Soft x-ray Spectroscopy Adventures in Pnictide Land …….

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Samples

F. Bondino, E. Magnano, M. Malvestuto, F. Offi, G. Panaccione, F. Parmigiani
PES, XAS, XES – 1111 system

P. Vilmercati, A. Fedorov, I. Vobornik, G. Panaccione
ARPES – 122 system

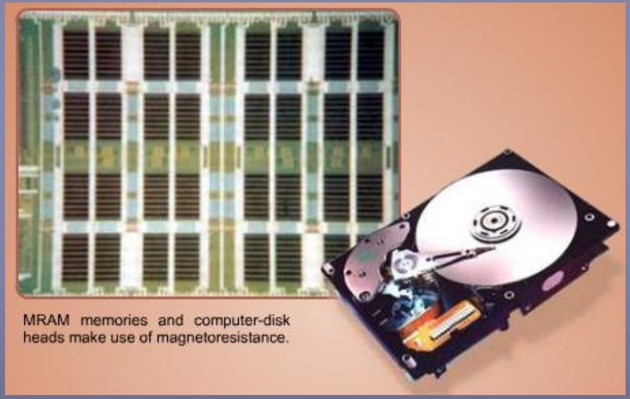
C. Parks Cheney, F. Bondino, P. Vilmercati, T. Callcott, J. Freeland
XAS – 122 system

D. J. Singh – Theory
E. W. Plummer, M. Stocks – Discussions

THE UNIVERSITY of TENNESSEE

Complex Electron Systems

High Temperature Superconductivity
(Cu Oxides)



Colossal Magnetoresistance
(Mn Oxides)

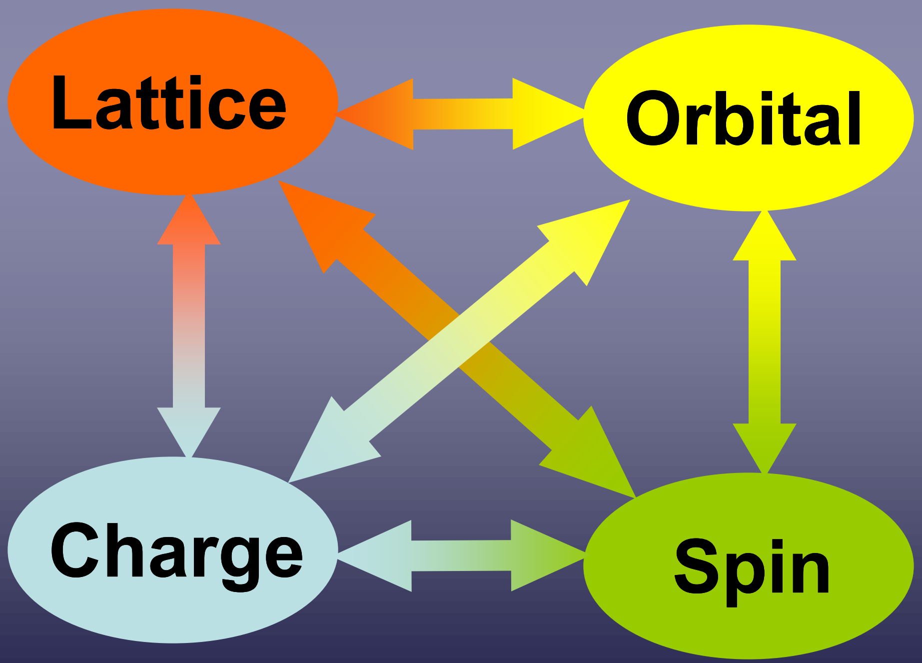
Dilute Magnetic Semiconductors
(Mn:GaAs)

Large Thermoelectric Effect
(Co Oxides)

Complex Electron Systems

Complex electron systems exhibit spectacular and unexpected phenomena arising from the interactions between the electrons or other degrees of freedom (such as the lattice or spin).

Interactions are strong ⇒ Beyond the usual approximation schemes based on single particle approximations ⇒ MANY BODY PROBLEM



Research Interest: interplay and competition of several degrees of freedom

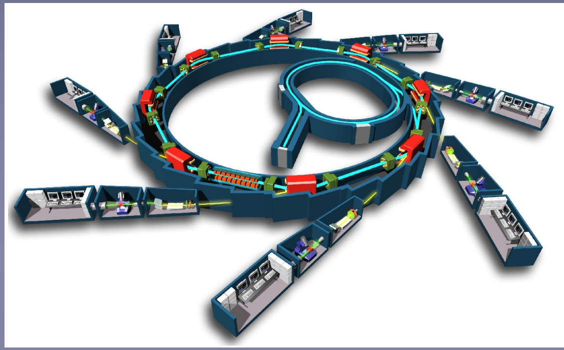
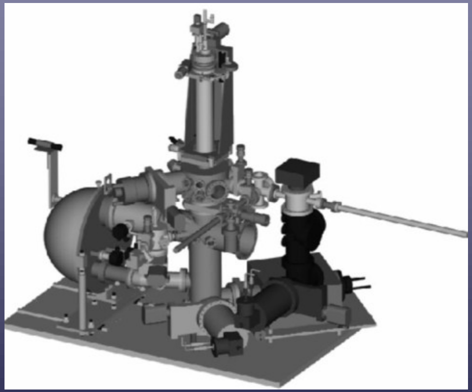
Spallation Neutron Source

Cray XT3 supercomputer
~250 Teraflops—use by proposal

Center for Nanophase Materials Sciences

Complex Electron Systems

Exciting opportunities

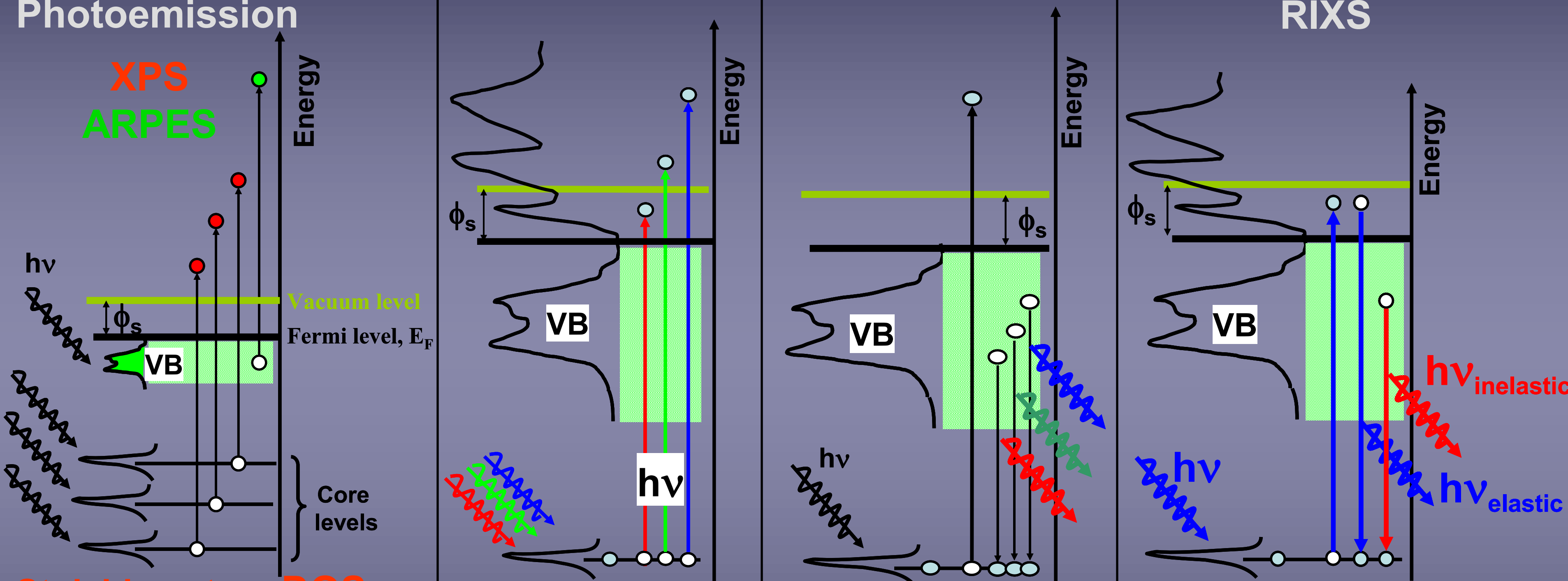
What	How	Where
Fe-based SC		**Synchrotron radiation**
Manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$	PE ARPES XAS XES EXAFS	
Cobaltates Na_xCoO_2 $GdBaCo_2O_{5+\delta}$		**Serf 310 - UTK**
Delafossites $CuRh_{1-x}Mg_xO_2$	ARPES LASER-ARPES MBE STM	
Binary Oxides VO_2, V_2O_3, Fe_3O_4, EuO		

nmannell@utk.edu, 974-6123, http://www.phys.utk.edu/faculty_mannella.htm

Experiments performed at UTK and Synchrotron Radiation Facilities ALS, Elettra, CAMD, Aladin, SSRL …

The Soft X-Ray Spectroscopies

Core Level and Angle Resolved Photoemission	X-Ray Absorption XAS	X-Ray Emission XES	Resonant Inelastic X-Ray Scattering RIXS



Stoichiometry - DOS Chemical Environment Band Structure Quasi-particles	Unoccupied states	Occupied states	Elementary Excitations d-d Transitions

Surface	Near-Surface Bulk	Bulk

Core levels ⟹ Element-specific Methods

Energy Crisis

Saving energy loss from transmission lines is one of the most important applications of High T_c superconductors

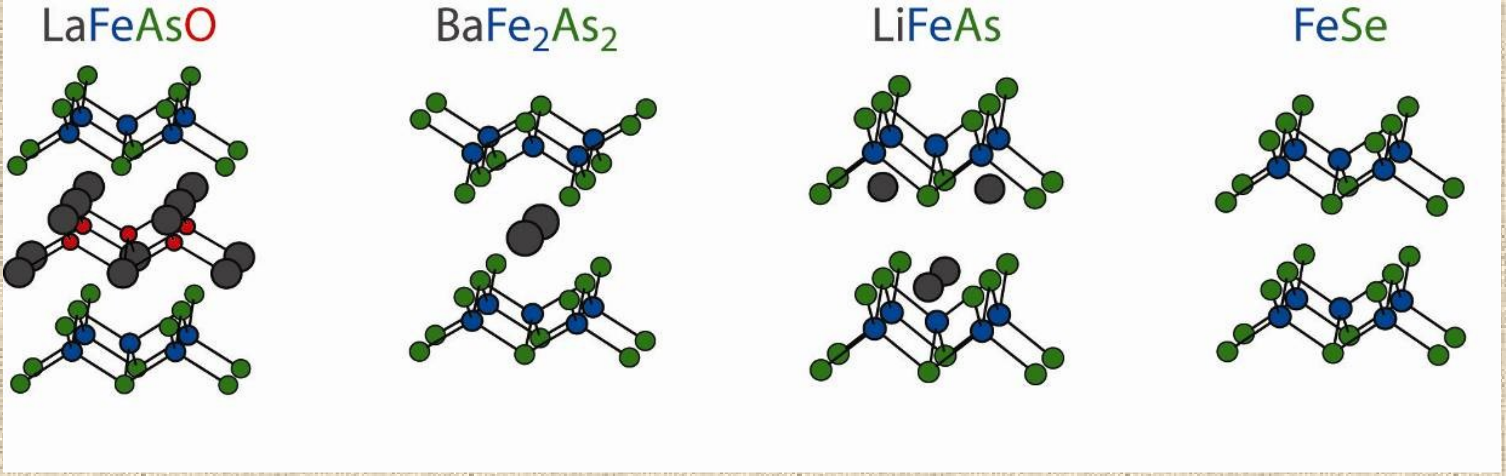
Breaking the supremacy of Cuprates

Brief History of Quaternary Rare Earth Transition Metal Pnictide Oxides- and *other Iron-based superconductors*

- Jeitschko group reports first RETPnO compounds (1994)
- Jeitschko group reports 18 quaternary arsenides, eg. LaFeAsO (2000)- *J.Alloys and Compounds 302 (2000) 70*
- Superconductivity at 4 K reported for LaFePO, raised to 7 K with F doping- *Kamihara et al. JACS 128 (2006) 10012*
- Feb. 2008 Superconductivity at 26 K reported for F doped LaFeAsO- *Kamihara et al. JACS 130 (2008) 3296* Pressure increases T_c to 41 K Takahashi et al. Nature Letters.
- March-April 2008 Groups in Beijing IOP push Tc up to about 50 K by replacing La by other light rare earths (Ce, Pr, Nd,Sm Gd). First materials prepared and studied in US at ORNL- *Sefat et al. Phys. Rev. B. 77* (2008) 174503.
- May 2008 Rotter et al. (Chemistry group in Munich) report superconductivity at 38 K for $Ba_{1-x}K_xFe_2As_2$ in the $ThCr_2Si_2$ structure- Single crystals can be grown from Sn or FeAs flux. No Oxygen

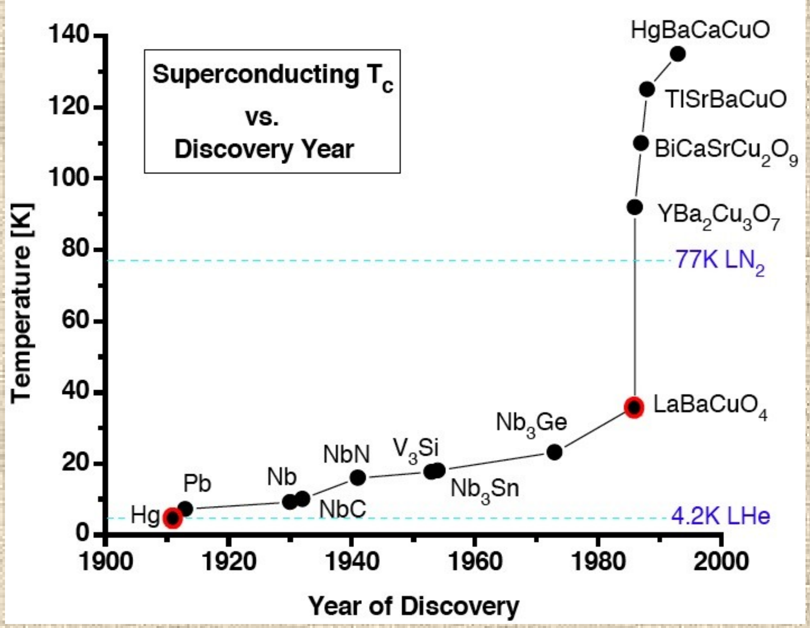
Brief History of Quaternary Rare Earth Transition Metal Pnictide Oxides- and *other Iron-based superconductors (cont'd)*

- **June 2008** Superconductivity at 18 K reported for Li_xFeAs by IOP group- **3rd structure type** (we also observed sc in our lab 2 days before preprint appeared on server).
- **July 2008** Superconductivity at 8K in $Fe_{1+x}Se$, reported by Hsu et al.(group from Taiwan), increases to 27 K under pressure (Mizuguchi et al Japan) Single crystals can be grown **4th structure type- NO arsenic or oxygen**

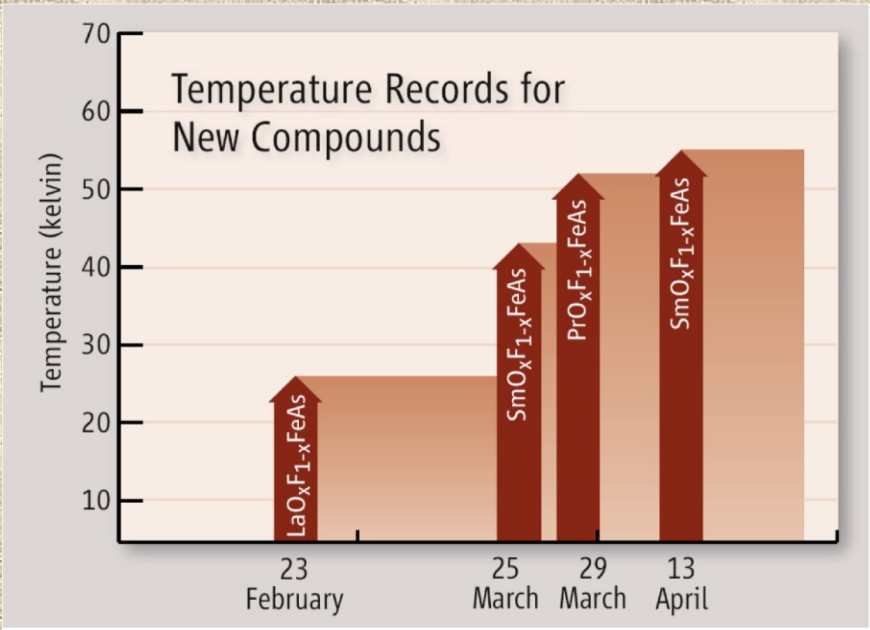


Square planar nets of Fe atoms in a tetrahedral environment is the common feature of all four superconducting structure types

How high is the T_c now?



Cuprate



Iron-based SC

Why Fe-based superconductors are so exciting

Excellent model systems for unconventional SC

--a lot can be done with DFT
--structurally simple & homogeneous
--nice crystals can be grown

Huge "materials space" to look for new SCs

--good test of predictive ability of modern theory

LaFeAsO Structure
Iron in tetrahedral coordination, Fe-Fe distance 2.85 Å
Fe-Fe distance 2.477 Å in iron metal
Large Number of Compounds!

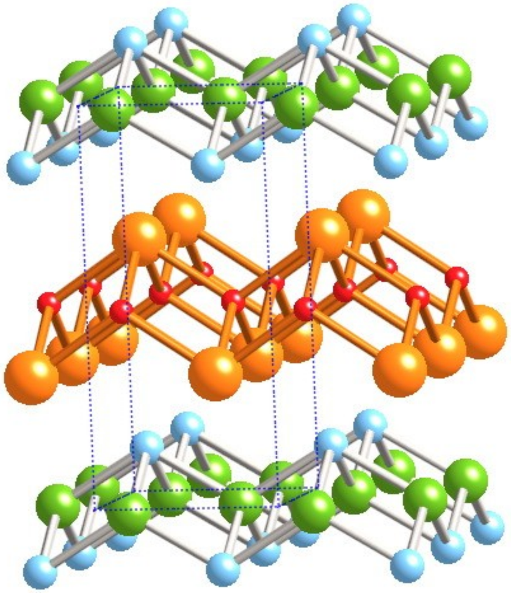


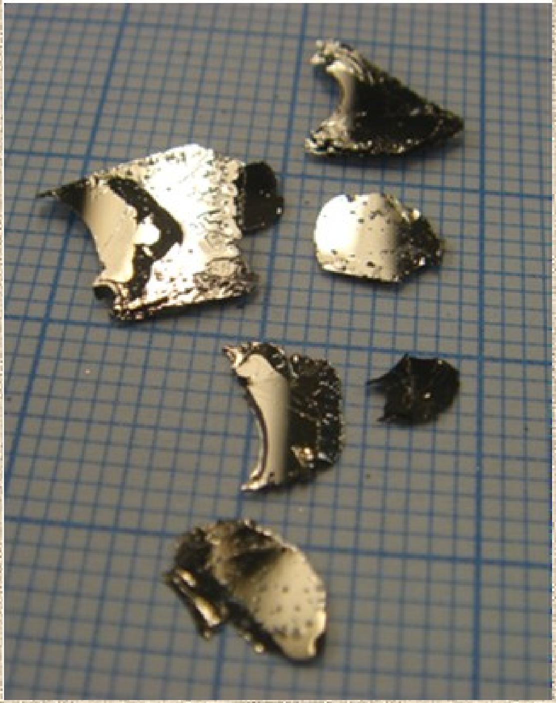
Table 1
Lattice constants of the tetragonal compounds RTAsO[a]

Compound	a (pm)	c (pm)	c/a	V (nm^3)
LaFeAsO	403.8(1)	875.3(6)	2.168	0.1427
CeFeAsO	400.0(1)	865.5(1)	2.164	0.1385
PrFeAsO	398.5(1)	859.5(3)	2.157	0.1365
NdFeAsO	396.5(1)	857.5(2)	2.163	0.1348
SmFeAsO	394.0(1)	849.6(3)	2.156	0.1319
GdFeAsO	391.5(1)	843.5(4)	2.155	0.1293
LaRuAsO	411.9(1)	848.8(1)	2.061	0.1440
CeRuAsO	409.6(1)	838.0(3)	2.046	0.1406
PrRuAsO	408.5(1)	833.7(1)	2.041	0.1391
NdRuAsO	407.9(1)	829.2(2)	2.033	0.1380
SmRuAsO	405.0(2)	819.1(7)	2.022	0.1343
GdRuAsO	403.9(1)	811.8(6)	2.010	0.1324
TbRuAsO	402.7(1)	807.8(1)	2.006	0,1310
DyRuAsO	402.2(2)	805.0(3)	2.001	0.1302
LaCoAsO	405.4(1)	847.2(3)	2.090	0.1392
CeCoAsO	401.5(1)	836.4(2)	2.083	0.1348
PrCoAsO	400.5(1)	834.4(2)	2.083	0.1338
NdCoAsO	398.2(1)	831.7(4)	2.089	0.1319

Table from Quebe et al. J. Alloys and Compounds **302** (2000) 74

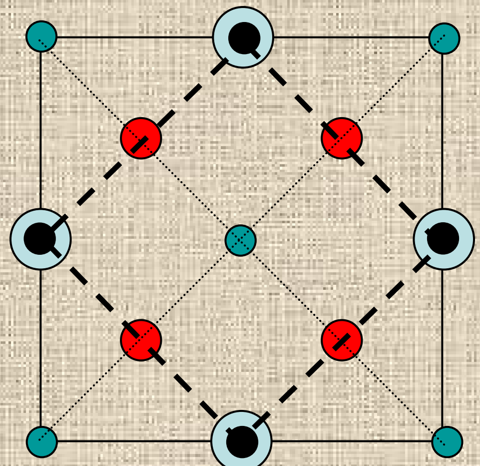
Some of Known Fe compounds (Before 1991) with the $ThCr_2Si_2$ Structure

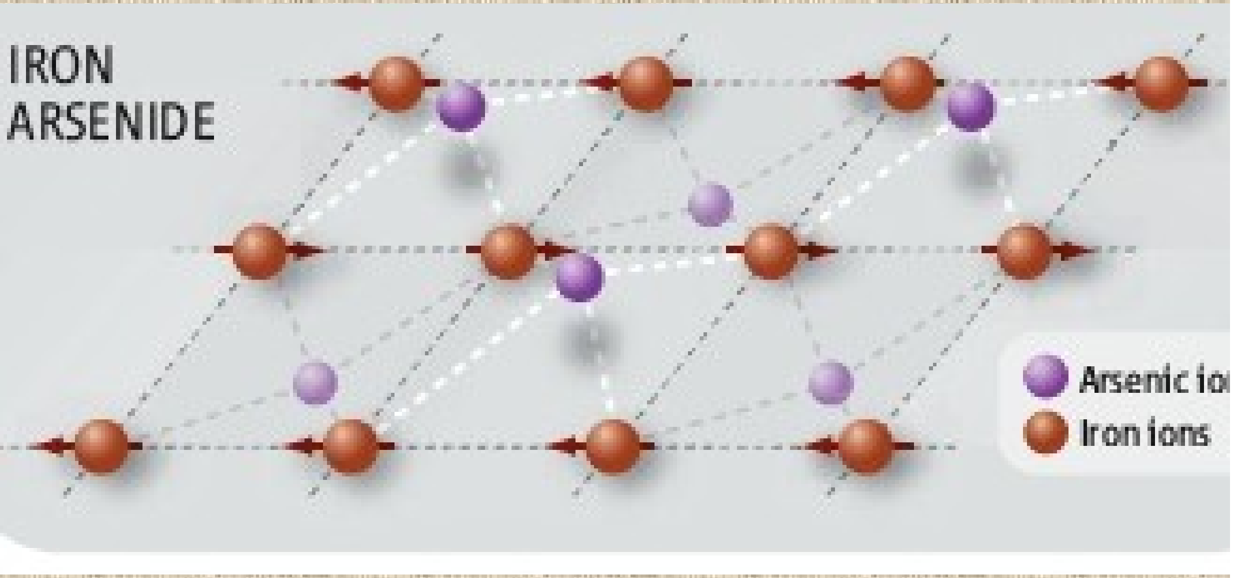
$EuFe_2As_2$	KFe_2As_2	$BaFe_2As_2$	$SrFe_2As_2$	$DyFe_2B_2$	$HoFe_2B_2$	$TmFe_2B_2$	$BaFe_2P_2$
$CaFe_2P_2$	$CeFe_2Ge_2$	$ErFe_2B_2$	$LuFe_2B_2$	YFe_2B_2	$CeFe_2P_2$	$GdFe_2B_2$	$TbFe_2B_2$
$CeFe_2Si_2$	$DyFe_2Si_2$	$ErFe_2Ge_2$	$EuFe_2P_2$	$DyFe_2Ge_2$	$ErFe_2Si_2$	$EuFe_2Si_2$	$LaFe_2Ge_2$
$LaFe_2P_2$	$SmFe_2Ge_2$	UFe_2Ge_2	$LaFe_2Si_2$	$NdFe_2Si_2$	$TlFe_2Se_2$	$ThFe_2Si_2$	YFe_2Si_2
UFe_2P_2	$GdFe_2Ge_2$	$NdFe_2Ge_2$	$TbFe_2Ge_2$	$YbFe_2Ge_2$	$LuFe_2Si_2$	$PrFe_2Si_2$	$SmFe_2Si_2$
$TmFe_2Si_2$	$YbFe_2Si_2$	$PrFe_2Ge_2$	$ThFe_2Ge_2$	$HoFe_2Si_2$	$SrFe_2P_2$	$TbFe_2Si_2$	$TlFe_2S_2$
UFe_2Si_2	$ZrFe_2Si_2$						

