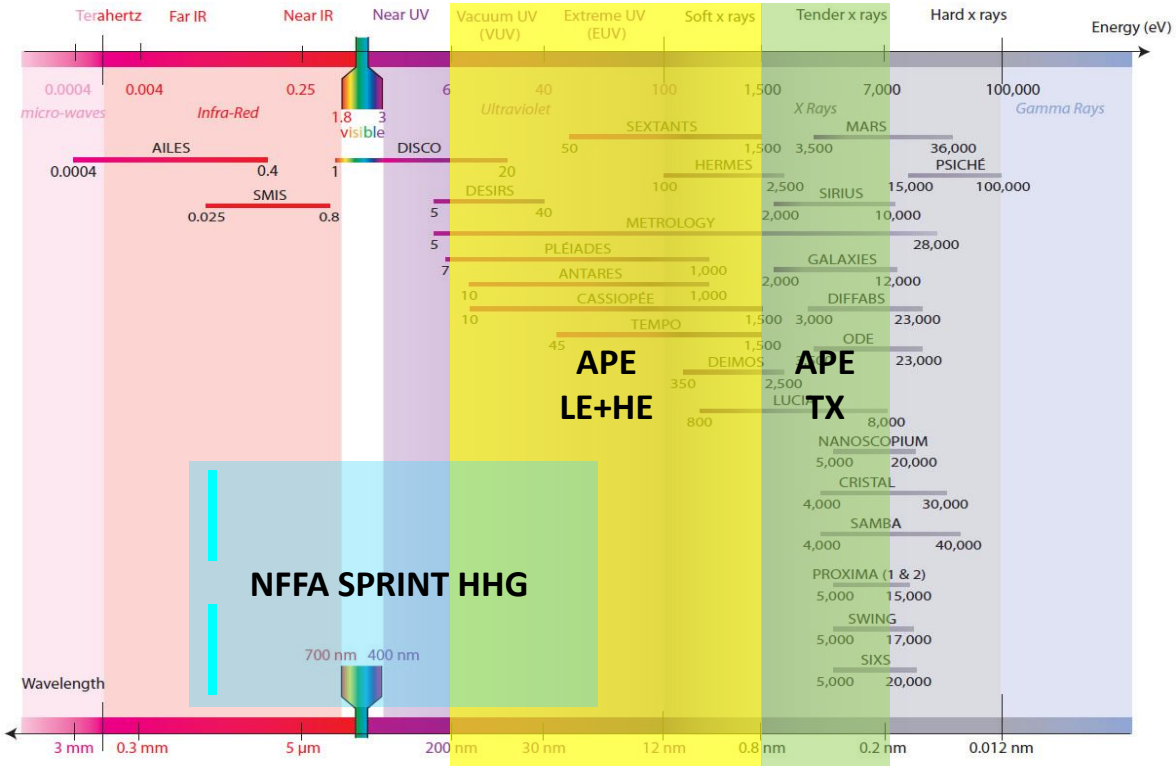
APE*-HIVE



Three APE beamlines are the offer of NFFA and our contribution to the upgrade of the Elettra 2.0 suite of user facilities along with SPRINT for 50-200 fs / >200 kHz time resolved spectroscopy

*Advanced Photoelectric-effect Experiments – APE in Italian is also “bee” as well as the most versatile utility vehicle ever!

nffa trieste

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nffa trieste

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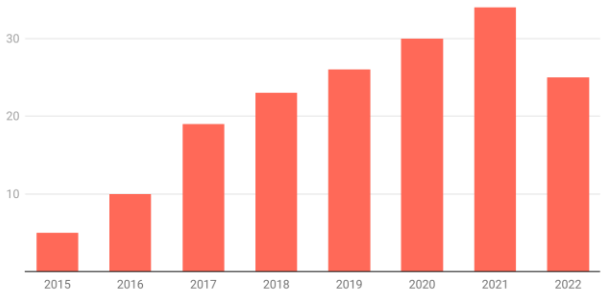
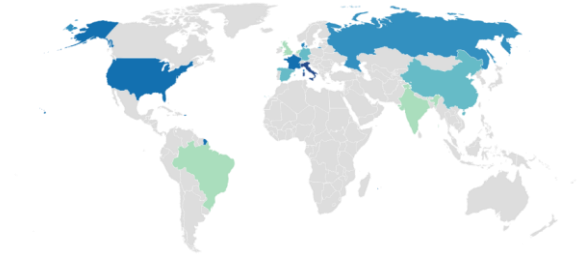
Publications

