

# X-ray spectra, electronic structure and correlation effects in FeAs-superconductors

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# Outline

- Introduction
- Cuprates and pnictides: Similarity and differences
- RIXS spectra of FeAs-superconductors
- Electronic structure calculations and correlation effects in pnictides: LDA and LDA+DMFT
- Summary

# The FeAs-superconductors – the iron age revisited



***Iron Man*** : In cinemas now from Paramount Pictures and Marvel Entertainment

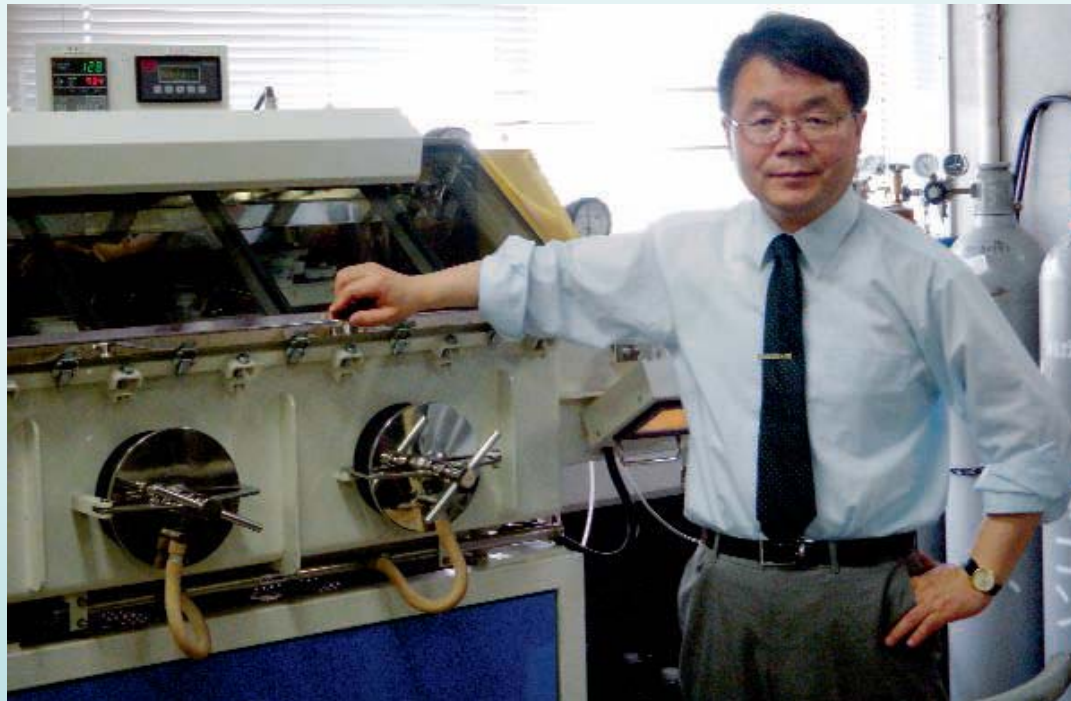
# The FeAs-superconductors

The discovery of FeAs high- $T_c$  superconductors in 2008 is the most extraordinary, unexpected and unprecedented event in the condensed matter physics for the last 20 years.

- Why extraordinary? It was considered that cuprates are absolutely unique compounds where high- $T_c$  can be realized.
- Why unexpected? At first time high- $T_c$  superconductivity is observed in compounds containing iron.
- Why unprecedented? During one year more than 1000 papers were prepared and displayed on <http://xxx.lanl.gov> web site.

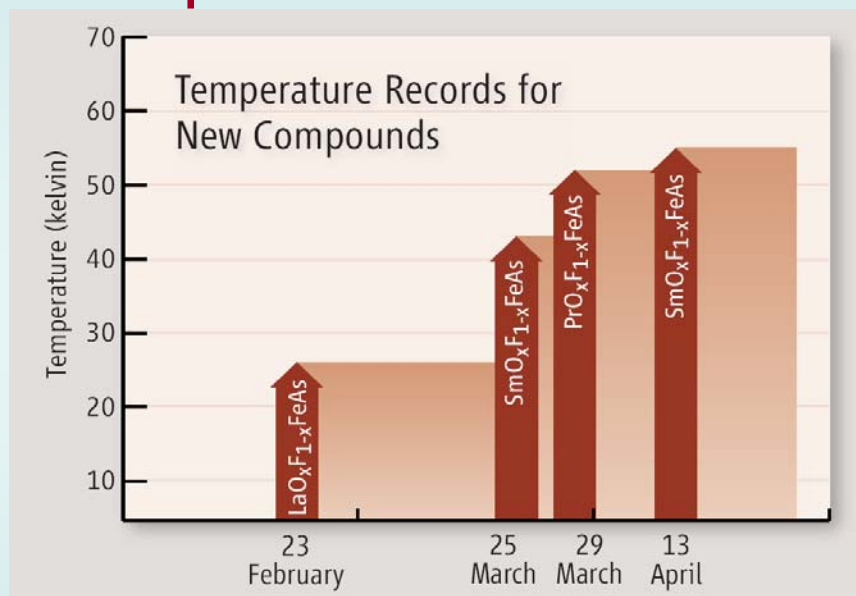
# The FeAs-superconductors: *races on a vertical*

- Hideo Hosono, at the Tokyo Institute of Technology, and colleagues found the first compound, fluorine-doped lanthanum oxygen iron arsenide ( $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ ), as they reported online 23 February 2008 in the *Journal of the American Chemical Society*. It weighed in with a  $T_c$  of 26 Kelvin.



# FeAs-superconductors: *races on a vertical*

## First family of FeAs-superconductors



Four Chinese groups quickly pushed the critical temperatures higher by replacing the lanthanum with other rare earth elements.

Y. Kamihara et.al., Tokyo, JACS (2008)

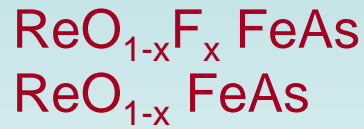
G.F. Chen, et.al., Beijing, arXiv: 0803.3790

