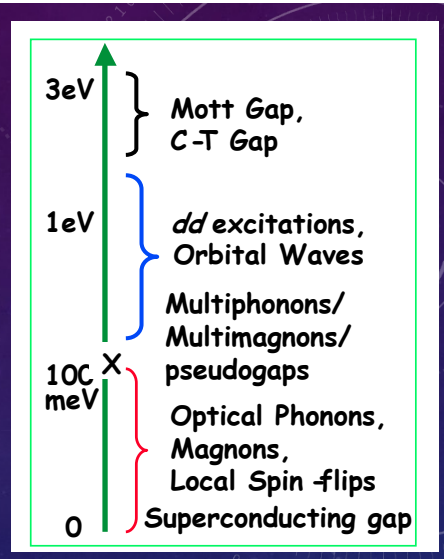
the ‘right’ energy scale



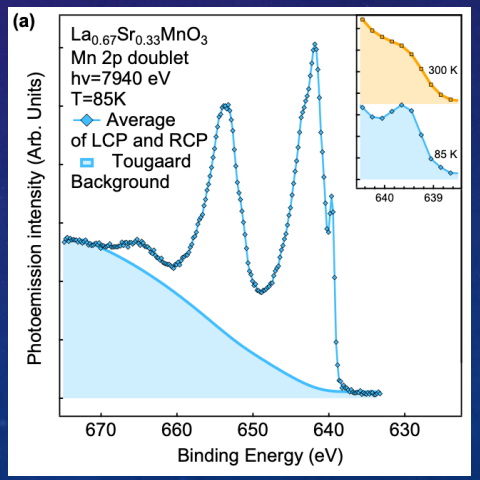
High Energy Resolution

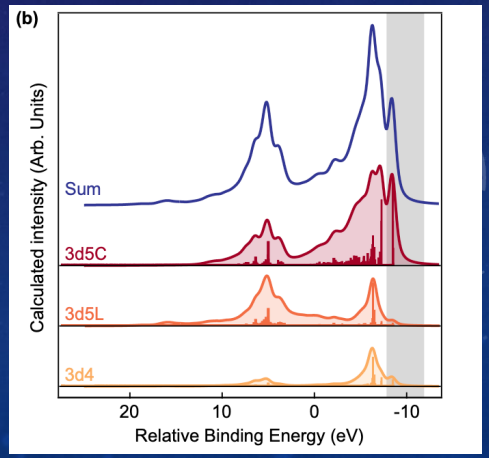
$E = E(\mathbf{k})$

- Superconducting gap ~ 1 - 100meV
- Optical Phonons: ~ 40 - 70 meV
- Magnons: ~ 10 meV - 40 meV
- Pseudogap ~ 30-300 meV
- Multiphonons and multimagnons ~ 50-500 meV
- Orbital fluctuations (originated from optically forbidden d-d excitations): ~100 meV-1.5 eV



(almost) Straightforward comparison with theory

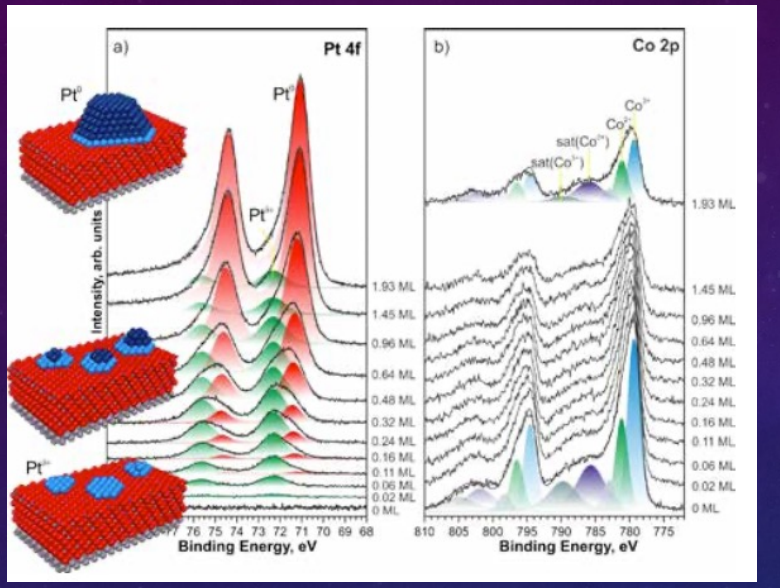




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Monitoring vs. surface environment (interfaces and adsorbates)

Evolution in $Pt/Co_3O_4(111)$



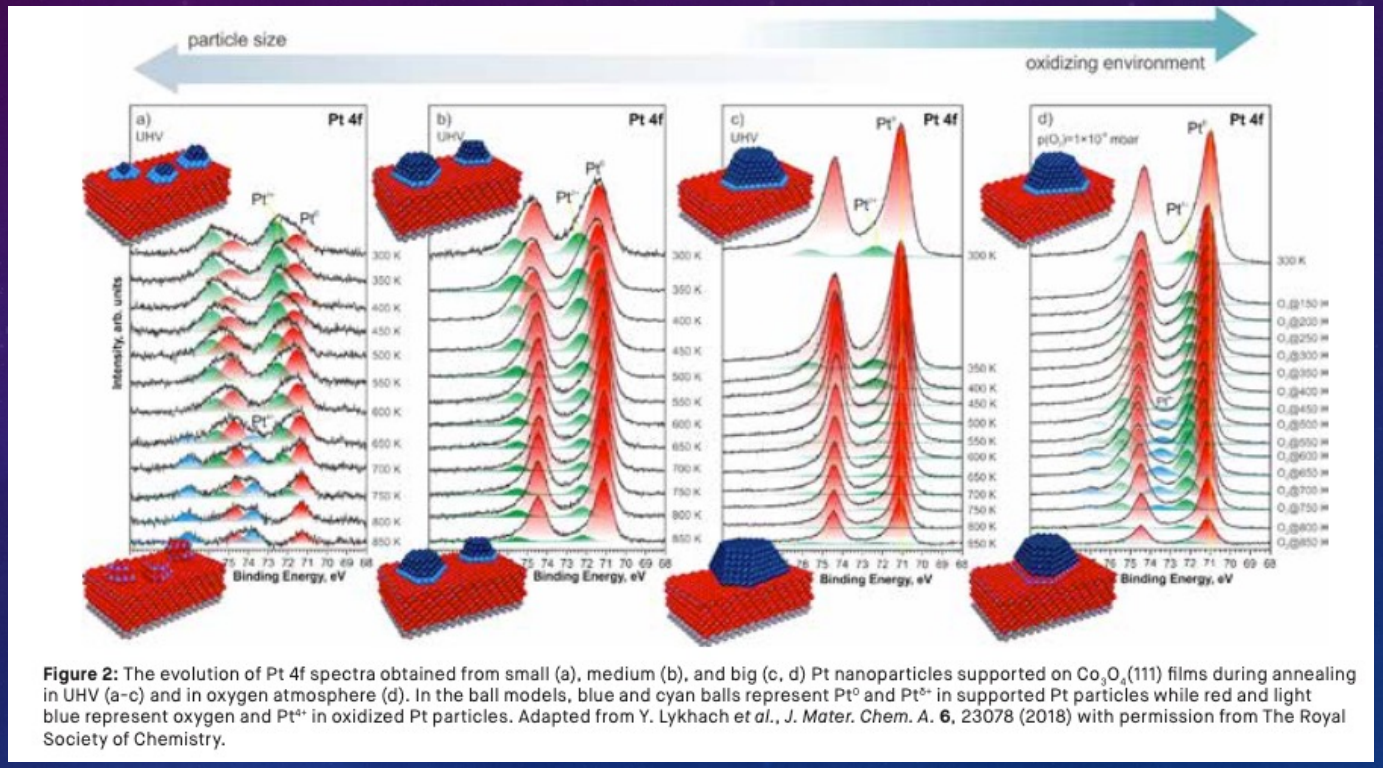


Figure 2: The evolution of Pt 4f spectra obtained from small (a), medium (b), and big (c, d) Pt nanoparticles supported on $Co_3O_4(111)$ films during annealing in UHV (a–c) and in oxygen atmosphere (d). In the ball models, blue and cyan balls represent Pt^0 and $Pt^{\delta+}$ in supported Pt particles while red and light blue represent oxygen and Pt^{4+} in oxidized Pt particles. Adapted from Y. Lykhach *et al.*, *J. Mater. Chem. A.* **6**, 23078 (2018) with permission from The Royal Society of Chemistry.

ISTITUTO OFFICINA DEI MATERIALI

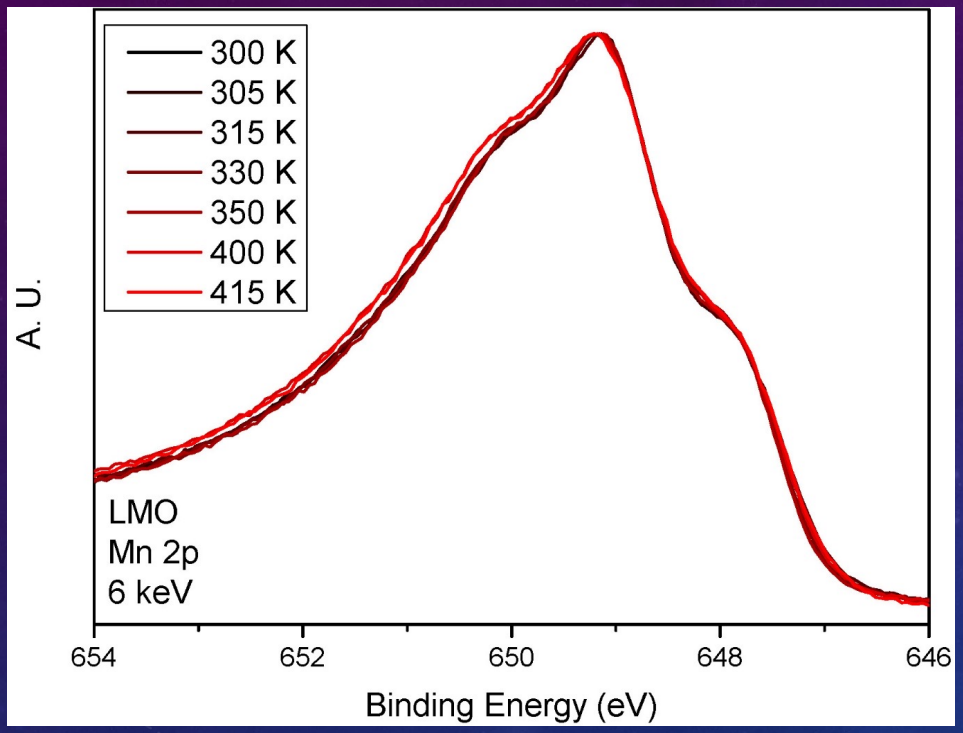
Y. Lykhach et al. J. Mater. Chem. A. 6, 23078 (2018)
Elettra Highlights 2019

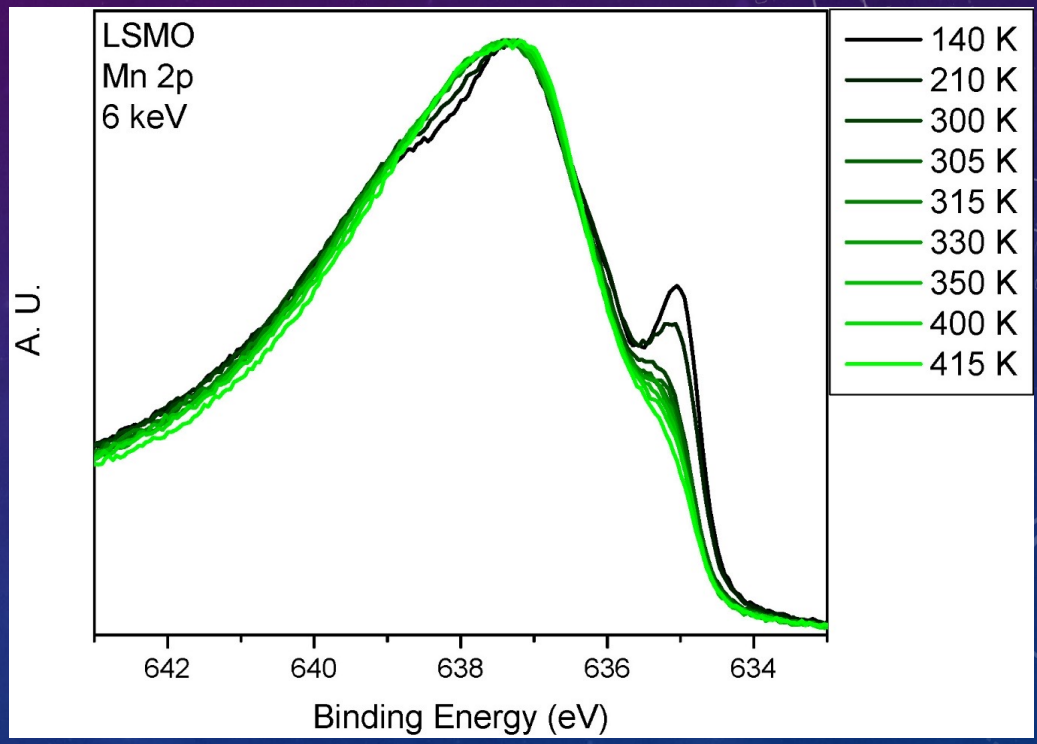
Evolution as a function of temperature: phase transition

Spectral change across the metal-insulator transition

Mn 2p core level vs temp.

$La_{0.65}Sr_{0.35}MnO_3$ 100 u.c.





