Separation of magnetism and high-T_c superconductivity in $Ca_{1-x}R_xFe_2As_2$ under pressure

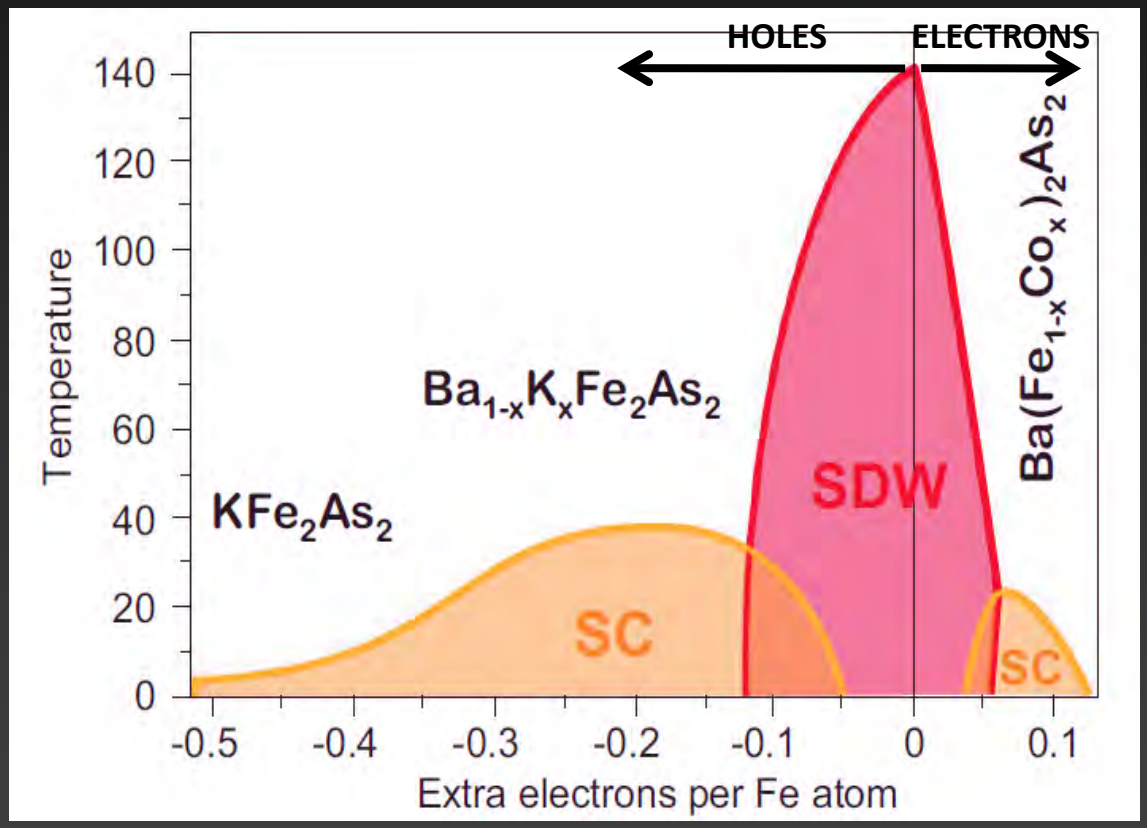
Johnpierre Paglione

Center for Nanophysics and Advanced Materials
Physics Department, University of Maryland

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

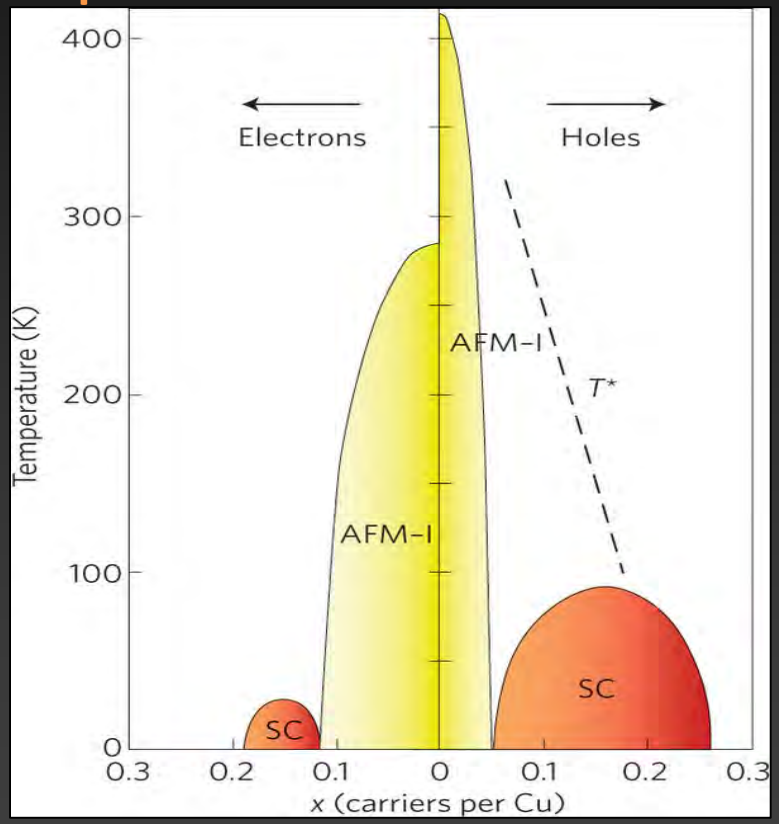
Electron/Hole Asymmetry?

Intermetallic iron-pnictides



Kordyuk et al (2010)

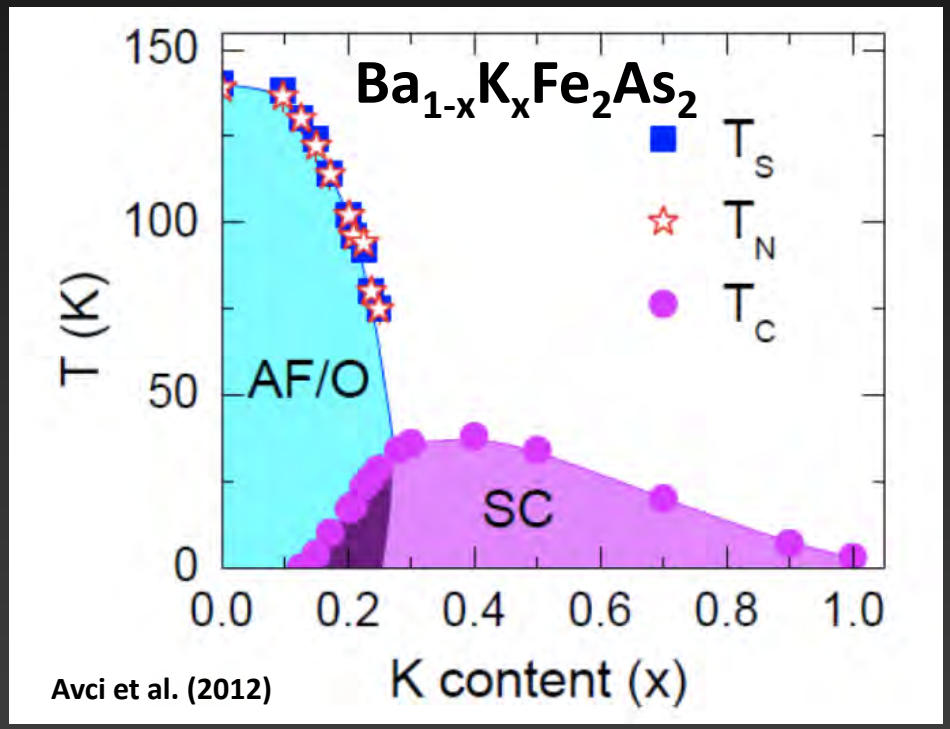
cuprates



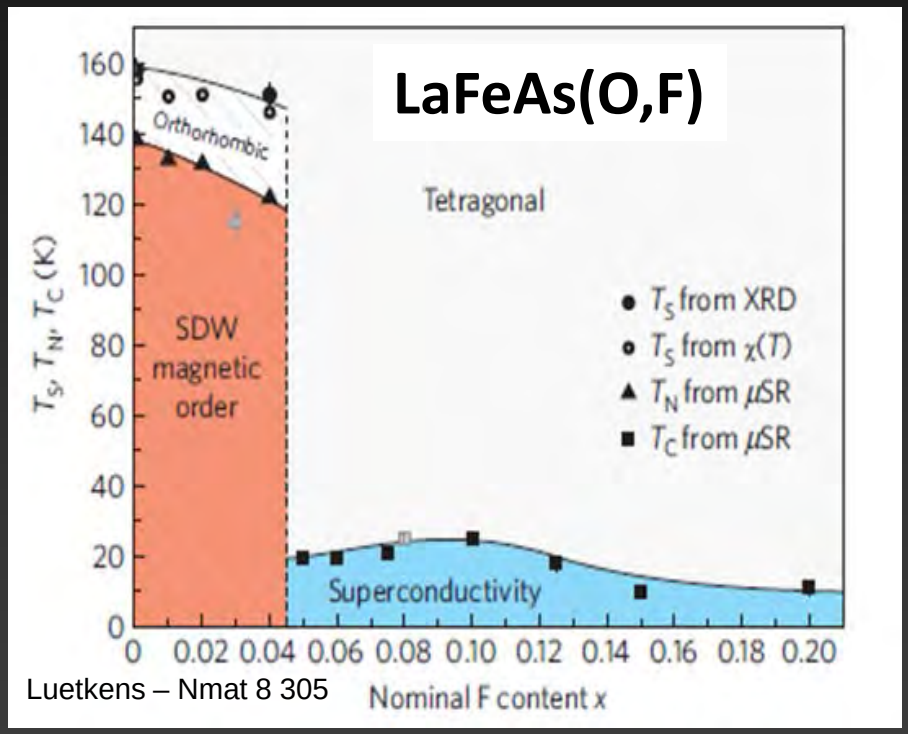
Orenstein/Vishwanath, Nature (2010)

$Ca_{1-x}La_xFe_2As_2$ under pressure

AFM/SC Coexistence?



Avci et al. (2012)

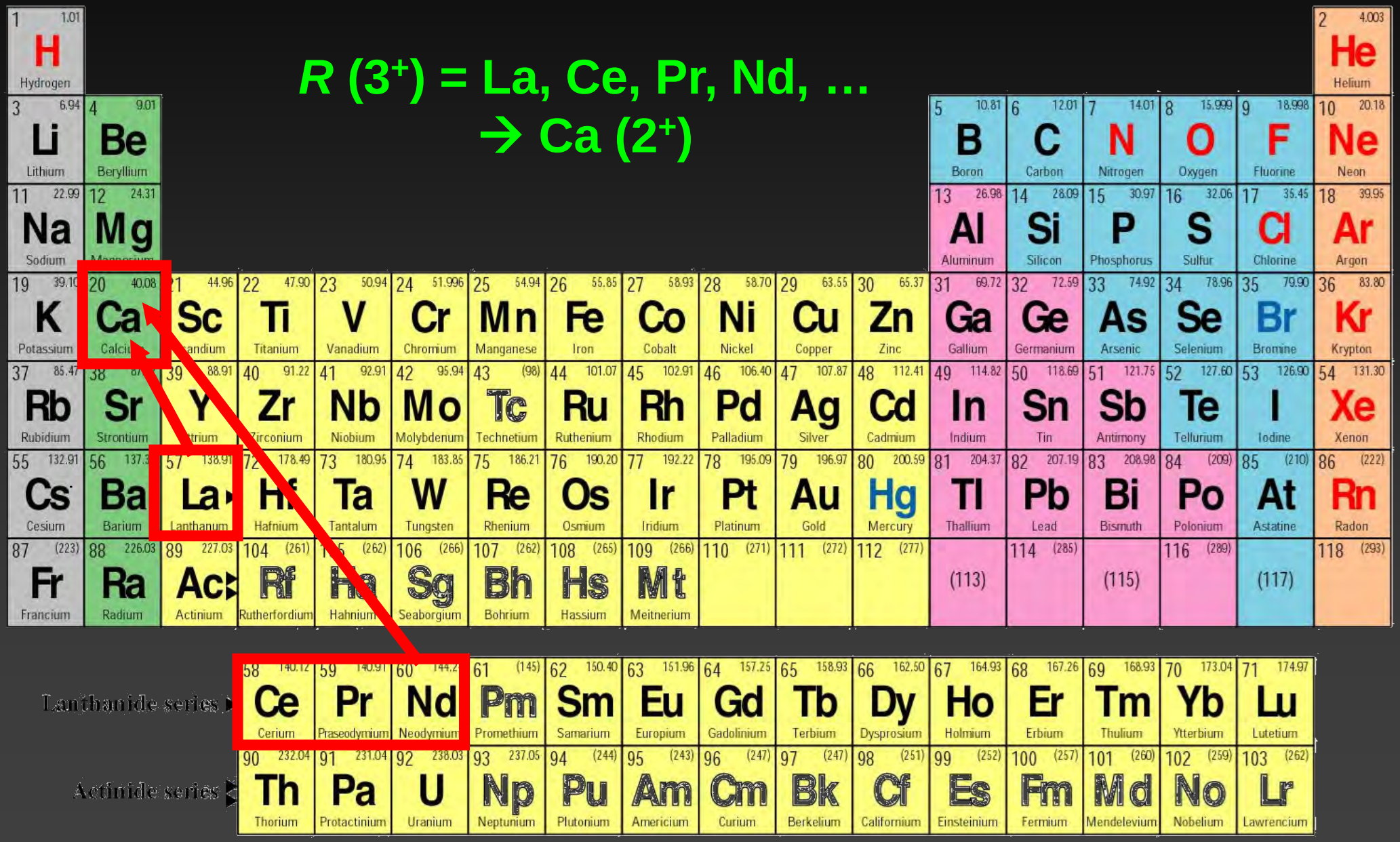


Luetkens – Nmat 8 305

- A-, T- and P-doped systems exhibit microscopic coexistence
- Oxypnictides do not!?

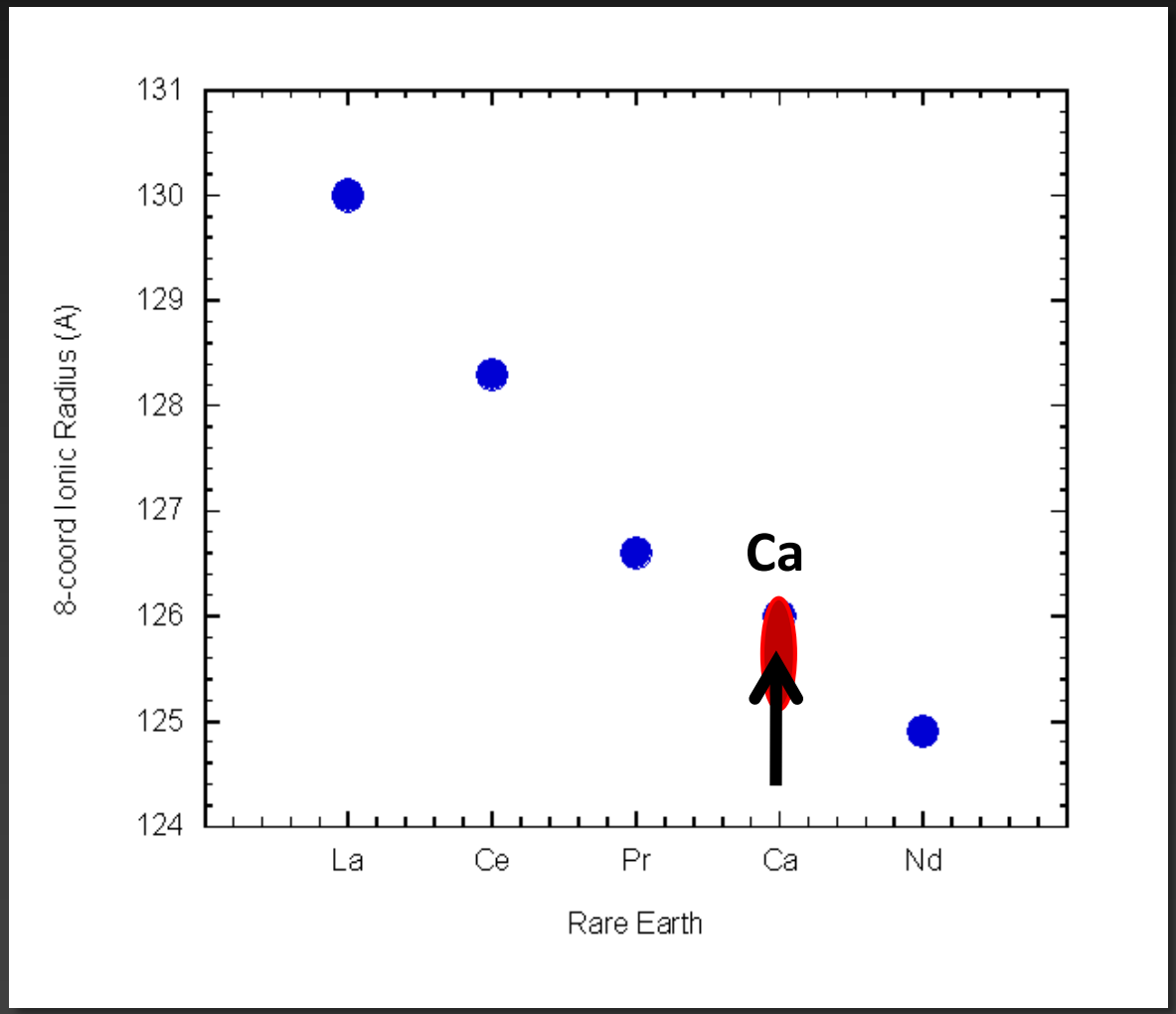
Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

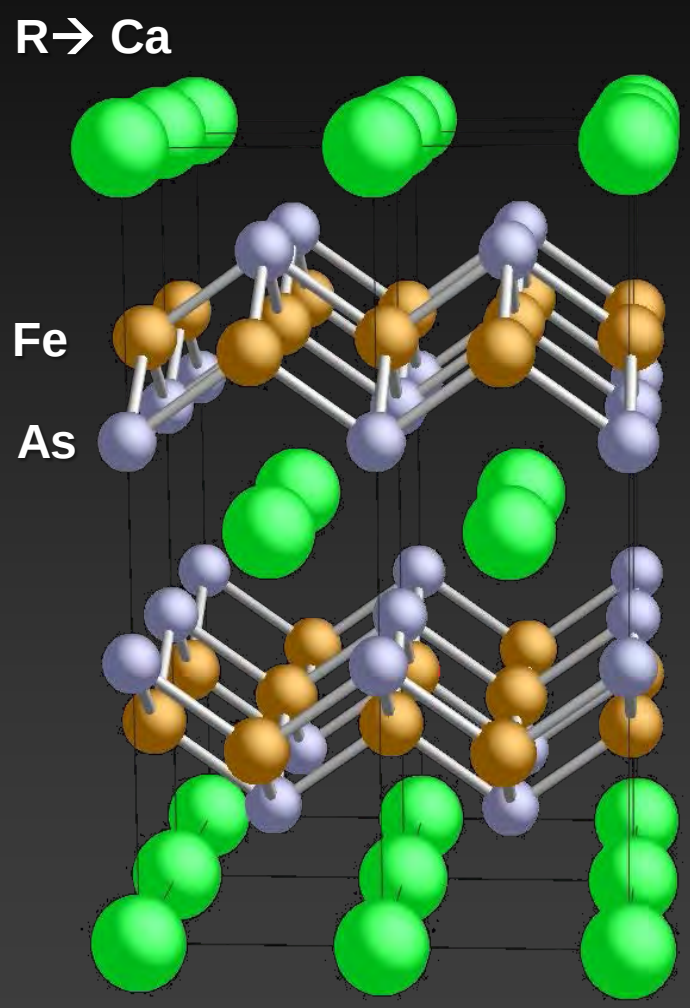
R **(3^+) = La, Ce, Pr, Nd, …**
→ Ca (2^+)



Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

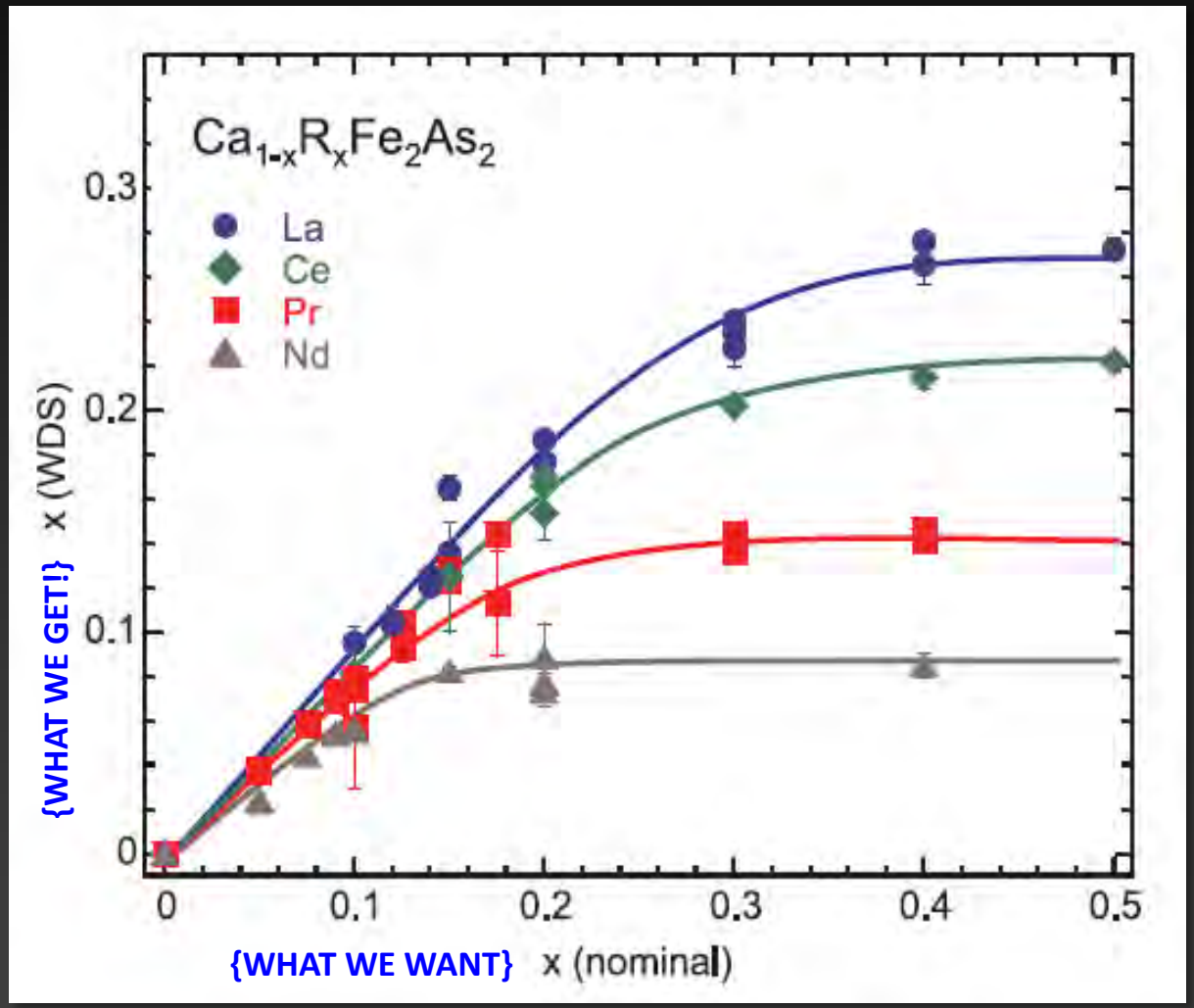
Lanthanide Contraction





Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Single-Crystal Synthesis

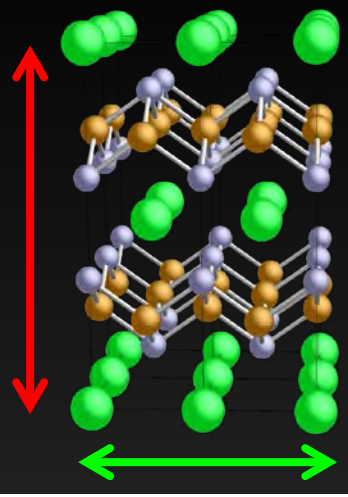


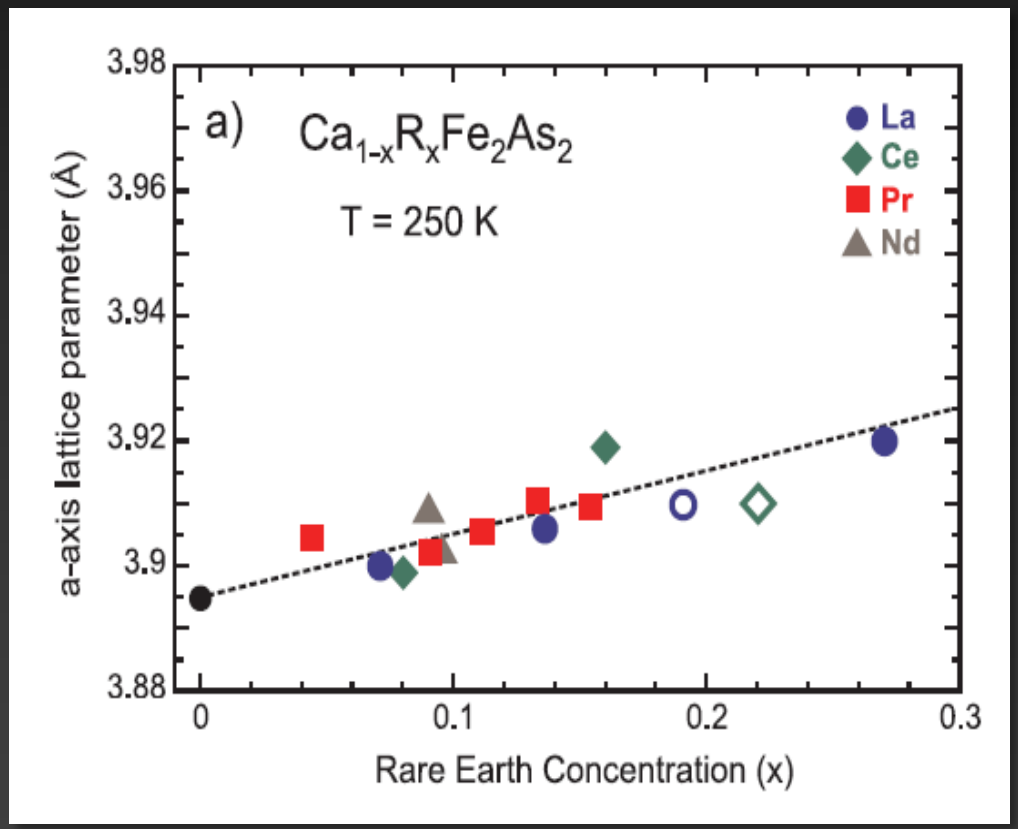
- large (~few mm) crystals
- self-flux method
- solubility limit vs RE

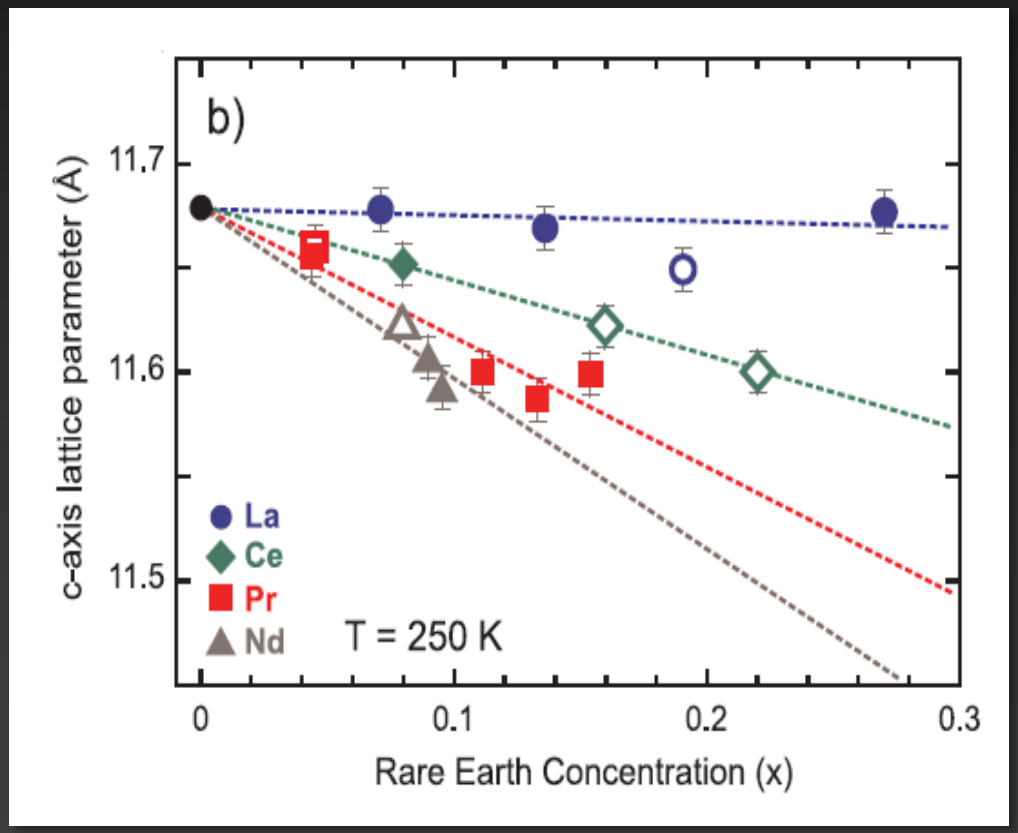
S.R. Saha *et al*, PRB 85, 024525 (2012)

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

X-ray Characterization





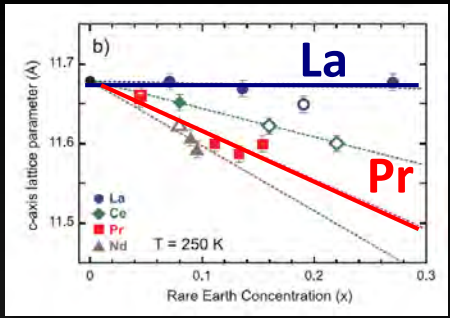


a-axis: ***same for all R***

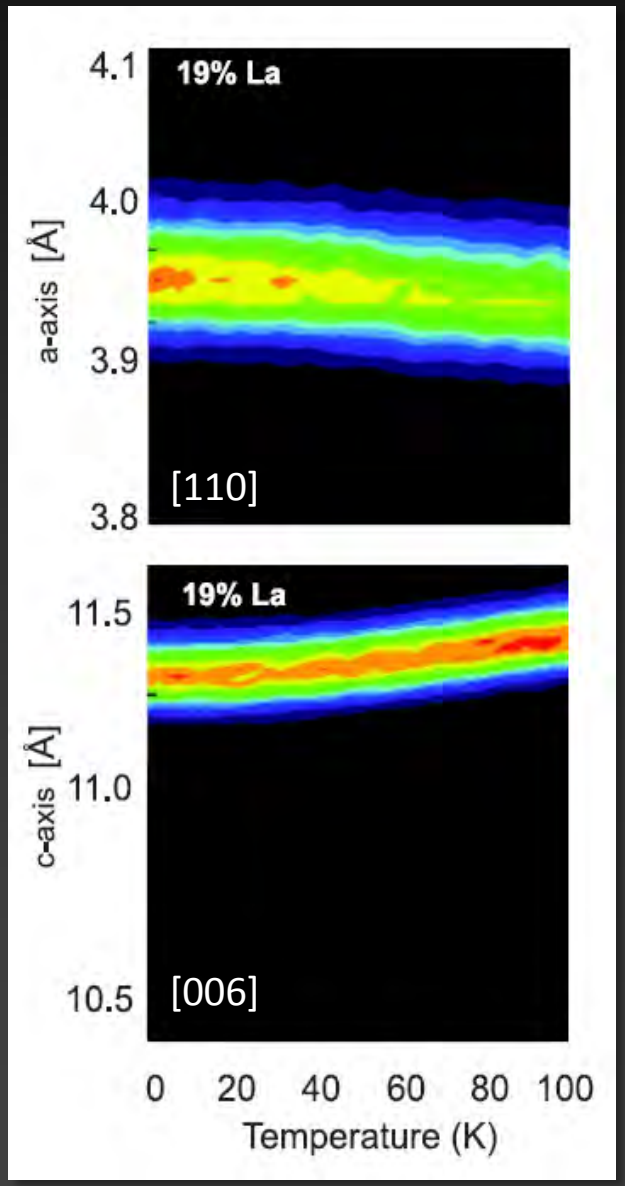
c-axis: ***depends on R***

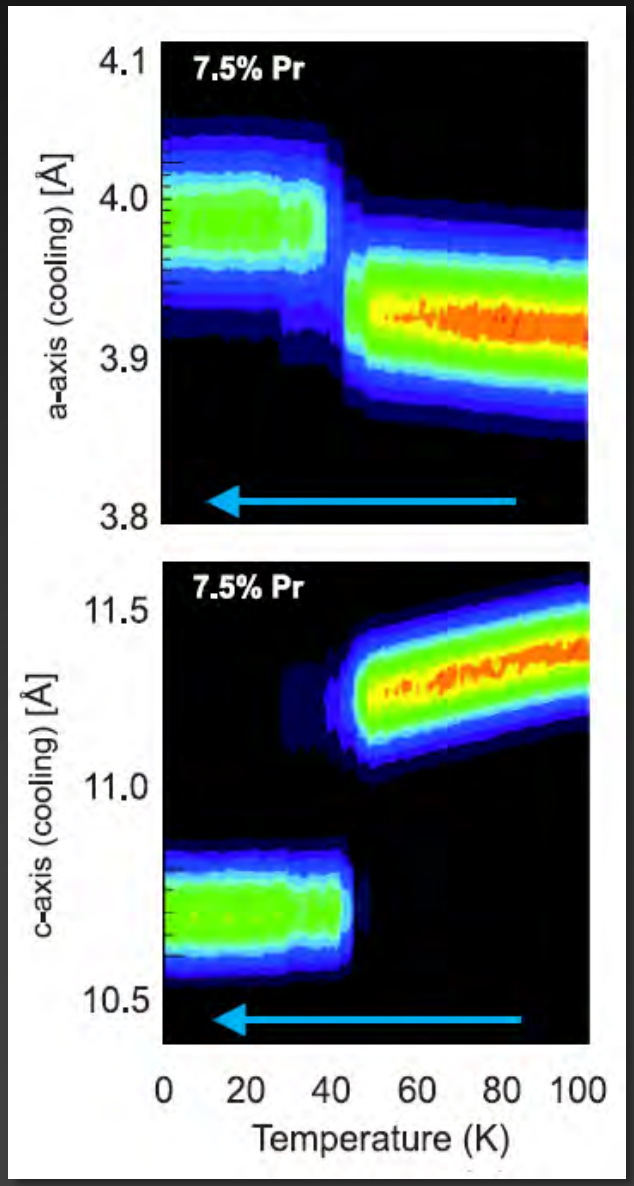
S.R. Saha *et al*, PRB 85, 024525 (2012)

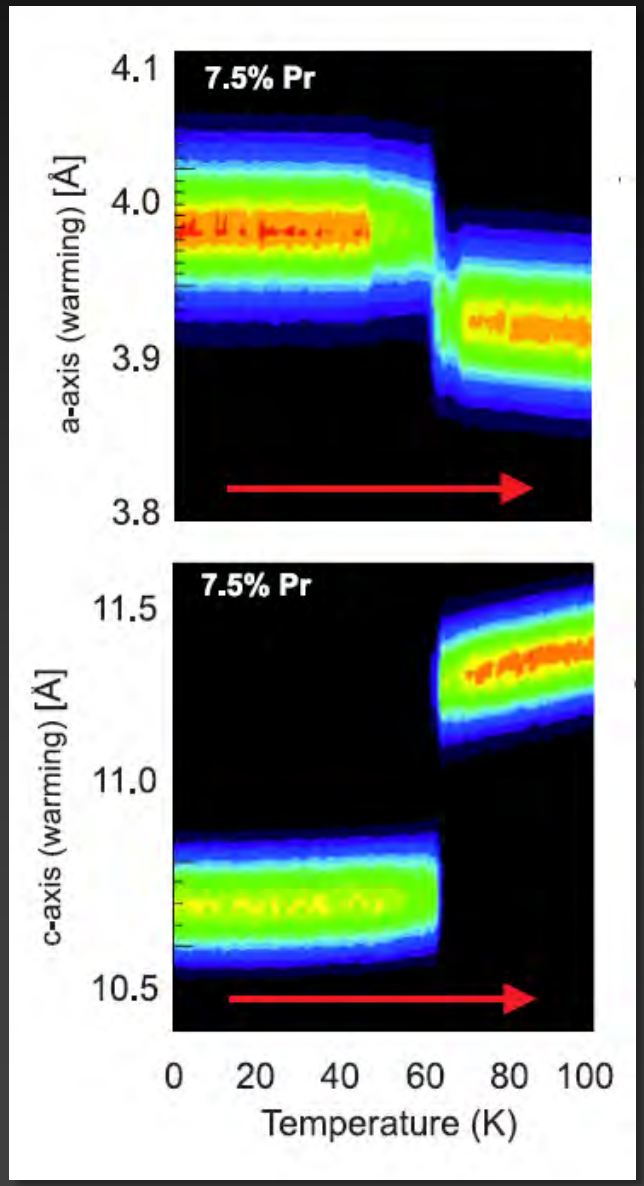
Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$



