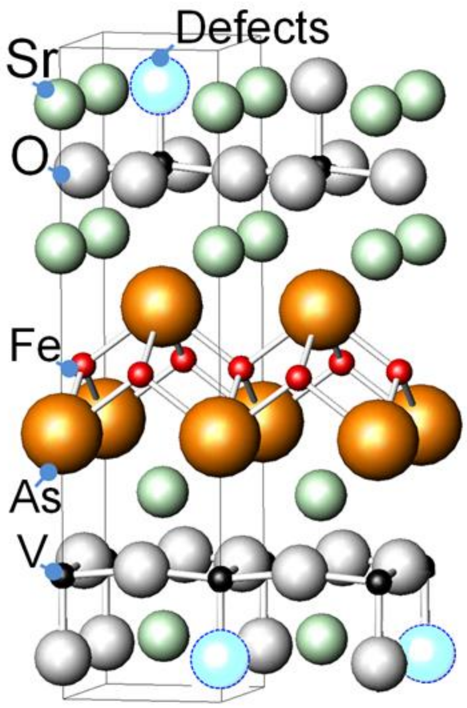
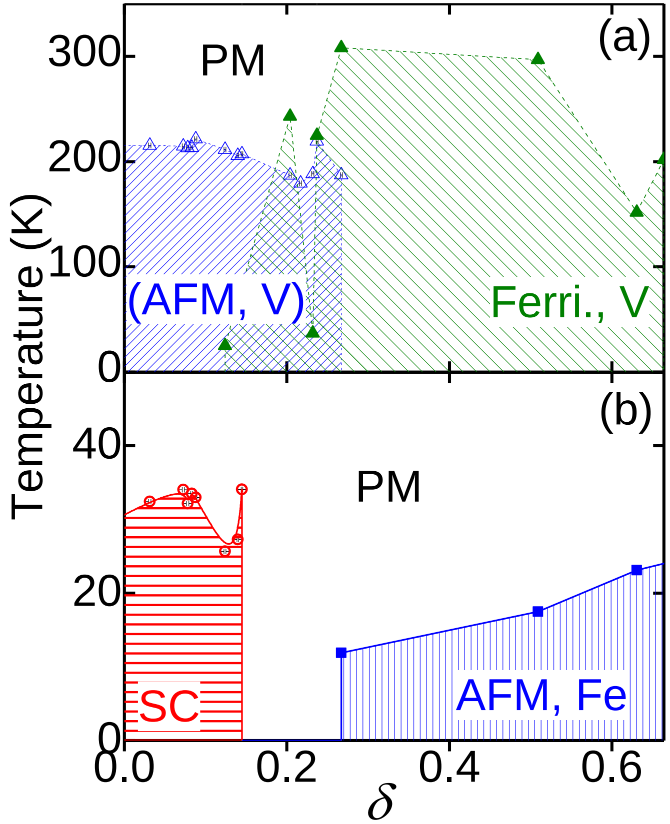
エネルギー材料としてのペロブスカイト関連混合アニオン化合物
Electronic Functionality of Superconducting Mixed Anion Layered Compounds (MALCs)



$Sr_2VFeAsO_{3-\delta}$



Tojo et al (2018)
URL: https://arxiv.org/abs/1802.03907

Yoichi Kamihara, Keio Univ., Japan

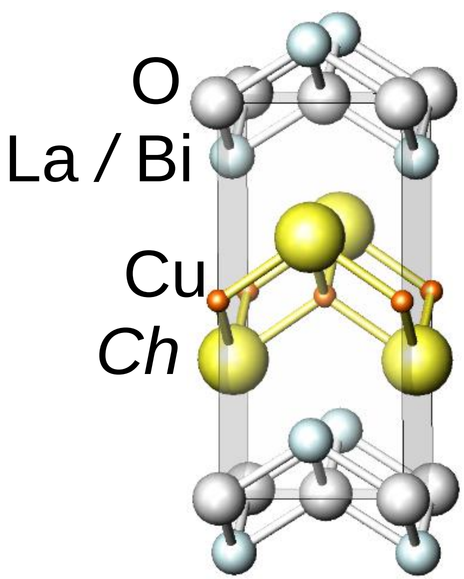
Outline

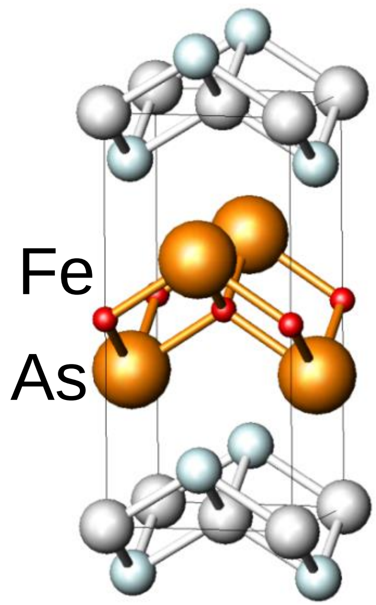
- Background, 10-15 min.
  - Mixed Anion Layered Compounds (MALCs)
    - Short history
    - Representative MALC, 1111
  - Iron-based superconductors
  - Recent reports for applications; Superconducting wires

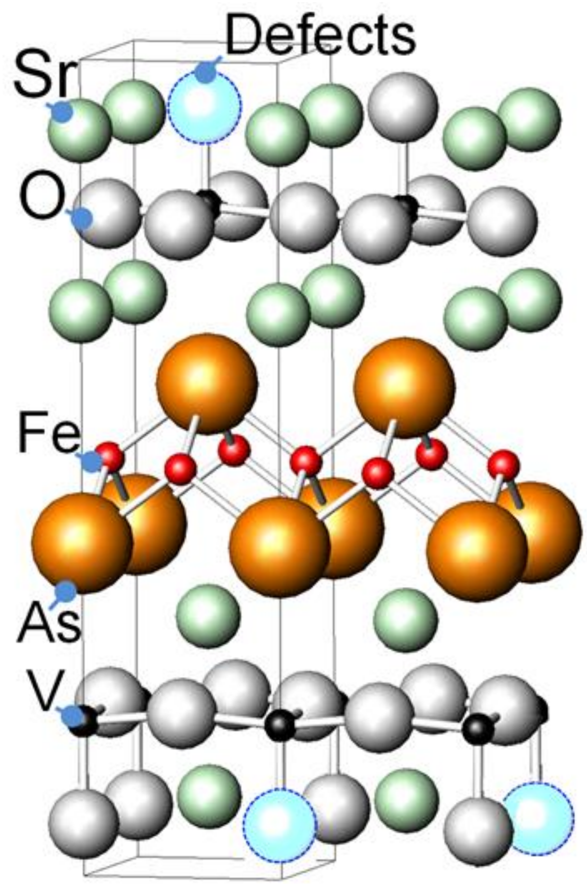
    Comments on
    - Self introduction (YK)
    - Gibbs' phase rule
    - Goodenough's Electronic and magnetic phase diagram
- Magnetic and electronic phase diagram for $Sr_2VFeAsO_{3-\delta}$
  - Experimental
  - Results
- Supplementary, our motivation
  - Update of J. B. Goodenough's scheme

Background: Mixed anion layered compounds (MALCs)

- LaCu*Ch*O (*Ch* = S, Se)
  - Transparent semiconductors , Hiramatsu, JACS (2010) & Goto, APL (2014)
- BiCuSeO
  - Thermoelectric material, ZT~0.76@900 deg.C, Zhao, APL (2010)
- Iron-based superconductors
  - $LaFeAsO_{1-x}F_x$, $Sr_2VFeAsO_{3-\delta}$, Zhu PRB (2009)





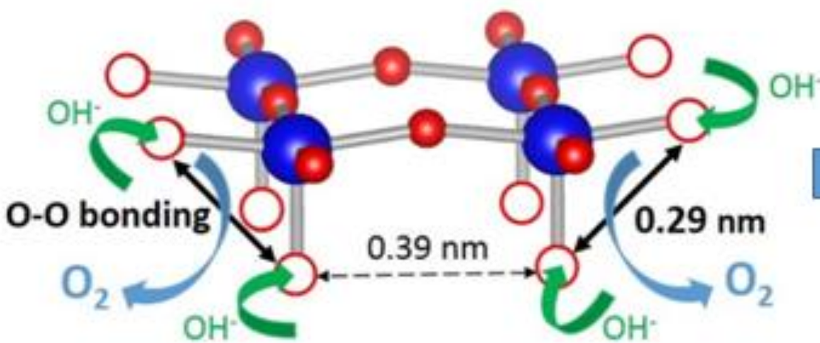


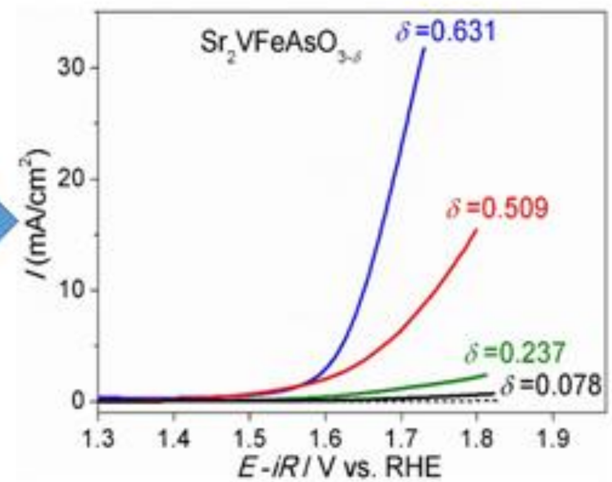
Supplementary, our motivation
Update of J. B. Goodenough's scheme

IUMRS-ICEM 2018

Proposal of New Electrochemistry in Mixed Anion Compounds

We-B2-1





Shigeto Hirai[1], Kazuki Morita[2], Taizo Shibuya[3], Yujiro Tojo[2], Tomoya Ohno[1], Kenji Yasuoka[2], Shunsuke Yagi[4], Yoichi Kamihara[2] and Takeshi Matsuda[1]

[1]Kitami Institute of Technology, [2]Keio University, [3]NEC Corporation, [4]The University of Tokyo

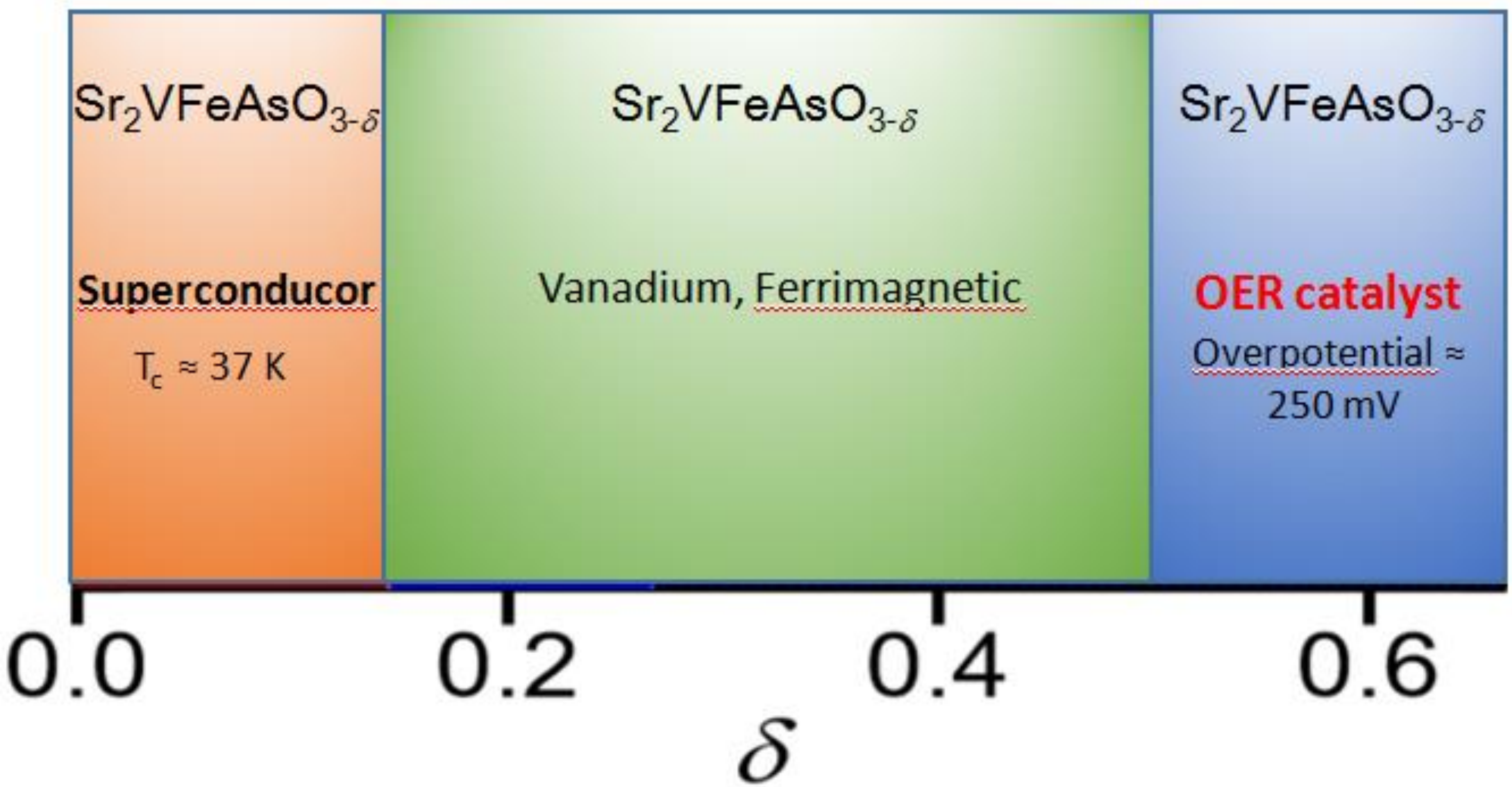
Keio University

Kitami Institute of Technology
105 Koen-cho kitami, Hokkaido 090-8507, JAPAN

東京大学

Supplementary, our motivation

Updated phase diagram of $Sr_2VFeAsO_{3-\delta}$



Bifunctional material that adopts **OER catalyst** or **superconductor**

We-B2-1

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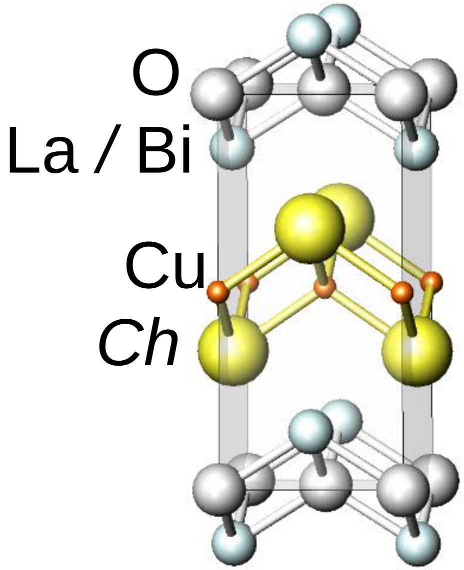
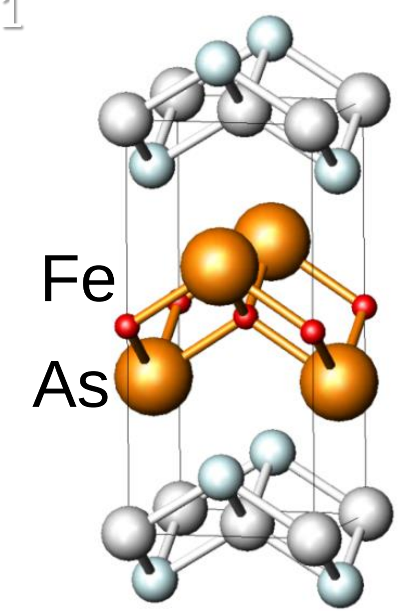
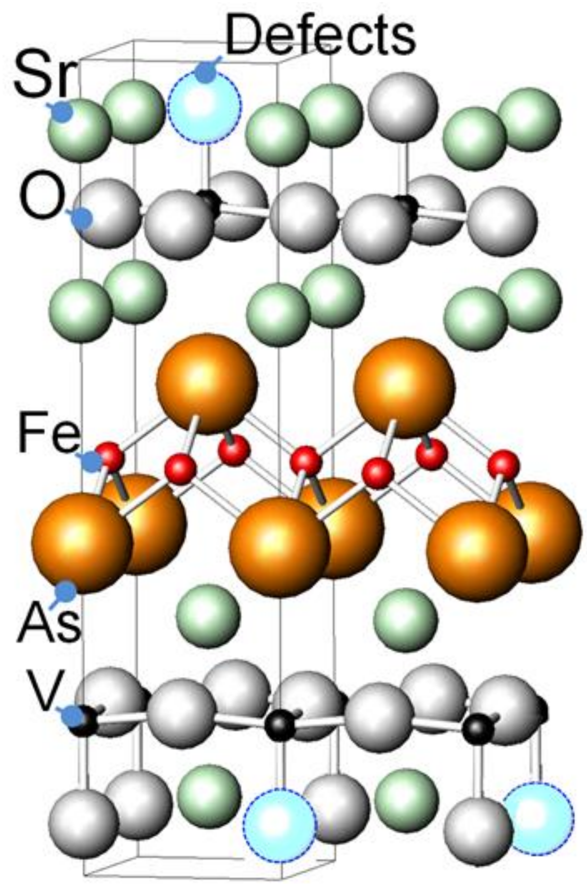
- Oxygen evolution reaction
  - Hirai, JMCA (2018), We-B2-1