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T. Pincelli et al. Nat. Comm. **8**, 16051 (2017)

Circular Dichroism in PES: access to magnetism

G. van der Laan / Journal of Electron Spectroscopy and Related Phenomena 200 (2015) 143–159

Zen and the art of dichroic photoemission

Gerrit van der Laan

Magnetic Spectroscopy Group, Diamond Light Source, Didcot OX11 0DE, United Kingdom

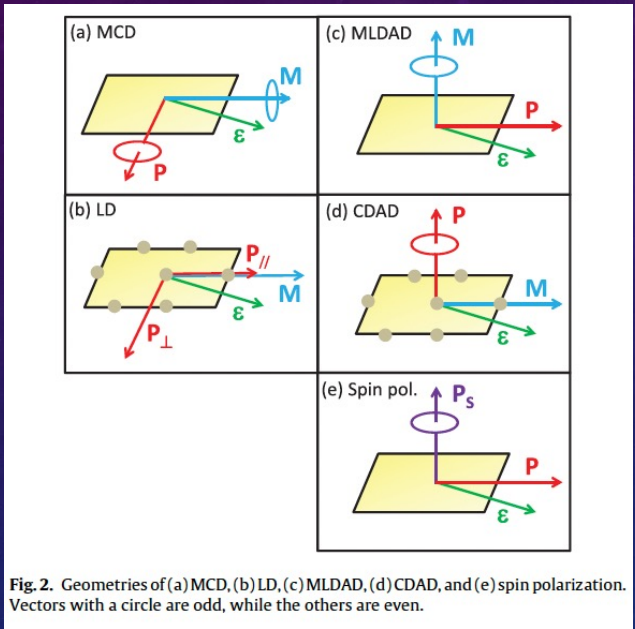
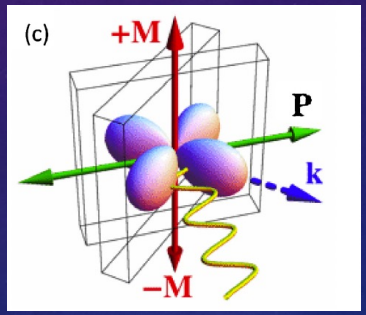
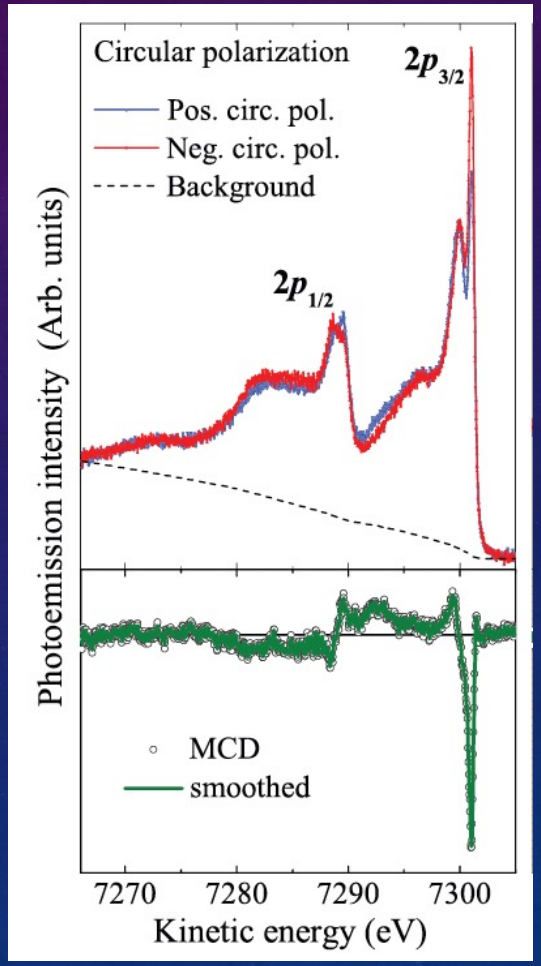


Fig. 2. Geometries of (a) MCD, (b) LD, (c) MLDAD, (d) CDAD, and (e) spin polarization. Vectors with a circle are odd, while the others are even.





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J. Fujii et al. PRL111 (2013) 097201.

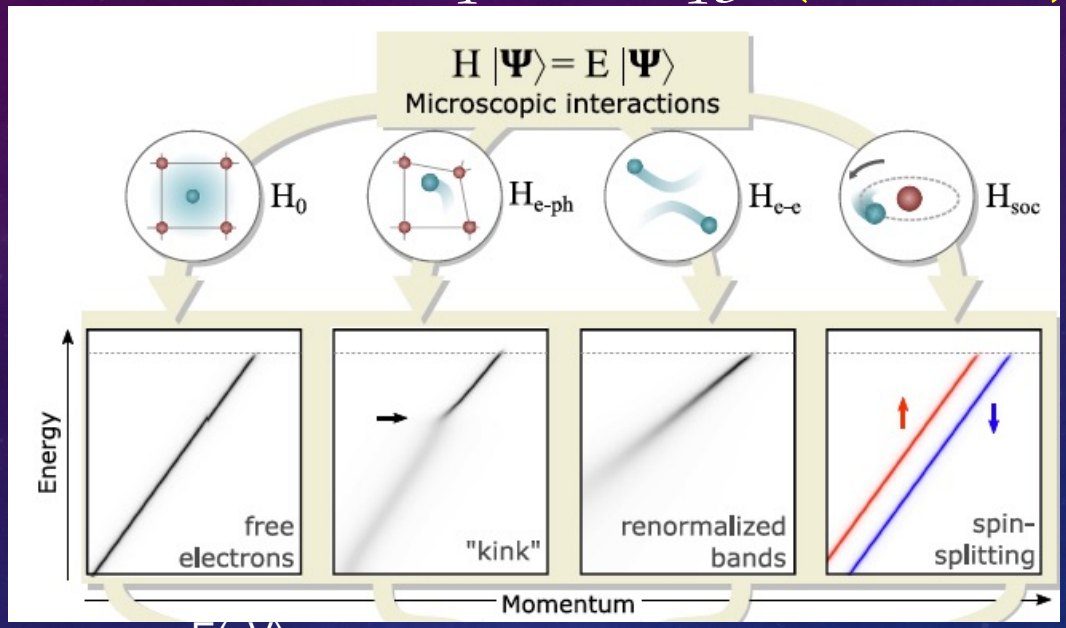
Why PES? Direct access to the electronic bands in a solid



Why PES? . (‘vision’ of interaction in a solid)

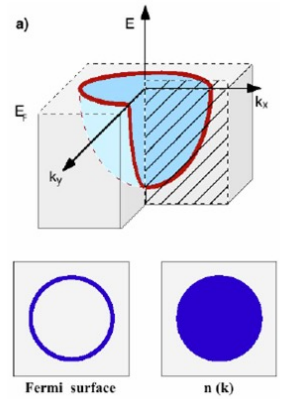
Angular Resolved PhotoElectron Spectroscopy (ARPES):

The k space

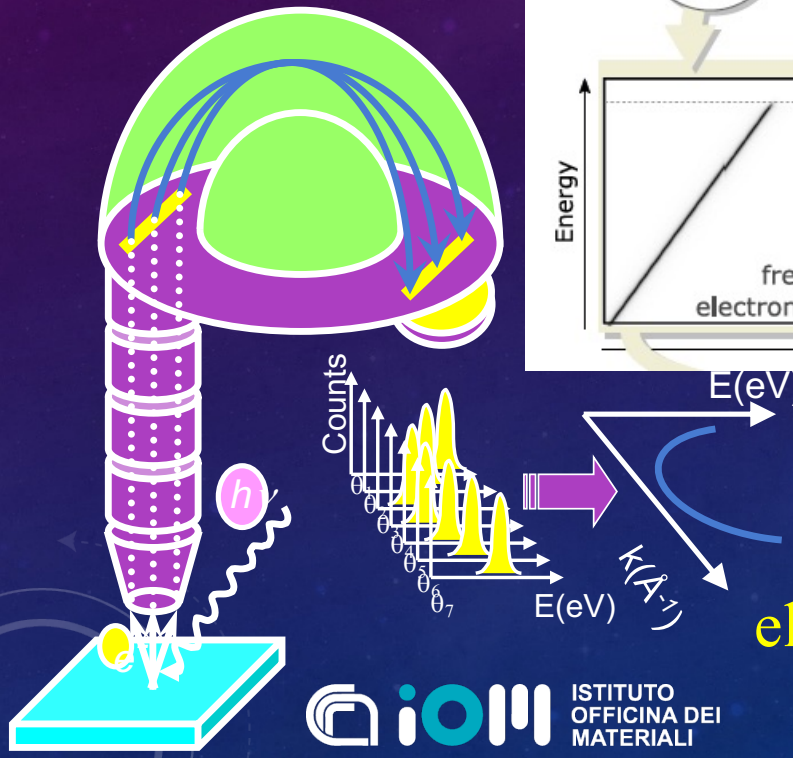


Courtesy of A. Damascelli

Many properties of solids are determined by valence electrons near E_F (conductivity, superconductivity, magnetoresistance, magnetism …)



Only a narrow energy slice around E_F is relevant for these properties (KT=25 meV at room temperature)

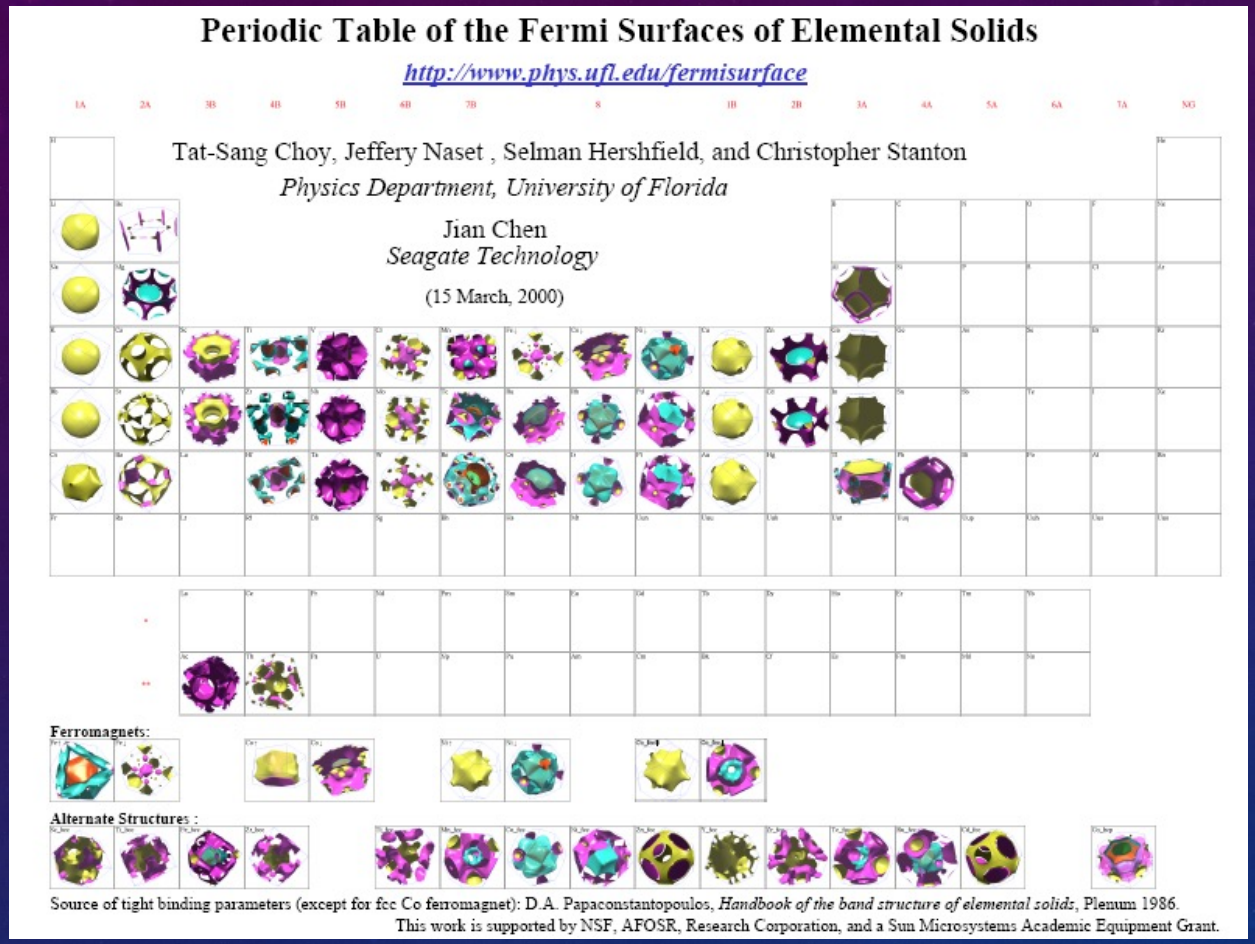


Direct access to k space enables study of electrons ‘dressed’ by interactions

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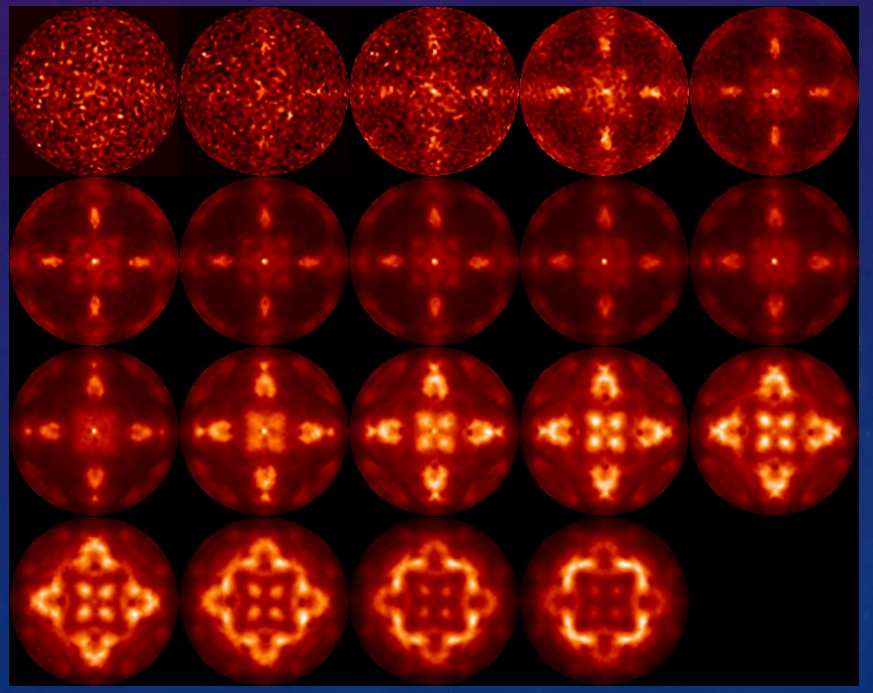
J.A. Sobota et al. Rev. Mod. Phys. 93, 025006 (2021)
P.D.C. King et al , Chem. Reviews, 121, 2816 (2021)