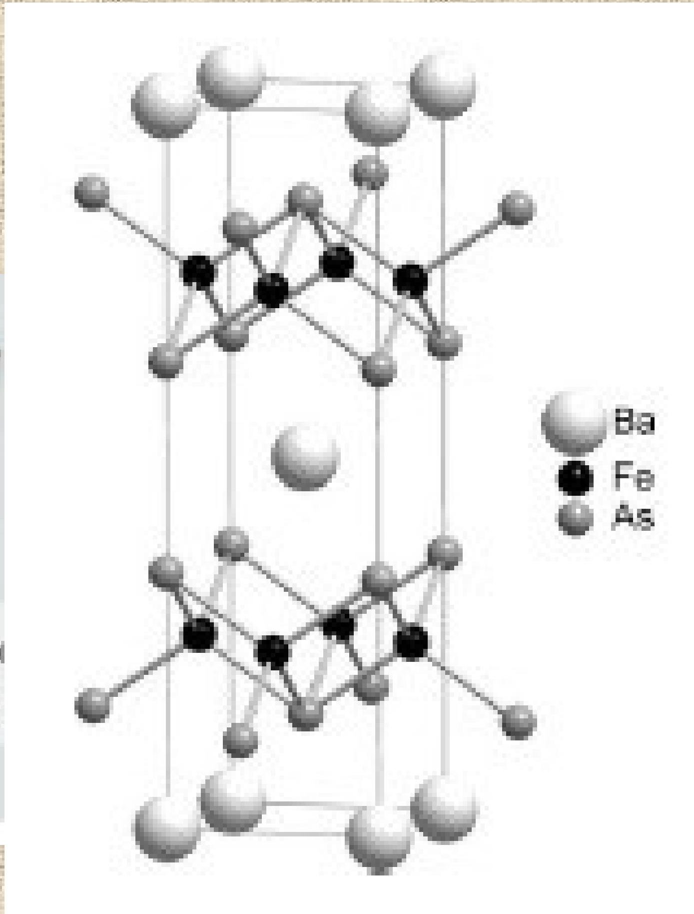


Crystals with $ThCr_2Si_2$ Structure ($BaFe_{1.84}Co_{0.16}As_2$)

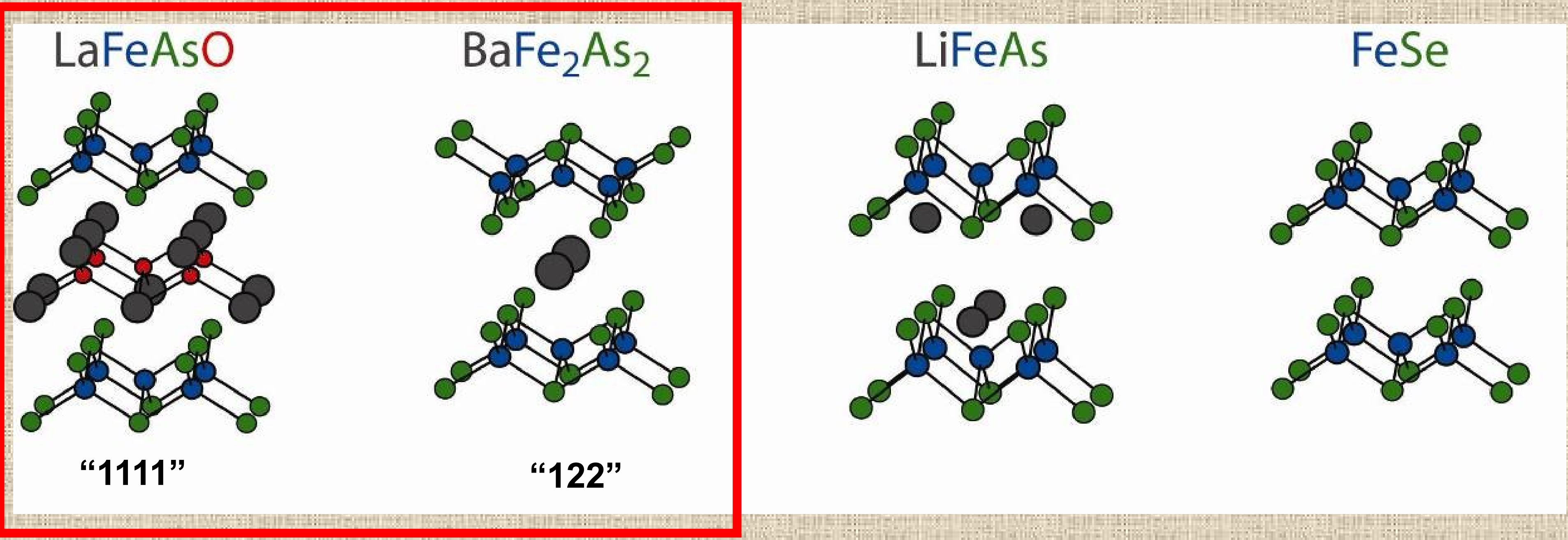
Lattice and Magnetic Structure



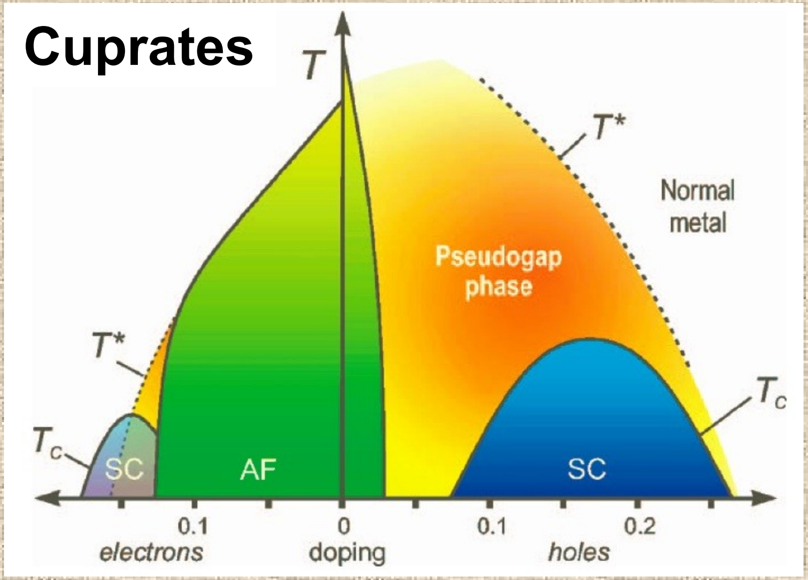




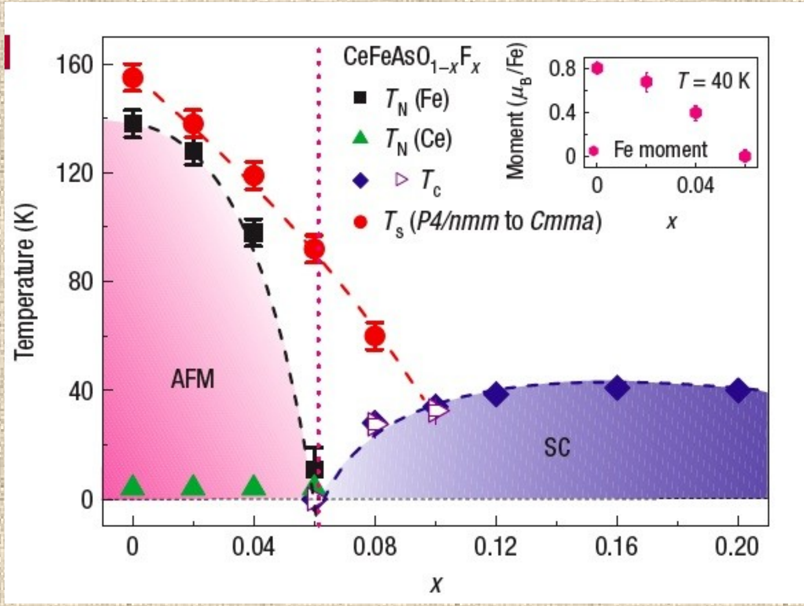
Adrian Cho, Science 320, 870(2008)



Square planar nets of Fe atoms in a tetrahedral environment is the common feature of all four superconducting structure types



Rev. Mod. Phys. 79, 353 (2007)



J. Zhao et al., Nature Materials 7, 953 (2008).

Similarities

Spin, charge both involved
2D crystal structure
Similarity of phase diagrams

Differences Lower Tc

CuO_2 Planes (Octahedral) vs. Tetrahedral coordination
Mott insulator AFM vs. Metallic "SDW" groundstate
Single Band vs. Multi-band

Some Key Questions

Are the new FeAs SCs similar or dissimilar to the cuprates HTSC?

Phase diagram shows competition between a magnetically ordered, Spin Density Waves state and Superconductivity

? = signatures of fluctuations associated with the proximity to AF state?

⇒ Clarify interplay between magnetism and superconductivity, i.e. competition between SC and SDW

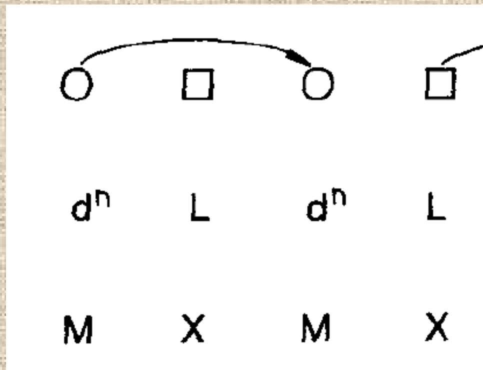
Are the new FeAs SCs similar or dissimilar to the cuprates HTSC?

Electronic structure of the normal state

A hallmark of cuprates HTSC: The non-Fermi liquid normal state

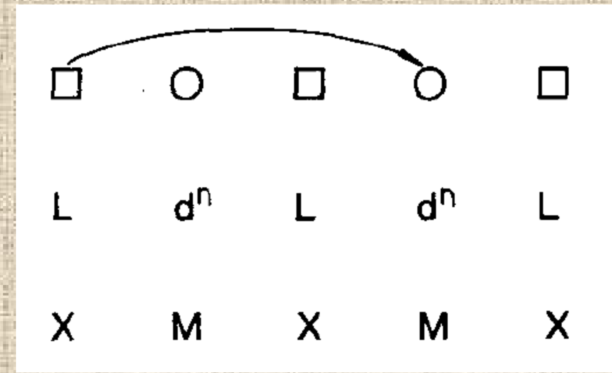
Strong electron correlations (i.e. on-site Coulomb repulsions) in the narrow Cu 3d bands

$Cu^{2+}O^{2-}Cu^{2+} + U \rightarrow Cu^{1+}O^{2-}Cu^{3+}$



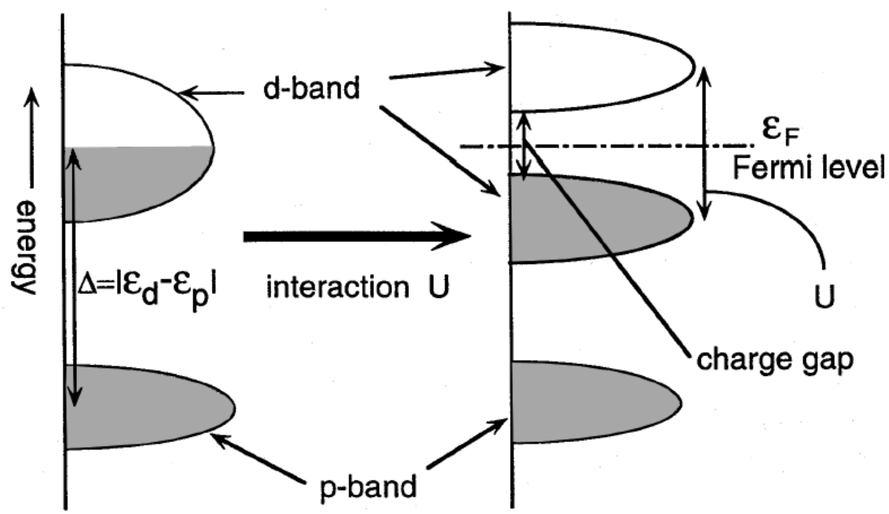
$2E(d^n) + U \rightarrow E(d^{n+1}) + E(d^{n-1})$

$Cu^{2+}O^{2-}Cu^{2+} + \Delta \rightarrow Cu^{1+}O^{1-}Cu^{2+}$



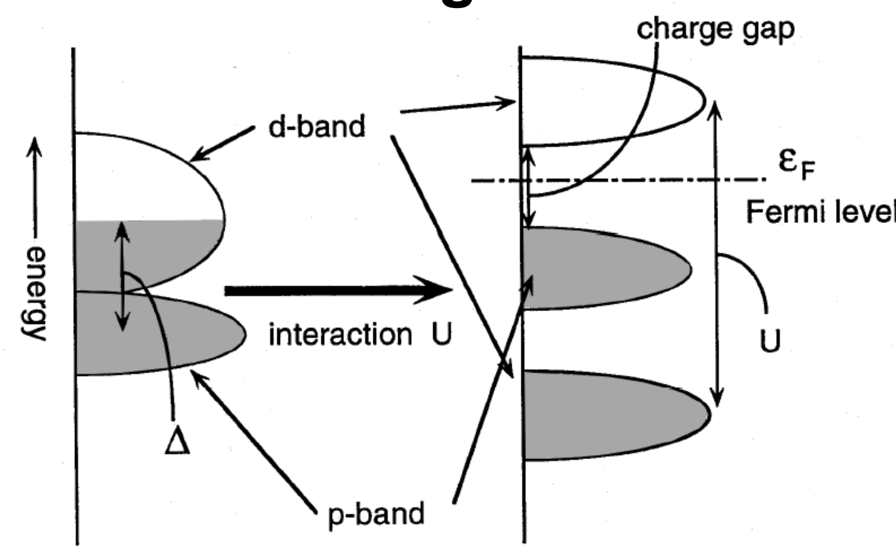
$E(d^n) + E(L) + \Delta \rightarrow E(d^{n+1}) + E(L^{-1})$

U < Δ Mott Hubbard



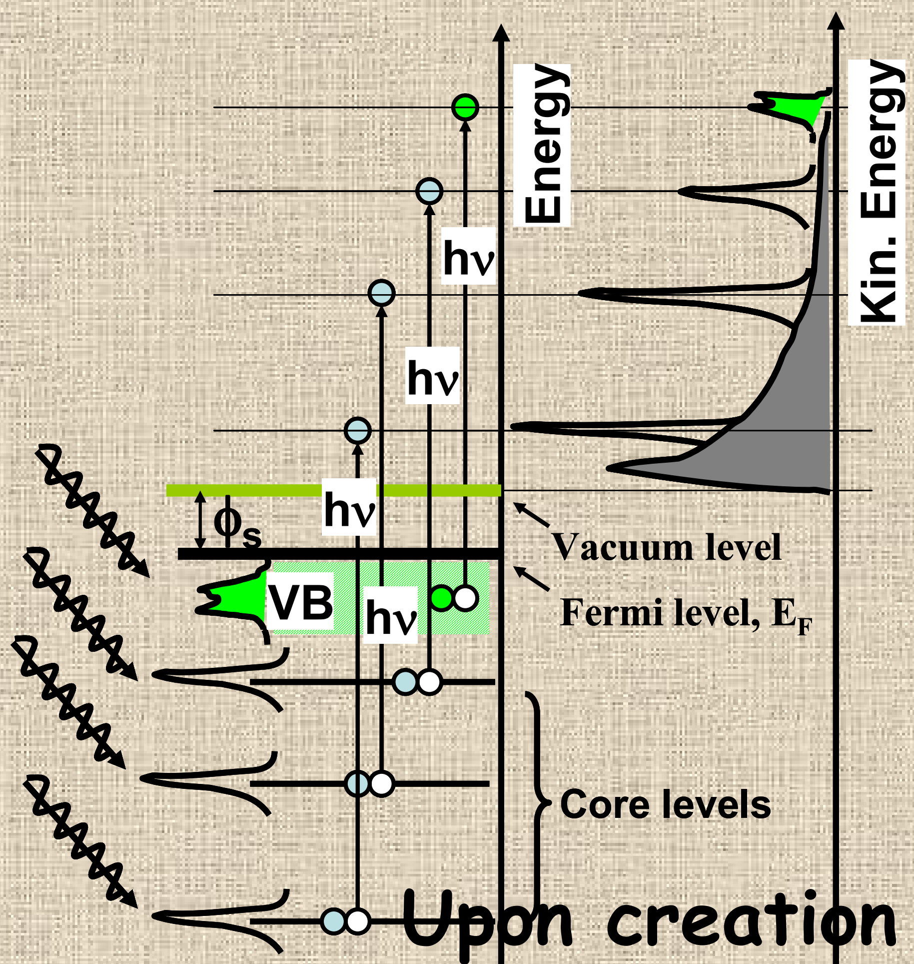
(a) Mott-Hubbard Insulator

U > Δ Charge Transfer

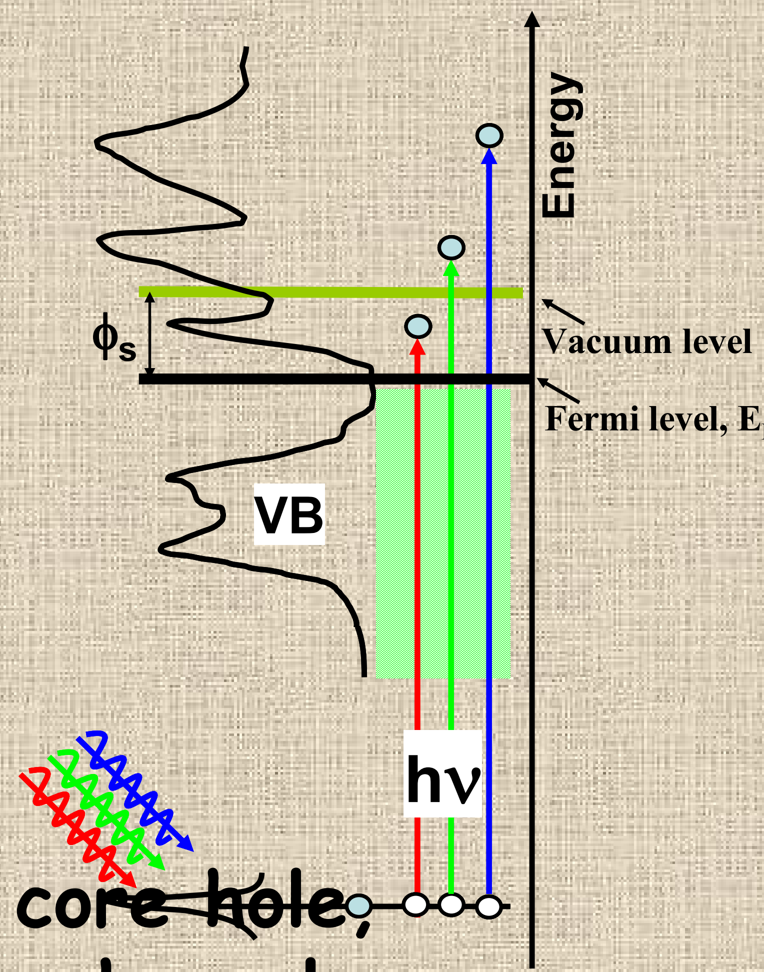


(b) Charge Transfer Insulator

Photoemission

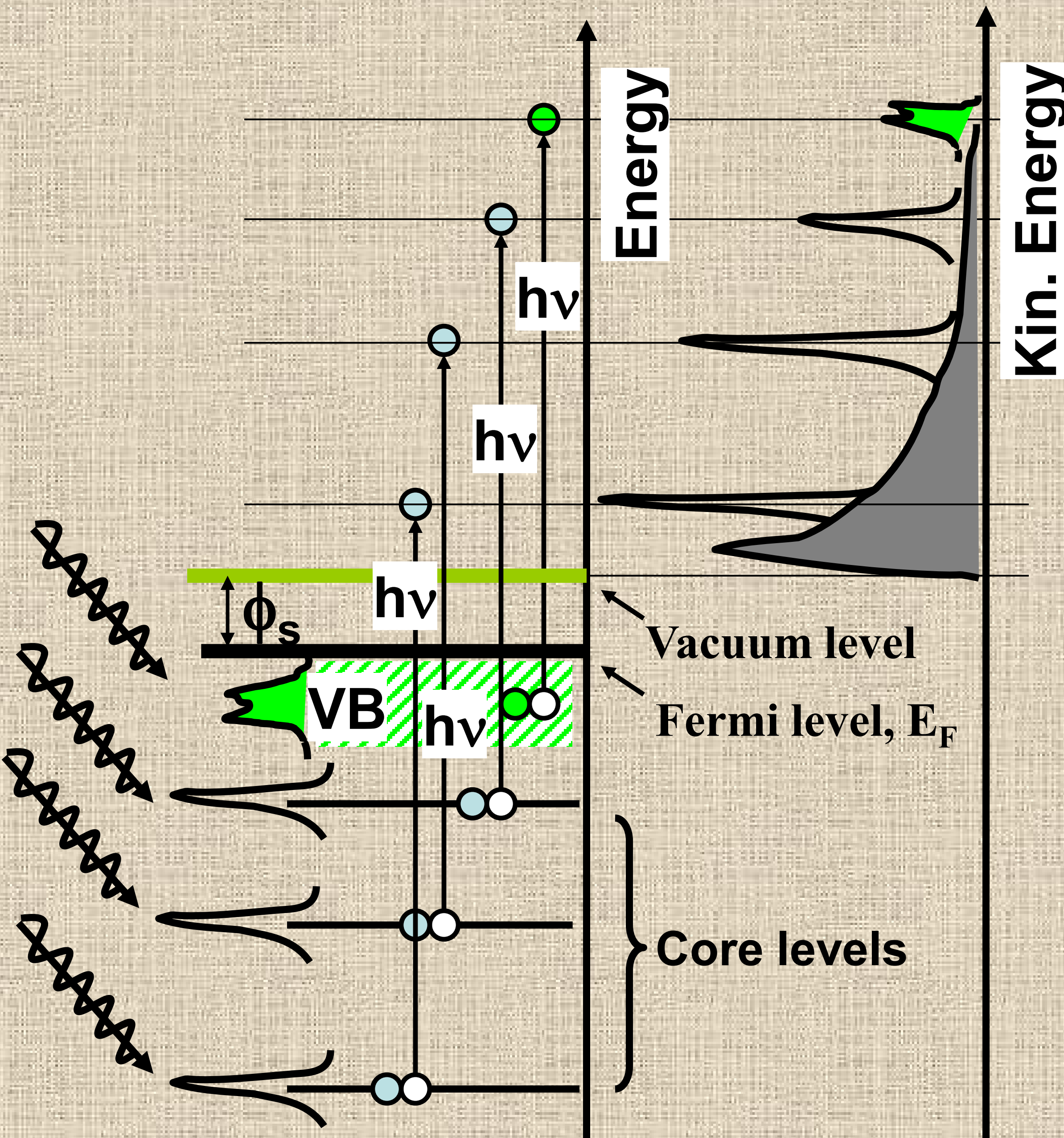


X-ray absorption (XAS)

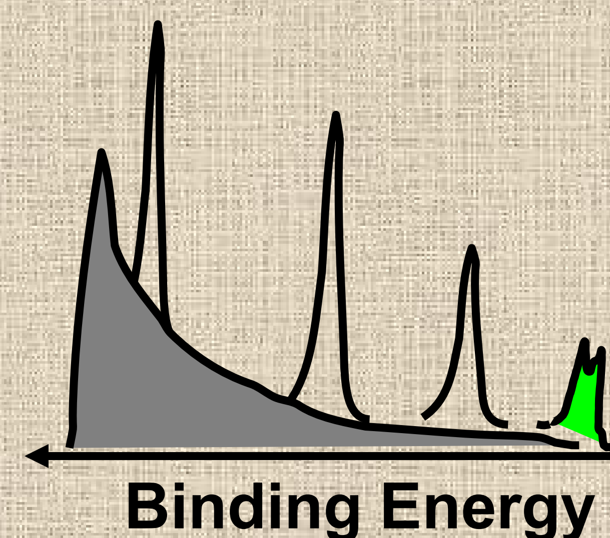


Upon creation of a core hole,
different screening channels
leave definite signatures
in photoemission and absorption spectra

