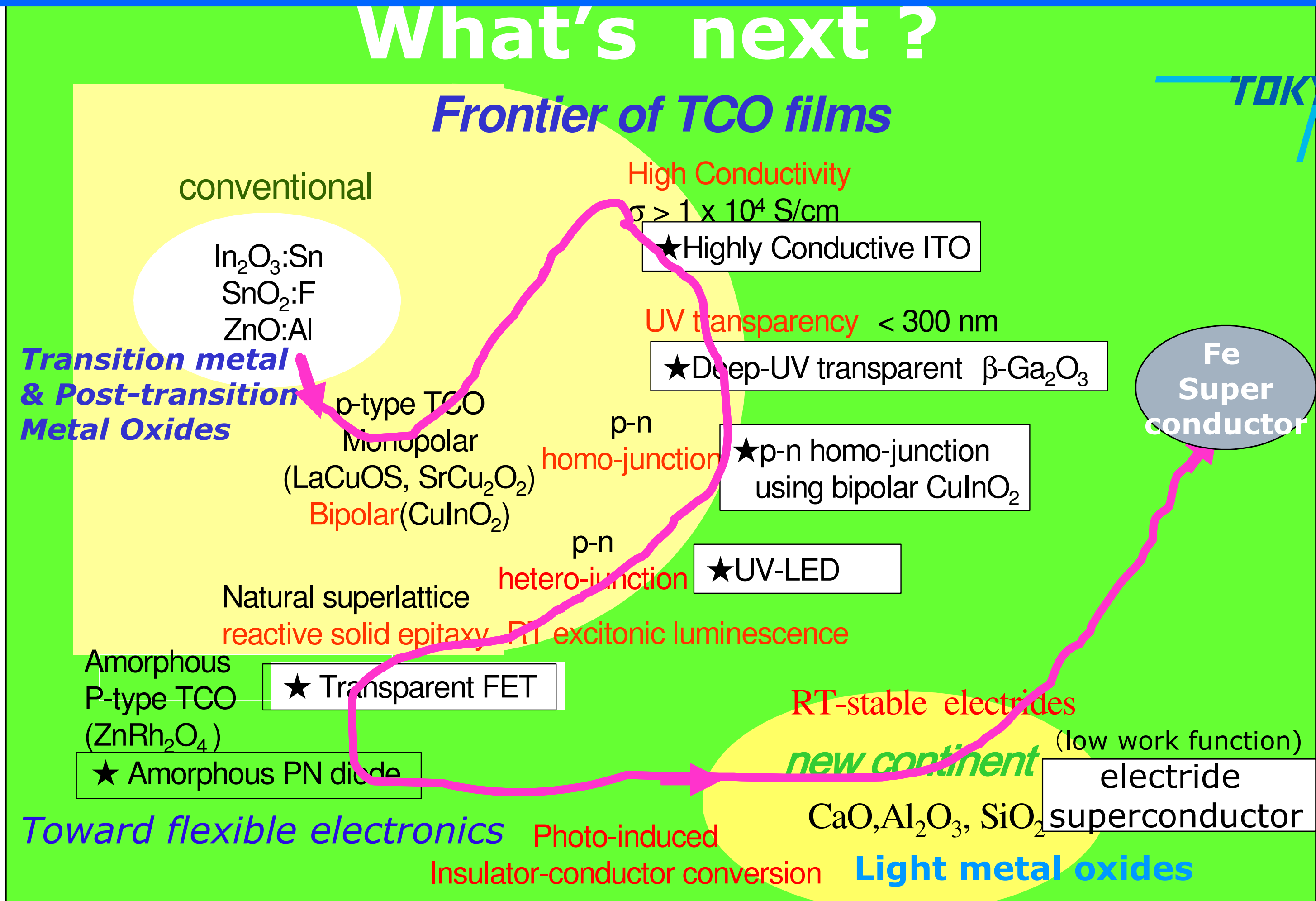
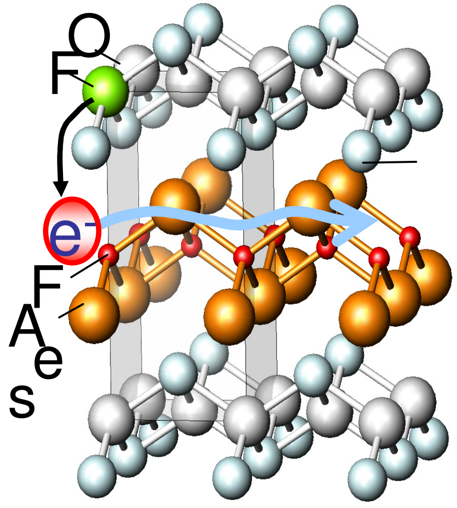
A New Continent of High Tc Superconductors: Layered Iron Pnictides

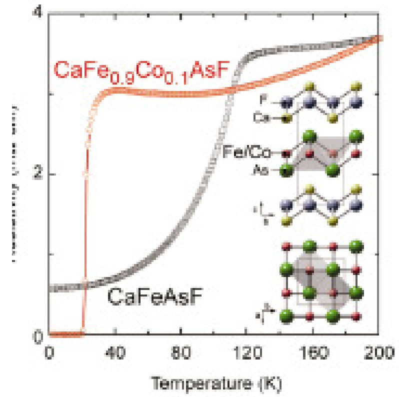


Hideo HOSONO

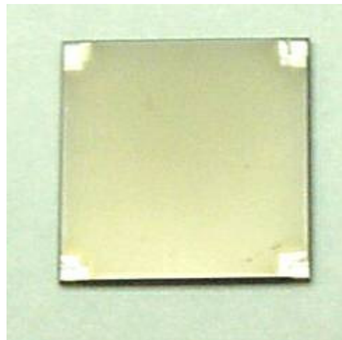
Frontier Research Center & Materials and Structures Lab.
Tokyo Institute of Technology, JAPAN

OUTLINE

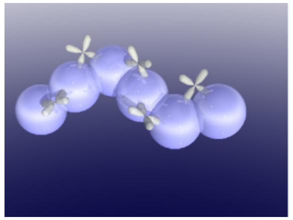




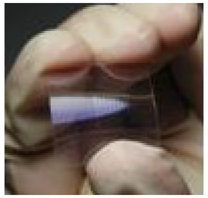
- Background
- Discovery of Fe(Ni)-pnictide superconductor
- Requirement for High Tc
- Ca(Sr)FeAsF, new insulating layer
- Epitaxial Thin Film Growth
- Water vapor-induced superconductivity
- Perspective



3大素材(鉄、セメント、ガラス)から生まれた電子機能材料



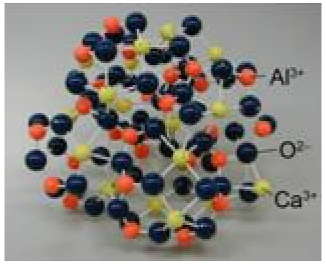
透明アモルファス酸化物
半導体の提案(1995)



透明トランジスタの試作
(2004、Nature)

ガラスから高性能透明トランジスタ

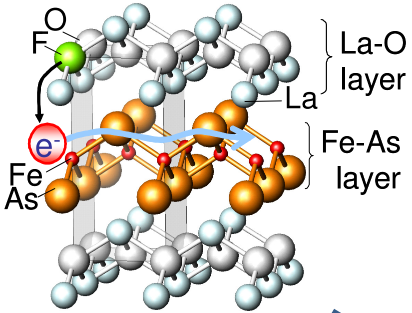
12インチ有機ELディスプレイ
の駆動に応用(2008,サムスン)



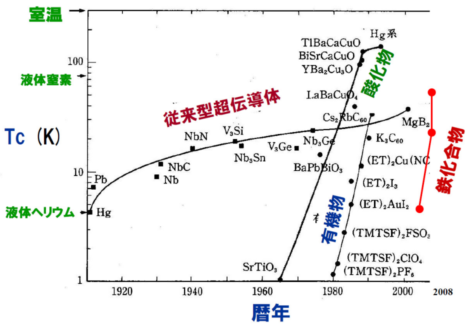
C12A7のナノ構造に注目
(1999)

セメントから透明金属

透明金属に変身。ITO代替物質。
(2004年　Science)



鉄の化合物は超電導に
ならないという常識を破る
(2006)



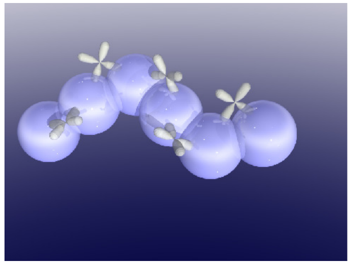
20年ぶりの高温超電導物質の発見

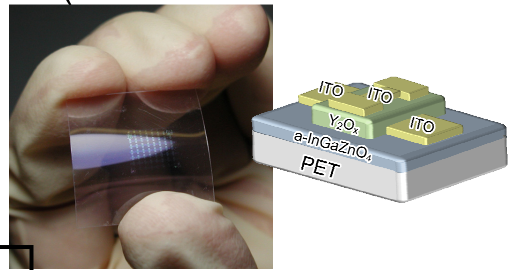
銅酸化物を除くと最高のTCを実現。世界的ブーム
(2008年,Nature)

透明アモルファス酸化物半導体(TAOS)の提案と進展

細野グループ

1995　透明アモルファス酸化物半導体の提案 @ICANS-16
1996　透明N型物質探索指針 (*J.Non-Cryst.Sol*)
2002　特徴的電子輸送特性の解明 *(Phys.Rev.B)*
2003　P型物質の発見とPN接合ダイオードの室温形成 (*Adv.Materials*)
2004　酸化物半導体単結晶薄膜を用いた高性能透明トランジス(*Science*)
2004　AOSを用いた曲がる高性能トランジスタ(*Nature*)
2008　世界初のPチャネル酸化物*TFT(Appl.Phys.Lett)*


(物質設計、東工大)



(透明で曲がるTFT,東工大)

国際動向

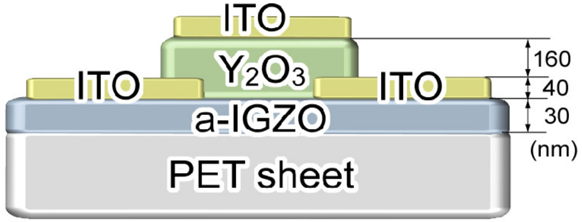
2005.9　アモルファス酸化物半導体(AOS) がメイントピックス
　　　　として採用@ICAN21(2005.9)
2005.12　10 papers @ MRS(ボストン)
2006.4　キヤノン　スパッターで高性能TAOS-TFTを発表
　　　　@E-MRS(ニース)
2006.12　凸版印刷、新型電子ペーパを提案@IDW(大津)
2007.5　透明酸化物半導体TFT@SID(カリフォルニア)
2007.8　AOSが全論文の15%に@ICANS22(コロラド)
2007.8　Samsung,LG がOLEDを試作発表@IMIS(韓国)
2008.5　サムソン電子AOS-TFT駆動12インチOLED,15インチLCD発表
　　　　@SID(US)
2008.12　日立　TAOS-TFTで1.5V動作を実現、フレキシブル・デバイス
　　　　に道 @国際電子デバイス会議(IEDM)

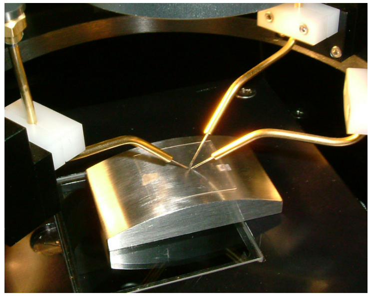

(電子ペーパ、凸版印刷)

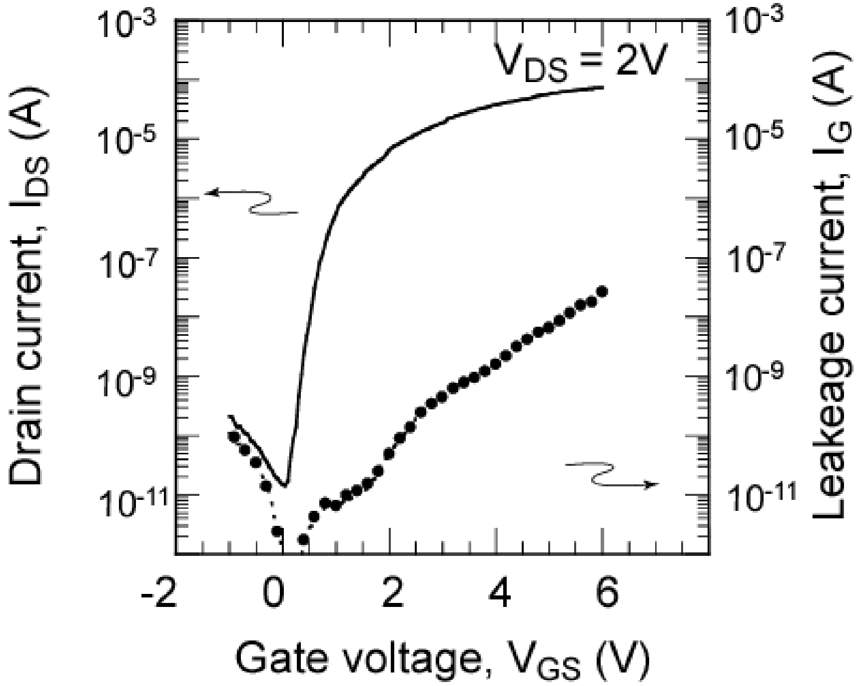

(有機EL,LG電子)