Neutron Scattering

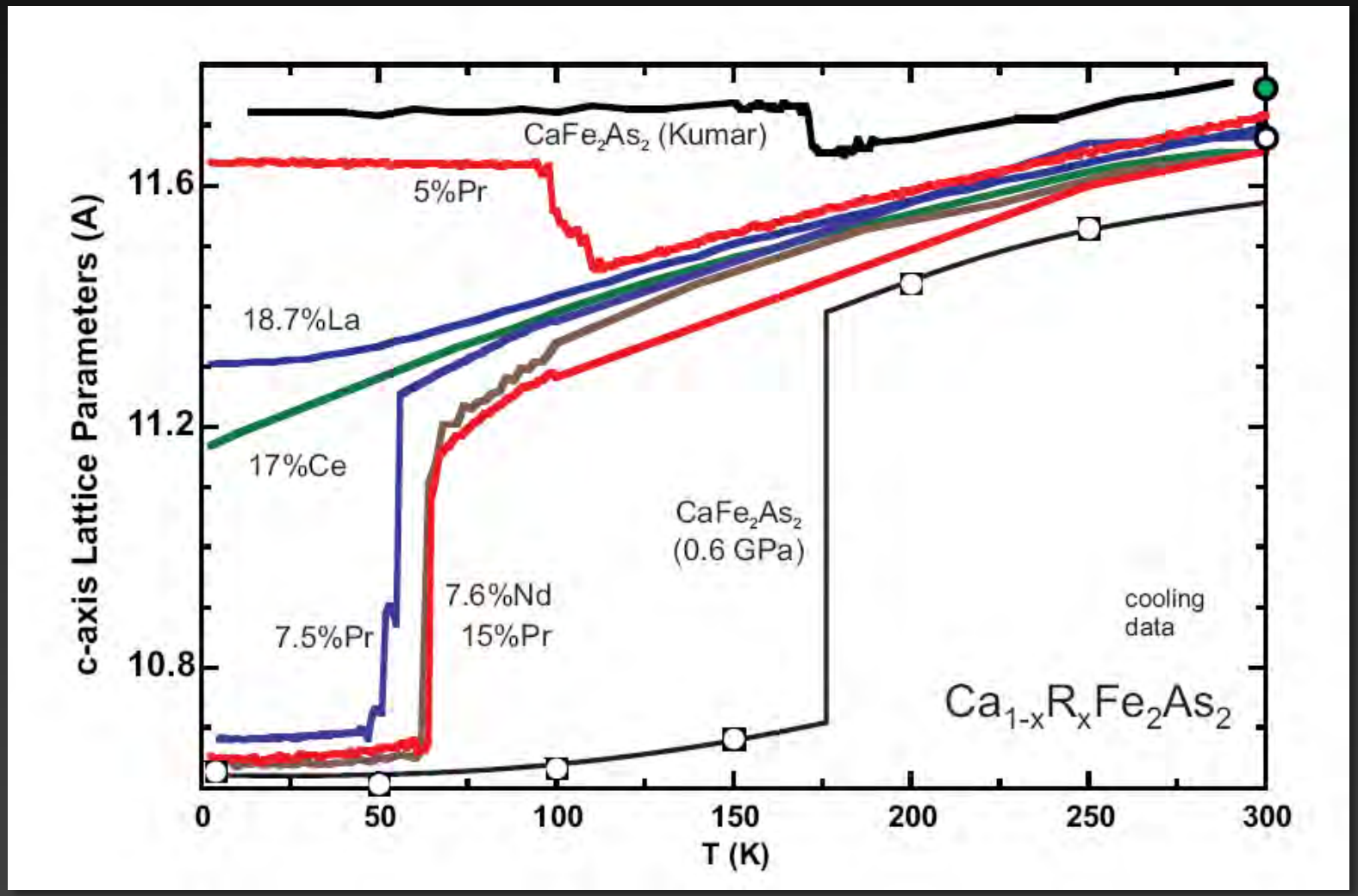






Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

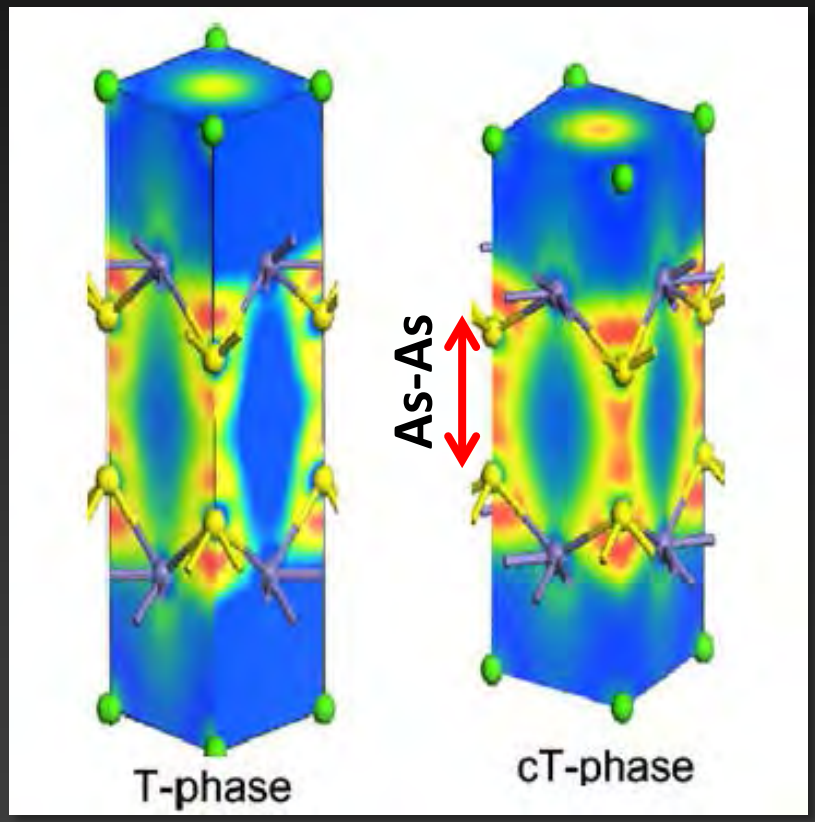
C-axis structural collapse



- structural collapse comparable to $CaFe_2As_2$ under pressure

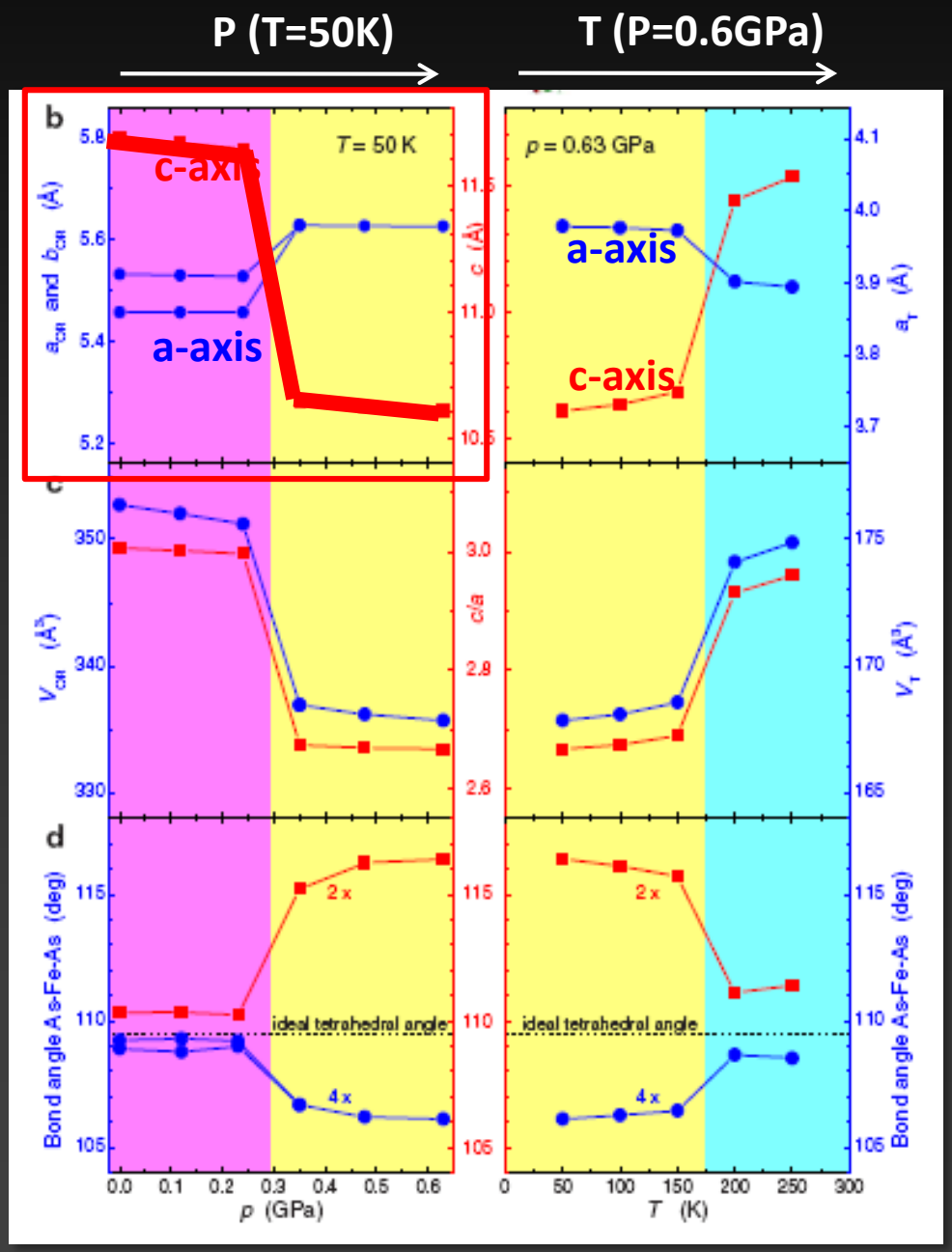
Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

$CaFe_2As_2$ under pressure



R. Hoffman (1985)
T. Yildirim (2008)

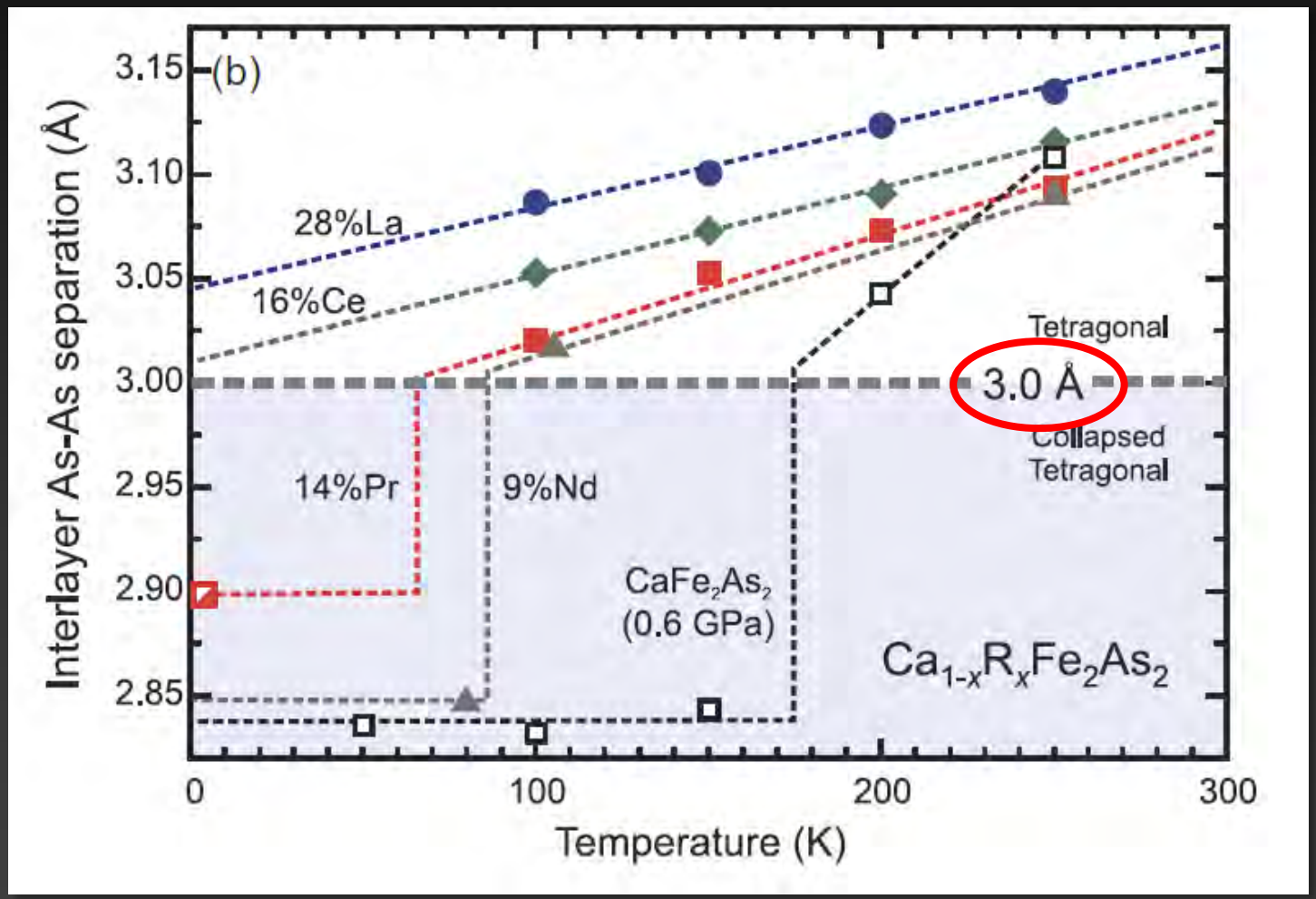
- "collapse" of tetragonal unit cell
- dramatic change in bonding structure

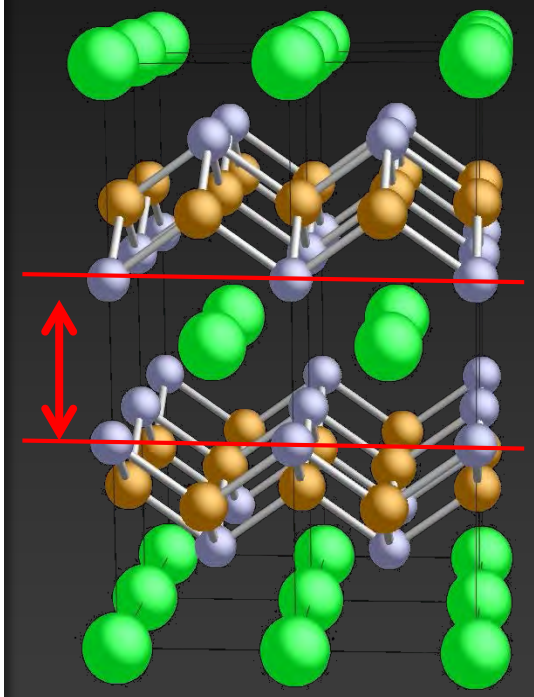


Kreyssig *et al.* (2008)

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

C-axis structural collapse



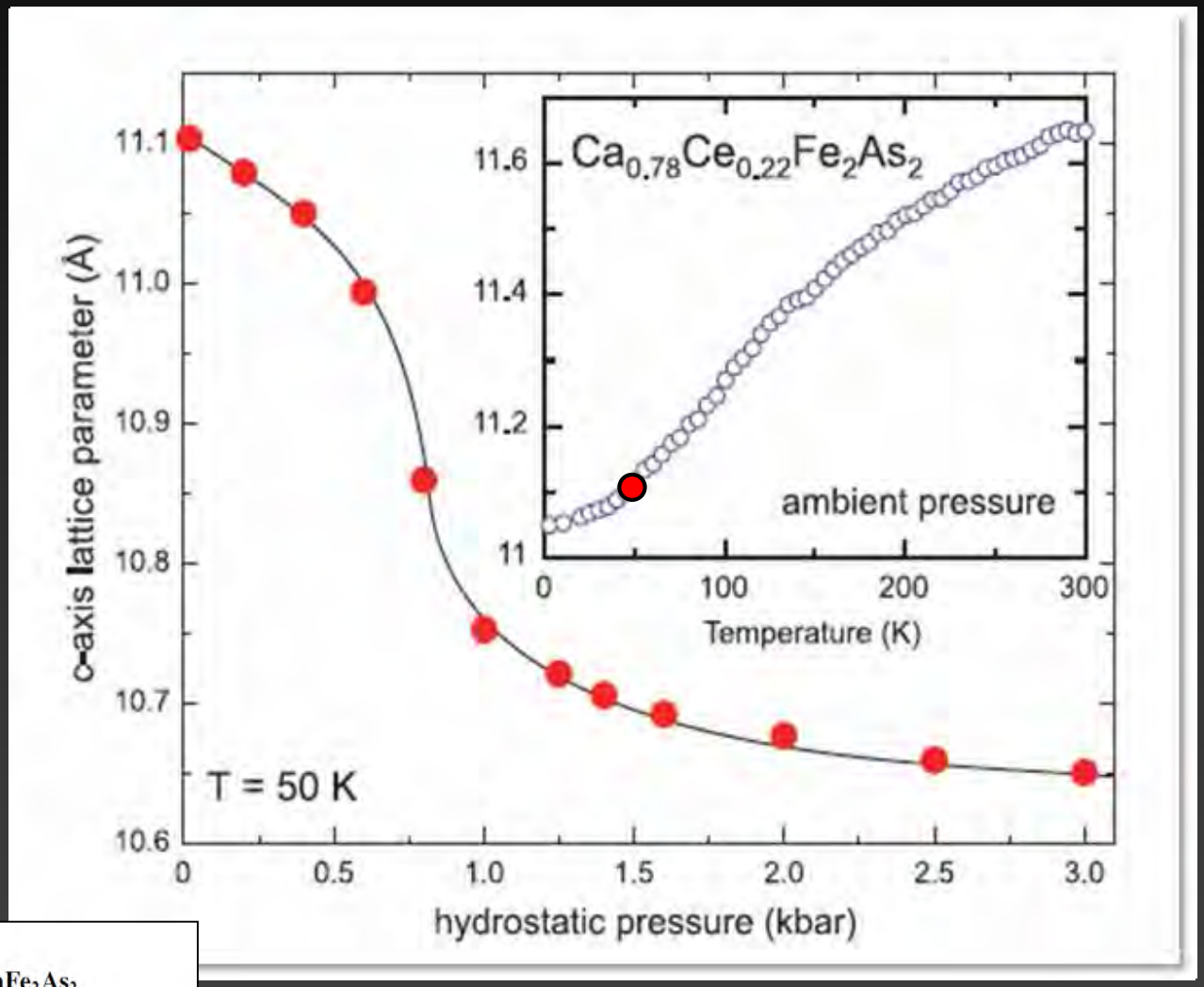


- **key parameter is As-As separation**

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

C-axis structural collapse

- controllable collapse
- **180 x 10^{-6} K^{-1} thermal expansion!!**



PHYSICAL REVIEW B **86**, 104303 (2012)