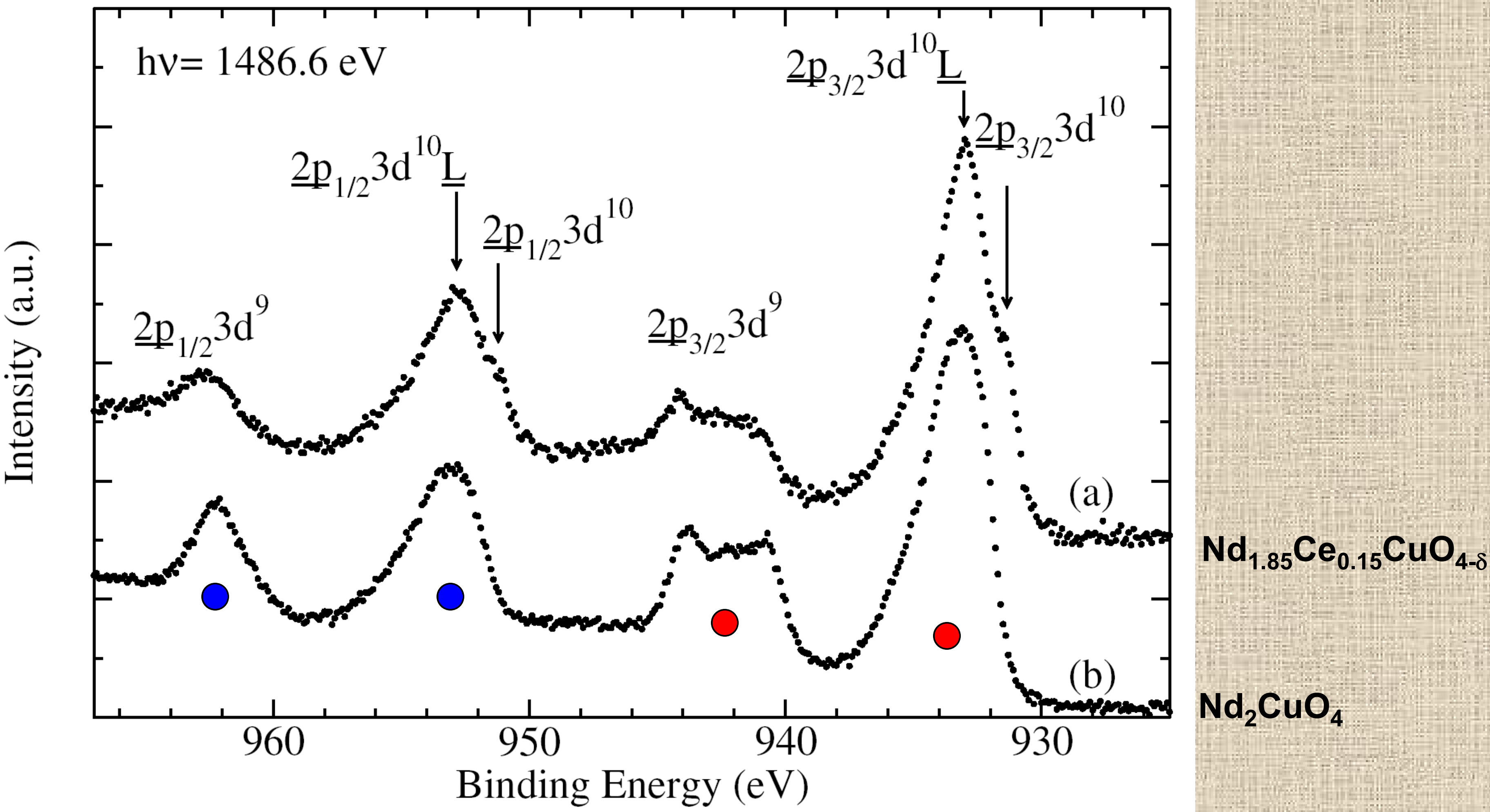
Core PE - stoichiometry, BE shifts, satellites



$$E_B = h\nu - KE$$

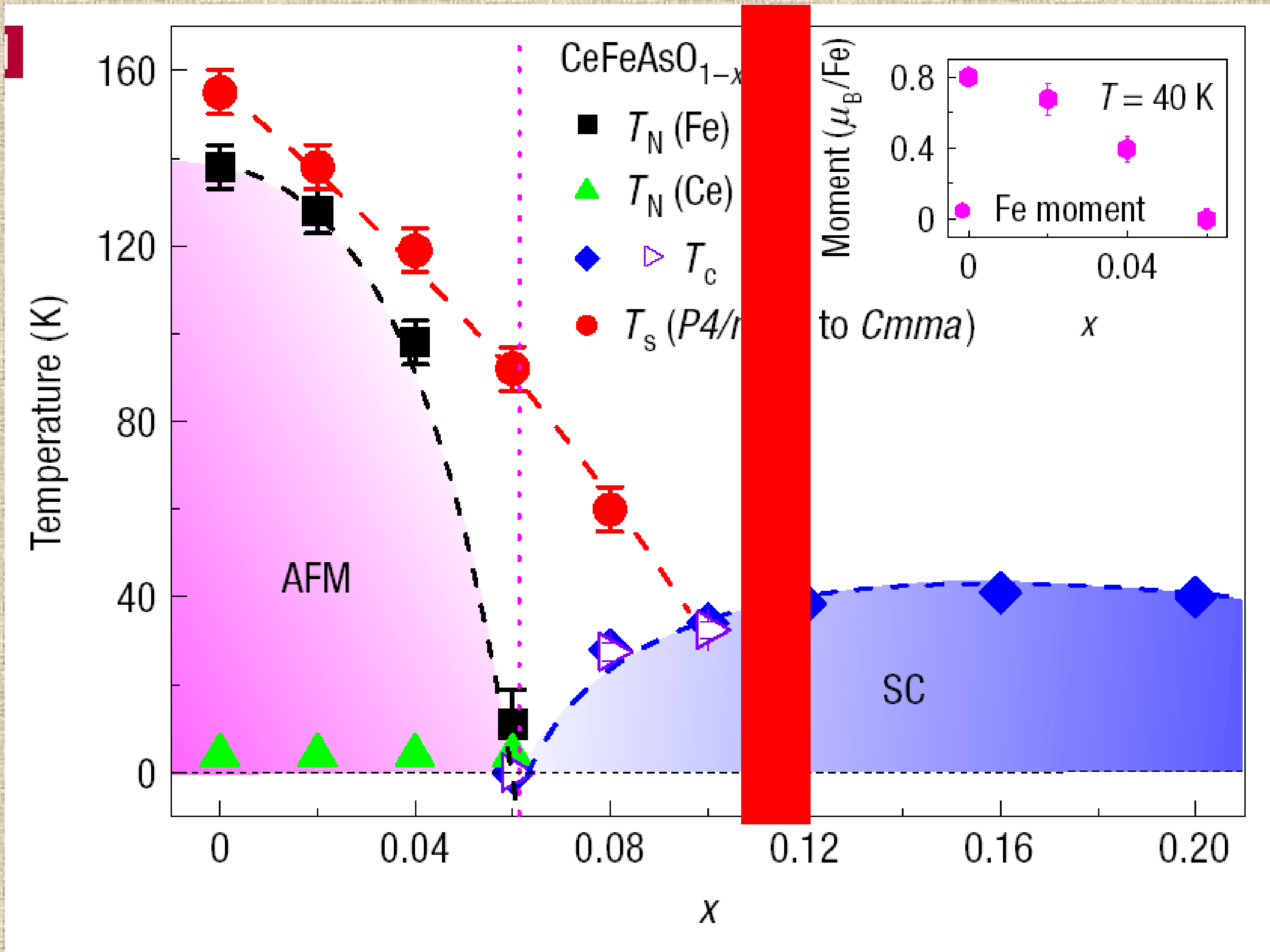


Cu 2p - XPS



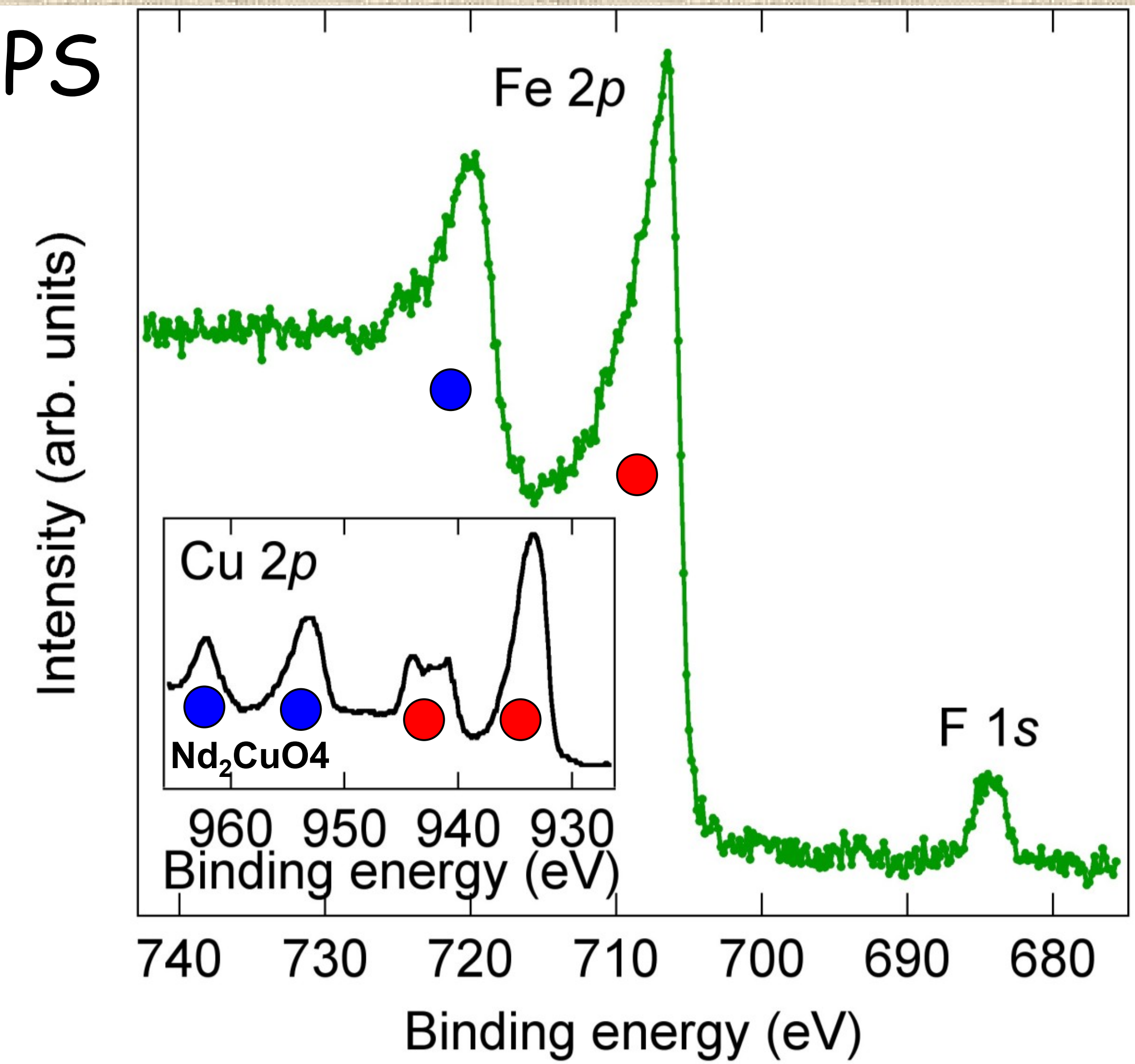
Steeneken et al., Phys. Rev. Lett. 90, 247005 (2003)

$CeFeAsO_{0.89}F_{0.11}$

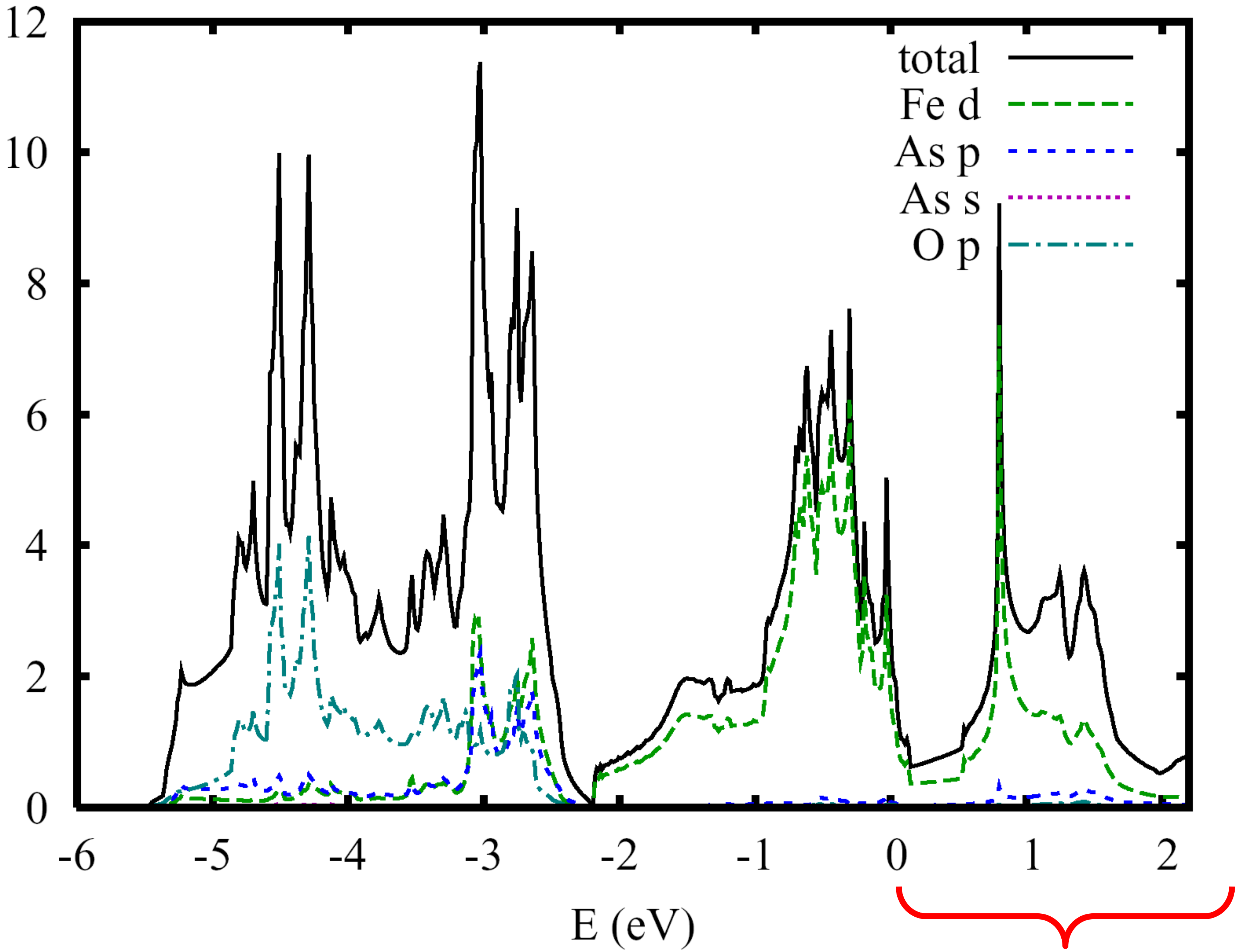


J. Zhao et al., Nature Materials 7, 953-959 (2008).

Fe 2p - XPS

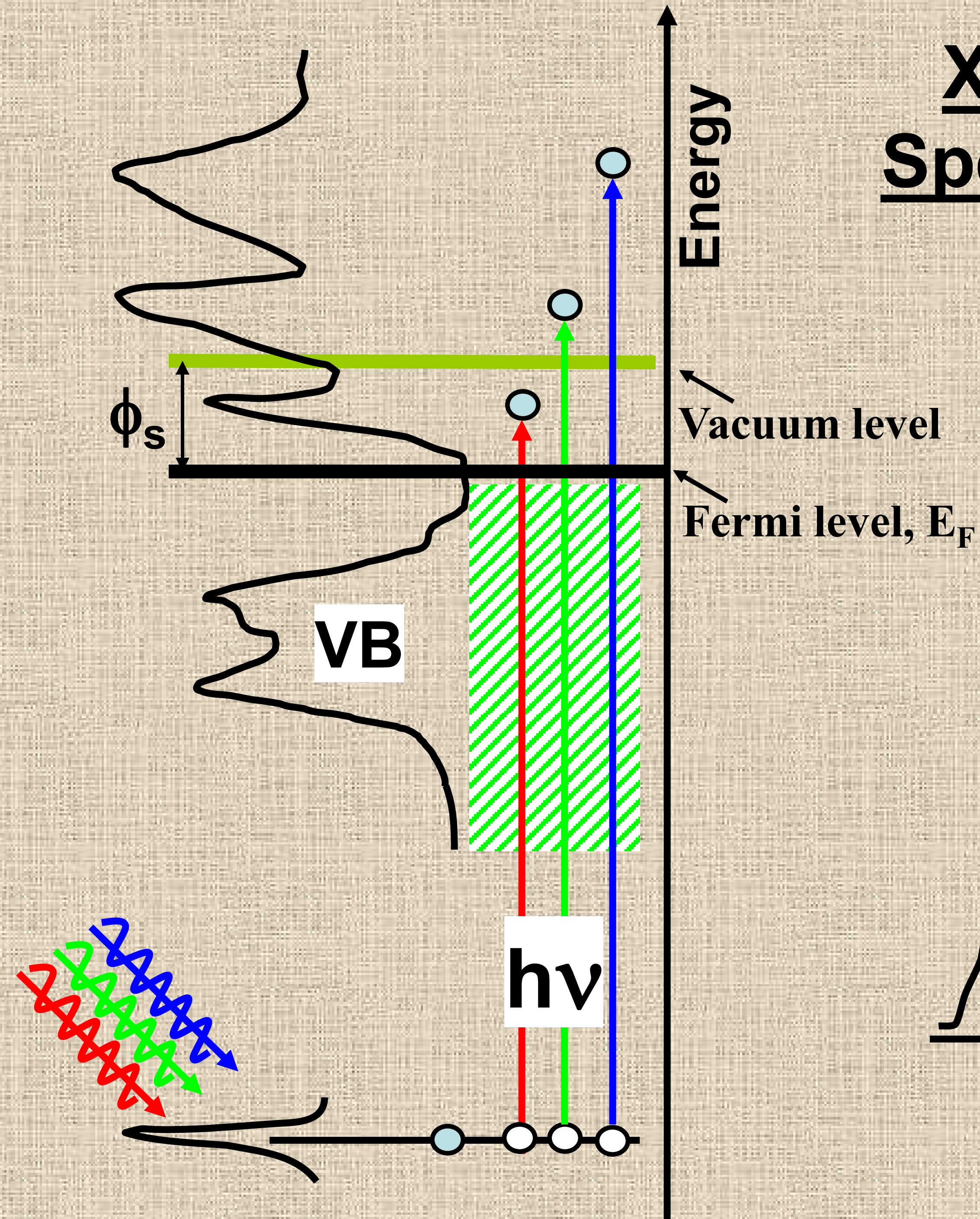


Similar to Fe 2p in metallic iron or iron intermetallics

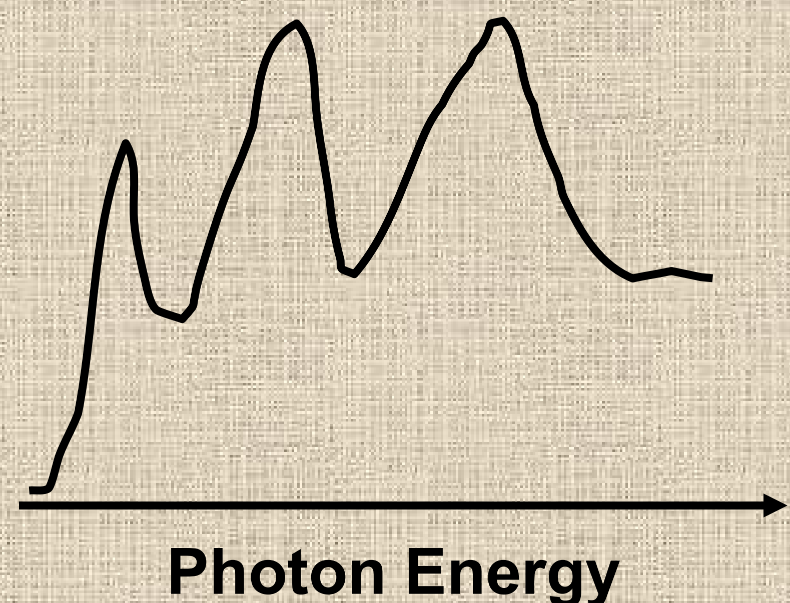


12
10
8
6
4
2
0
-6
-5
-4
-3
-2
-1
0
1
2
E (eV)
total
Fe d
As p
As s
O p

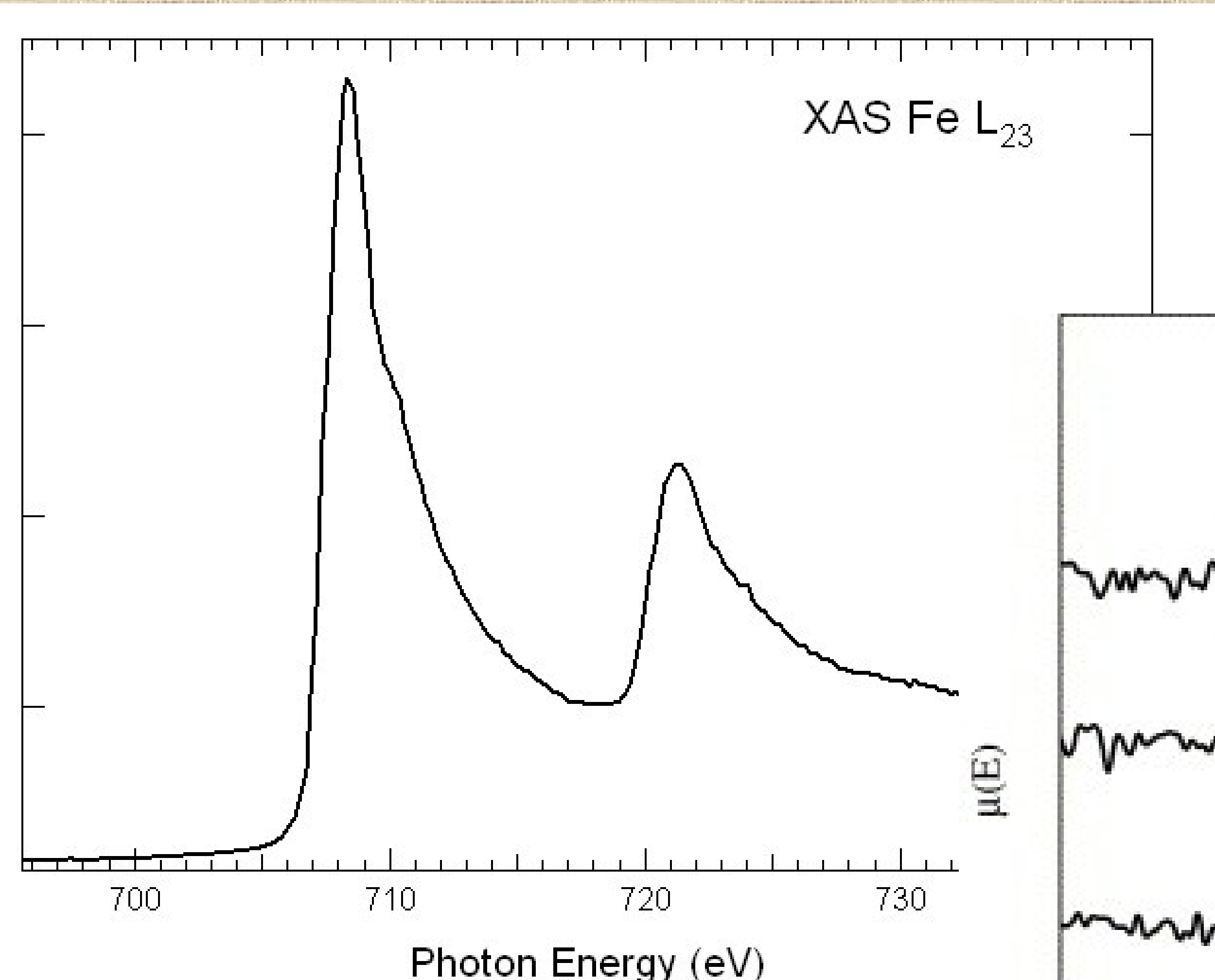
X-ray absorption Spectroscopy (XAS)

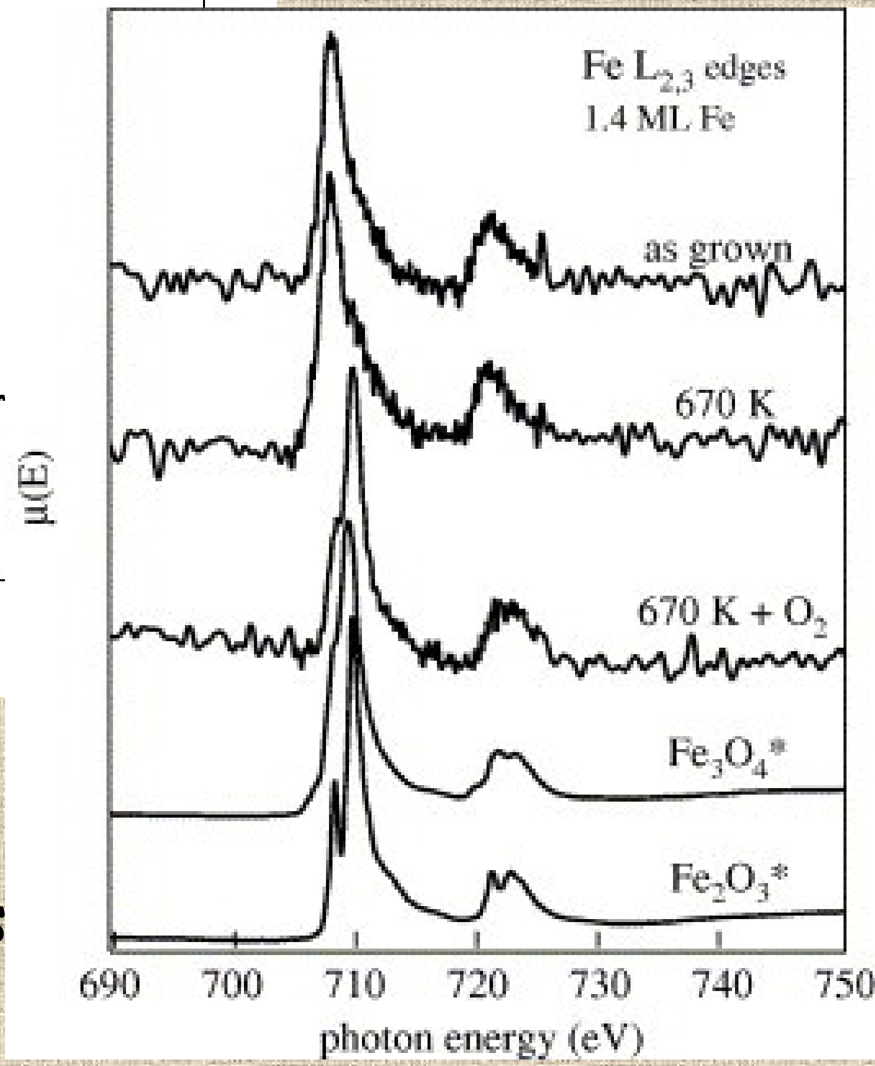


unoccupied DOS
(Matrix elements…)