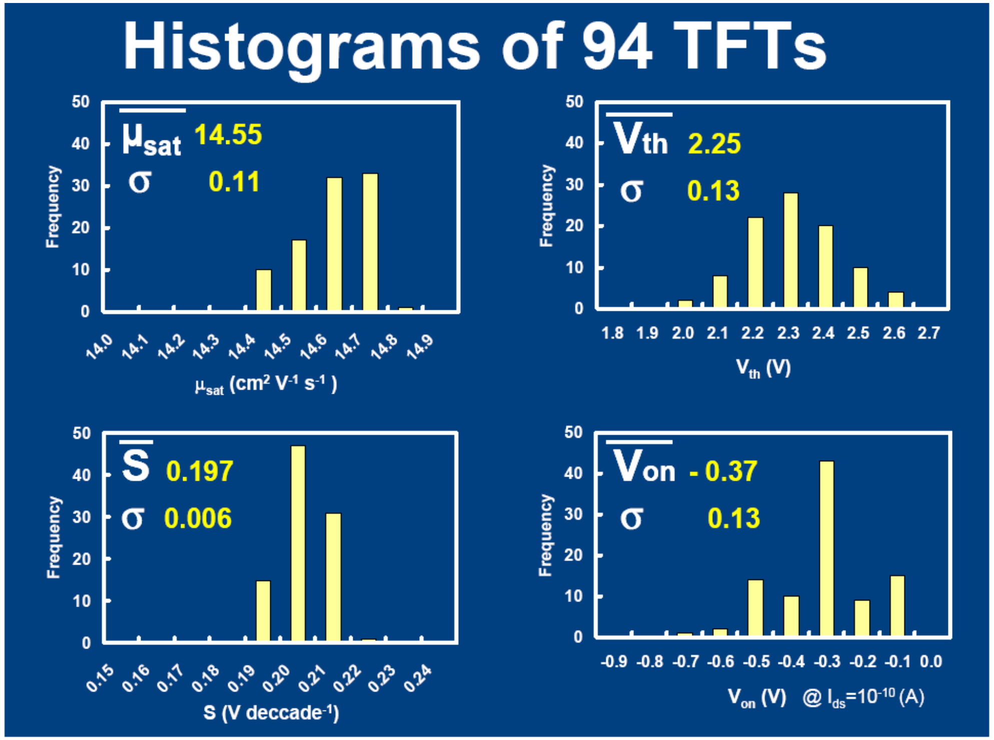
室温でPETフィルム上に作製した薄膜トランジスタ

電界効果移動度μ
= 12 cm²(Vs)⁻¹









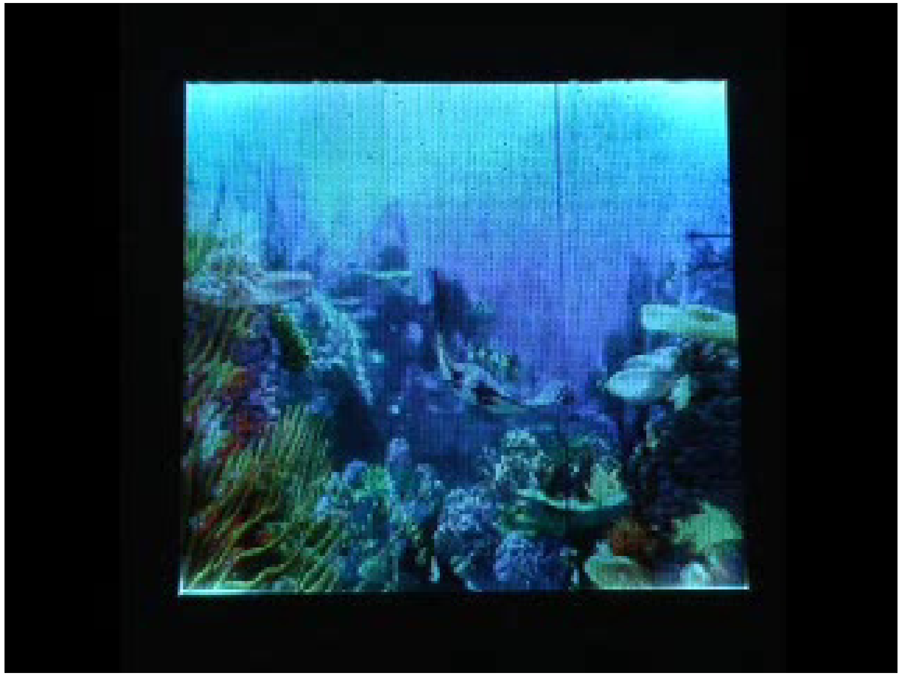
Cf. 水素化アモルファスシリコン
μ=~1cm²(Vs)⁻¹

Display Application

Full Color Image
Driven by TAOS - TFTs

AM-OLED Panel

4-inch



LG Electronics @SID'07

12-inch

Samsung Electronics @SID'08

SID 2009

Solution-derived TFT

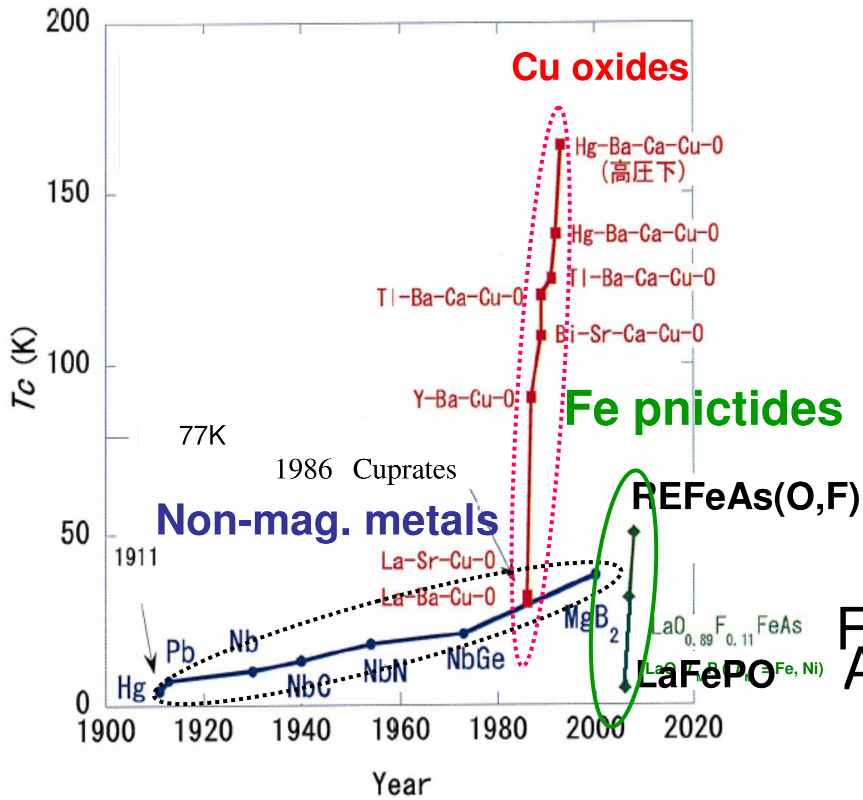
Trend in Superconductor Research

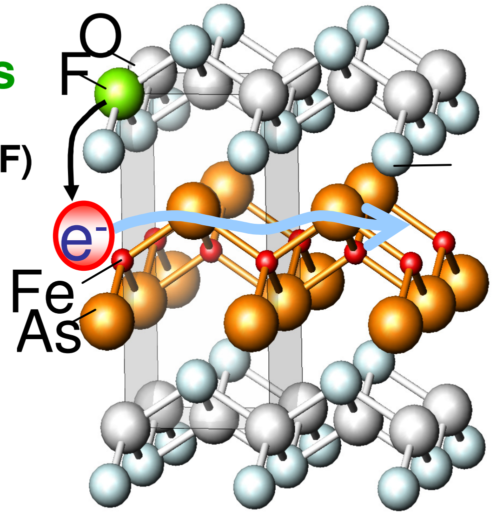
Bronze(Cu) age ➡ Iron age

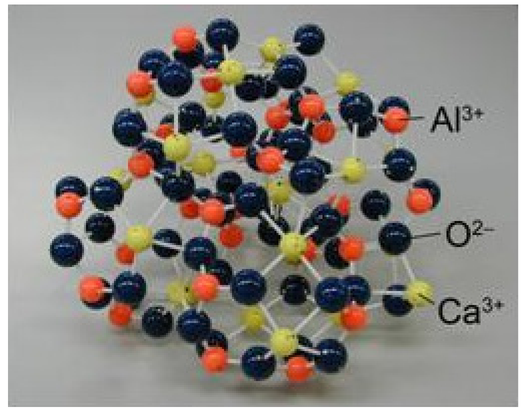
Stone age

$12CaO \cdot 7Al_2O_3$

Superconducting Cement

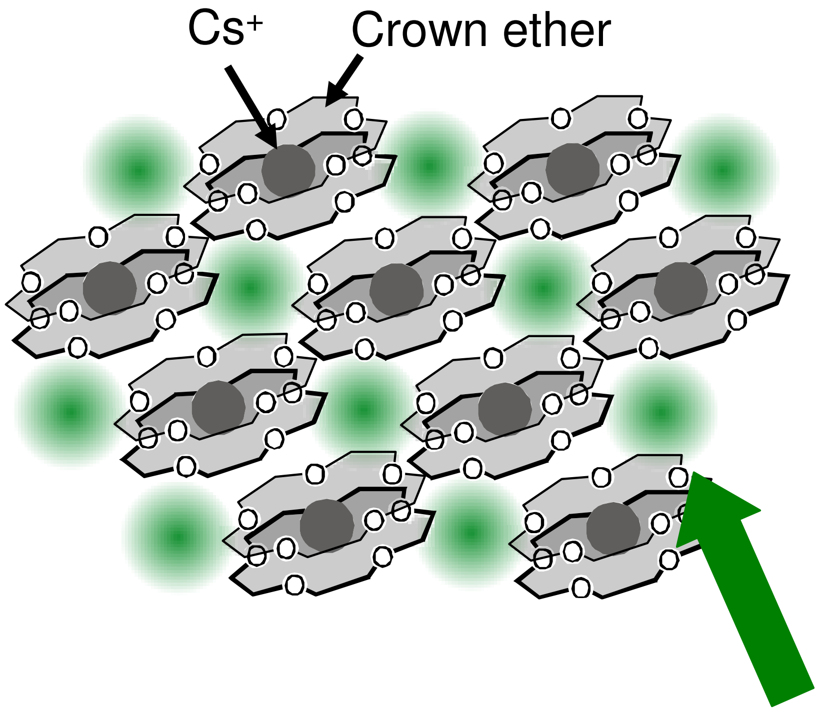


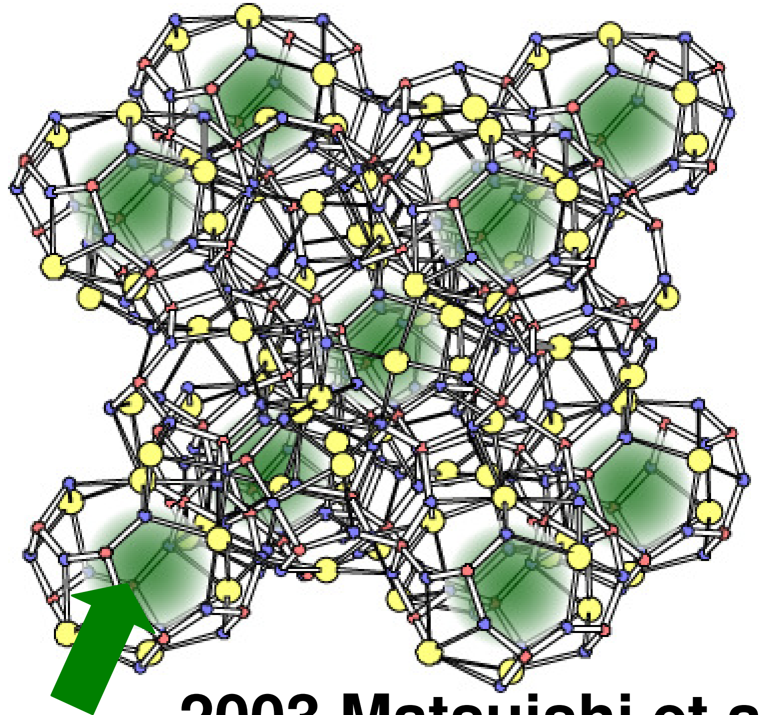




C12A7 electride

$Cs^+[15\text{-crown-}5]_2(e^-)$ **$[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$**





1983 ~ Dr. J. L. Dye
(Nature)

- Stable condition

  max -40 ℃ in vacuum

2003 Matsuishi et al.
(Science)

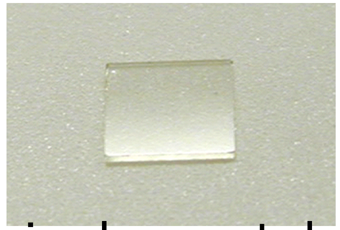
- Stable condition

  Up to ~ 400 ℃ in Air
  Up to melting point(~1300C) in vacuum

C12A7 electride is thermally and chemically stable

12CaO·7Al$_2$O$_3$ (C12A7)

powder



single crystal

- A constituent of alumina cements
- Large band gap ~7 eV
- Cubic (a = 1.199 nm, I$\bar{4}$3d)
- Unit cell: $Ca_{24}Al_{28}O_{66} = [Ca_{24}Al_{28}O_{64}]^{+4} + 2O^{2-}$

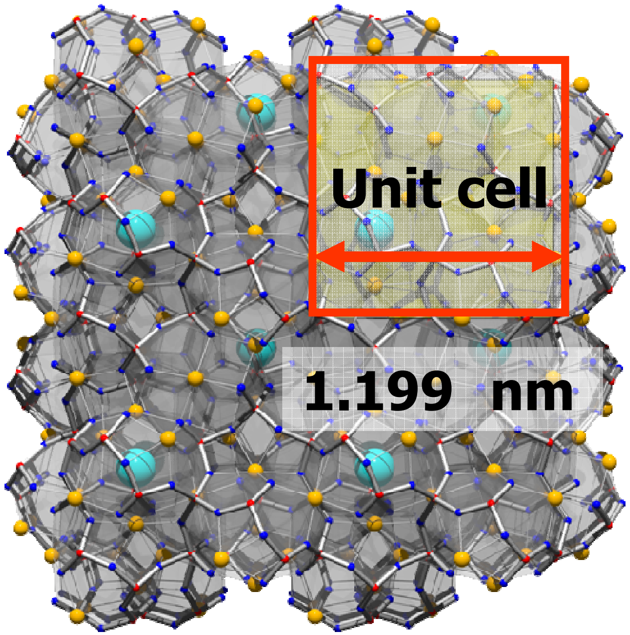
Mp. 1415 ºC

Free Oxygen Ions

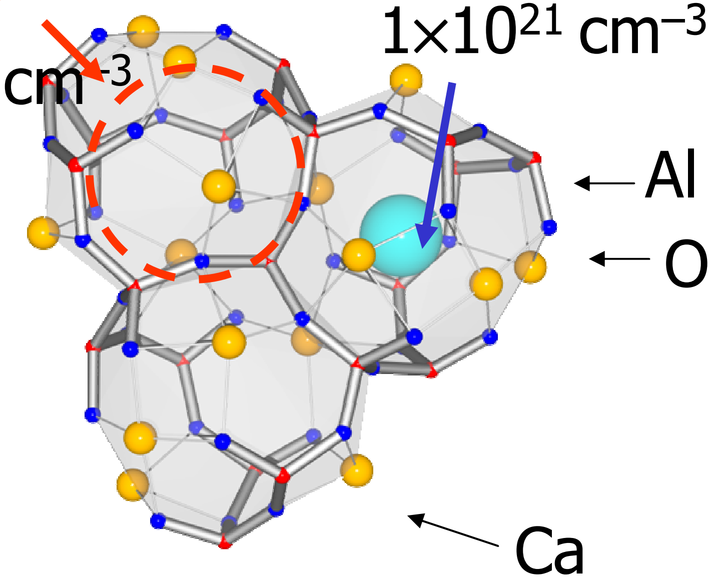
12 Cages

6×10^{21} cm^{-3}

1×10^{21} cm^{-3}



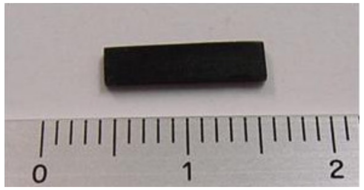
Densely Packed Sub-nano-sized Cages

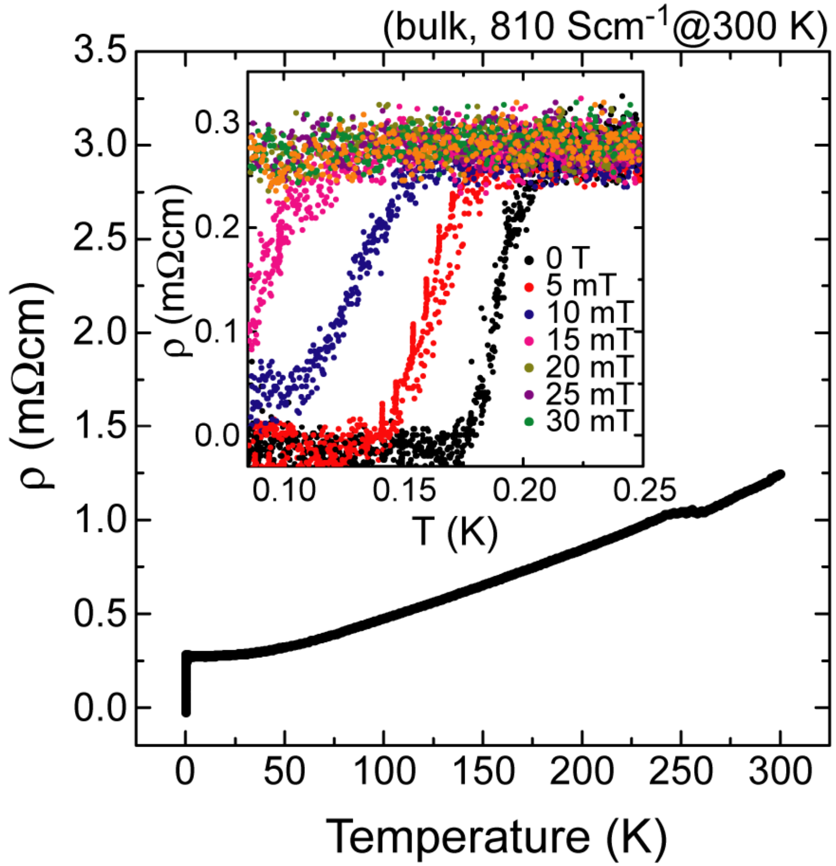


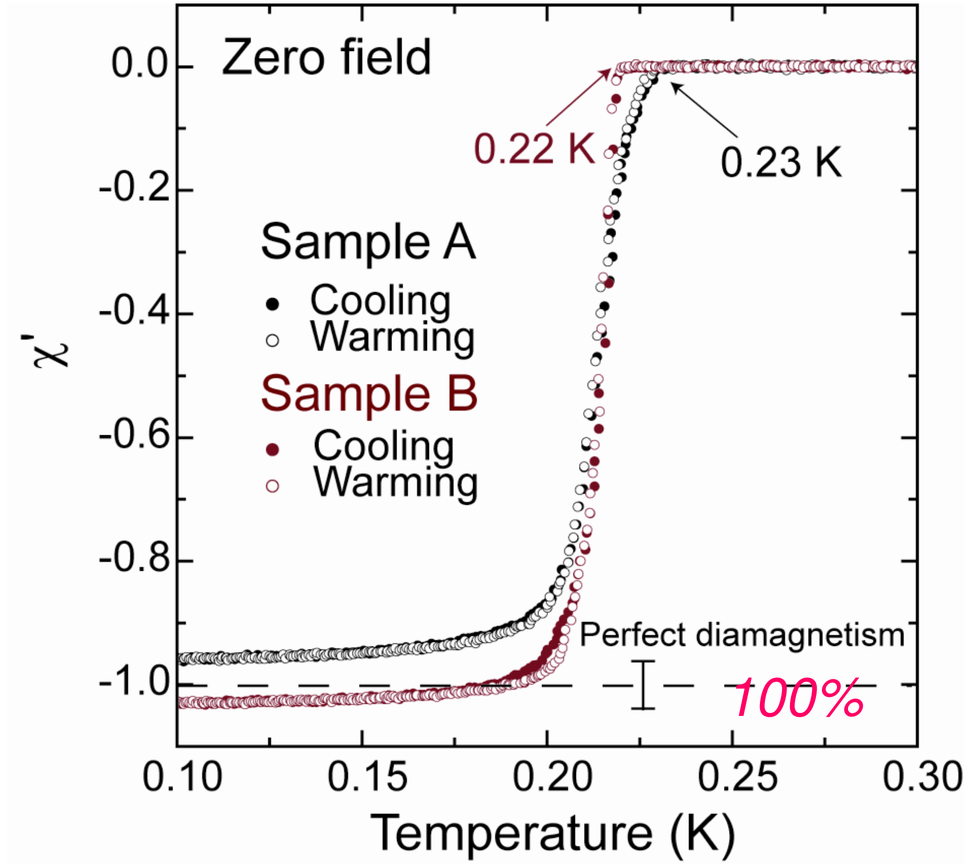
Fast Oxygen Ion Conductor

Metal-Superconducting Transition

Superconducting Cement







First s-metal superconductor

J.Am.Chem.Soc.(2007)

Superconducting cement:
beyond imagination ?

Vol 444|23 November 2006 nature

NEWS & VIEWS

SOLID-STATE PHYSICS

Super silicon

Robert J. Cava

Silicon is the archetypal semiconductor, and base material of the microelectronic age. But it turns out that, treated the right way, silicon the semiconductor can become silicon the superconductor.

If someone were to stop me in the street and ask me to name the most important materials on Earth, I would say concrete, steel, glass and silicon. To witness the importance of the first three, just look up from your page or screen. For the last, close your eyes and imagine yourself back in the BS (before-silicon) world of, say, Myrna Loy in *The Thin Man* or Humphrey Bogart in *Casablanca*. One might reasonably argue a preference for the softer focus of those earlier times; but the differences in lifestyle between then and now make it hard to argue against the assertion that silicon has become the technologically most important material of the past 50 years.

It is for this reason that Bustarret and colleagues' report (page 465 of this issue)[1] is such a breakthrough: they have succeeded in turning silicon, the consummate semiconductor, into a superconductor at ambient pressure. Admittedly, the treatment they meted out to silicon to force its conversion ('doping' with high levels of boron) can only be termed abusive, and the temperature at which they measured it (0.3

Window on the world: silicon is arguably the material most central to modern life.

D. HALLINAN/ALAMY

NEWS & VIEWS NATURE|Vol 444|23 November 2006

Performing experiments using such high-powered lasers, and testing materials for superconductivity at such low temperatures, is no small matter. So why bother? The authors are motivated by the possibility that, if silicon could be made superconducting — even under conditions too extreme to be useful in practical devices — the integration of superconducting silicon into the sophisticated world of microelectronics processing might uncover new electronic functions. It will be interesting, for example, to see whether an electron-rich superconductor can be made out of silicon through extreme doping with electron-rich phosphorus or arsenic, rather than hole-rich boron. That would allow the gamut of microelectronics concepts and processing to be applied to superconductors, but is far from an obvious extension of the present work.