Zhi-An Ren, Beijing, arXiv: 0803.4283

Zhi-An Ren, Beijing, arXiv: 0804.2053

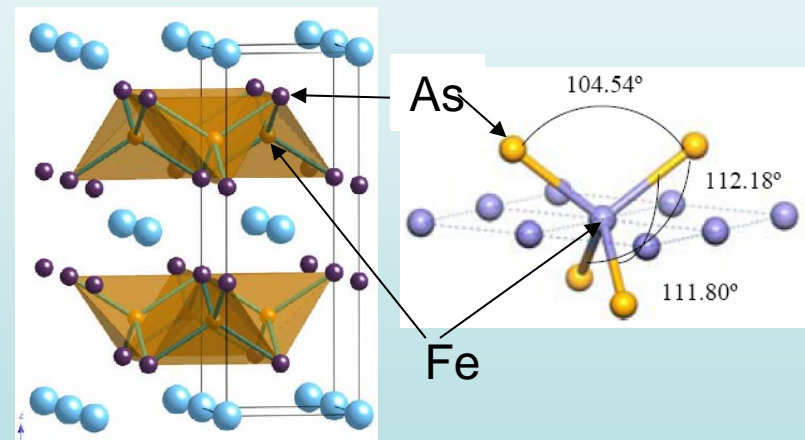
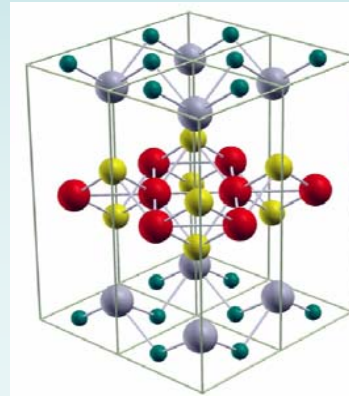
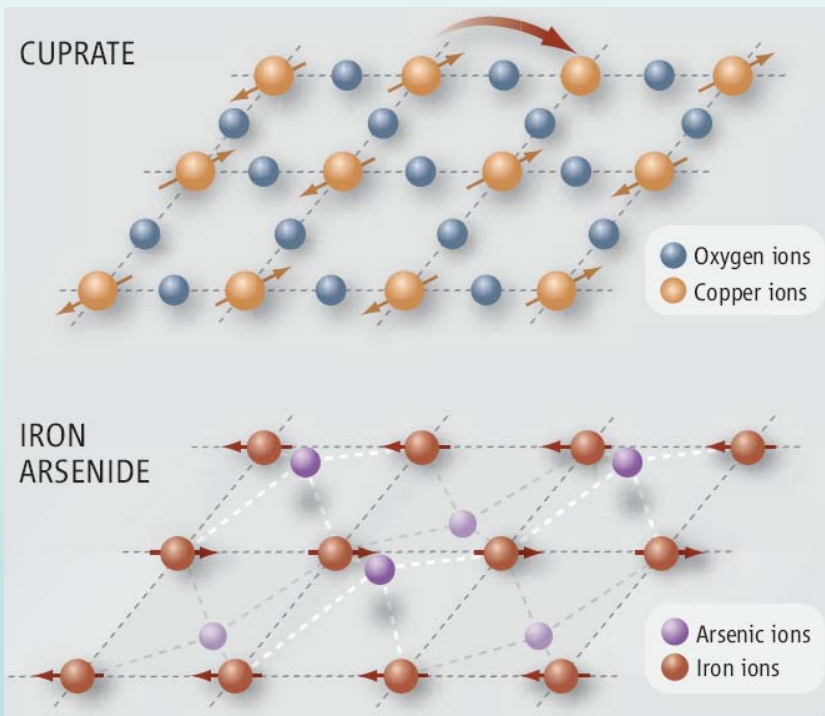
|  |  |
|--|--|
| SmF <sub>x</sub> O <sub>1-x</sub> FeAs<br>x~0.2 d) | T <sub>c</sub> =55K,<br>cm/0803.3603<br>a=3.933Å,<br>c=8.4287Å   |
| PrF <sub>x</sub> O <sub>1-x</sub> FeAs c)          | T <sub>c</sub> =52K,<br>cm/0803.4283<br>a=3.985Å,<br>c=8.595Å    |
| CeF <sub>x</sub> O <sub>1-x</sub> FeAs b)          | T <sub>c</sub> =41 K,<br>cm/0803.3790<br>a=3.996Å,<br>c=8.648Å   |
| LaF <sub>x</sub> O <sub>1-x</sub> FeAs a)          | T <sub>c</sub> =26 K,<br>JACS-2008<br>a=4.036Å, c=8.739<br>Å     |
| La <sub>1-x</sub> Sr <sub>x</sub> OFeAs            | T <sub>c</sub> =25K,<br>cm/0803.3021,<br>a=4.035Å, c =<br>8.771Å |

# Crystal Structure: Tetragonal $I4/mmm$



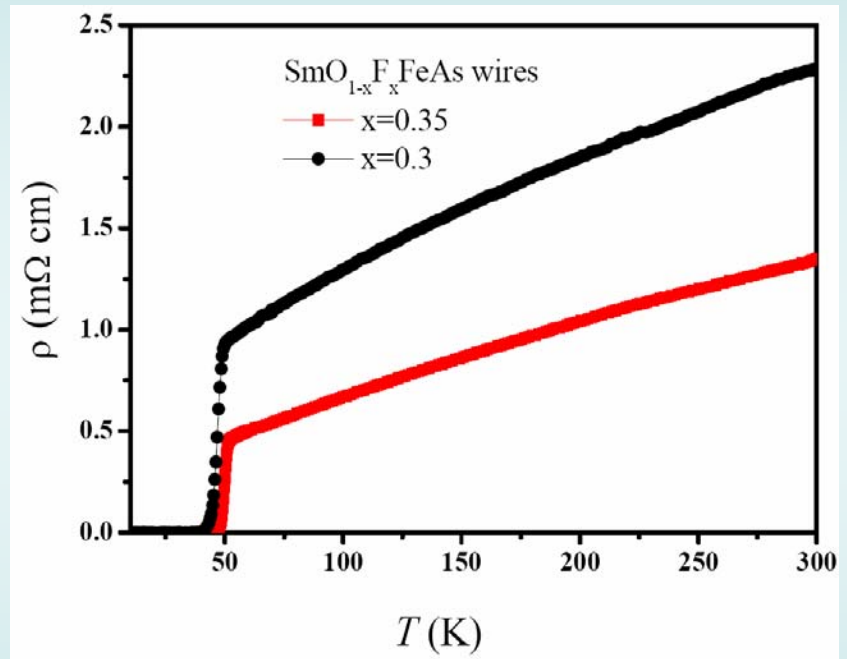
F not important, vacancy fine

- 2D square lattice of Fe
- Fe - magnetic moment
- As-similar then O in cuprates



# Technologically relevant

Wires fabricated by the powder-in-tube (PIT) method:



Zhaoshun Gao, et.al., arXiv 0806.2451

$J_c$  up to  $2 \times 10^5$  A/cm<sup>2</sup>

( $H_{c2}$ ) up to 120 T

More three-dimensional than cuprates

# Variety of materials

**SmO<sub>1-x</sub>F<sub>x</sub>FeAs** ( $T_c=55$  K,  $x\sim 0.2$ )

electron doped

**(Ba<sub>1-x</sub>K<sub>x</sub>)Fe<sub>2</sub>As<sub>2</sub>** ( $T_c=38$ K,  $x\sim 0.4$ ),

hole doped (not electron doped)

Marianne Rotter et.al., arXiv:0805.4630

**BaFe<sub>2</sub>As<sub>2</sub>**, ( $T_c=29$ K @ 35 kbar),

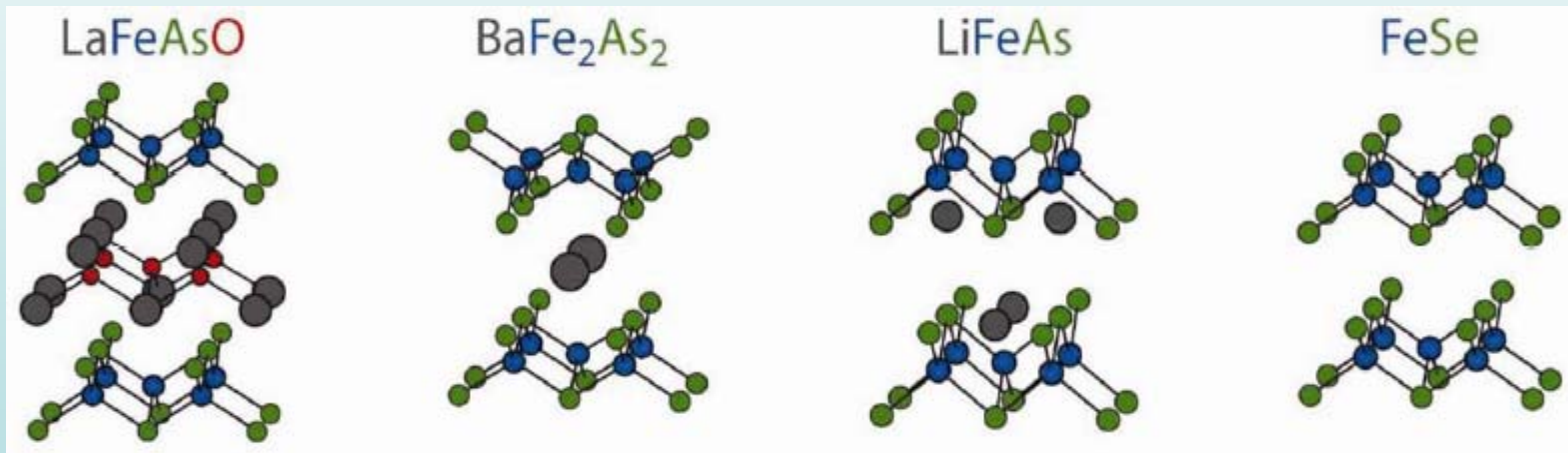
Milton S. Torikachvili, PRL (2008)

**Li<sub>1-x</sub>FeAs**, ( $T_c=18$ K),

X.C.Wang et.al., arXiv:0806.4688

**FeSe<sub>1-0.08</sub>**, ( $T_c=34$ K @ 22 GPa), **No arsenic ☺!**

G. Garbarino et.al., arXiv: 0903.3888



# A big class of new materials

(> 2000 compounds)

- Re-O-TM-Pn.