ARPES: the Fermi surface



https://www.youtube.com/watch?v=BejOga-L4kw
ARPES visualization

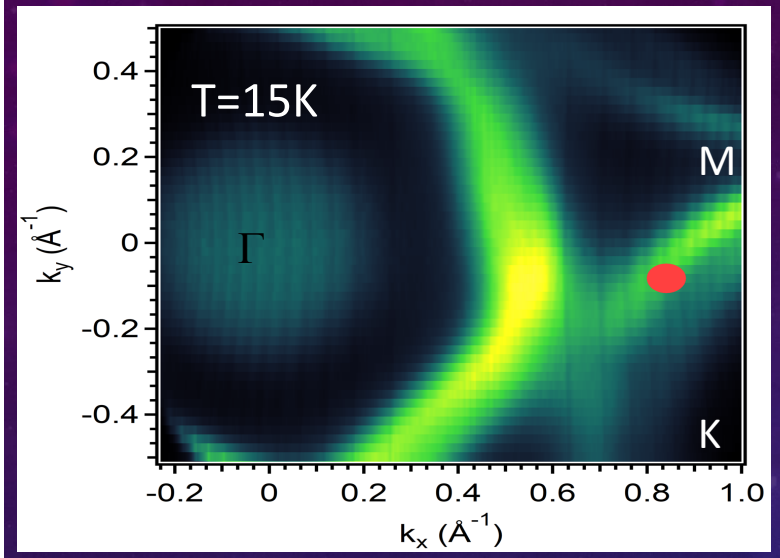
Fe(100) fermi surface cut



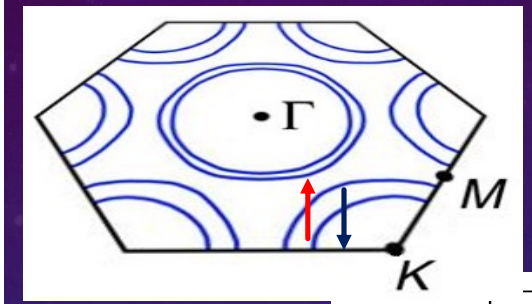
APE-LE beamline CNR-IOM @Elettra

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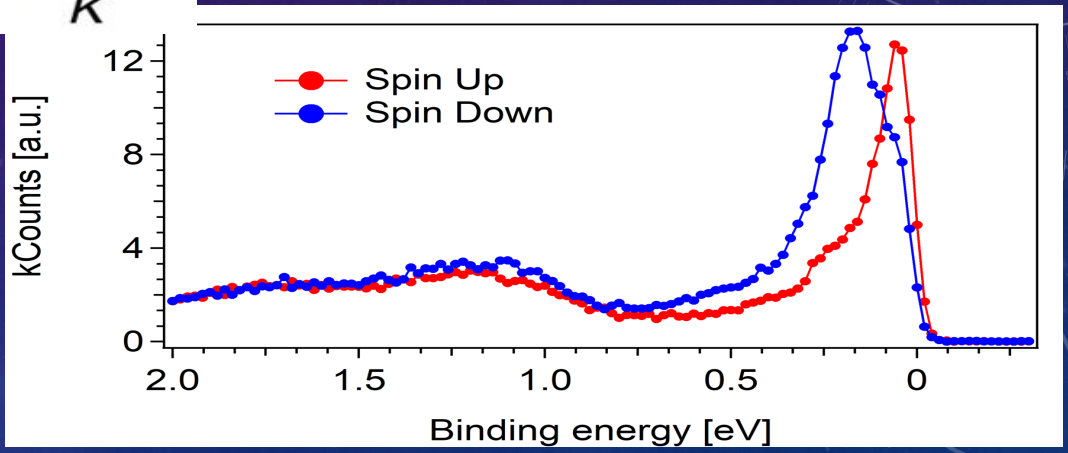
Specialization of ARPES: Spin- Resolved ARPES



$NbSe_2$ Fermi Surface and spin texture



Out of plane spin polarization





C. Bigi et al. JSR 24, 750 (2017)
C. Bigi et al. PRB 103, 245142 (2021)
J. M. Riley et al. Nature Nanot. **10**, 1043 (2015)
L. Bawden et al. Nature Comm. **7**, 11711 (2016)

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FUTURE: Time resolved PES

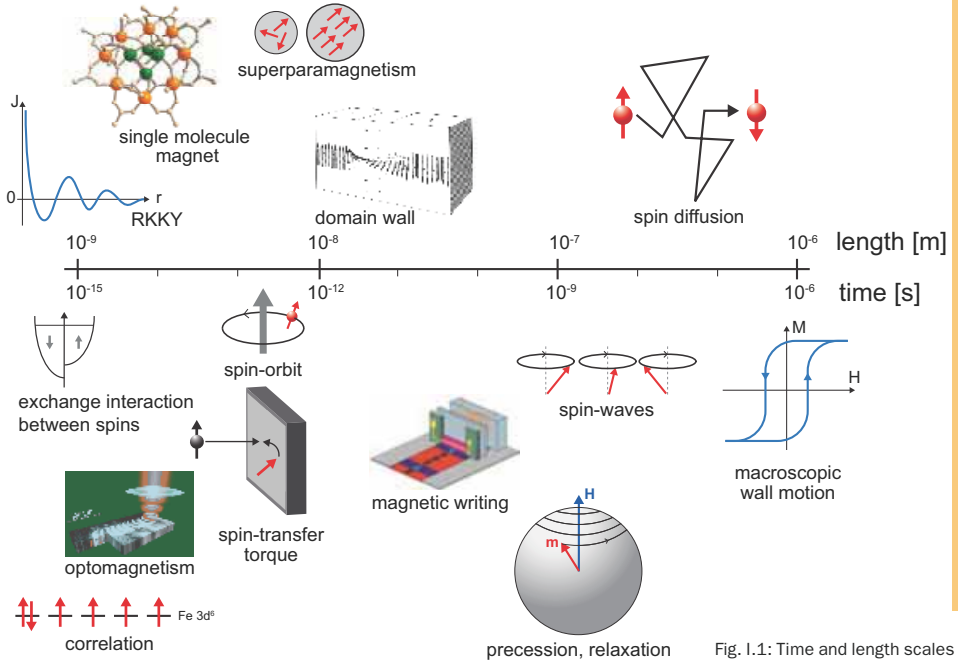


Fig. I.1: Time and length scales in magnetism.

Atomic moment reversal due to field- or current-induced domain wall motion, with a velocity of ~ 100 m/s	d_{wall}/v_{wall} ~ **200 ps**
Magnetization precession and damping, according to the LLG-equation (see Infobox)	~ **50 ps**
Spin-orbit interaction between the electron spin and its orbital motion	1–100 meV → τ ~ **50–5000 fs**
Jahn-Teller interaction, which stabilizes an elastic distortion to avoid a degenerate electronic ground-state	~ 50 meV → τ ~ **100 fs**
Spin-wave energy, at intermediate wave-vector	1–1000 meV, → τ **5–5000 fs**
Electrostatic crystal-field interaction of oriented 3d-orbitals with neighboring ions	~ 1 eV → τ ~ **5 fs**
Inter-electronic exchange energy *J* arising from the Pauli principle	~ 5 eV → τ ~ **1 fs**
Correlation energy, responsible within an atom for enforcing Hund's rules	~ 5 eV → τ ~ **1 fs**

Table I.2: Magnetic time scales

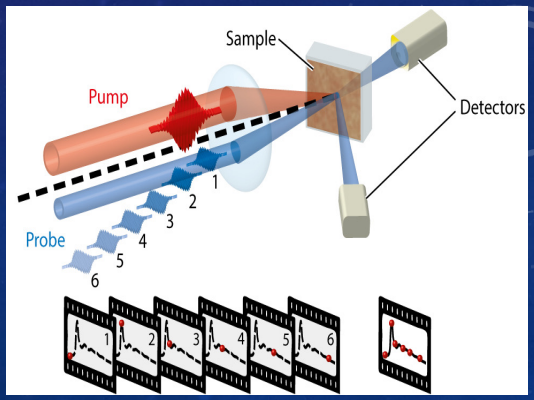
Pump-probe methods

The system is pumped again after each measurement.

The time between the excitation and the probe is scanned.

low probe fluence, spectroscopy

Time resolution is given by **pulse duration** and **timing accuracy**.



From SwissFEL science case

Opportunity (and challenge)

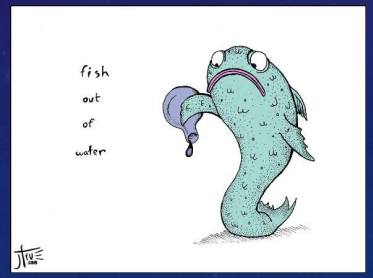
Decoupling spin-lattice-electrons due to different critical timescale

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Magnetic properties as seen by X-ray based Electron Spectroscopies (the basics of the game: PART 2)



Giancarlo Panaccione
Istituto Officina dei Materiali (IOM)
Consiglio Nazionale delle Ricerche (CNR)
Trieste, Italy



Examples on quantum materials and van der Walls systems

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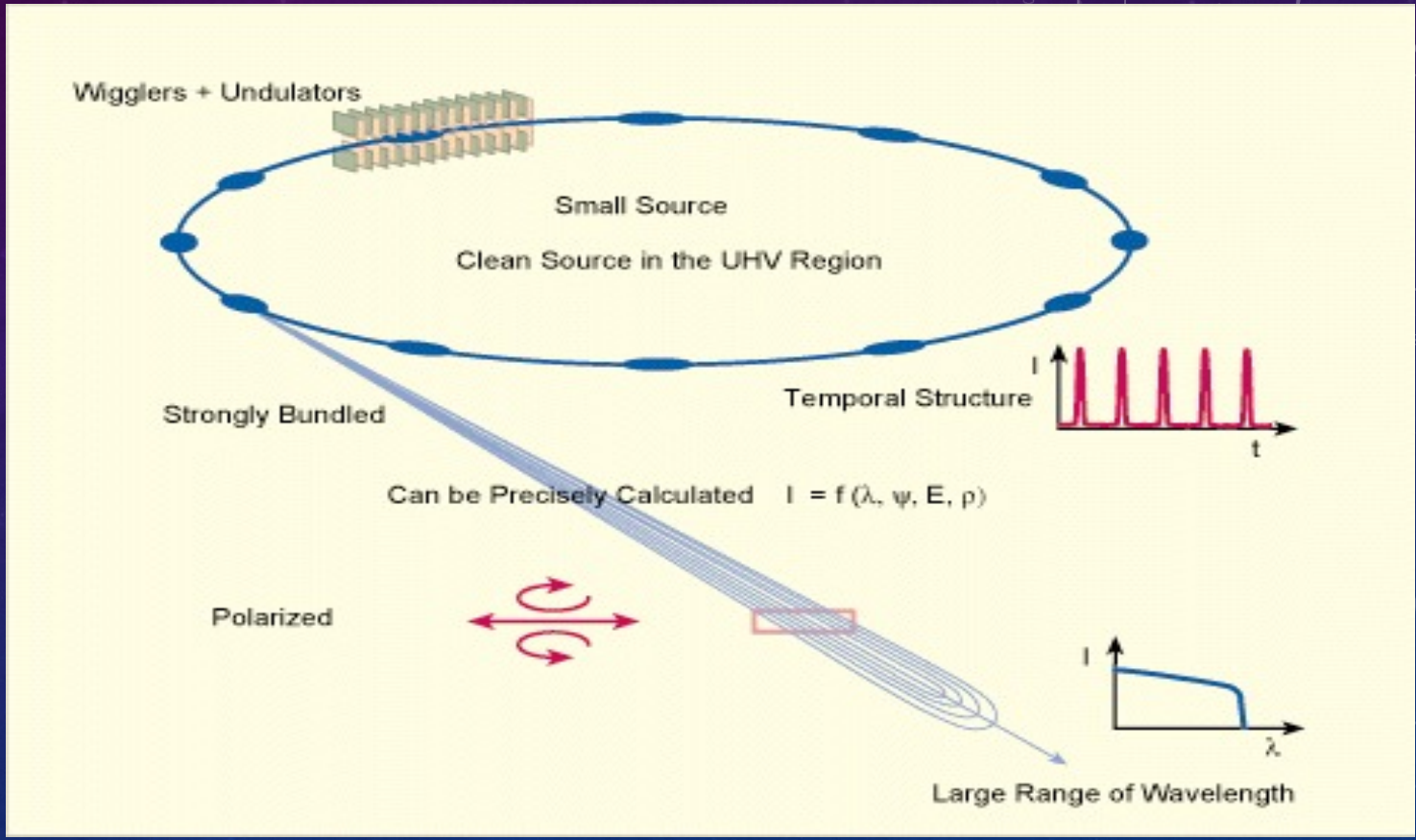
AIMagn - Associazione Italiana di Magnetismo

School on Magnetic Nanomaterials
Perugia
Oct 20th – 24th

SYNCHROTRON RADIATION

Versatile tool for X-ray production

- **Tunable Energy** (Element Selective)
- **High Intensity** (High energy resolution)
- Time Structure
- **Polarization** (Symmetry control)
- Coherence
- Focalisation



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Low-dimensional magnetic phenomena

generalized Heisenberg spin Hamiltonian

$$H = -\frac{1}{2}\sum_{i,j} J\boldsymbol{S}_i \cdot \boldsymbol{S}_j \quad +\Lambda S_i^z S_j^z - \sum_i A(S_i^z)^2$$

Exchange coupling

Exchange anisotropy

"On-site" anisotropy

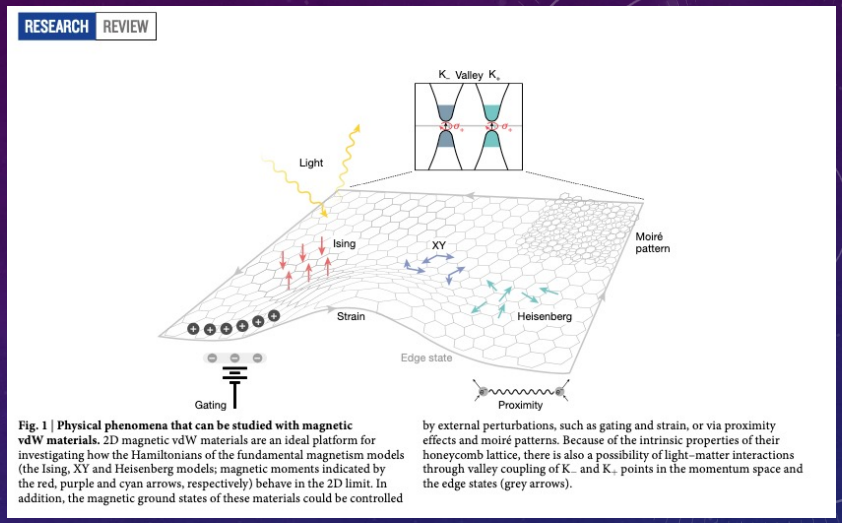
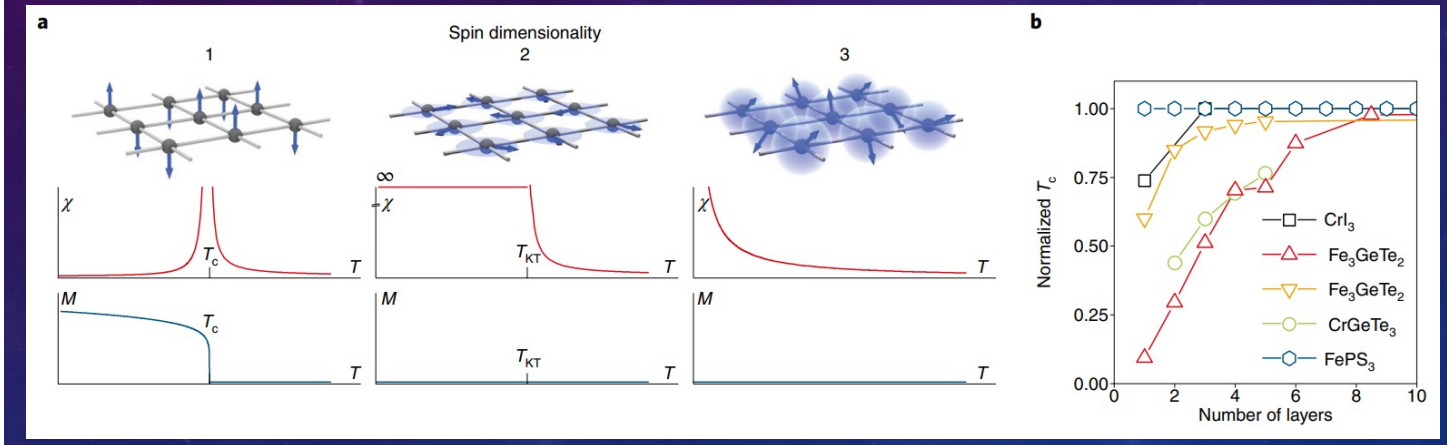


Fig. 1 | Physical phenomena that can be studied with magnetic vdW materials. 2D magnetic vdW materials are an ideal platform for investigating how the Hamiltonians of the fundamental magnetism models (the Ising, XY and Heisenberg models; magnetic moments indicated by the red, purple and cyan arrows, respectively) behave in the 2D limit. In addition, the magnetic ground states of these materials could be controlled by external perturbations, such as gating and strain, or via proximity effects and moiré patterns. Because of the intrinsic properties of their honeycomb lattice, there is also a possibility of light–matter interactions through valley coupling of K_ and K+ points in the momentum space and the edge states (grey arrows).