So, are Bustarret and colleagues' results[1] just an amusing diversion in the search for new superconductors, or a herald of more and better devices and materials? It's too early to tell. The main thrusts in the search for new superconducting materials nowadays are towards exotic systems in which magnetism can be transformed into superconductivity by changing a carefully controlled experimental parameter, and towards materials based on metallic elements that have high superconducting transition temperatures and are easy to process. Such a material could change the way electrical current is carried. I remain convinced that we could wake up any morning to the announcement that someone, somewhere, has found it. If that superconductor is made by doping concrete, I'll know it's time for me to retire. ■

Robert J. Cava is in the Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA.
e-mail: rcava@princeton.edu

1. Bustarret, E. *et al. Nature* 444, 465–468 (2006).
2. Lee, P. A. & Ramakrishnan, T. V. *Rev. Mod. Phys.* 57, 287–337 (1985).
3. Thomas, G. A. *Phil. Mag.* B52, 479–498 (1985).
4. Rosenbaum, T. F. *et al. Phys. Rev. Lett.* 45, 1723–1726 (1980).
5. Dai, P., Zhang, Y. & Sarachick, M. P. *Phys. Rev. Lett.* 66, 1914–1916 (1991).

any two randomly chosen genomes than suggested previously by studying SNPs alone. More than half of the CNVs that were identified overlap known annotated genes in the genome. So it is likely that CNVs play a role in so-called complex diseases, in which multiple genes and/or gene–environment interactions are involved.

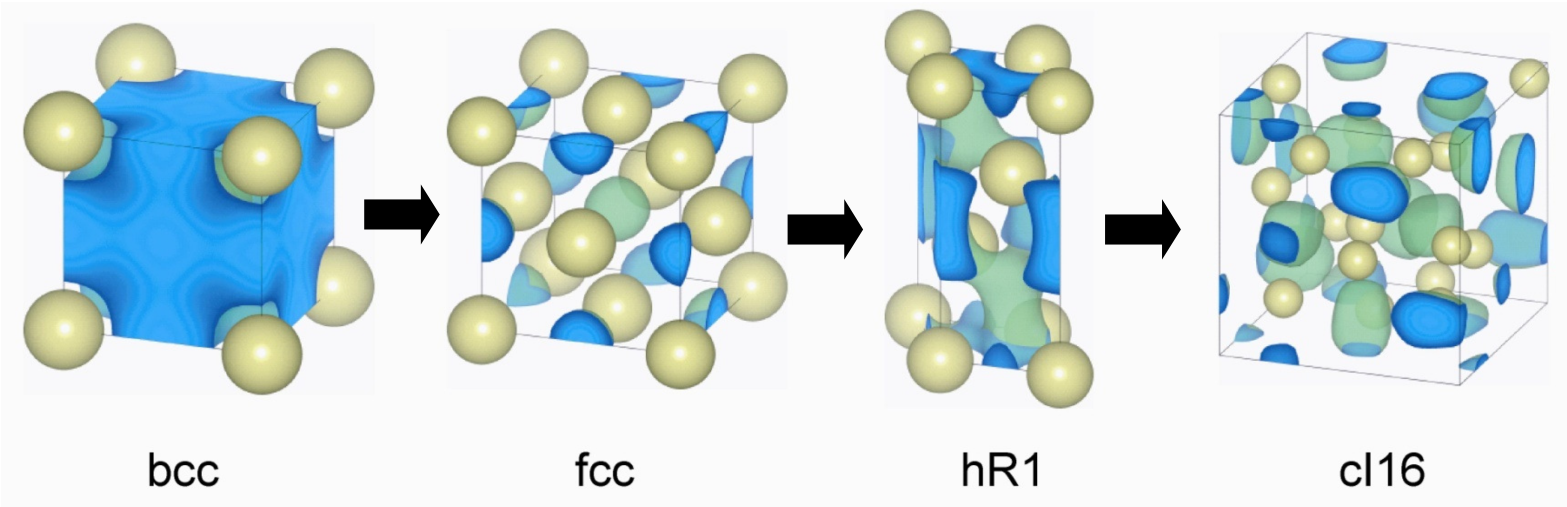
Mechanistically, how might copy-number variation be involved with complex disease? When deletions or duplications are present within a gene or its regulatory region, there is a reasonable chance that there will be an imbalance in the appropriate level of RNA and thus protein production from that gene. For genes and pathways in which the amount of a functional product produced is critical, it seems likely that CNVs could underscore variation in susceptibility to disease. Classically, variation in the copy number of the globin genes was shown to be responsible for various disorders of haemoglobin, such as the α-thalassaemias[6]. More recently, variable copy number of the *CCL3L1* gene was reported to be

Nature, Nov.27,2006

If that superconductor is made by *doping concrete*, I'll know it's time for me to retire *(Robert J.Cava, Princeton U.)*

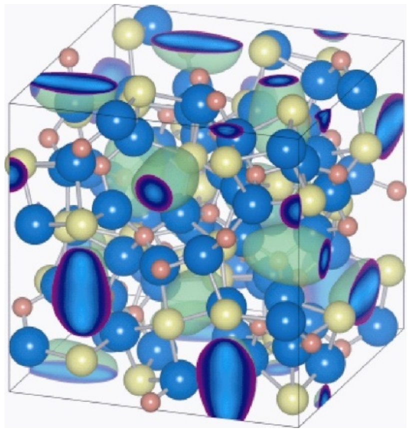
High P-phase of s-band metals and C12A7:e^-

Pressure-driven Li phase



(Superconductor
Tc=20K @ High P

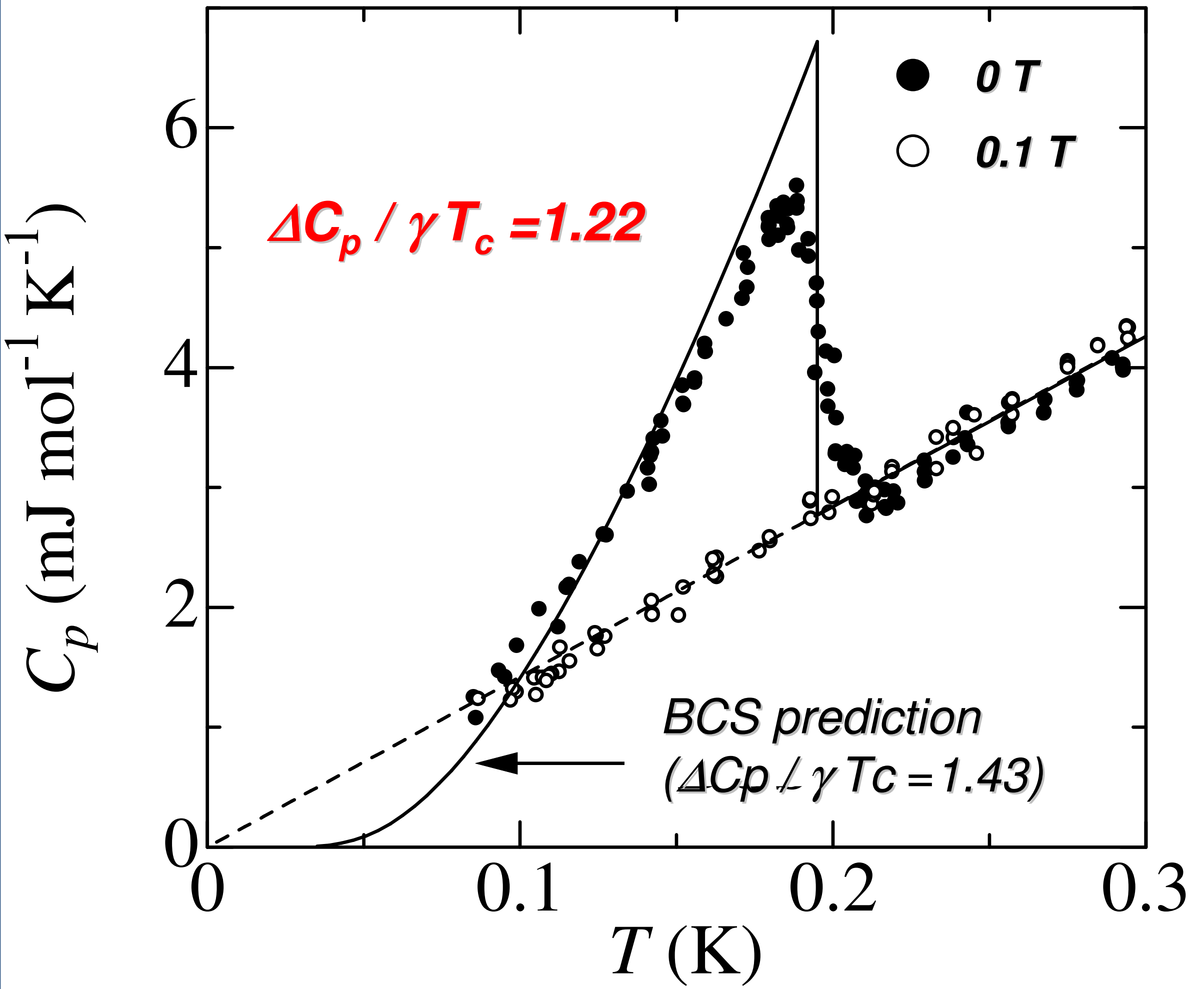
Metallic C12A7:e-



The Same Space Group
(Id3-4)!!!

Heat Capacity

Sample ; FZ grown single crystal



$$C_p = \beta T^3 + \gamma T,$$

$$\gamma = \frac{1}{3}\pi^2 k_B{}^2 N_\gamma(0),$$

$$\Theta_D = \left(\frac{12\pi^4 Rr}{5\beta}\right)^{1/3},$$

$N_\gamma(0) = 7.0\times10^{21}\ \mathrm{eV}^{-1}\ \mathrm{cm}^{-3}$

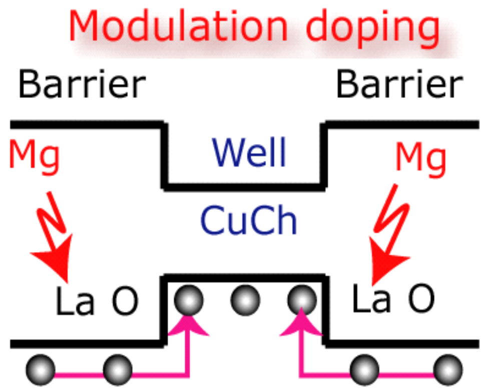
Θ_D = 628K

($C12A7:O^{2-}$; 604K)

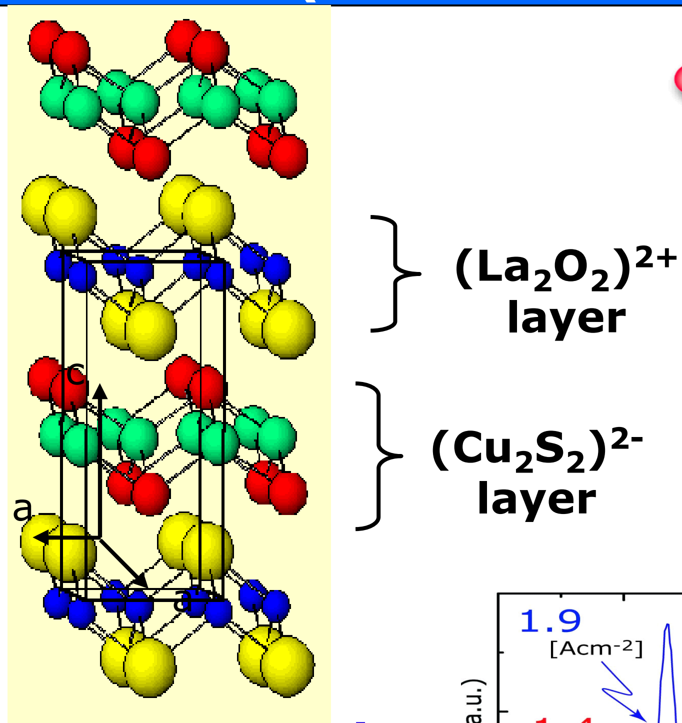
PRB(2008)

Unique Optoelectric Properties of
LaCuOCh(Ch=S,Se)

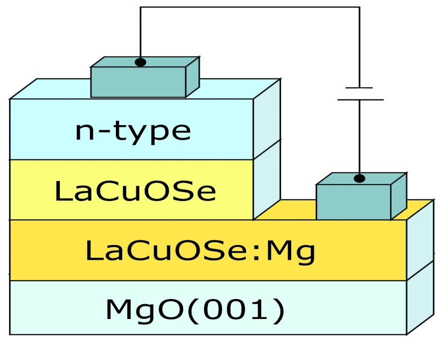
- **Transparent p-type degenerate semicon.**

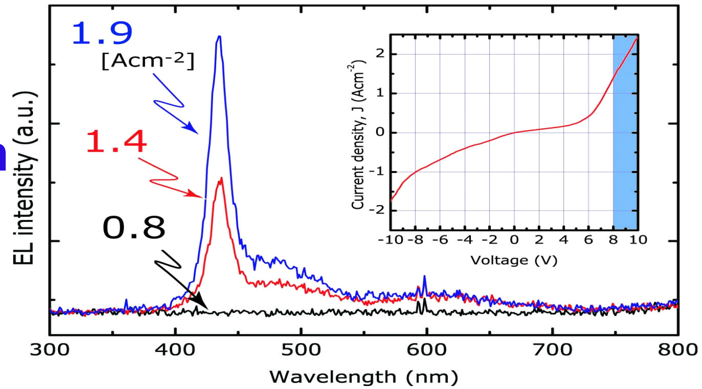


$N=4\times10^{20}cm^{-3}$
$\sigma=140\ Scm^{-1}$

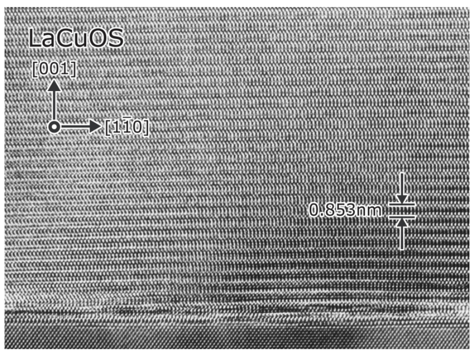


- **Blue LED**





- **RT-stable exciton**
- **Large NLO**



APL(2002), PRB(2003), OPL(2003),APL(2005)

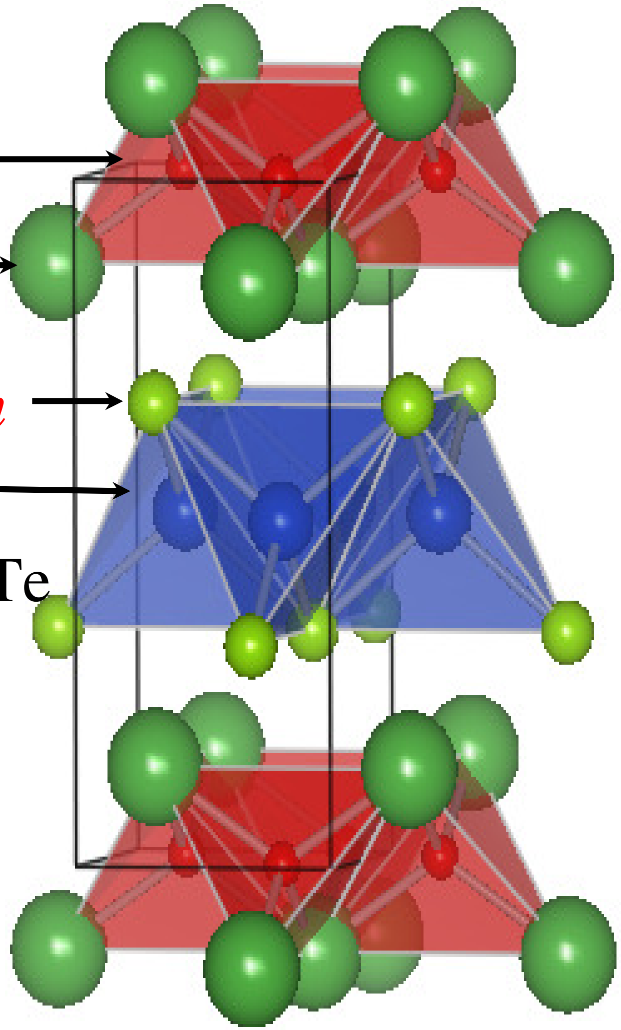
From LaCuOCh (p-type semicond.) to LaTMOPn (magnetic semicond.)