Total publications: 172



Users' Nationality

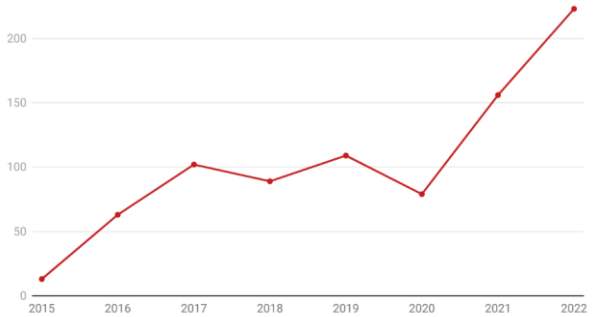
Total users: 141



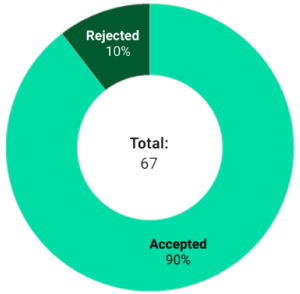
Nationality based on the affiliation

Days allocated to users

Total days: 834

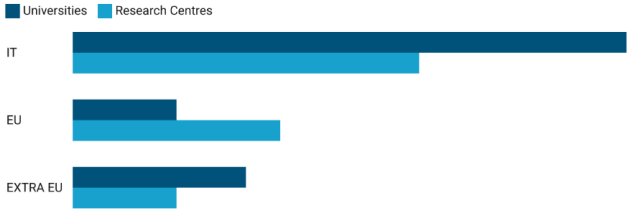


Proposals

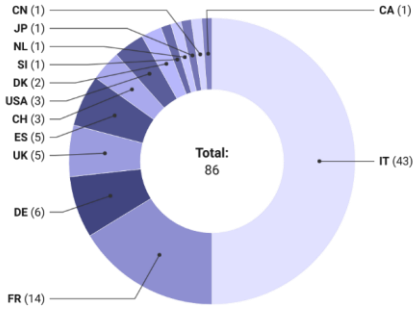


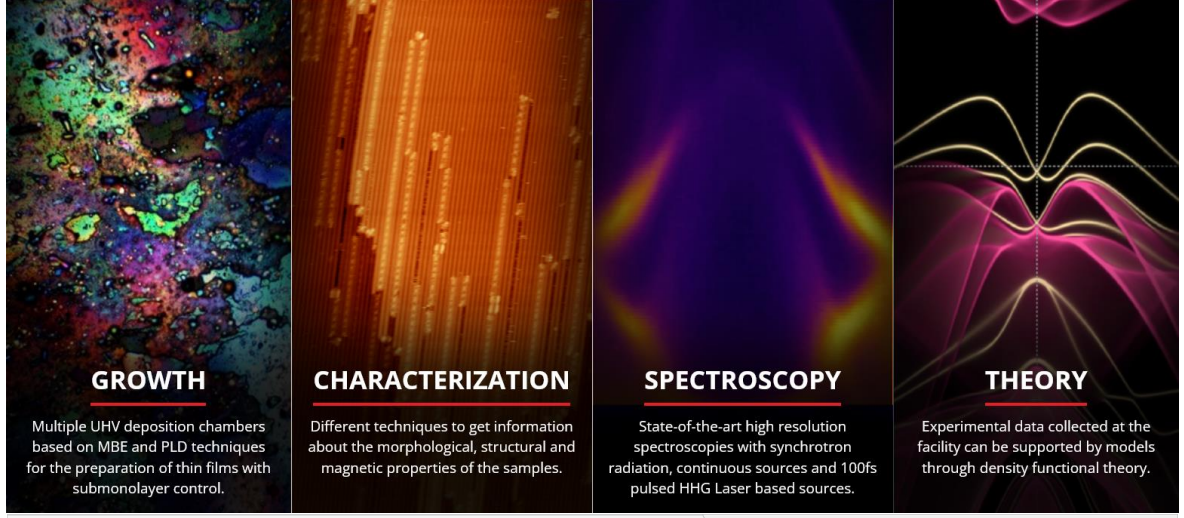
Involved institutions

Total institutions: 43

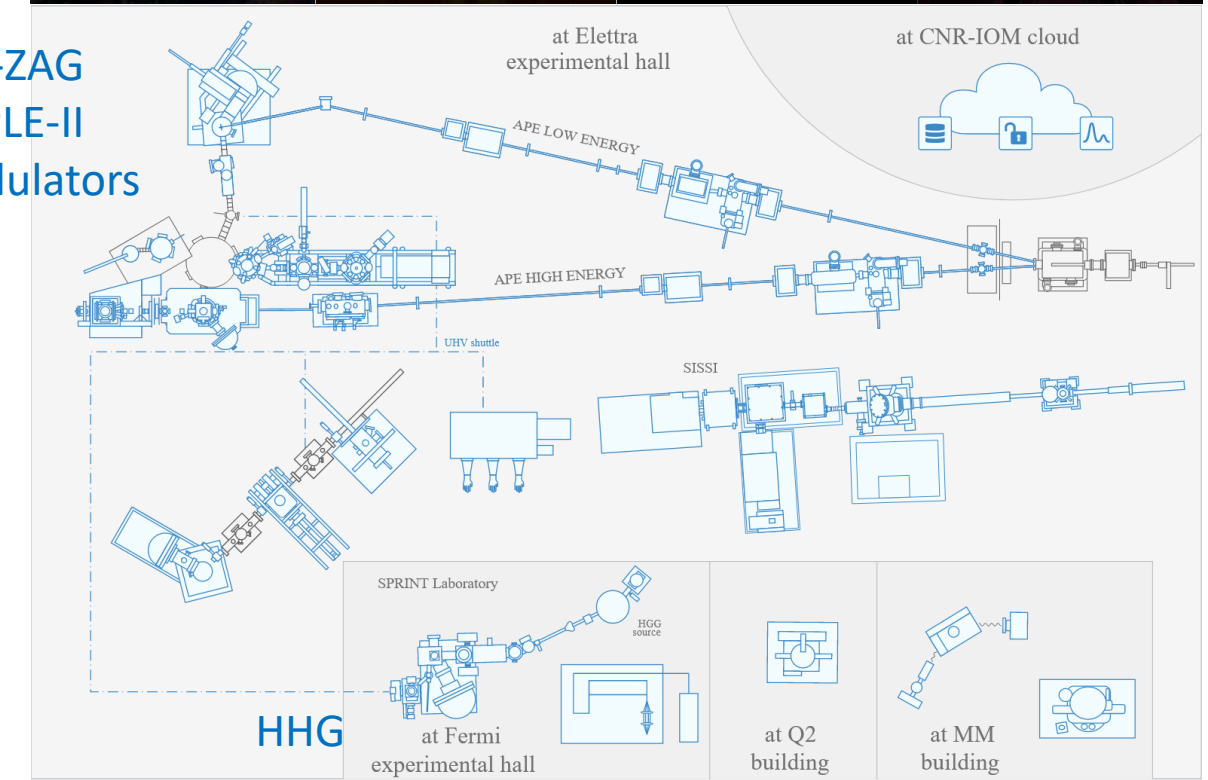


External referees





ZIG-ZAG
APPLE-II
Undulators



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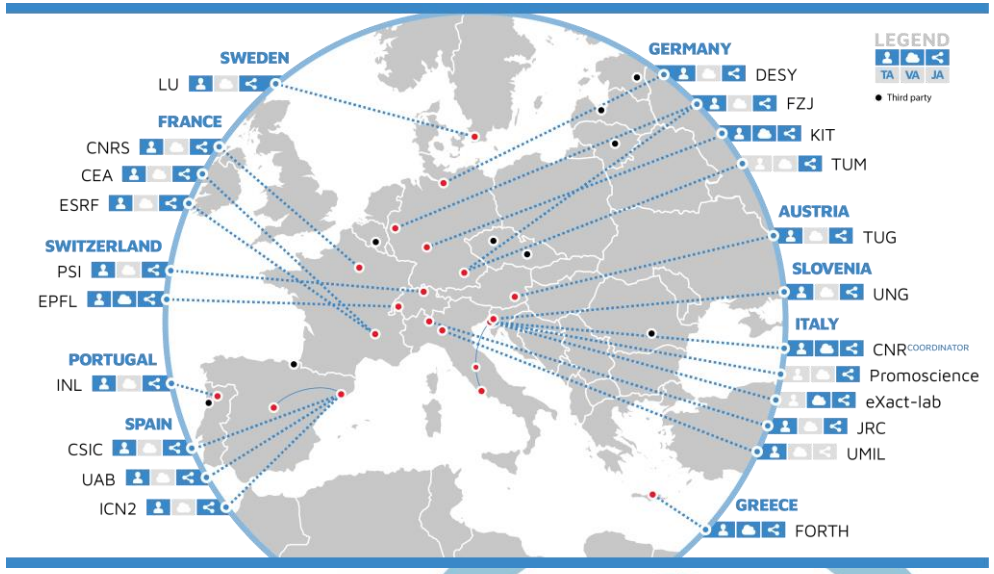
European Spin-OFF ← nffa trieste → **NRRP Italian Spin-OFF**

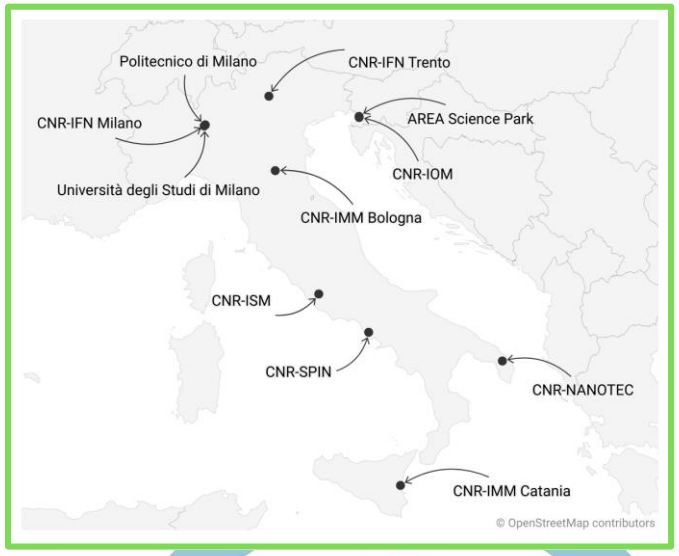
nffa.eu research infrastructure

nffa-di

Piano Nazionale di Ripresa e Resilienza



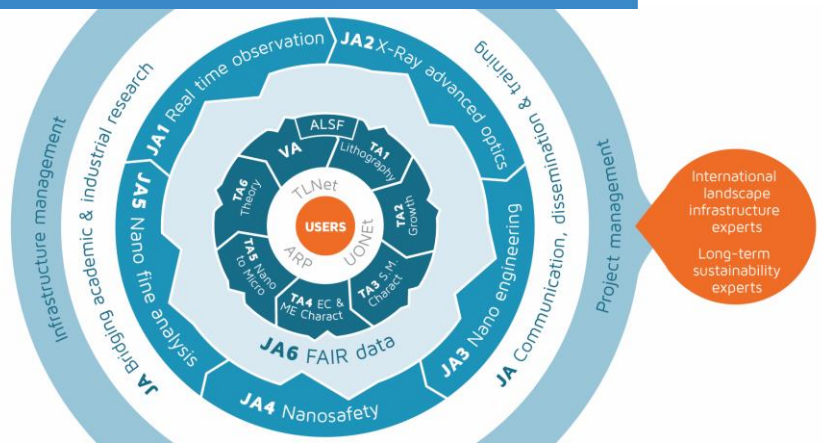
Ongoing discussion at CNR for optimal investments on Elettra 2.0



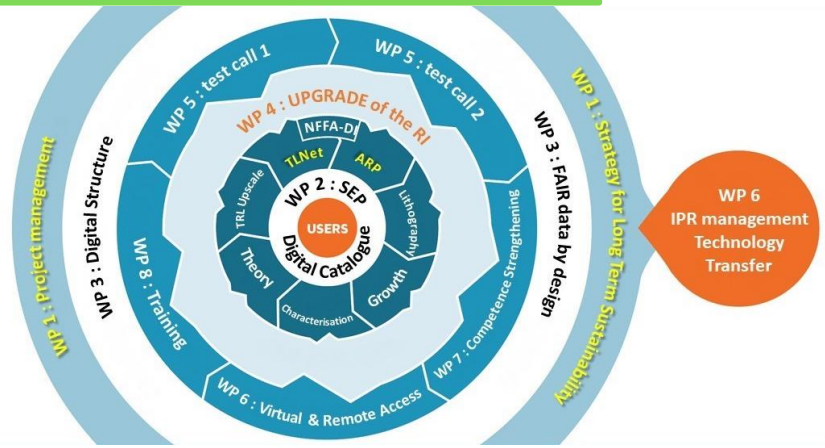
23 partners + 12 TP

186 methods
650 instruments

SR, Neutrons, EM



4 partners – 9 nodes
Polimi: nanofab
AREA: TEM, hydrogen
Unimi: surf. Magnetism
CNR: nanofabs, ultrafast Optics, TEM



APE-LE

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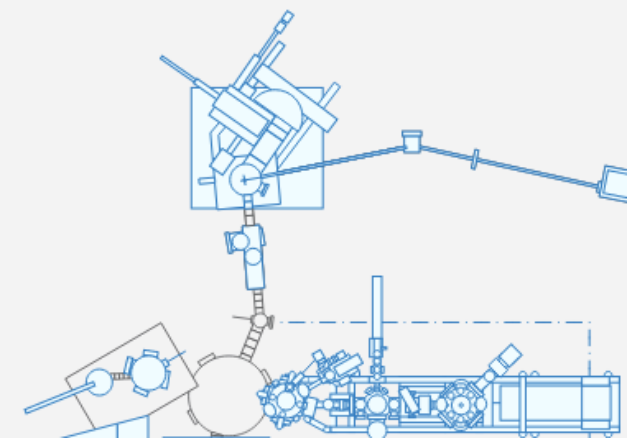
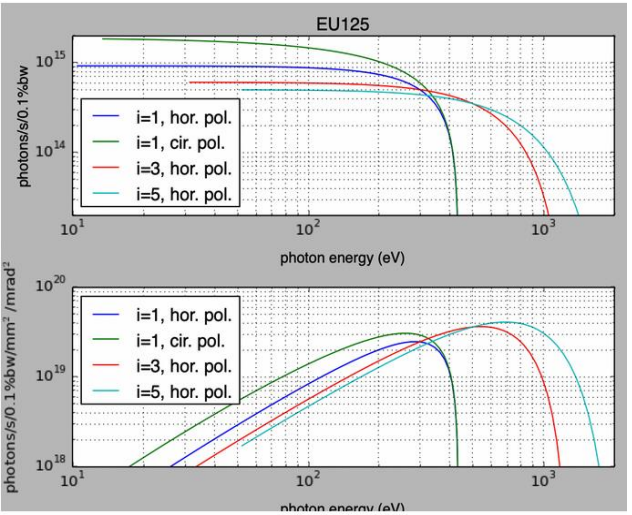
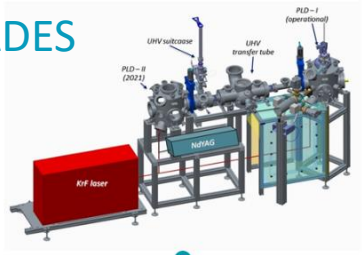
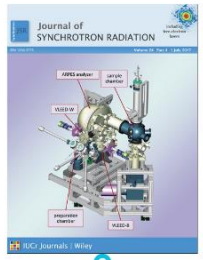
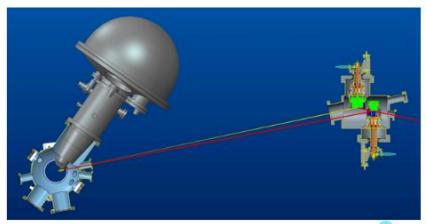


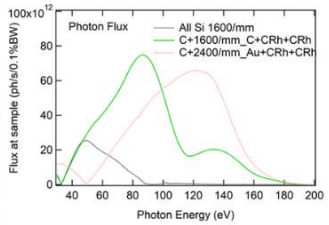


MAJOR UPGRADES









2003 APE open to users

2015 In-situ PLD

2016 Spin-ARPES

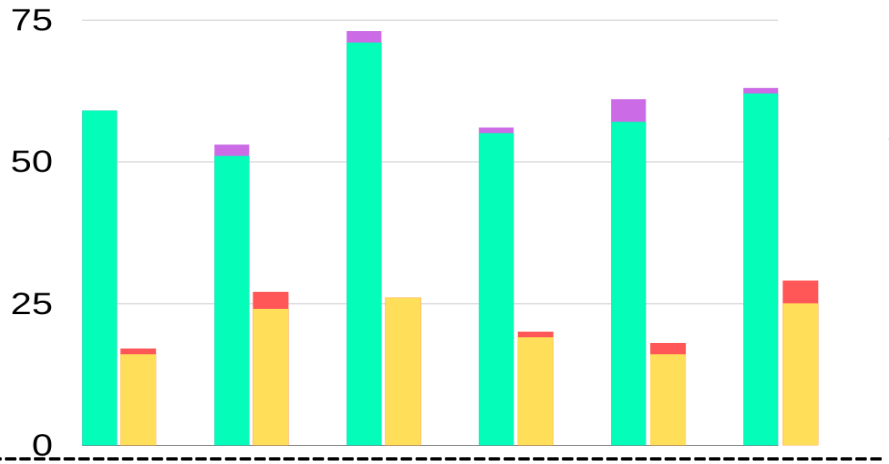
2022 Permanent cryo

ELETTRA 2.0: APE-ELE Microfocus + extended range

User proposals: Elettra submitted · NFFA submitted · Elettra allocated · NFFA allocated