Background: short (private) history on MALCs

Transparent oxides as active electronic materials and their appliations, edited by H. Hosono and M. Hirano (CMC publishing, Tokyo, 2006), p. 71-93, Layered compounds (in Japanese),
ISBN：978-4-88231-656-5

第3章 Layered compounds

Hidenori Hiramatsu
Yoichi Kamihara

1 はじめに

半導体超格子は，目的機能を実現するように，物質の化学組成と厚さを綿密に計算し，それらを原子層オーダーで正確に積層することによって，人工的に作製されている。この人工超格子は，分子線エピタキシー（MBE）や有機金属気相堆積法（MOCVD）などの薄膜成長技術の発展と2次元電子構造の理解が進展したことにより実現されたと言って過言ではない。これらの成果に基づき，一原子層からの厚さ制御，界面急峻性，大面積均一性が実現され，さらに，シングルまたはダブルヘテロ構造の特徴を生かし，量子井戸レーザーや高電子移動度トランジスタなどの光・電子デバイスが実用化している。一方，一分子層に相当する層厚と化学組成が自然に制御された層状化合物が数多く存在し，それら化合物の中には，特異な性質を示すものがある。よく知られ

Background: short (private) history on MALCs

電子デバイスが実用化している。一方，一分子層に相当する層厚と化学組成が自然に制御された層状化合物が数多く存在し，それら化合物の中には，特異な性質を示すものがある。よく知られている例としては，YBCO などの Cu 系高温超伝導体がある。

我々はそういった層状化合物群の中から，特に，アニオンを2種類以上含有する「混合アニオン層状化合物」に注目した。図1(a)に層状オキシカルコゲナイド *Ln*CuO*Ch* の結晶構造を示す[1~4]。例えば，LaCuOS では，酸化ランタン層と硫化銅層が交互に積層した層状構造で構成さ

We have focused on a Mixed Anion Layered Compounds (MALCs), which contains two or more kinds of anions at crystallographic sites in a unit cell.

Transparent oxides as active electronic materials and their appliations, edited by H. Hosono and M. Hirano (CMC publishing, Tokyo, 2006), p. 71-93, Layered compounds (in Japanese),
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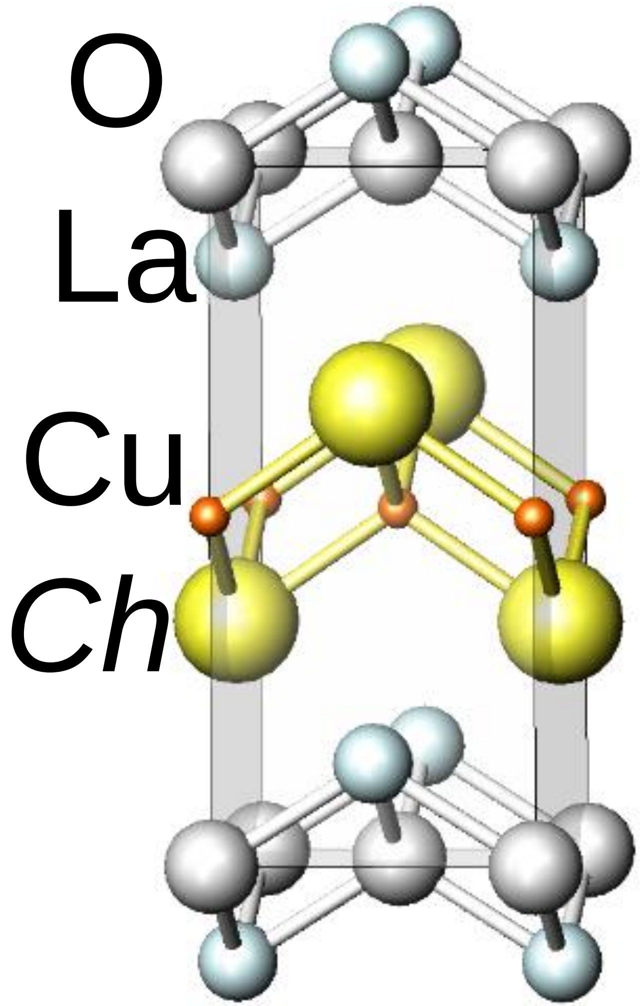
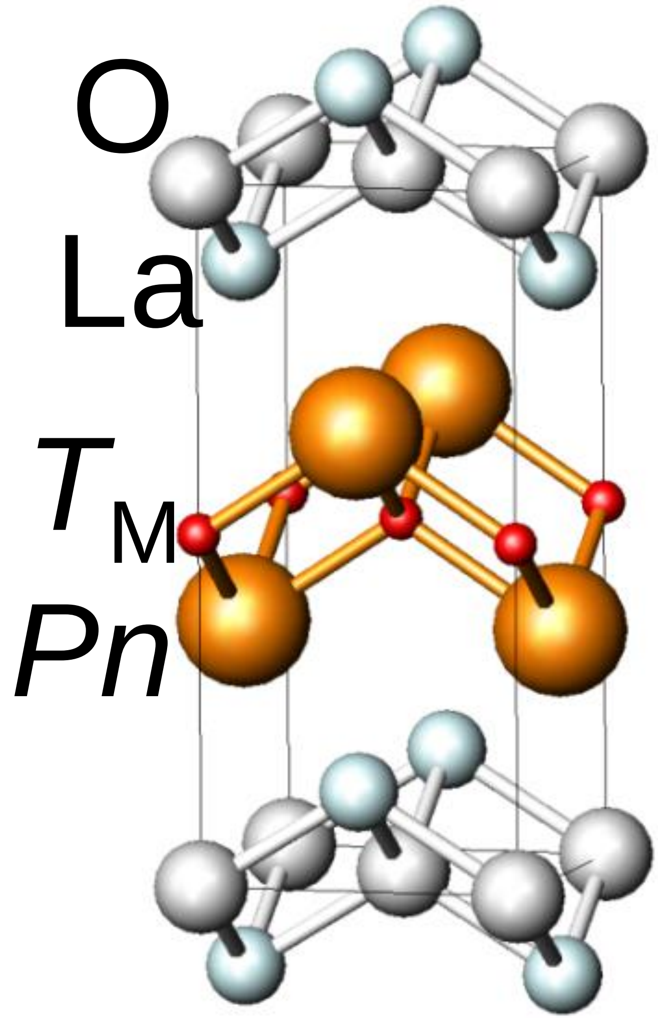
e.g. Electronic properties of representative MALCs

LaCu*Ch*O & LaT_M*Pn*O (T_M: Transition metal) 1111 system



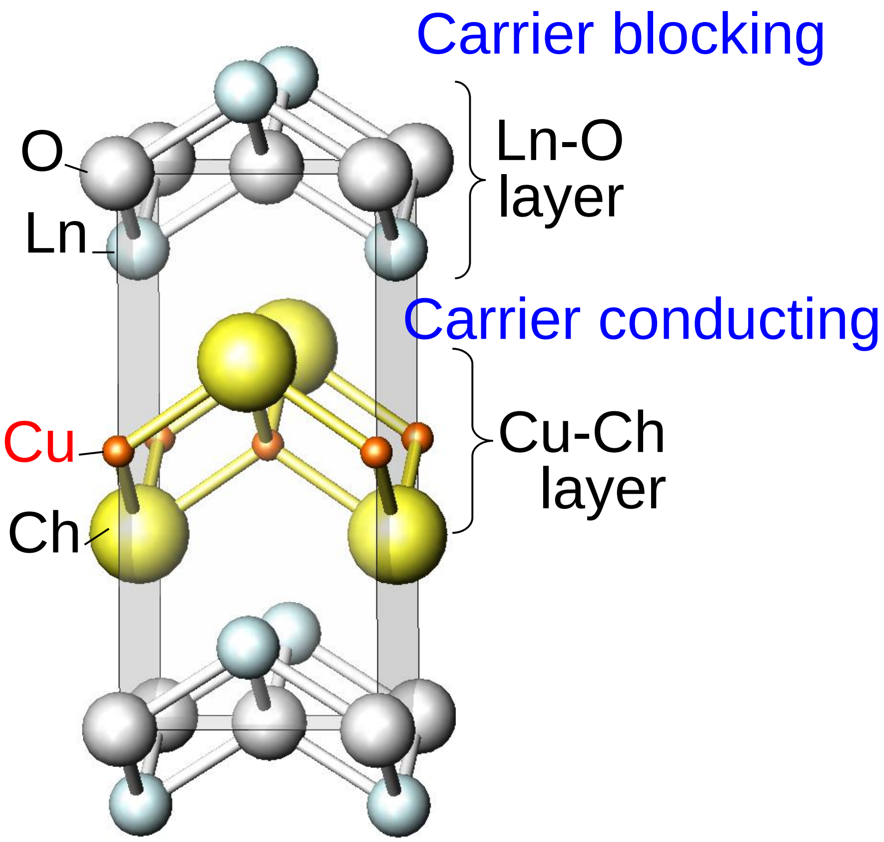
Transparent semiconductors

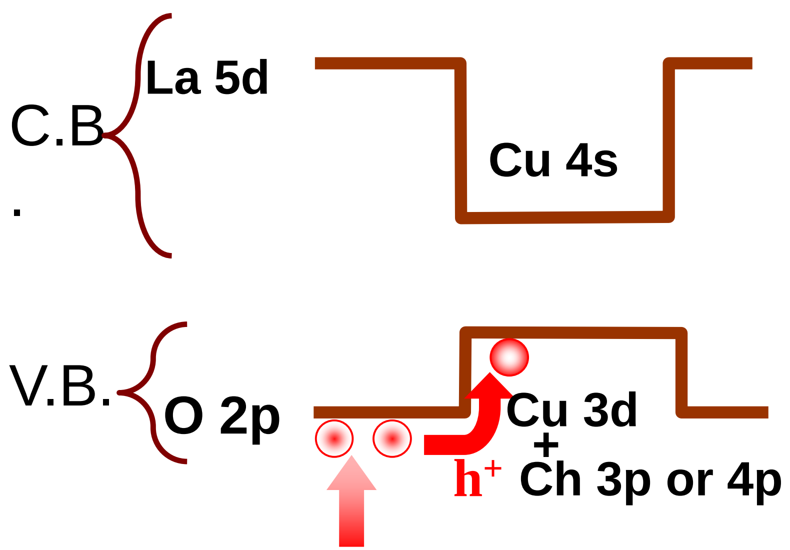
Eg ~ 3 eV



Unknown In 2005

e.g. Electronic properties of LaCu*Ch*O





Cu vacancy (~1 at%)

M. Palazzi et al, Acad. Sci., Paris, C. R. (1981).
K. Ueda et al, Appl. Phys. Lett. (2000).
H. Hiramatsu, et al, J. Am. Chem. Soc. 132, 15060 (2010).
Y. Goto, et al, Appl. Phys. Lett. 105, 022104 (2014).