O

La

Ch

Cu



$(\mathbf{La}^{3+}\,\mathbf{O}^{2-})(\mathrm{Cu}^{+}\,Ch^{2-})$ *Ch*=S, Se, Te

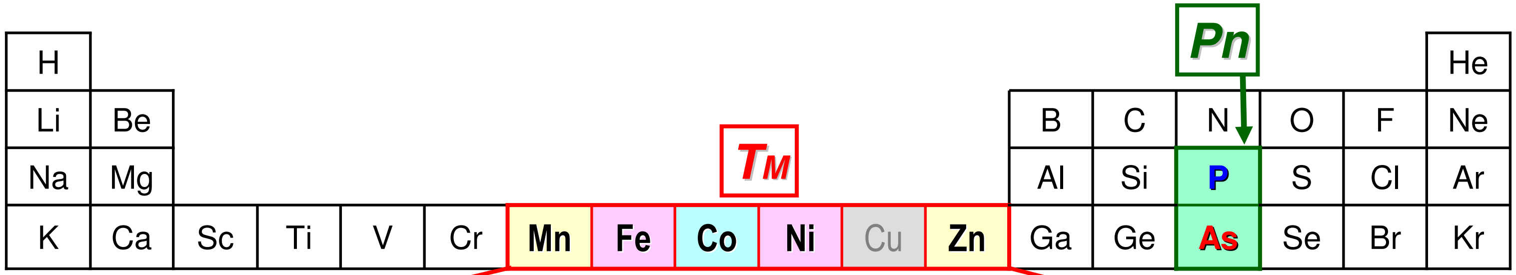
La => Nd, Ce, Pr, Bi

$(\mathrm{La}^{3+}\,\mathrm{O}^{2-})(TM^{2+}Pn^{3-})$ *Pn*=P, As, Sb

Ln = La, Nd, Sm, Gd

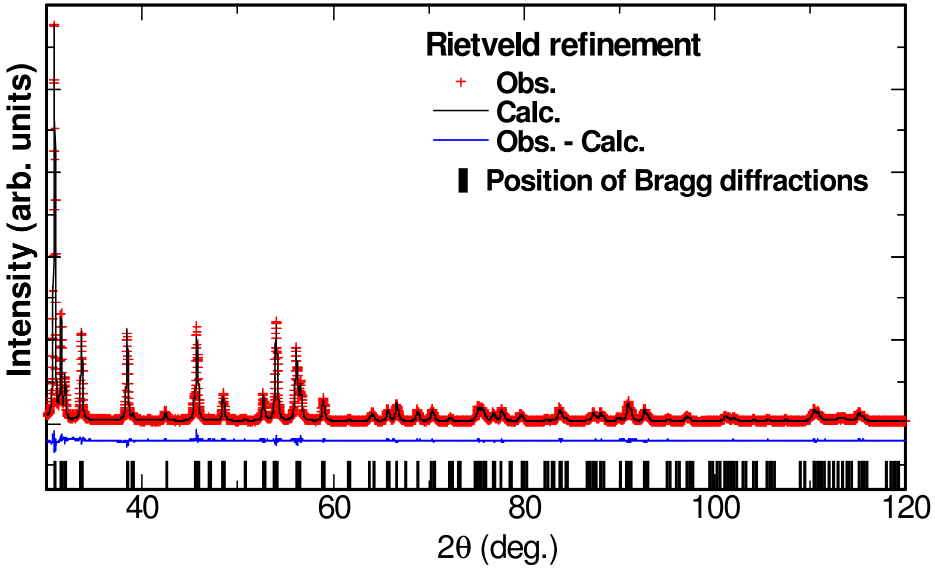
***TM* = Mn, Fe, Co, Ni, (Zn)**

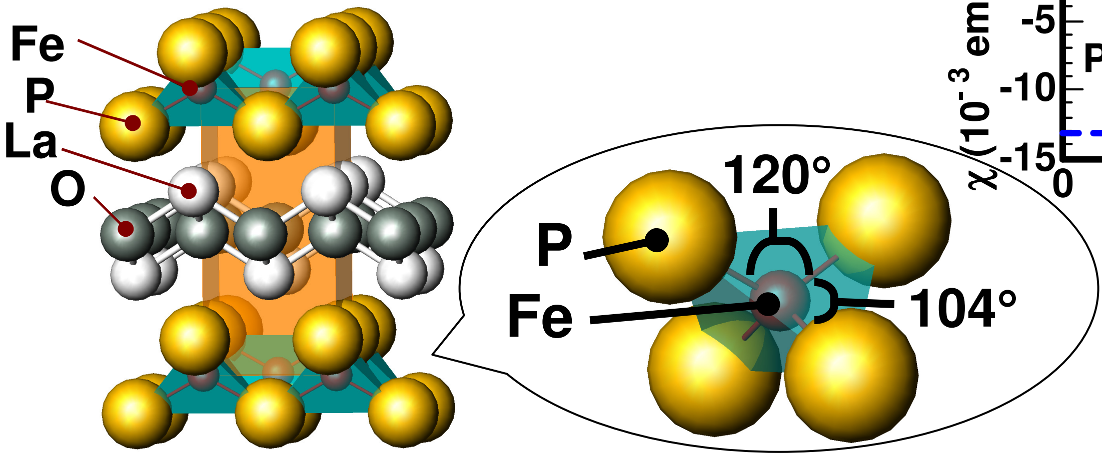
Properties of LaTMPnO

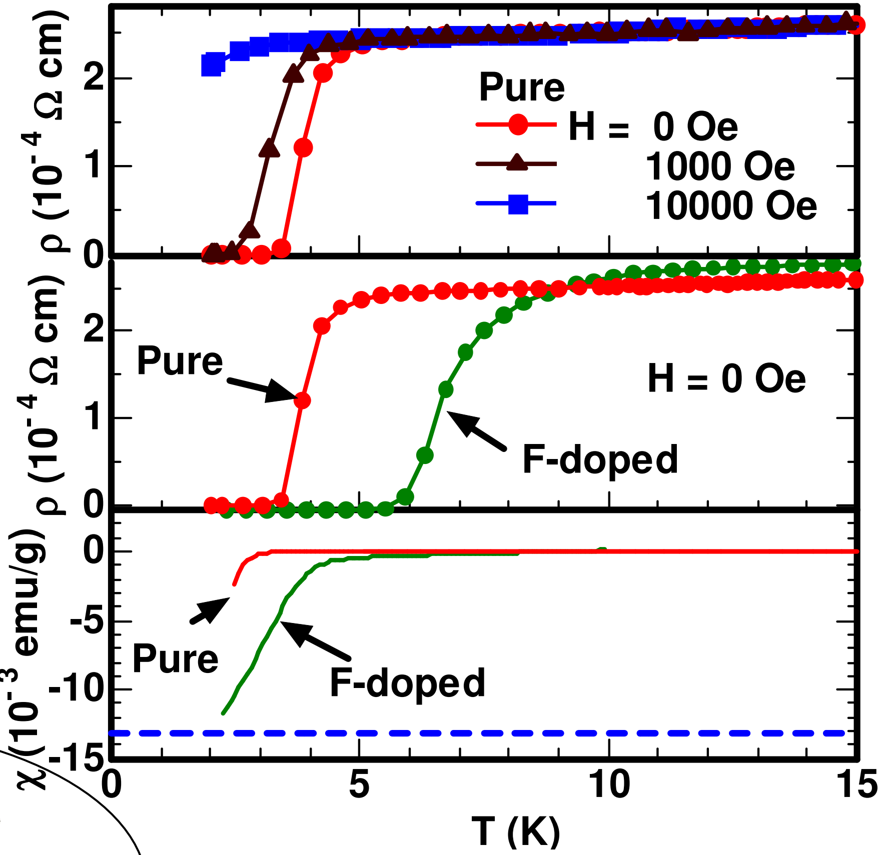


TM^{2+}	Mn($3d^5$)		Fe($3d^6$)		Co($3d^7$)		Ni($3d^8$)		(Cu)	Zn($3d^{10}$)	
Pn	P	As	P	As	P	As	P	As		P	As
Elect. Prop.	Semiconductor		Super-conductor		Metal		Super-conductor		—	Semiconductor	
Magnetism	AFM				FM				—	nonmagnetic	
E_g	~1 eV		—		—		—		—	~1.5 eV	
T_C / T_N	> 400 K		Undoped: 5 K	Undoped: X F-doped: 26 K	43 K	66 K	Undoped: 3 K	Undoped: 2.4 K		—	
Ref.	Yanagi et al. JAP submitted		Kamihara *et al.* JACS(2006), Kamihara *et al.* JACS (2008)		Yanagi et al. PRB (2008)		Watanabe *et al.* IC (2007), Watanabe *et al.* JSSC (in press)		—	Kayanuma *et al.* PRB (2007), Kayanuma *et al.* TSF (2008)	

Discovery of Tc in LaFePO



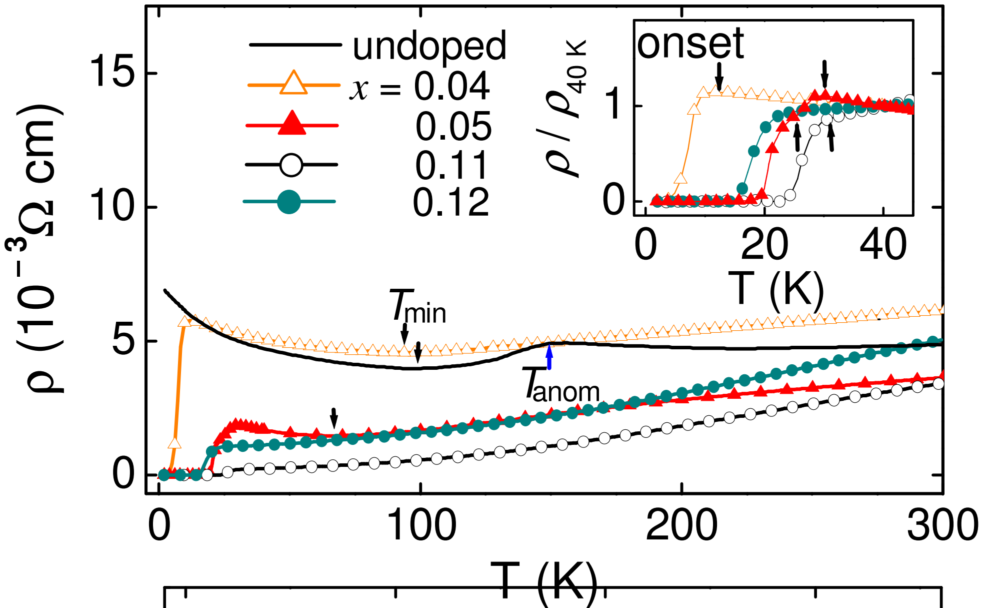


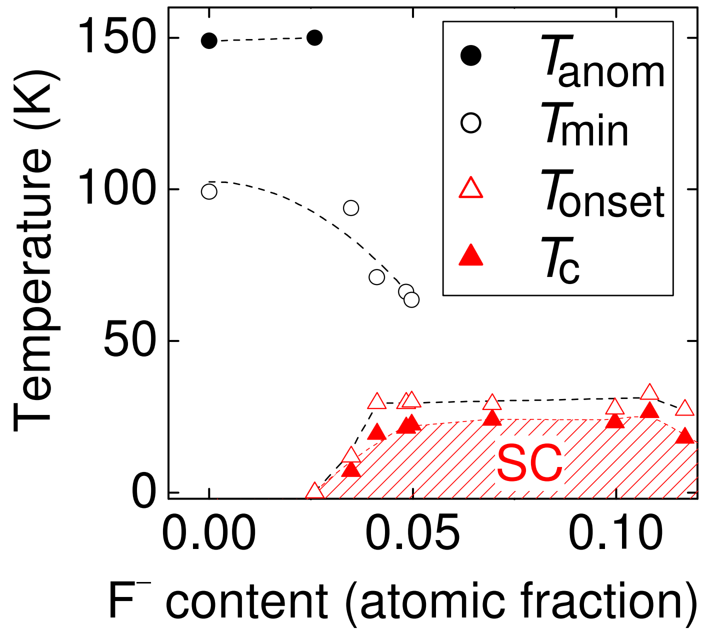


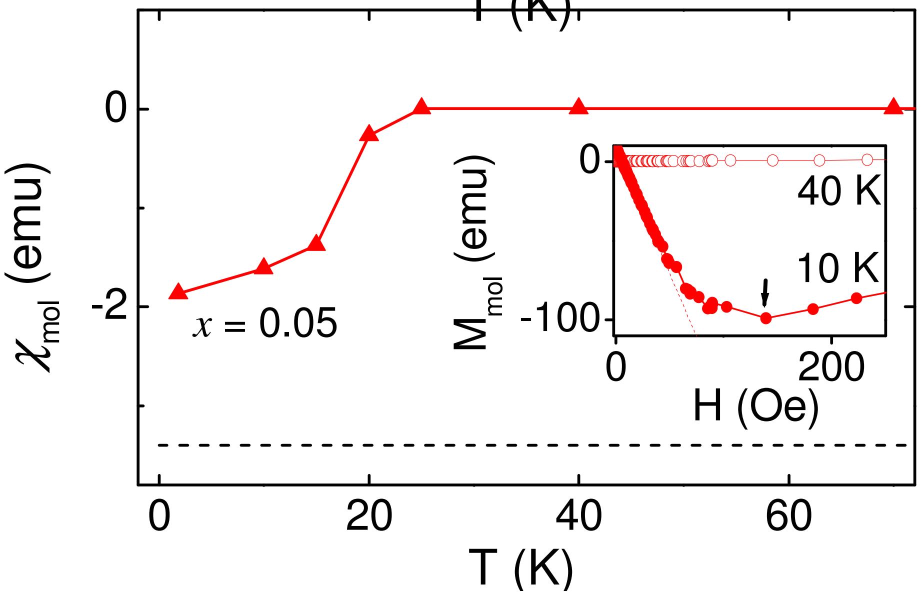
JACS,128,10012(2006)

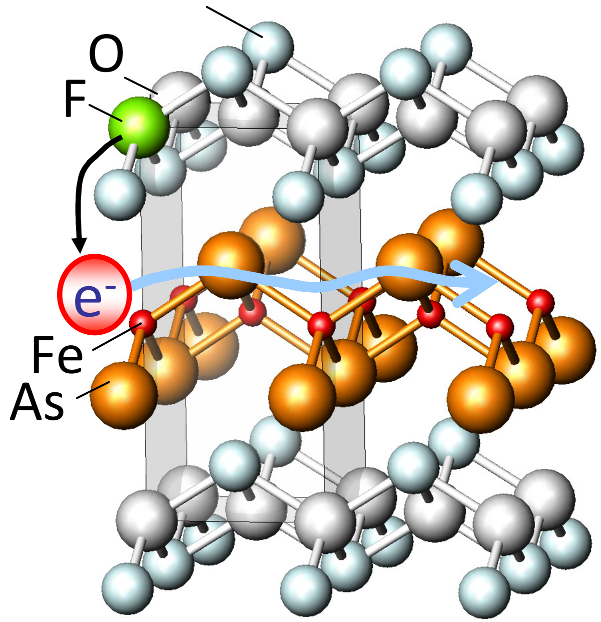
F-doped LaFeAsO

published on- line in JACS (2008) on Feb 23

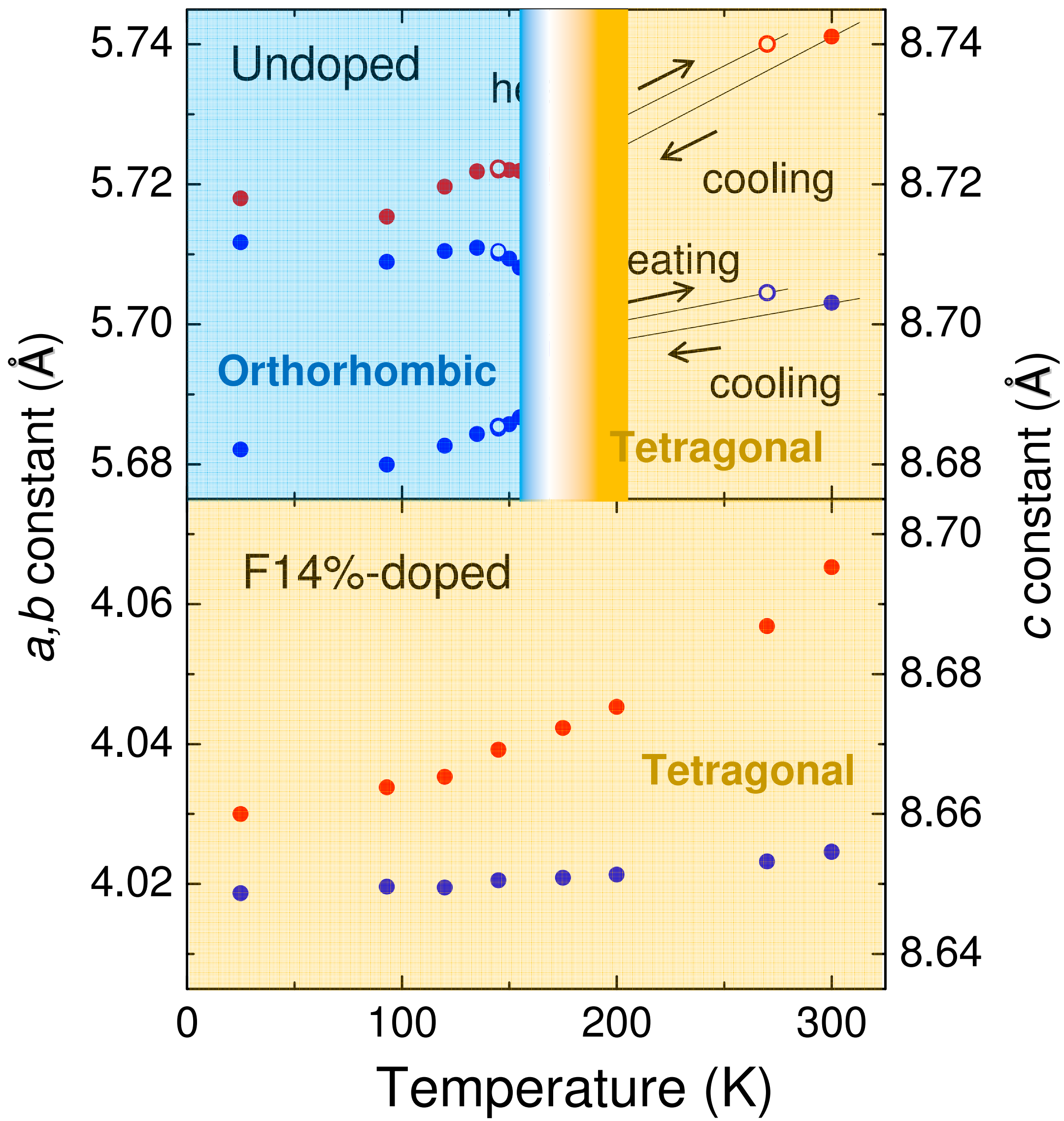








Lattice constant vs. T



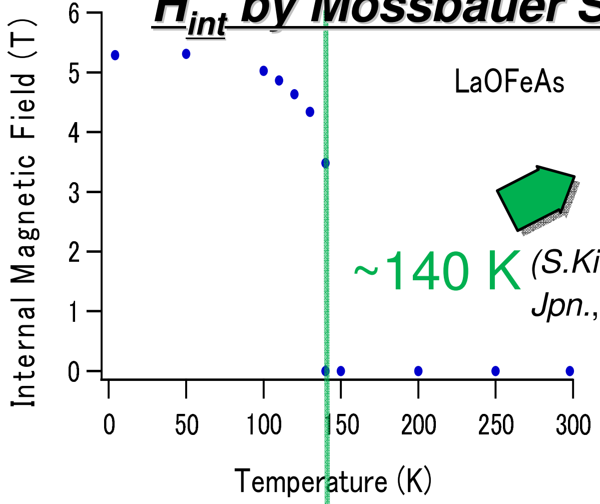
$LaFeAsO_{1-x}F_x$

- *a*, *b* lattice constants drastically separate at ~160 K.
- ~0.5 % difference between *a* and *b* @ 120 K.
- F-doping keeps the tetragonal symmetry down to 25 K>.

T.Nomura et al. Cond-mat/0804.3569 (April 22), Supercond.Sci & Technol. (2008)

What happens at ~150K?