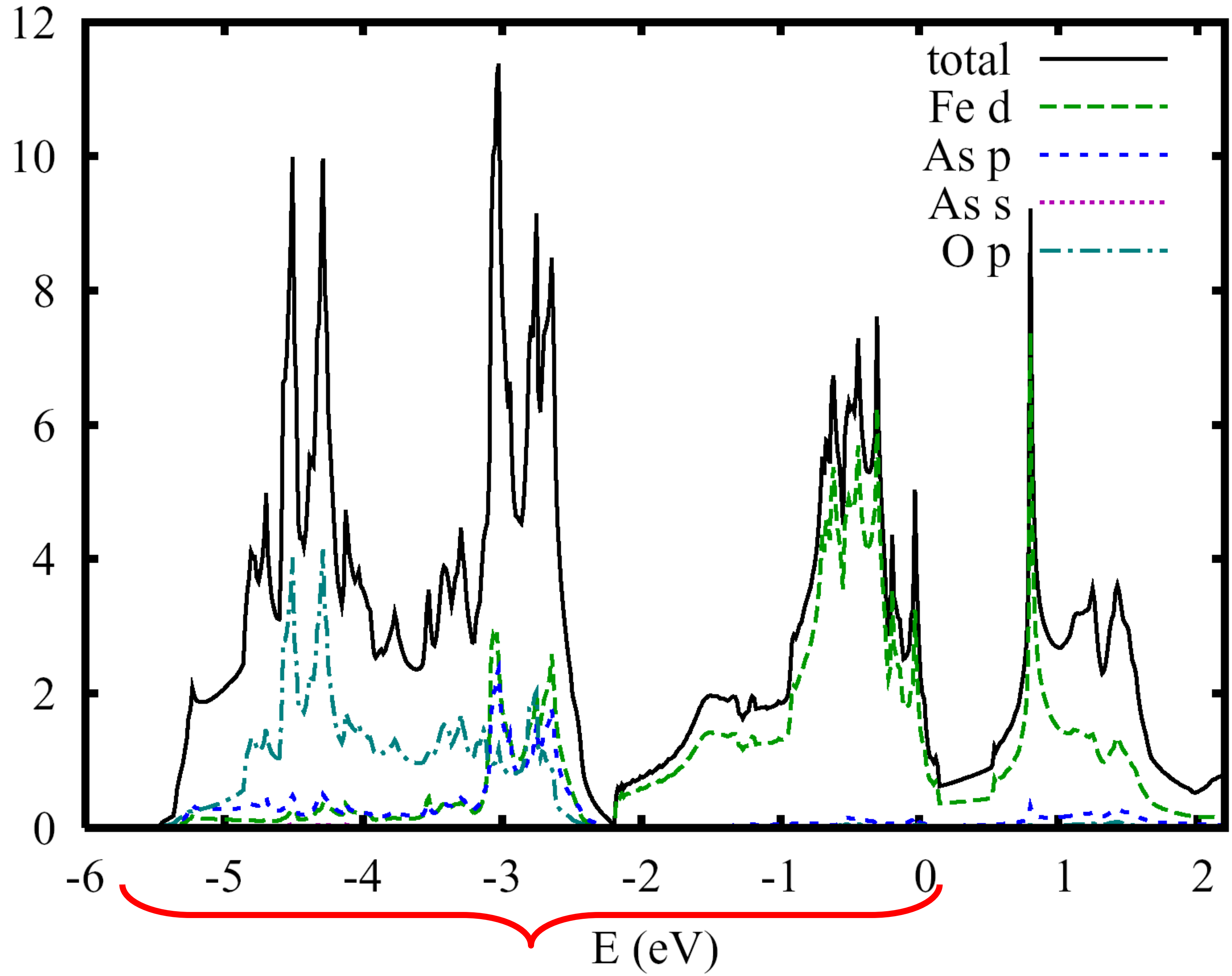


Fe 2p - XAS

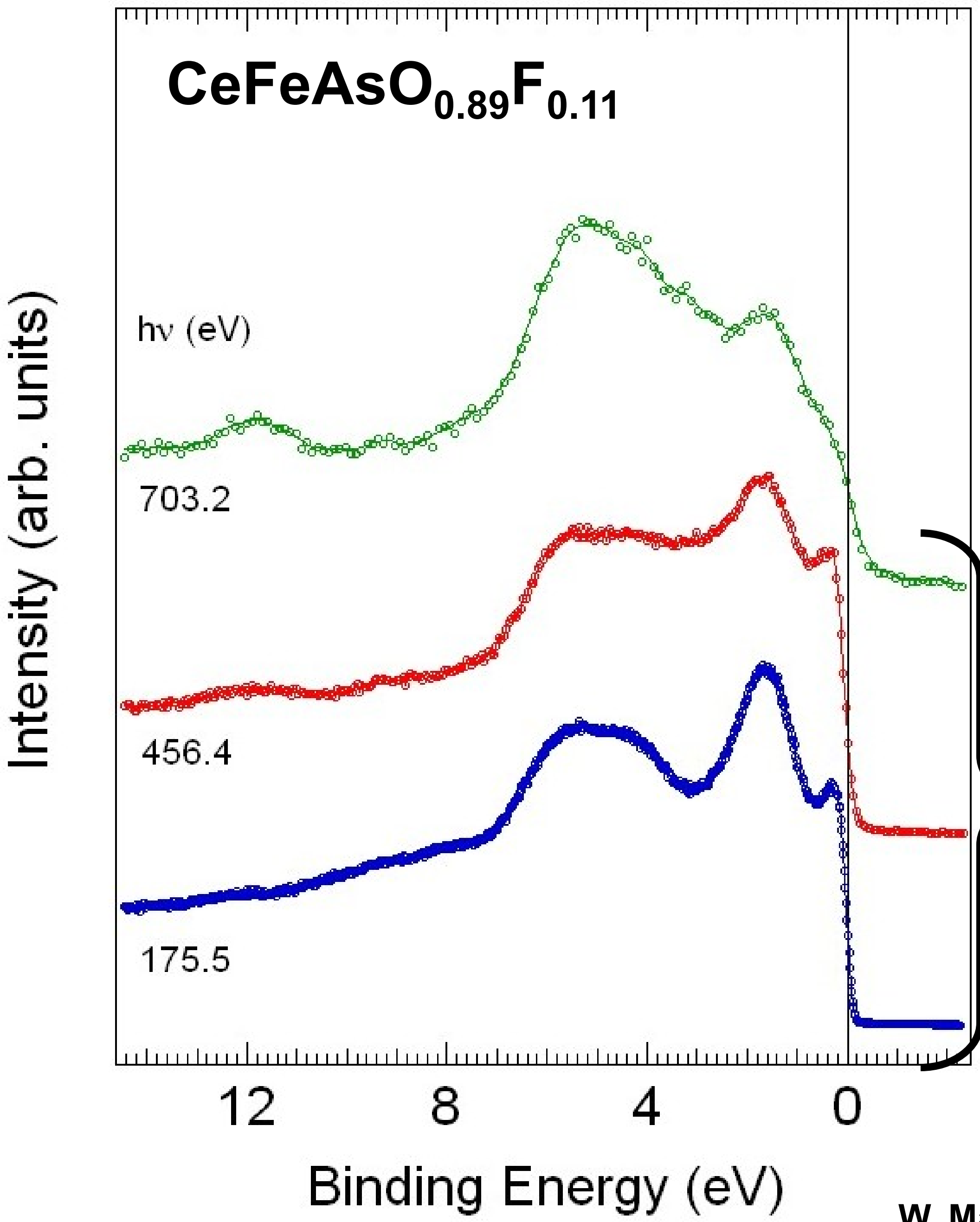


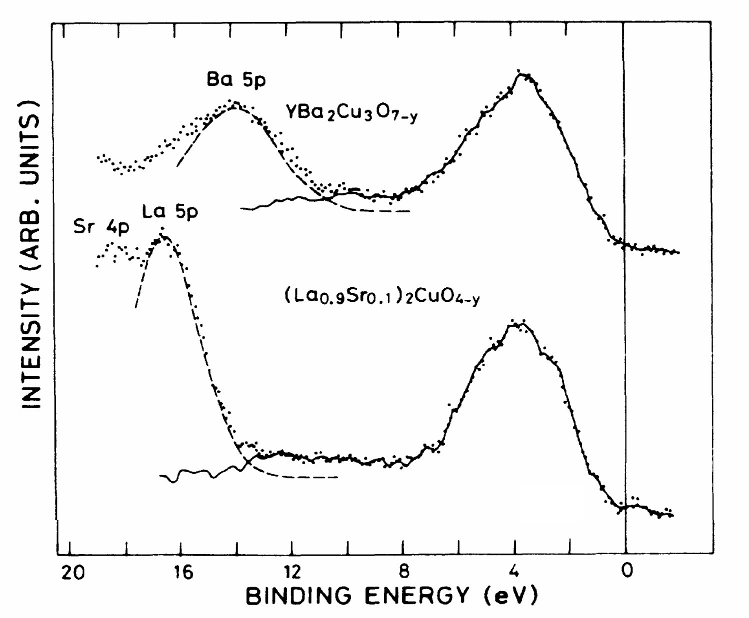


Appears more similar to that of metallic iron or iron intermetallics



total
Fe d
As p
As s
O p
12
10
8
6
4
2
0
-6
-5
-4
-3
-2
-1
0
1
2
E (eV)

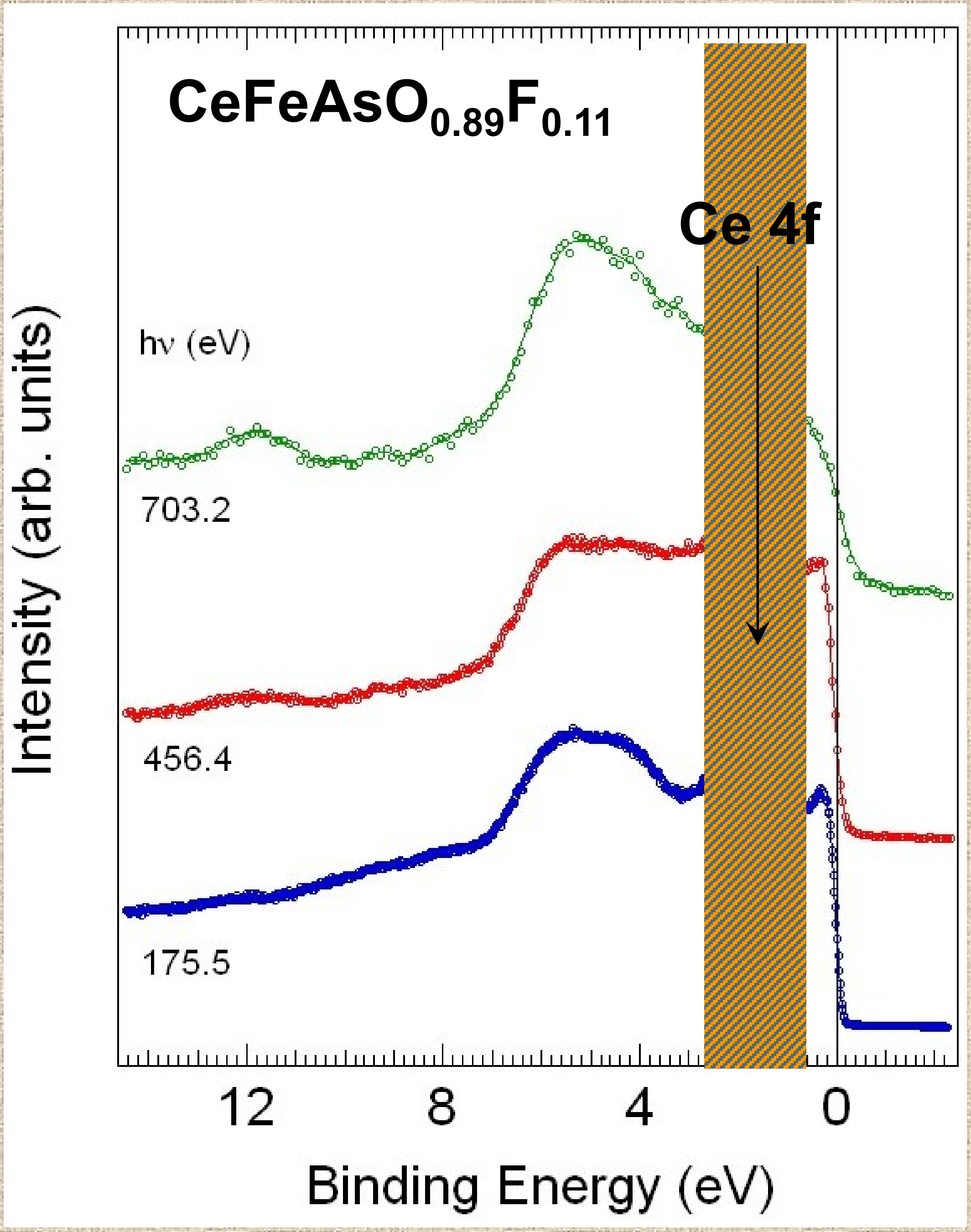


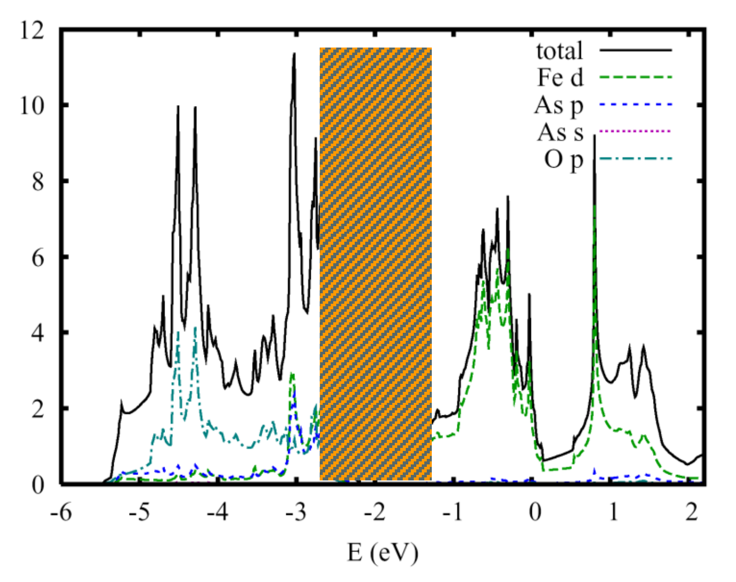


HIGH DOS at the Fermi Level

D. H. Lu et al., Nature 455, 81 (2008)

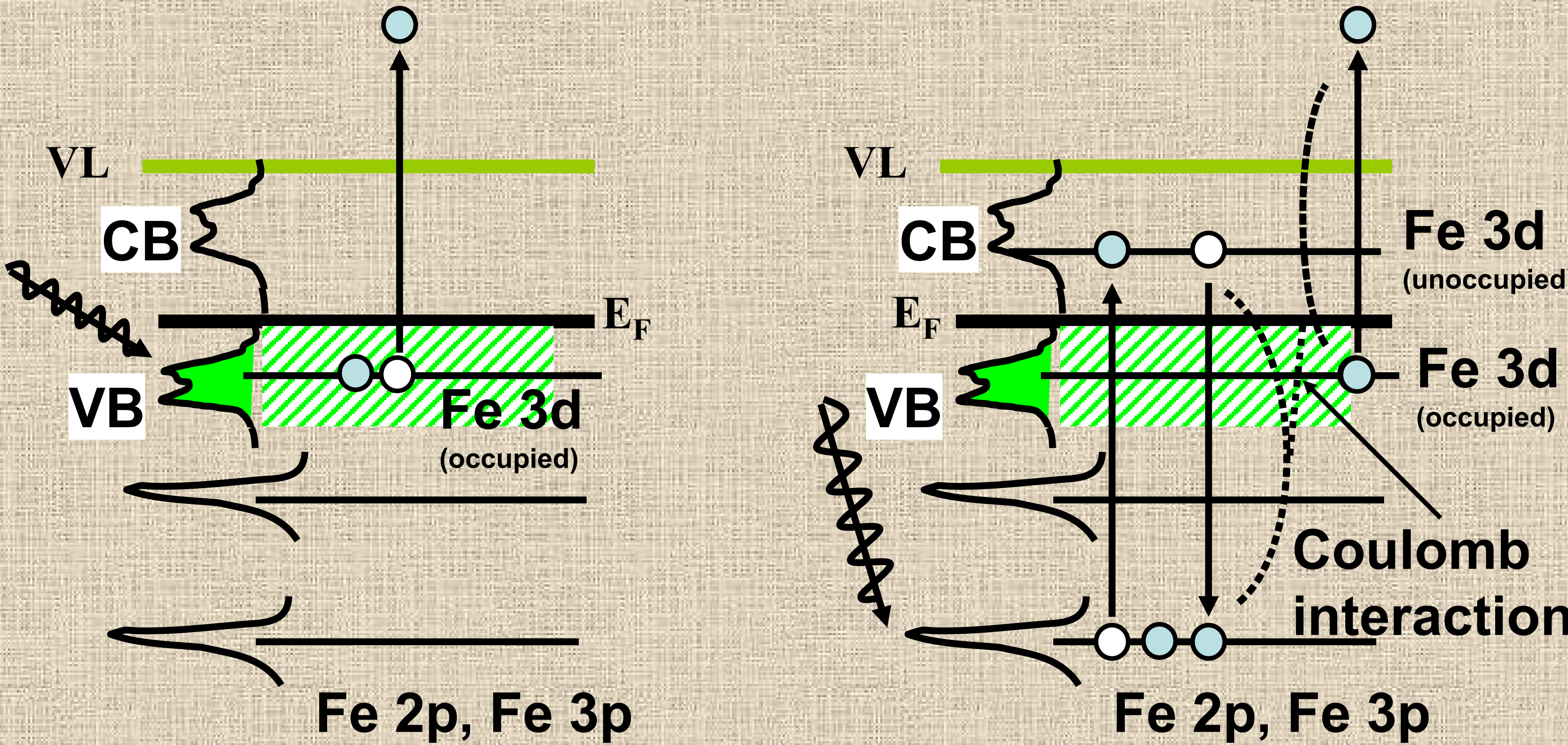
W. Malaeb et al., J. Phys. Soc. Jpn. 77, 093714 (2008)