Giant negative thermal expansion in La-doped $CaFe_2As_2$

A. Rebello and J. J. Neumeier
Department of Physics, P. O. Box 173840, Montana State University, Bozeman, Montana 59717-3840, USA

Zhaoshun Gao, Yanpeng Qi, and Yanwei Ma
Key Laboratory of Applied Superconductivity, Institute of Electrical Engineering, Chinese Academy of Sciences, Beijing 100190, China

S.R. Saha *et al*, PRB 85, 024525 (2012)

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

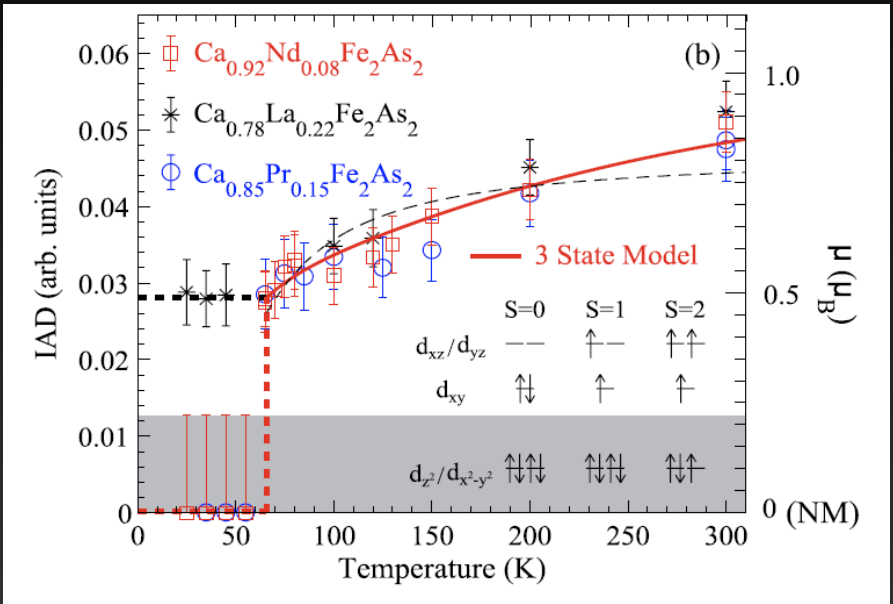
Quenched Fe Moment

PRL 110, 047003 (2013) PHYSICAL REVIEW LETTERS week ending 25 JANUARY 2013

Spin-State Transition in the Fe Pnictides

H. Gretarsson,[1] S. R. Saha,[2] T. Drye,[2] J. Paglione,[2] Jungho Kim,[3] D. Casa,[3] T. Gog,[3] W. Wu,[1] S. R. Julian,[1] and Young-June Kim[1,*]

[1]Department of Physics, University of Toronto, 60 Saint George Street, Toronto, Ontario M5S 1A7, Canada
[2]Center for Nanophysics and Advanced Materials, Department of Physics, University of Maryland, College Park,
[3]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

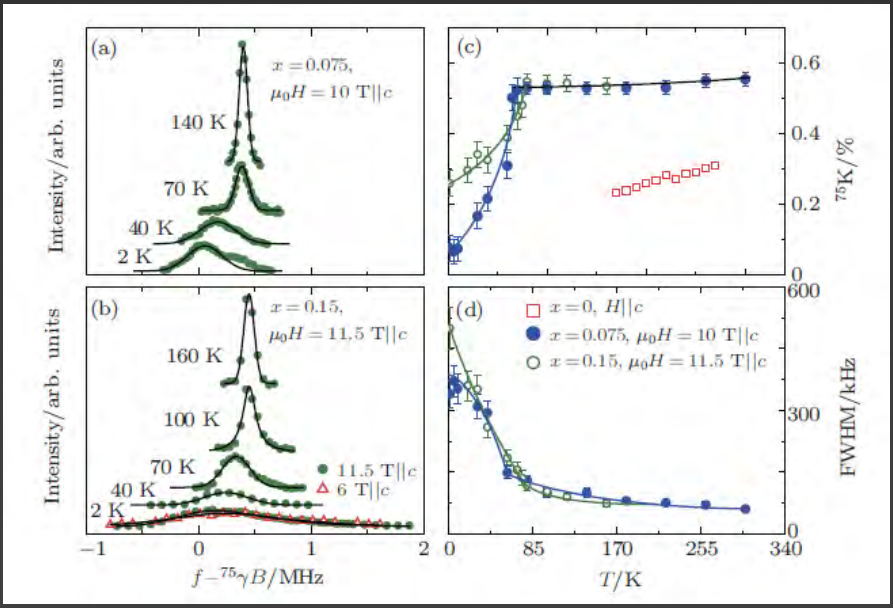


RAPID COMMUNICATION Chin. Phys. B Vol. 22, No. 5 (2013) 057401

Quenched Fe moment in the collapsed tetragonal phase of $Ca_{1-x}Pr_xFe_2As_2$*

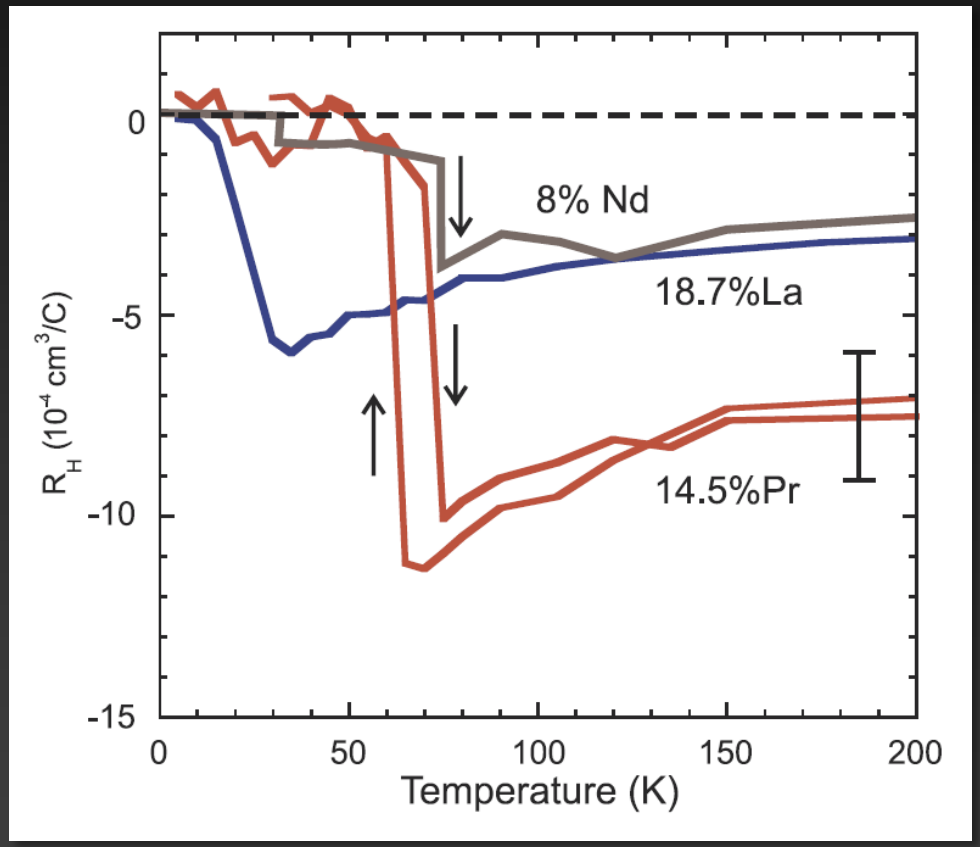
Ma Long(马 龙)[a], Ji Gao-Feng(吉高峰)[a], Dai Jia(代 佳)[a], Saha S R[b], Drye T[b], Paglione J[b], and Yu Wei-Qiang(于伟强)[a]†

[a]Department of Physics, Renmin University of China, Beijing 100872, China
[b]Center for Nanophysics and Advanced Materials, Department of Physics, University of Maryland, College Park, MD 20742, USA

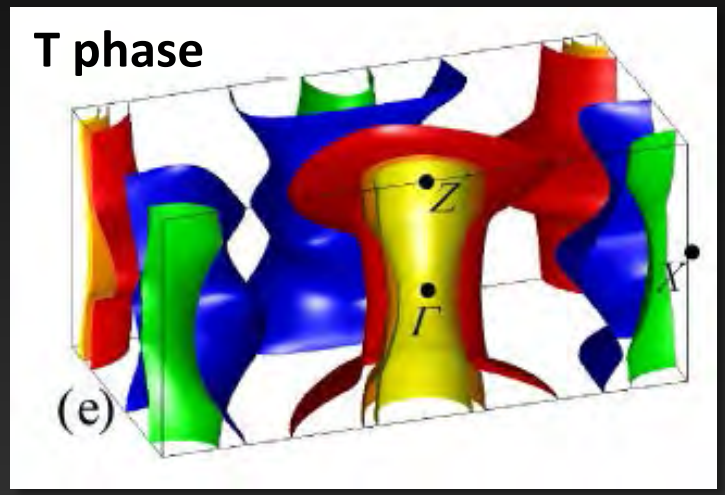


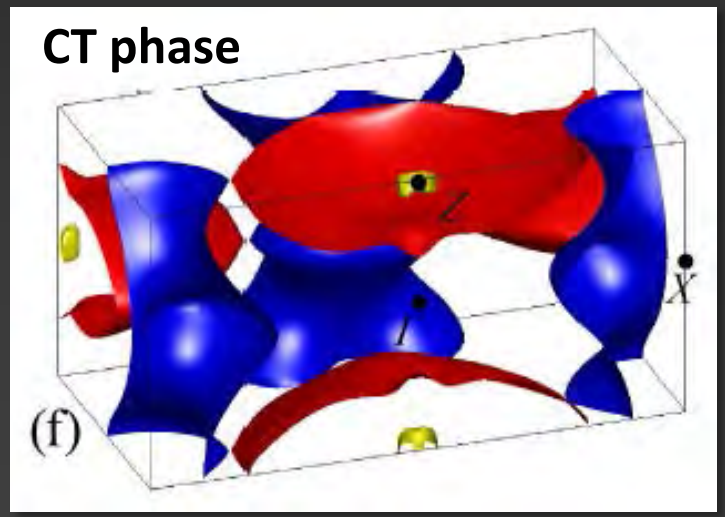
Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Electronic reconstruction



S.R. Saha *et al*, PRB 85, 024525 (2012)

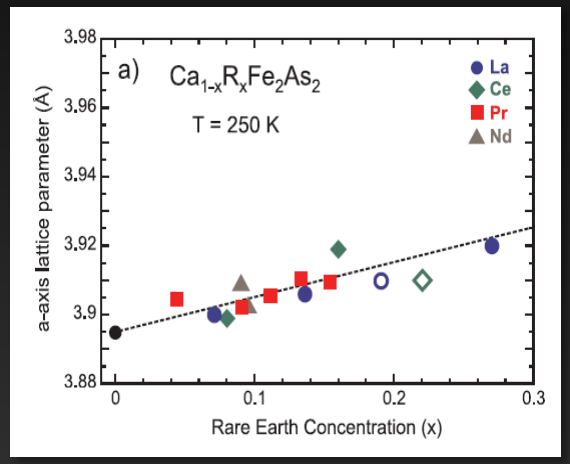


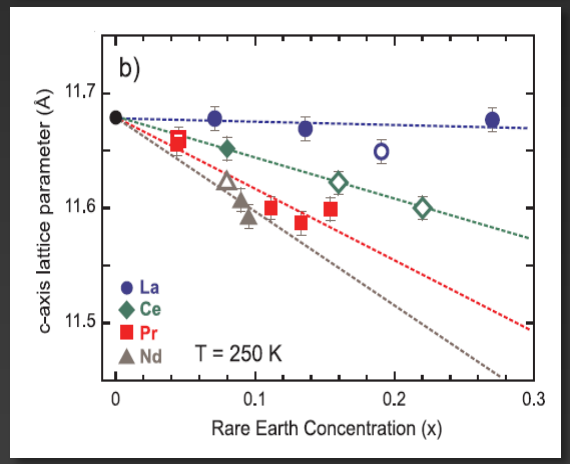


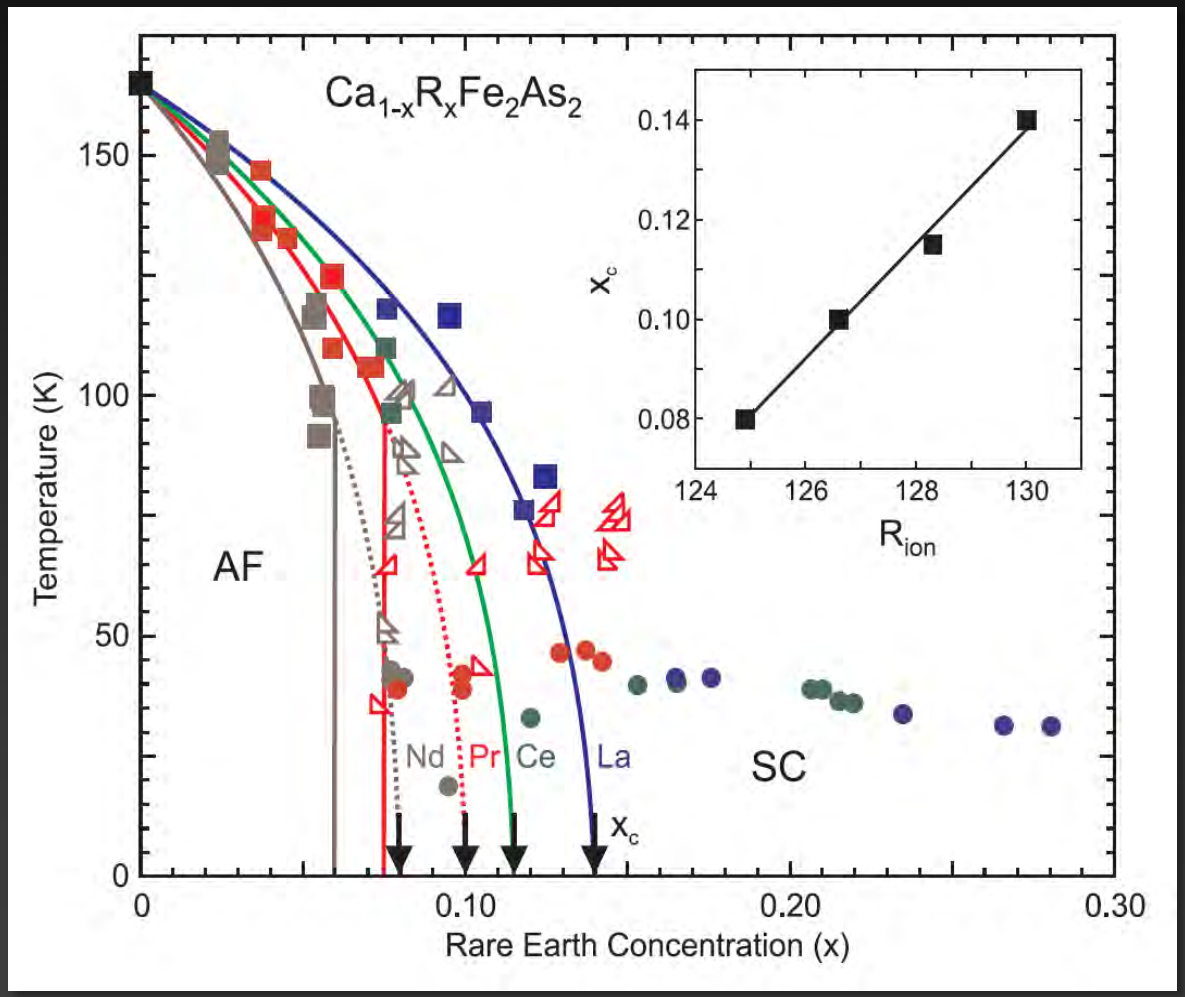
Kasahara (2010)

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Phase Diagram





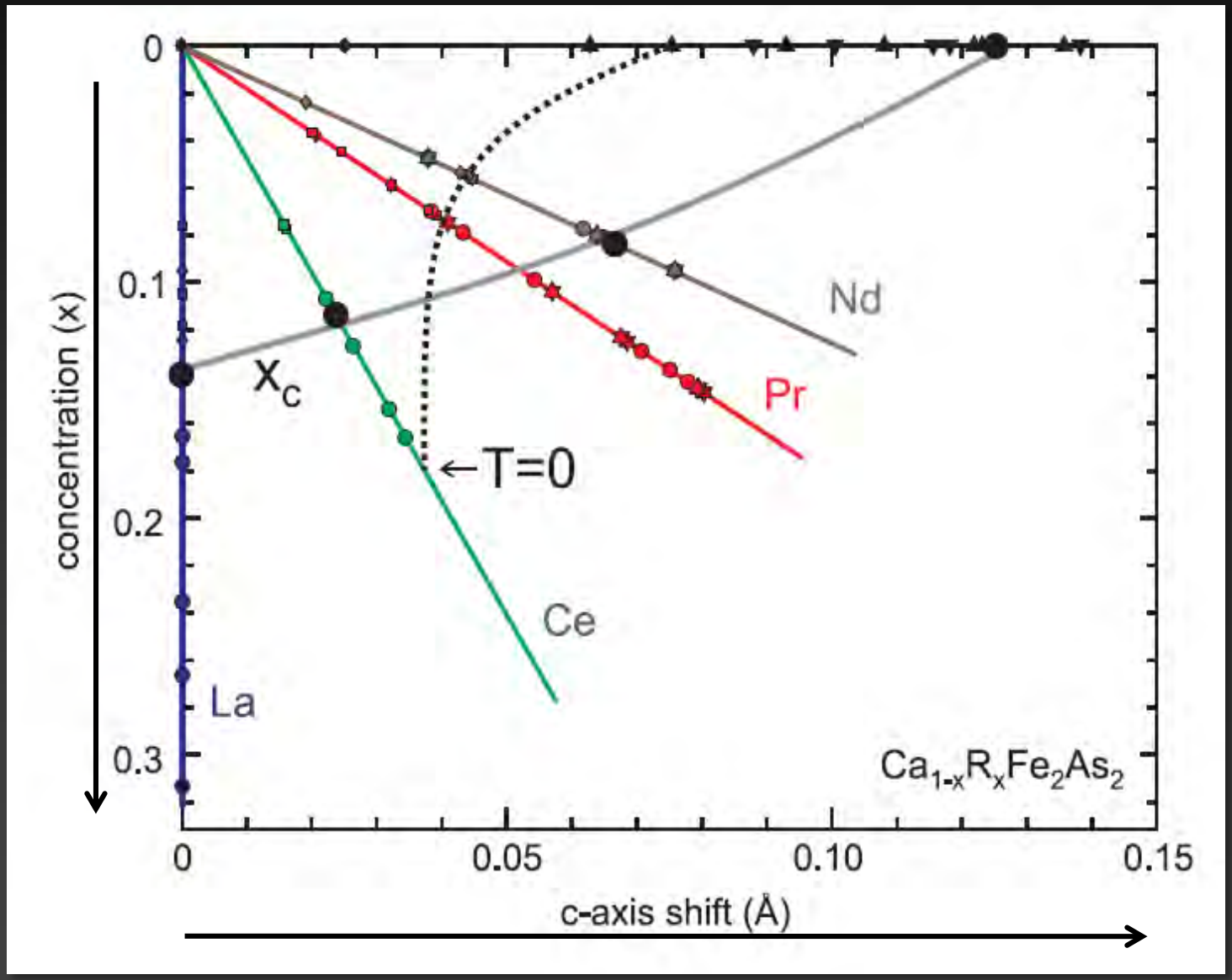


- suppression of AFM phase dependent on rare earth

S.R. Saha *et al*, PRB 85, 024525 (2012)