H_{int} by Mössbauer Spectroscopy



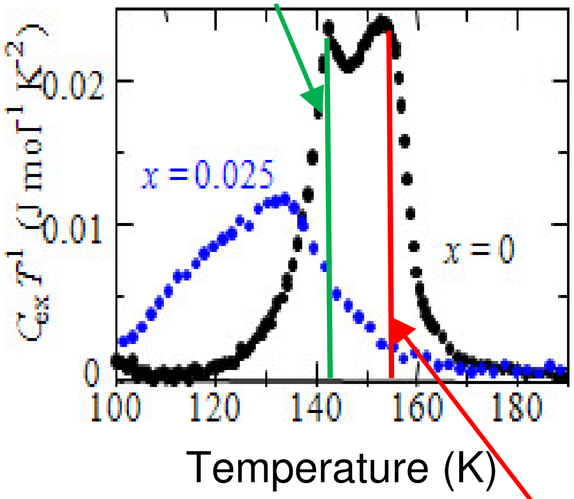
~140 K

(*S.Kitao et al J.Phys. Soc. Jpn.*, **77**, 103706, (2008).)

Magnetic Phase Transition

~140 K

Heat Capacity

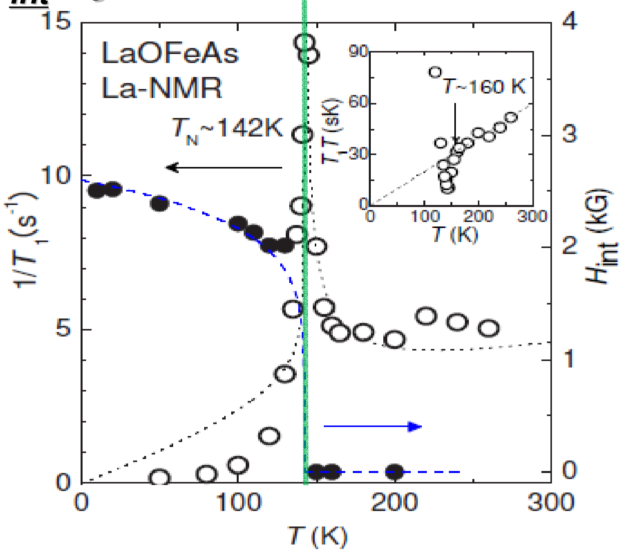


（Y.Kohama et al. PRB. **78**,020512,2008）

~155 K

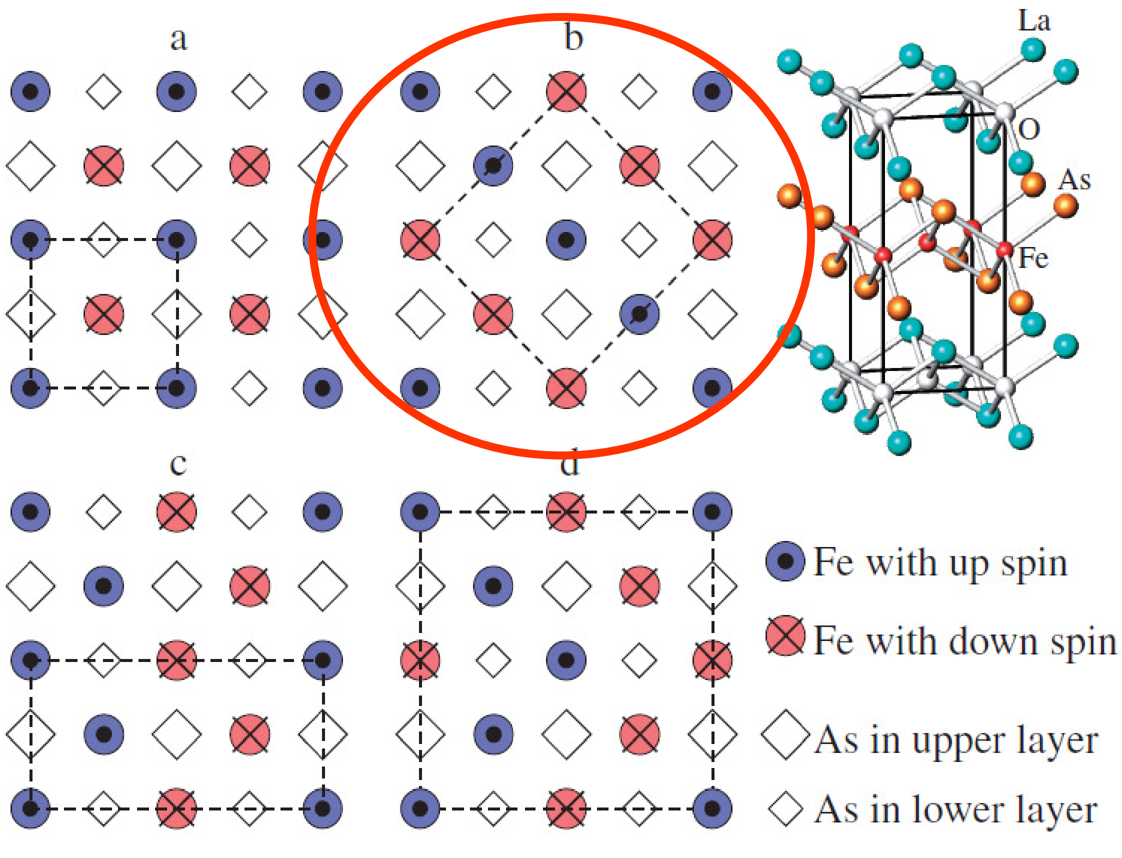
Structural phase transition

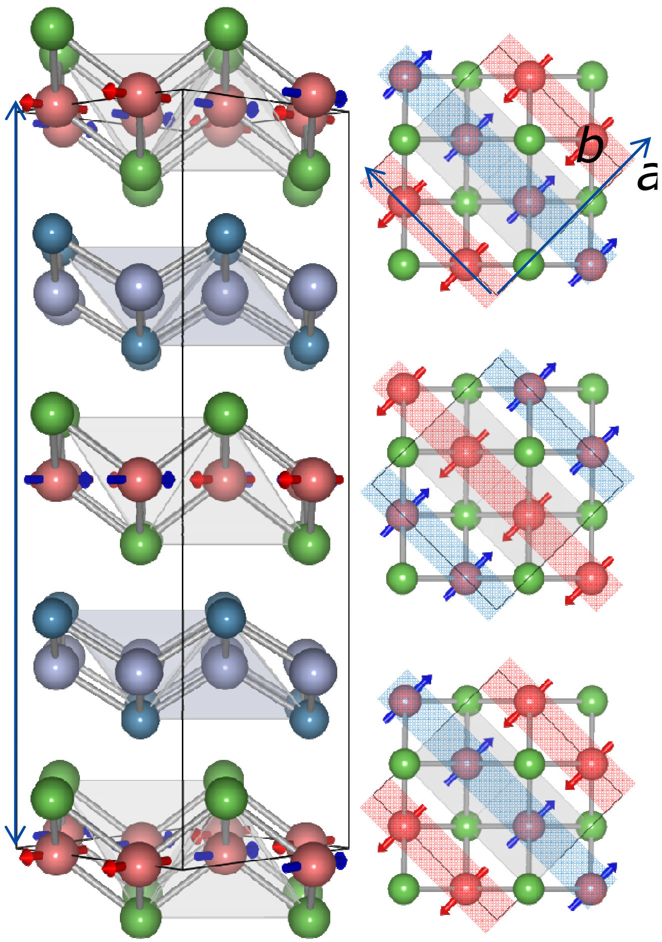
H_{int} by NMR



(Y. Nakai et.al. *J. Phys. Soc. Jpn.*, **77**, 073701, (2008)).

Most stable magnetic ordering in ortho-phase





Most stable AF-phase (stripe-type)

Magnetic moment/Fe = $2\mu_B$

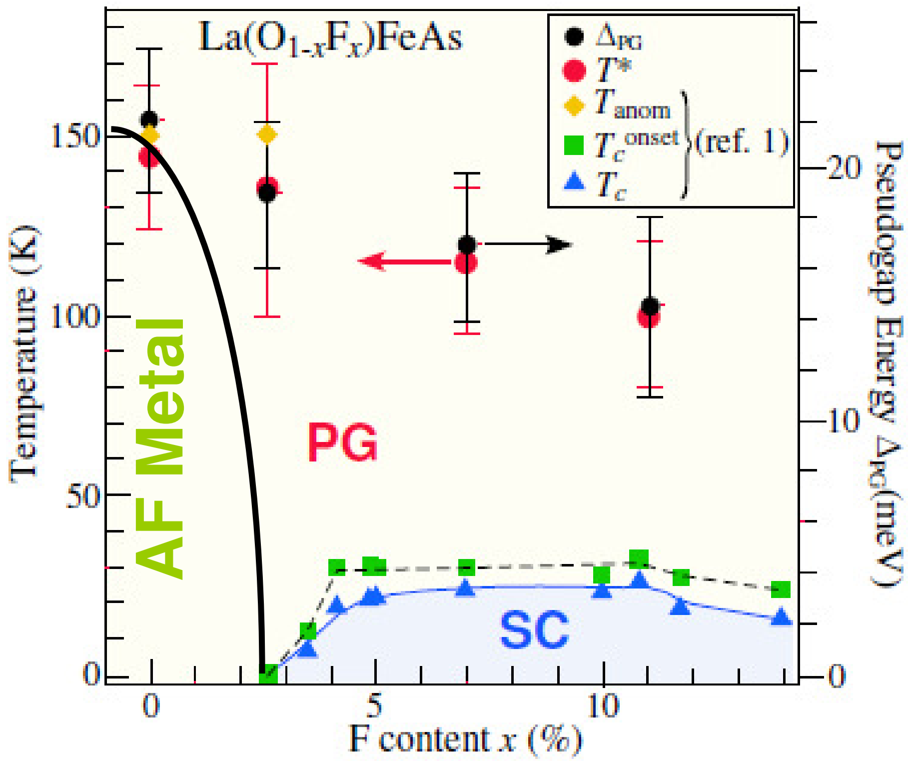
Ishibashi, Terakura,Hosono, JPSJ, 77, 053709 (2008).

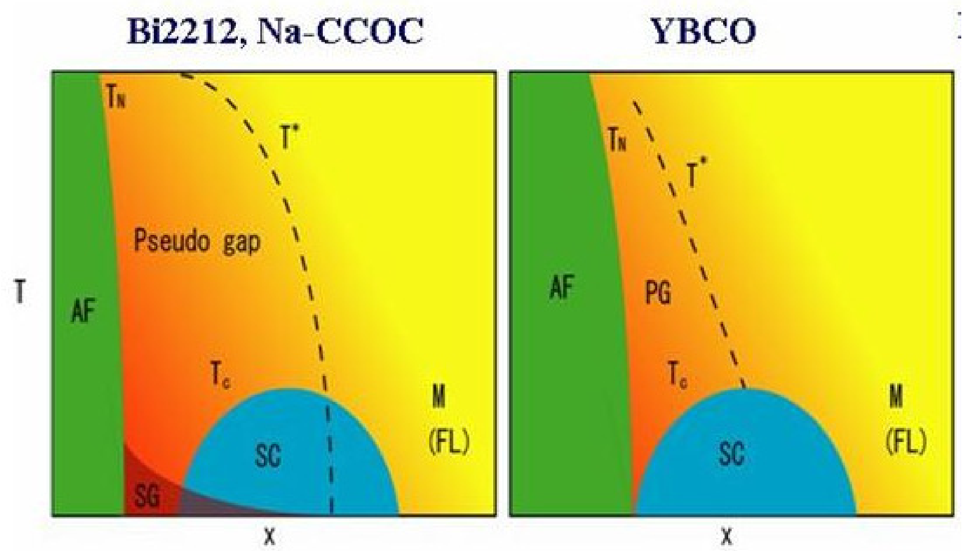
Neutron diffraction

$0.4\mu_B$/Fe

PRB(2008)

Phase Diagram:
A close similarity to Cuprates

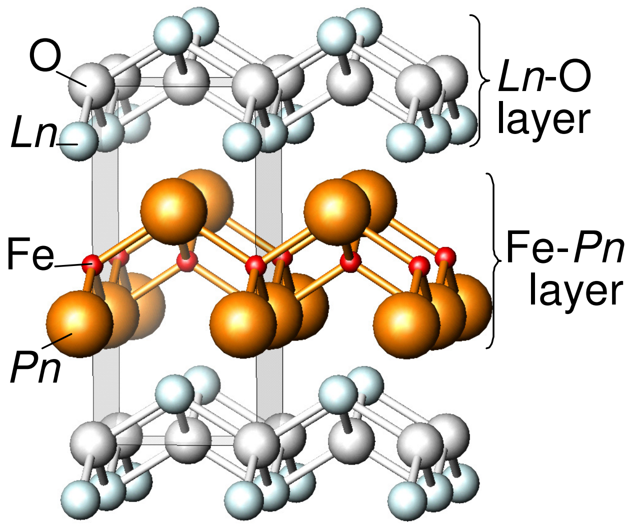




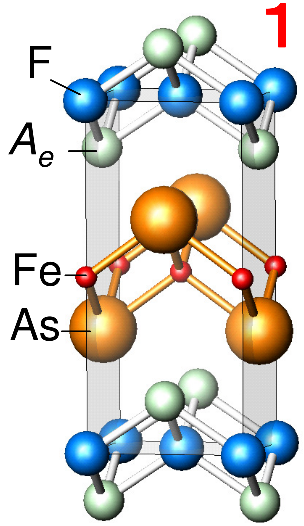
The presence of Pseudo-Gap was observed by PE (Takahashi G, Tohoku U. + Shin G, Tokyo U. + Hosono G. TIT)

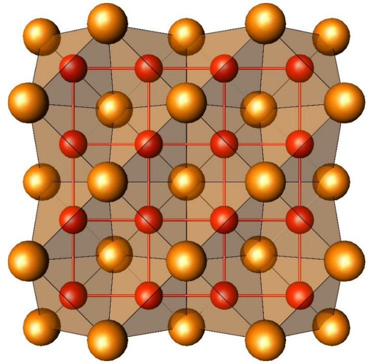
Crystal Structures for Fe-based Superconductors