- Pn

- TM =

Periodic Table of the Elements

|   |    |    |    |    |     |     |     |     |    |     |    |     |    |     |    |     |    |     |    |     |    |     |    |     |    |     |    |    |    |    |    |    |    |    |    |    |    |
|---|----|----|----|----|-----|-----|-----|-----|----|-----|----|-----|----|-----|----|-----|----|-----|----|-----|----|-----|----|-----|----|-----|----|----|----|----|----|----|----|----|----|----|----|
| 1 | IA | 1  | H  | I  | IIA | 2   | He  | O   |    |     |    |     |    |     |    |     |    |     |    |     |    |     |    |     |    |     |    |    |    |    |    |    |    |    |    |    |    |
| 2 |    | 3  | Li | 4  | Be  | 5   | B   | 6   | C  | 7   | N  | 8   | O  | 9   | F  | 10  | Ne |     |    |     |    |     |    |     |    |     |    |    |    |    |    |    |    |    |    |    |    |
| 3 |    | 11 | Na | 12 | Mg  | 13  | Al  | 14  | Si | 15  | P  | 16  | S  | 17  | Cl | 18  | Ar |     |    |     |    |     |    |     |    |     |    |    |    |    |    |    |    |    |    |    |    |
| 4 |    | 19 | K  | 20 | Ca  | 21  | Sc  | 22  | Ti | 23  | V  | 24  | Cr | 25  | Mn | 26  | Fe | 27  | Co | 28  | Ni | 29  | Cu | 30  | Zn | 31  | Ga | 32 | Ge | 33 | As | 34 | Se | 35 | Br | 36 | Kr |
| 5 |    | 37 | Rb | 38 | Sr  | 39  | Y   | 40  | Zr | 41  | Nb | 42  | Mo | 43  | Tc | 44  | Ru | 45  | Rh | 46  | Pd | 47  | Ag | 48  | Cd | 49  | In | 50 | Sn | 51 | Sb | 52 | Te | 53 | I  | 54 | Xe |
| 6 |    | 55 | Cs | 56 | Ba  | 57  | *La | 72  | Hf | 73  | Ta | 74  | W  | 75  | Re | 76  | Os | 77  | Ir | 78  | Pt | 79  | Au | 80  | Hg | 81  | Tl | 82 | Pb | 83 | Bi | 84 | Po | 85 | At | 86 | Rn |
| 7 |    | 87 | Fr | 88 | Ra  | +Ac |     | 104 | Rf | 105 | Ha | 106 | Sg | 107 | Ns | 108 | Hs | 109 | Mt | 110 |    | 111 |    | 112 |    | 113 |    |    |    |    |    |    |    |    |    |    |    |

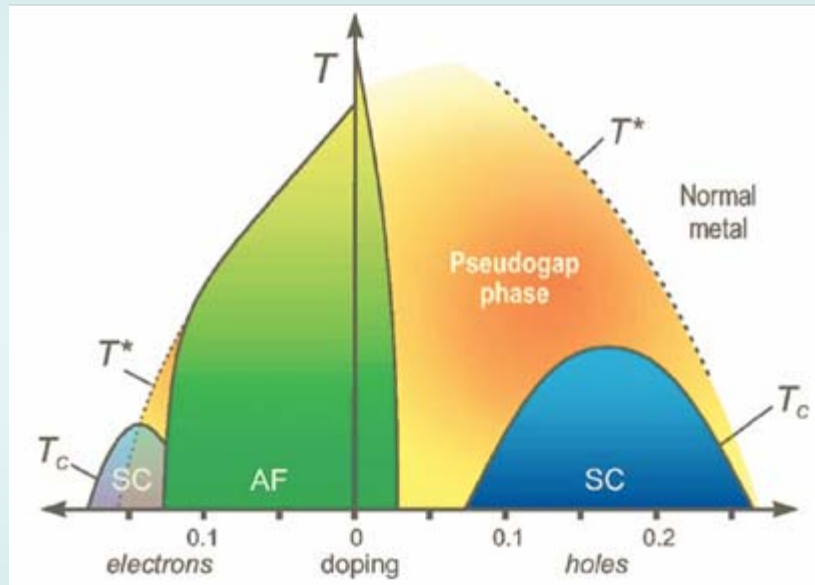
  

|                     |    |    |    |    |    |    |    |    |    |    |     |     |     |     |
|---------------------|----|----|----|----|----|----|----|----|----|----|-----|-----|-----|-----|
| * Lanthanide Series | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68  | 69  | 70  | 71  |
|                     | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er  | Tm  | Yb  | Lu  |
| + Actinide Series   | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 |
|                     | Th | Pa | U  | Np | Pu | Am | Cm | Bk | Cf | Es | Fm  | Md  | No  | Lr  |

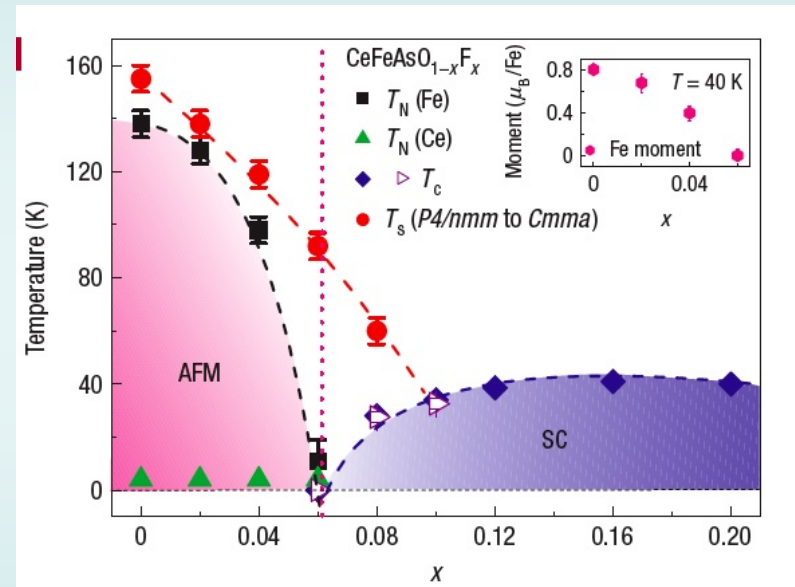
- Re = La+

# Cuprates and pnictides: similarity and difference

## Cuprates

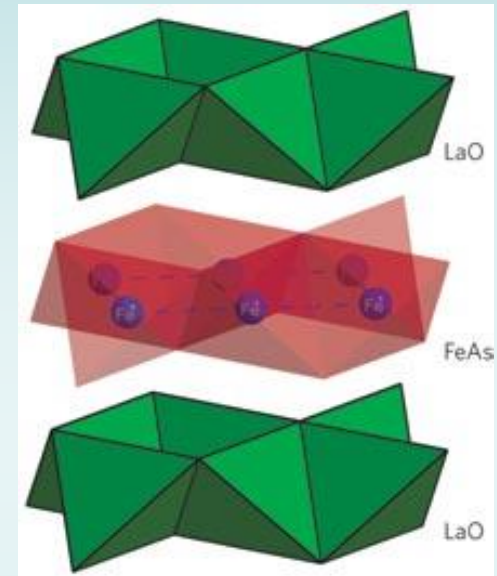
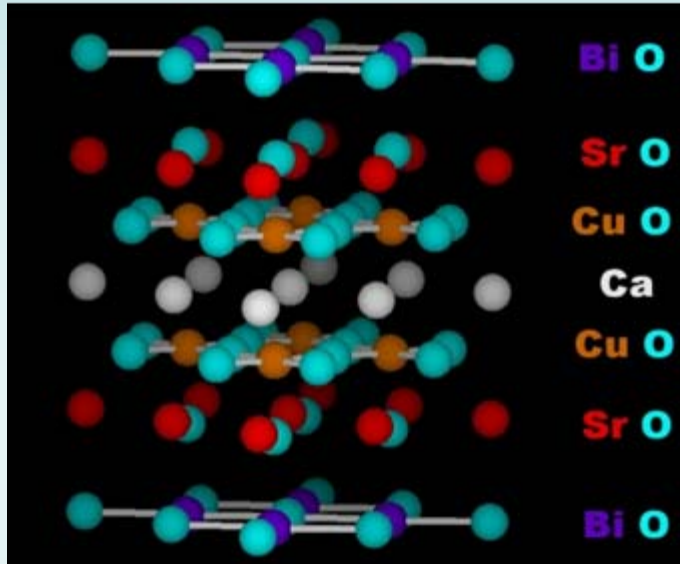


## $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$



In both cases doping induces carriers (electrons and holes) which suppress AFM ordering and provides conditions for Cooper pairing.