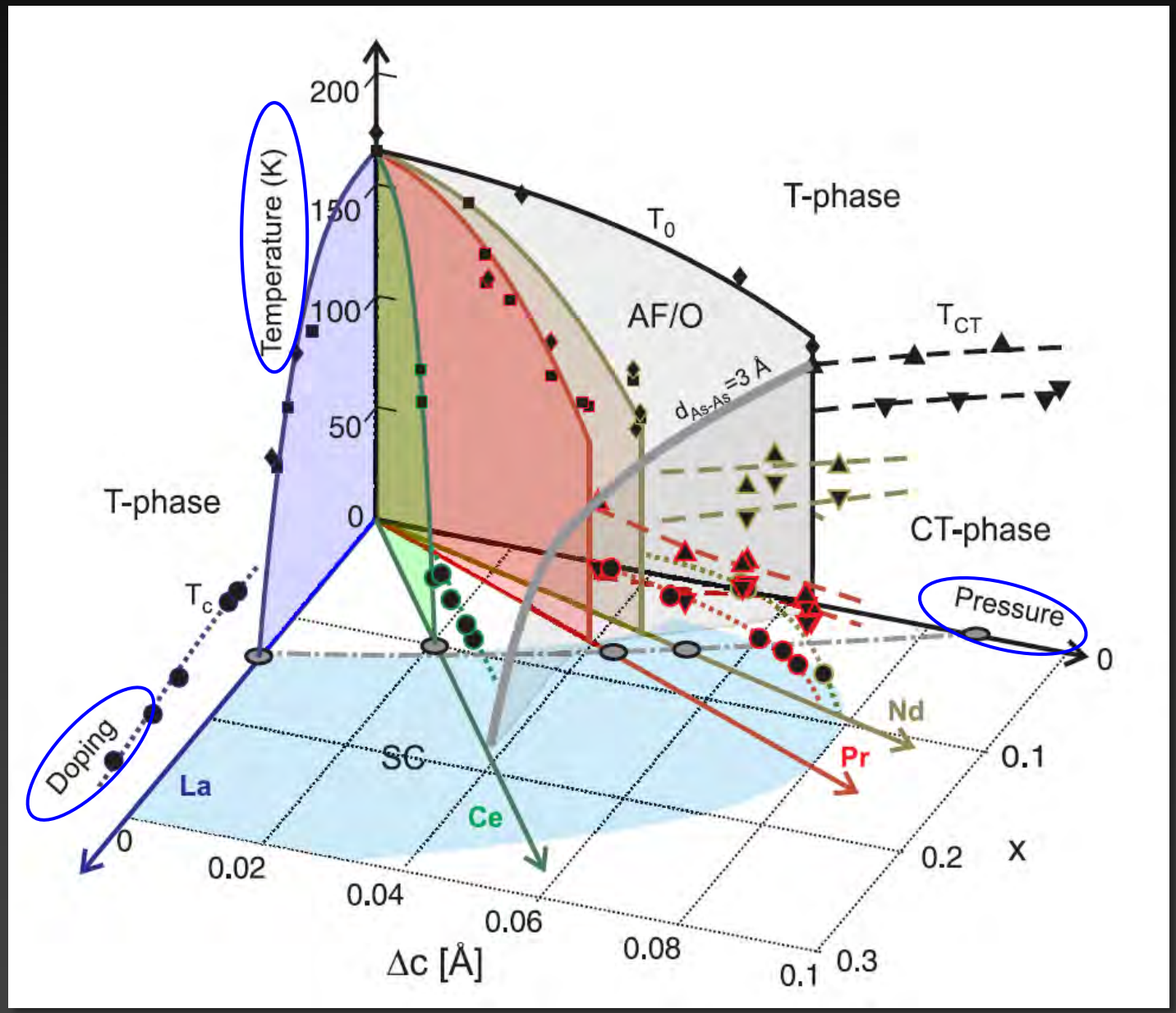
Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Phase Diagram



S.R. Saha *et al*, PRB 85, 024525 (2012)

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$



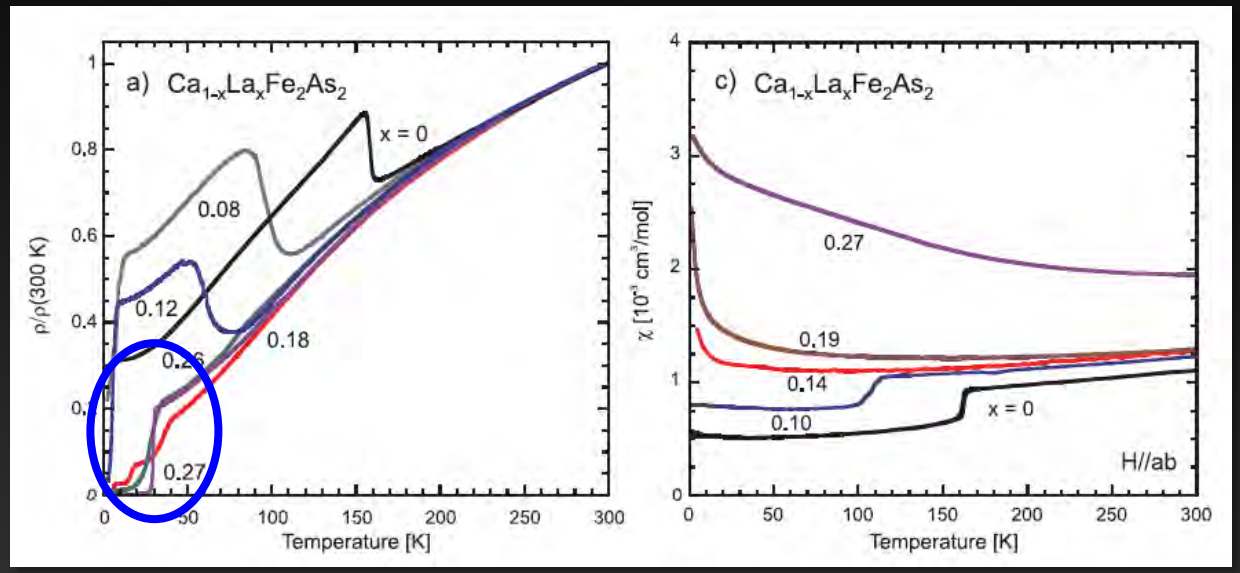
S.R. Saha *et al*, PRB 85, 024525 (2012)

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Physical Properties

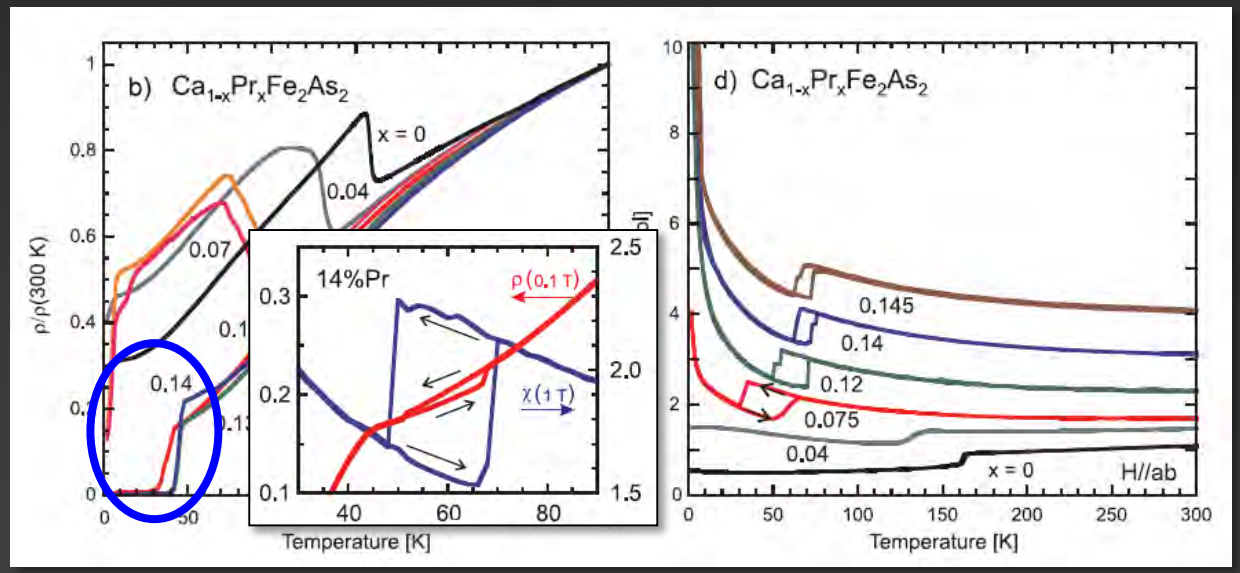
La-doping:

- NO structural collapse
- Superconductivity!



Pr-doping:

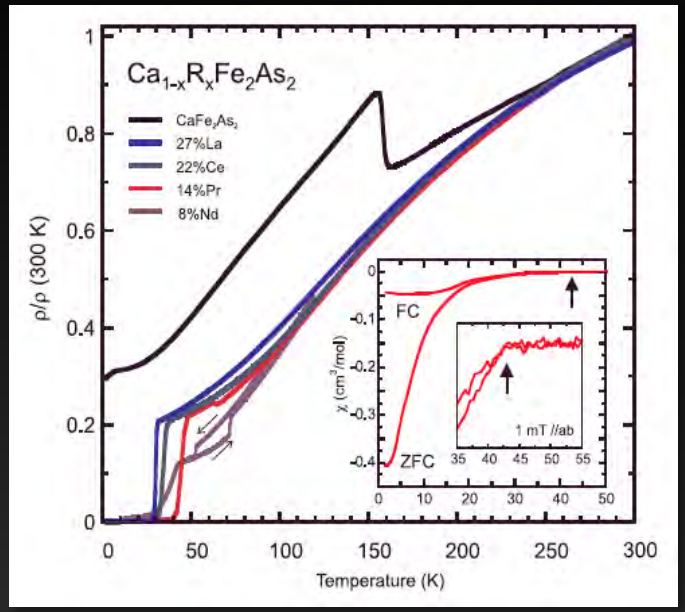
- Structural collapse
- Superconductivity!?



- *R*= La, Ce, Pr, Nd suppress magnetic order and induce superconductivity with max T_c onset of ~50 K
- **No apparent coexistence of AFM and high-Tc superconductivity phase**

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Superconductivity up to 49 K!



S.R. Saha *et al*, PRB 85, 024525 (2012)

PHYSICAL REVIEW B **85**, 024525 (2012) arXiv:1105.4798

Structural collapse and superconductivity in rare-earth-doped $CaFe_2As_2$

S. R. Saha,[1] N. P. Butch,[1] T. Drye,[1] J. Magill,[1] S. Ziemak,[1] K. Kirshenbaum,[1] P. Y. Zavalij,[2] J. W. Lynn,[3] and J. Paglione[1,*]
[1]*Center for Nanophysics and Advanced Materials, Department of Physics, University of Maryland, College Park, Maryland 20742, USA*
[2]*Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, USA*
[3]*Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*
(Received 3 November 2011; revised manuscript received 5 December 2011; published 13 January 2012)

arXiv:1106.1837

epl A Letters Journal Exploring the Frontiers of Physics

EPL, 95 (2011) 67002

Synthesis and properties of La-doped $CaFe_2As_2$ single cry
with $T_c = 42.7$ K

Zhaoshun Gao[(a)], Yanpeng Qi[(a)], Lei Wang, Dongliang Wang, Xianping Zhang, Chao Yao, Chunlei Wang and Yanwei Ma[(b)]

Key Laboratory of Applied Superconductivity, Institute of Electrical Engineering, Chinese Academy of Scie
Beijing 100190, China

Physica C xxx (2012) xxx–xxx

Superconducting properties of $Ca_{1-x}RE_xFe_2As_2$ (*RE*: Rare Earths)

T. Tamegai[a,b,*], Q.P. Ding[a,b], T. Ishibashi[a], Y. Nakajima[a,b]

PHYSICAL REVIEW B **86**, 104303 (2012)

Giant negative thermal expansion in La-doped $CaFe_2As_2$

A. Rebello and J. J. Neumeier
Department of Physics, P. O. Box 173840, Montana State University, Bozeman, Montana 59717-3840, USA
Zhaoshun Gao, Yanpeng Qi, and Yanwei Ma

arXiv:11

PNAS | September 20, 2011 | vol. 108 | no. 38 | 15705–15709

Unusual superconducting state at 49 K in electron-doped $CaFe_2As_2$ at ambient pressure

Bing Lv[a], Liangzi Deng[a,b], Melissa Gooch[a], Fengyan Wei[a,b], Yanyi Sun[a], James K. Meen[a,c], Yu-Yi Xue[a,b], Bernd Lorenz[a,b], and Ching-Wu Chu[a,b,d,1]

[a]Texas Center for Superconductivity, University of Houston, Houston TX 77204-5002; [b]Department of Physics, University of Houston, Houston TX 77204-5005; [c]Department of Chemistry, University of Houston, Houston TX 77204-5003; and [d]Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley CA 94720

Contributed by Ching-Wu Chu, July 26, 2011 (sent for review June 23, 2011)

IOP Publishing — Superconductor Science and Technology
Supercond. Sci. Technol. **26** (2013) 095003 (6pp) doi:10.1088/0953-2048/26/9/095003

Upper critical fields and anisotropy of $Ca_{1-x}La_xFe_2As_2$ single crystals

W Zhou, F F Yuan, J C Zhuang, Y Sun, Y Ding, L J Cui, J Bai and Z X Shi

PHYSICAL REVIEW B **87**, 201108(R) (2013) RAPID COMMUNICATIONS

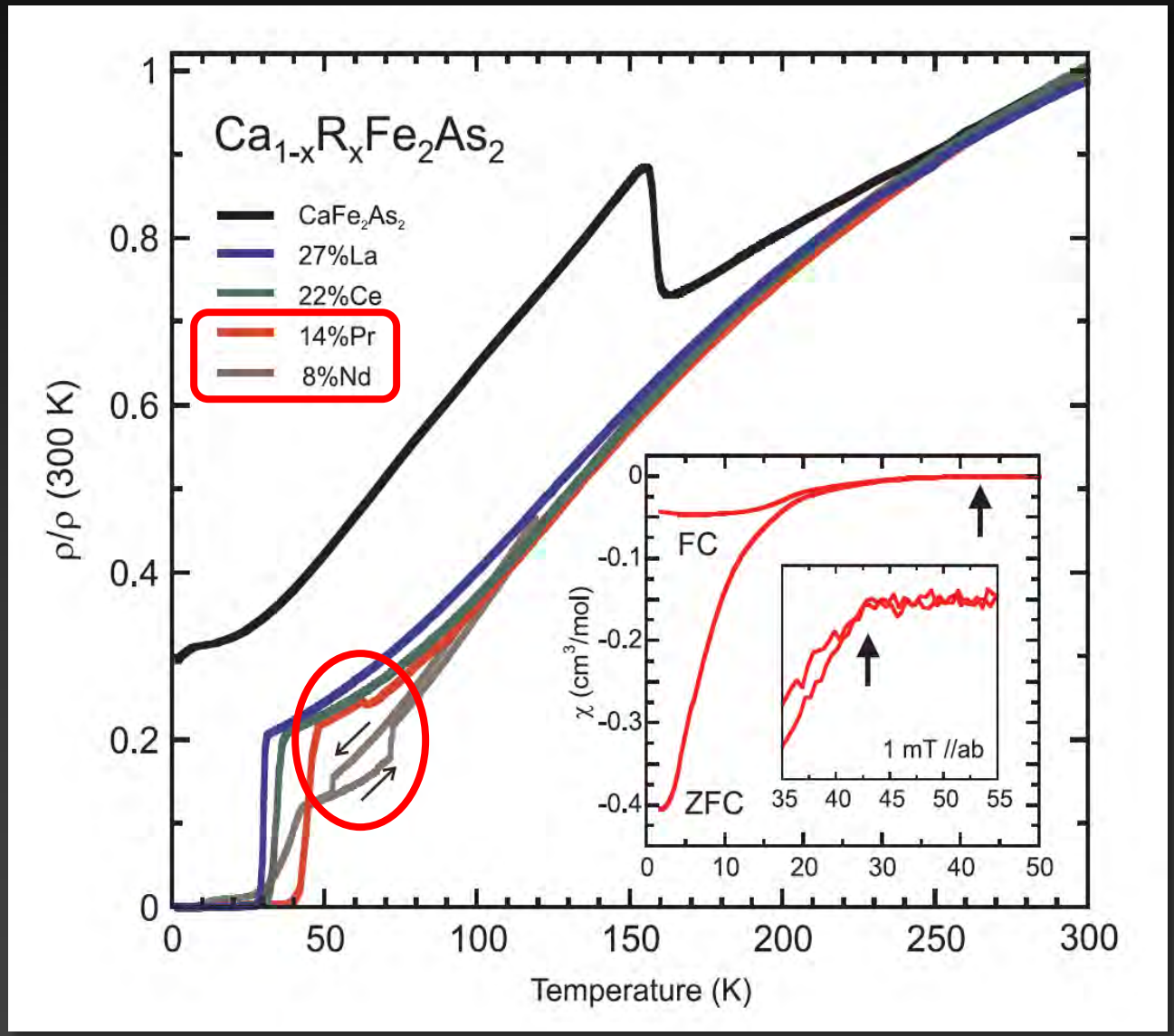
Nanoscale surface element identification and dopant homogeneity in the high-T_c superconductor $Pr_xCa_{1-x}Fe_2As_2$