1111—LnO



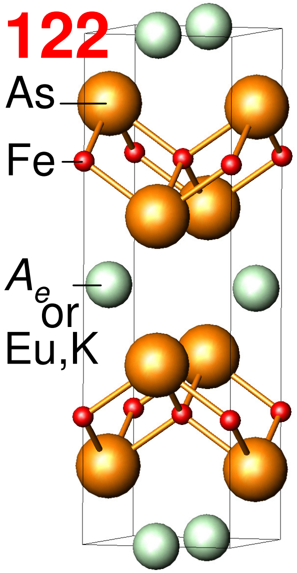
1111—AeF



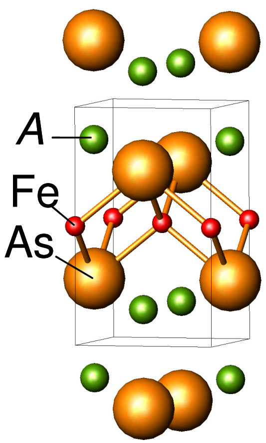


Fe^{2+} square lattice

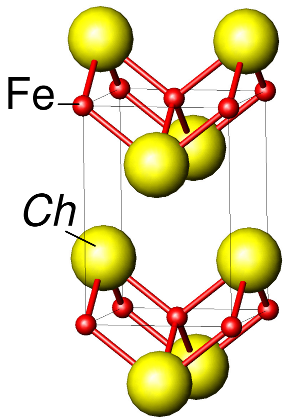
122

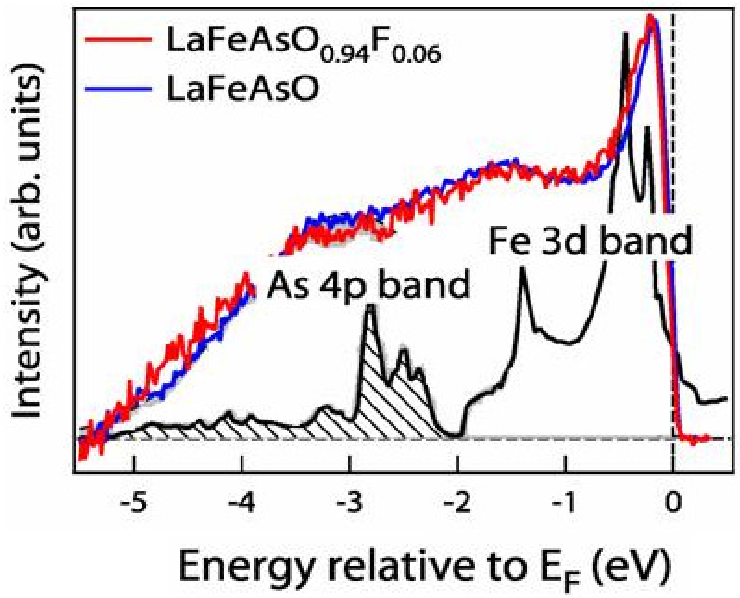


111

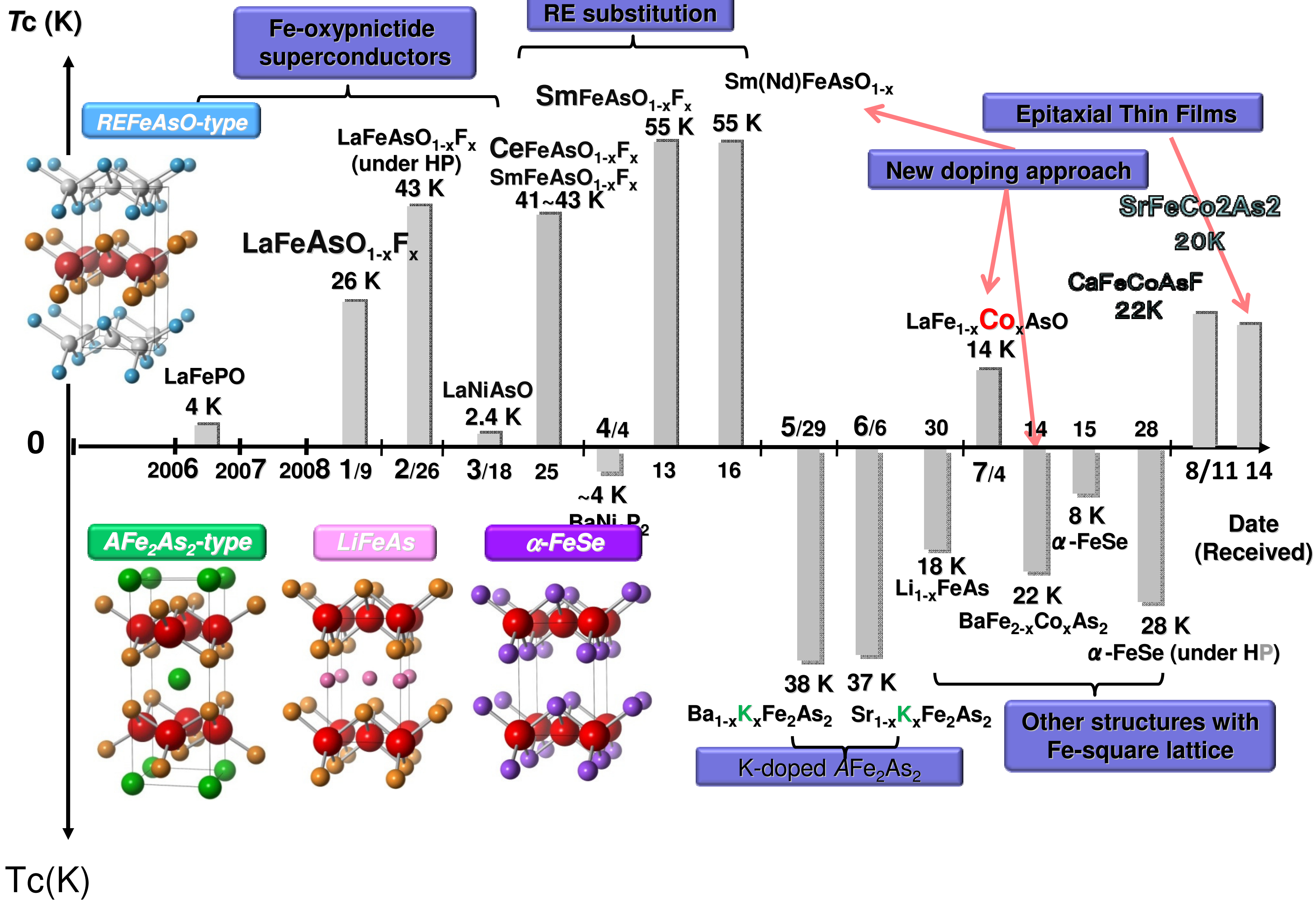


11

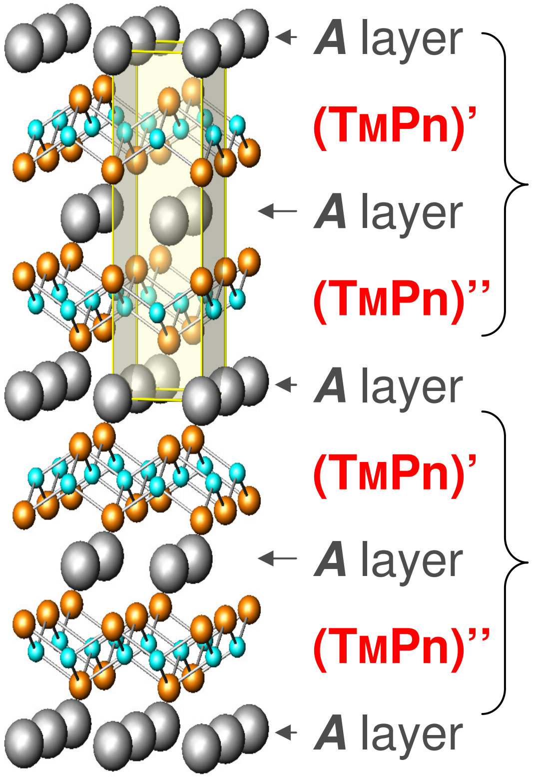


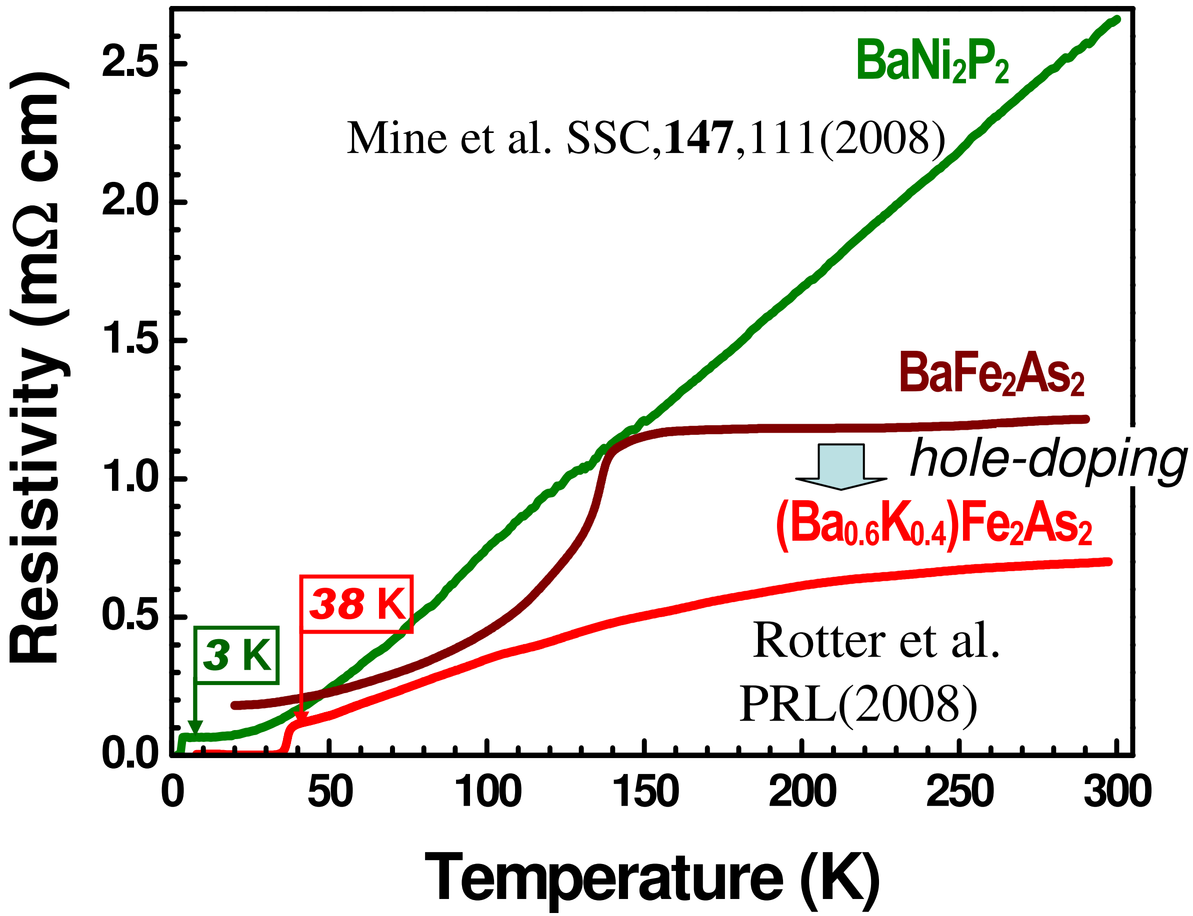


Advances in superconductors with square Fe(Ni) lattice



ATM$_2$*Pn*$_2$: bi-layer structure

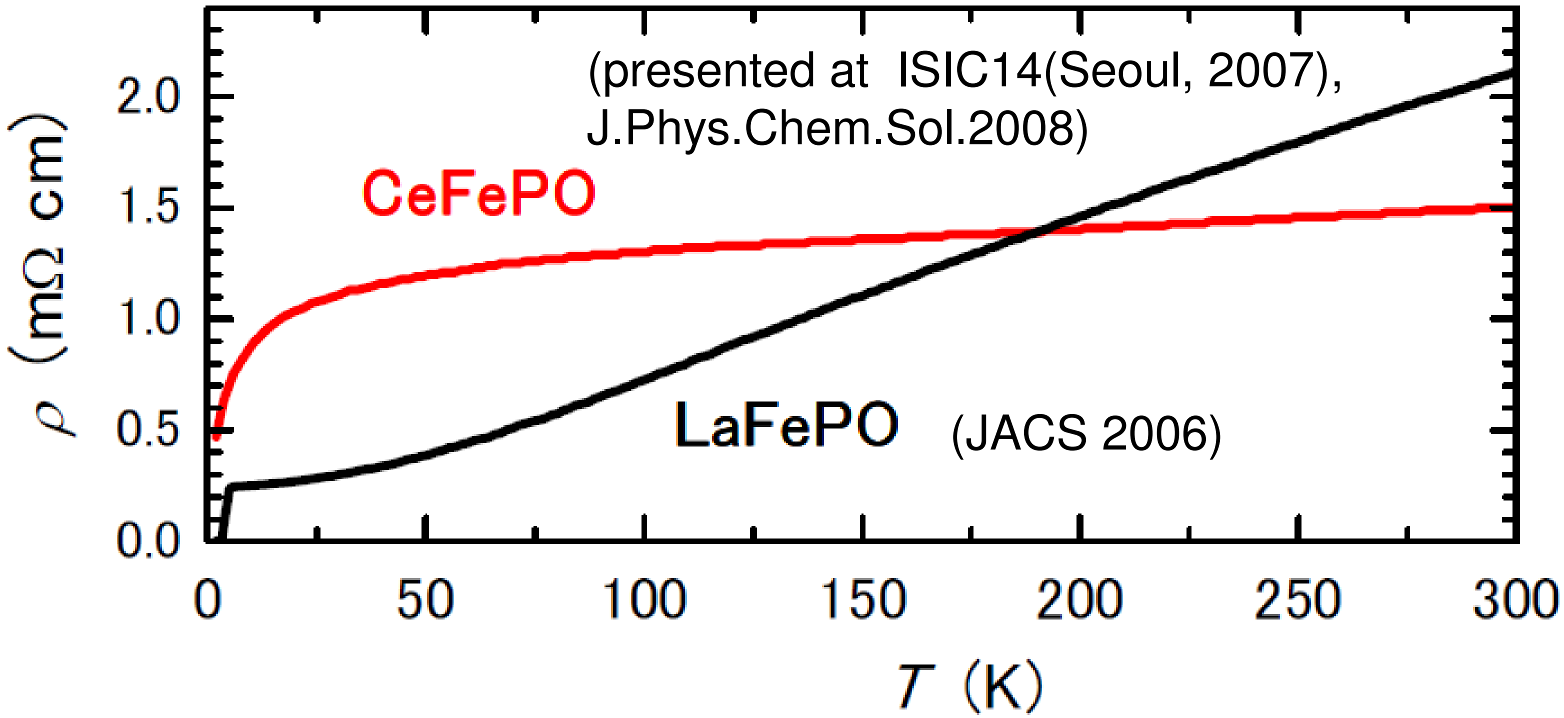




Structural (magnetic) phase transition at high temperature is required for high Tc.

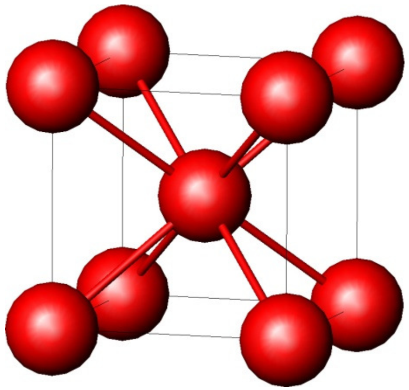
Why we skipped REFeAsO (RE= Ce,----)?

Heavy Fermion(Bruning et al PRL,2008)
γ=700mJmol^{-1}K^{-2}



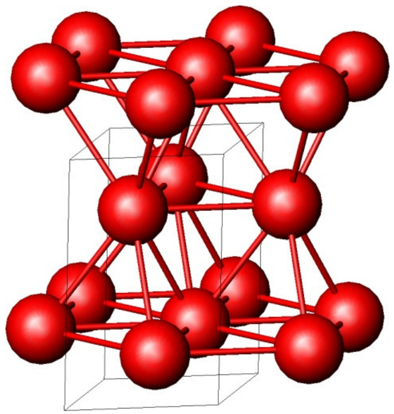
Carrier doping kills magnetism of Fe lattice

- α-Fe (bcc)



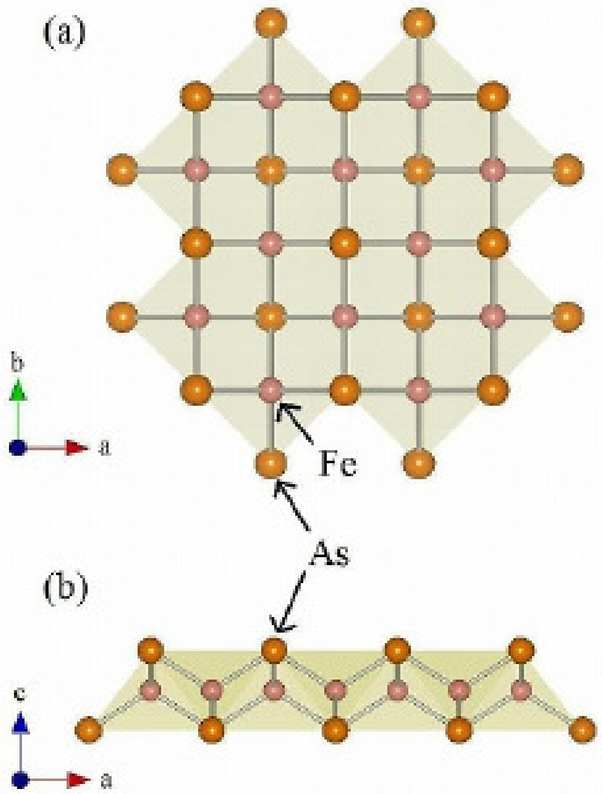
・Ferromagnetic Metal
・d(Fe-Fe) ~0.248 nm

- ε-Fe (hcp)

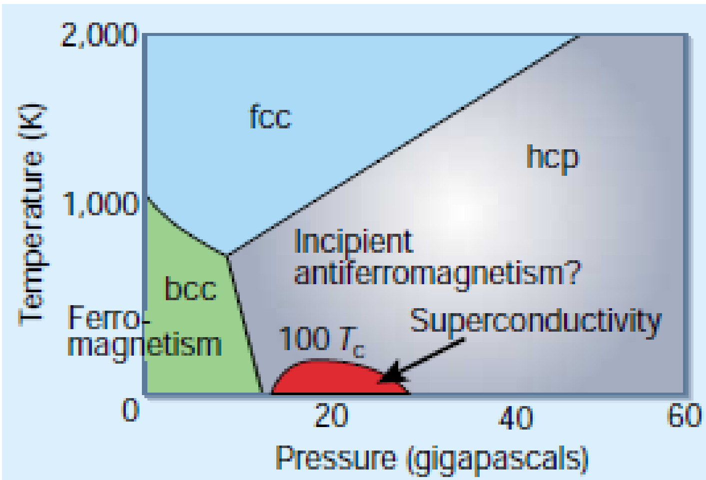


・Superconductors
(~20 GPa, T_c < 2 K)
・d(Fe-Fe)~0.244 nm

- FeAs layer in ReFeAsO



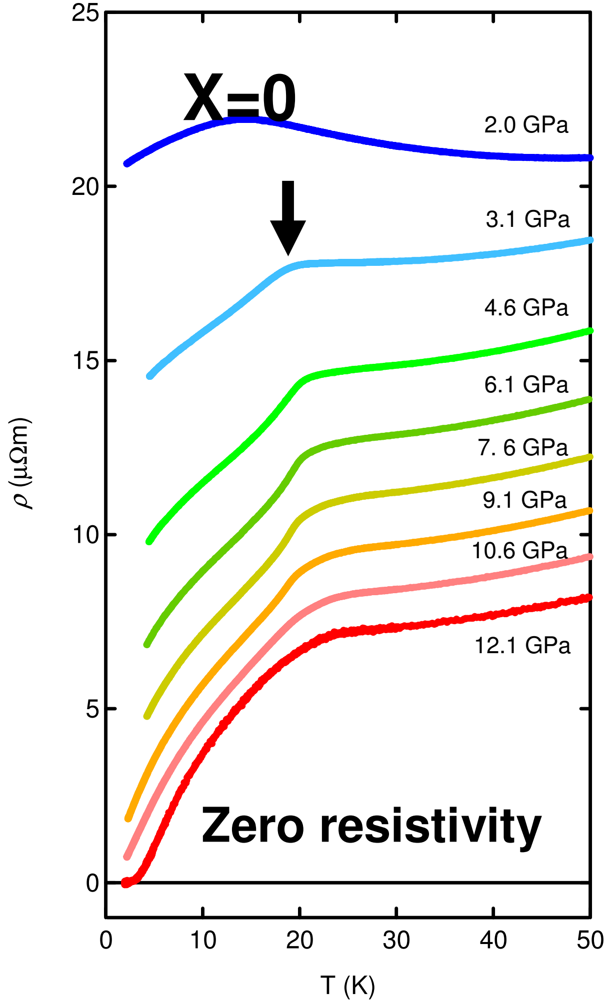
・Superconductors
(Ambient P, T_c > 26 K)
・d(Fe-Fe)~0.285 nm