# Cuprates and pnictides: similarity and difference



In both cases, the superconductivity is in metallic layers, there is a charge reservoir and they are antiferromagnetic in their undoped state.

# Cuprates and pnictides: similarity and difference

## Similarity:

- Layered structure
- AFM for undoped compounds
- Suppression of magnetic order with doping

## Difference:

- Undoped cuprates - AFM insulators with localized description of magnetic moments,  $U \geq W$
- Undoped pnictides - metals with itinerant description of magnetic order,  $U < W$

# Are Fe-pnictides correlated systems?

Open questions:

- Very high electrical resistivity (bad metals)
- Very large uniform susceptibility in the normal state
- Very low constant of electron-phonon coupling which is not sufficient for BCS-theory
- Close to M-I transition (predicted by DMFT theory)

Is it strongly correlated superconductivity?

# X-ray spectra of FeAs-superconductors:

7 May 2008: E.Z. Kurmaev et al., arXiv: 0805.0668; PRB, 78, 220503R (2008).

Fe RIXS, O 1s XAS, O  $K\alpha$  XES:  $\text{ReO}_{1-x}\text{F}_x\text{FeAs}$  (Re=La,Sm).

12 June 2008: T. Kroll et al., arXiv: 0806.2625; PRB 78, 220502 (2008).

O 1s XAS, Fe 2p XAS:  $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ .

15 August 2008: A. Ignatov et al., arXiv; 0808.2134. Fe 1s XAS, As 1s XAS, La 2p XAS:  $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ .

20 November 2008: C.J. Zhang et al., arXiv: 0811.3268. Fe 1s and As 1s EXAFS:  $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ .

6 February 2009: E.Z. Kurmaev et al., arXiv: 0902.1141. Fe RIXS:  $\text{CaFe}_2\text{As}_2$ .

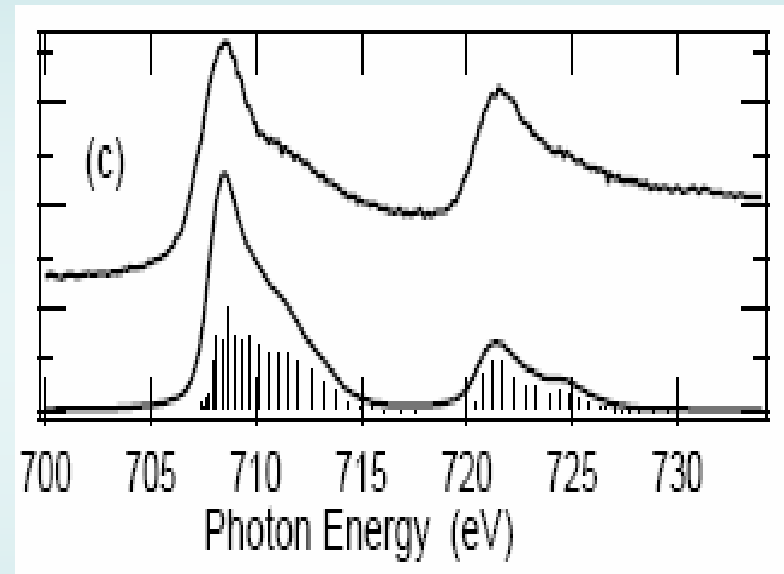
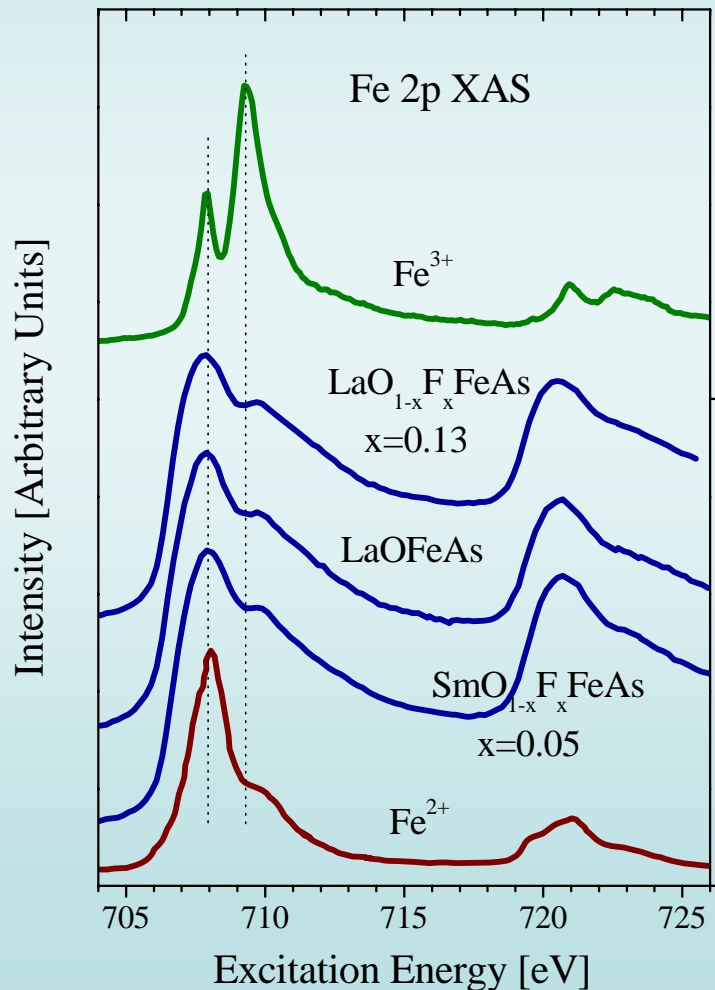
27 March 2009: E.Z. Kurmaev et al.: arXiv: 0903.4901, Fe RIXS:  $\text{LiFeAs}$  and  $\text{NaFeAs}$ .

15 May 2009: W.L. Yang et al., Fe RIXS:  $\text{Sm}_{0.85}\text{FeAs}$ ,  $\text{BaFe}_2\text{As}_2$ ,  $\text{LaFe}_2\text{P}_2$ .

# RIXS spectra of FeAs-superconductors

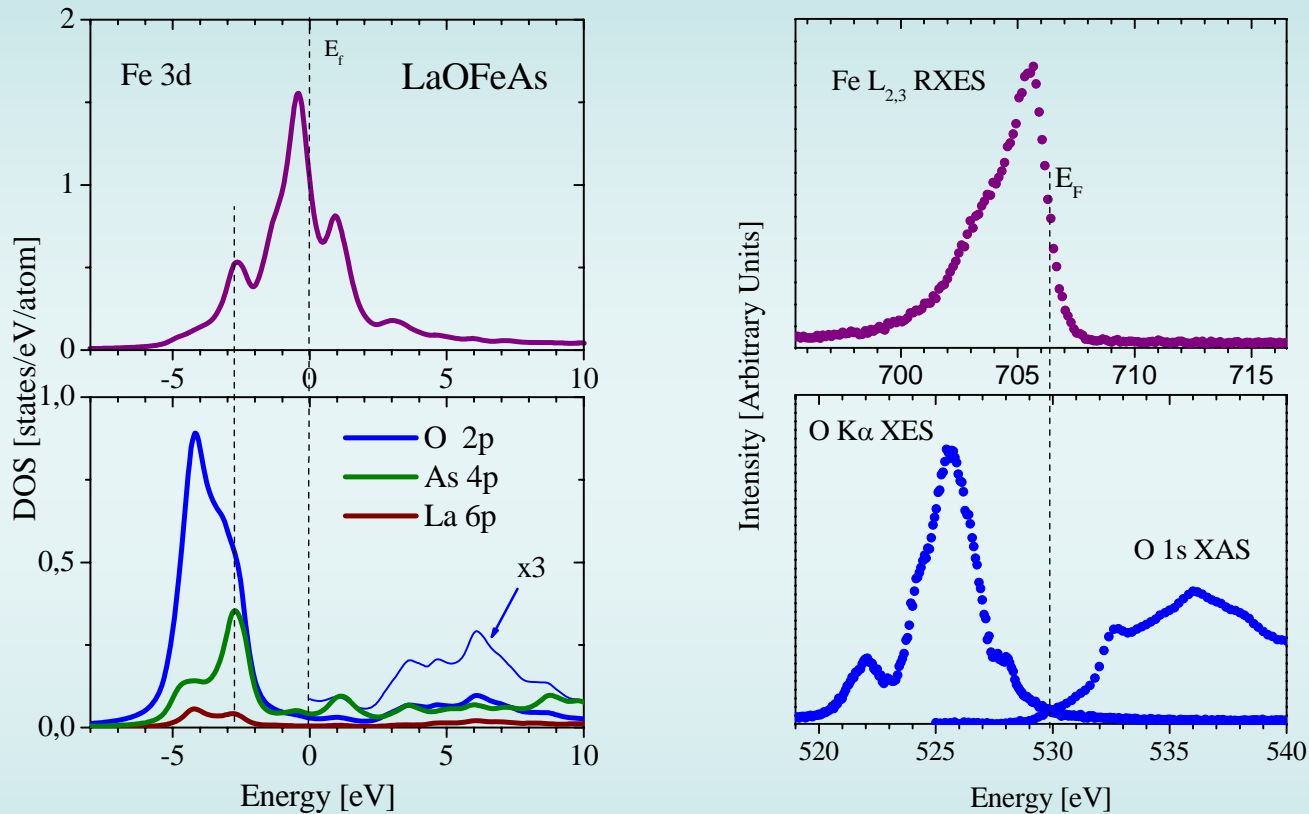
E.Z. Kurmaev et al.