Ilija Zeljkovic,[1] Dennis Huang,[1] Can-Li Song,[1] Bing Lv,[2] Ching-Wu Chu,[2] and Jennifer E. Hoffman[1,*]
[1]*Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA*
[2]*Texas Center for Superconductivity, University of Houston, Houston, Texas 77204, USA*
(Received 18 January 2013; published 17 May 2013)

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Superconductivity

- appears in all R-doped samples

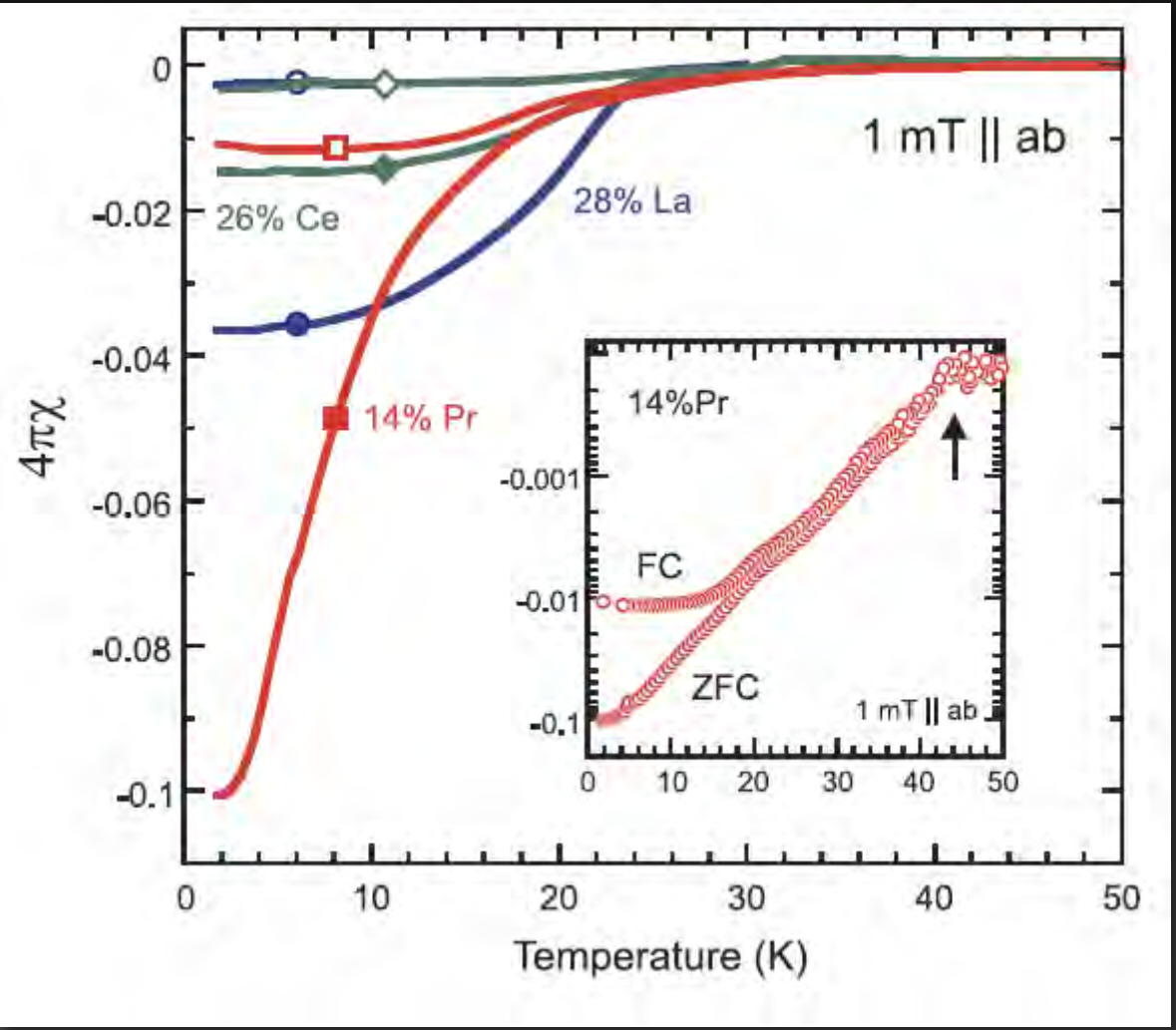


S.R. Saha *et al*, PRB 85, 024525 (2012)

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Superconductivity

- appears in all R-doped samples
- **small volume fractions**



S.R. Saha *et al*, PRB 85, 024525 (2012)

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Superconductivity

- appears in all R-doped samples
- **small volume fractions**

The simultaneous occurrence of superparamagnetism and superconductivity in nominal single crystalline $(Ca_{1-x}Pr_x)Fe_2As_2$ with $0 \leq x \leq 0.13$

B. Lv, F. Y. Wei, L. Z. Deng, Y. Y. Xue, and C. W. Chu*

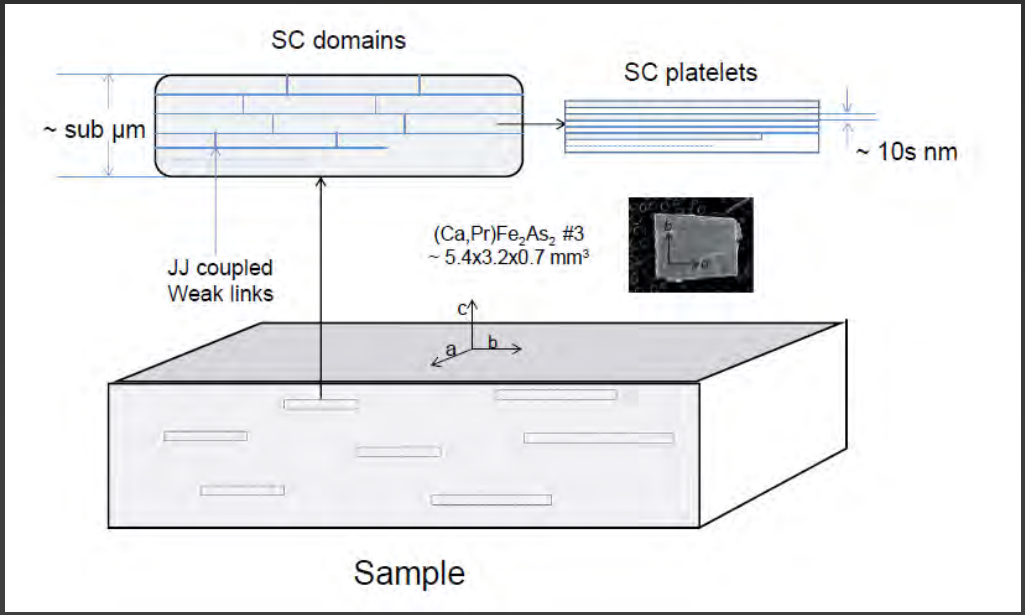
Arxiv:1308.3129

Why is the superconducting T_c so high in rare-earth-doped $CaFe_2As_2$?

Authors: F. Y. Wei,[1] B. Lv,[1] L. Z. Deng,[1] J. K. Meen[2], Y. Y. Xue[1], J. E. Hoffman[3] and C. W. Chu[1,4,*]

Arxiv:1309.0034

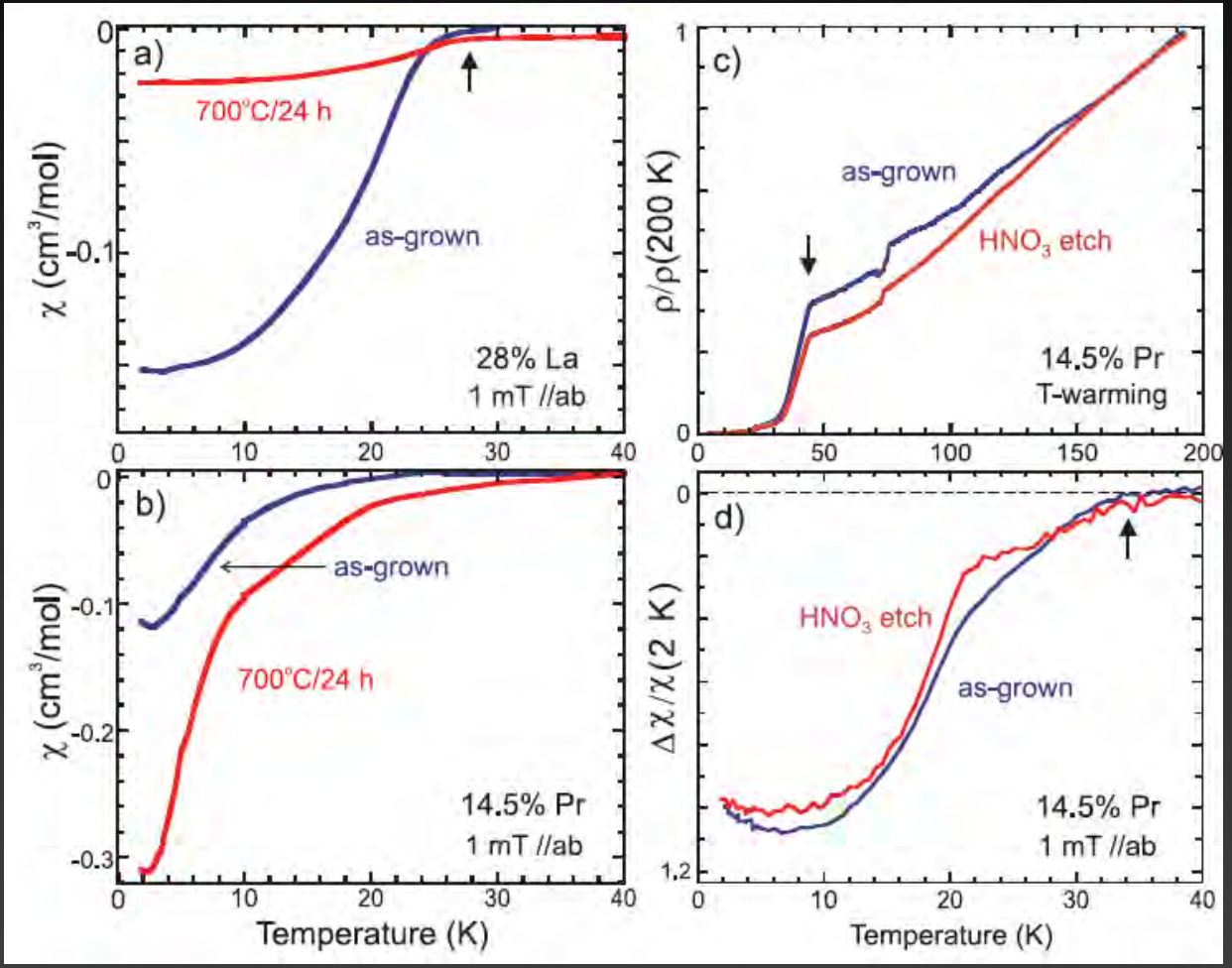
Defect-based SC mechanism?



Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Superconductivity

- appears in all R-doped samples
- small volume fractions
- **impervious to annealing, etching**

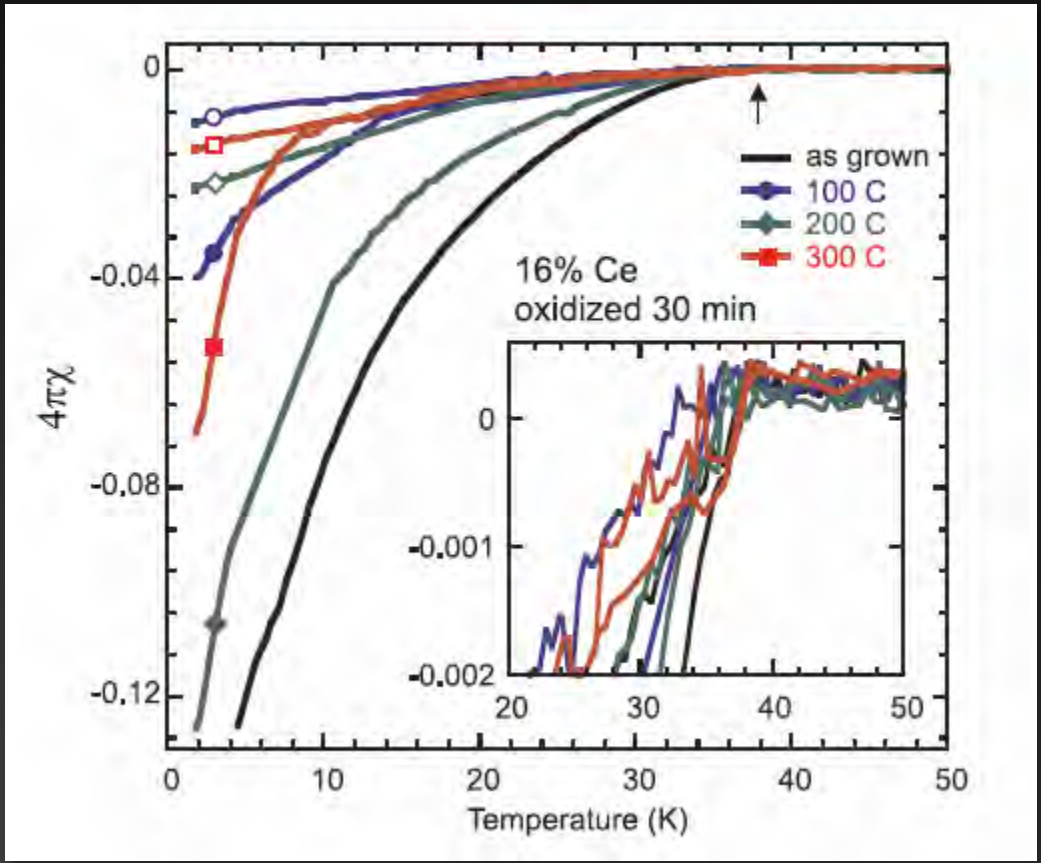


S.R. Saha *et al*, PRB 85, 024525 (2012)

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Superconductivity

- appears in all R-doped samples
- small volume fractions
- impervious to annealing, etching
- **oxidation not cause**

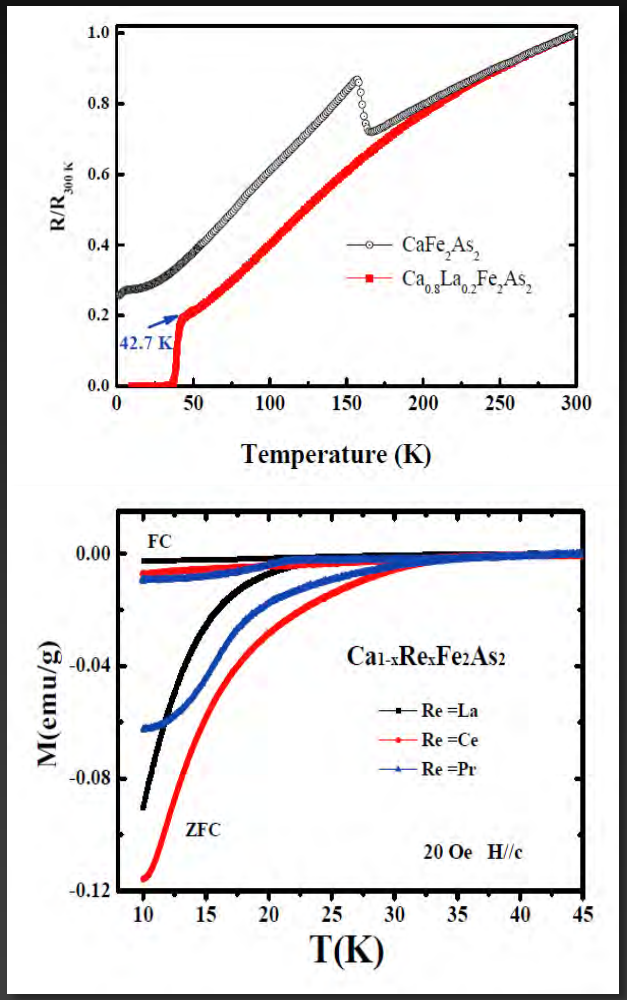


S.R. Saha *et al*, PRB 85, 024525 (2012)

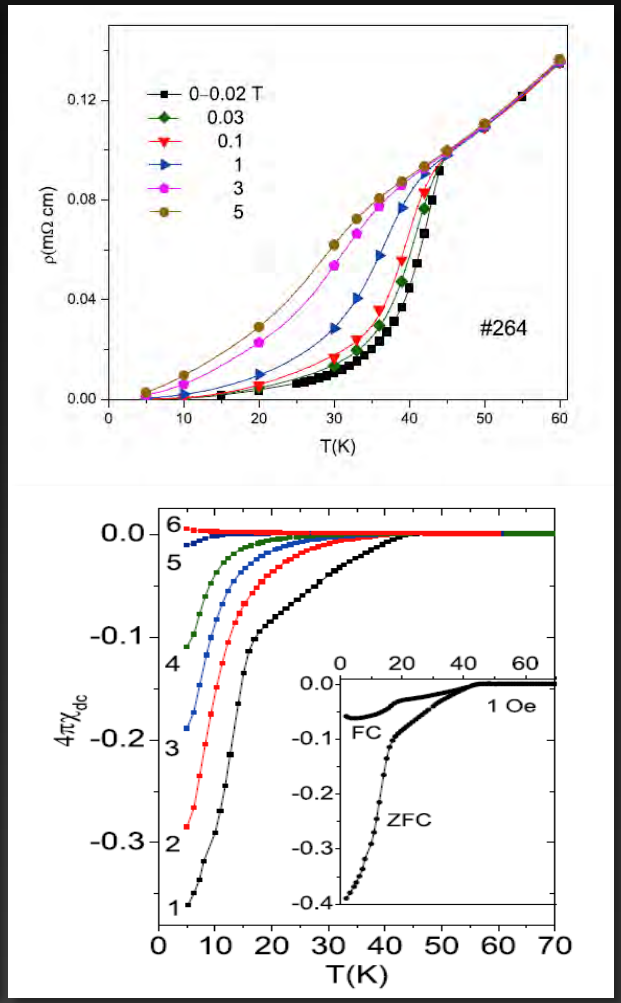
Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Superconductivity

- appears in all R-doped samples
- small volume fractions
- impervious to annealing, etching
- oxidation not cause
- **observed independently by other groups!**