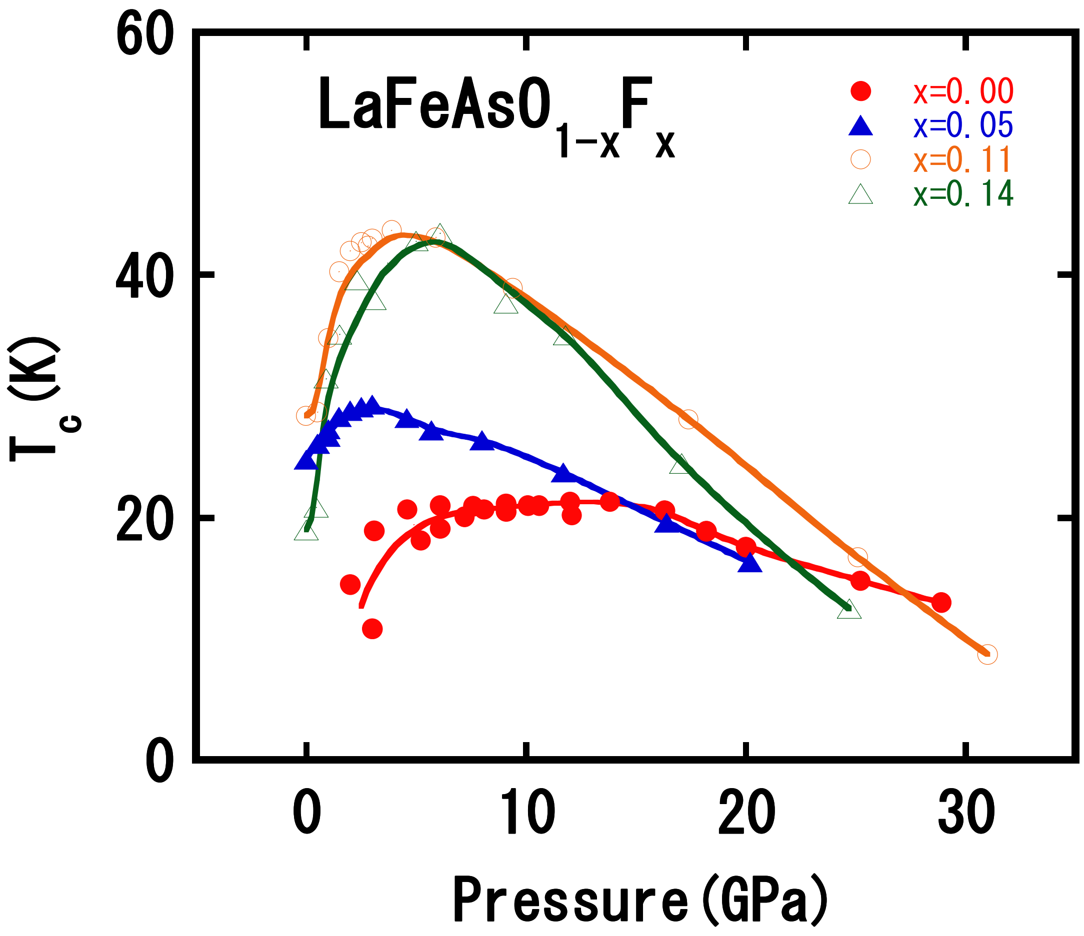


(Saxena et.al. *Nature*, 2001)

Tc-Pressure phase diagram

P-induced Tc in Parent material



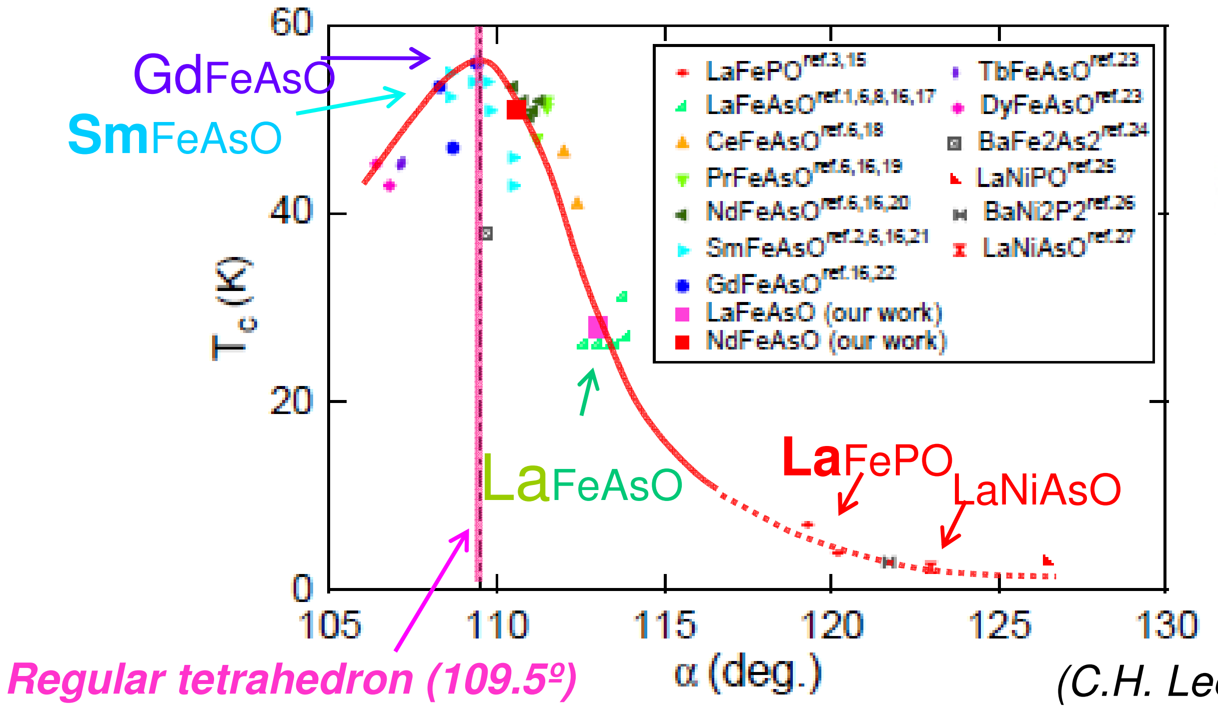


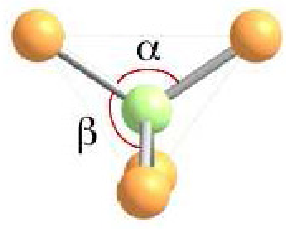
Okada et al (JPSJ 2009)

Takahashi Group (Nihon U.)+ Hosono G(TIT)
*Nature **453,**376(2008)*

Local structure and TC

Tc vs α (As-Fe-As angle)



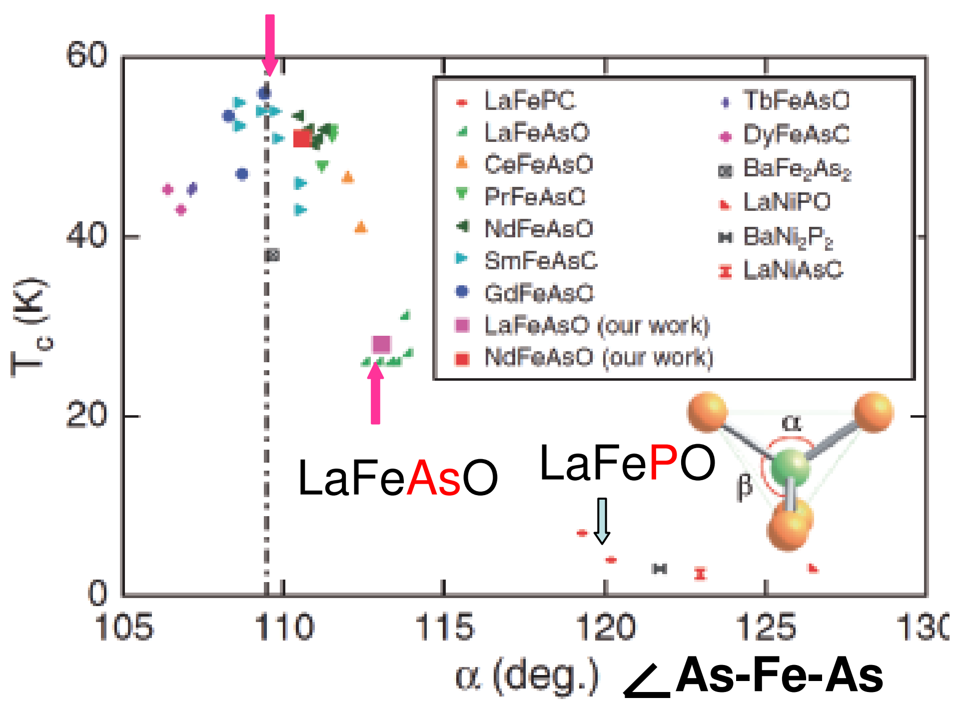


$FeAs_4$-tetrahedron

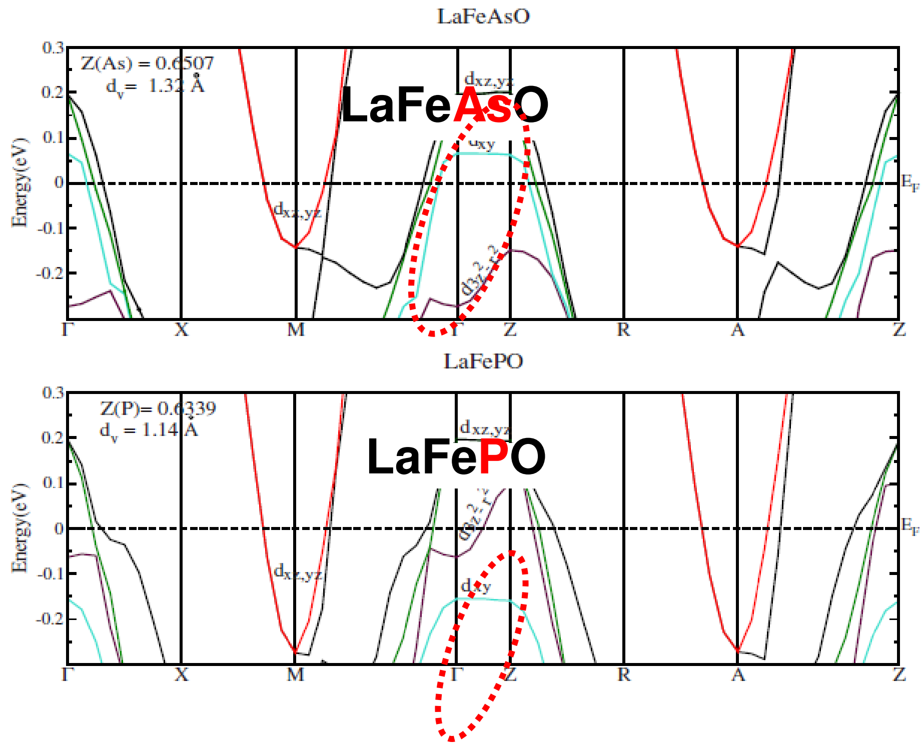
(C.H. Lee et al., JPSJ, 2008)

Higher symmetry of $FeAs_4$ tetrahedron leads to higher *Tc* in *Ln*FeAsO system.

Local Structure and Tc



Lee et al.(JPSJ 2008)



d_{x2-y2} and d_{xy} are shifted

New Fe-1111 member AeFeAsF (Ae = Ca & Sr)

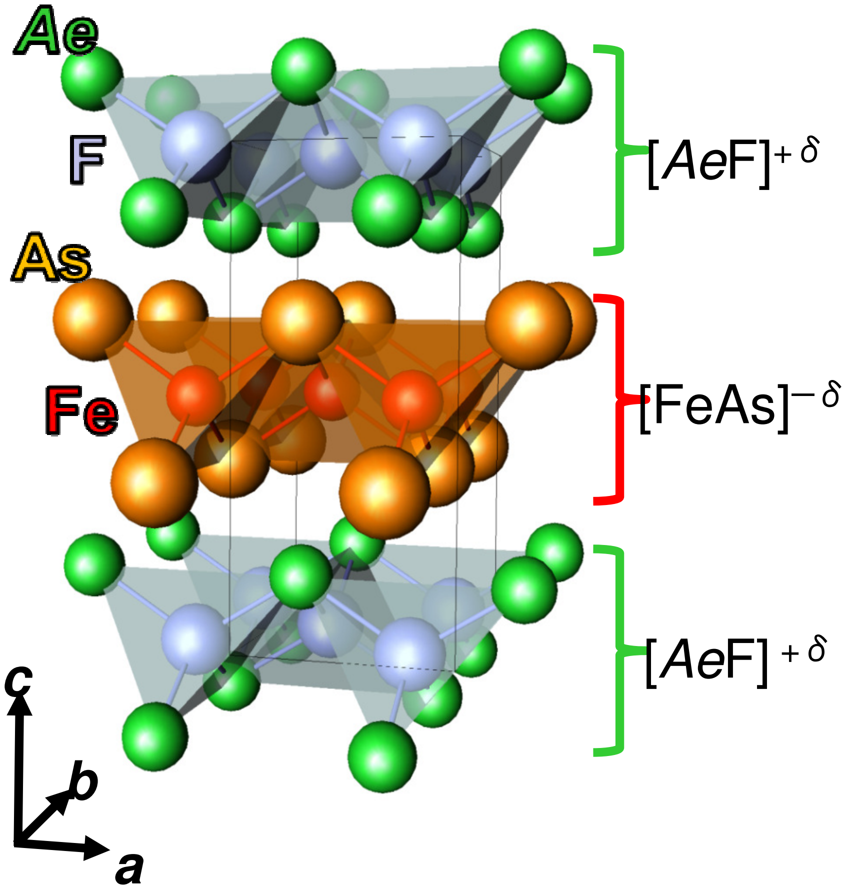
Substitution of blocking layer

[$Ln^{3+}O^{2-}$] layer

Ln: rare-earth element
ex. La, Ce, Sm … etc

[$Ae^{2+}F^{-}$] layer

Ae: alkali-earth element
ex. Ca, Sr



Doping method

① Doping to AeF layer: *Ae*, F → ? ✕

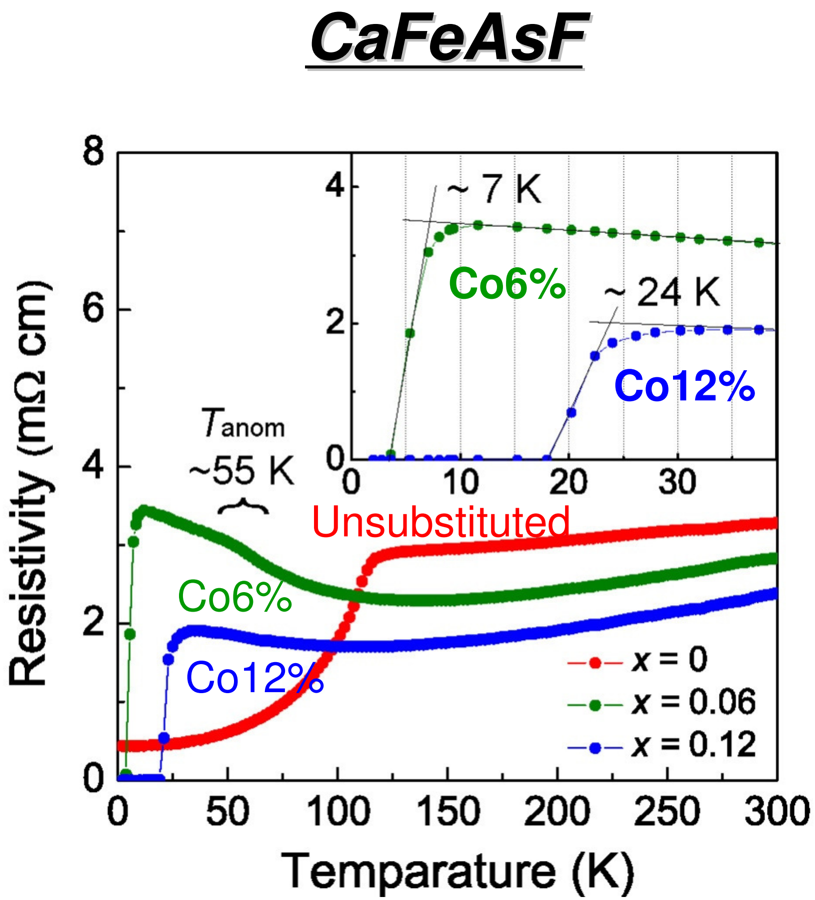
② Doping to FeAs layer: Fe → Co, Ni ○

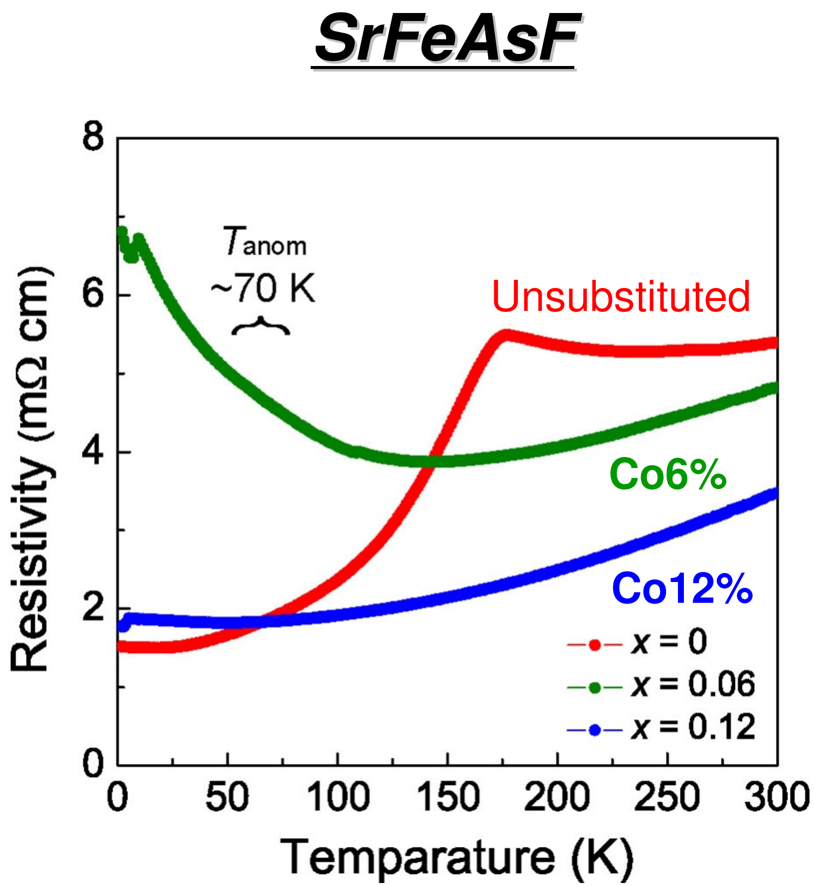
$CaFe_{1-x}Co_xAsF$ Tc = ~22 K

$SrFe_{1-x}Co_xAsF$ Tc = ~4 K

(Matsuishi et al., JACS, JPSJ(2008))