Long range magnetic order

Anisotropy

ISTITUTO OFFICINA DEI MATERIALI

See M. Gilbertini et al *Nat.. Nanotechnol.* **14**, 408–419 (2019).

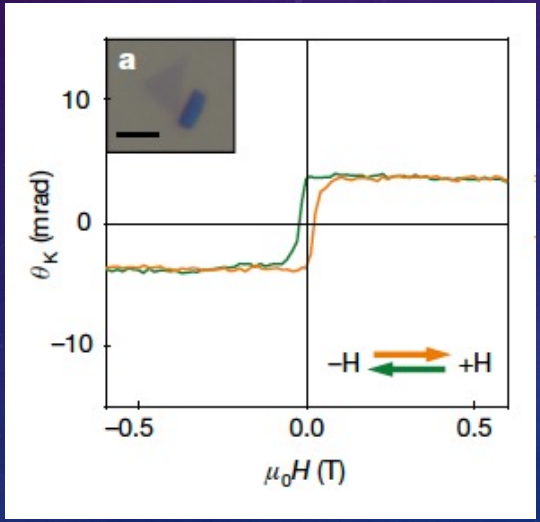
VI_3 and CrI_3 : 2D van der Walls magnets

LETTER

doi:10.1038/nature22391

Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit

Bevin Huang[1]*, Genevieve Clark[2]*, Efrén Navarro-Moratalla[3]*, Dahlia R. Klein[3], Ran Cheng[4], Kyle L. Seyler[1], Ding Zhong[1], Emma Schmidgall[1], Michael A. McGuire[5], David H. Cobden[1], Wang Yao[6], Di Xiao[4], Pablo Jarillo-Herrero[3] & Xiaodong Xu[1,2]



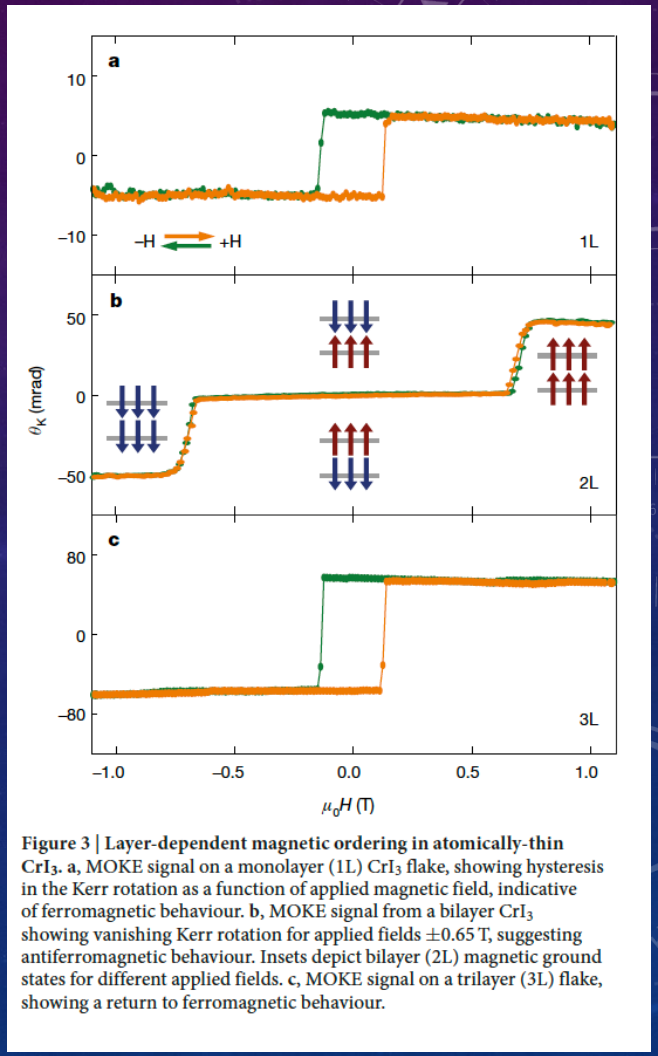


Figure 3 | Layer-dependent magnetic ordering in atomically-thin CrI_3. **a**, MOKE signal on a monolayer (1L) CrI_3 flake, showing hysteresis in the Kerr rotation as a function of applied magnetic field, indicative of ferromagnetic behaviour. **b**, MOKE signal from a bilayer CrI_3 showing vanishing Kerr rotation for applied fields ±0.65 T, suggesting antiferromagnetic behaviour. Insets depict bilayer (2L) magnetic ground states for different applied fields. **c**, MOKE signal on a trilayer (3L) flake, showing a return to ferromagnetic behaviour.

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A. De Vita et al. *Nano Lett.* **22, 7034** (2022)

M. Gibertini et al. Nat. Nanotechn.. 14 , 408 (2019)

VI_3 and CrI_3 : 2D van der Walls magnets

- Structural transition

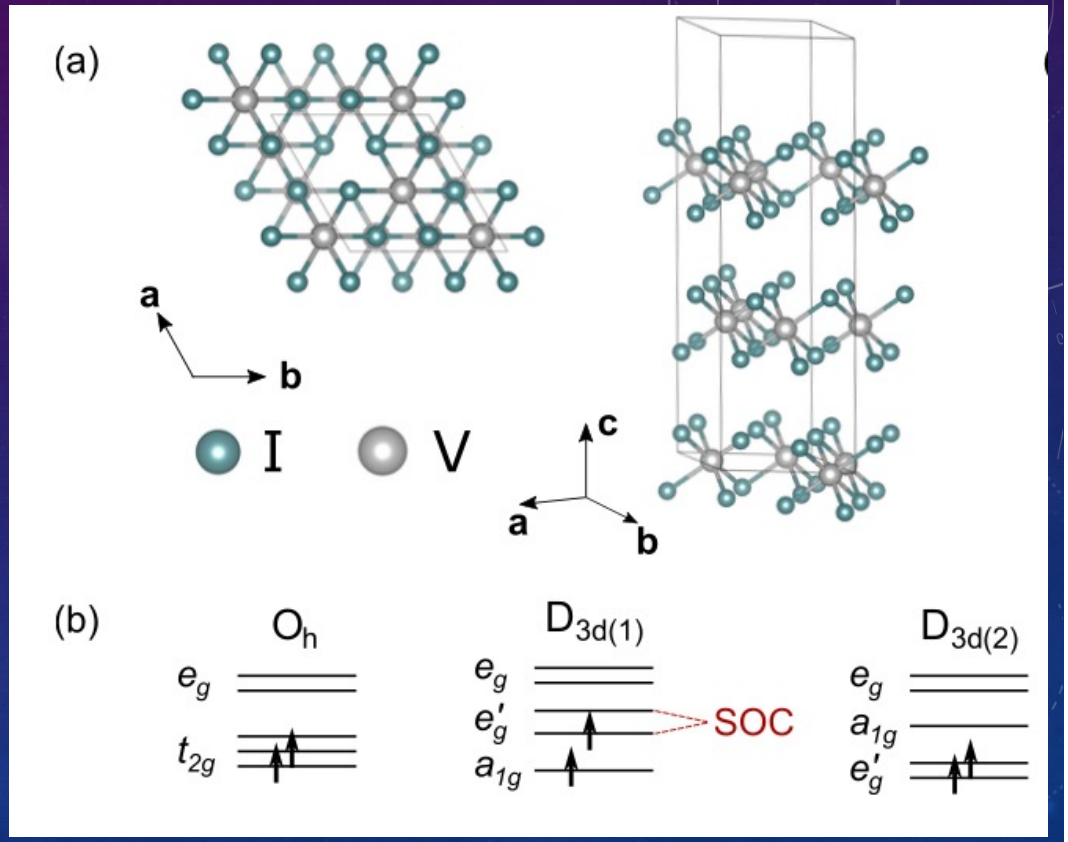
(rombohedral to monoclinic VI_3 T=79 K
(monoclinic to rombohedral CrI_3 T=220 K)

- Magnetic transitions in VI_3

FM1@50 K
FM2@35 K with spin canting

OPEN QUESTIONS

- Uncertainties in ground states
- Role of SOC and correlation
- Relevant spin character

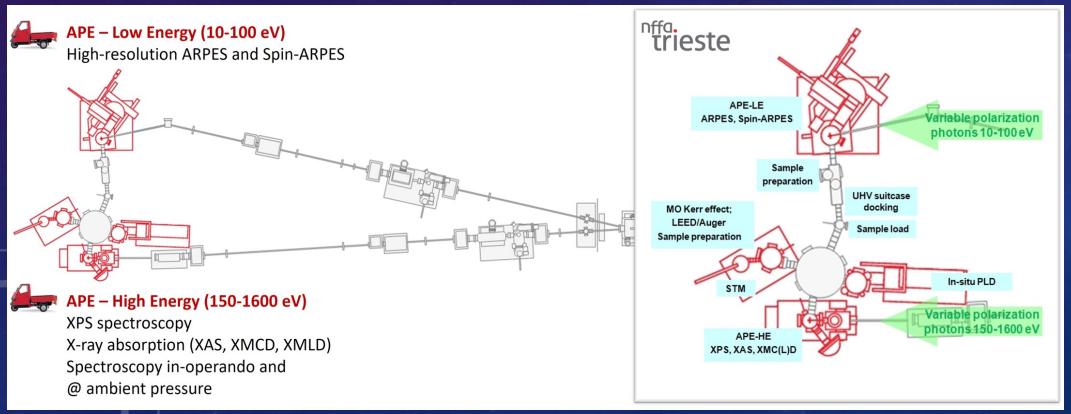


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The Playground(s): Elettra and ESRF