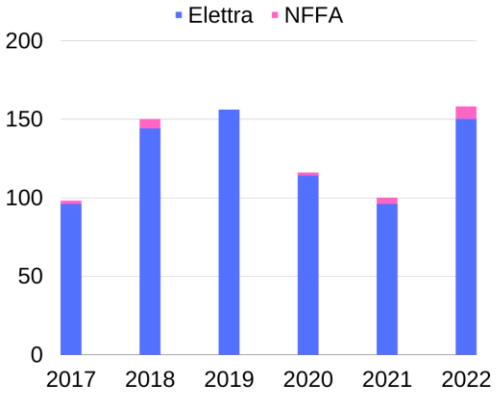
365 proposals (> 30 per semester; max 73 per year)

137 allocated (oversubscription 2.7; acceptance 37.5%)



2002 2012 2017 2018 2019 2020 2021 2022

Allocated days



since 2016: 93 papers on international journals, 29 with IF >9 , 7 theses (Master, PhD)

SCIENCE at APE-LE

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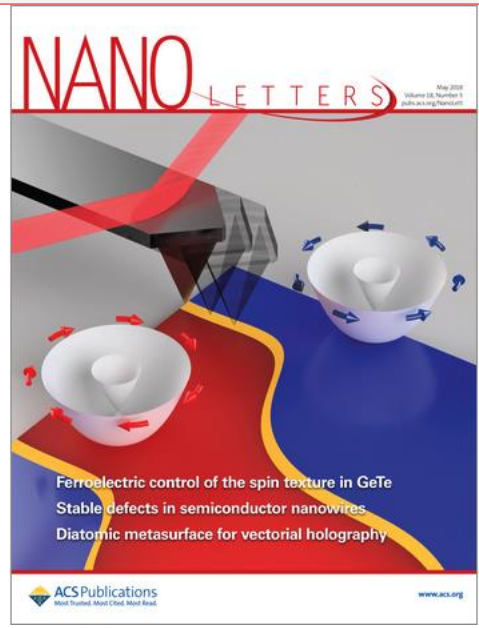
Spin Texture of Topological Matter

Electronic states in anomalous metals, low dimensional materials (graphene, topological insulators, transition metal dichalcogenides), highly correlated metallic oxides and 2D electron gases confined on surfaces/interfaces

Magnetic ordering and coupling in diluted magnetic systems, magnetic topological insulators; interfaces with ferromagnets; electronic/ magnetic properties of complex oxides and "out of equilibrium" systems

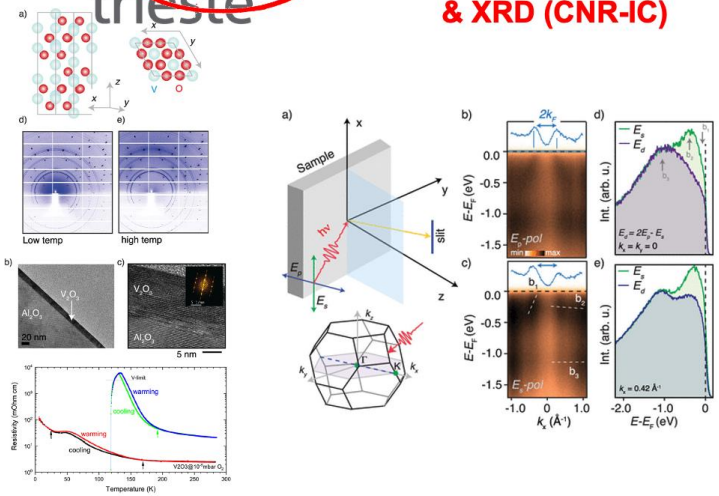
Fundamental aspects of photoemission spectroscopy, matrix element effects, **dichroism**

Growth morphology, electron states and magnetism of **hybrid organic/inorganic interfaces**, charge transfer at the interfaces, doping effects on the molecular layer



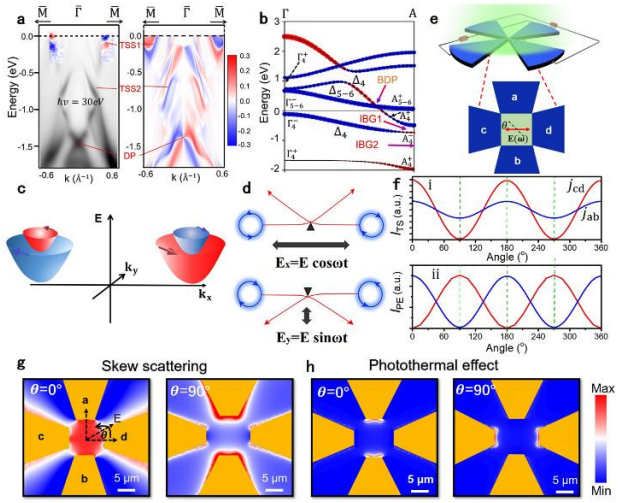
Nano Lett. 22, 14, 5990–5996 (2022)

nffa trieste **In-situ PLD, TEM, ARPES & XRD (CNR-IC)**



Genuine Mott transition undressed of any symmetry breaking effects in thin films of V_2O_3

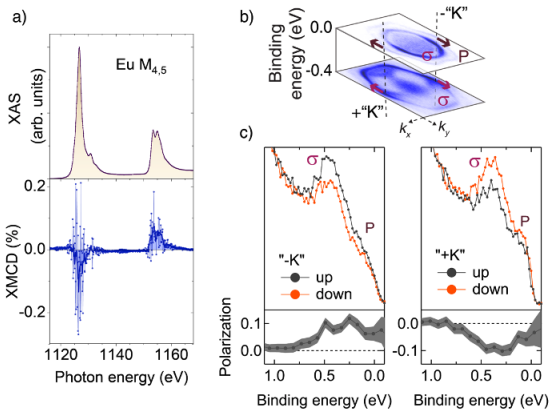
Nature Comm. 12, 1584 (2021)



Spin polarized surface states in $NiTe_2$ exploited in **high-frequency rectifiers**

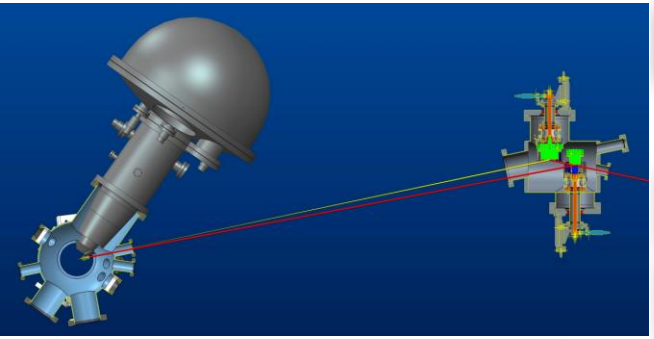
PNAS 119(4), e2116575119 (2022)

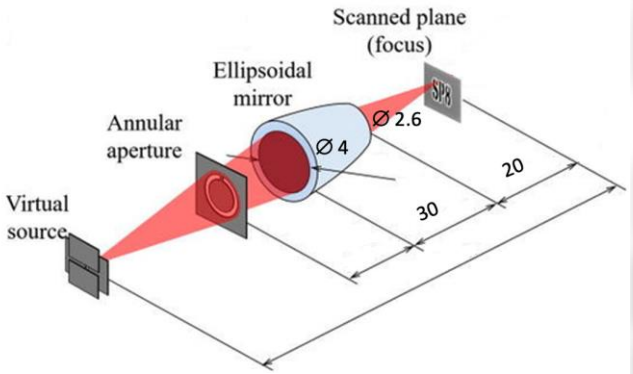
nffa trieste **QI lab, XMCD, Spin ARPES**



Interplay between **magnetism and topological properties** in the axion insulator candidate $EuSn_2P_2$

ENHANCED PERFORMANCE: APE-ELE





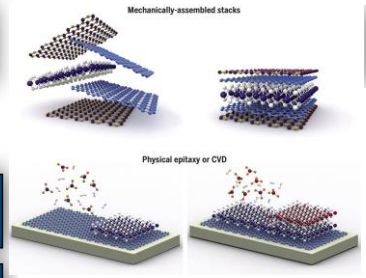
Capillary mirror and micro-focusing

Scientifically — *Advantages*

- Surface-to-bulk connectivity
- Local magnetism
- size-effects

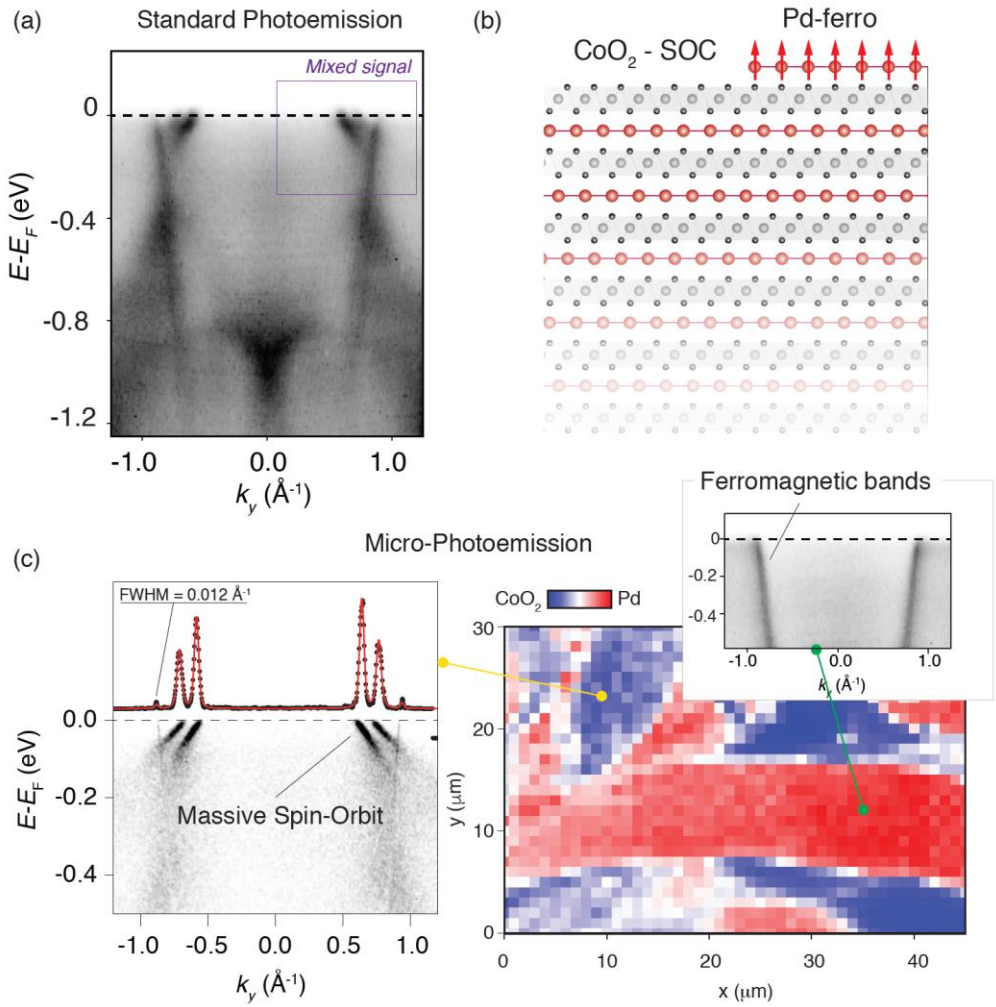
Technologically

- Noise reduction (clean areas)
- No spurious effects (domains/rotation)
- Measurements on real devices