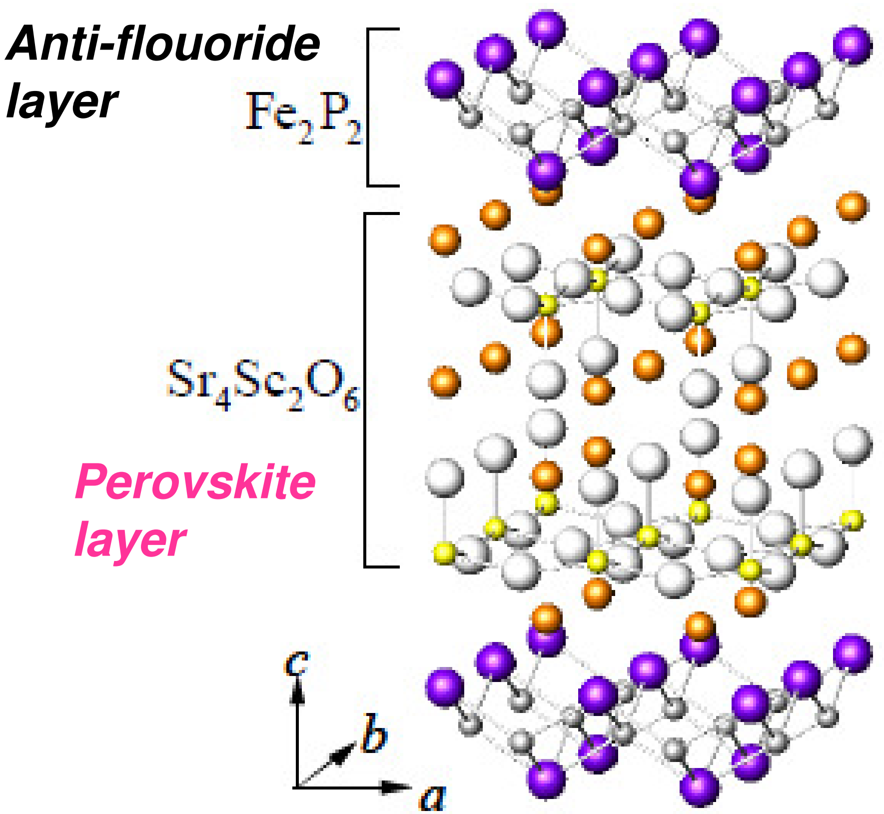
Superconductivity in $AeFe_{1-x}Co_xAsF$

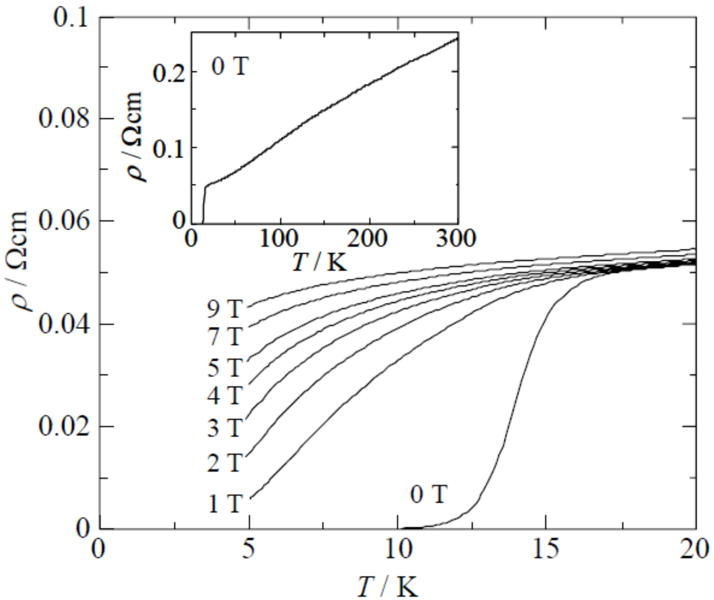


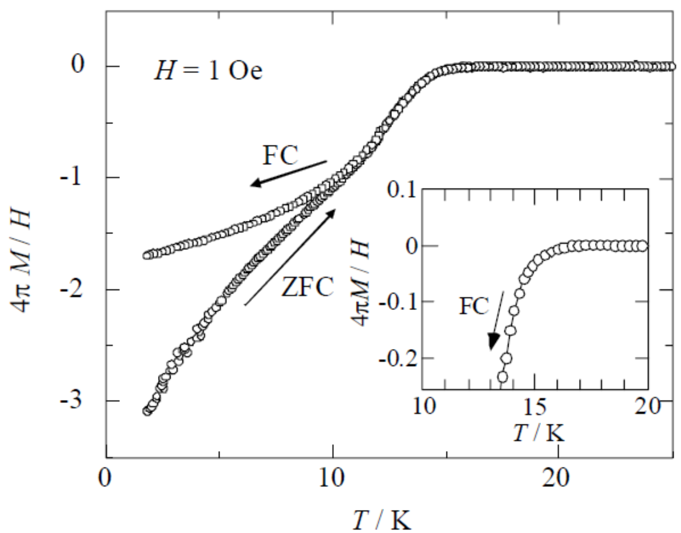


Fe^{2+} $3d^6$ Co^{2+} $3d^7$

Perovskite-blocking layer







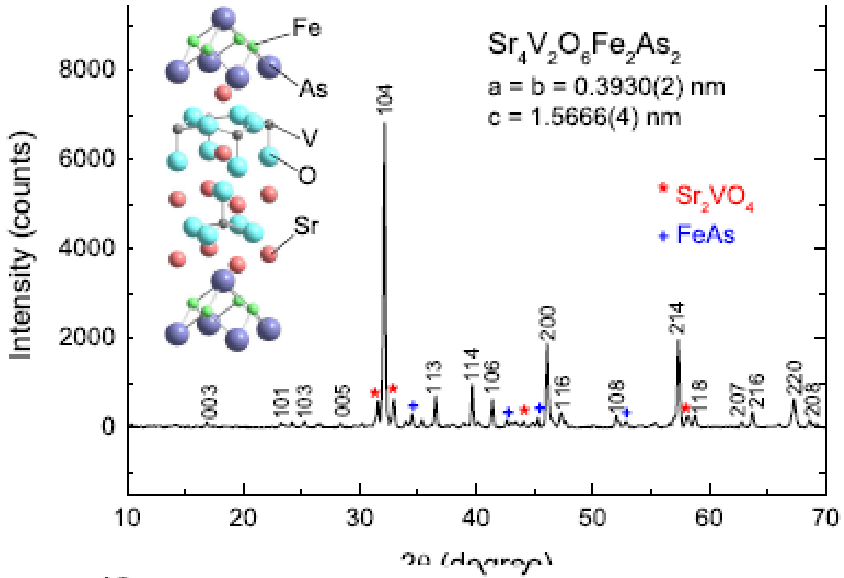
H.Ogino et al.
Presented at APS(March)

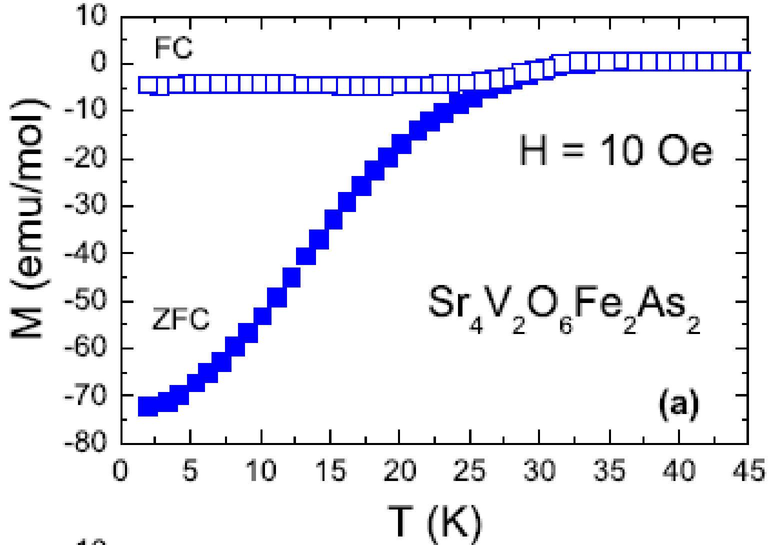
April 12,2009

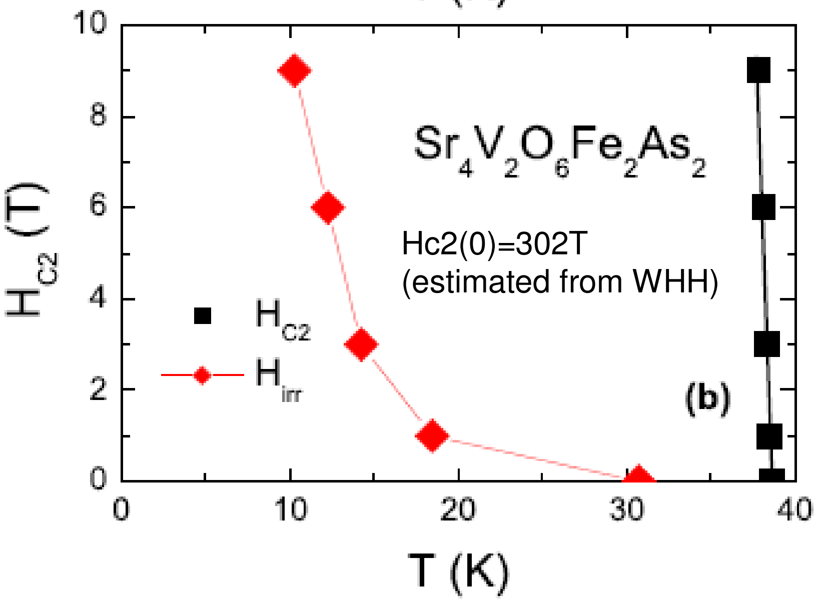
Superconductivity at 37.2 K in the Parent Phase $Sr_4V_2O_6Fe_2As_2$

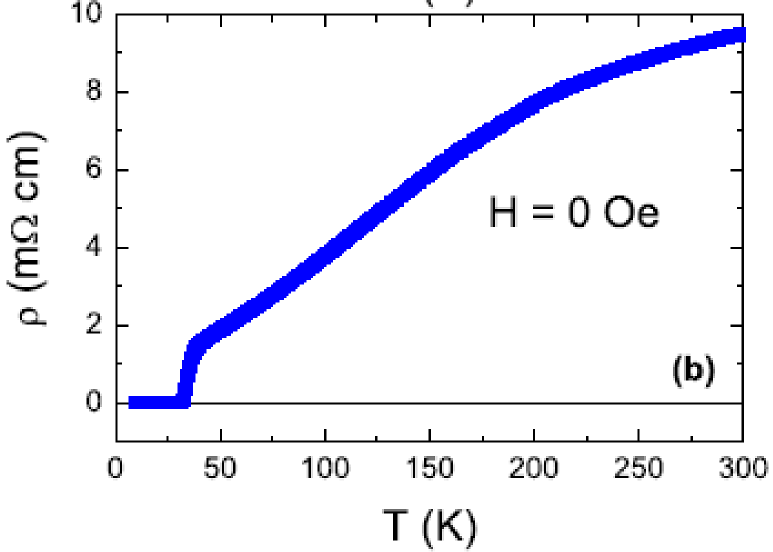
Xiyu Zhu, Fei Han, Gang Mu, Peng Cheng, Bing Shen, Bin Zeng, and Hai-Hu Wen*

National Laboratory for Superconductivity, Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, P. O. Box 603, Beijing 100190, China









A Tentative Mechanism

Intercalation

H_2O (~0.3nm) is larger than Sr^{2+} (0.23nm)

OH^- is more plausible

$SrFe_2As_2 \Rightarrow Sr(OH)_xFe_2As_2$ **Tc (max)= 25K**

Hole-doping to FeAs layer
via OH^- insertion to Sr-layer

Cf. $Sr(Fe_{2-x}Co_x)As_2$
Tc(max)=22K

Chemical doping with H_2O is possible in Sr122.

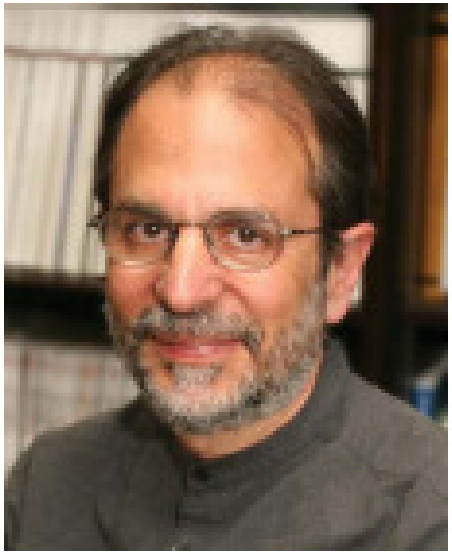
Comparison with Cuprates and MgB_2

	Fe-oxypnictides	MgB_2	Cuprates
Parent Material	(bad) metal (T_N~150K)	metal	Mott Insulator (T_N~400K)
Fermi Level	3d 5-bands	2-bands	3d single band
Max Tc	56K	40K	~140K
Impurity effect	robust	sensitive	sensitive
Sc gap symmetry	extended-s-wave(?)	s-wave	d-wave
$Hc^2(0)$	100-200T>	~40T	~100T
Jc	?		

Contemporary superconducting materials

Chemical Communications **2005**,5373-5377.

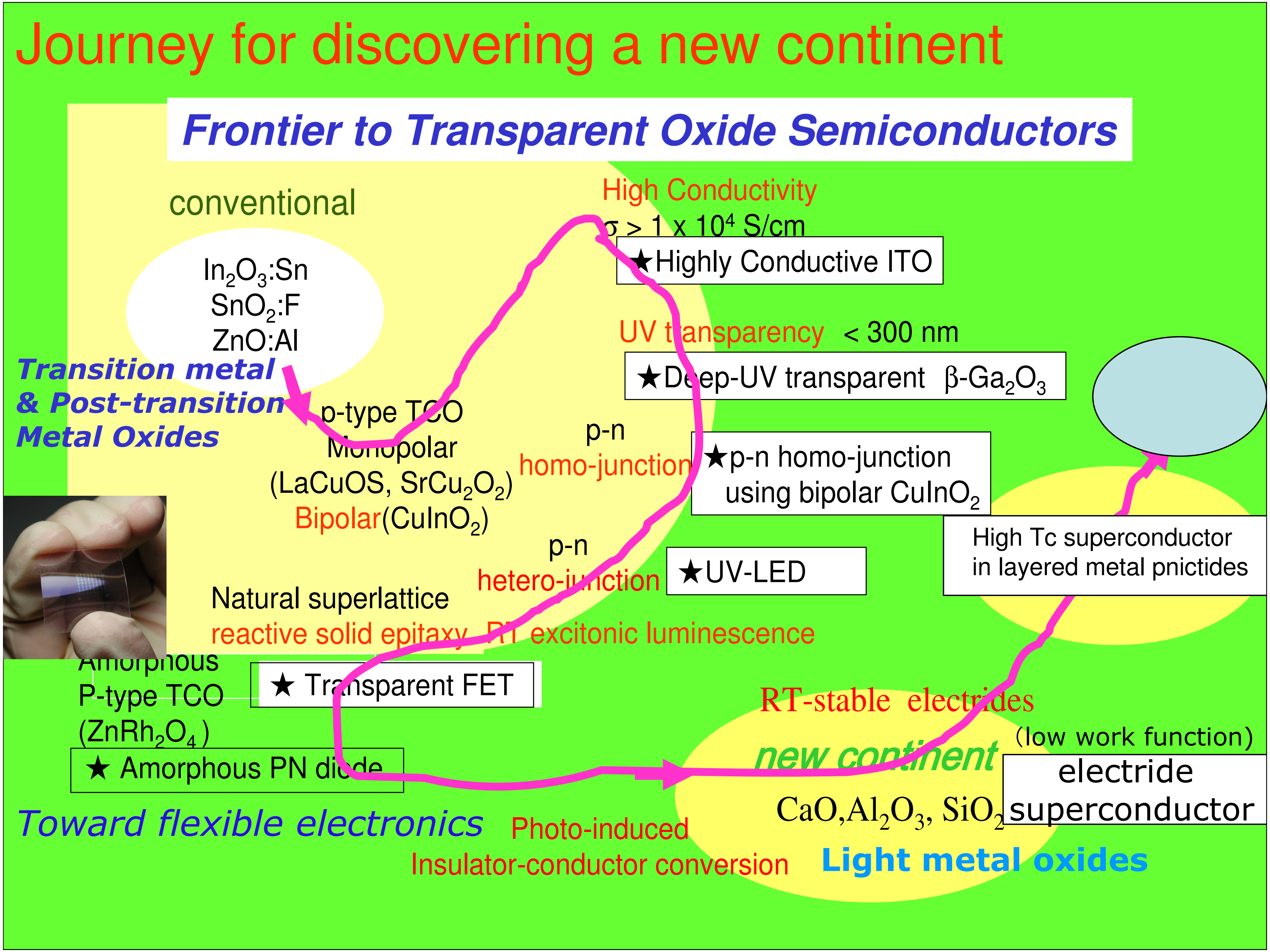
By Bob Cava



Robert Cava is Chair of the Department of Chemistry at Princeton and a Professor in Chemistry and Materials. He is a Fellow of the American Physical Society and the American Ceramic Society, and a member of the US National Academy of Sciences. He was Acting Director of the Princeton Materials Institute from 2001 to 2002. He began at Princeton in 1997 after working at Bell Laboratories from 1979 to 1997, where he was a Distinguished Member of Technical Staff. He was a National Research Council Postdoctoral Fellow at NIST from 1978 to 1979 after receiving his Ph.D. in Ceramics from MIT in 1978.

New superconductors are currently being discovered at 2-4 per year.

The search for new superconductors has largely been *the domain of condensed matter physicists* knowledgeable in the synthesis of intermetallic or oxide compounds. *Chemists have much to offer the field*, and have also found new superconductors, both in focused searches and by accident in the synthetic programs with other goal.



Journey for discovering a new continent
Frontier to Transparent Oxide Semiconductors
conventional
In_2O_3:Sn
SnO_2:F
ZnO:Al
Transition metal
& Post-transition
Metal Oxides
High Conductivity
$\sigma > 1 \times 10^4$ S/cm
★Highly Conductive ITO
UV transparency < 300 nm
★Deep-UV transparent β-Ga_2O_3
p-type TCO
Monopolar
(LaCuOS, $SrCu_2O_2$)
Bipolar($CuInO_2$)
p-n
homo-junction
★p-n homo-junction using bipolar $CuInO_2$
p-n
hetero-junction
★UV-LED
High Tc superconductor in layered metal pnictides
Natural superlattice
reactive solid epitaxy
RT excitonic luminescence
Amorphous
P-type TCO
($ZnRh_2O_4$)
★ Transparent FET
★ Amorphous PN diode
RT-stable electrides
new continent
(low work function)
electride
superconductor
CaO, Al_2O_3, SiO_2
Toward flexible electronics
Photo-induced
Insulator-conductor conversion
Light metal oxides