T. Kroll et al., PRB 78, 220502 (2008)



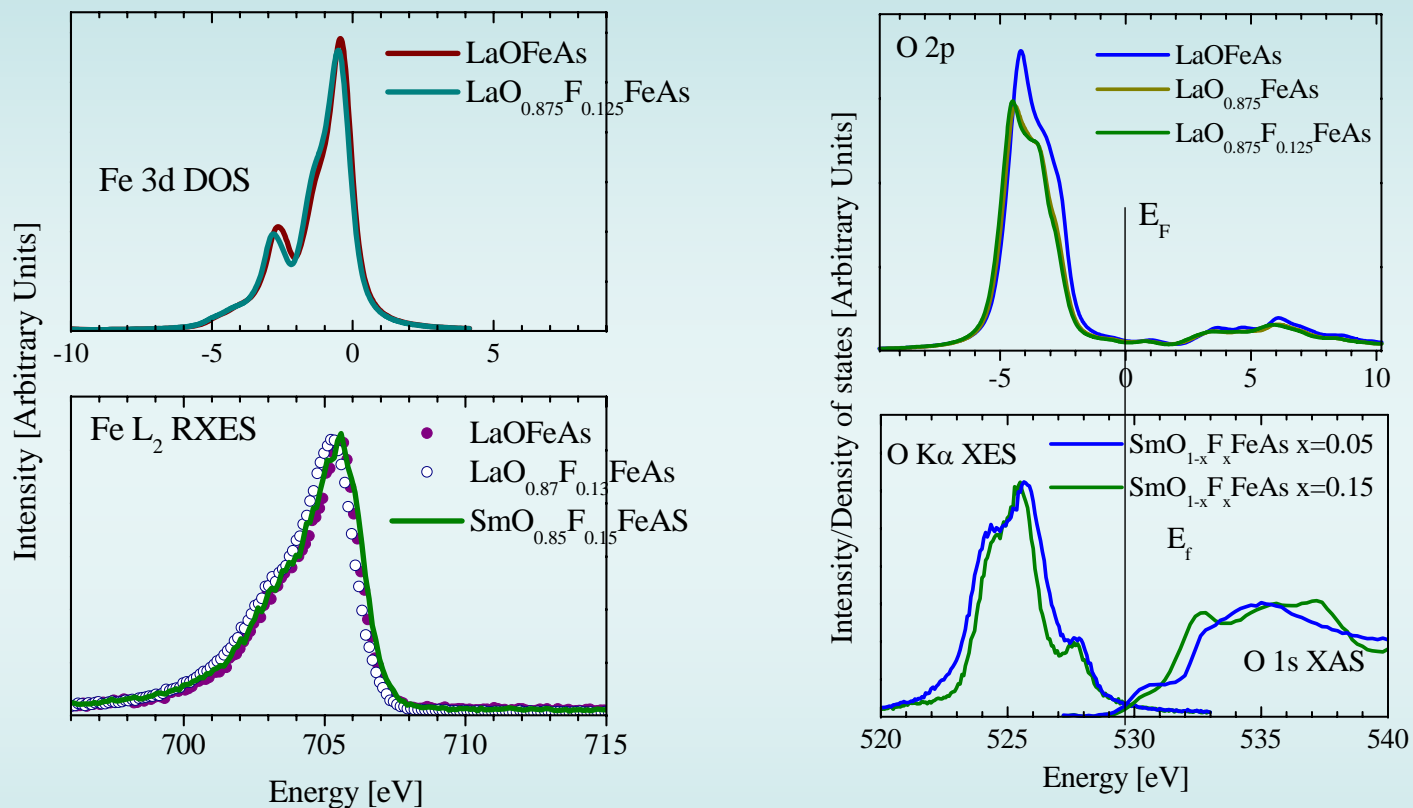
Results of multiplet calculation for  $\text{Fe}^{2+}$  ( $d^6$ ) are in accordance with experimental Fe 2p XAS of  $\text{LaOFeAs}$

# X-ray spectra and LDA of undoped LaOFeAs



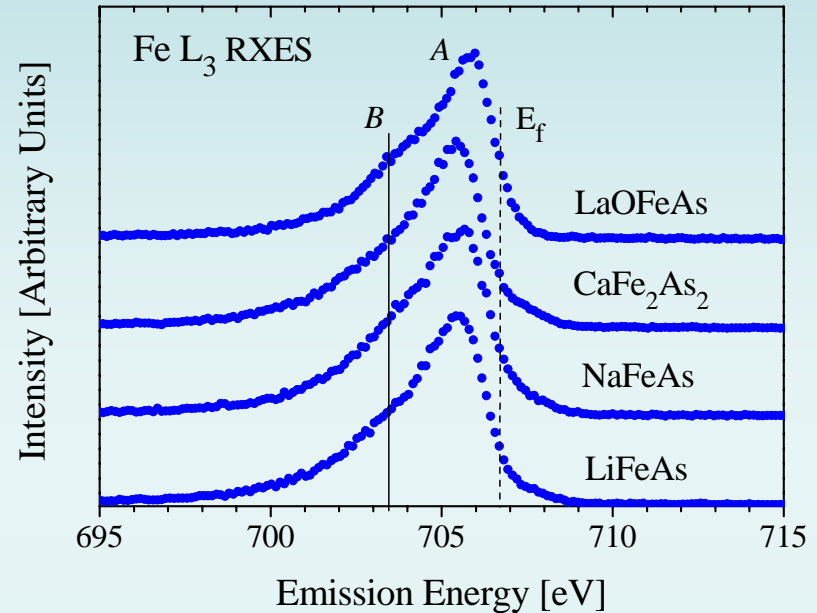
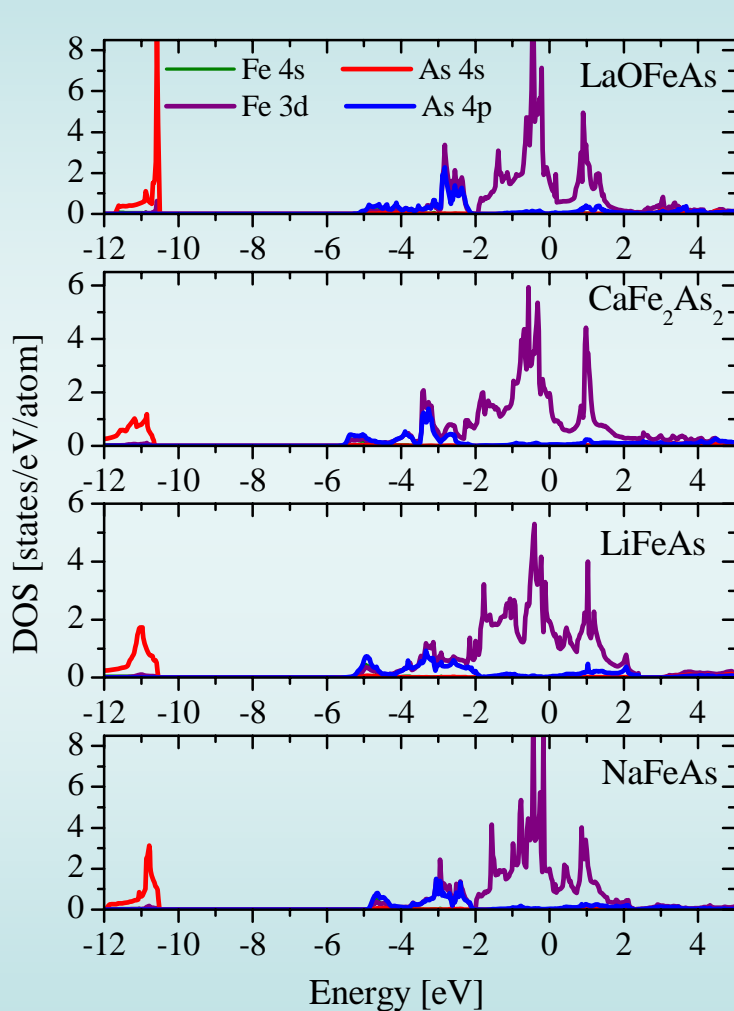
Fe 3d-states dominate at the Fermi level; the contribution of O 2p-states in the vicinity of  $E_F$  is negligible.