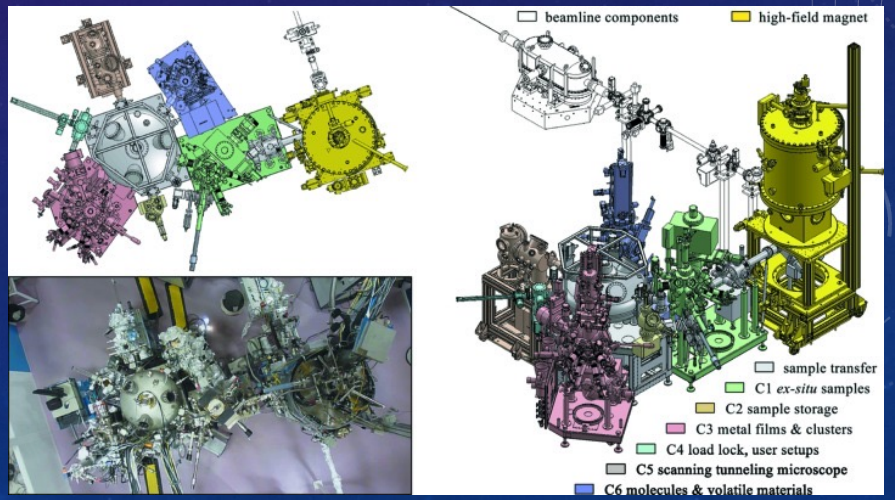


APE beamline –LE branch



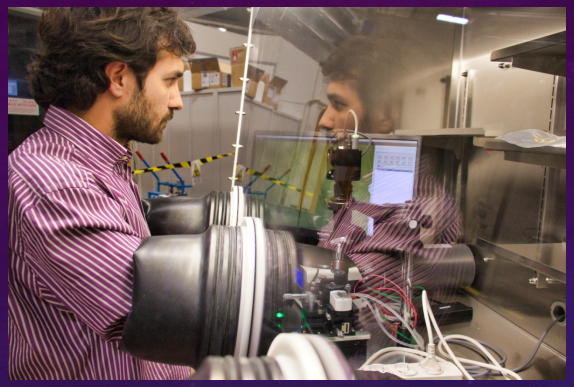


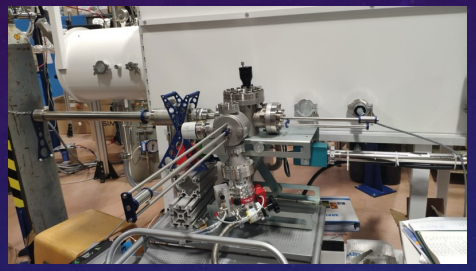
ID32 beamline – XMCD branch



VI_3 and CrI_3 : samples dissolve in 'normal' atmosphere

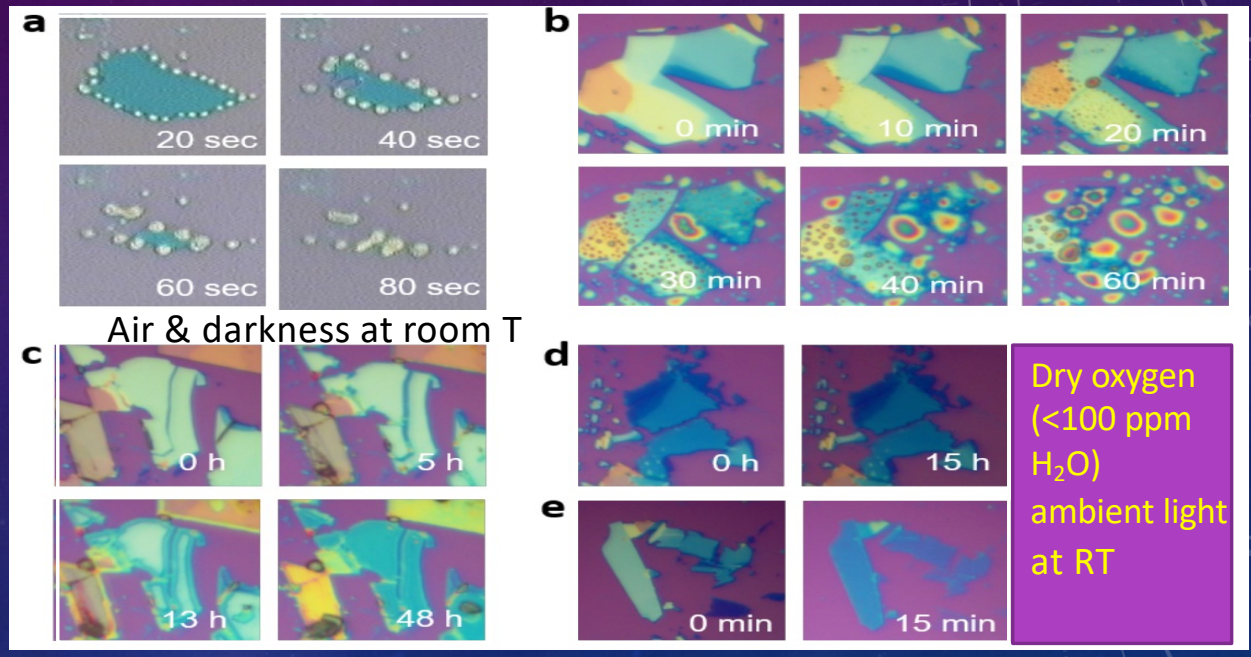
High reactivity. Need of controlled environment





Air & focused optical light

Humid Argon & Ambient light



1. Exfoliation (Full scale glovebox, Ar atmosphere: H_2O < 0.1 ppm)
2. UHV transfer with Suitcase, no air exposure

Air sensitive
Light sensitive

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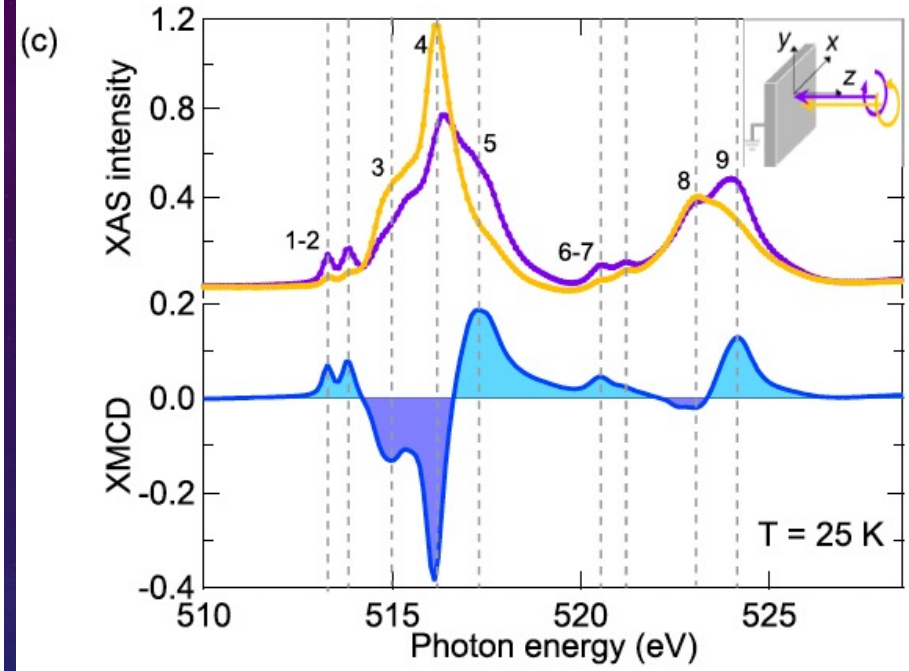
I^- substitution by water creates $CrI_{3-x}(H_2O)_x^{x+}$.
Initiated by *d-d* transitions starting at 1.4 eV.

From D. Shcherbakov et al. *Nano Lett*. 2018, **18**, 4214

Long range magnetic order via XMCD

De Vita et al. *Nano Lett.* ***24*, 1487** (2024)
R Sant et al. *J. Phys.:Condens. Matter* **35** 405601 (2023)

Vanadium L $_{2,3}$ edges
20 K – 0,5 T out of plane

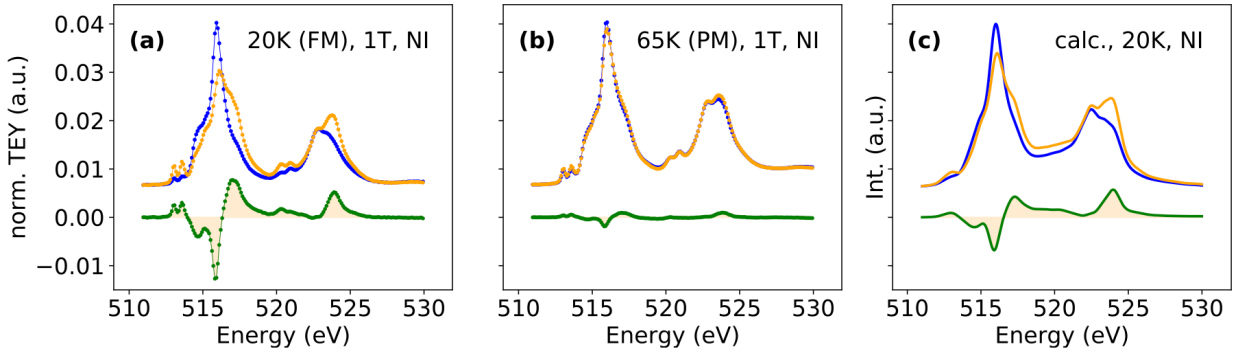


Lsrge magnetic signal

1-2 and 6-7 features (sharp, i.e. localized states)
Transitions to unoccupied t2g states
Signature of V^{3+} valence, e.g. V2O3
De Groot et al., Phys. Rev. B 1990: Caputo et al., Appl. Surf. Sci. 2022

Exp

Mult Cluster Calculation

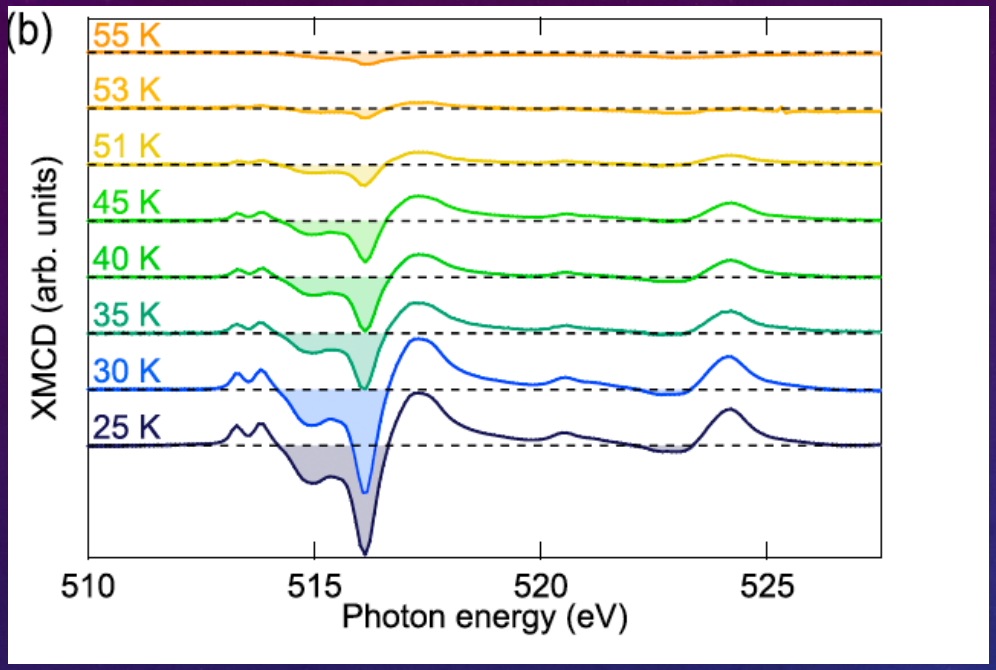


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QUANTY code , M. W. Haverkort 2016 J. Phys.: Conf. Ser. 712 012001

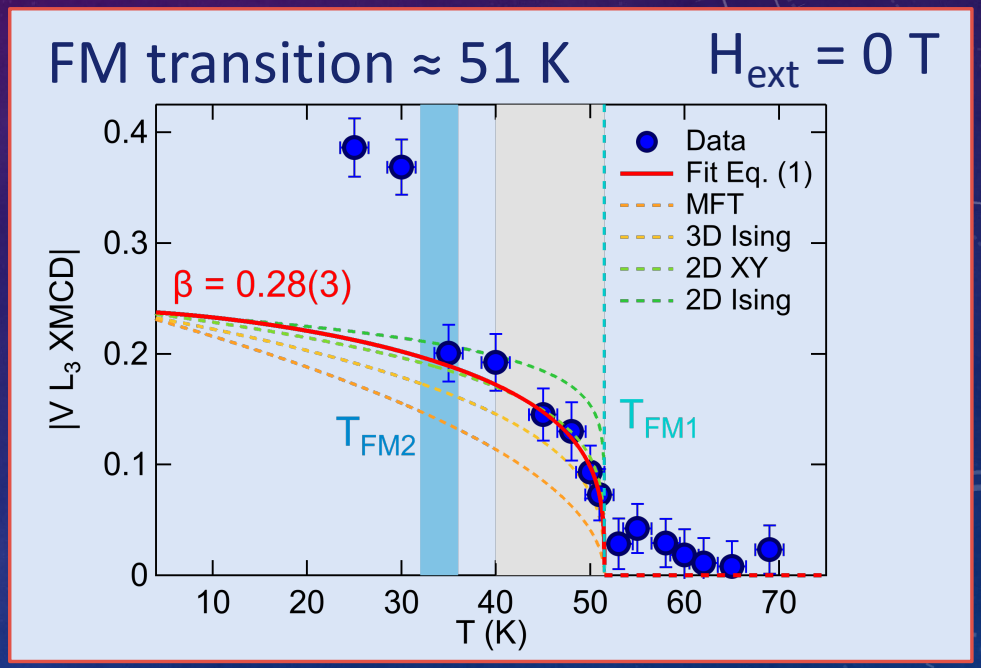
Spin dimensionality via XMCD vs. T

De Vita et al. *Nano Lett.* ***24, 1487*** (2024)
R Sant et al. *J. Phys.:Condens. Matter* **35** 405601 (2023)



Critical behaviour:

Information on universality class



$$m = m_0\left(1 - \frac{T}{T_C}\right)^{\beta}$$

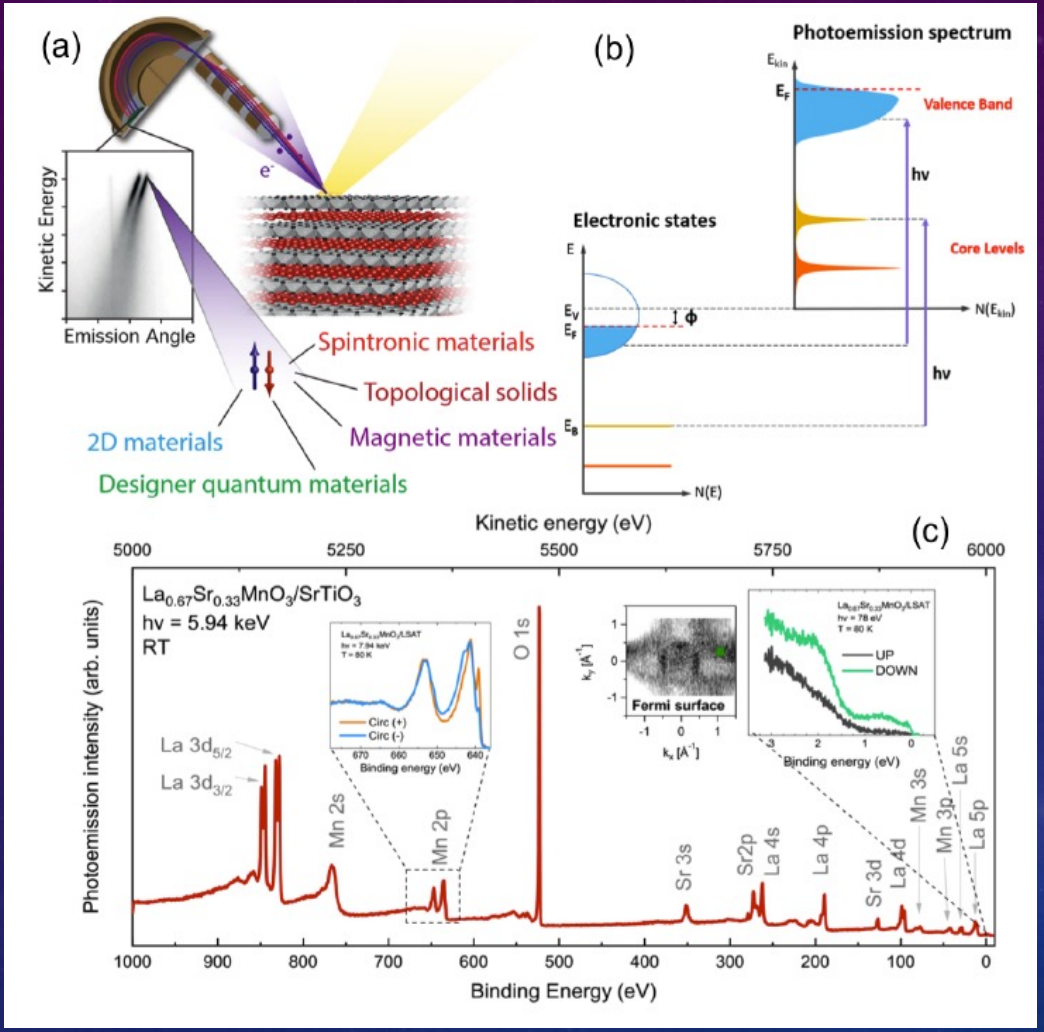
$\beta = 0.28(3)$ → Reduced spin dimensionality