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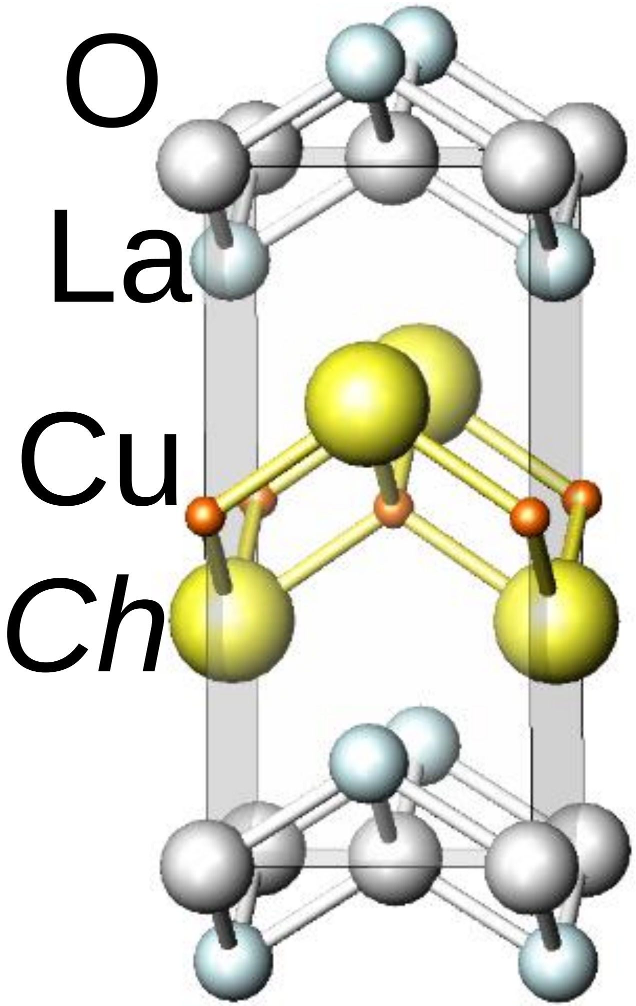
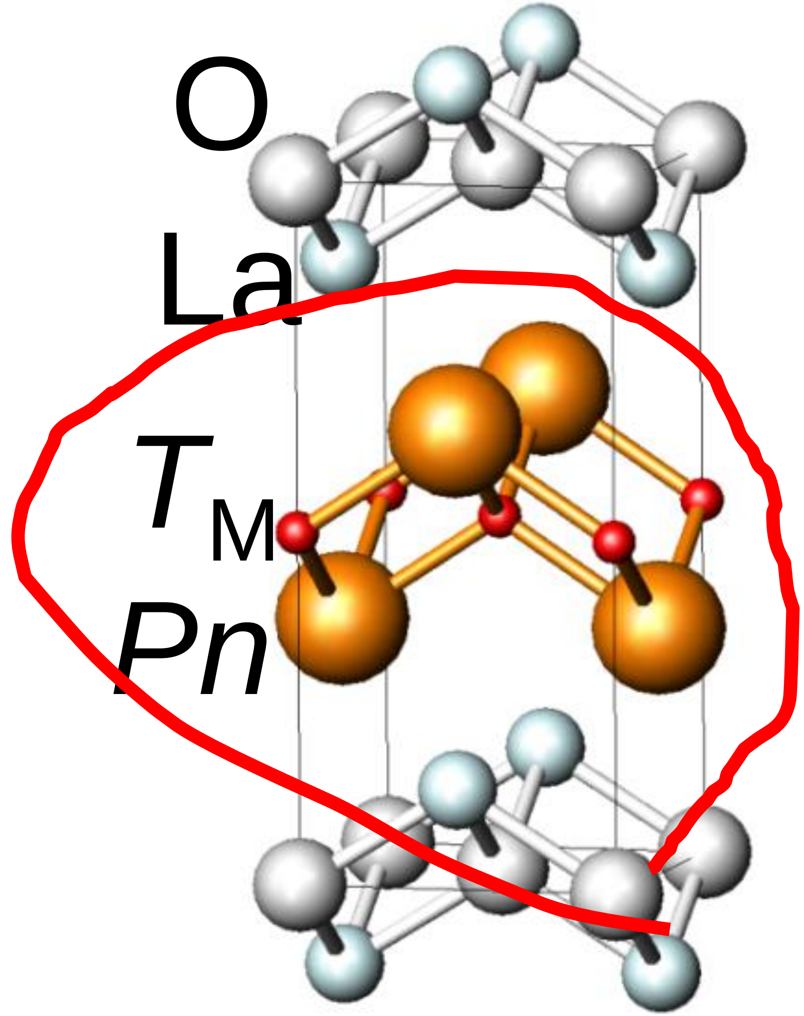
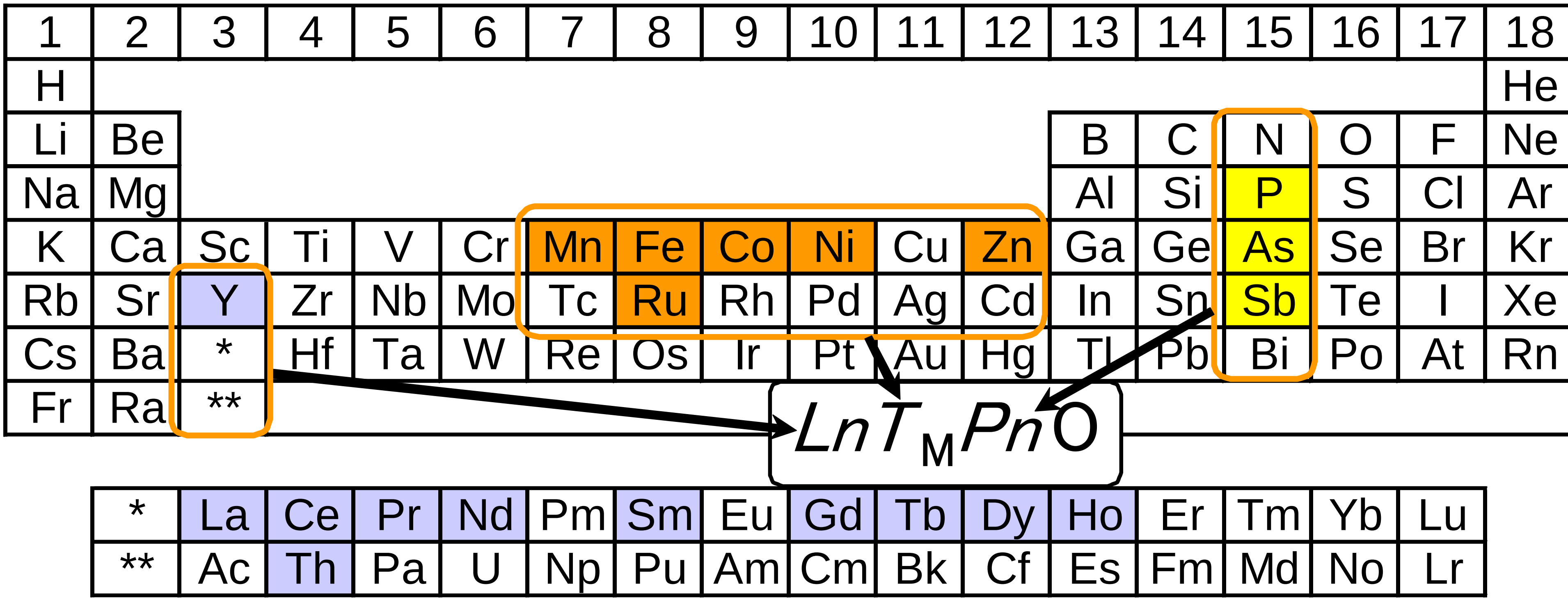




Transparent semiconductors
Eg ~ 3 eV

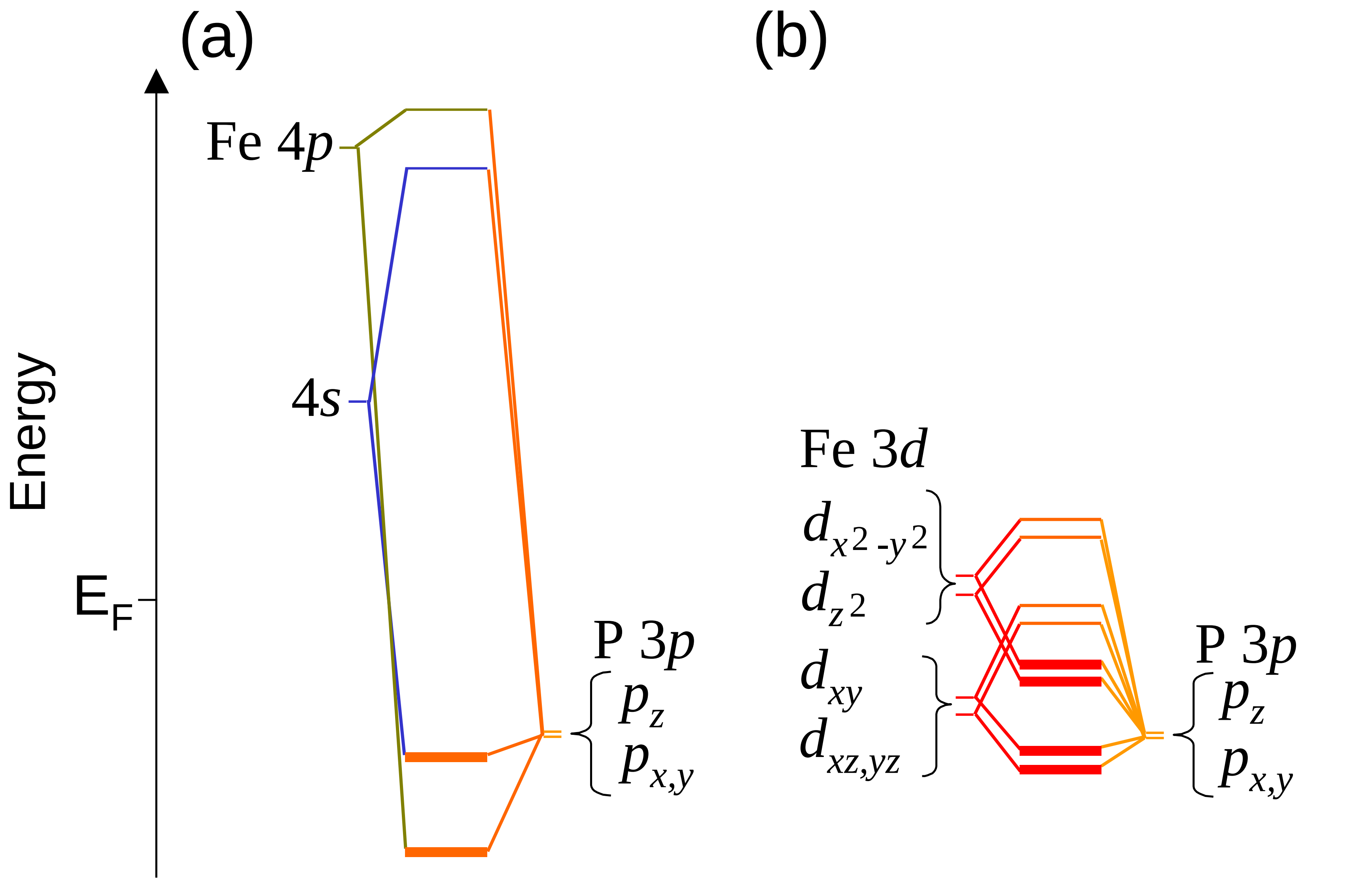
Unknown In 2005

An mixed anion compound; La$T_M Pn$O

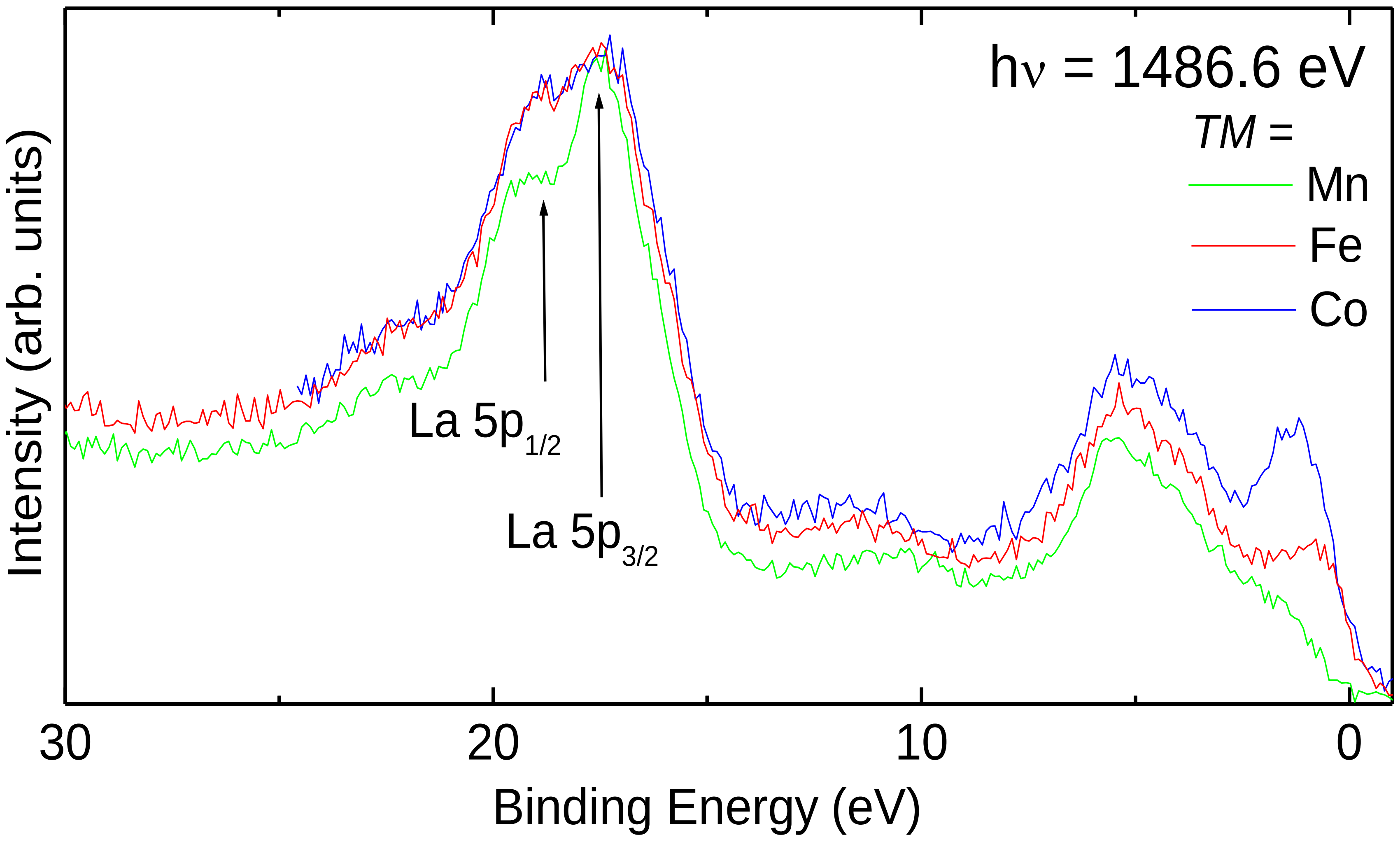


Many electronic properties
(Functionalities) appears in MALCs

e.g. Simplified energy diagram of Fe-P in LaT_MPO



e.g. Valence band of LaT_MPO



Electronic and magnetic properties of La$T_M$$Pn$O

T_M	Mn		Fe		Co		Ni		(Cu)	Zn	
Pn	P	As	P	As	P	As	P	As		P	As
Elect. Prop.	Mott Insulator		SC	Metal	Metal		SC			Insulator	
Magnetism	AFM		SC	AFM (F) SC	FM		SC			-	
Eg	~ 1 eV		-		-		-			~ 1.5 eV	
T_N, T_c (FM)	> 400 K		-	150 K	43 K	66 K	-	-		-	
T_c (SC)	-		4 K	(F) ~26 K	-	-	3 K	2.4 K		-	
Ref.	1		-	-	2		3	4,5		6,7	6,7

1. H. Yanagi, et al J. Applied Phys. (2009)
2. H. Yanagi, et al, Phys. Rev. B (2008)
3. T. Watanabe, et al, Inorganic Chem. (2008)
4. T. Watanabe, et al, J. Sol. State Chem.(2008)
5. L. Fang, et al, Phys. Rev. B (2008)
6. K. Kayanuma, et al, Thin Solid Films (2008)
7. Y. Takano, et al, J. Alloy Compd. (2008)

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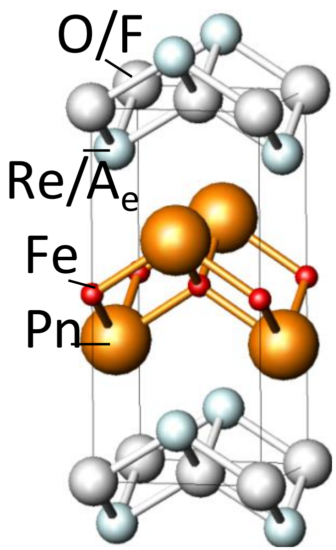
Iron (Fe) is

Pure Fe

Ferromagnetic in pure metal

Ferri. magnetc in oxides

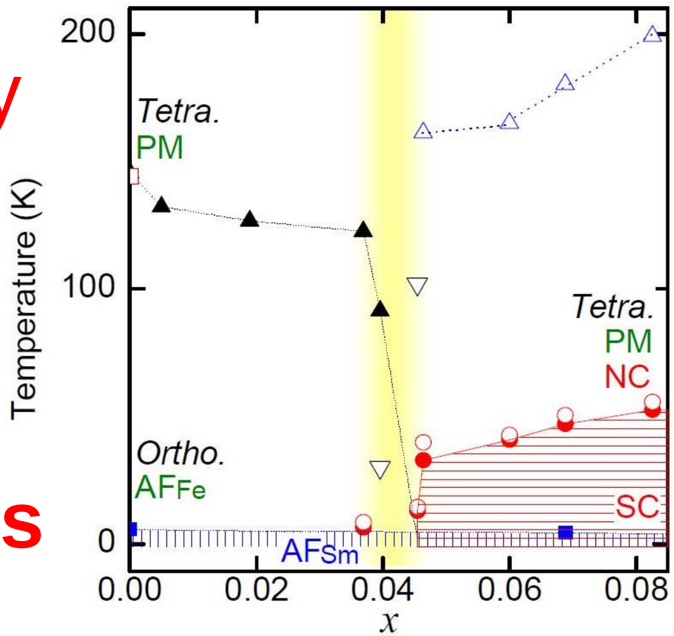
Magnetite, Fe_3O_4



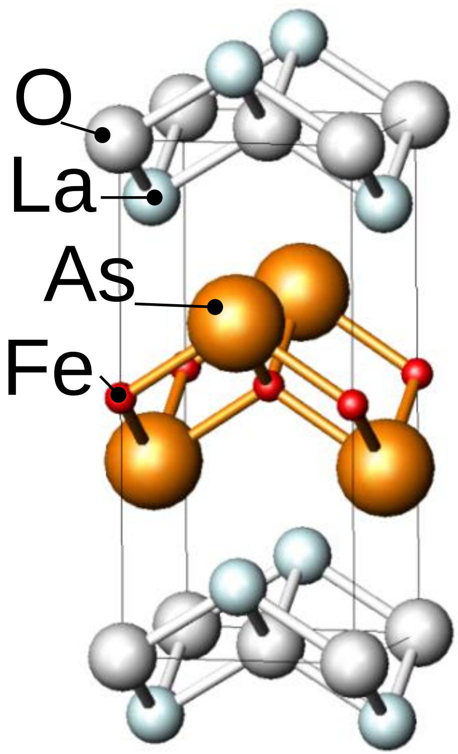
LaFePnO$_{1-x}$F$_x$ (Pn = P, As)