# X-ray spectra and LDA of $\text{ReO}_{1-x}\text{F}_x\text{FeAs}$



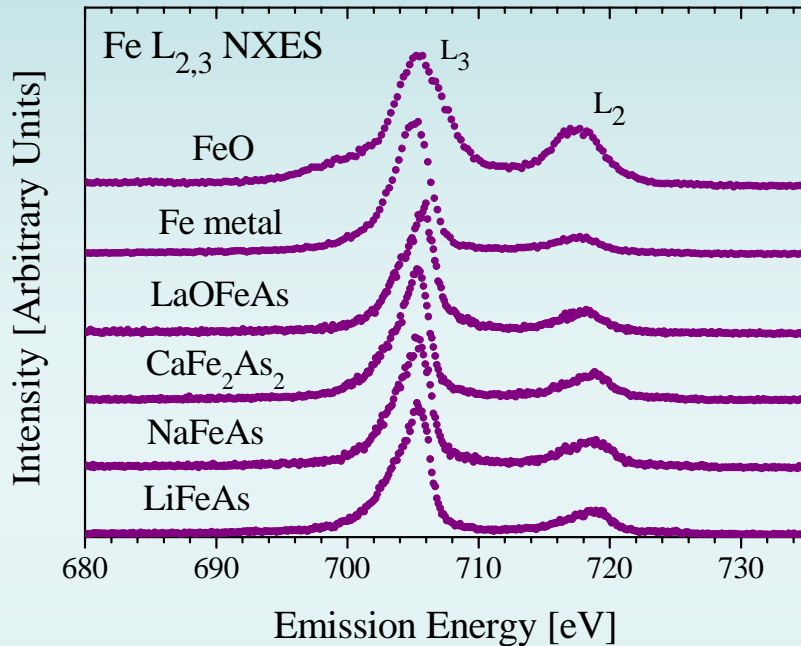
The same level of oxygen deficiency and fluorine doping (12.5%) gives the similar reduction of O 2p band width. This means that carriers in FeAs-reservoir are provided by oxygen vacancies or F 2p-electrons.

# RIXS spectra of FeAs-superconductors



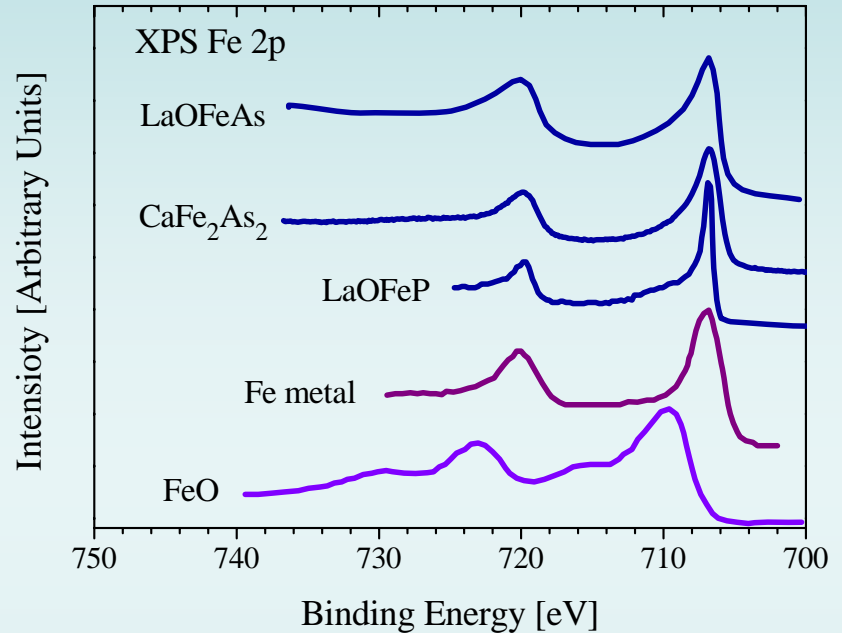
In accordance with LDA calculations Fe L<sub>3</sub> RXES show that Fe 3d-states have the similar distribution and dominate at E<sub>F</sub> for all FeAs-compounds. Therefore superconductivity in FeAs-systems may be described within minimal model, taking into account only essential Fe 3d-bands which are close to the Fermi level.

# X-ray spectra of FeAs-superconductors



$I(L_2)/I(L_3)$  intensity ratio is almost identical for all FeAs-compounds and more close to that of Fe metal than of FeO.

Conclusion: X-ray emission and photoelectron spectra show itinerant character of Fe 3d-electrons in FeAs-compounds.



XPS Fe 2p of FeAs-systems are narrow, have a simple shape as in Fe-metal and do not show the presence of satellite structure typical for FeO.

Computational scheme for  
correlated electron materials:

Material specific electronic structure  
(Density functional theory/LDA)

+

Electronic correlations  
(Many-body theory/DMFT)



LDA+DMFT

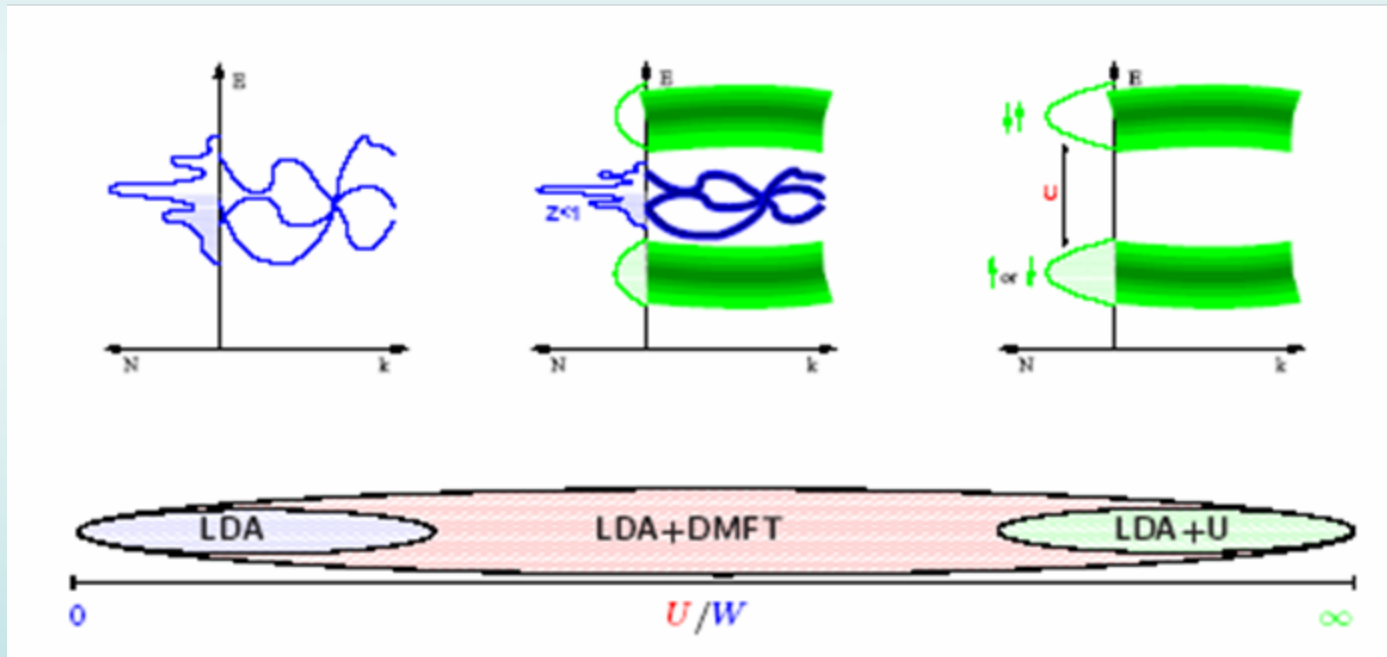
Anisimov, Poteryaev, Korotin, Anokhin, Kotliar (1997);  
Lichtenstein, Katsnelson (1998);  
Augsburg - Ekaterinburg collaboration (2001)