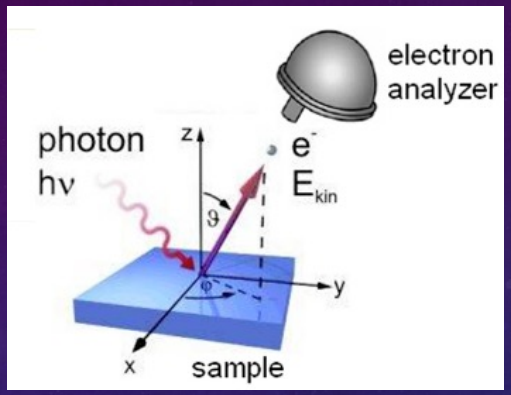
$\beta = 0.23$: **2D XY**

Spin canting @ 35 K P. Dolezal Phys. Rev. Mater. 3, 121401(R) 2019

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The technique: PhotoElectron Spectroscopy (PES) in a 'nutslide'





Kai Siegbahn
Nobel Prize 1981
'for his contribution to the development of electron spectroscopy'

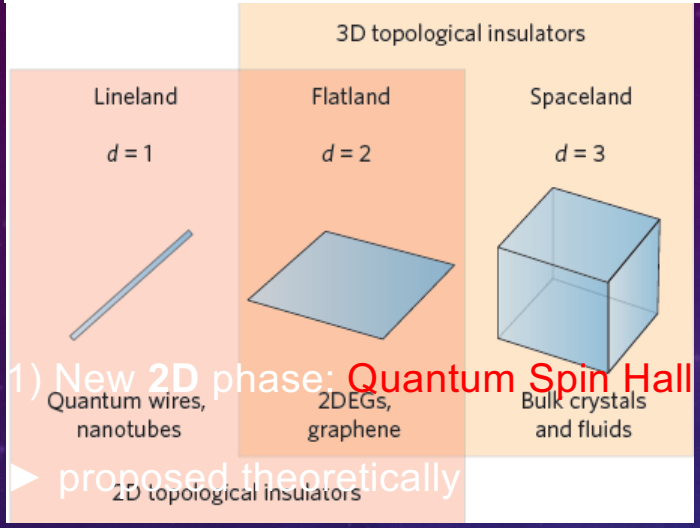
$$E_{kin} = h\nu - \phi - |E_B|$$

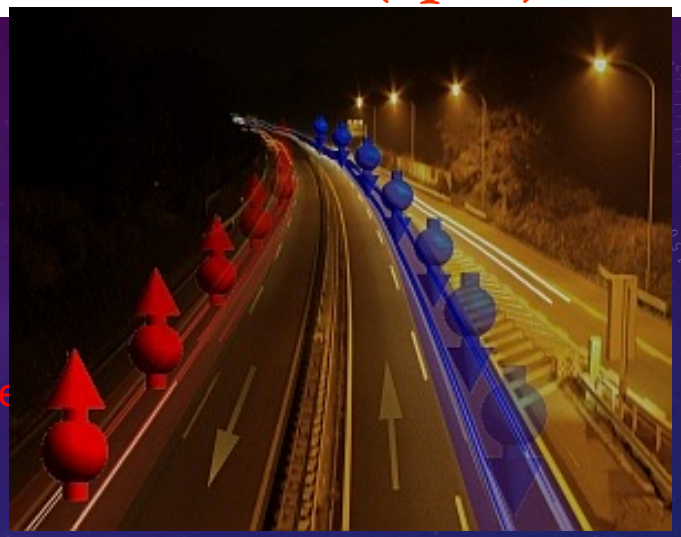
- Direct probe of electronic properties
- Chemical sensitive
- Depth Sensitive
- Non destructive

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For a review, see e.g. P.D.C. King et al , Chem. Reviews 2021, 121, 2816 (2021)

Dimensionality + Electron(spin) flow





Konig et al. Science 318 (2007)

Topological Insulators

1) New **2D** phase: Quantum Spin Hall effe

- proposed theoretically

2) New **3D** phase: 3D Topological Insulators

- The physics of topological insulators involves interactions between hosts of dimension d and boundaries of dimension d-1. Topological electronic states have been observed at the edges of 2D systems and at the surface of 3D material.

- proposed theoretically in 2007

Fu, Kane and Mele PRL98 (2007)
Moore and Balents PRB75 (2007)

- found experimentally in 2008

Hsieh et al. Nature 452, 970 (2008)

- 3D Topological insulators are materials that conduct electricity only at their surface via special electronic states. with special properties arising from the laws of quantum mechanics

3) Generalized theory and classification (2008-2010)

Moore and Balents; Zhang et al
Fu, Kane and Mele; M. Franz
And many others

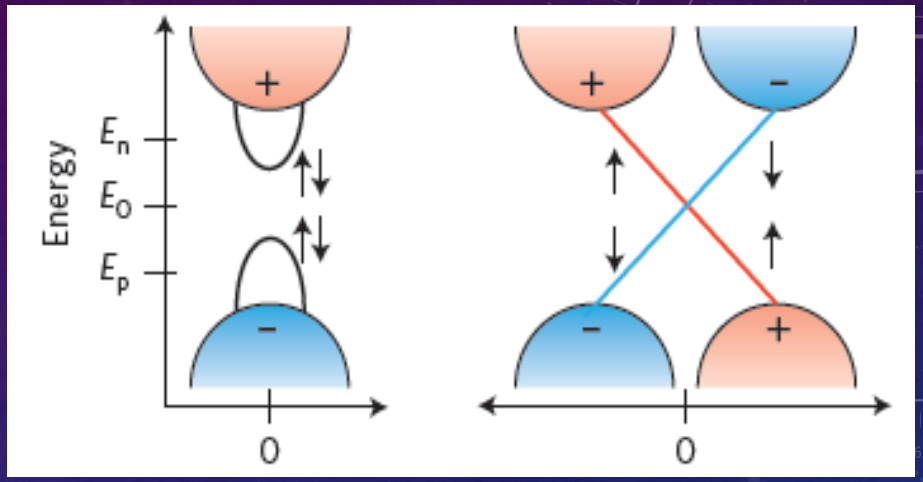
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Topological Insulators: role of spin-orbit/**band inversion**

3D case

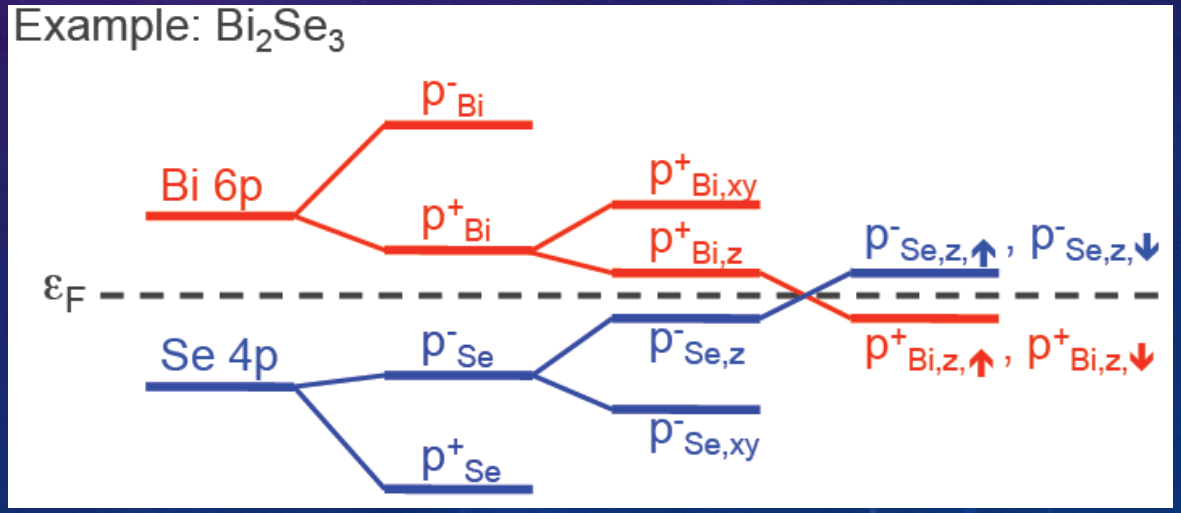
➔Without spin-orbit interaction

Valence (antibonding orbitals, antisymmetric wave functions) and conduction (bonding orbitals, symmetric wave functions) bands; spin up and down electrons have the same energies



➔With spin-orbit interaction

The **inversion** of symmetric and antisymmetric states may occur (topological twisting);



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H. Zhang et al. Nat. Phys. 5, 438 (2009)- H.C. Manoharan, Nature Nanotechnology 5, 477 (2010)

Topological Insulators: role of spin-orbit/**edge 2D states**

3D gap – 2D conductive states

➔**With spin-orbit interaction**

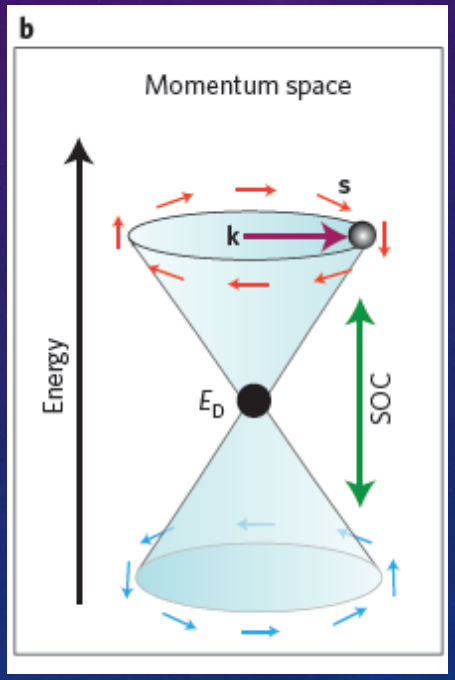
- **inversion** of symmetric and antisymmetric states occurs

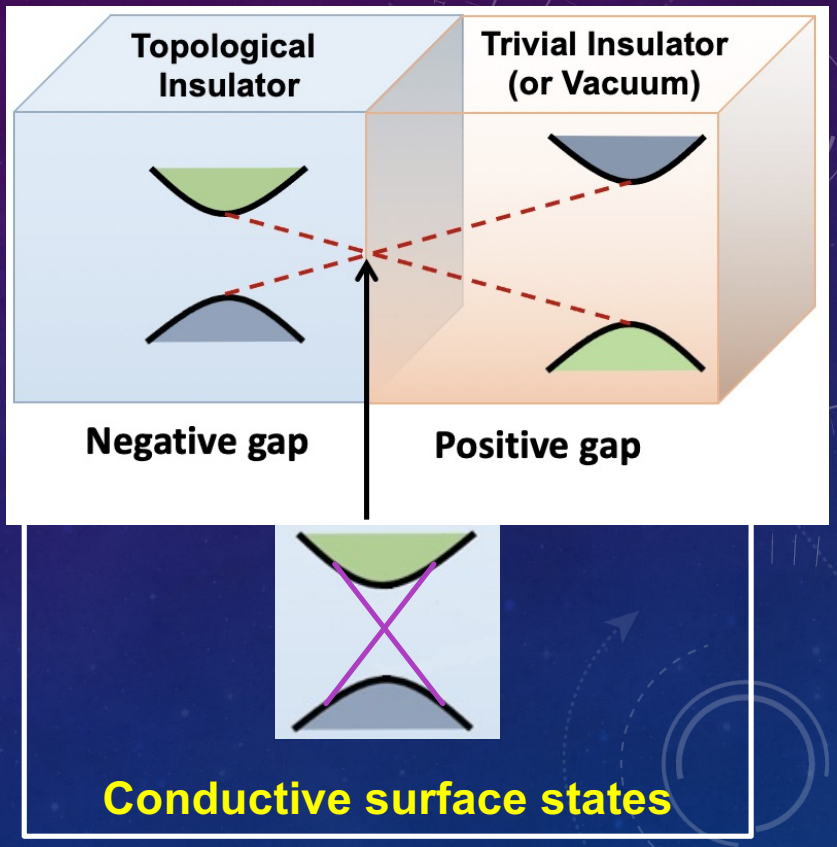
- **Time-inversion symmetry** is preserved

Gap must close at the interface!