Superconductivity In most MALCs

Iron-based superconductors



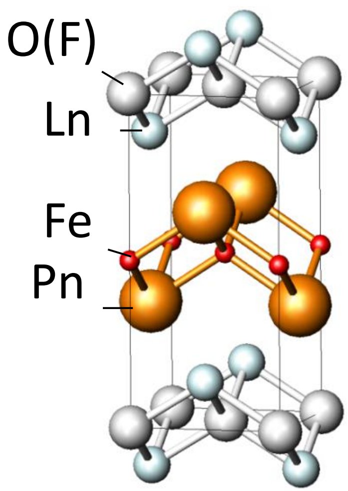
e.g. LaFeAsO, a mother compound for superconductors



Chemical formula	T_c onset (K)
$LaFeAsO_{1-x}F_x$	29
$LaFeAsO_{1-x}$	28
LaFeAs(O, H)	38.5
$LaFe_{1-x}Co_xAsO$	14
$LaFe_{1-x}Ni_xAsO$	7
$LaFeAs_{1-x}P_xO$	12
LaFeAsO (HP)	21
$LaFeAsO_{0.89}F_{0.11}$ (HP)	43

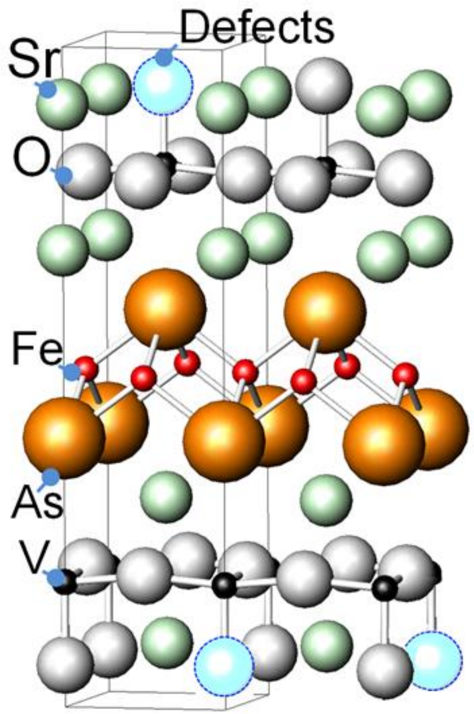
Review: Kamihara, Hosono, Denshi-Zairyo (2010) Japanese
Ref. K. Miyazawa, et al, Appl. Phys. Lett. 96, 072514 (2010).

Iron-based superconductors in MALCs



1111

Highest T_c ~58 K



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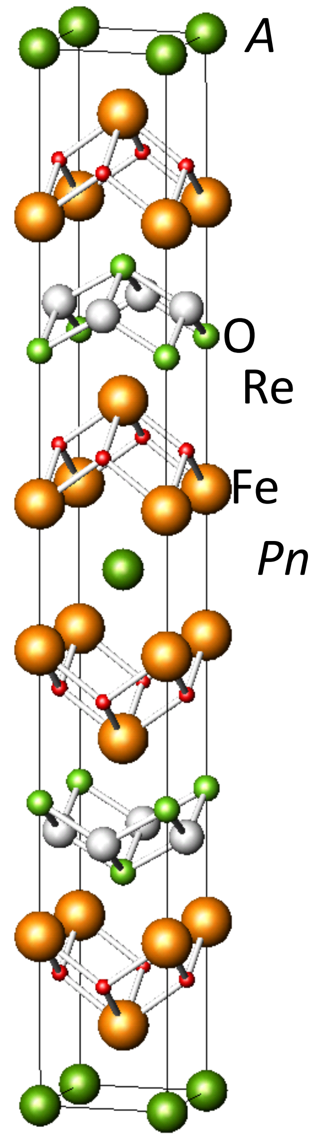

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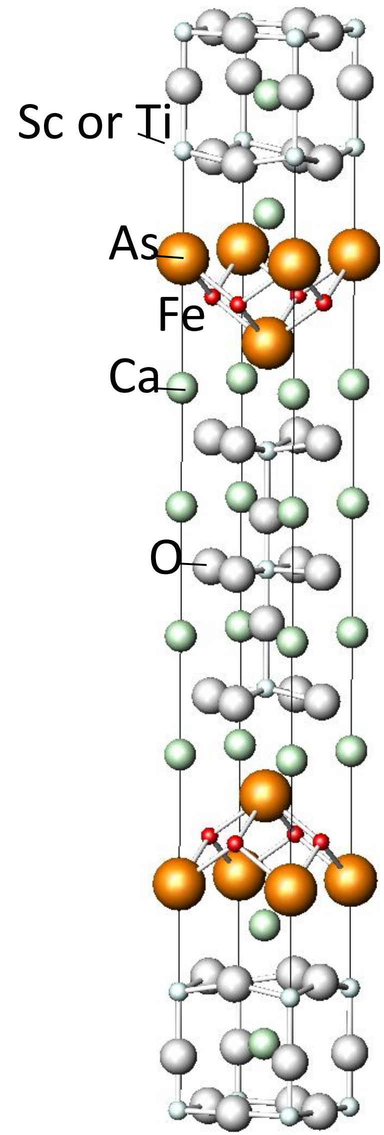

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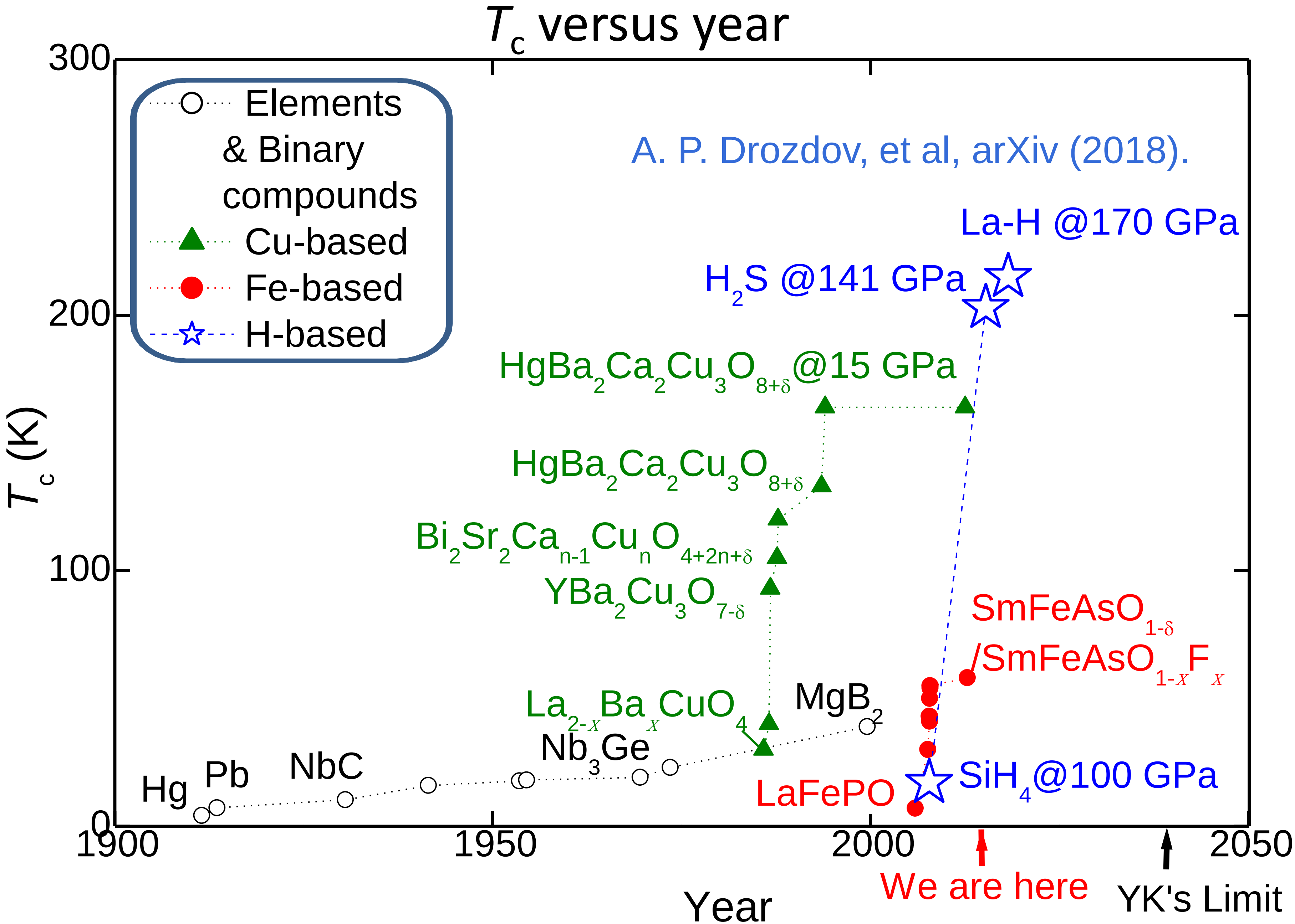


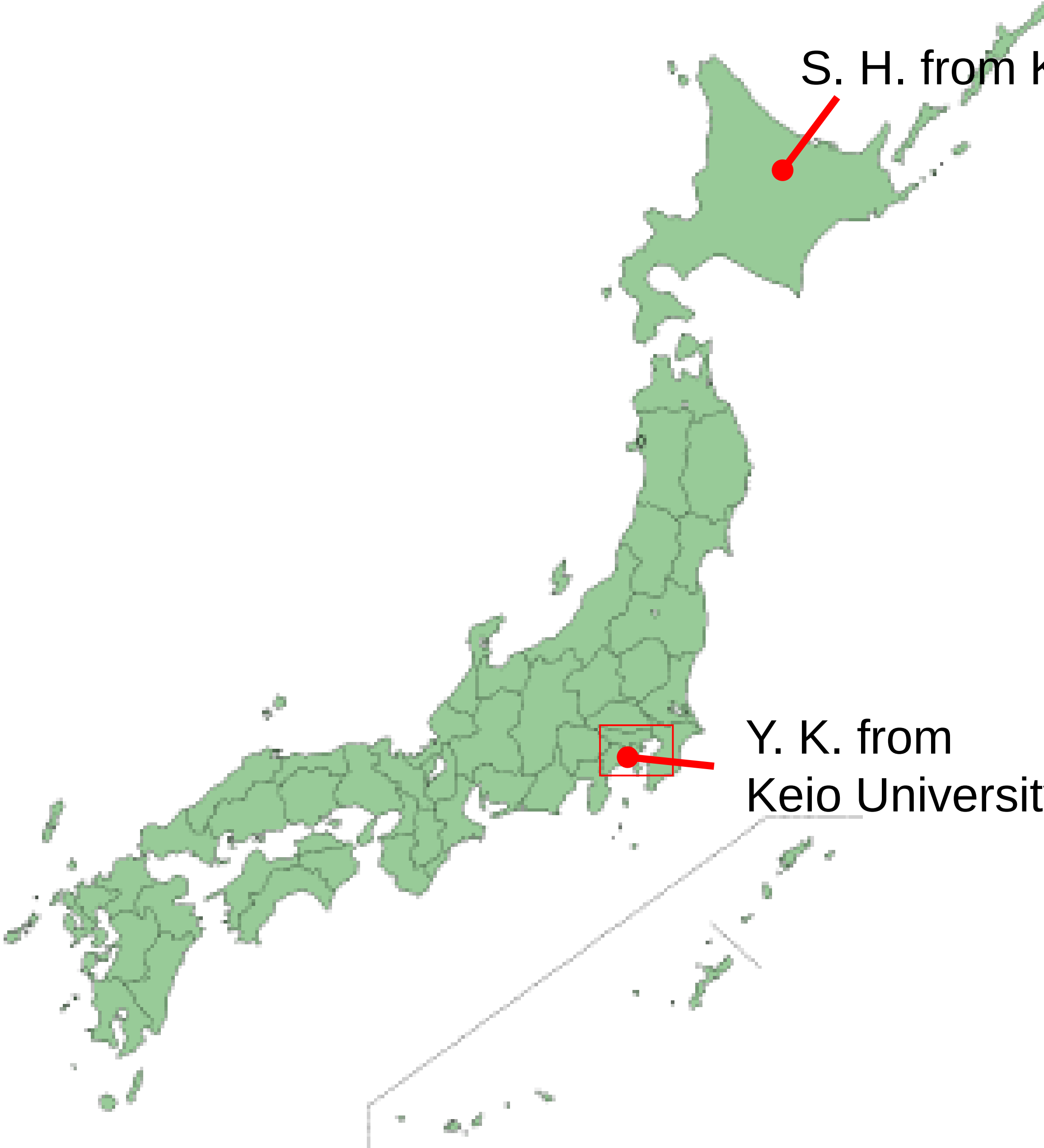
Iron-based superconductors shows “Second highest T_c under ambient Pressure”

Recommended Reviews & Books on iron-based superconductors

- G. R. Stewart, Rev. Mod. Phys. 83, 1589-1652 (2011). Superconductivity in iron compounds
- J. Shimoyama, Supercond. Sci. Technol. 27, 044002_1-7 (2014). Potentials of iron-based superconductors for practical future materials
- K. Tanabe, and H. Hosono, Jpn. J. Appl. Phys. 51, 010005_1-17 (2012). Frontiers of research on iron-based superconductors toward their application
- M. Fujioka, Wiley encyclopedia of electronics Engineering 1-30, 2014. Iron-based superconductors, SmFeAsO1-xFx
- H. Hosono, K. Kuroki, Physica C 514, 399-422 (2015). Iron-Based Superconductors: current status of materials and pairing mechanism
- M. Fujioka, Wiley encyclopedia of electronics Engineering 1-30, 2014. Iron-based superconductors, SmFeAsO1-xFx
- Y. Kamihara, H. Hosono, “Superconductivity in Iron Oxypnictide induced by F-doping” in “Photonic and Electronic Properties of Fluoride Materials, 1st Edition” Chapter 19 (2016).
- Y. Kamihara, TEION KOGAKU (J. Cryo. Super. Soc. Jpn.) 52, 383-388 (2017). A private story, discovery of iron-based high Tc superconductors II (in Japanese)
- Y. Kamihara, TEION KOGAKU (J. Cryo. Super. Soc. Jpn.) 52, 415-421 (2017). Electronic properties of 1111 superconducting materials and superconducting wires made from 1111 via powder-in-tube process (in Japanese)

Self-Introduction

Introduction for our university



S. H. from Kitami Institute of Technology

Y. K. from
Keio University

Keio University

CALAMVS GLADIO FORTIOR
1858

https://zh.wikipedia.org/wiki/神原陽一

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自由的百科全書

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神原陽一 [编辑]

维基百科，自由的百科全书

神原陽一（日语：神原 陽一 / かみはら よういち *Kambara Yoichi* ?），日本物理學家、材料科學家。工學博士。現任慶應義塾大學副教授。

目录 [隐藏]