Extension of energy range to 160 eV : $K_\perp$ and shallow core levels

Terminations on cleaved $PdCoO_2$ @ IO5-Diamond
30X50 μm^2 < APE-LE vs. **Ø 1µm as APE-ELE**



Mazzola et al., npj Quantum Materials 2022

ARPES: Micro, Nano, SPIN VLEED commissioning, SPIN VLEED operational, SPIN Mott

Synchrotron	ARPES / Spin-ARPES	Spot size	
ALS	ARPES (Maestro)	Capillary 10 µm	ZP 120 nm
	Spin-ARPES (VLEED commissioning; BL10)	50 µm	
BNL	ARPES (ESM-ARPES)	20 µm	KB 100 nm under dev.
Soleil	Spin-ARPES (VLEED commissioning; Cassiopee)	~ 500 µm	
	ARPES (ANTARES)	ZP <100 nm	
Alba	Spin-ARPES (VLEED; Lorea)	20-30 µm	
Diamond	ARPES (IO5)	Capillary 4-5 µm	ZP 400 nm
Bessy	Spin-ARPES (Mott, U125-PGM)	70 X 20 µm²	
Max IV	Spin-ARPES (VLEED commissioning; Bloch)	10 µm	
SLS	Spin ARPES (Mott Cophee; SIS)	50 X 100 µm²	
HiSOR	Spin ARPES (VLEED Espresso; BL9)	~ 1 mm	
Elettra	ARPES (Spectromicroscopy)	<1 µm (Schwarzschild; 27 & 74 eV)	

APE-HE

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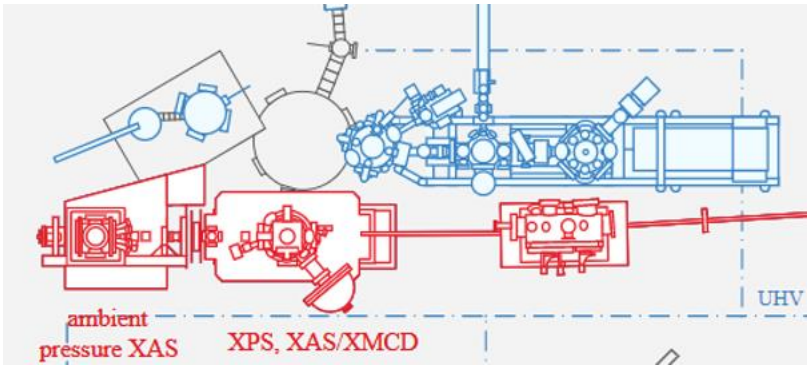
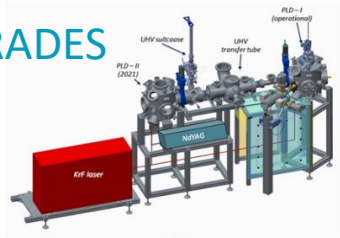
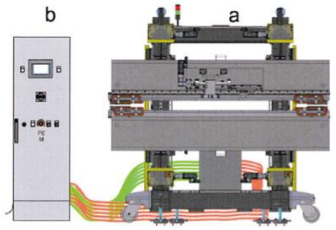
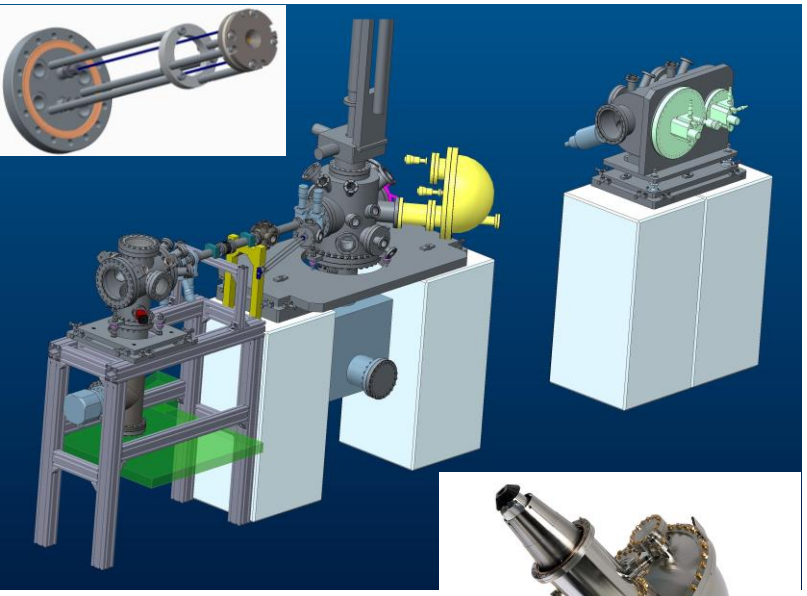


MAJOR UPGRADES





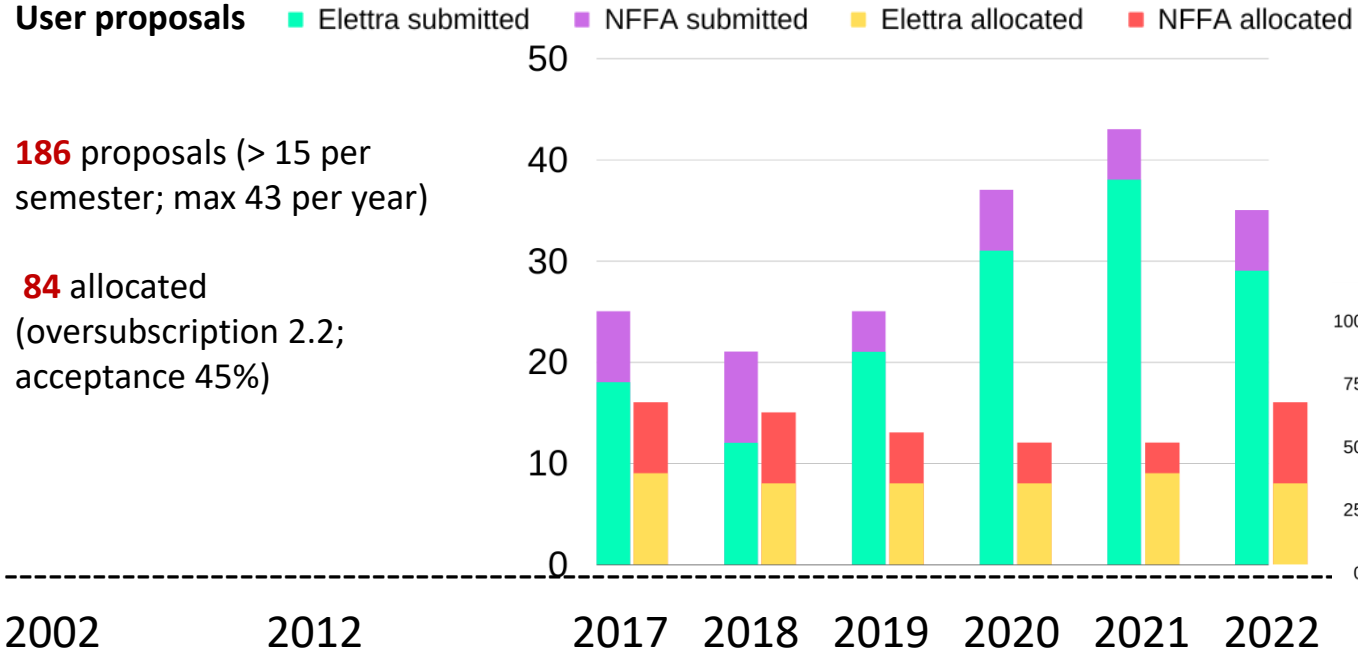
- **2003** APE open to users
- **2014** MBE MOKE Cluster
- **2015** In-situ PLD
- **2019** In-operando amb pr XAS
- **2020** R3000 with 2D Delay Line
- **2021** Amb pr XAS dedicated chamber
- **ELETTRA 2.0: APE-EHE** Microfocus + New Apple



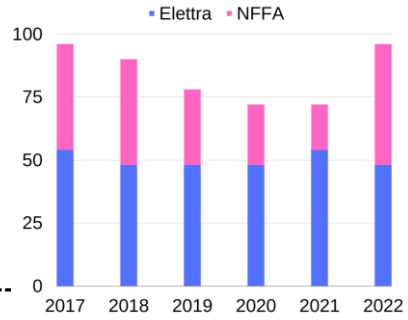
User proposals

186 proposals (> 15 per semester; max 43 per year)

84 allocated (oversubscription 2.2; acceptance 45%)



Allocated days



since 2016: 91 papers, 26 with IF >9 , 6 theses (Master, PhD)

Surface and Interface Magnetism / Multiferroism

Voltage control **Strain control**
Light control
Magnetocalorics
Hybrid-Spinterface

ACS NANO
www.acsnano.org
ARTICLE

Magnetoelectric Coupling at the Ni/ $Hf_{0.5}Zr_{0.5}O_2$ Interface

Anna Dmitriyeva, Vitalii Mikheev, Sergei Zarubin, Anastasia Chouprik, Giovanni Vinai, Vincent Polewczyk, Piero Torelli, Yury Matveyev, Christoph Schlueter, Igor Karateev, Qiong Yang, Zhaojin Chen, Lingling Tao, Evgeny Y. Tsymbal,* and Andrei Zenkevich*

Cite This: ACS Nano 2021, 15, 14891−14902 Read Online

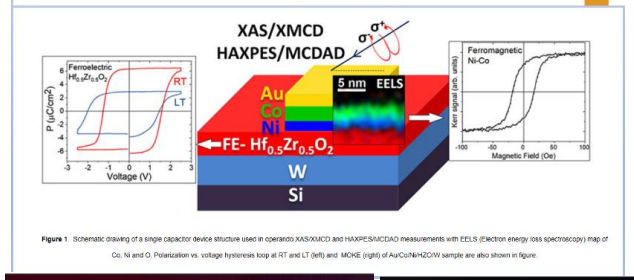


Figure 1. Schematic drawing of a single capacitor device structure used in operando XAS/XMCD and HAXPES/MCDAD measurements with EELS (Electron energy loss spectroscopy) map of Co, Ni and O. Polarization vs. voltage hysteresis loop at RT and LT (left) and MOKE (right) of Au/Co/Ni/HZO/W sample are also shown in figure.