- Formation of edge states (2D) at interface

Dirac (cone) dispersion of electron with 'locked' spin direction



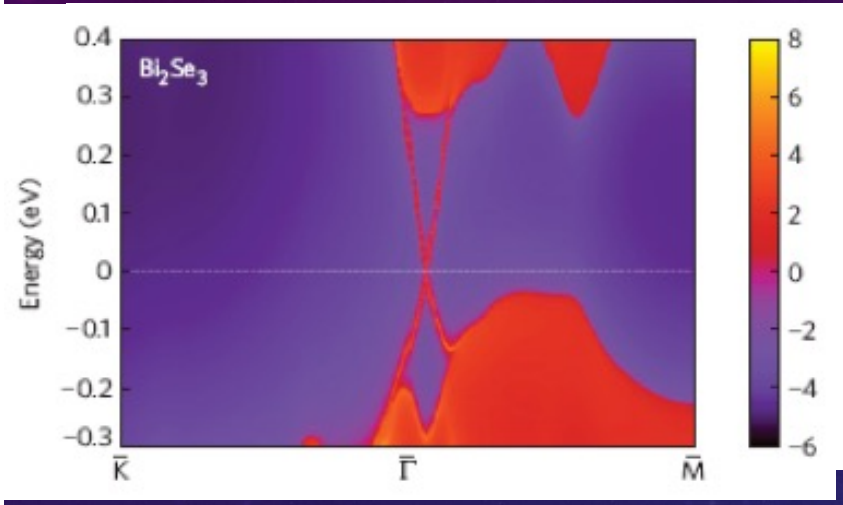


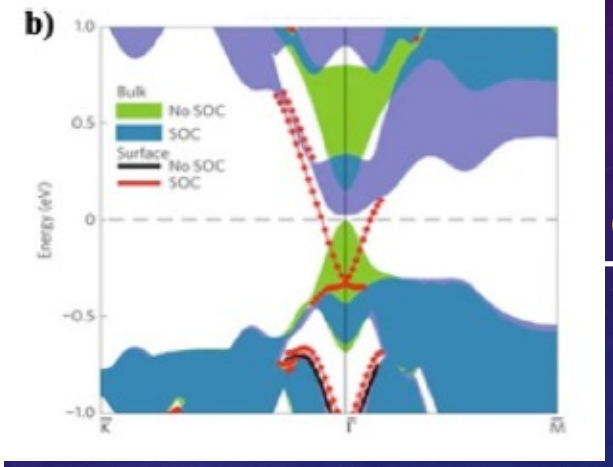
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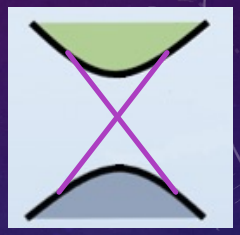
H. Zhang et al. Nat. Phys. 5, 438 (2009)- H.C. Manoharan, Nature Nanotechnology 5, 477 (2010)

Topological Insulators: theoretical predictions

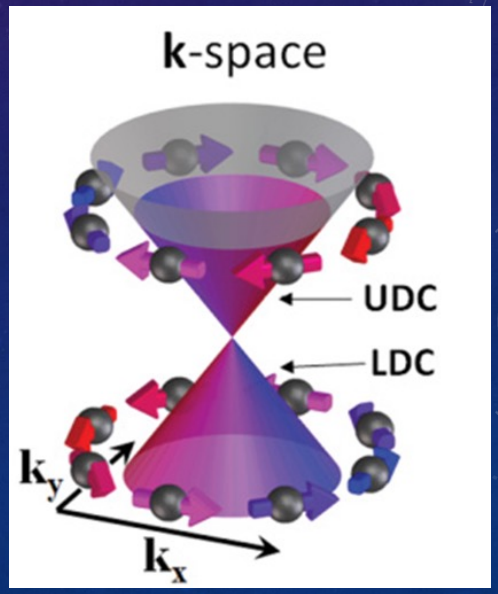
3D gap – 2D conductive states







Conductive surface states



Need of surface sensitive technique (2D vs 3D)
Need of element selectivity
Need of spin sensitivity

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H. Zhang et al. Nat. Phys. 5, 438 (2009) H.C. Manoharan, Nature Nanotechnology 5, 477 (2010)

Magnetic Topological materials: coupling functionalities

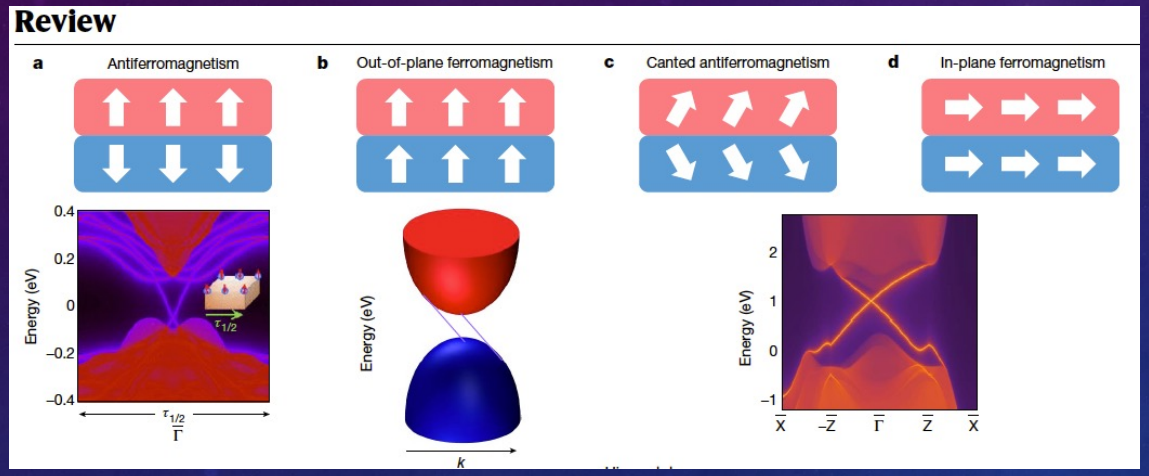
Review

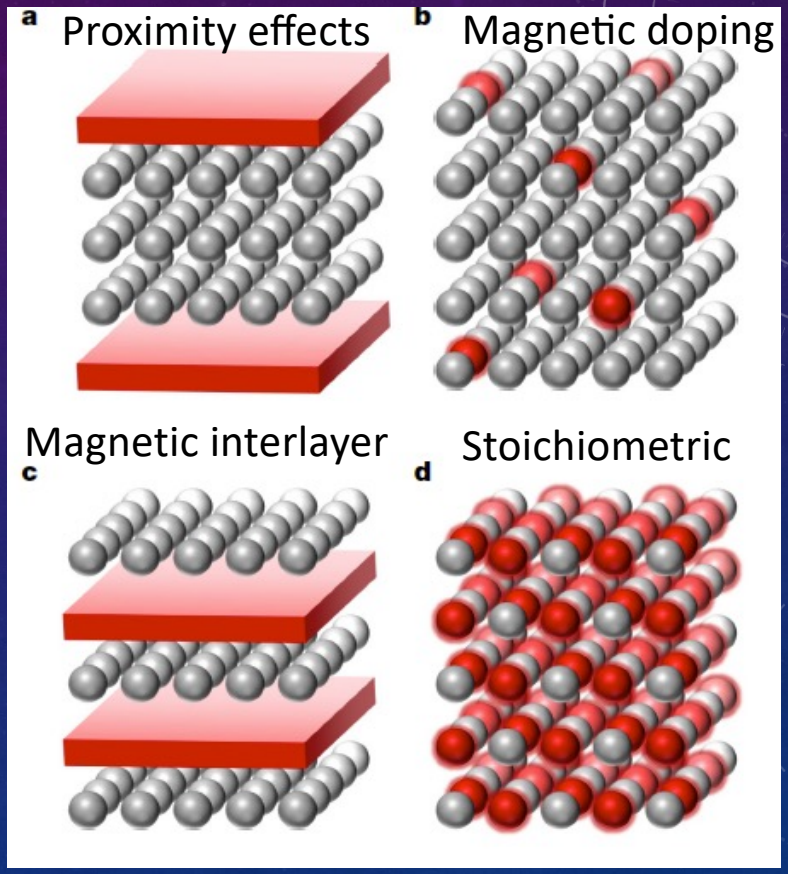
Progress and prospects in magnetic topological materials

https://doi.org/10.1038/s41586-021-04105-x

B. Andrei Bernevig[1], Claudia Felser[2] & Haim Beidenkopf[3]

Received: 8 December 2020



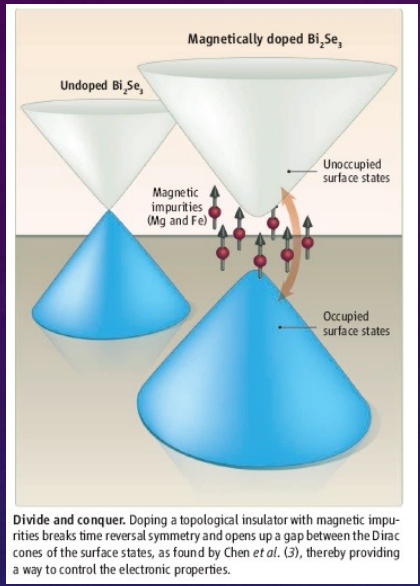


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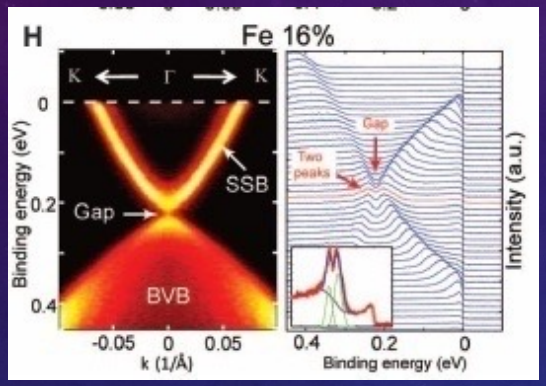
D. Pesin, A. Mac Donald, Nature Mater **11**, 409–416 (2012)

Magnetic Topological materials: 1) magnetic doping

➢**Use of Ferromagnetic impurities**

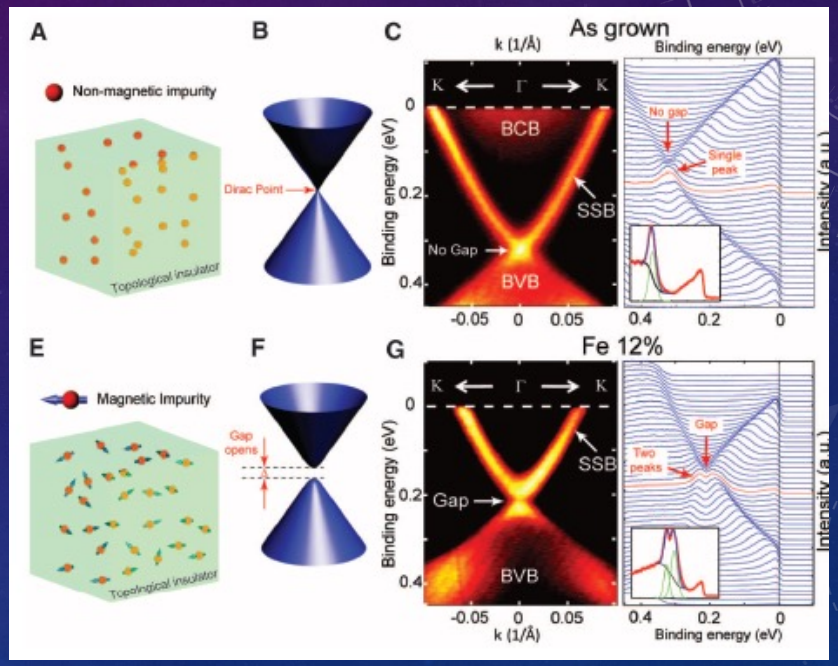


Divide and conquer. Doping a topological insulator with magnetic impurities breaks time reversal symmetry and opens up a gap between the Dirac cones of the surface states, as found by Chen *et al.* (3), thereby providing a way to control the electronic properties.



Magnetic impurities **break time-reversal symmetry** –

gap in the surface state opens?



Doubt on Fe% , out of solubility limit?
Formation of segregated species or cluster
J. Huiwen et al. PRB85, 165313 (2012)

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Y.L. Chen et al., Science 329, 659 (2010);
L.A. Wray et al., Nat. Physics 7, 21 (2011))
(I. Garate & M. Franz, PRL 104, 146802 (2010)
M. Franz, Science 329, 639 (2010)

Magnetic Topological materials: 1) magnetic doping

➢**Use of Ferromagnetic impurities**

T_C~12 K, with easy magnetization parallel to c

Evidence of Bulk ferromagnetism

(Mn doping) $Bi_{2-x}Mn_xTe_3$

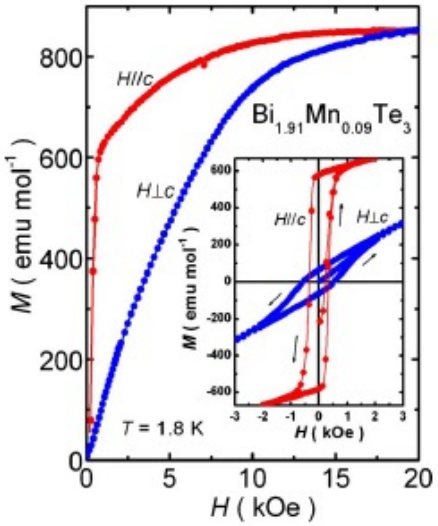
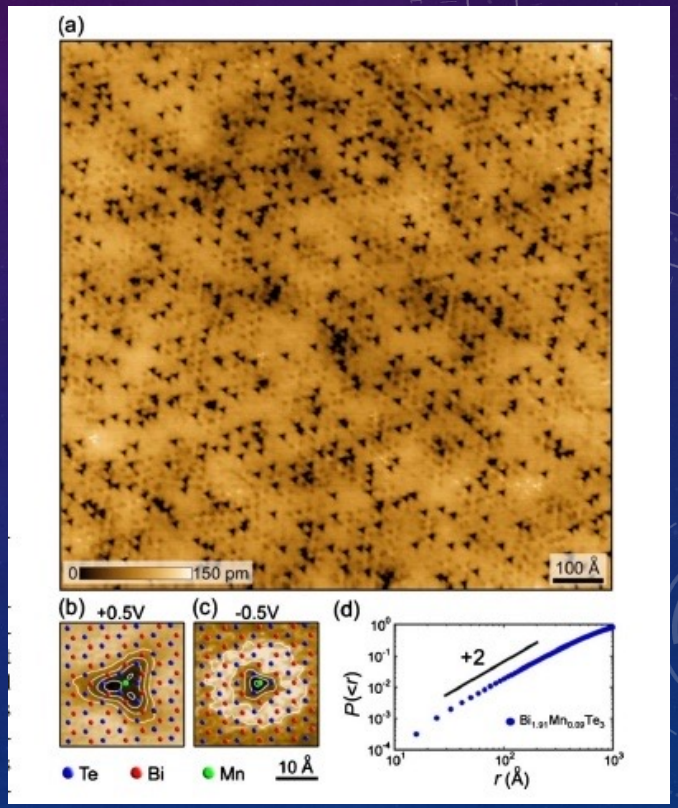


FIG. 6. (Color online) Magnetic-field-dependent magnetization of a $Bi_{1.91}Mn_{0.09}Te_3$ crystal under the applied field parallel to the c axis, $H \| c$, and perpendicular to the c axis, $H \perp c$, at $T = 1.8$ K. Inset shows the hysteresis MH loops of this $Bi_{1.91}Mn_{0.09}Te_3$ crystal for both field directions.