1 生平與成就
2 經歷
3 所屬學會
4 受賞
5 參見
6 參考資料
7 外部連結

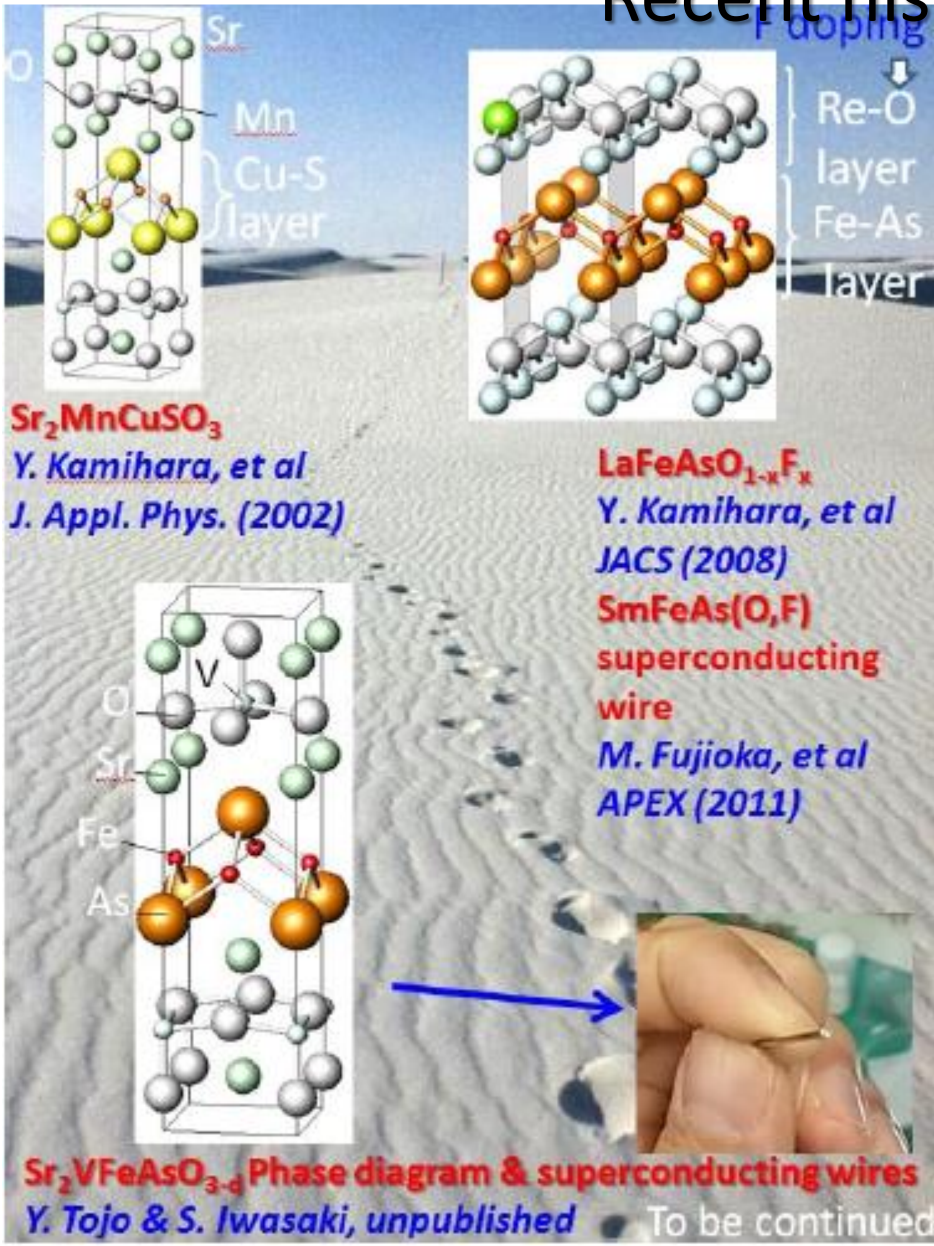
生平與成就 [编辑]

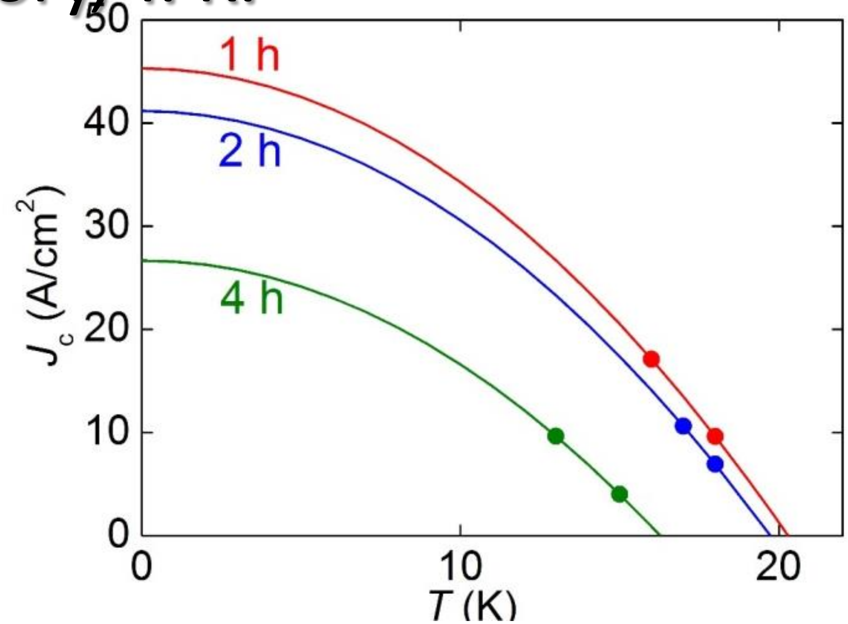
神原陽一出生於日本東京都町田市，慶應義塾大學畢業，工學博士（慶應義塾大學）。

2008年在細野秀雄的團隊中，參與發現鐵基超導體LaFeAs(O,F)[1]。神原陽一參與執筆的研究經過湯森路透統計，是世界引用次數最多的鐵基超導體論文。細野秀雄與神原發現「超導材料」的論文，曾於2008年被《科学》評選為「世界十大科技進展」之一，與山中伸彌（2012年諾貝爾生理學或醫學獎）的「基於iPS細胞的細胞再編成」並列。

Highly cited paper in 2008.

Recent history, Y. K.





S. Iwasaki, M. Matoba, and Y. Kamihara, Mater. Sci. Tech. Jpn. 55, 77-82 (2018). Superconducting critical current densities for $Sr_2VFeAsO_{3-\delta}$ wires fabricated by ex-situ powder-in-tube process

Japanese Unexamined Patent Application Publication No. 2018-055975

Y. Kamihara, J. Cryo. Super. Soc. Jpn. 52, 383-388 (2017). (in Japanese)

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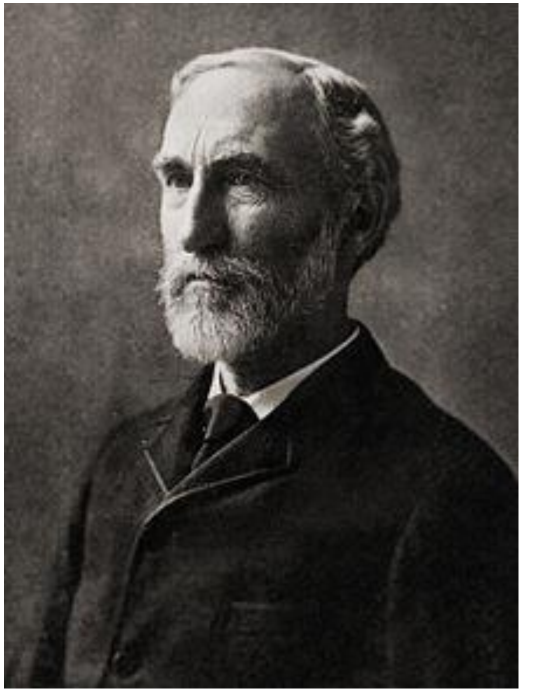
Gibbs' Phase rule

- is essential to verify a chemical state and phase diagram, and an electronic & an magnetic functionality.



$$F = C - P + 2$$

Degrees of Freedom (F)

Number of Components (C)

Number of Phases (P)

Goodenough's Electronic and magnetic phase diagram

F = C – P + 2

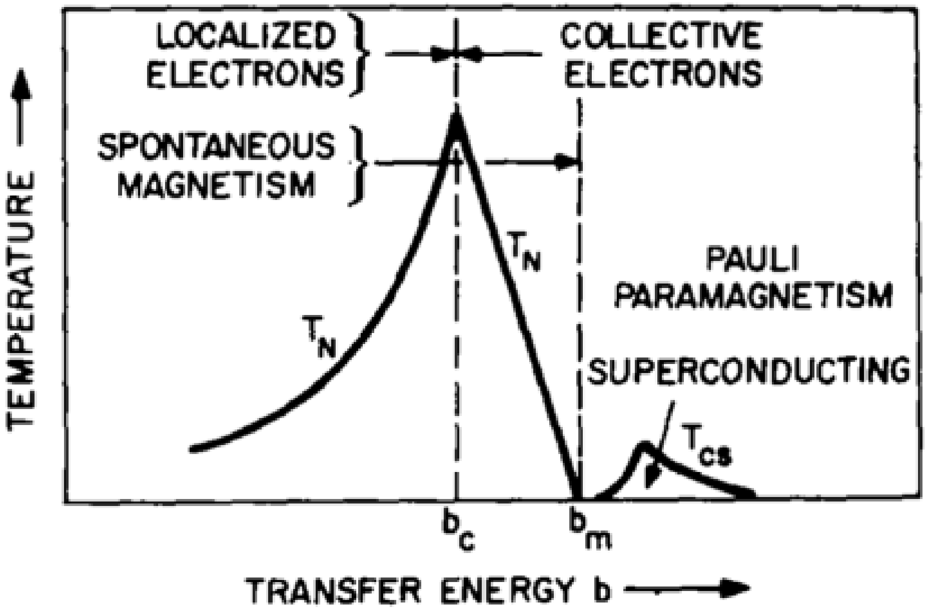
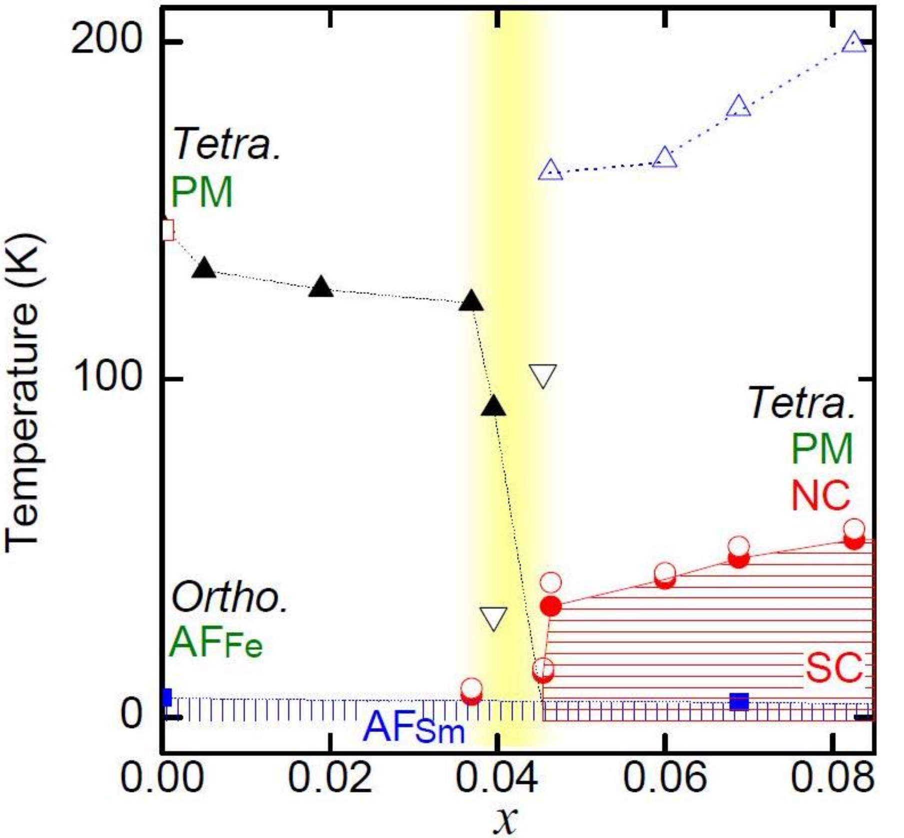


Fig. 8. Schematic, electronic *T*-*b* diagram for one electron per interacting *d* orbital.

J. B. Goodenough (1969).
"Descriptions of outer *d* electrons"



e.g. $SmFeAsO_{1-x}F_x$
Y. Kamihara (2010).

3d transition metal based superconductors obey the Goodenough's phase diagram

Outline

- Background, 10-15 min.
  - Mixed Anion Layered Compounds (MALCs)
    - Short history
    - Representative MALC, 1111
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  - Recent reports for applications; Superconducting wires

    Comments on
    - Self introduction (YK)
    - Gibbs' phase rule
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- Magnetic and electronic phase diagram for $Sr_2VFeAsO_{3-\delta}$
  - Experimental
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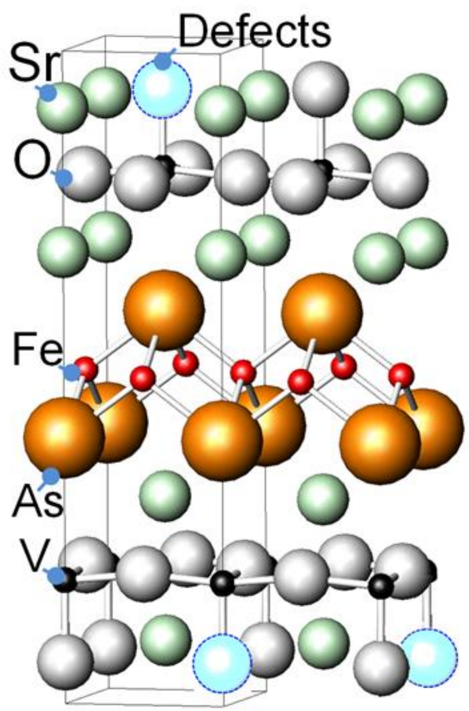
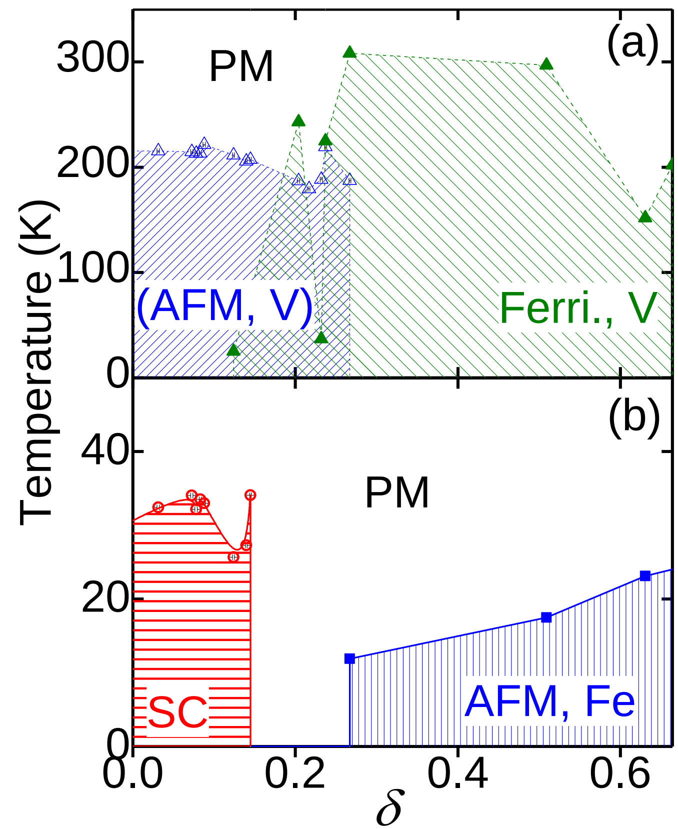
- Supplementary, our motivation
  - Update J. B. Goodenough's scheme