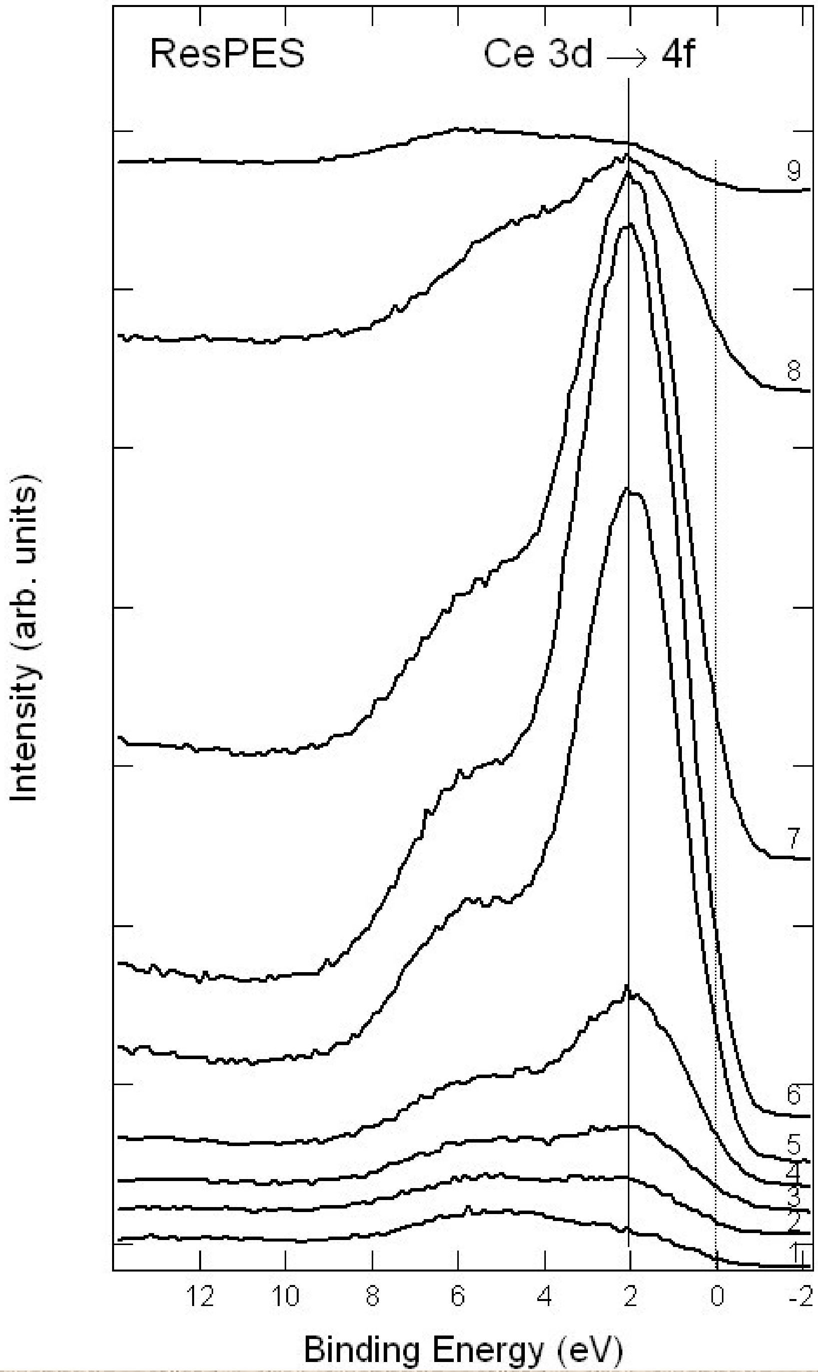


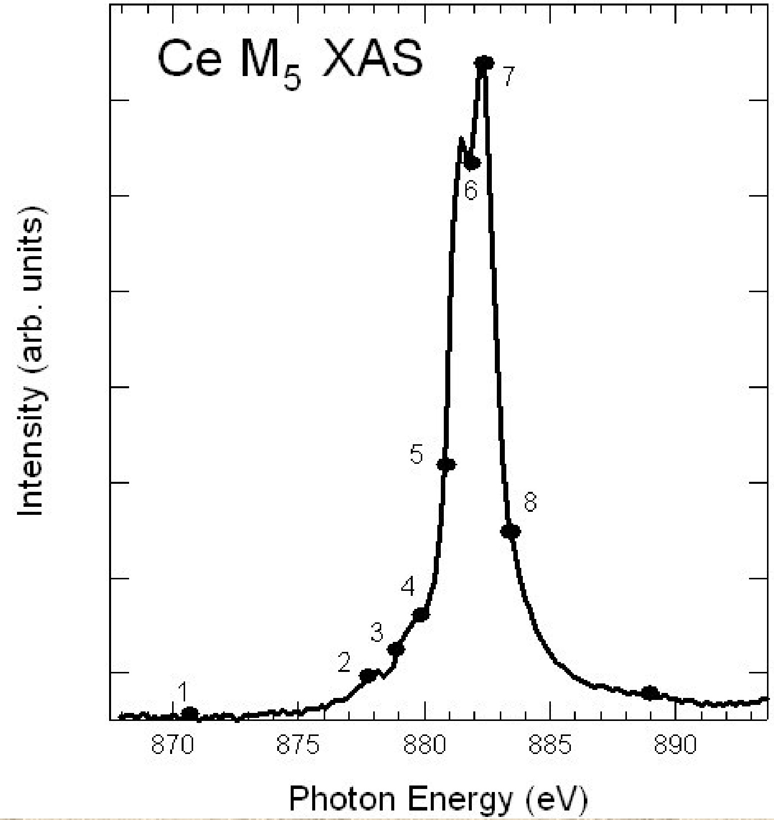


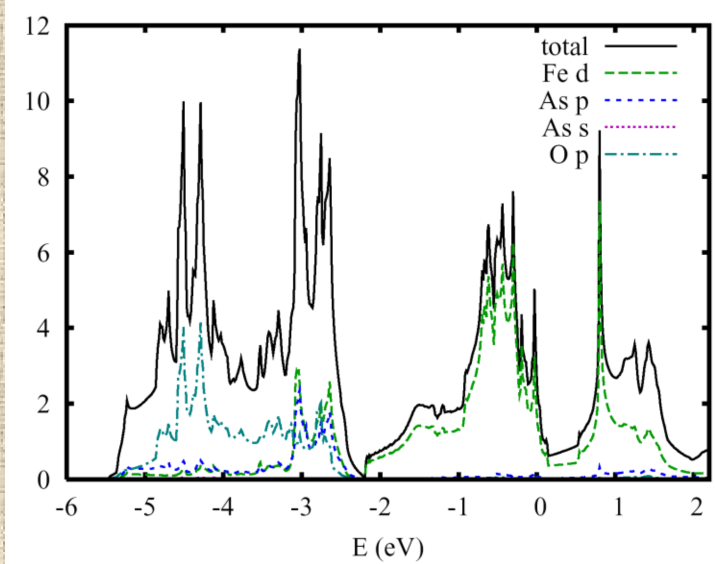
$LaFeAsO_{0.89}F_{0.11}$

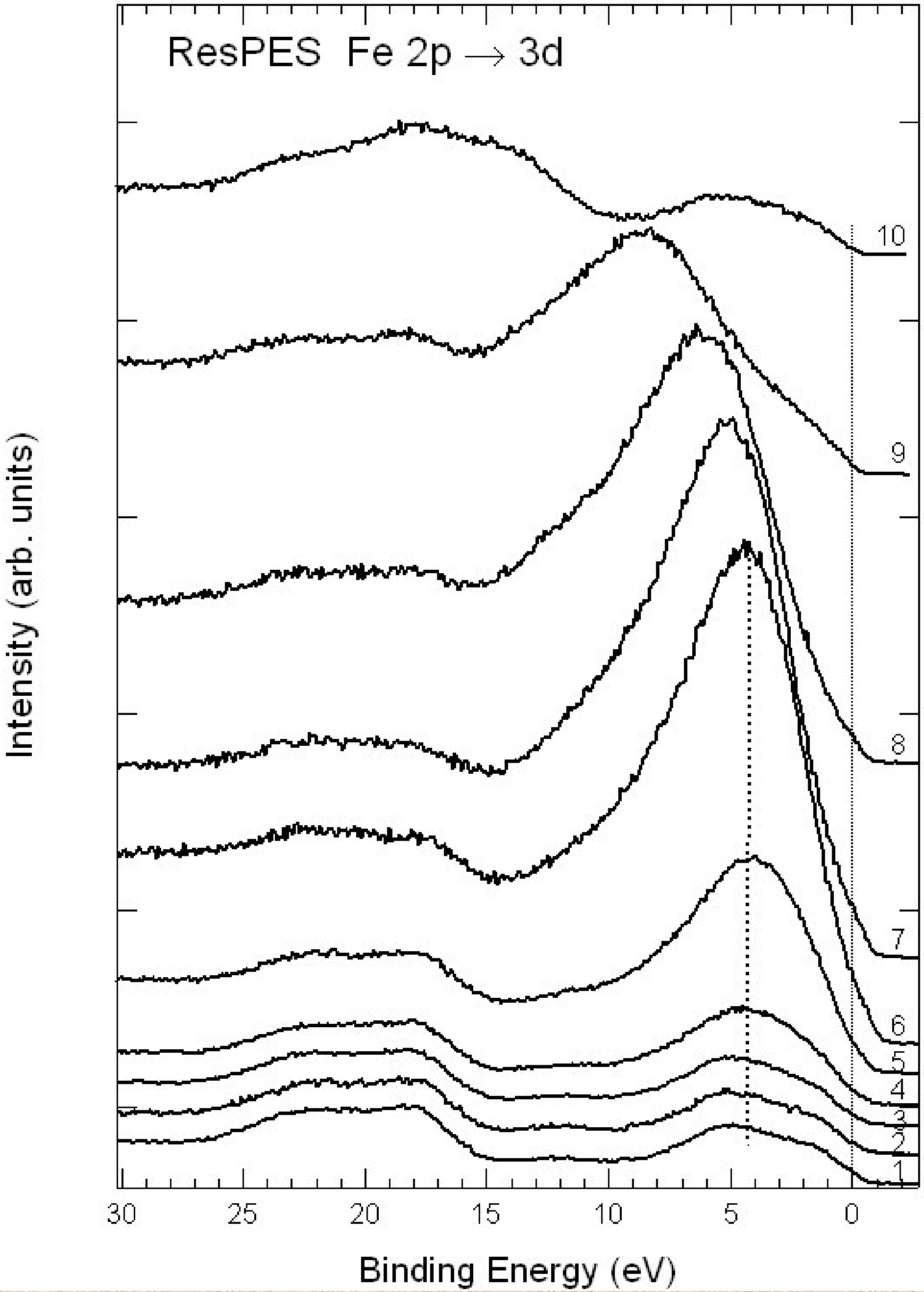
Resonant Photoemission

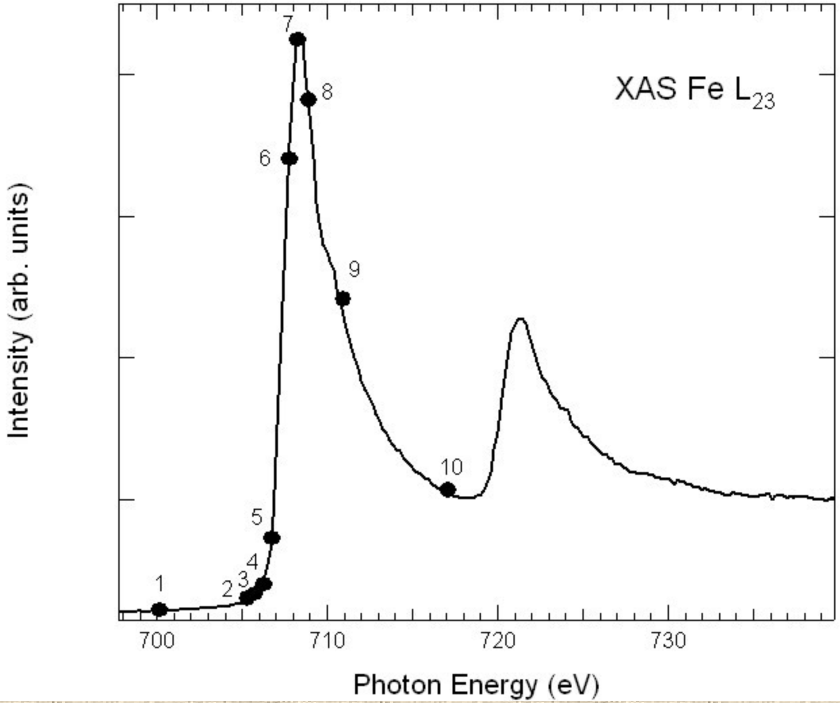



ResPES
Ce 3d → 4f
Intensity (arb. units)
Binding Energy (eV)
12 10 8 6 4 2 0 -2
9
8
7
6
5
4
3
2
1


Ce M_5 XAS
Intensity (arb. units)
Photon Energy (eV)
870 875 880 885 890
1
2
3
4
5
6
7
8


total
Fe d
As p
As s
O p
E (eV)
-6 -5 -4 -3 -2 -1 0 1 2
0 2 4 6 8 10 12



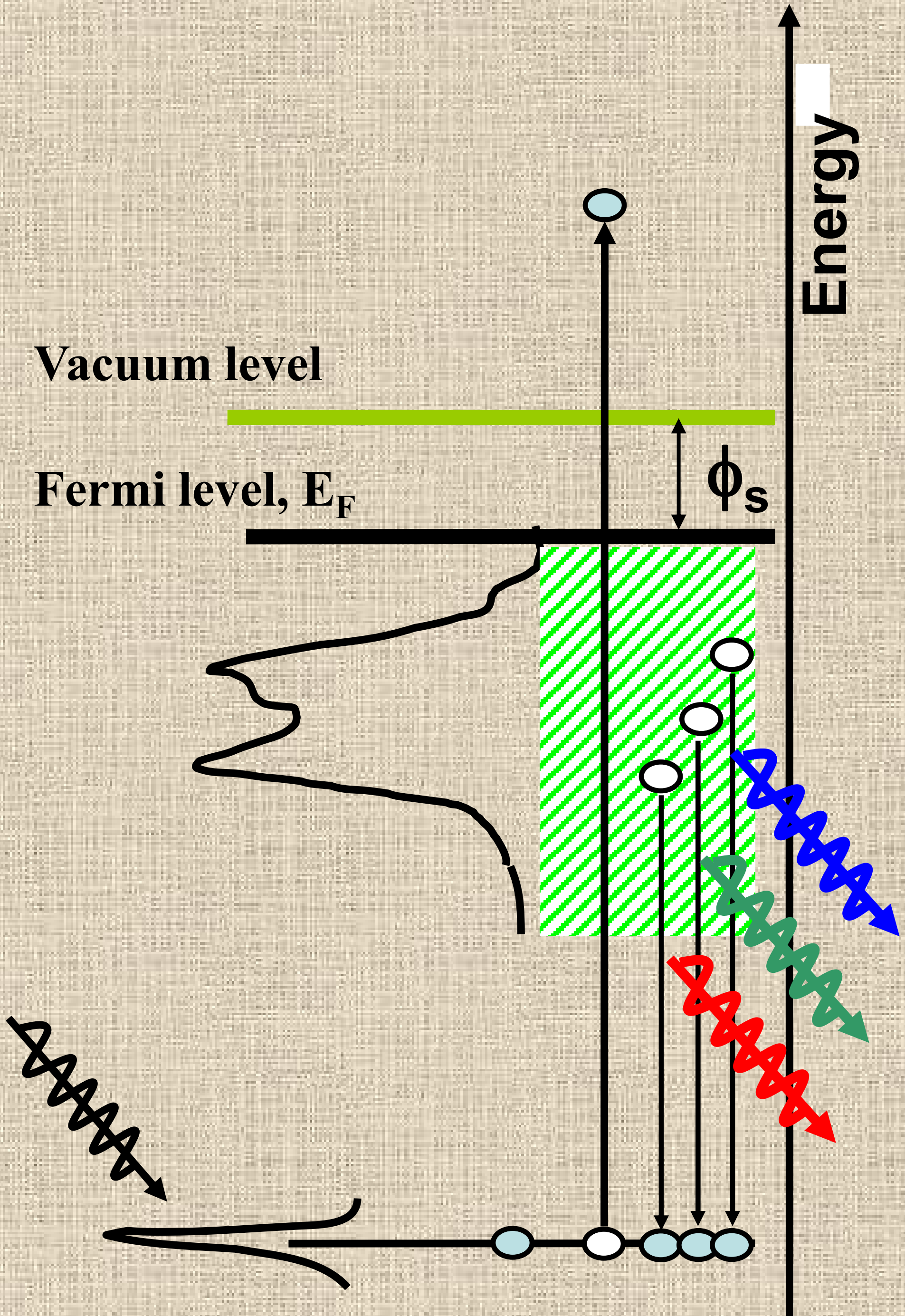


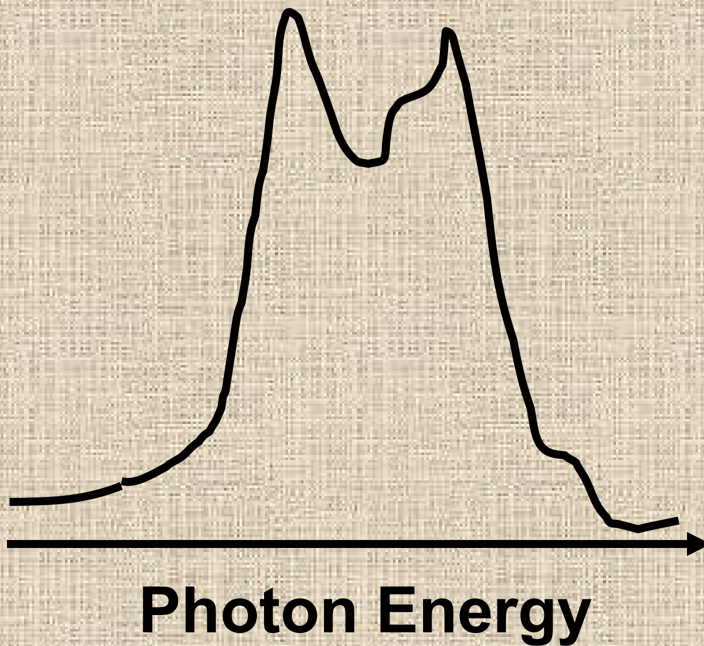
Behavior similar to that of metallic Ni and Fe

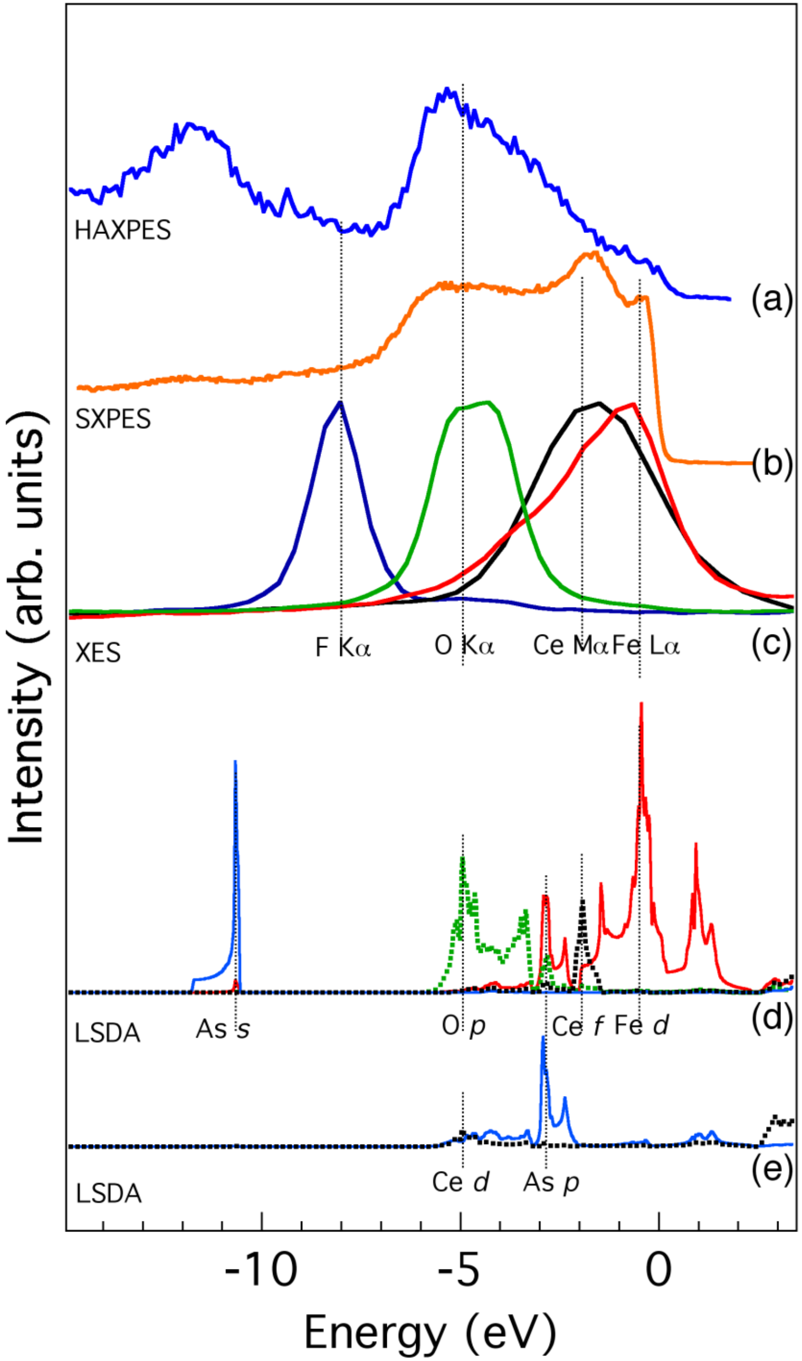
M. Weinelt et al., PRL. 78, 967 (1997)

S. Hufner et al., PRB 61, 12582 (2000)

XES
Band structure, PDOS






HAXPES
(a)
SXPES
(b)
XES
F Kα
O Kα
Ce Mα
Fe Lα
(c)
LSDA
As s
O p
Ce f
Fe d
(d)
LSDA
Ce d
As p
(e)
-10
-5
0
Energy (eV)
Intensity (arb. units)

Are the new FeAs SCs similar or dissimilar to the cuprates HTSC?

FeAs-SC do NOT show apparent signatures of Mott physics – Itinerant Fe electrons

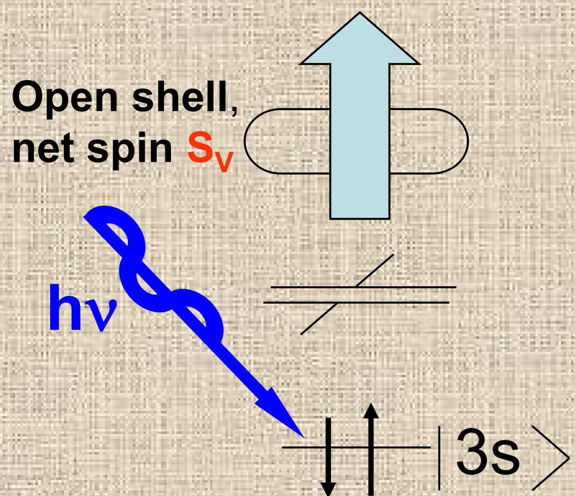
---

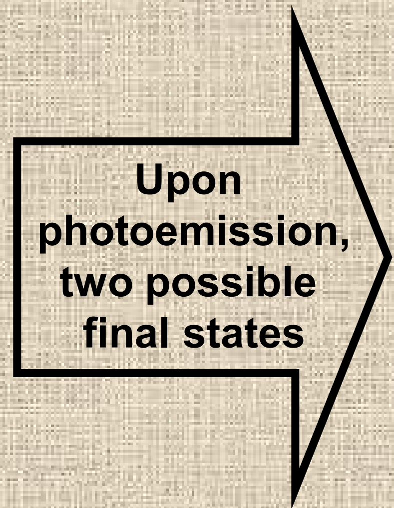
Phase diagram shows competition between a magnetically ordered, Spin Density Waves state and Superconductivity

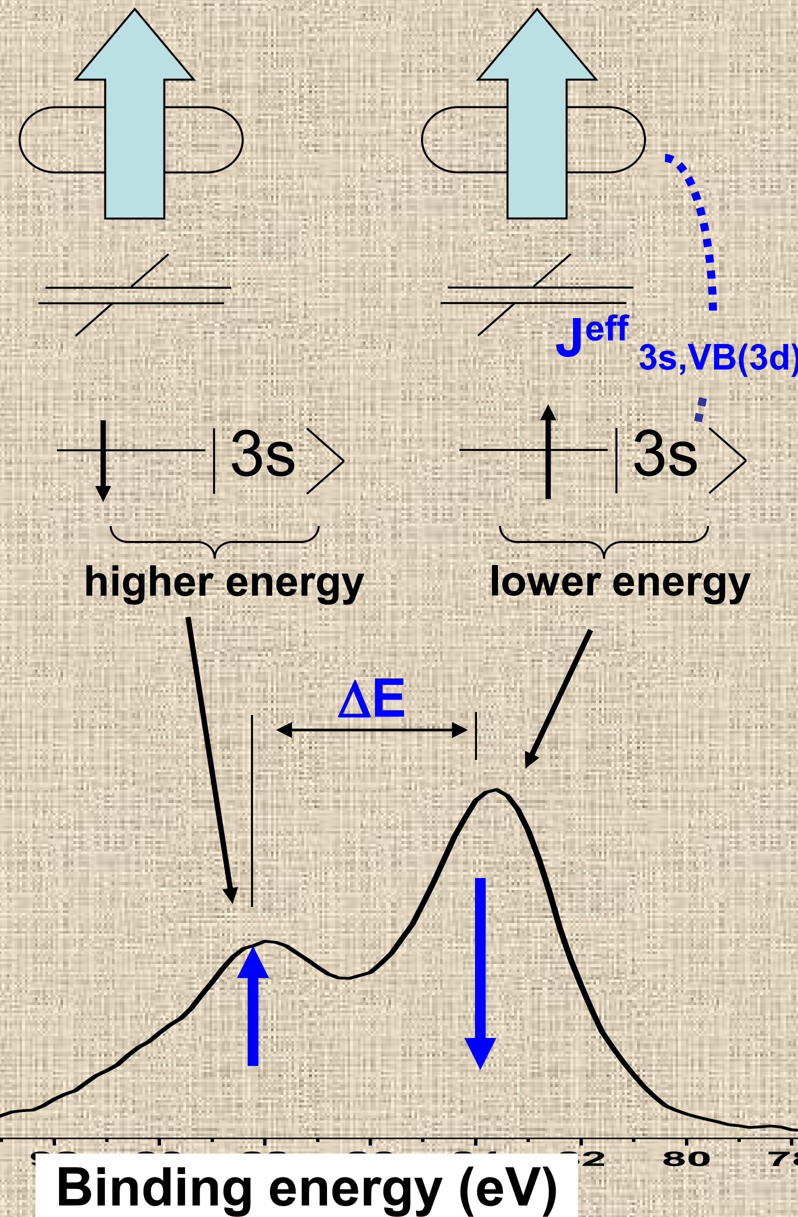
? = signatures of fluctuations associated with the proximity to AF state?

Multiplet splitting in core levels of transition metal oxides

$$BE = h\nu - E_{kin} = \underbrace{E^*(N-1)}_{\text{Final state}} - \underbrace{E_0(N)}_{\text{Initial state}}$$





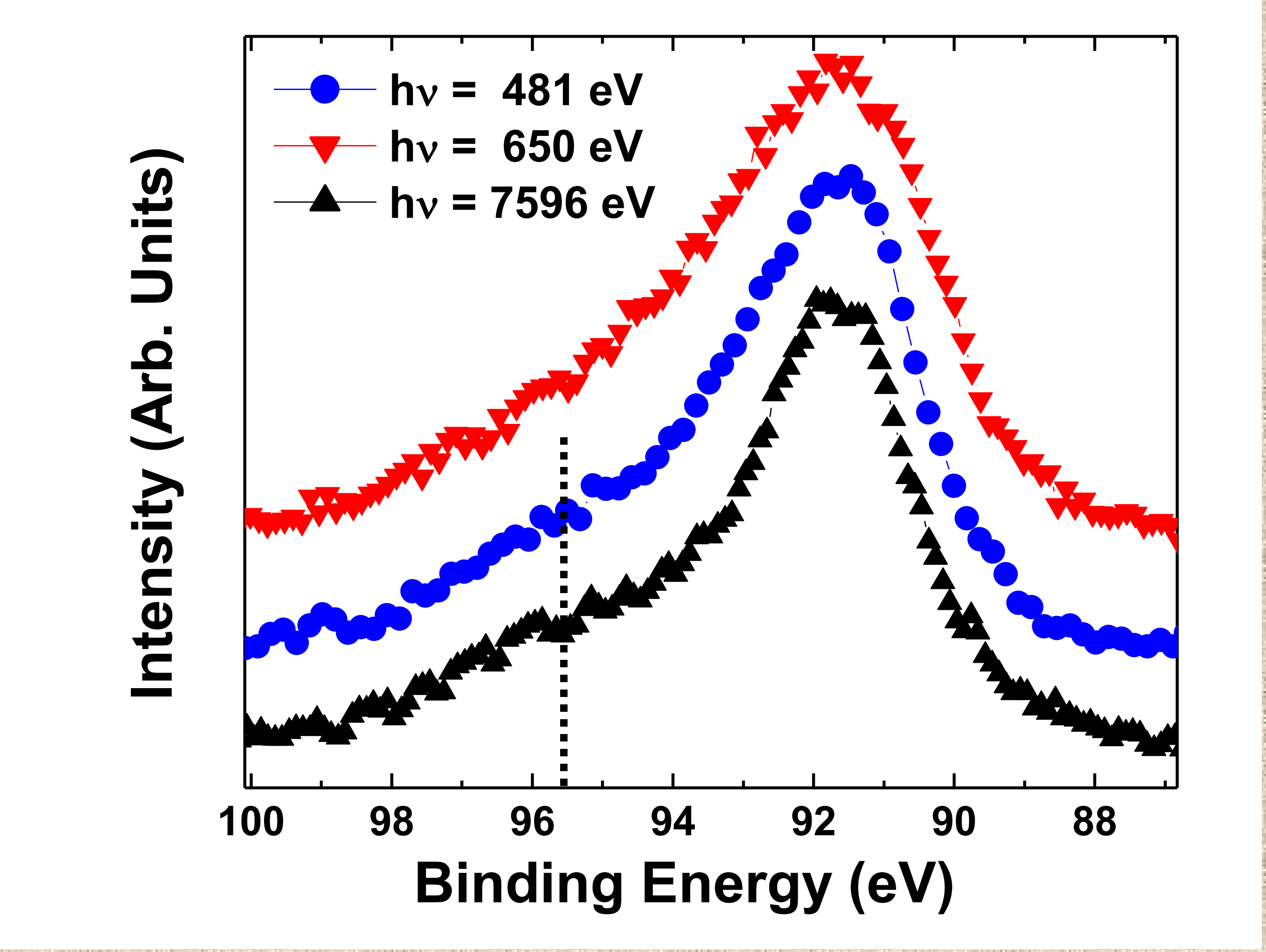


The splitting between the two peaks is given by

$$\Delta E \approx (2S_V + 1)\, J^{eff}_{3s,VB(3d)}$$

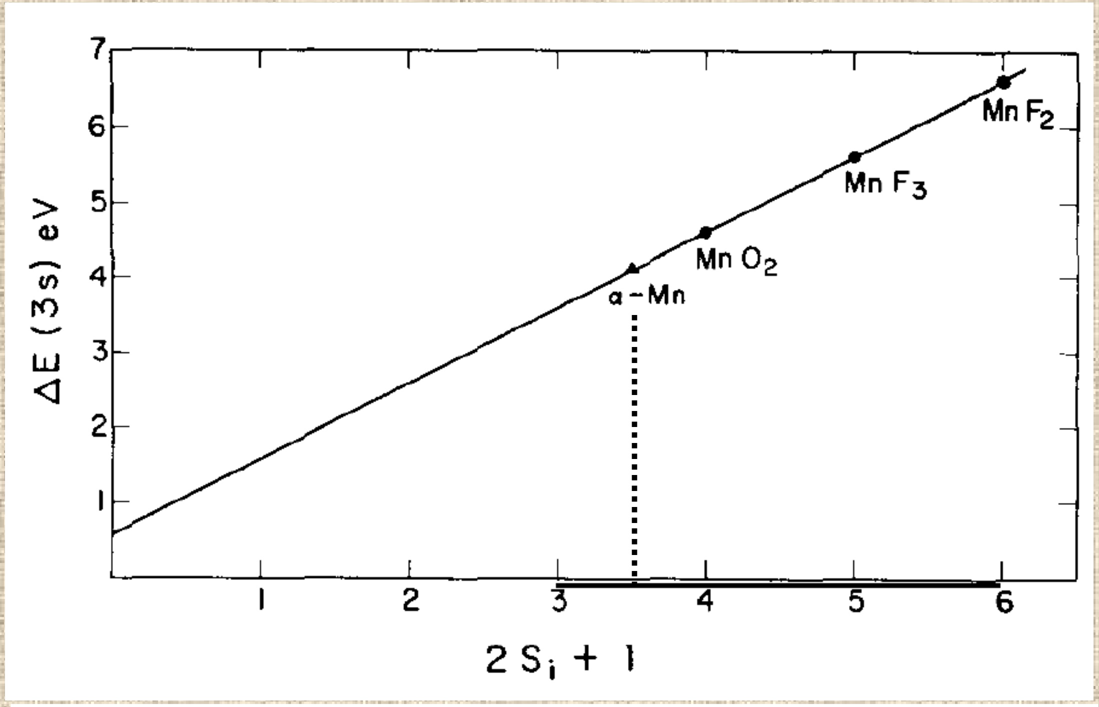
(Van Vleck Theorem)

Detection of Multiplet Splittings in Fe 3s Photoemission Spectra



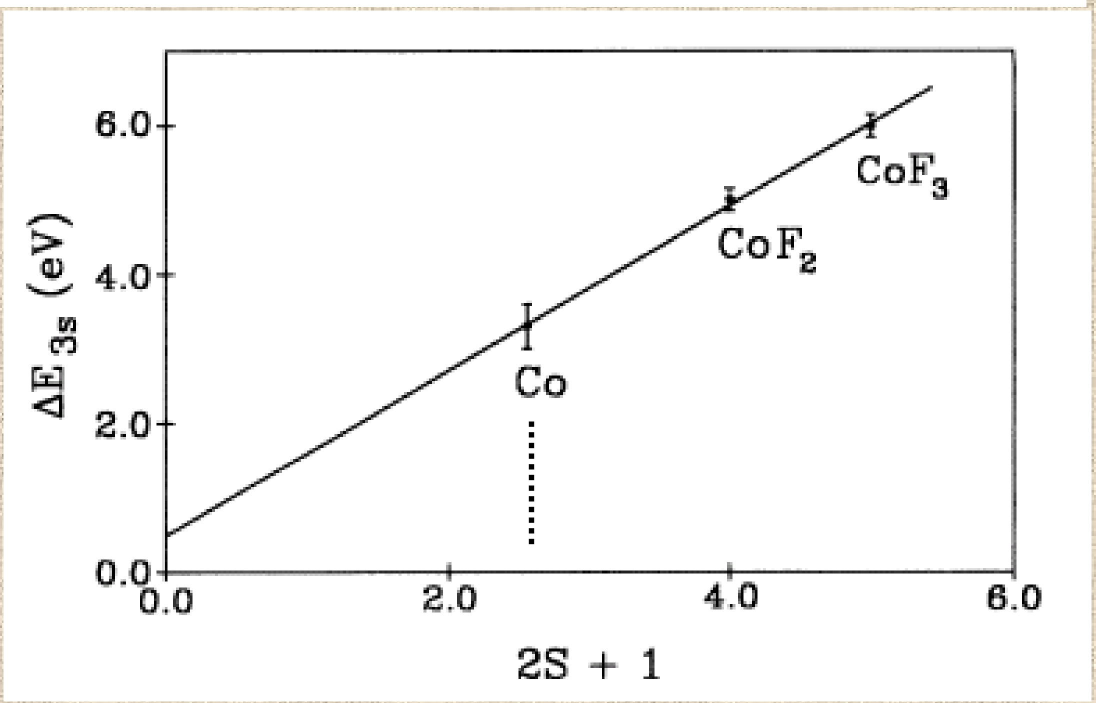
Multiplet splittings are usually interpreted as local moments

How to handle itinerant systems?