COMMUNICATION
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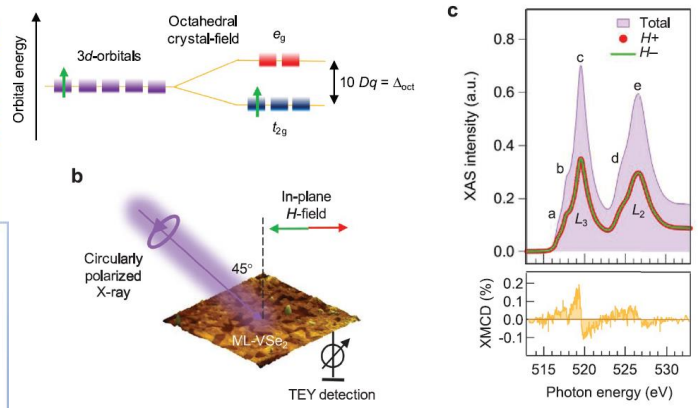
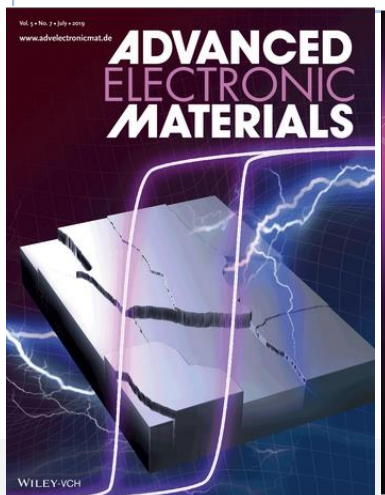
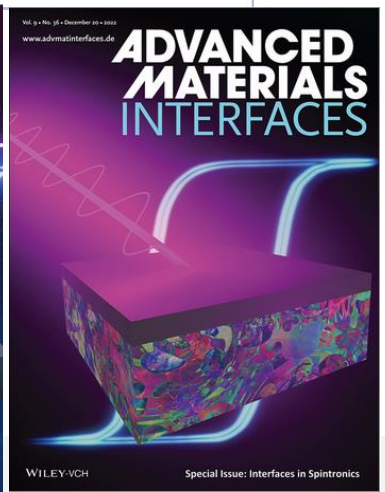
Evidence of Spin Frustration in a Vanadium Diselenide Monolayer Magnet







In-operando Ambient Pressure Spectroscopy

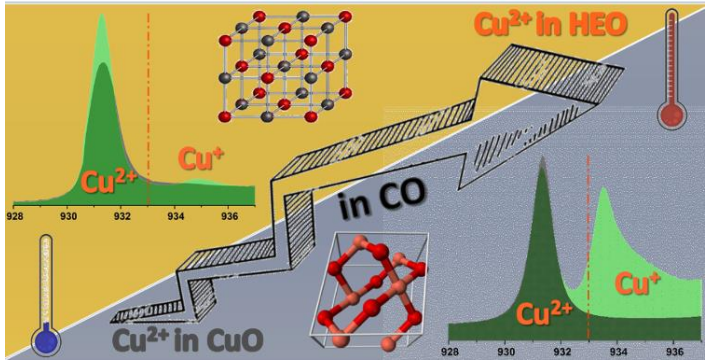
In operando
Up to 5 bar
Temperature control
100-800K
Photocatalysis

THE JOURNAL OF PHYSICAL CHEMISTRY Letters
pubs.acs.org/JPCL
Letter

Stabilization by Configurational Entropy of the Cu(II) Active Site during CO Oxidation on $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$

Martina Fracchia, Paolo Ghigna,* Tommaso Pozzi, Umberto Anselmi Tamburini, Valentina Colombo, Luca Braglia, and Piero Torelli

Cite This: J. Phys. Chem. Lett. 2020, 11, 3589−3593 Read Online



ACS Catalysis
pubs.acs.org/acscatalysis
Research Article

Electronic Properties of Ti Sites in Ziegler−Natta Catalysts

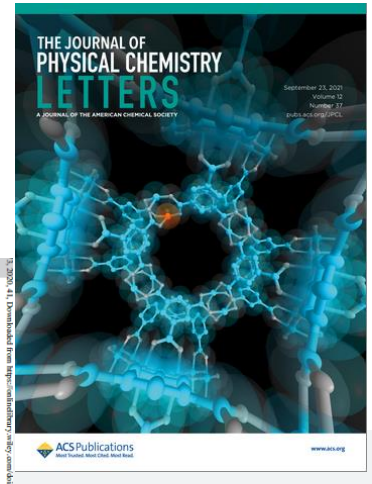
Alessandro Piovano, Matteo Signorile, Luca Braglia, Piero Torelli, Andrea Martini, Toru Wada, Gentoku Takasao, Toshiaki Taniike, and Elena Groppo*

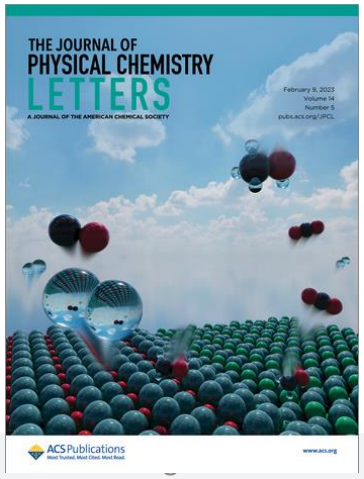
Cite This: ACS Catal. 2021, 11, 9949−9961 Read Online

Zeolites
How to cite: Angew. Chem. Int. Ed. 2020, 59, 18145−18150
International Edition: doi.org/10.1002/anie.202005841
German Edition: doi.org/10.1002/ange.202005841

Titanium Defective Sites in TS-1: Structural Insights by Combining Spectroscopy and Simulation

Matteo Signorile+, Luca Braglia+, Valentina Crocellà, Piero Torelli, Elena Groppo, Gabriele Ricchiardi, Silvia Bordiga, and Francesca Bonino*





ENHANCED PERFORMANCE: APE-EHE

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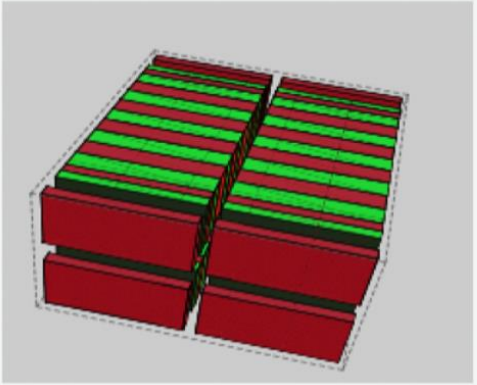
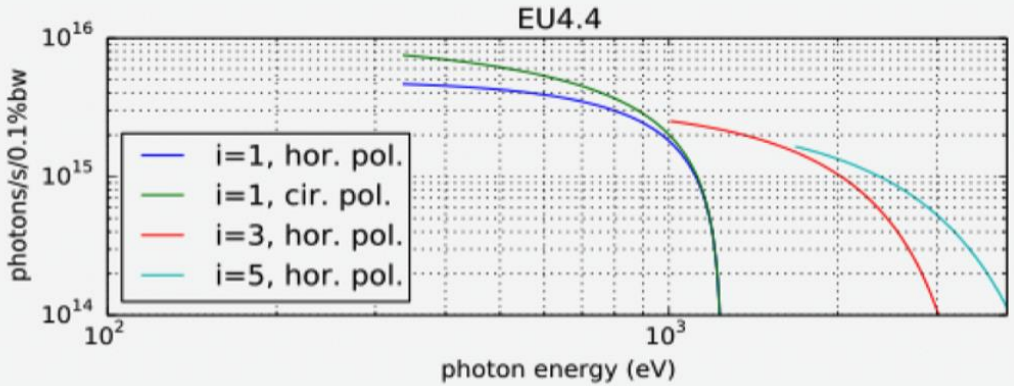
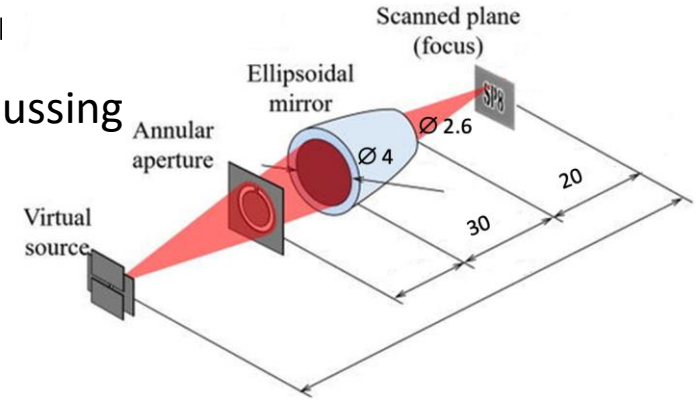




First harmonic will cover up to 1keV full polarization co

Achromatic fosussing

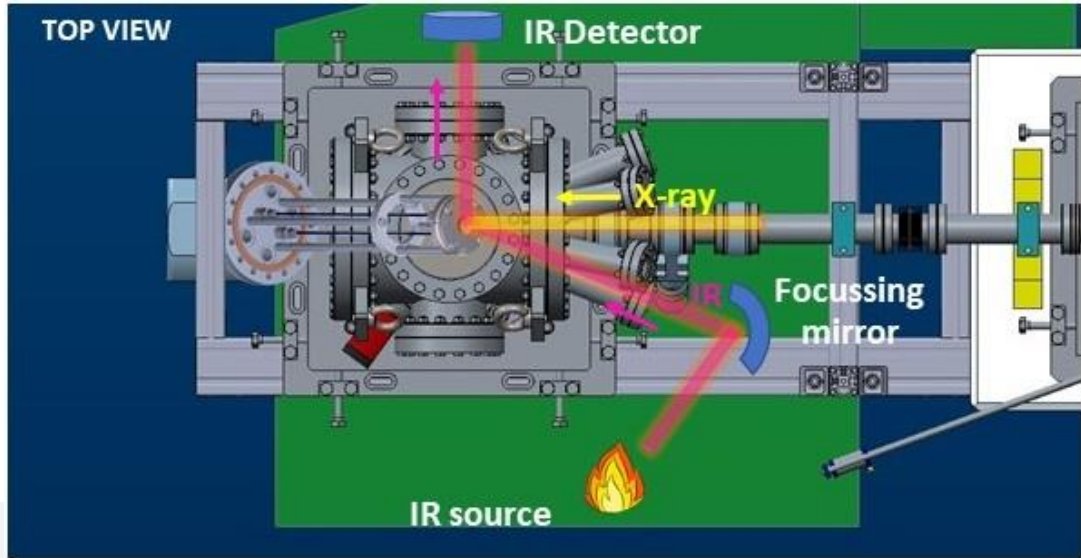


Esfoliation facility with transfer

Single domain XMCD/PES on Ferromagnets/multiferroics Magnetic dichroism in PES (LMDAD)

SR-facility	beamline	XAS/XMCD	in operando AP-XAS
Diamond	i10	XMCD, XMLD, 0.5-420 K, 14 T	
	B07 - versox	XAS, XPS, 120-1250 K	AP XAS for gas and liquid cells (300-450 K), AP-XPS up to 30 mbar, 250-750 K
SLS	Xtreme	XMCD, XMLD, 2-350 K, 7 T, prep chamber	
Soleil	Deimos	XMCD, XMLD, 0.2-370 (1000) K, 7 (30) T, *in situ*	liquid cell for ferrofluids in FY
	Tempo	XMCD (10 mT), XMLD, XPS, prep chamber, 50-1200 K, time resolved	
ESRF	ID32	XMCD, XMLD, 3-325 K, 9 T, prep chamber	
Alba	Boreas	XMCD, XMLD, 3-350 K, 6 T, prep chamber	
Bessy	Vekmag	XMCD, XMLD, 0.3-500 K, 9 T, time resolved	
ALS	4.0.2	XMCD, XMLD, 15-750 K, 4 T	
	9.3.2	200-900 eV, XAS	200-900 eV, ambient pressure XPS