Y.S. Hor et al. PRB 81, 195203 (2010)

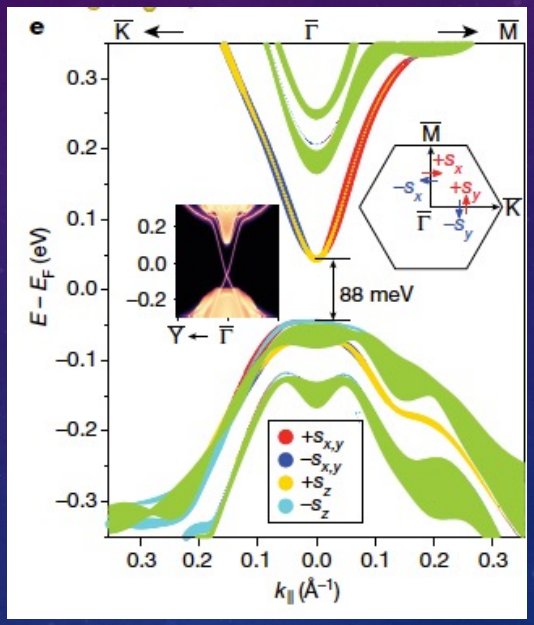
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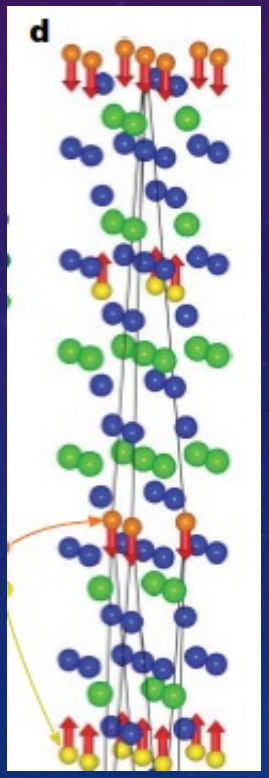
Magnetic Topological insulators: stoichiometric systems

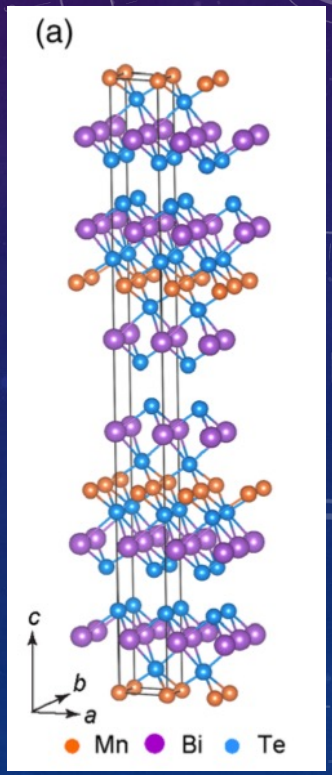
Antiferromagnetic topological insulator $MnBi_2Te_4$

3d Based- Mn layer
Out of plane magnetization
Mn bands close to Ef

DFT theory





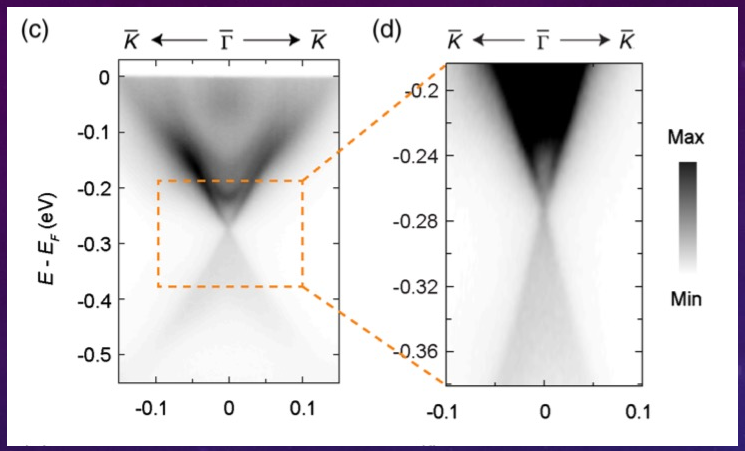


Hou et al., Nano Lett. 2019, 19, 2472−2477
M. . Otrokov et al. Nature 576: 416- 422 (2019)
A. M. Shikin et al. Sci. Rep. **10**, 13226 (2020)

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Magnetic Topological insulators: 3) stoichiometric systems

Antiferromagnetic topological insulator: 3d vs. 4f



3d – based

$MnBi_2Te_4$

4f – based

$EuIn_2As_2$

$EuSn_2P_2$

$EuSn_2As_2$

2D ferromagnetism

3D A-type antiferromagnetism

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Hou et al., Nano Lett. 2019, 19, 2472−2477
F. Mazzola et al. Nano Lett. 2023, 23, 17, 8035

Teng et al., 2019 J. Semicond. 40 081507
Y.J. Chen et al. Phys. Rev. X 9, 041040 (2019)

Magnetic Topological insulators: $EuSn_2P_2$

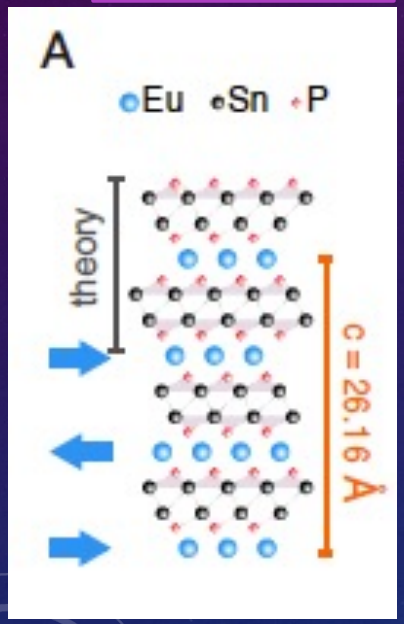
A-type antiferromagnetism

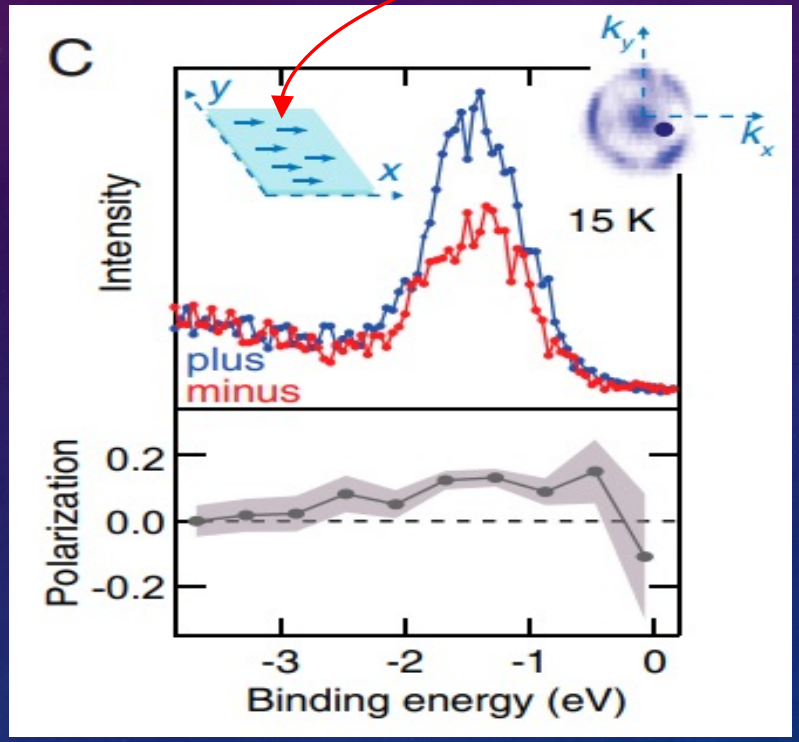
4f – based

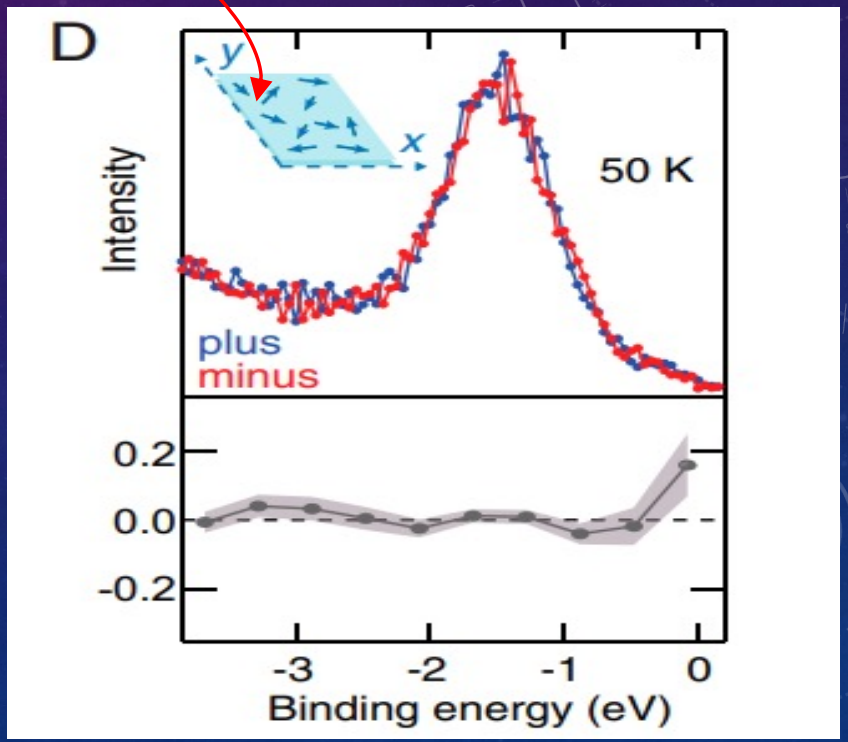
In-plane spin polarization signal on Eu 4f

$T_{Néel} \sim 30$ K

$EuSn_2P_2$







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G. M. Pierantozzi, A. Devita et al., PNAS, 119(4), e2116575119 (2022)

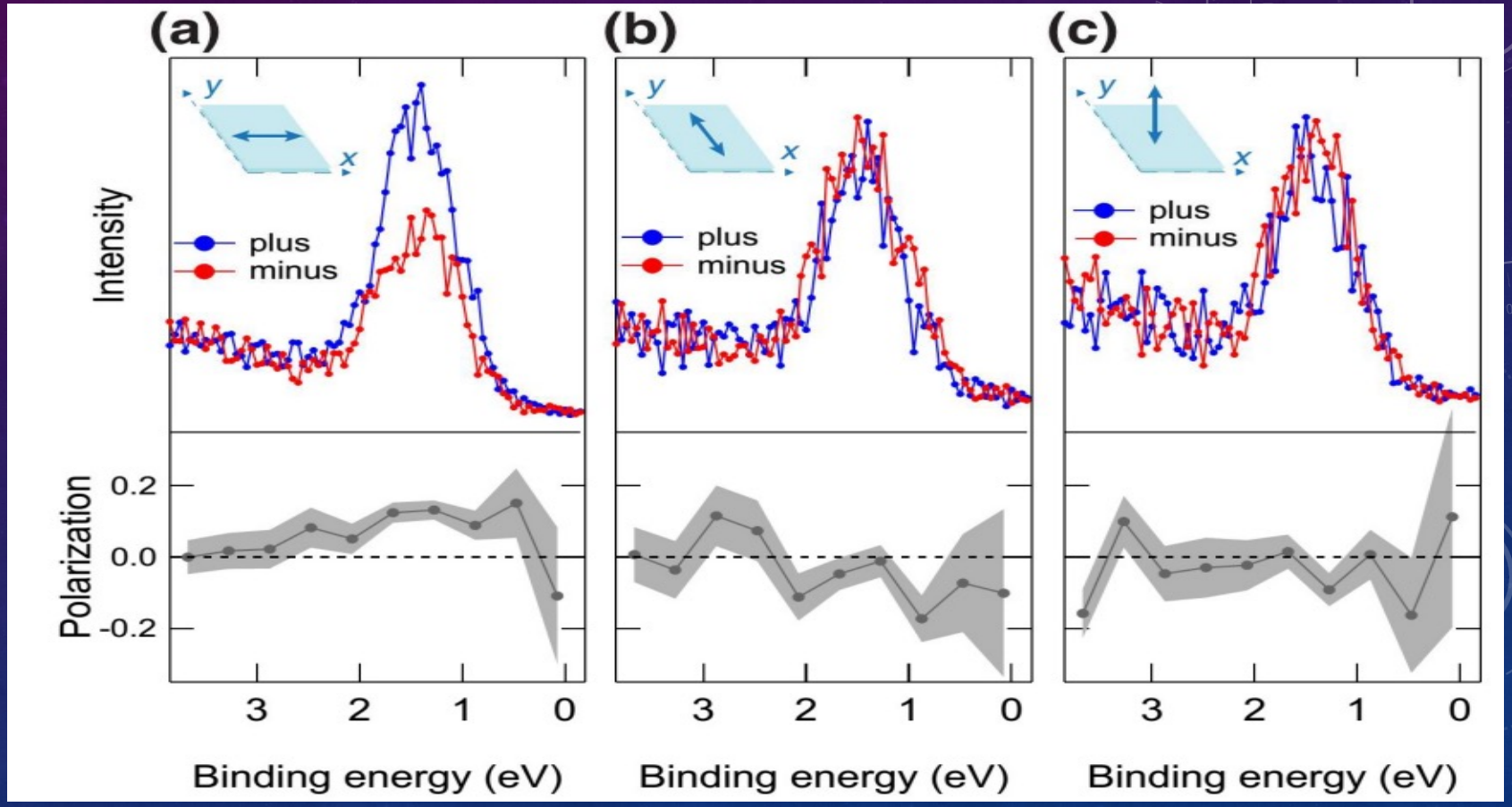
Magnetic Topological insulators: $EuSn_2P_2$

A-type antiferromagnetism → Spin directions?

Spin- resolved

ARPES

4f Eu level



G. M. Pierantozzi, A. Devita et al., PNAS, 119(4), e2116575119 (2022)

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References and useful reading

1) Handbook on Synchrotron Radiation, ed., E.-E. Koch, North-Holland Publishing Company; (North Holland, Amsterdam, 1983)

2) www.lightsource.org

3) F. Sette in New Directions in research with Third Generation Soft X-ray Synchrotron Radiation Sources, Ed. S. Schlachter and F.J. Wuilleumier, NATO ASI series, Applied Sciences Vol. 254, 1993, pp.251

4) J. Stöhr and Y. Wu, in New Directions in Research with Third-Generation Soft X-Ray Synchrotron Radiation Sources, eds. A. S. Schlachter and F. J. Wuilleumier (Kluwer, Netherlands, 1994), p. 221.

5) R. P. Feynman, R. B. Leighton and M. Sands, The Feynman Lectures on Physics, Vol. I,II,III (Addison-Wesley, Reading, 1964).

6) N.W.Ashcroft, N.D.Mermin, "Solid State Physics"

7) M. Grioni, 'A Photoemission Primer' , in Very High Resolution Photoelectron Spectroscopy, Lecture notes in Physics, Vol. 565, Springer 2001

References and useful reading

Chemical Reviews **2021** , *121* (5), Focus issue



J.A. Sobota et al. Rev. Mod. Phys. 93, 025006 (2021)

A. Damascelli, Z. Hussain and Z.-X. Shen, Rev. Mod. Phys. **75**, 473 (2003)

N. Samarth, *Nature Mater* **16,** 1068 (2017)

J. Stohr, H.C. Siegmann, Magnetism, from fundamentals to Nanoscale dynamics, Springer 2006.

K.S. Novoselov (Nobel prize 2010, graphene)
et al. Science 353, aac9439 (2016)

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