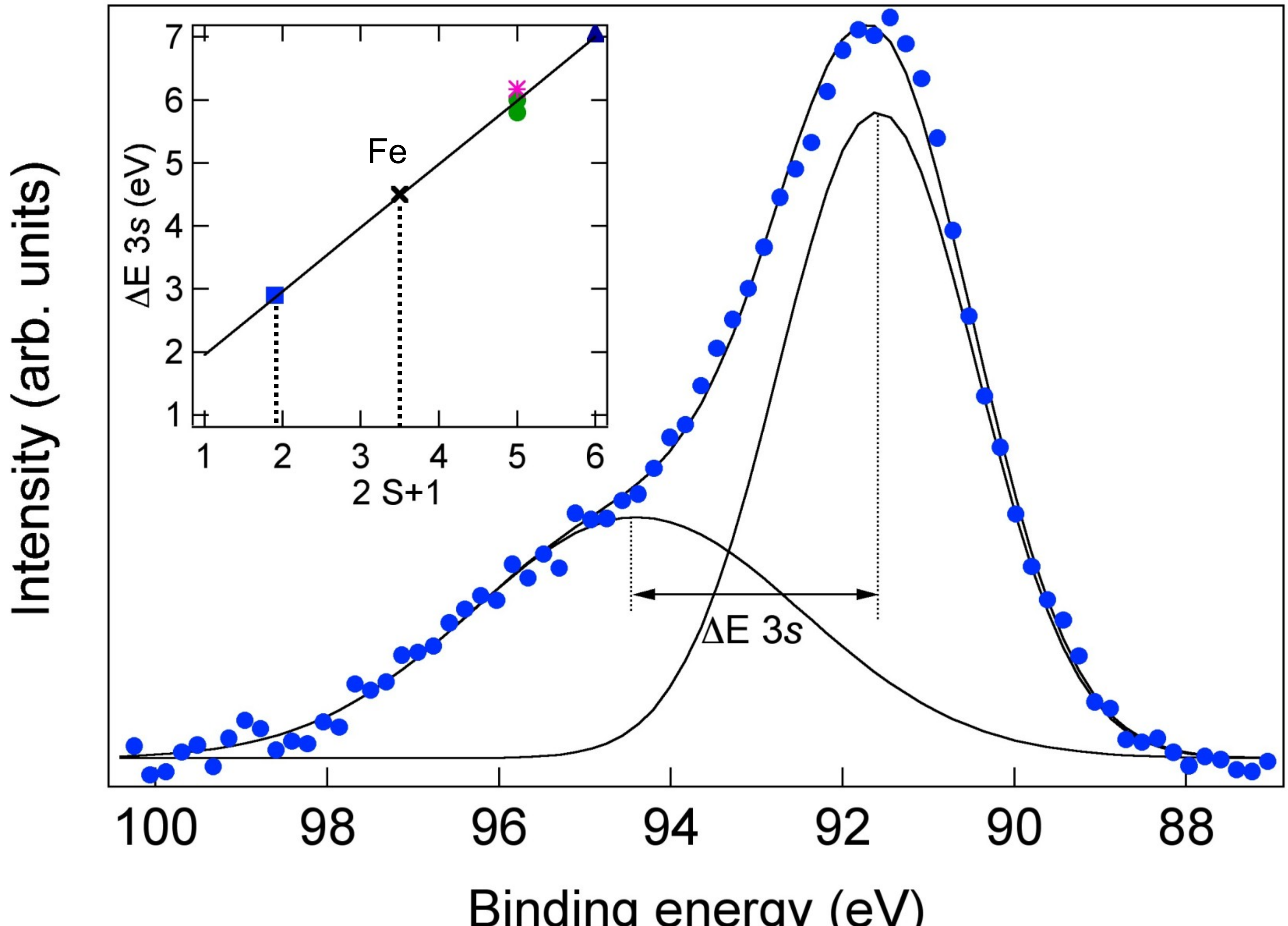


F. R. McFeely et al.,
Solid State. Com. 15, 1051 (1974)

The Van Vleck model holds for itinerant systems …..



D. G. van Campen & L. E. Klebanoff,
Phys. Rev. B 49, 2040 (1994)



Intensity (arb. units)
Binding energy (eV)
100
98
96
94
92
90
88
ΔE 3s
ΔE 3s (eV)
2 S+1
Fe
1
2
3
4
5
6
7

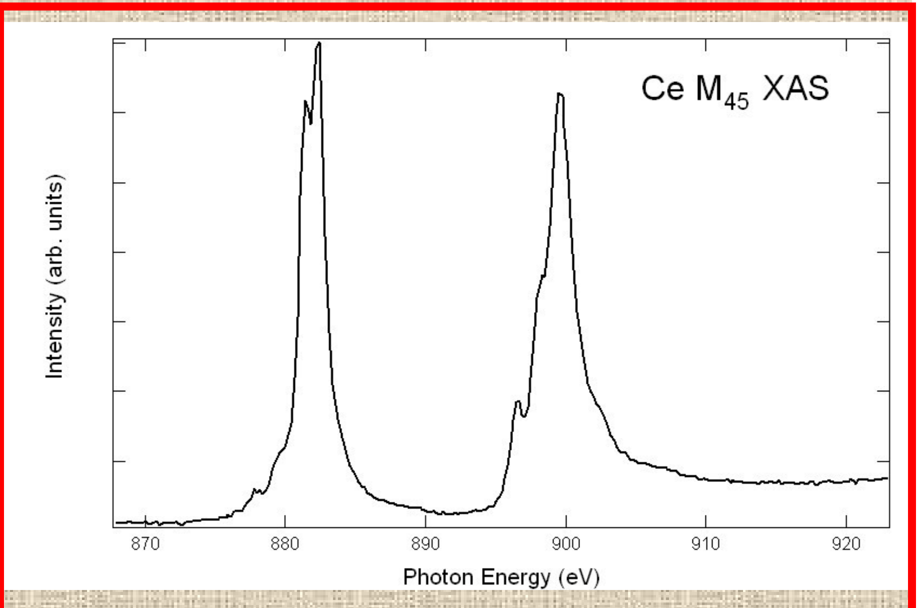
According to

Mossbauer,
NMR,
magnetic susceptibility

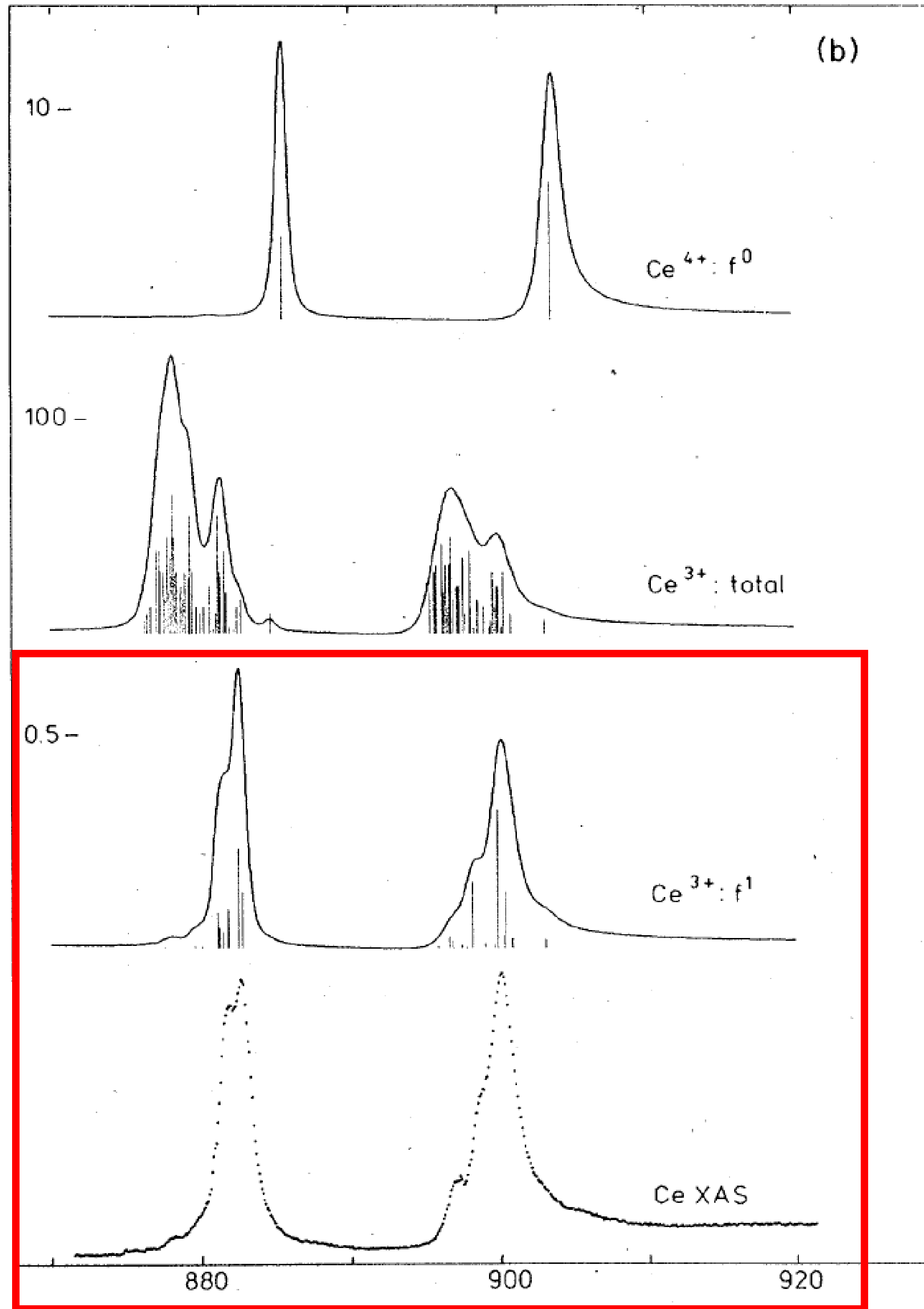
….. Fe is NON magnetic

…… magnetic susceptibility accounted by a free Ce ion (3^+, i.e.f^1)

Ce 3d - XAS



Ce is 3$^+$, i.e. f^1

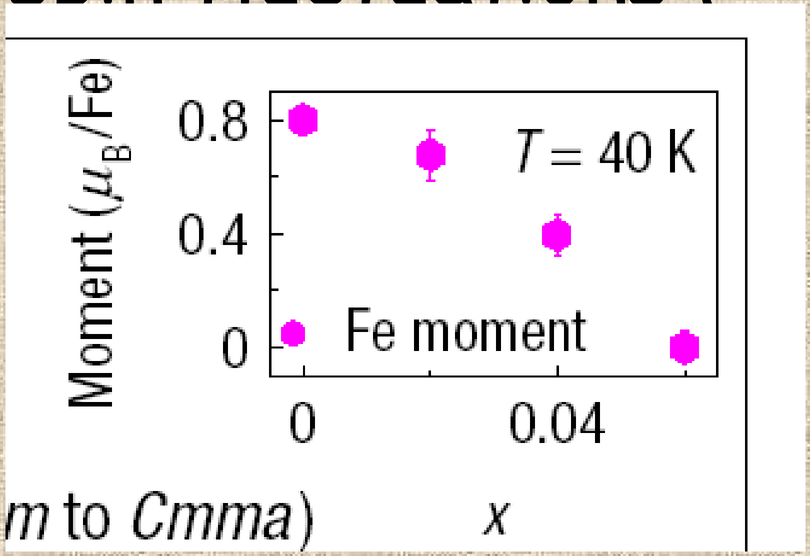


Fast time scale in PES (10^{-16} - 10^{-15} s)

+

absence of local moment $\Rightarrow$

Fe 3s multiplet splitting indicates Fe spin fluctuations ($\approx$ 0.9 - 1.0 μB)



Same scenario in FeAl, non-magnetic with fluctuating magnetism

Are the new FeAs SCs similar or dissimilar to the cuprates HTSC?

FeAs-SC do NOT show apparent signatures of Mott physics – Itinerant Fe electrons

---

Phys. Rev. Lett. 101 (2008), 267001.

? – signatures of fluctuations associated with the proximity to AF state?

Fe 3s multiplet splitting indicates Fe spin fluctuations (≈ 0.9 – 1.0 mB) in the normal state

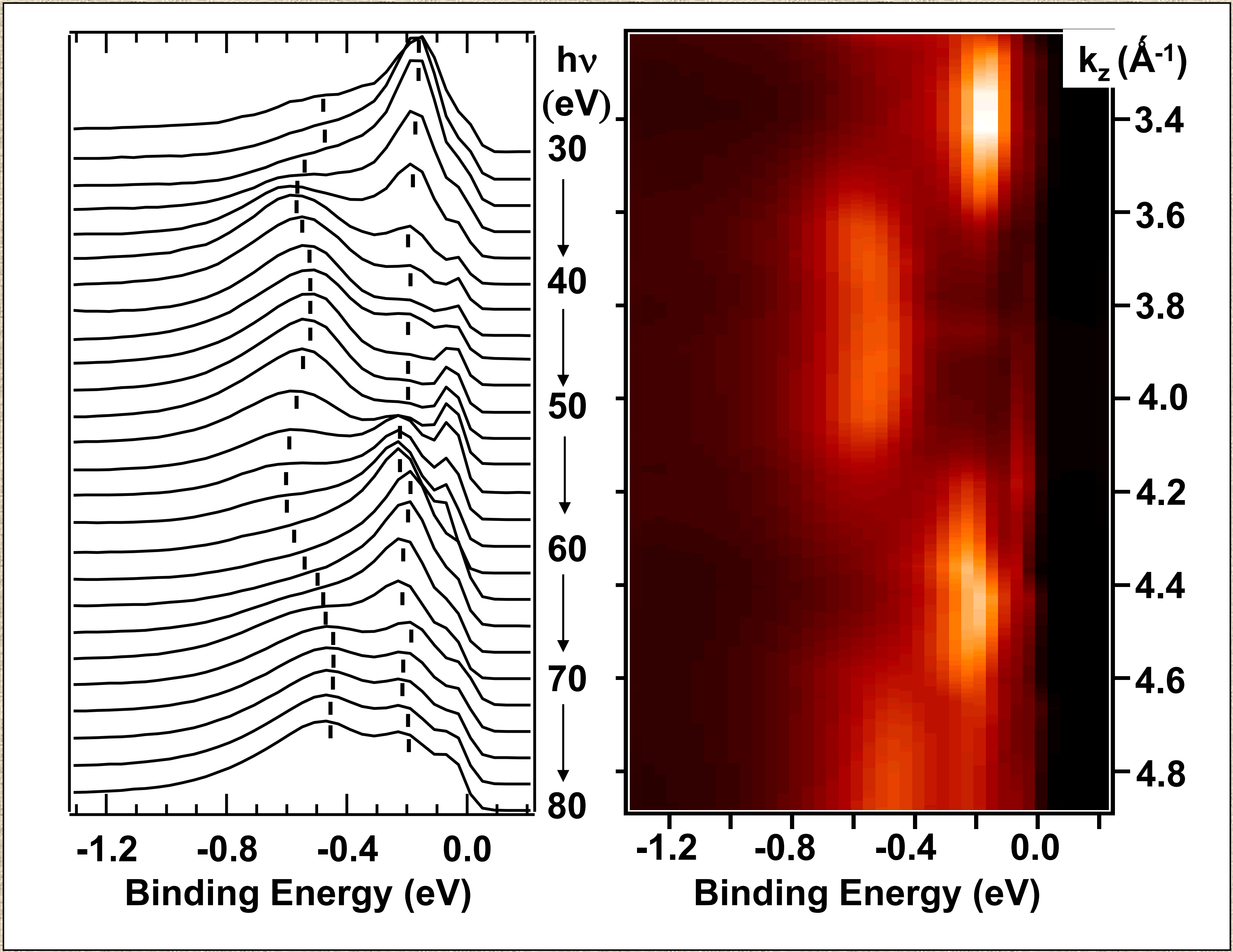
H. Q. Yuan et al., *Nature* 457, 565 (2009)

Despite their layered structure,

$(Ba,K)Fe_2As_2$ exhibit superconducting properties that are quite isotropic, a behavior drastically different compared to that of other layered superconductors.

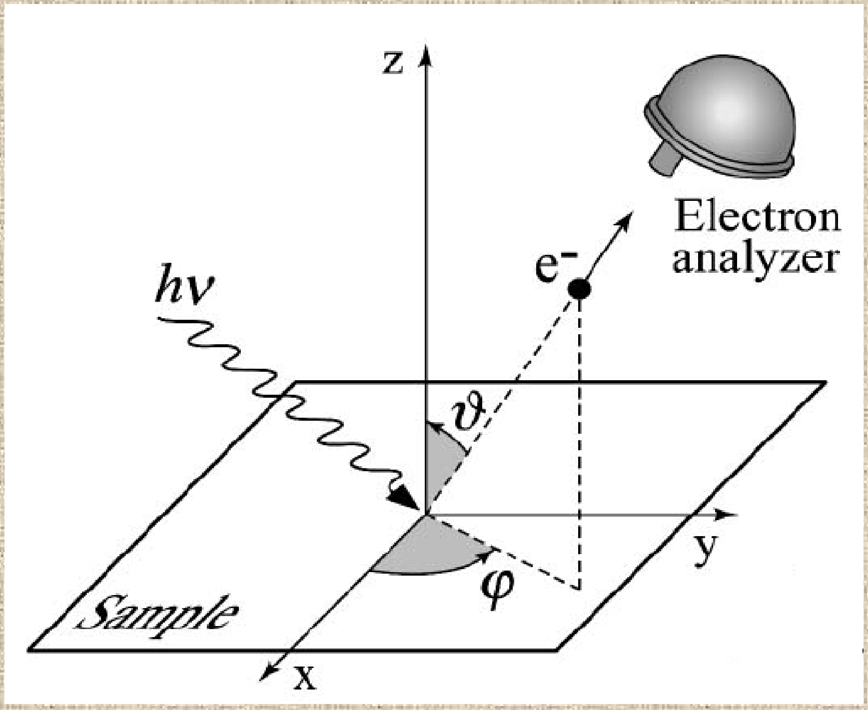
It has been proposed that the nearly isotropic critical field of $(Ba,K)Fe_2As_2$ might be linked to its distinctive three-dimensional electronic structure and Fermi surface (FS) topology,

→ the reduced dimensionality is not a prerequisite for high temperature superconductivity, contrary to what has been suggested for cuprate HTSC



hν
(eV)
30
40
50
60
70
80
-1.2
-0.8
-0.4
0.0
Binding Energy (eV)
k_z (Å^{-1})
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
-1.2
-0.8
-0.4
0.0
Binding Energy (eV)

Angle Resolved PhotoEmission Spectroscopy (ARPES)

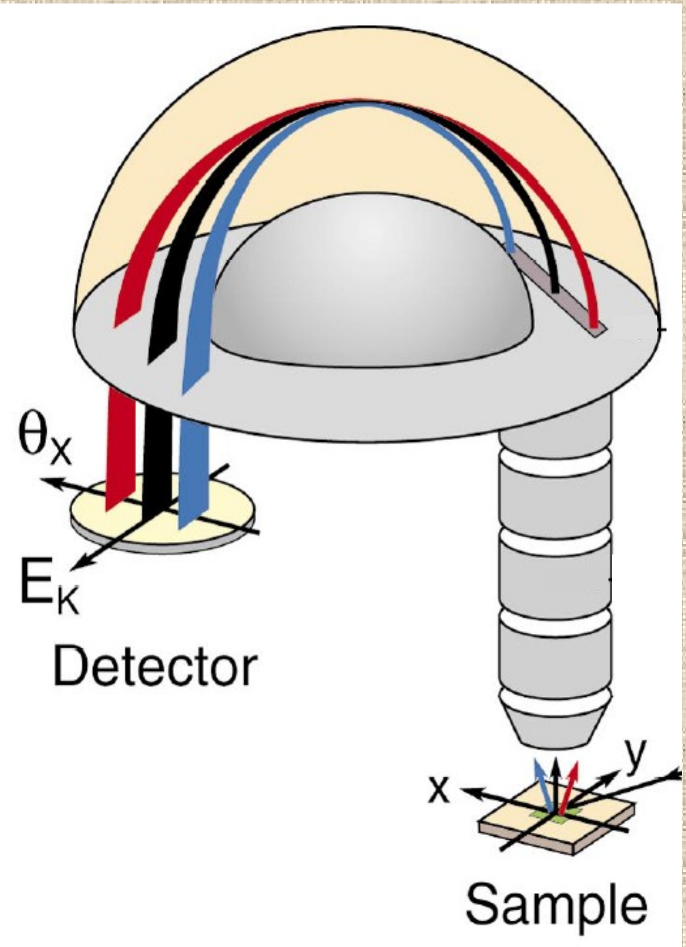


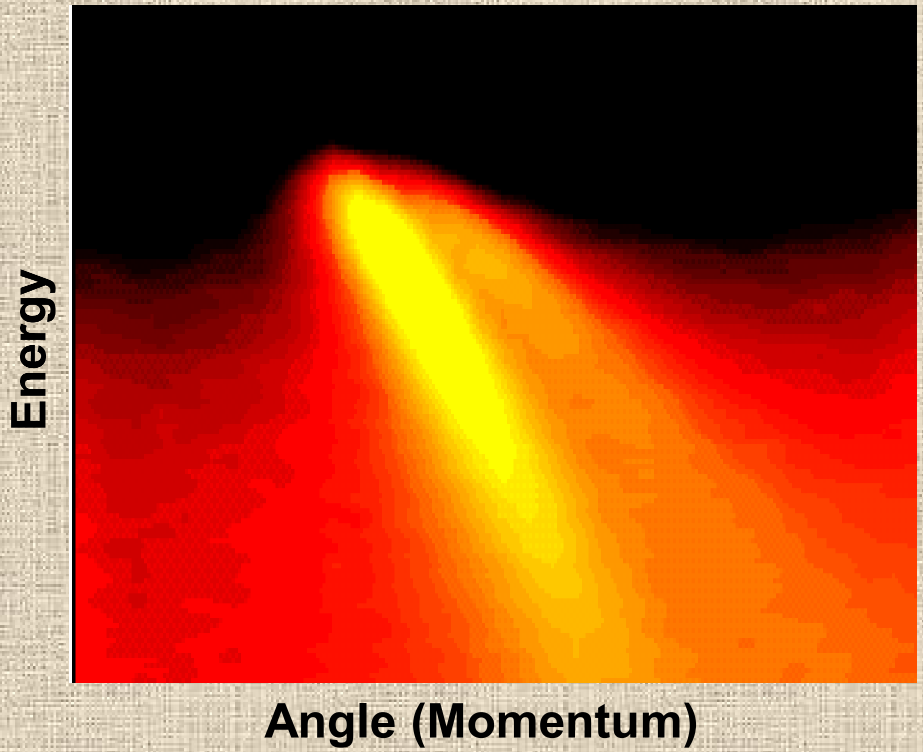
$$E_B = h\nu - \phi - E_{kin}$$

$$p_{\ldots} = \hbar \ldots \sqrt{\ldots mE_{kin}} \sin \vartheta$$

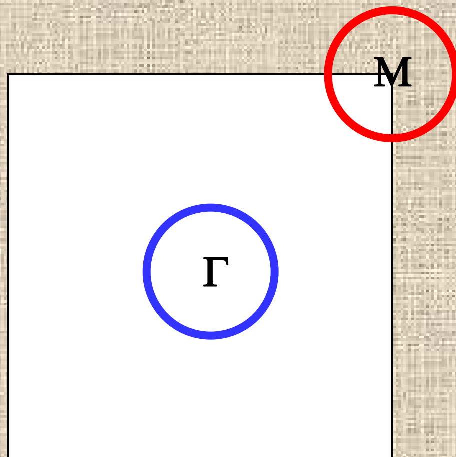
Direct measurement of the electronic structure in 2D materials