# Computational scheme for correlated electron materials:

Weakly correlated metal ( $U \ll W$ )

Strongly correlated metal ( $U/W \gg 1$ )

Mott insulator  $U \gg W$



K. Held, Adv. Phys. 56, 829 (2007).

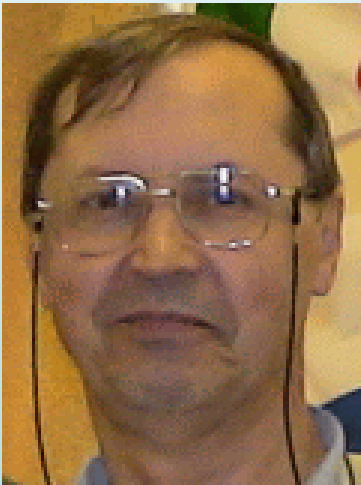
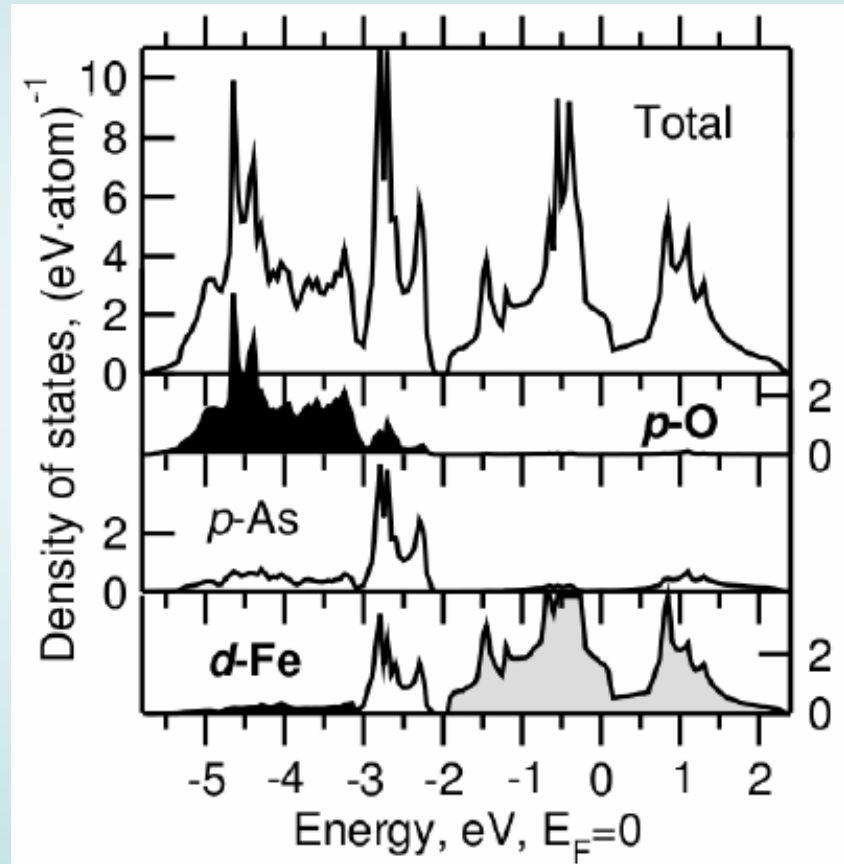
# LDA and LDA+DMFT calculations of LaOFeAs

Total and partial DOS (LDA) of LaOFeAs

LDA:

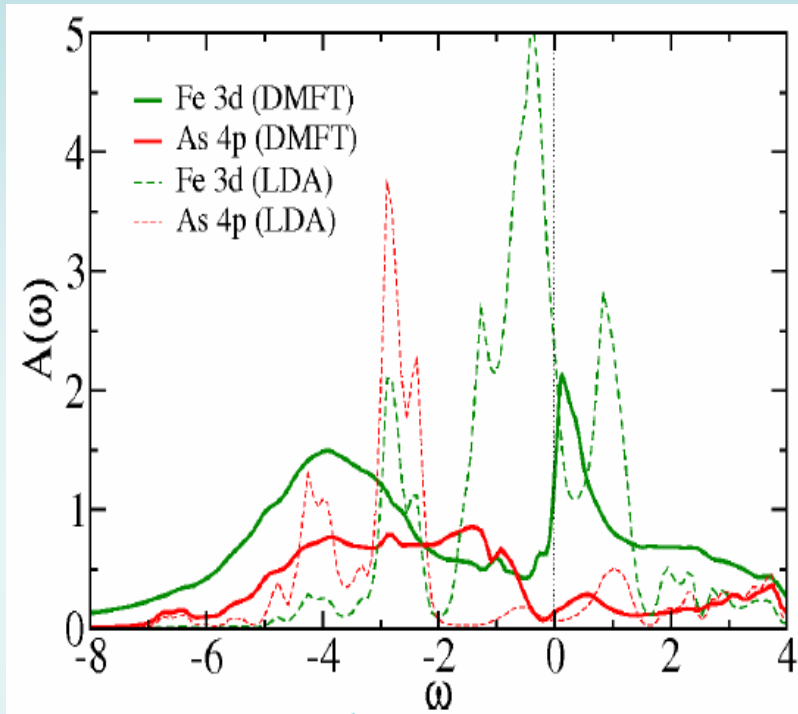
Fe 3d:  $-3 \div +2$  eV

Electronic structure is typical for  
metallic systems



V.I. Anisimov et al., arXiv: 0810.2629  
(2008); Physica C 469, 442 (2009).

# LDA+DMFT for LaOFeAs



$U=4 \text{ eV}, J_H=0.7 \text{ eV};$

Fe 3d-states:  $-8 \text{ eV} \div +4 \text{ eV}$

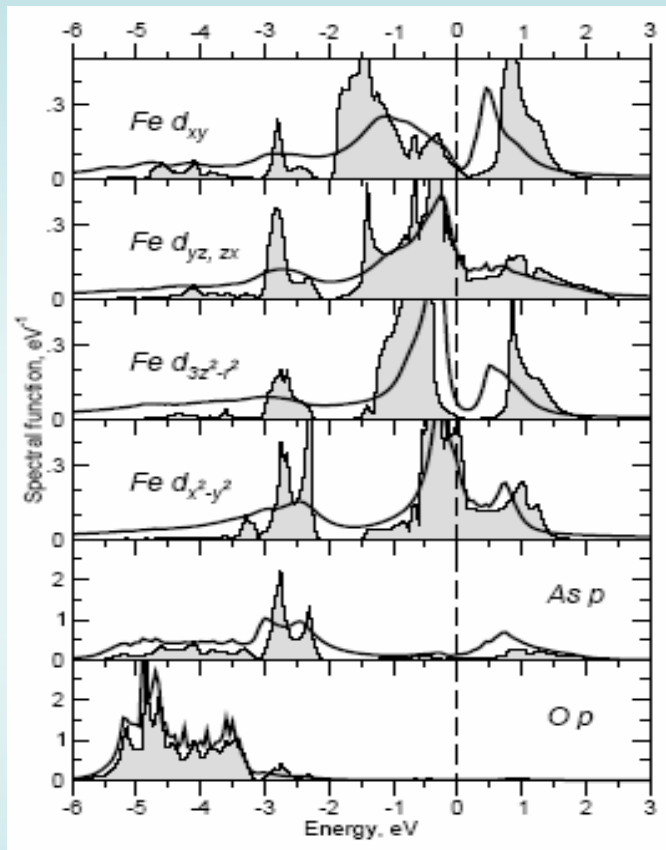
Low Hubbard d-band and quasiparticle peak at  $E_F$  are formed.