Y. Qi *et al.* (2011)



B. Lv *et al.* (2011)

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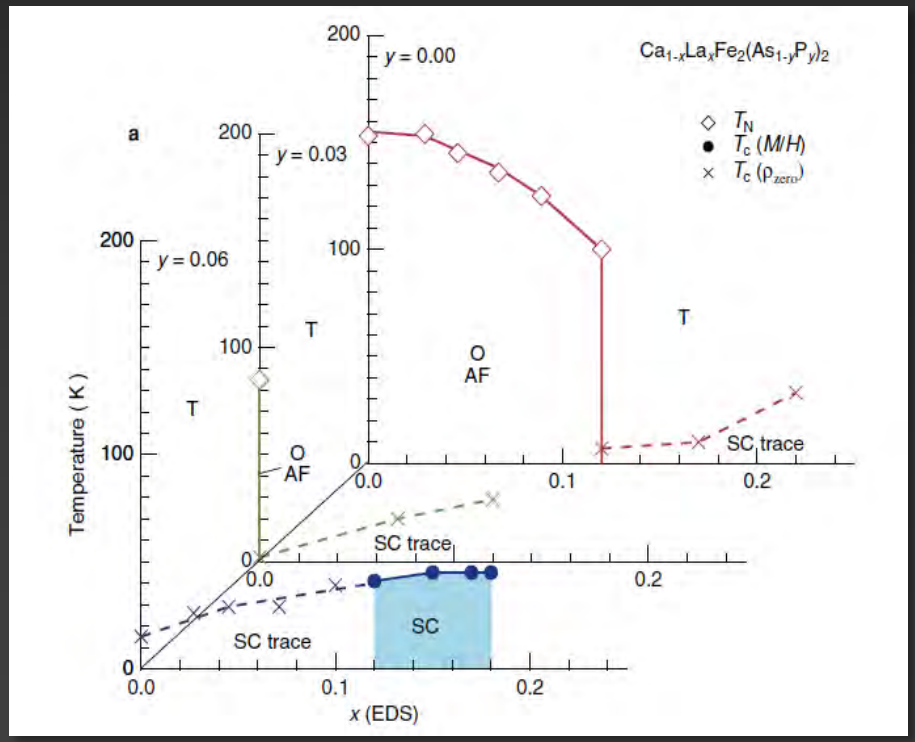
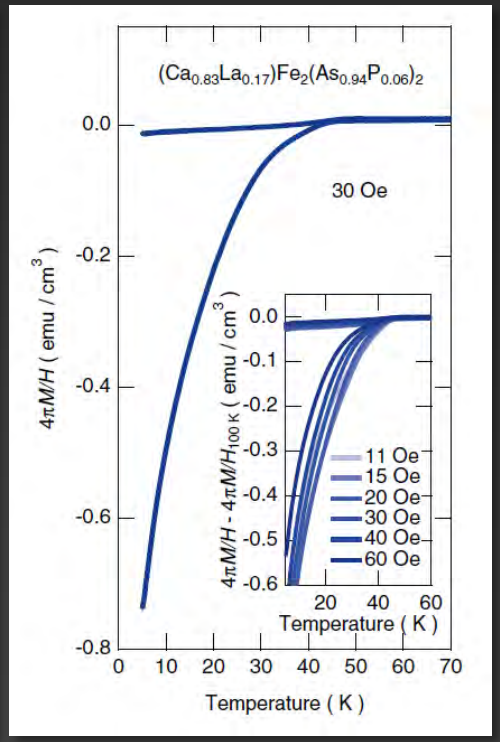
SCIENTIFIC REPORTS | 3 : 1478 | DOI: 10.1038/srep01478

Emergence of superconductivity at 45 K by lanthanum and phosphorus co-doping of $CaFe_2As_2$

Kazutaka Kudo, Keita Iba, Masaya Takasuga, Yutaka Kitahama, Jun-ichi Matsumura, Masataka Danura, Yoshio Nogami & Minoru Nohara





First observation of bulk phase??

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

Superconductivity

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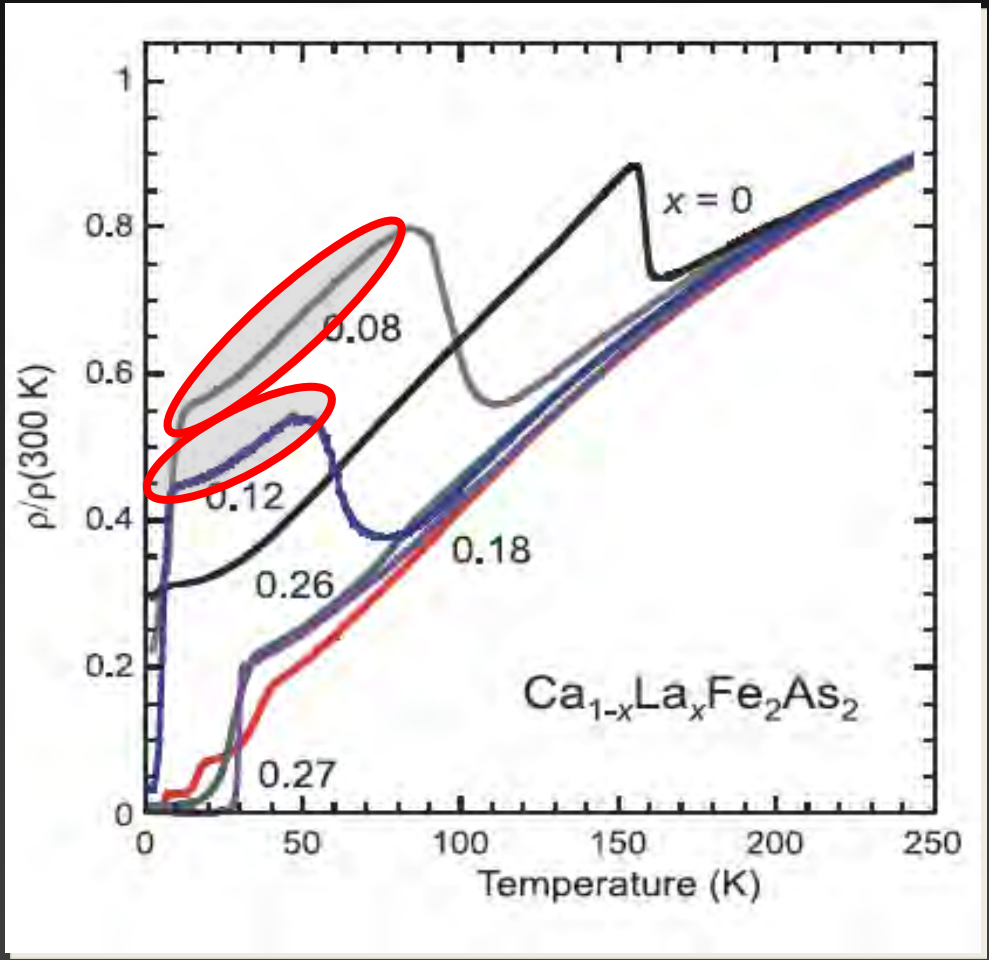
- small volume fractions
- impervious to annealing, etching
- oxidation not cause
- observed independently by other groups!
- **only in paramagnetic (non-AFM) state**



S.R. Saha *et al*, PRB 85, 024525 (2012)

Rare Earth Tuning $Ca_{1-x}R_xFe_2As_2$

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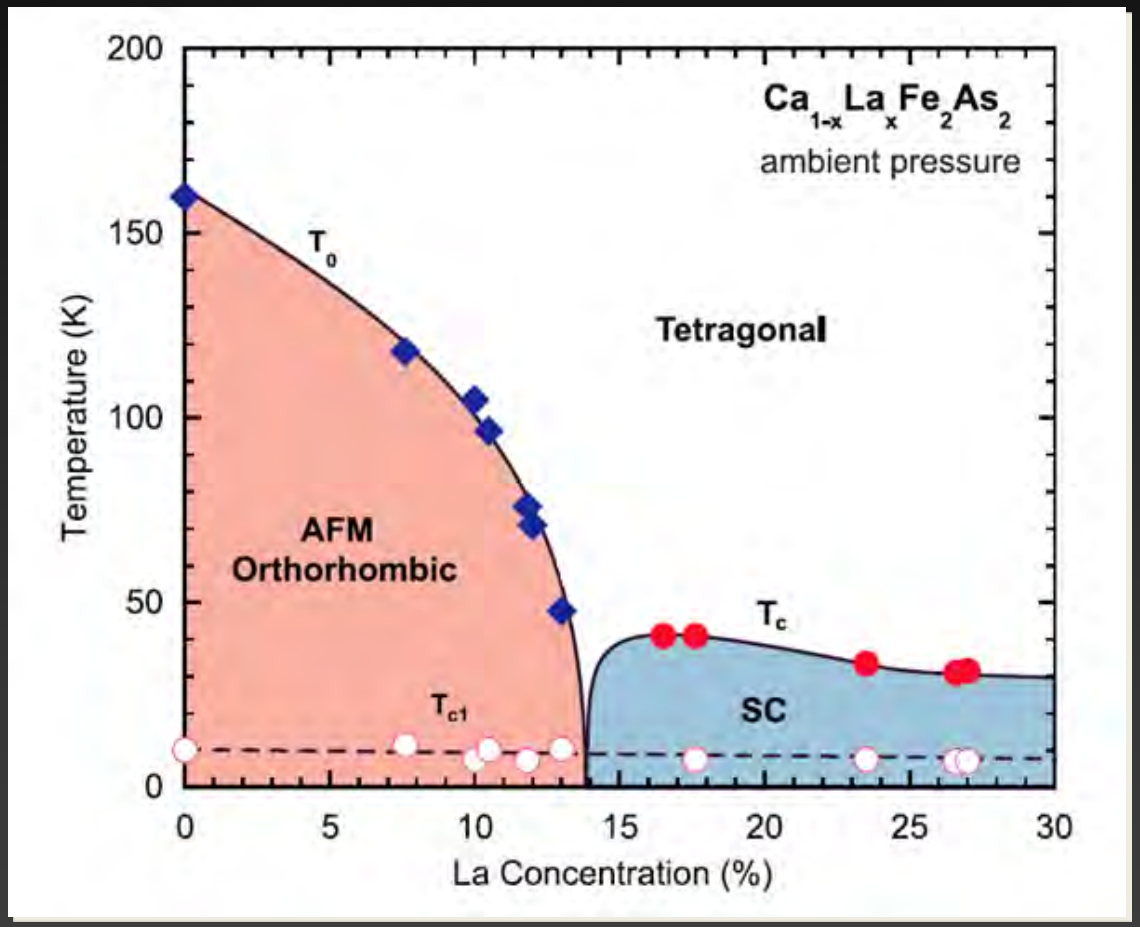
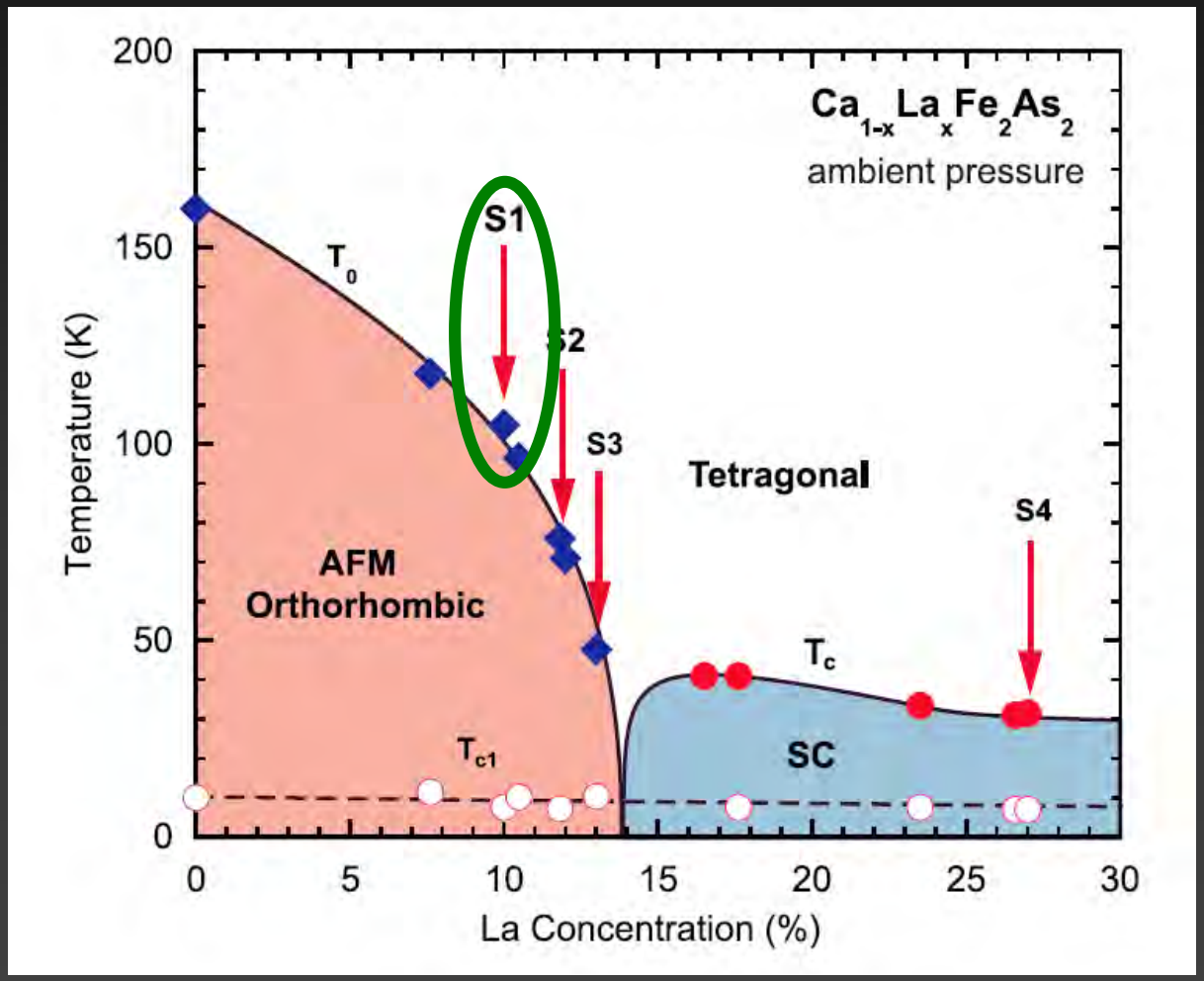


No coexistence of AFM and SC phases?

S.R. Saha *et al*, preprint

$Ca_{1-x}La_xFe_2As_2$ under pressure



S1. Clamp cell (UMD)

0 – 14 kbar

resistivity

S2. helium cell (NIST)

0 – 4 kbar

neutron scattering

S3. helium cell (McMaster)

0 – 4 kbar

resistivity

S4. Anvil cell (Cambridge)