Angle Resolved PhotoEmission Spectroscopy (ARPES)

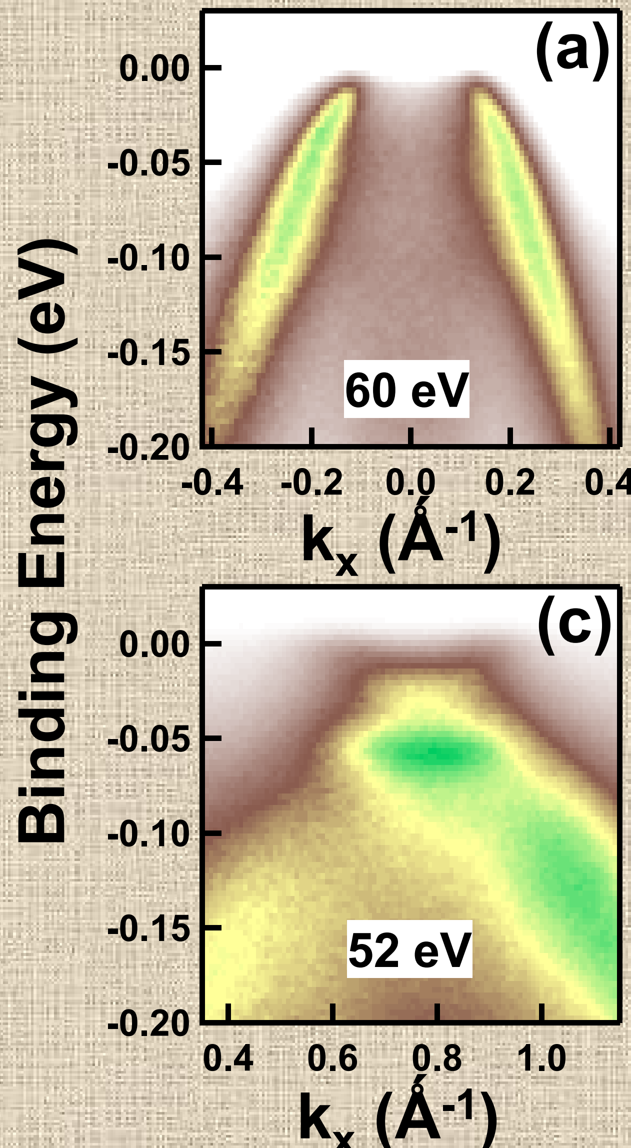


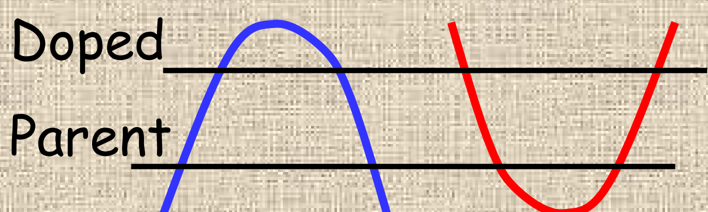


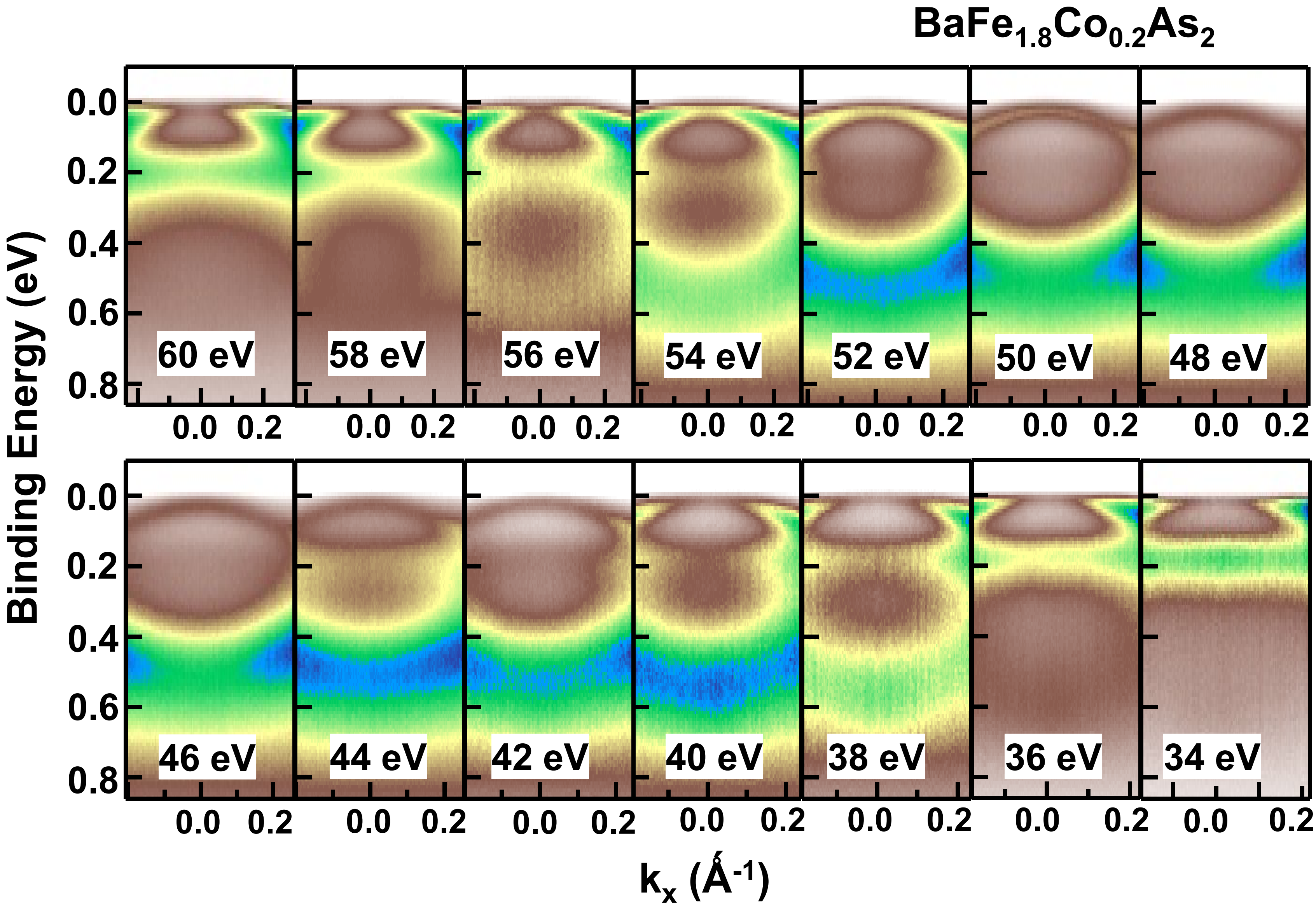
$Ba(Fe_{1-x}Co_x)_2As_2$



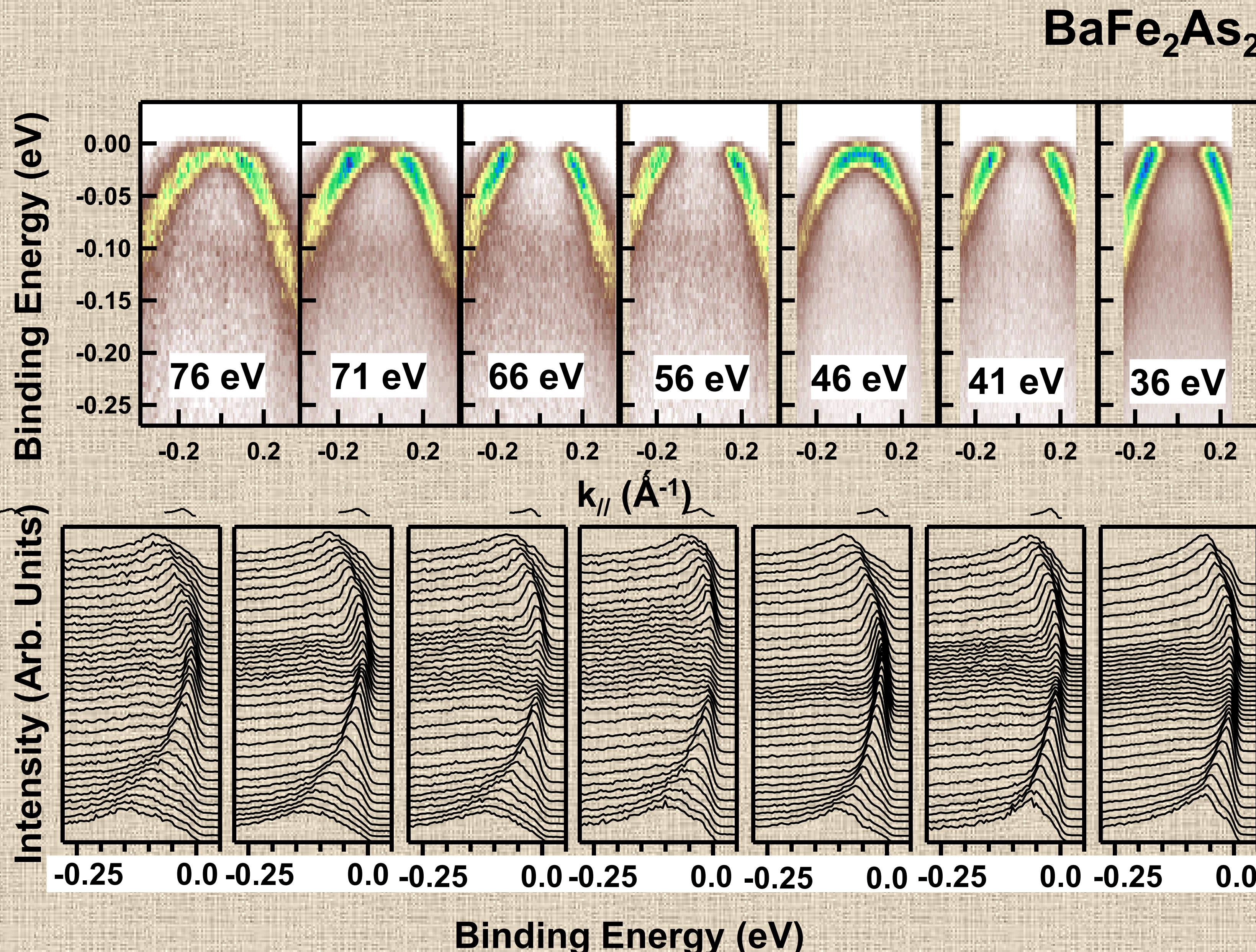
Parent (x=0)







Band at 200 meV → captured by LDA using z_{LDA} but not z_{EXP}



BaFe2As2
Binding Energy (eV)
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
76 eV
71 eV
66 eV
56 eV
46 eV
41 eV
36 eV
-0.2
0.2
k// (Å-1)
Intensity (Arb. Units)
-0.25
0.0
Binding Energy (eV)

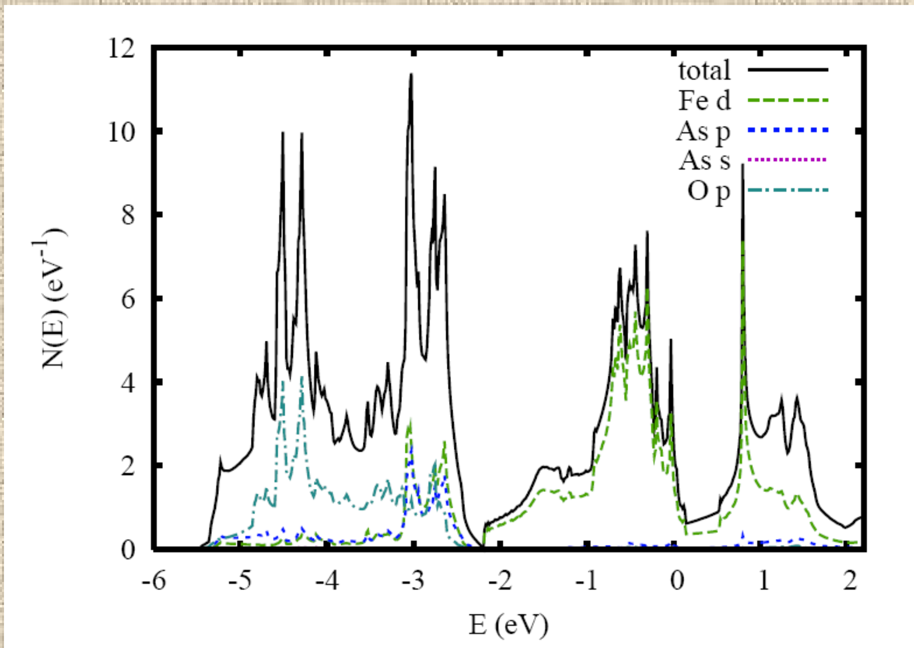
PRL **100,** 237003 (2008) PHYSICAL REVIEW LETTERS week ending 13 JUNE 2008

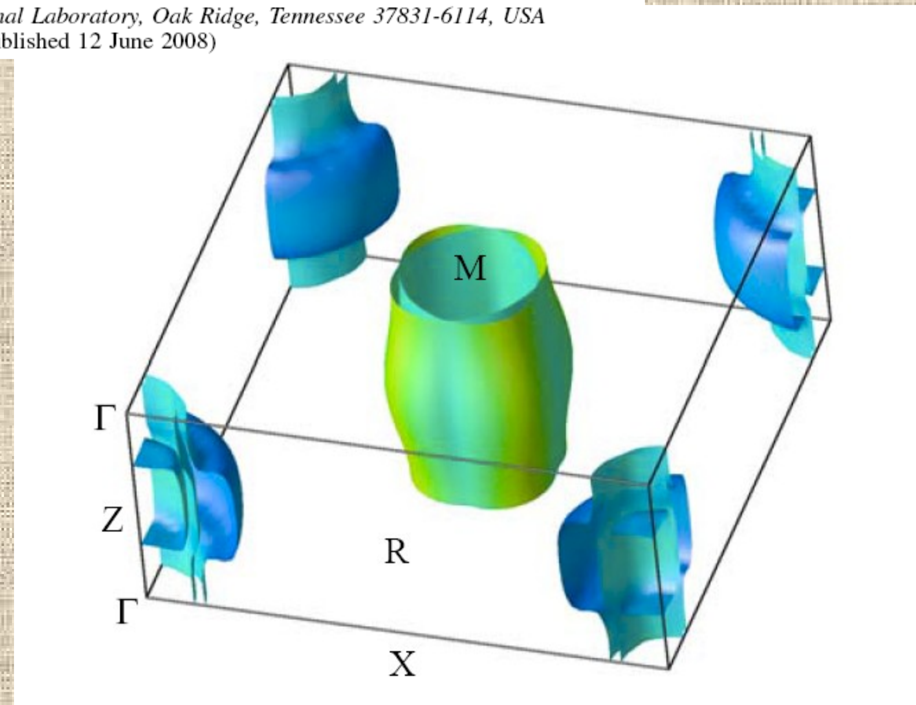
Density Functional Study of $LaFeAsO_{1-x}F_x$: A Low Carrier Density Superconductor Near Itinerant Magnetism

D. J. Singh and M.-H. Du

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6114, USA

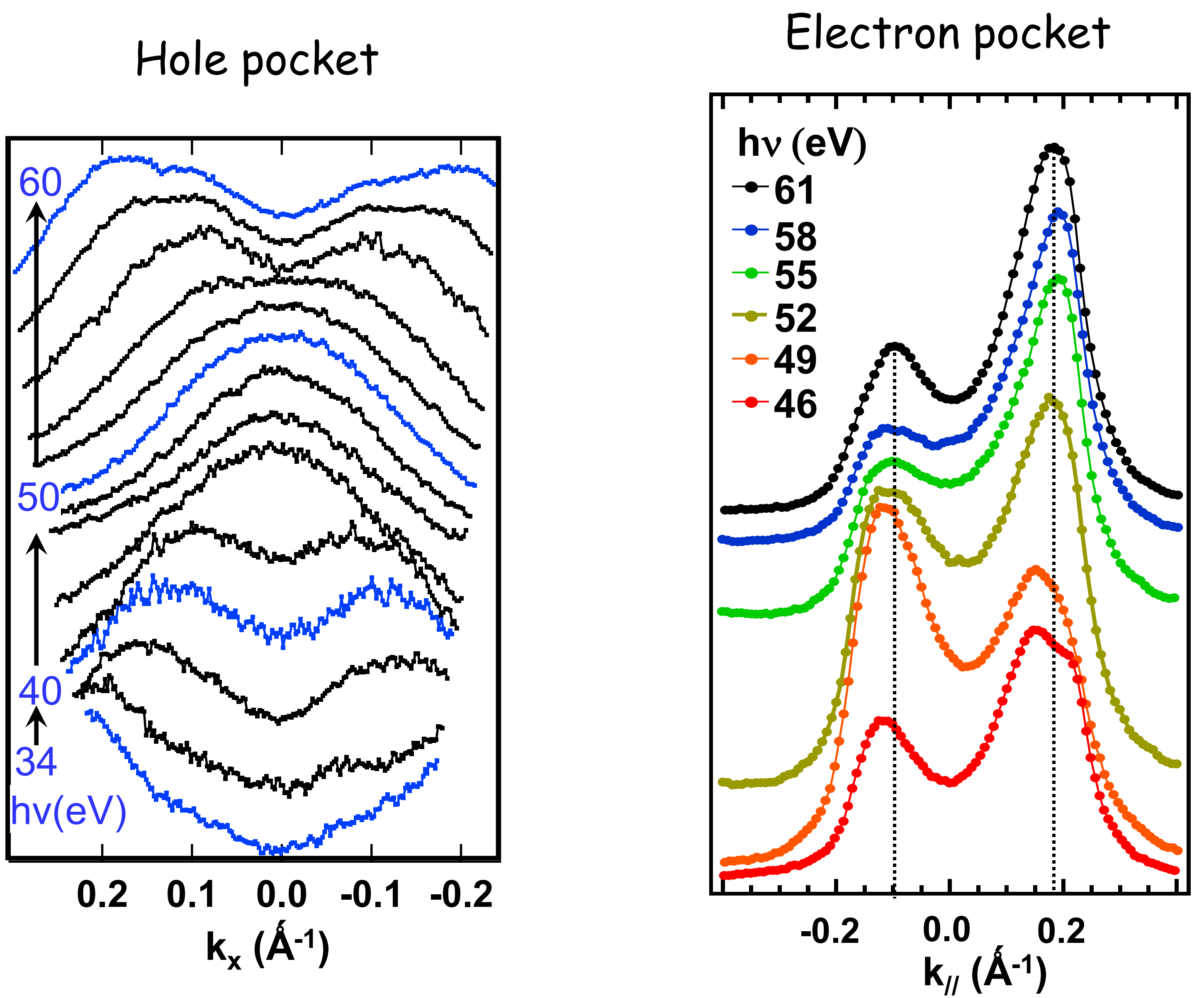
(Received 4 March 2008; published 12 June 2008)



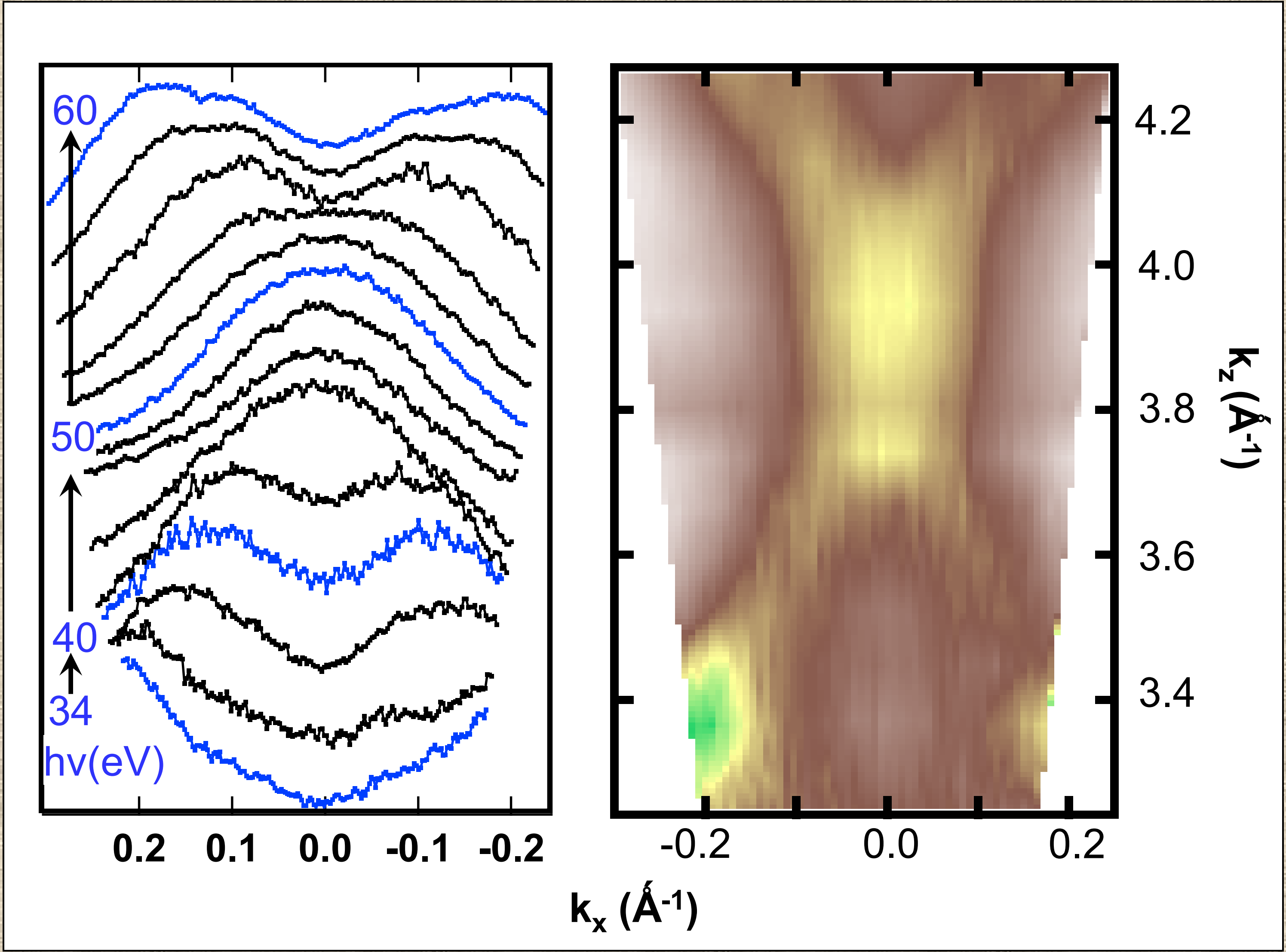


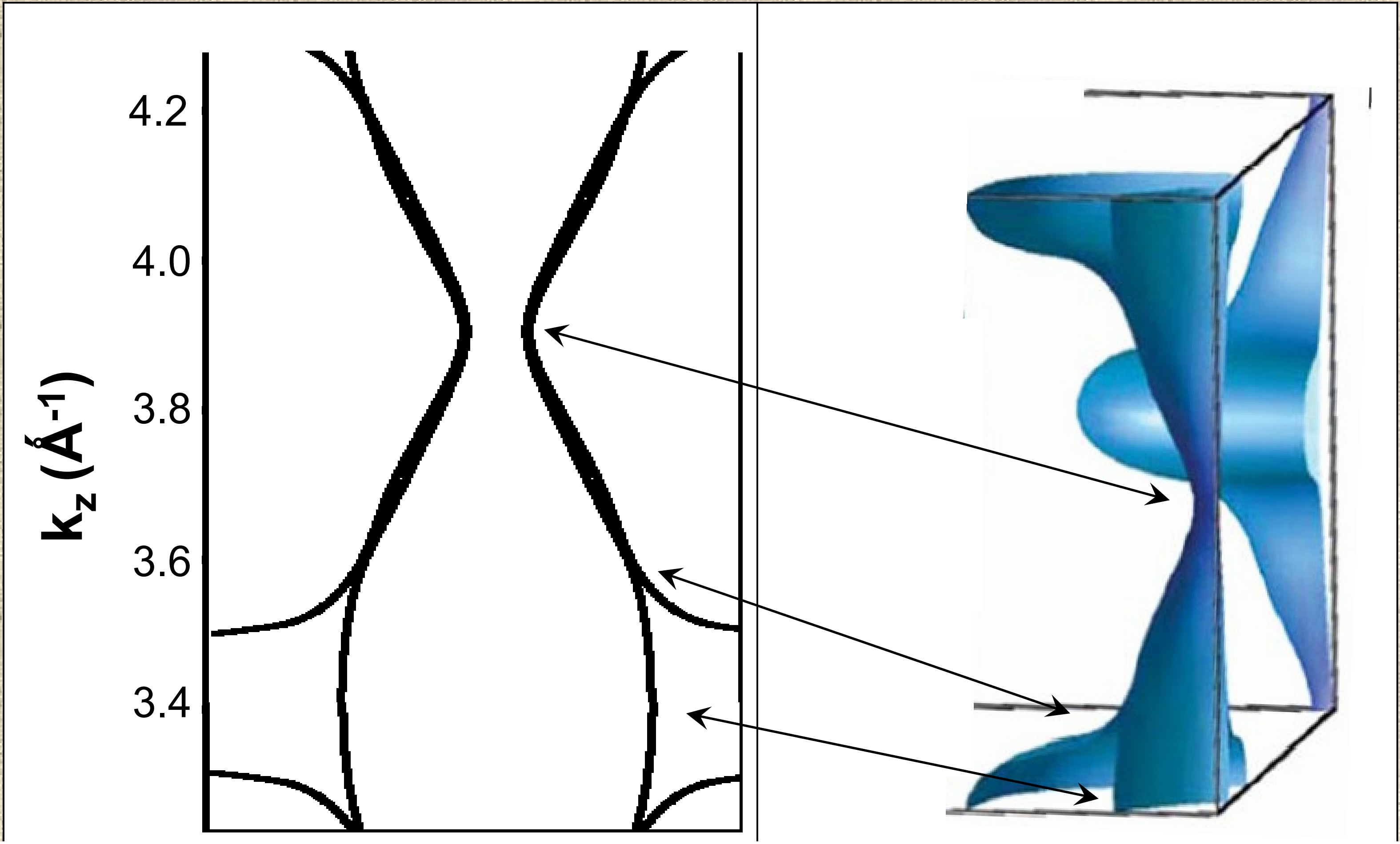
- Weak hybridization between Fe and As
- Nearly 2D electronic structure