Magnetic and electronic phase diagram for $Sr_2VFeAsO_{3-\delta}$



$Sr_2VFeAsO_{3-\delta}$



Tojo et al (2018)
URL: https://arxiv.org/abs/1802.03907

Yoichi Kamihara, Yujio Tojo, Manami Nakanishi, Suguru Iwasaki, Ryosuke Sakagami, Michitaro Yamaguchi, and Shigeto Hirai

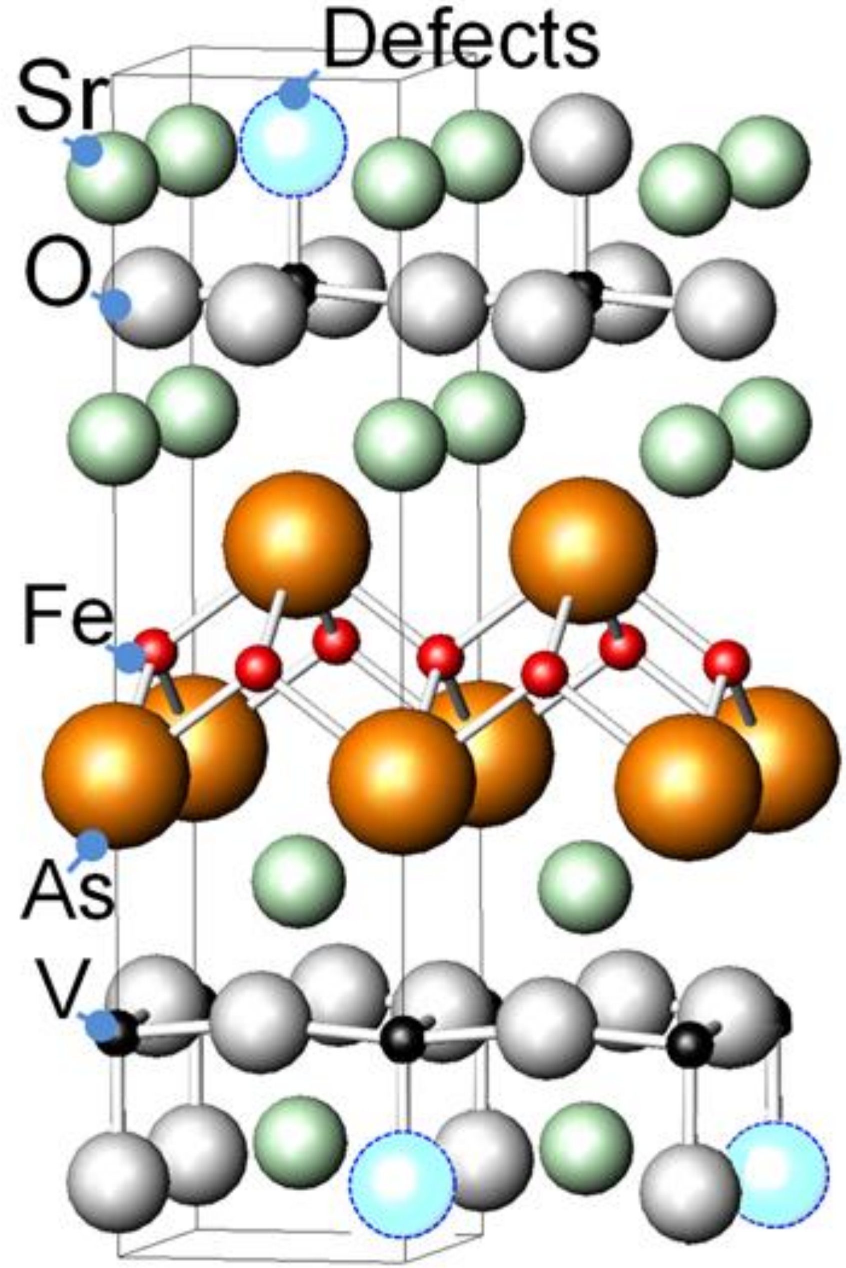
Keio Univ. & Kitami Inst. of Tech., Japan

$Sr_2VFeAsO_{3-\delta}$

To make Magnetic and electronic phase diagram

We have to verify

- Oxygen vacancy (δ)
- Two magnetic 3d transition metal ions in a unit cell
- Three electronic phase
  - Normal conducting
  - Superconducting
- Three magnetic phases for V & Fe.
  - Paramagnetic phase
  - Antiferromagnetic phase
  - Ferrimagnetic phase
  - Theoretical analysis using DFT



Acknowledgment

- Keio University-G; Synthesis, transport measurement, DFT
  Taizo Shibuya, Tetsuro Nakamura, Koichiro Shoji,
  Hirotaka Fujioka, Masanori Matoba
- Tokyo Institute of Technology-G; XRF, Specific heat
  Shintaro Yasui, Mitsuru Itoh, Soshi Iimura,
  Hidenori Hiramatsu, Hideo Hosono
- Stanford University-G; Synchrotron XRD
  Wendy Mao
- Kyoto University-G; Mössbauer spectroscopy
  Shinji Kitao, Makoto Seto

Tojo et al, arXiv (2018)
URL: https://arxiv.org/abs/1802.03907

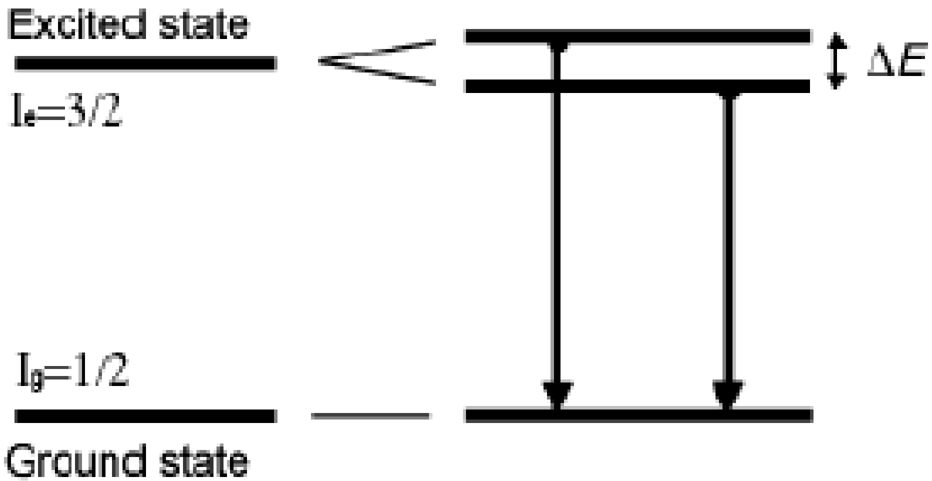
Experimental

- Samples preparation & characterization
  - Synthesis by solid state reactions
  - X-ray diffraction (XRD), Rigaku Rint2500, Cu-Kα
    - ✓Lattice constants
  - X-ray Fluorescence
    - ✓Atomic valence
    - ✓Chemical composition analysis

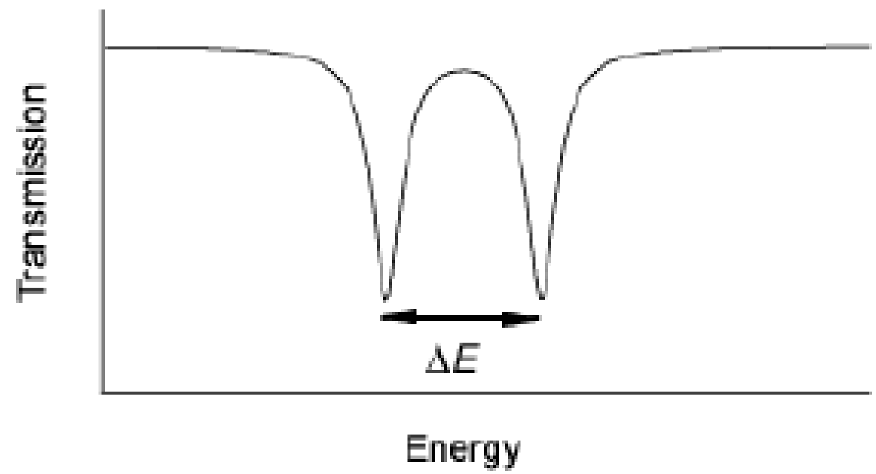
  (Lattice constants, atomic valence, chemical composition analysis:) To quantify δ

  - Heat capacity & Synchrotron XRD @ low temperatures
    - ✓Possible magnetic phase transitions
- DC 4 proved resistivity measurement
- Magnetic moment measured by SQUID magnetometer
- ^{57}Fe Mössbauer spectroscopy

Experimental: ^{57}Fe Mössbauer spectroscopy **using ^{57}Co source (hν = 14.4 keV)**



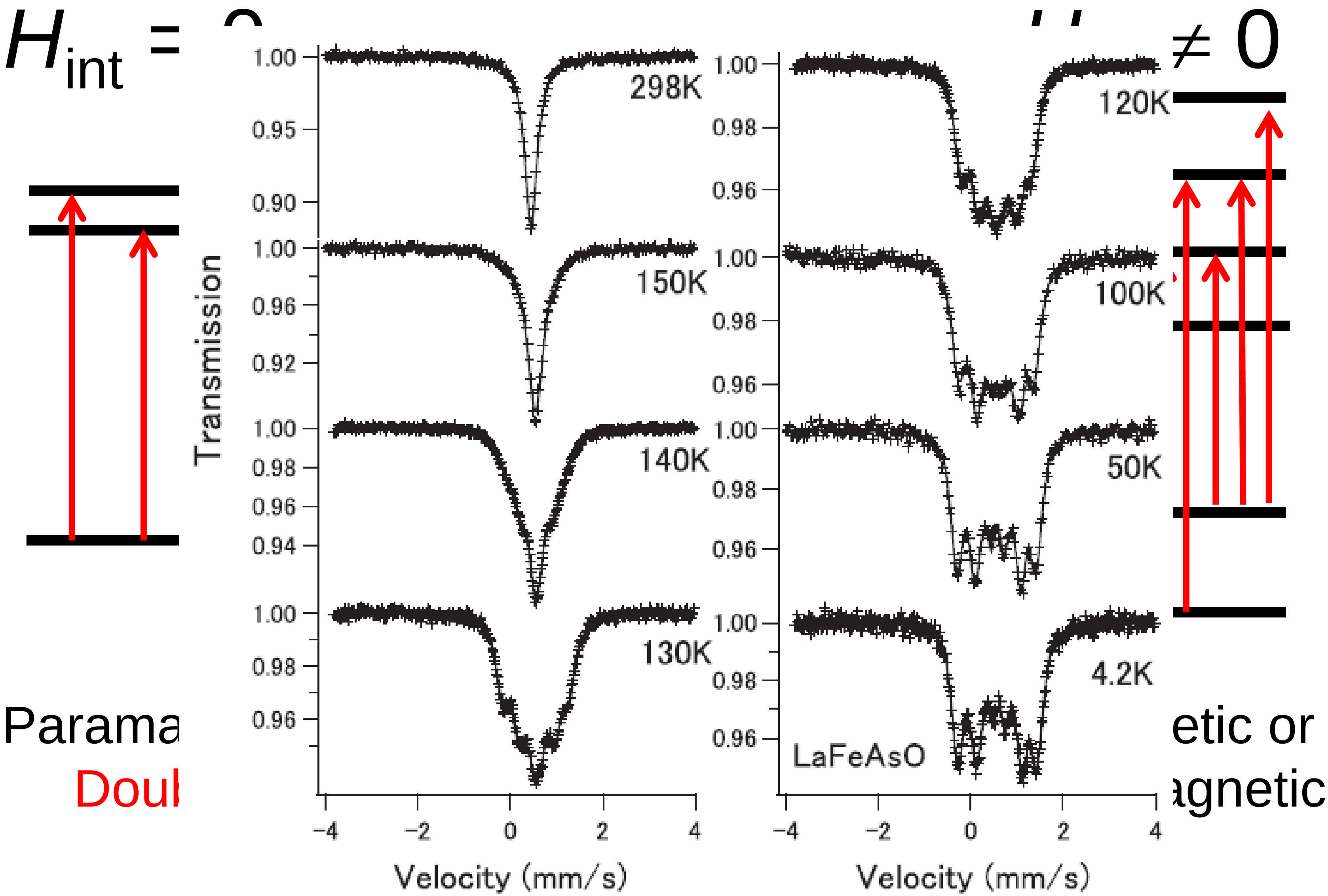
Nuclear level splitting



Mössbauer spectrum

Nuclear level splitting, ^{57}Fe Mössbauer spectroscopy using ^{57}Co source ($h\nu$ = 14.4 keV)