H-cell setup: in situ X-ray and IR spectroscopy



all new APE-Tender-X beamline

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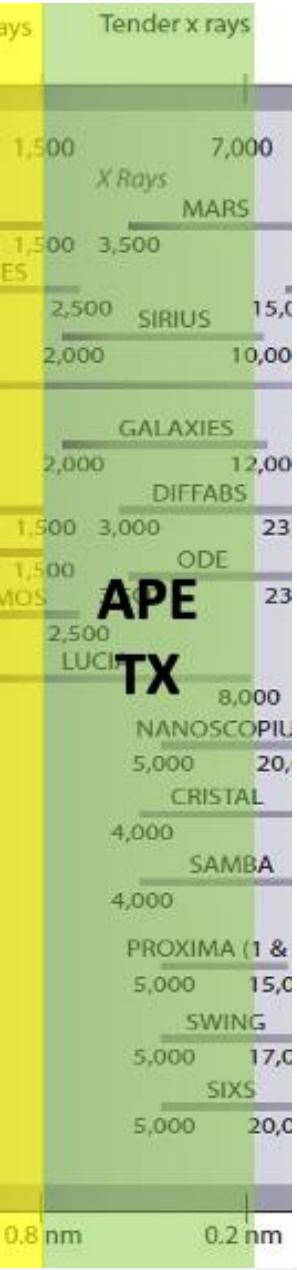


RATIONALE: 1) **electron mean free path varies from 0.5 to over 5 nm**
energy range favourable for PES/ARPES with depth sensitivity

- extending ARPES and core level photoemission spectroscopy from surface to bulk or buried layers allowing to probe **electron states**, **graded compositions**, **multilayered devices**
- access to 3rd and 4th period core edges (resonant photoemission and XAS/XMCD)
- in-operando setups

2) Elettra 2.0 can host a **dedicated short insertion with performances well adapted** for bridging the soft-X to hard-X ranges (as IO9 of Diamond, but with a unique – short – undulator)

Synchrotron	HAXPES	Energy range
Soleil	HAXPES + RIXS (GALAXIES)	2.3-12 Kev
PETRA III	HAXPES (P22)	2.4-15 keV
Diamond	HAXPES (IO9) 2 x > 2m undulators	0.1-20 keV
Bessy	HAXPES (HIKE)	2.5 -12 keV
	Ambient pressure HAXPES (Belchem-DCM, under constr)	2.5-10 keV
SLS	Ambient pressure HAXPES endstation	N/A

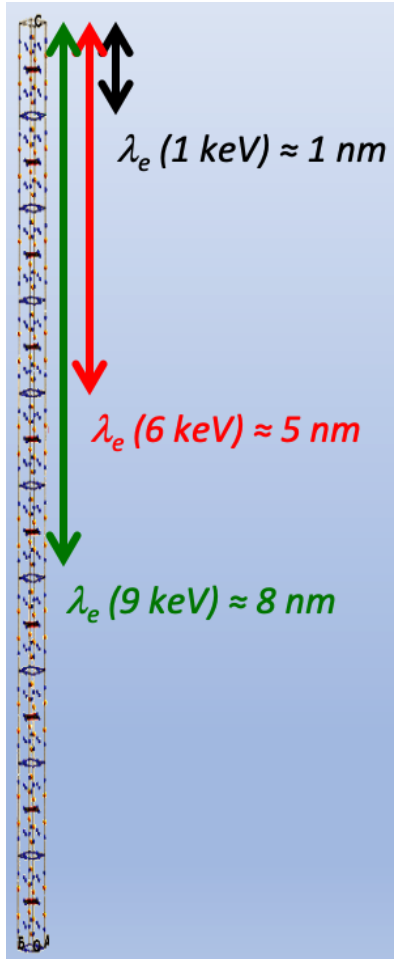
Benchmark IO9 vs. APE-TX

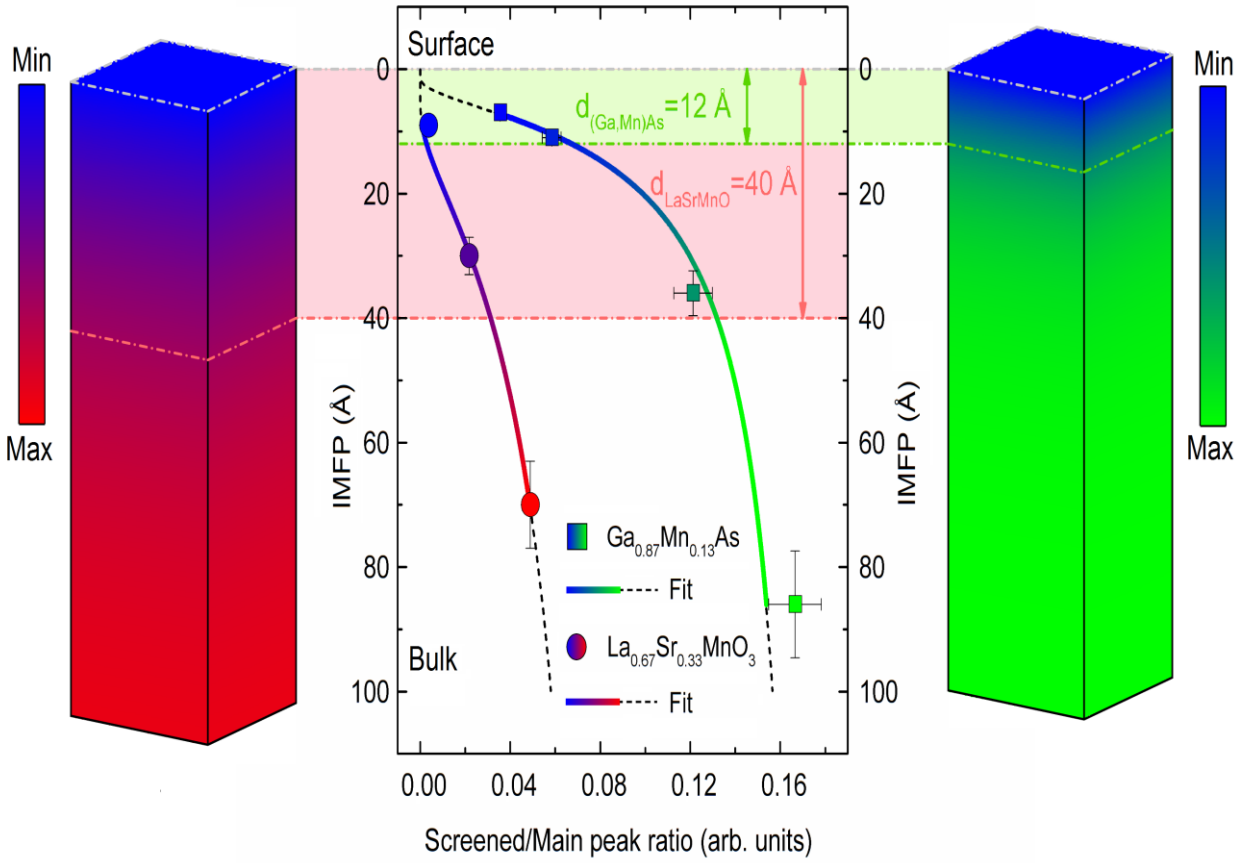
500 eV *~4x10^12 photon/s (slit 20um)*
1000 eV ~ 3x10^12 photon/s (slit 10um)

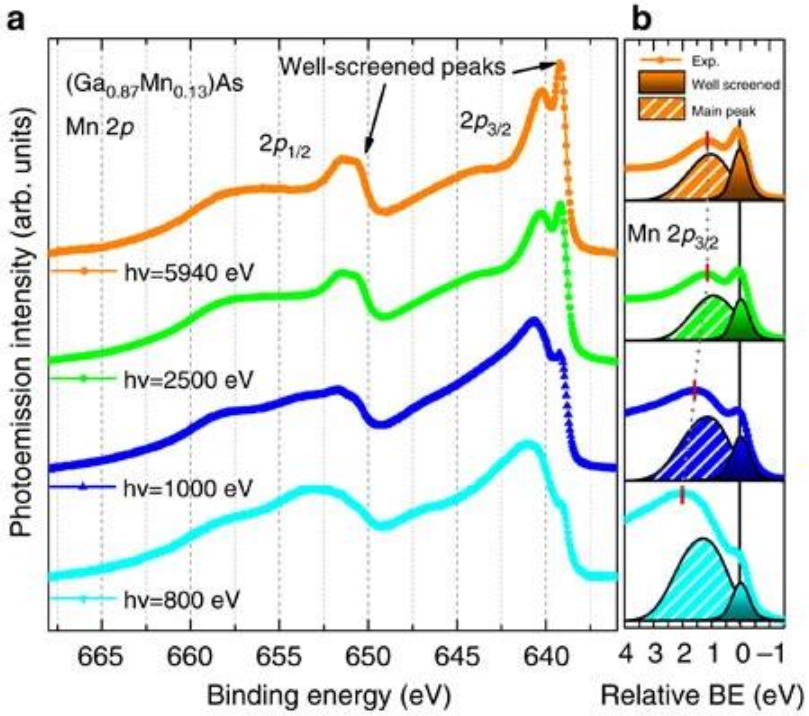
2.5 keV ~1x10^13 photon/s (Si(111) DCM)
2.5 keV ~ 3x10^12 photon/s (Si(111) DCM)
6 keV ~ 1.5x10^12 photon/s (Si(111) DCM)

Core Level PES from Soft-X to Tender-X

Example: critical thickness of 'metallic' bulk screening attenuation of bulk hybridization, localization of surface electrons.







T. Pincelli et al. Nat. Comm. **8**, 16051 (2017) IO9 – Diamond + BL19LXU Spring 8

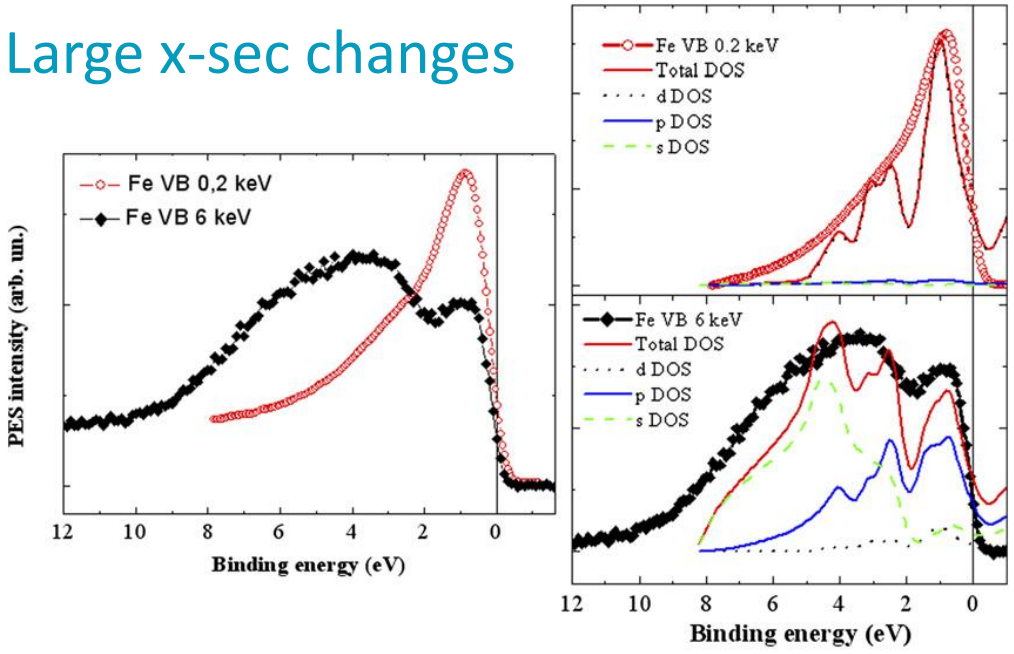
ARPES from Soft-X toTender-X

nature materials
ARTICLES
PUBLISHED ONLINE: 14 OCTOBER 2012 | DOI: 10.1038/NMAT3450