The band gap is opened for  $U=4.5 \text{ eV}, J_H=0.7 \text{ eV}$



Conclusion: LaOFeAs is close to M-I transition and belongs to class of strongly correlated systems

# LDA+DMFT for LaOFeAs

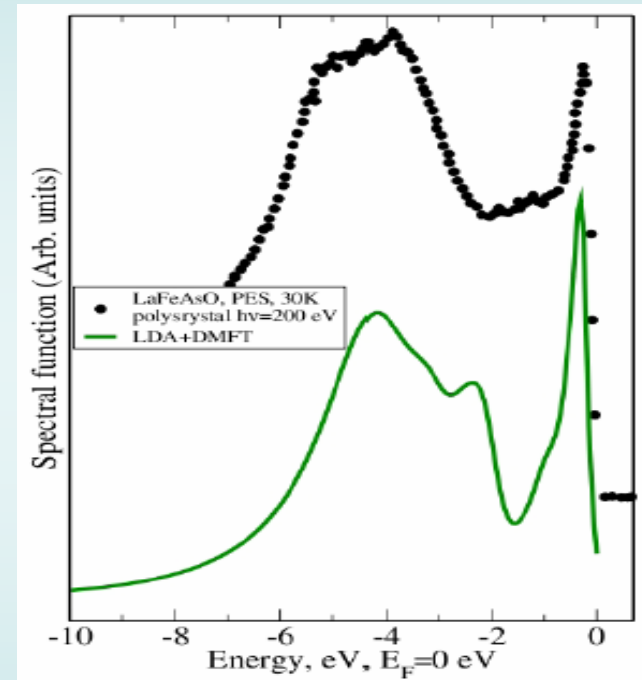
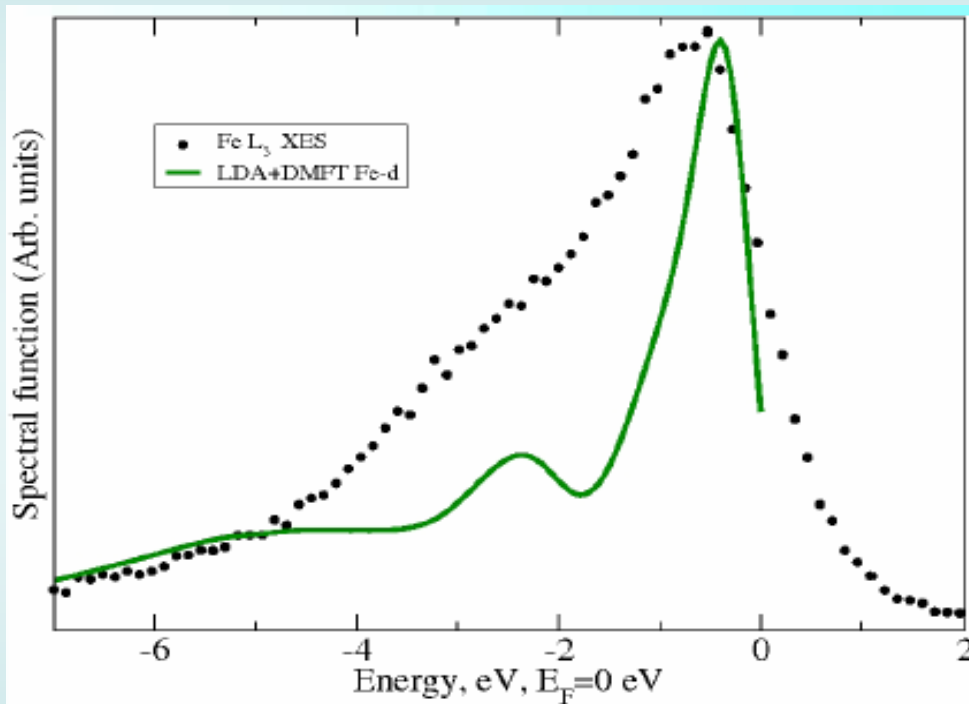


LDA+DMFT calculation is performed in extended basis including not only Fe3d but also As4p and O 2p-states. In this case the value  $U$  is reduced to  $U=3.1$  eV and LDA+DMFT calculation did not show low Hubbard  $d$ -band and quasiparticle peak near  $E_F$ .

Conclusion: LaOFeAs belongs to weakly correlated systems

V.I. Anisimov et al., arXiv: 0810.2629 (2008); Physica C 469, 442 (2009), A. Georges (private communication)

# Comparison of LDA+DMFT and experimental spectra of LaOFeAs



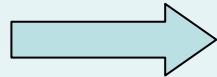
V.I. Anisimov et al., arXiv: 0810.2629 (2008); Physica C 469, 442 (2009)

# FeAs is different from $\text{CuO}_2$

FeAs

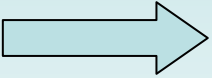
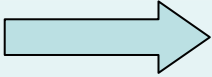


Charge carriers are more itinerant and less localized on atomic sites.



Multiband description is necessary, unlike an effective single band model of cuprates.

# Why the U (local correlations) are different in pnictides and cuprates?

- Cuprates  are very two-dimensional and the low-energy electrons reside in a single band of carriers formed by hybridization of Cu  $3d_{x^2-y^2}$  orbitals with O 2p-electrons.
- Pnictides  all five Fe 3d-orbitals contribute to the electronic structure in the vicinity  $E_F$ . This orbital mixing coupled to Fe 3d-As 4p hybridization strongly reduces the effective U as compared to the cuprates.

M.R. Norman, Physics 1, 21 (2008)

# Summary

Fe RIXS spectra show that Fe 3d-states dominate at the Fermi level for LaOFeAs, CaFe<sub>2</sub>As<sub>2</sub>, LiFeAs and NaFeAs. Therefore the superconductivity of FeAs systems can be described within the minimal model.

LDA-calculations and X-ray spectra show the similar reduction of O 2p-band due to oxygen deficiency and F-doping. This means that carriers in FeAs-reservoir are provided by oxygen vacancies or F 2p-electrons.

Experimental X-ray and photoemission spectra are found to be close to LDA+DMFT calculations which take into account Fe 3d-As 4p hybridization which weakens electron correlations.

# List of publications

1. Yu.A. Izyumov and E.Z. Kurmaev, FeAs systems: a new class of high-temperature superconductors, Review article: Physics-Uspekhi, 51, 1261 (2008).
2. Yu.A. Izyumov and E.Z. Kurmaev, High- $T_c$  superconductors on the base of FeAs-compounds, Book: 2009 (in press).
2. E.Z. Kurmaev et al., X-ray spectra and electronic structure of iron arsenide superconductors ( $RFeAsO_{1-x}F_x$ ,  $R=La,Sm$ ), PRB, 78, 220503 (2008); arXiv: 0805.0668 (7 May, 2008).
3. V.I. Anisimov, E.Z. Kurmaev and Yu.A. Izyumov, Strength of correlations in pnictides and its assesment by theoretical calculations and spectroscopy experiments, Physics C 469, 442 (2009).
4. E.Z. Kurmaev et al., Electronic structure of  $CaFe_2As_2$ : contribution of itinerant Fe 3d-states to the Fermi level, arXiv: 0902.1141 (2009).
5. E.Z. Kurmaev et al., The electronic structure of LiFeAs and NaFeAs probed by resonant inelastic X-ray scattering, arXiv: 0903.4901 (2009).
6. E.Z. Kurmaev et al., X-ray emission spectra, electronic structure and structural models of  $FeSe_x$  (to be published).
7. E.Z. Kurmaev et al., Electronic structure of LaONiP superconductor: X-ray spectra and LDA calculations (submitted to J. Phys.: Condensed Matter).

**Thank you very much!**