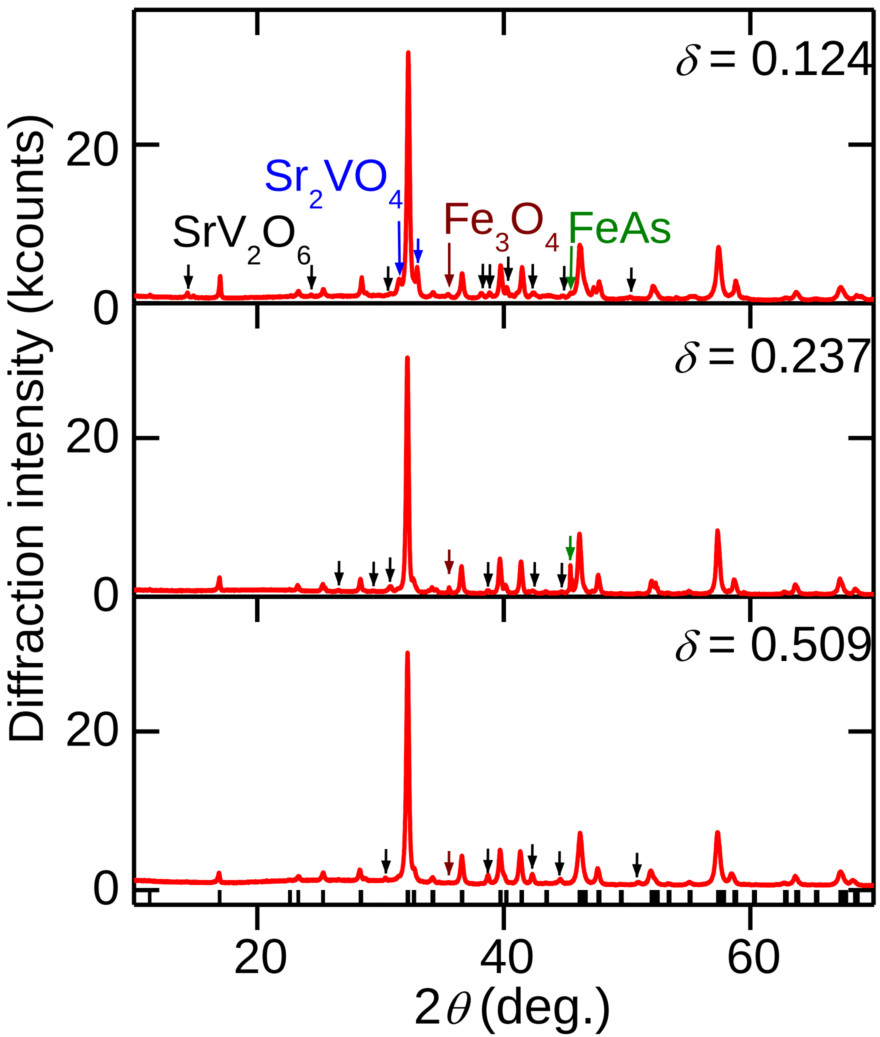
H_{int} = 0 $\neq 0$

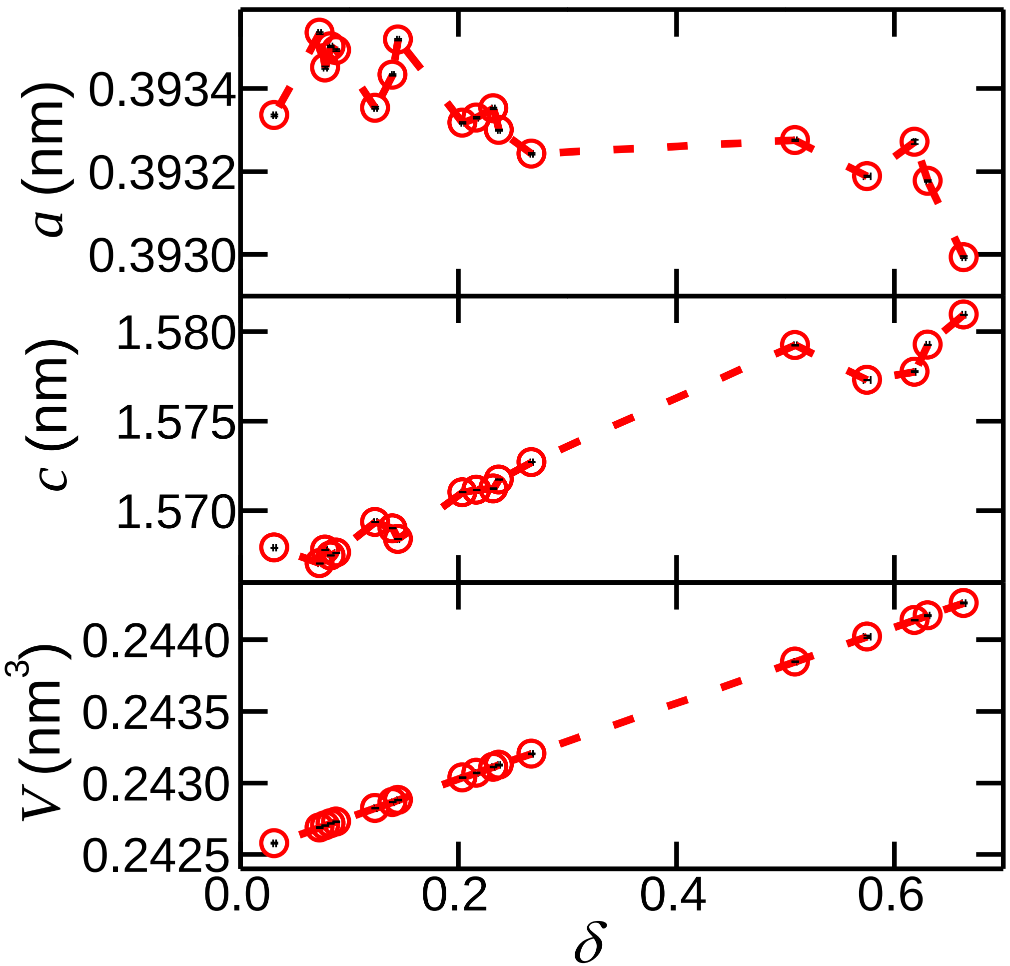


Parama... etic or

Doubl... agnetic

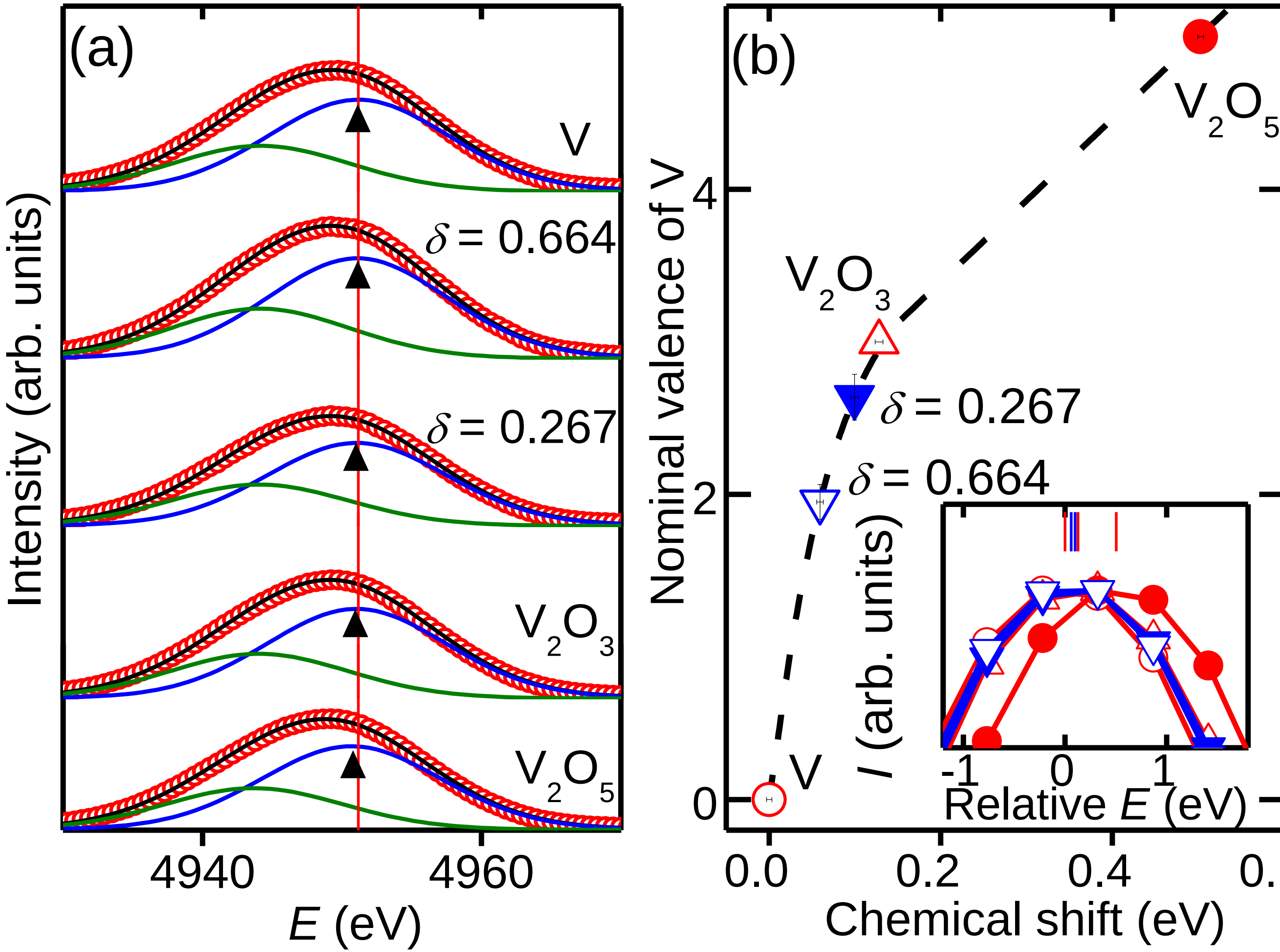
Results: XRD patterns & Lattice constants





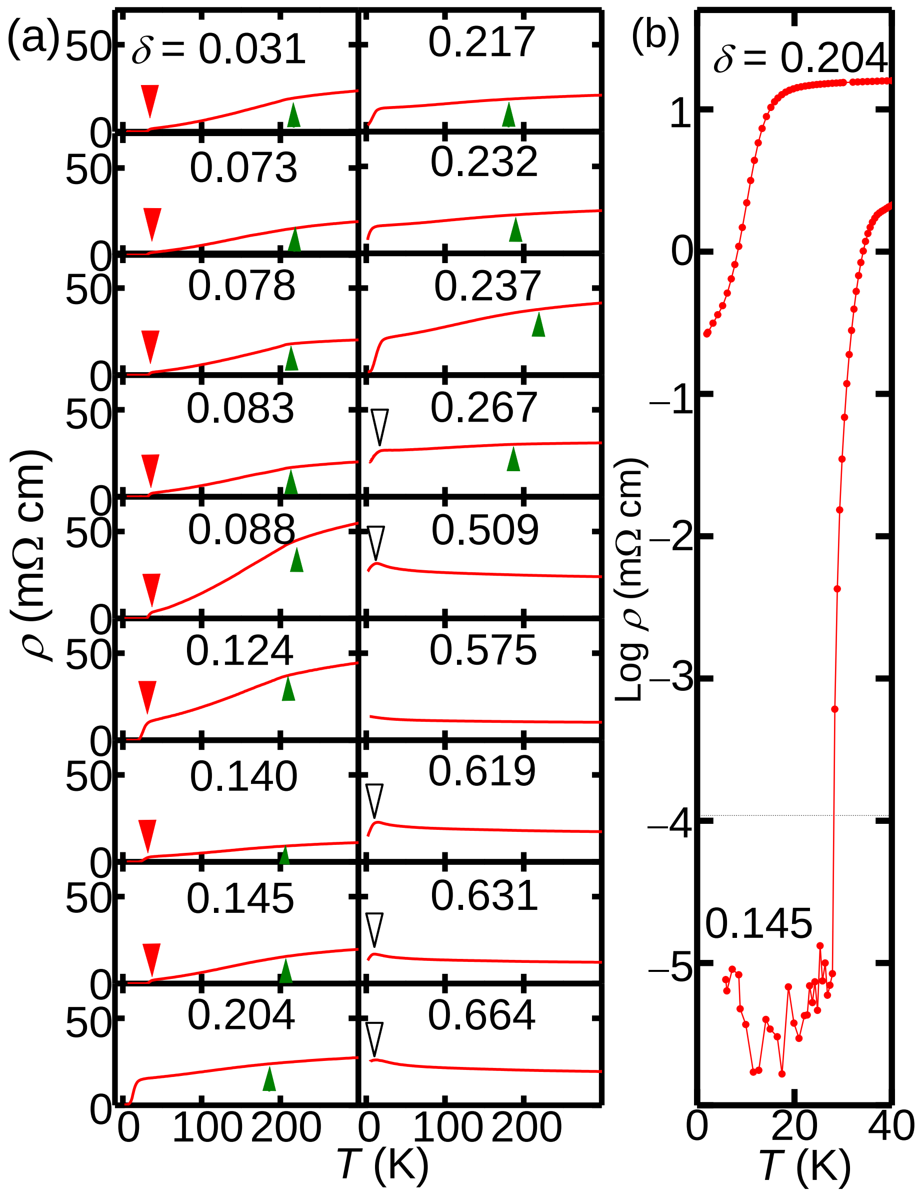
Tojo et al, arXiv (2018)

Results: XRF



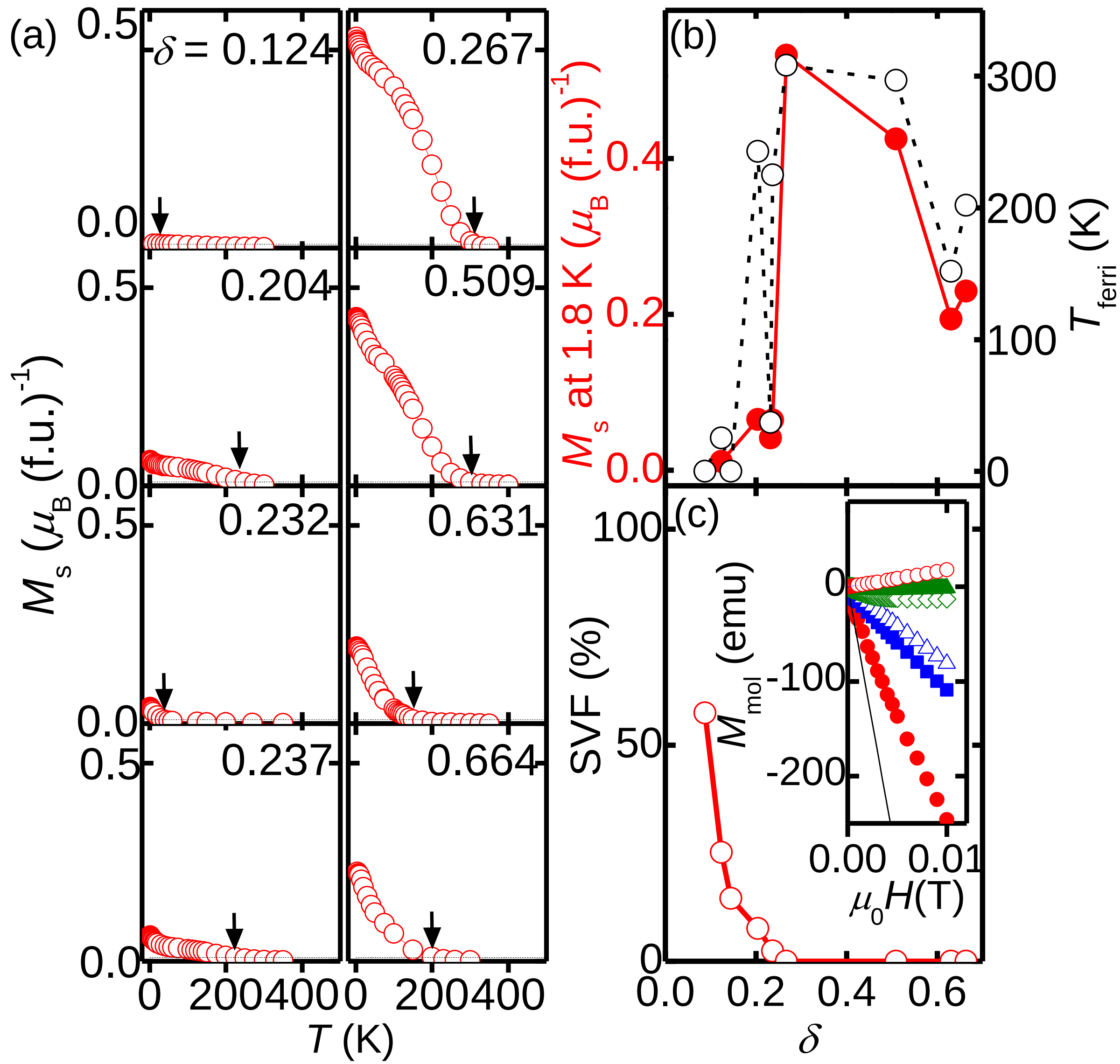
Tojo et al, arXiv (2018)