Bulk electronic structure of the dilute magnetic semiconductor $Ga_{1-x}Mn_xAs$ through hard X-ray angle-resolved photoemission

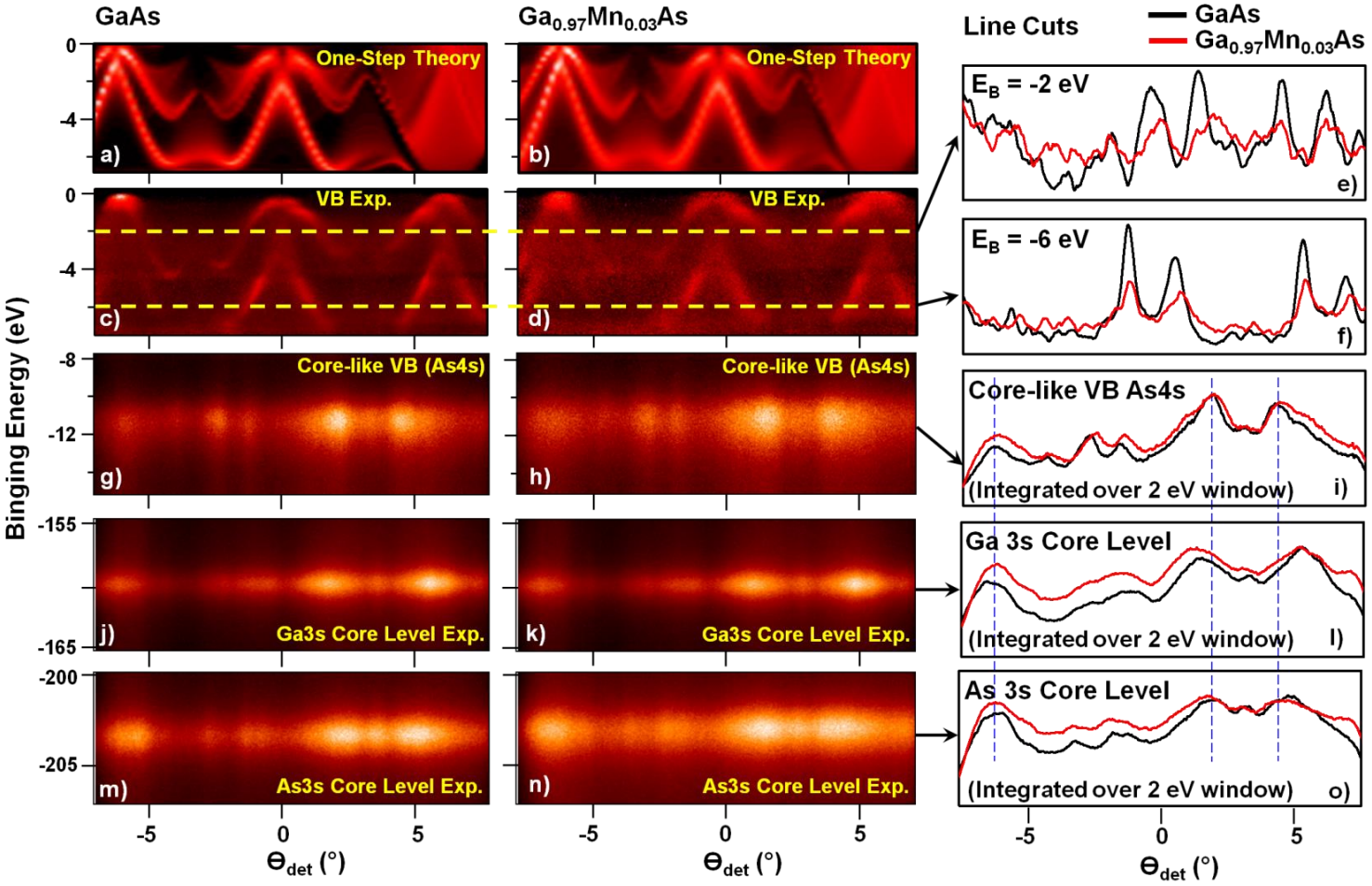
A. X. Gray[1,2,3]*, J. Minár[4], S. Ueda[5], P. R. Stone[2,6], Y. Yamashita[5], J. Fujii[7], J. Braun[4], L. Plucinski[8], C. M. Schneider[8], G. Panaccione[7], H. Ebert[4], O. D. Dubon[2,6], K. Kobayashi[5] and C. S. Fadley[1,2]

Large x-sec changes



(a) (b)

ARPES with 3.4 keV measured @ Spring-8



HAXPES FOR MATERIALS SCIENCE

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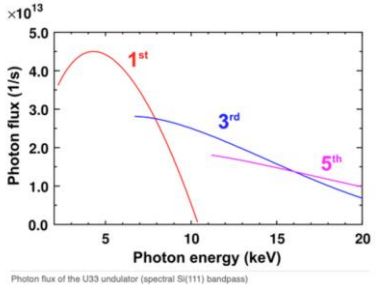
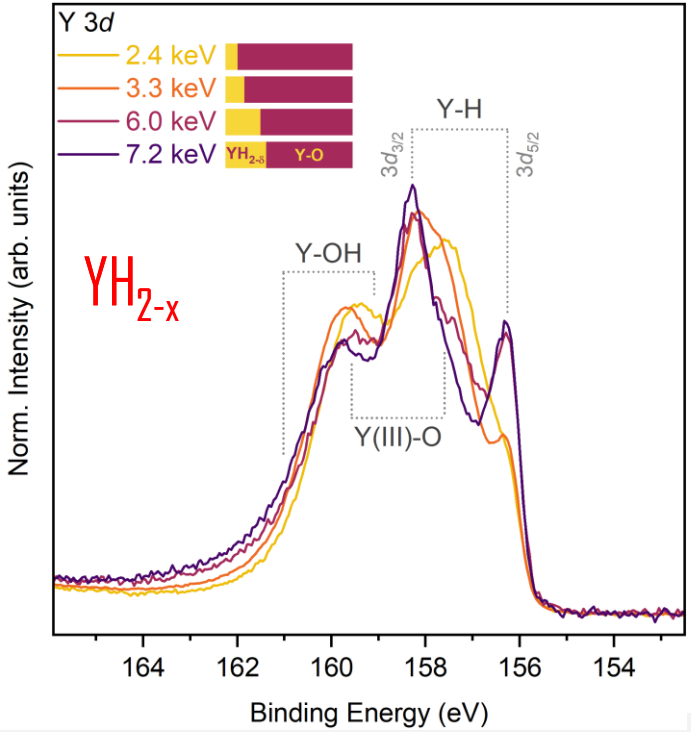
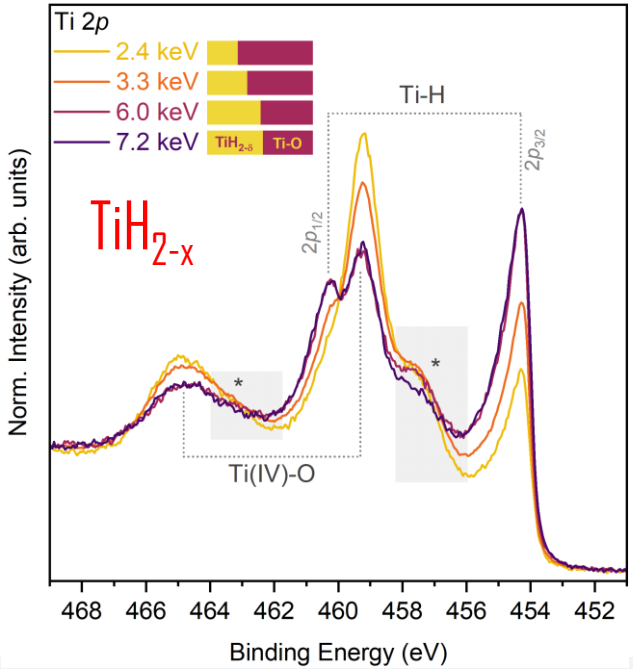
1. Identify chemical state distribution
2. Identify electronic character and bonding nature

HAXPES @ Petra III P22



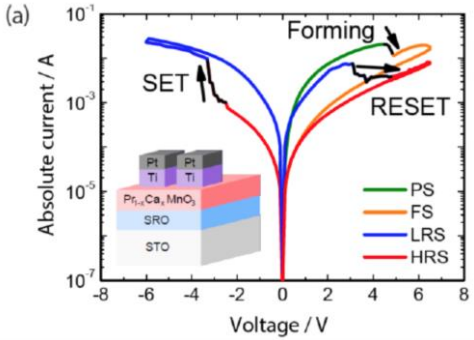
hν / keV	Optics	$E_{F,16/84}$ / meV
2.4106	Si(111) DCM	280
3.2691	Si(111) DCM + Si(220) PM	243
6.0054	Si(111) DCM + Si(333) PM	242
7.2310	Si(111) DCM + Si(333) PM (double bounce)	202





3. Chemical states of titanium for all the resistive states

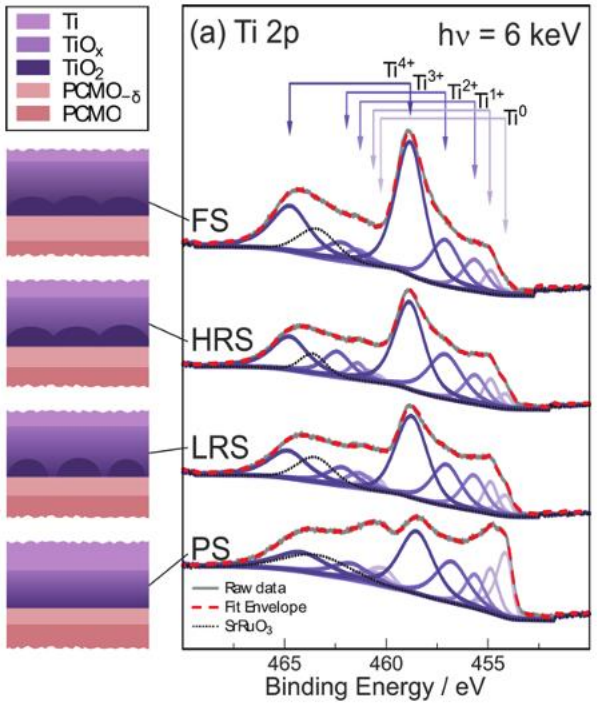
HAXPES @ SOLEIL Galaxy



TiO_2 CONTENT: FS > HRS > LRS > PS

Comparison **virgin** state with High/low resistance state (HRS/LRS)

Ti^0 = metallic titanium
Ti^{1+} = non stoichiometric titanium oxide*
Ti^{2+} = titanium monoxide (TiO)
Ti^{3+} = titanium sesquioxide (Ti_2O_3)
Ti^{4+} = titanium dioxide (TiO_2)
* but also TiC or TiN