- FS consists of 5 sheets:
- 2 high velocity electron cylinders
- 2 lower velocity hole cylinders
- 1 3D hole pocket
- 3D hole pocket shrinks with doping
- Theories focus on pairing interaction between elect. and hole bands



Hole pocket
60
50
40
34
hv(eV)
0.2 0.1 0.0 -0.1 -0.2
k_x ($Å^{-1}$)
Electron pocket
hν (eV)
61
58
55
52
49
46
-0.2 0.0 0.2
$k_{//}$ ($Å^{-1}$)


60
50
40
34
hv(eV)
0.2
0.1
0.0
-0.1
-0.2
4.2
4.0
3.8
3.6
3.4
-0.2
0.0
0.2
k_z (Å^-1)
k_x (Å^-1)

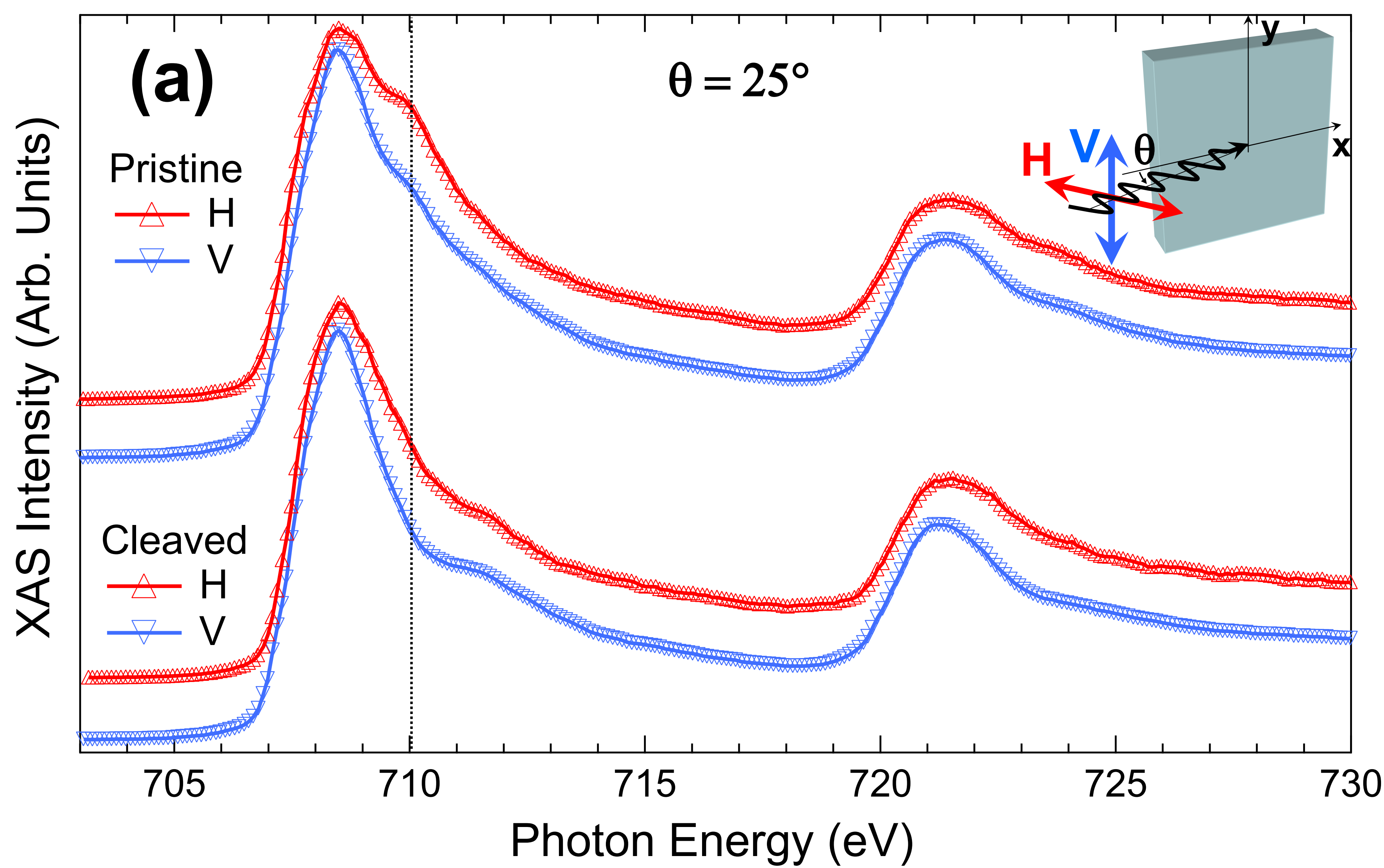


Phys. Rev. B 79, 220503(R) (2009))

Polarized XAS on $BaFe_2As_2$

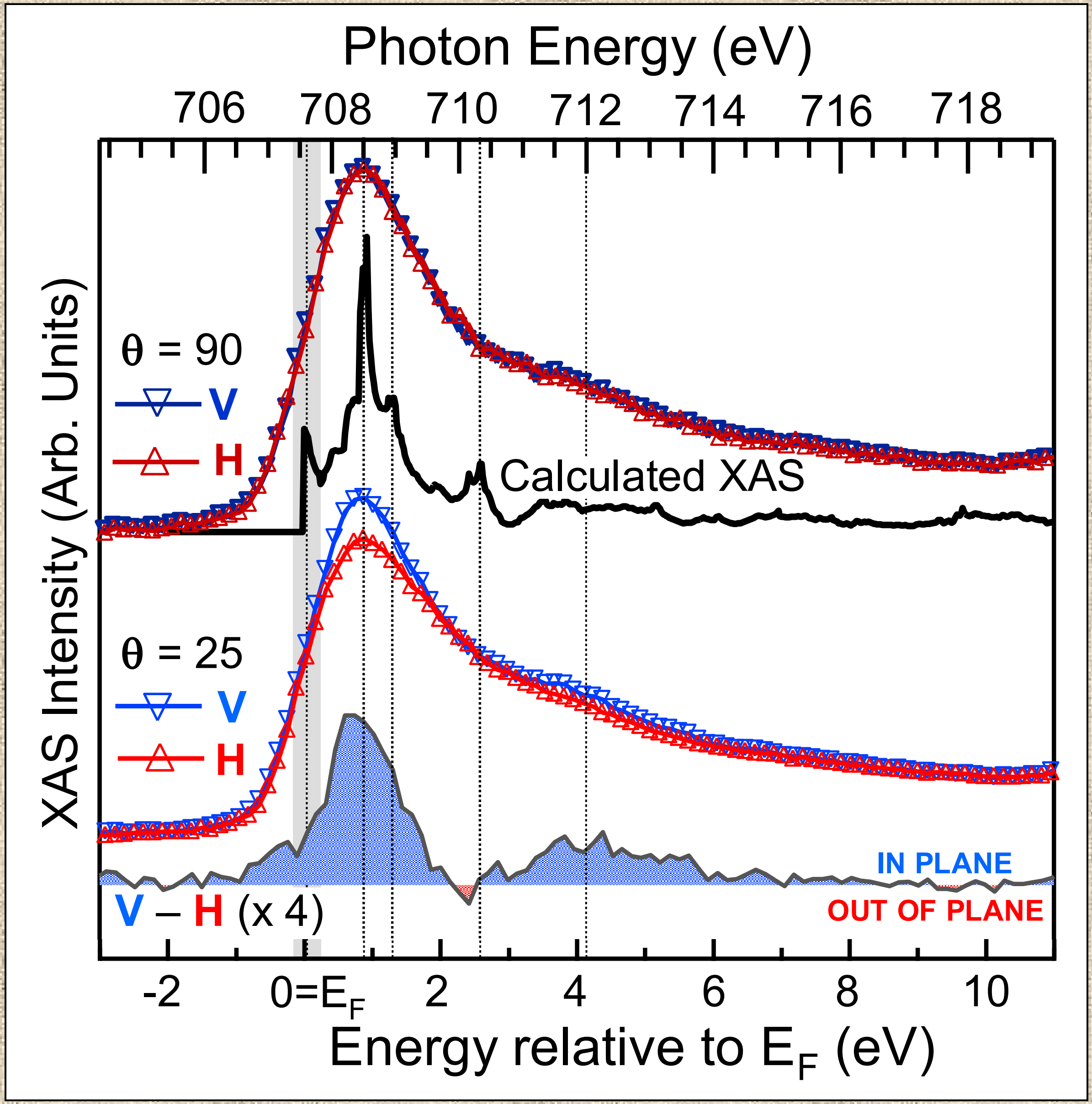
X-ray spectroscopy seems to suggest low U values
Full calculations including matrix elements and also effect of the core

W.L. Yang, T. Devereaux et al., PRB 80, 014508 (2009)

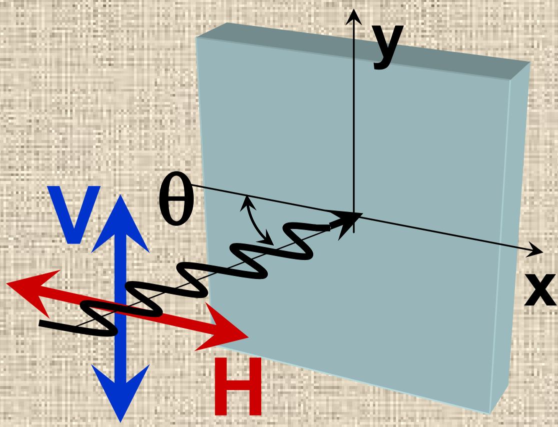


(a)
θ = 25°
y
x
H
V
θ
Pristine
H
V
Cleaved
H
V
XAS Intensity (Arb. Units)
705
710
715
720
725
730
Photon Energy (eV)

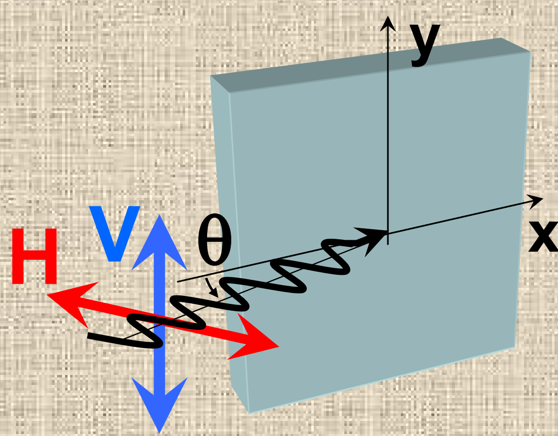
$BaFe_2As_2$



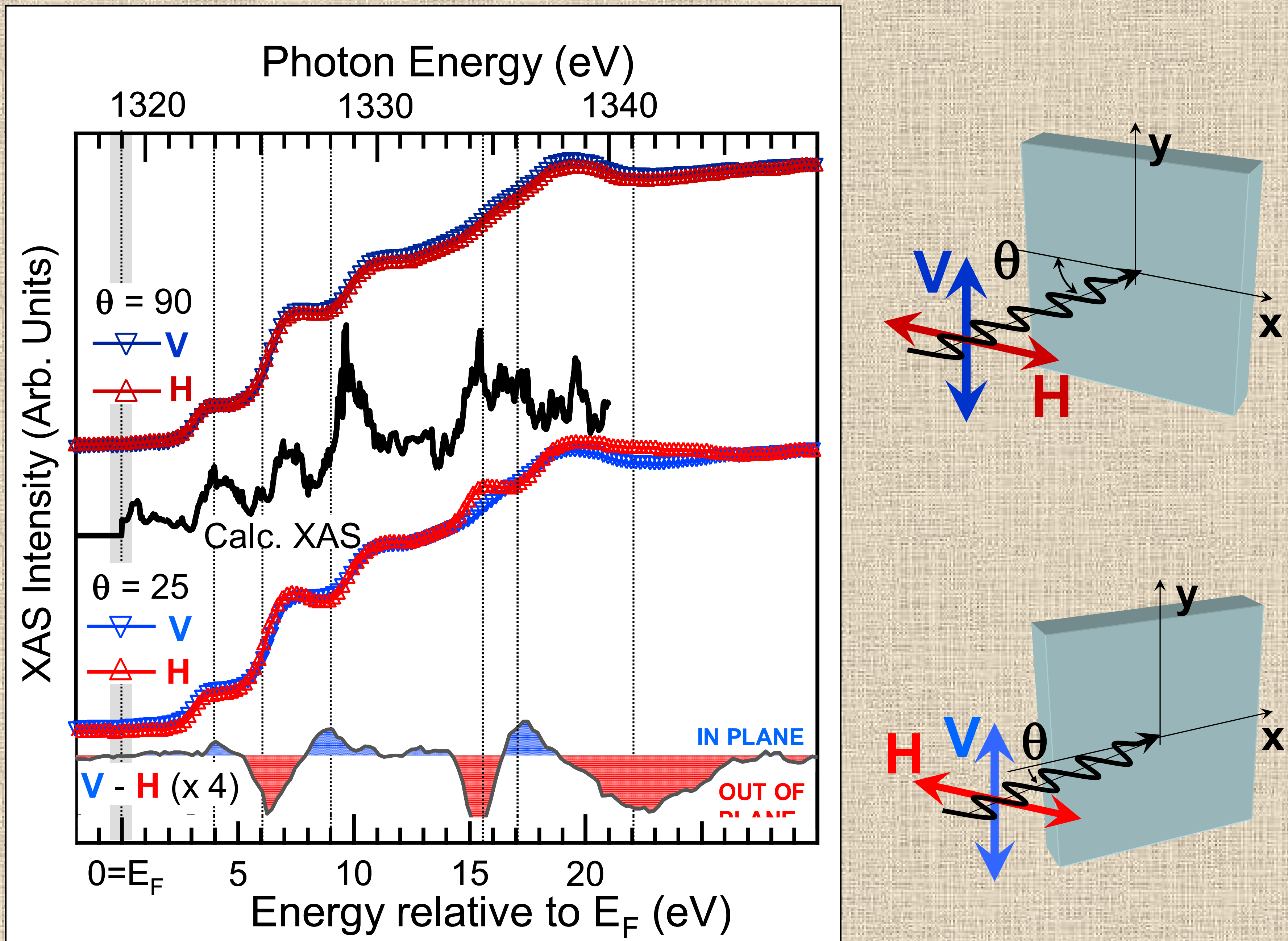
Photon Energy (eV)
706
708
710
712
714
716
718
XAS Intensity (Arb. Units)
θ = 90
V
H
Calculated XAS
θ = 25
V
H
IN PLANE
OUT OF PLANE
V – H (x 4)
-2
0=E_F
2
4
6
8
10
Energy relative to E_F (eV)



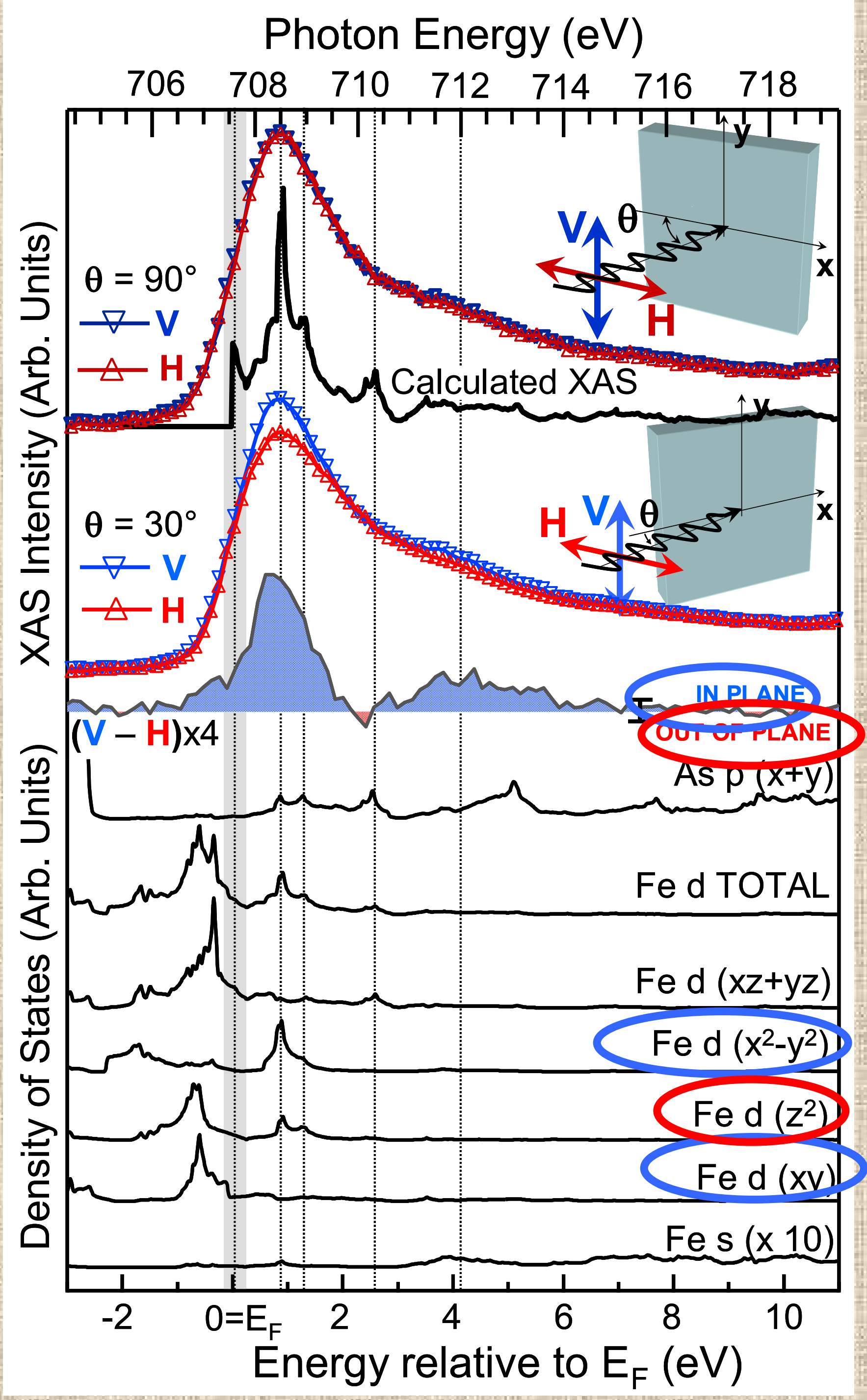
y
x
θ
V
H



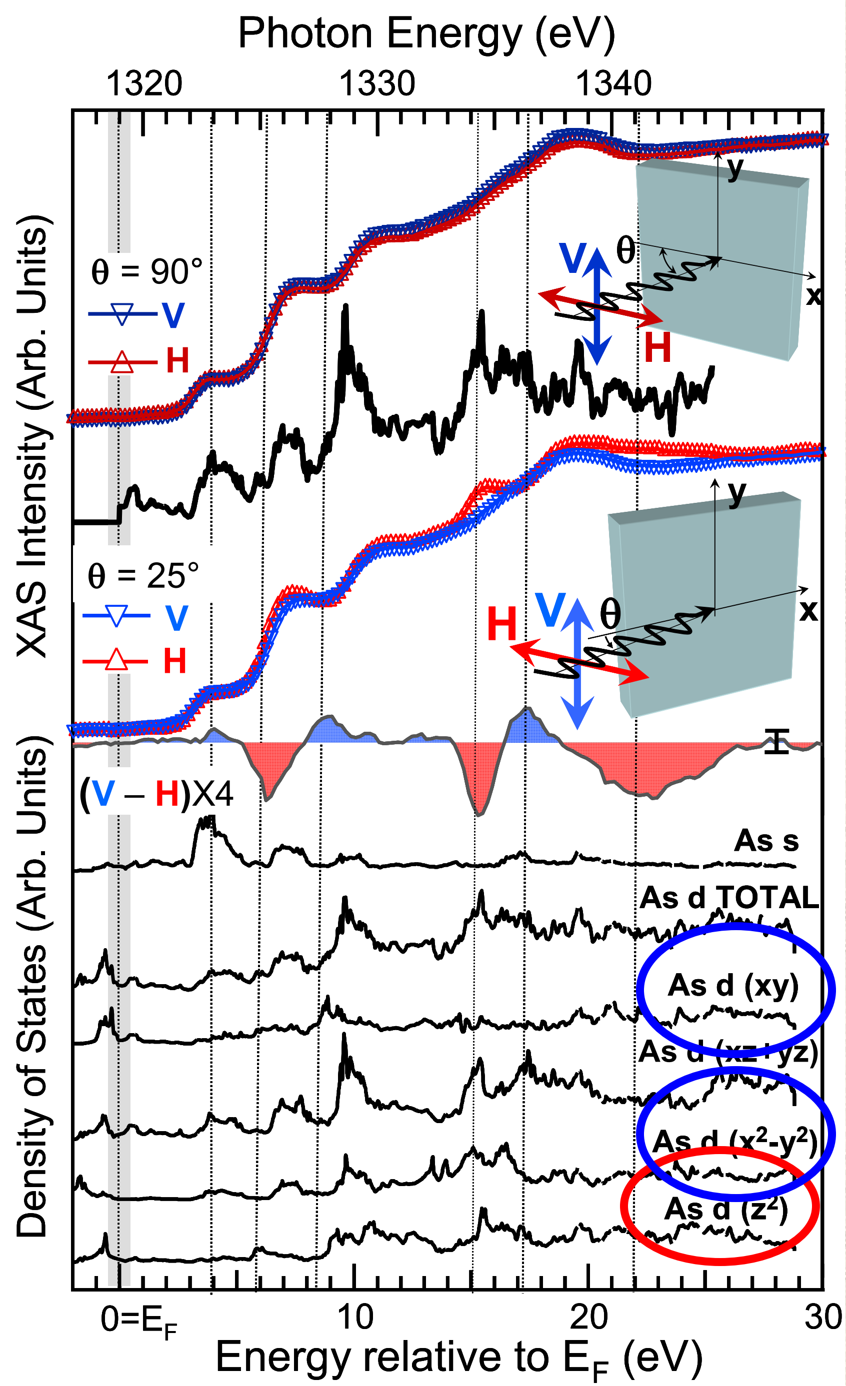
y
x
θ
H
V



Photon Energy (eV)
1320
1330
1340
XAS Intensity (Arb. Units)
θ = 90
V
H
Calc. XAS
θ = 25
V
H
IN PLANE
V - H (x 4)
OUT OF
0=E_F
5
10
15
20
Energy relative to E_F (eV)
y
θ
V
x
H
y
H
V
θ
x



710 and 712 eV
Hybridization with As



Photon Energy (eV)
1320
1330
1340
XAS Intensity (Arb. Units)
θ = 90°
V
H
θ
y
x
θ = 25°
(V – H)X4
As s
As d TOTAL
As d (xy)
As d (xz+yz)
As d (x²-y²)
As d (z²)
Density of States (Arb. Units)
0=E_F
10
20
30
Energy relative to E_F (eV)

FeSC are quite unique high temperature superconductors

- Itinerant Fe d-band character,
- High density of states at E_F,
- No signatures of strong local Mott-Hubbard type correlations that characterize cuprate HTSC.

(F. Bondino et al., Phys. Rev. Lett. 101, 26700 (2008)).

FeSC show three-dimensional FS topology (→ reduced dimensionality is not a necessary condition for high temperature superconductivity?)

(P. Vilmercati et al., Phys. Rev. B 79, 220503(R) (2009))

- High degree of Fe-As hybridization.
- The energies and directions of Fe and As d unoccupied orbitals in agreement with the predictions of DFT

(C. Parks Cheney et al., Phys. Rev. B, in press)

These results assist in establishing a unique character of the FeSC materials, a new class of high temperature superconductors, quite unlike the cuprates.

Itinerant Spin Fluctuations in the Normal State of $CeFeAsO_{0.89}F_{0.11}$

F. Bondino et al., Phys. Rev. Lett. 101, 26700 (2008)

3D Fermi Surface Topology in $Ba(Fe_{1-x}Co_x)_2As_2$

P. Vilmercati et al., Phys. Rev. B 79, 220503(R) (2009)

Orbital Symmetry and Bonding Topology in $Ba(Fe_{1-x}Co_x)_2As_2$

C. Parks Cheney et al., Phys. Rev. B, in press.