Results: ρ - T



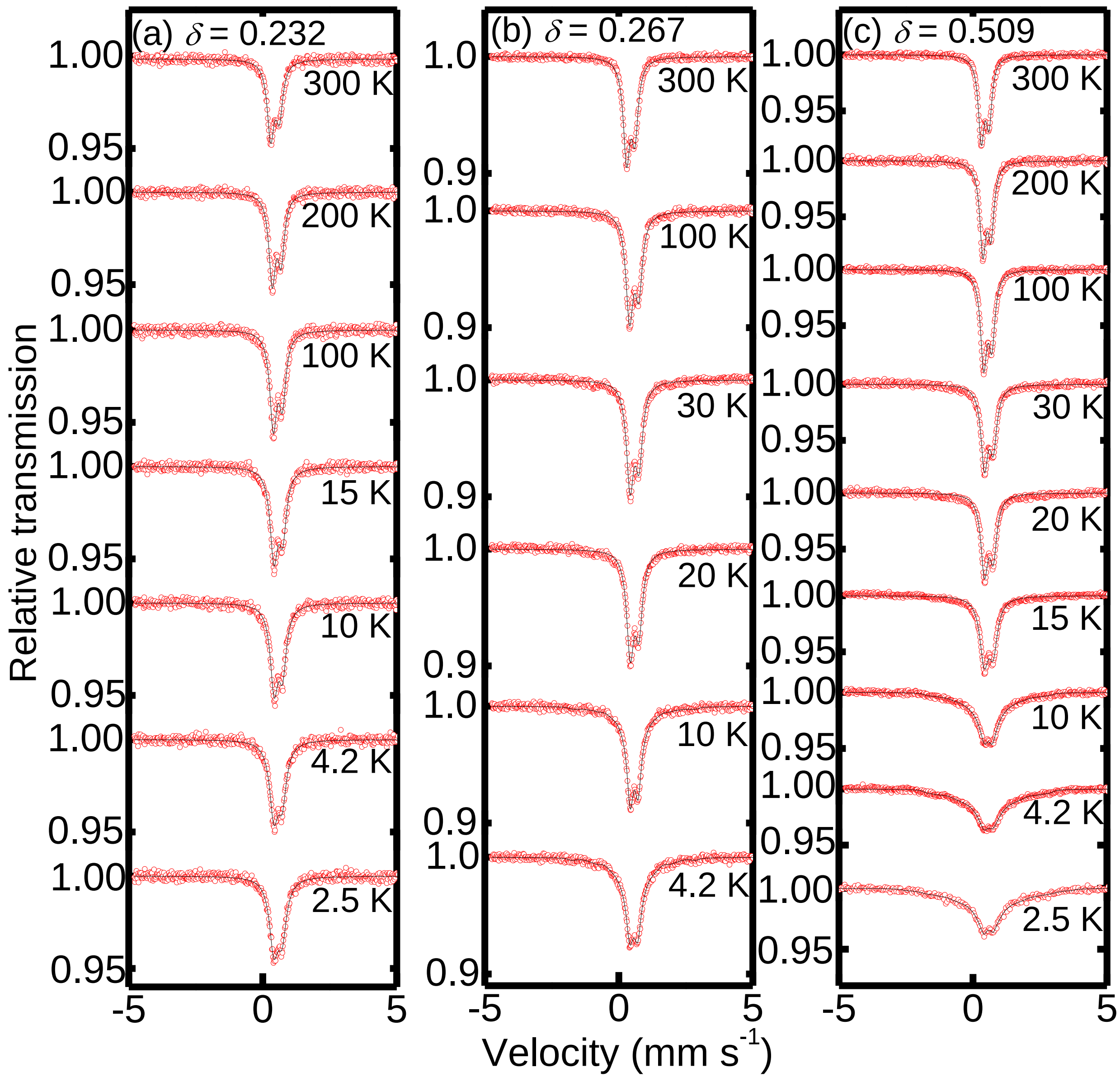
Tojo et al, arXiv (2018)

Results: *Ms*-*T*



Tojo et al, arXiv (2018)

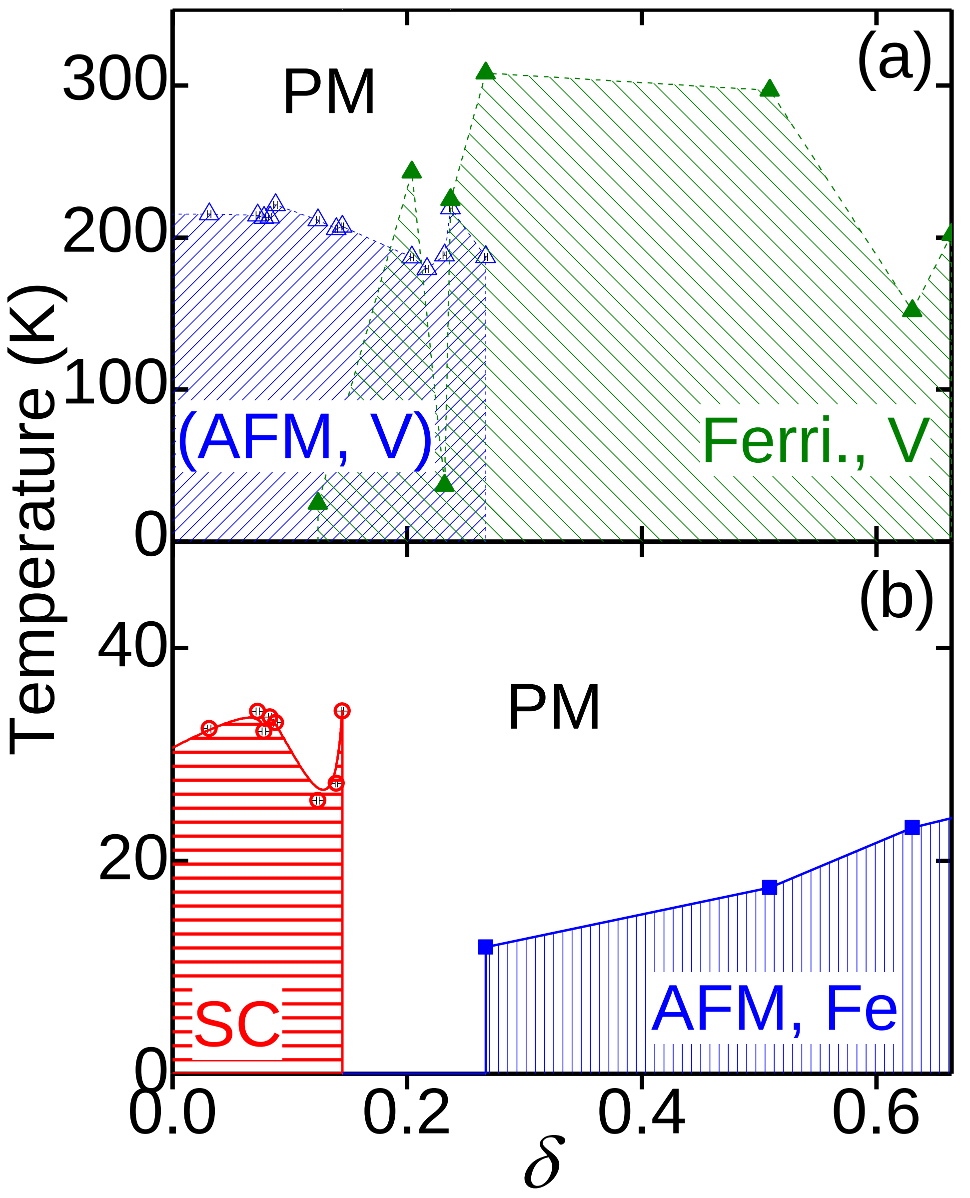
Results: ^{57}Fe Mössbauer spectroscopy



Results: DFT calculations on magnetism, Fe: s-AF

δ	Order	Moments (μ_B) V1	V2	V3	V4	ΔE (meV (f.u.)$^{-1}$)
0	A-AF	-1.9	-1.9	1.9	1.9	0
	FM	1.9	1.9	1.9	1.9	4
	c-AF	-1.9	1.9	-1.9	1.9	4
	c-AF	1.9	-1.9	-1.9	1.9	5
	Ferri.	-1.9	-1.9	1.9	-1.9	16
0.25	Ferri.	1.9	1.9	1.9	-2.2	0
	A-AF (Ferri.)	1.9	1.9	-1.9	-2.3	7
	FM	1.9	1.9	1.9	2.3	10
0.50	c-AF (Ferri.)	1.9	-2.3	1.9	-2.3	0
	FM	1.9	2.3	1.9	2.3	9
	A-AF	-1.9	-2.3	1.9	2.3	29

Results: Element specific phase diagram



Conclusions

- Magnetic and electronic phase diagrams for $Sr_2VFeAsO_{3-\delta}$ are demonstrated assuming linear relation between δ and lattice volume.
  - AFM of V coexists with SC of Fe in $Sr_2VFeAsO_{3-\delta}$
  - Ferrimagetism of V does not.
  - AFM of Fe does not...

- Our result supports "Goodenough's scheme "

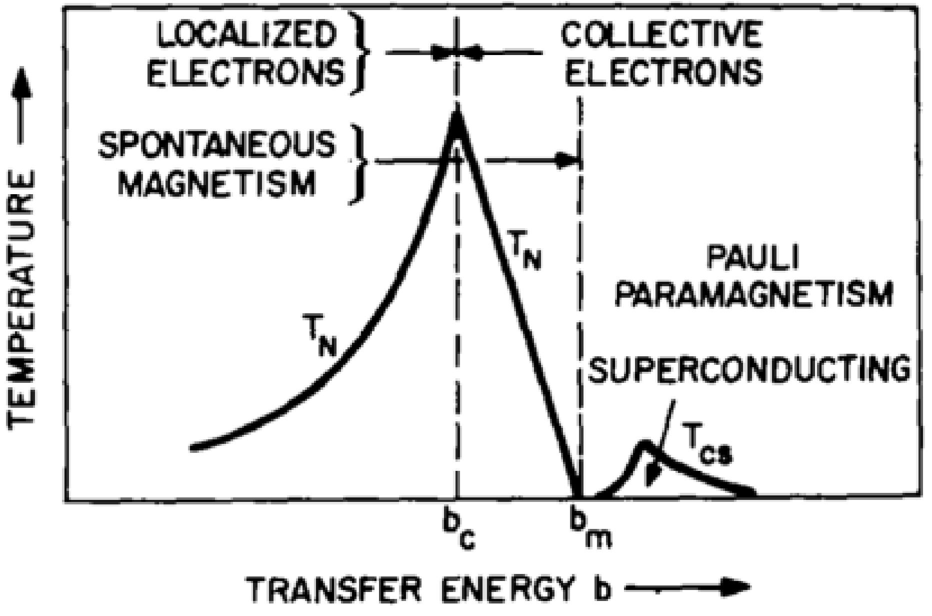


Fig. 8. Schematic, electronic *T*-*b* diagram for one electron per interacting *d* orbital.

J. B. Goodenough (1969).
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Supplementary, our motivation
Update of J. B. Goodenough's scheme

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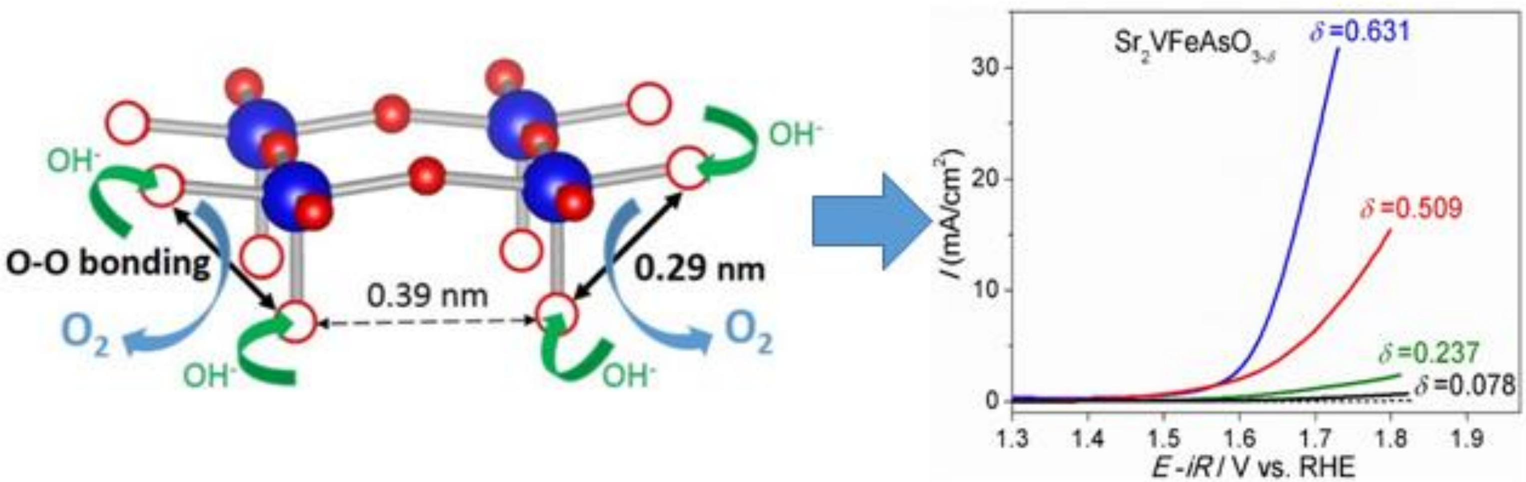
We-B2-1

Proposal of New Electrochemistry in Mixed Anion Compounds



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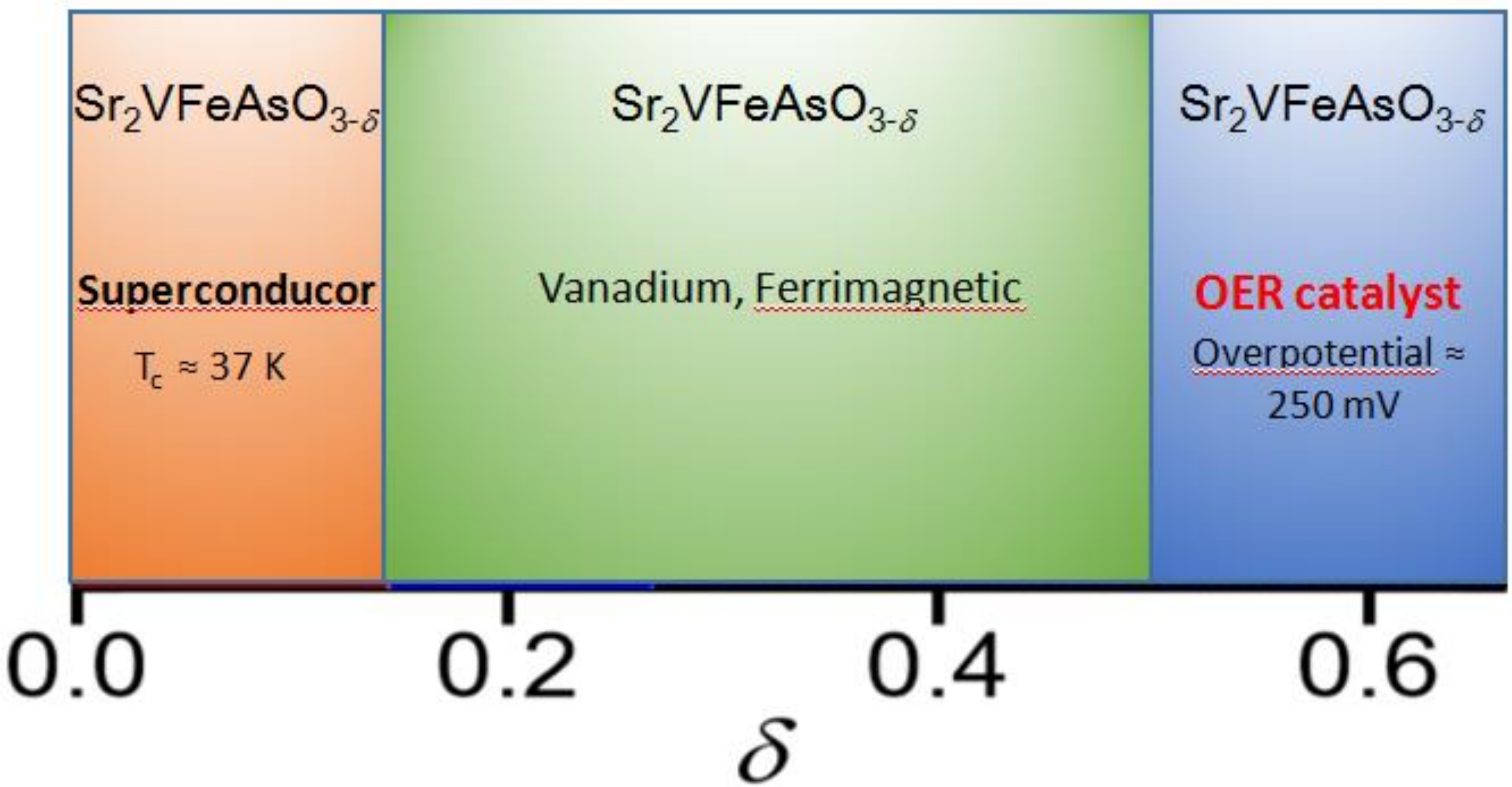
Keio University

東京大学
THE UNIVERSITY OF TOKYO

Supplementary, our motivation

Updated phase diagram of $Sr_2VFeAsO_{3-\delta}$



Bifunctional material that adopts OER catalyst or **superconductor**

We-B2-1

Dr. Hirai’s slides in IUMRS-ICEM

Thank you for your attention