F. Borgatti, et al. Nanoscale 5, 3954 (2013); A. Herper et al. , Adv. Mater. 26, 2730 (2014)
A. Regoutz et al. Adv. Funct. Mater. 26, 507 (2016); C. Baumer et al. Faraday Discuss., (2019), 213;

CONCEPT OF APE-Tender-X beamline

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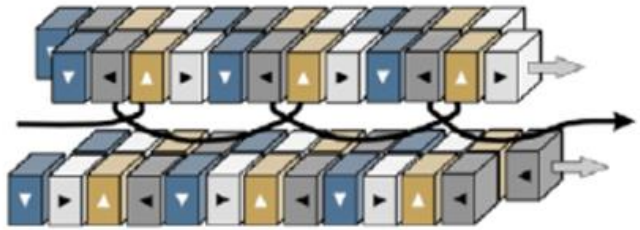
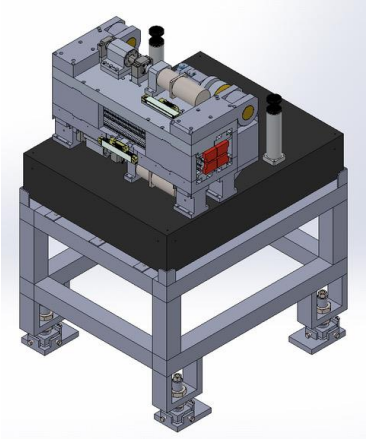
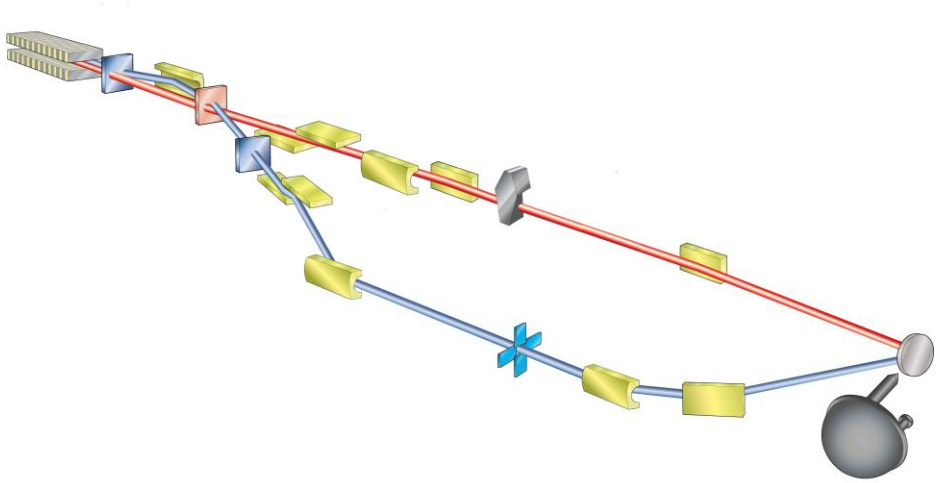
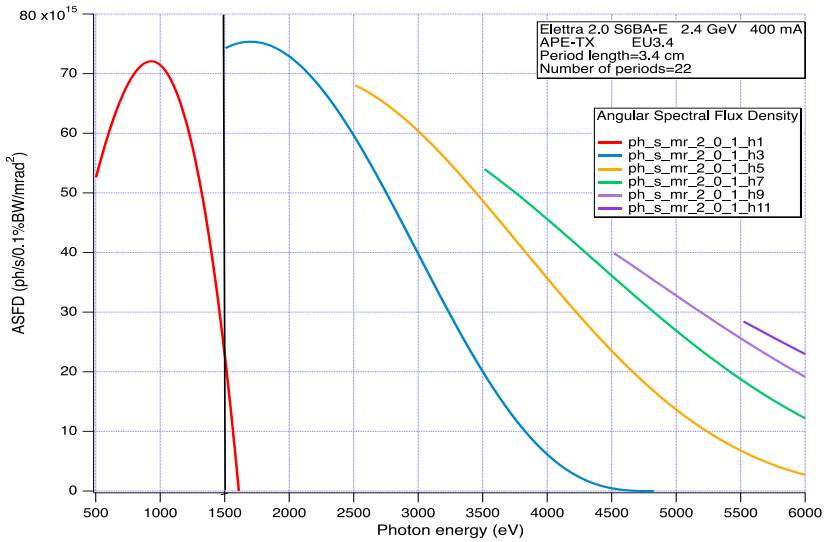


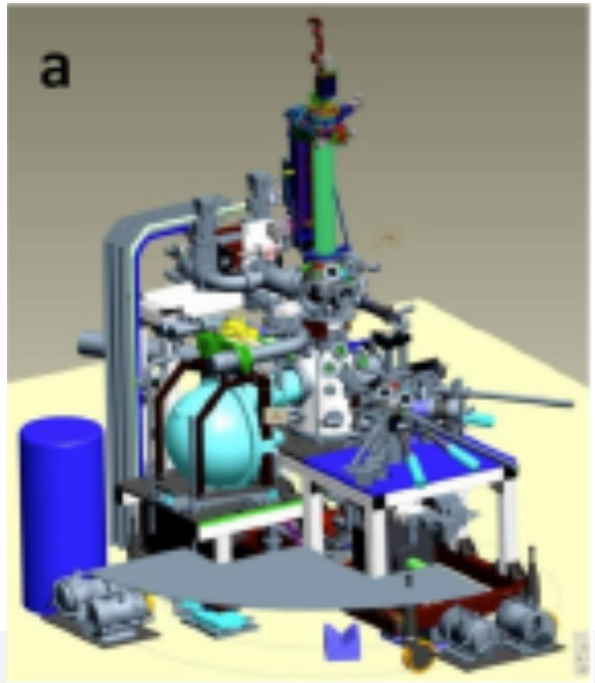


Concept and construction by Bruno Diviacco

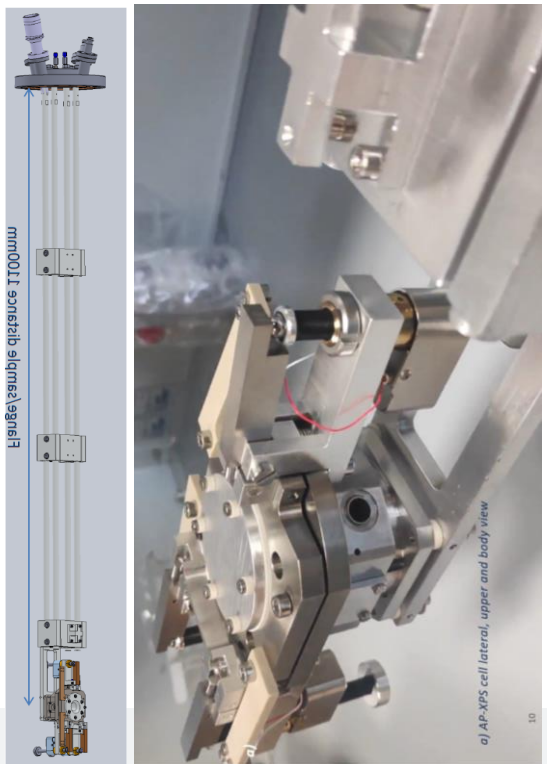


Preliminary concept under development by CNR and Elettra + international collaboration (IO9-like)





NFFA Prototype for AP-HAXPES experiment (collab. with I09) The sample volume is separated from the UHV by 2 SiN membranes (summer 2023).



- FIGURES OF MERIT OF THE APE-HIVE UPGRADES:

- APE-ELE : exploit beam brilliance for microfocussing, expand hv-range
- APE-EHE : exploit beam brilliance for for microfocussing and optimized 1st Harmonic source
- APE-TX : exploit Elettra 2.0 lattice (short section) and undulator technology to realize a continuous photon energy range for photoelectric effect measurements with variable (0.5 – 5 nm) depth sensitivity
- FAIR-by-design metadata acquisition -> towards ARWs in NFFA

- ONGOING DISCUSSION (2023) at CNR level for optimizing overall institutional investments on Elettra 2.0

Nanoscience research @ Elettra 2.0

nffa. trieste

ISTITUTO OFFICINA DEI MATERIALI

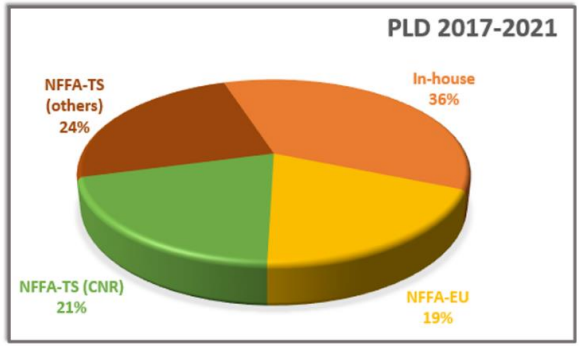
DigiMAT - Probing and controlling the electronic properties of materials by taking advantage of thin films technology

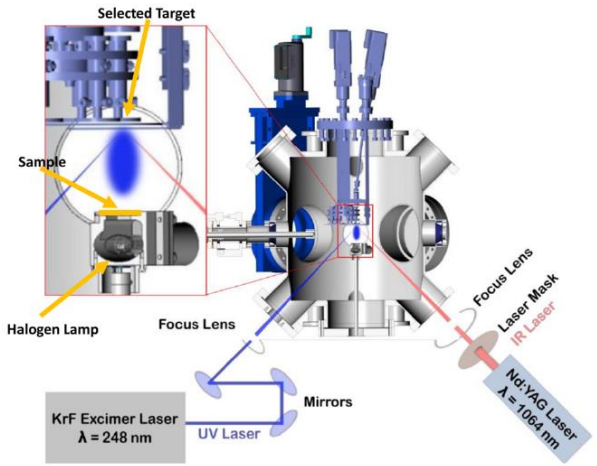
In-house	NFFA-TS		NFFA-Europe
Bi_2Se_3	* RE-doped $SrTiO_3$	* $LaAlO_3$	* V_2O_3
TiO_2	* $SrNbO_3$	* $Fe(Te_{0.5}Se_{0.5})$	*Fe-doped TiO_2
$SrRuO_3$	* FeTe	* $LaNiO_3$	*TM-doped $SrTiO_3$
$La_{0.7}Ba_{0.3}MnO_3$	* Fe	* $CaMnO_3$	* $BaTiO_3$
$La_{0.7}Ce_{0.3}MnO_3$	* WO_3	* Fe_3O_4	RE-doped CeO_2
$BiFeO_3$	* $LaVO_3$	* $MgGa_2O_4$	* RE-doped MgO
WO_3	* MoS_2	* $MgCr_2O_4$	* FeSe
FeSe	* CeO_2	* ZnO	* YSZ-8%
V_2O_3	* $YBa_2Cu_3O_7$	* Bi_2WO_6	
Cr_4Te_5	$La_{0.7}Sr_{0.3}MnO_3$	* WO_3	
	*MnSe2	* YIG - $Y_3Fe_5O_{12}$	

*growth protocol developed "on-demand"

*36 different materials / 30 user-driven / **28 growth protocols developed***

UV-ARPES experiments run on these materials





Dual pulsed laser deposition system for the growth of complex materials and heterostructures

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