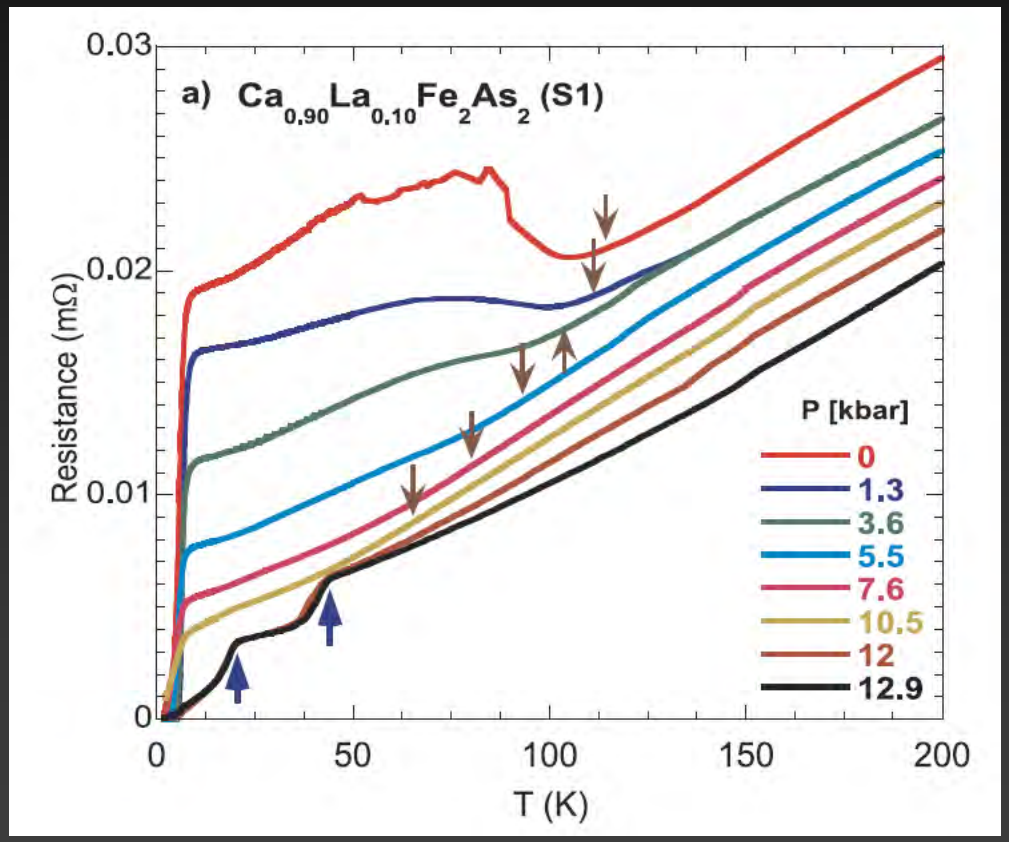
0 – 50 kbar

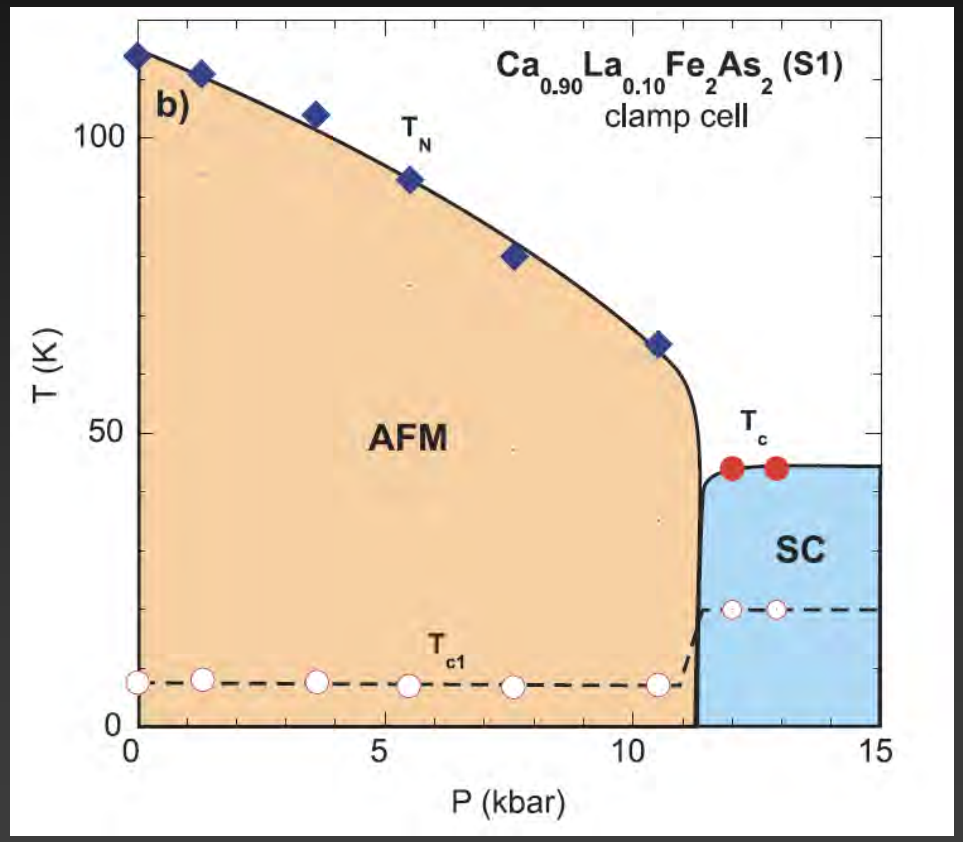
resistivity and TDO

S.R. Saha *et al*, preprint

$Ca_{1-x}La_xFe_2As_2$ under pressure

SAMPLE 1: *La10%, piston clamp cell (liquid)*

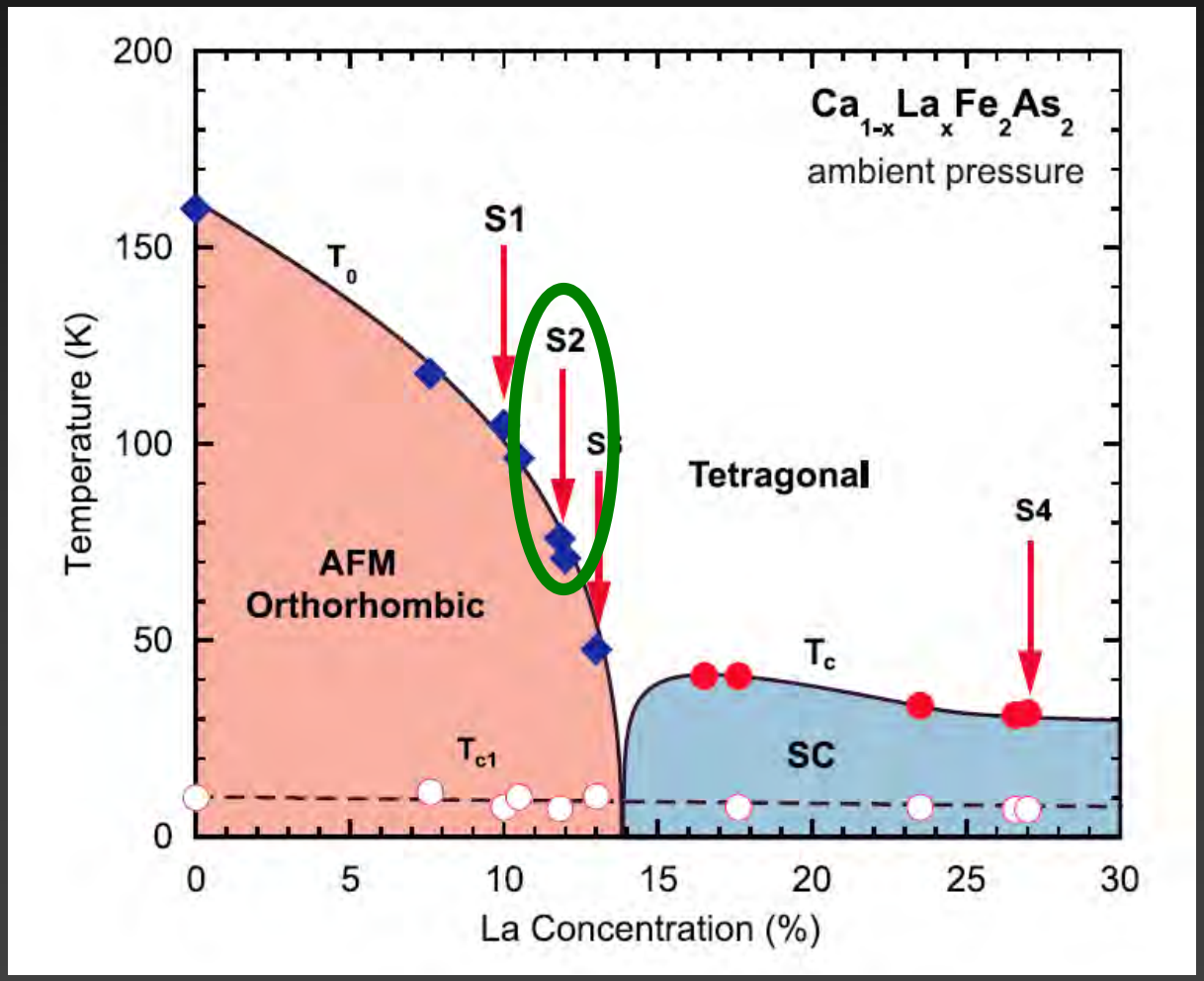




- **No trace of T_c > 10 K below 12 kbar**

S.R. Saha *et al*, preprint

$Ca_{1-x}La_xFe_2As_2$ under pressure



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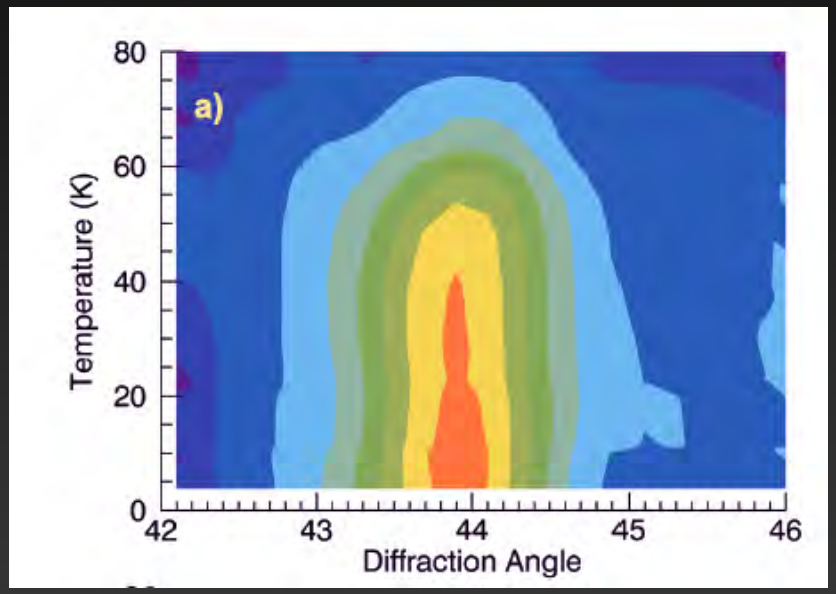
0 – 50 kbar

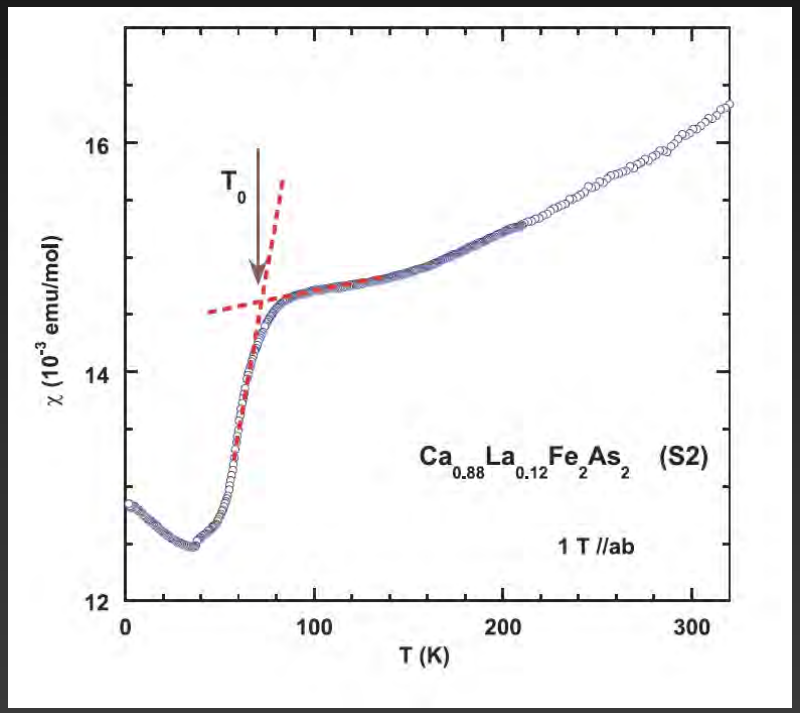
resistivity and TDO

S.R. Saha *et al*, preprint

$Ca_{1-x}La_xFe_2As_2$ under pressure

SAMPLE 2: ***La12%, hydrostatic (He) cell***



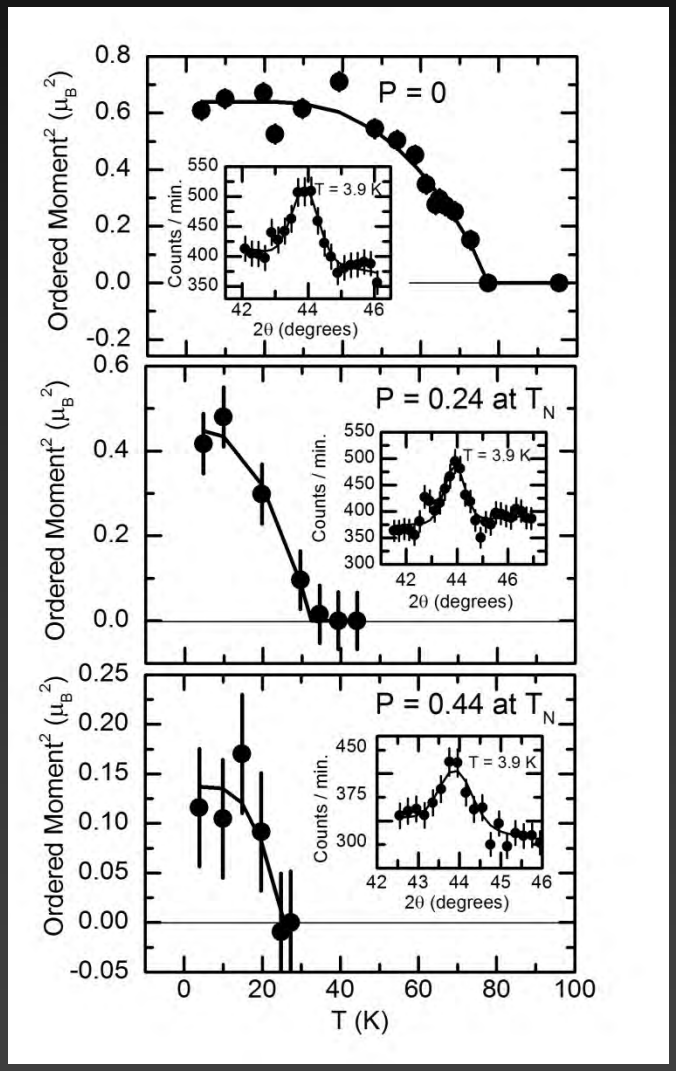


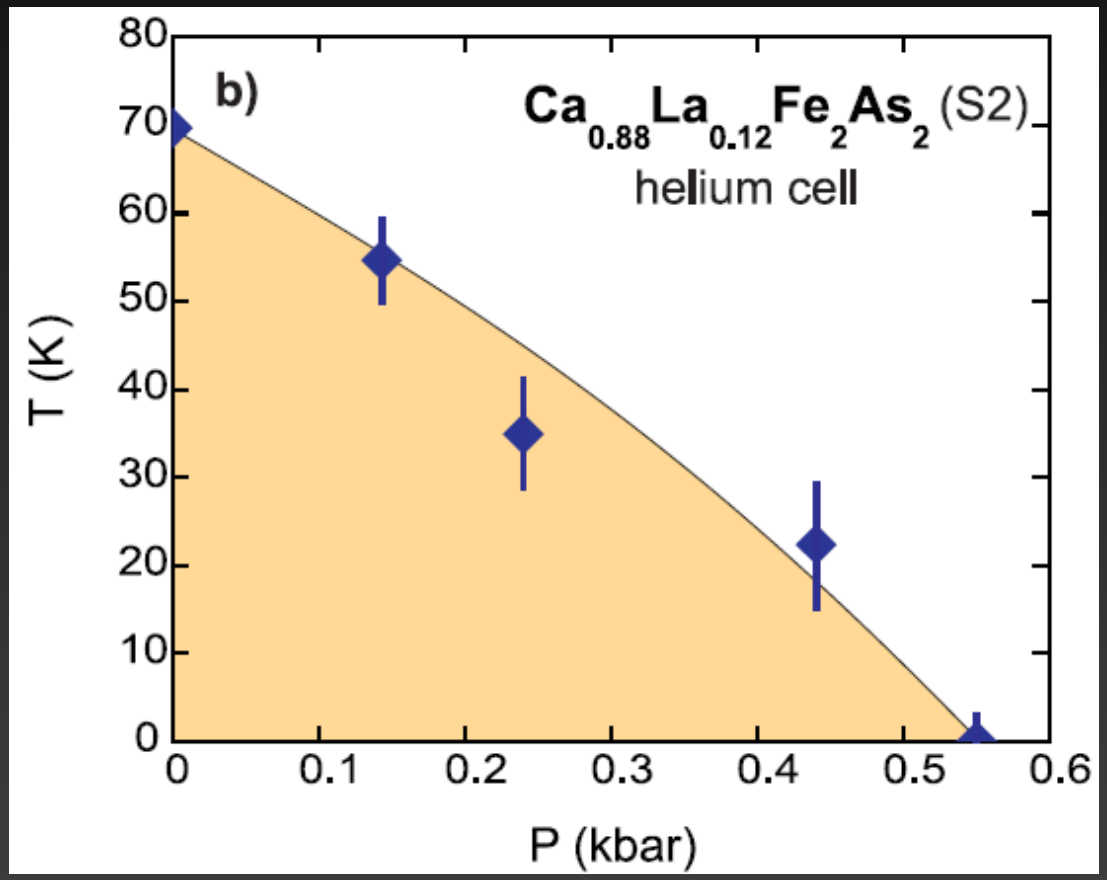
- **Measure AFM OP under He gas pressure**

S.R. Saha *et al*, preprint

$Ca_{1-x}La_xFe_2As_2$ under pressure

SAMPLE 2: ***La12%, hydrostatic (He) cell***





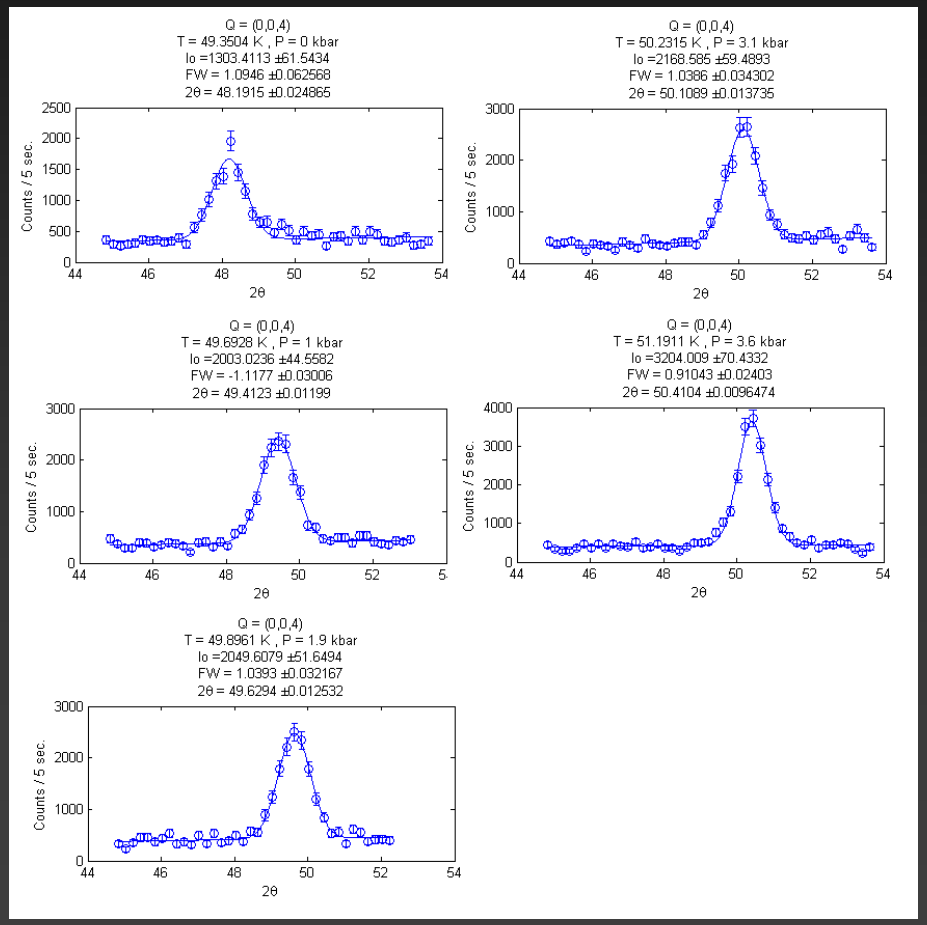
T_0 vanishes < 0.5 kbar

S.R. Saha *et al*, preprint

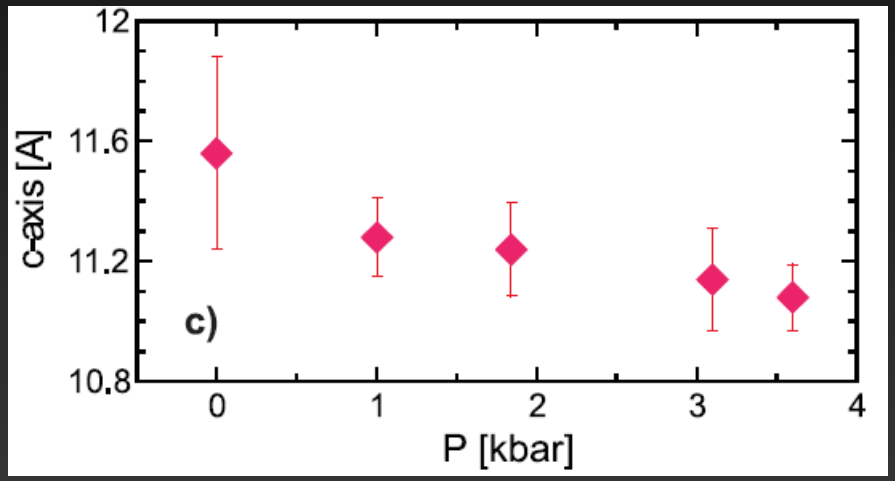
$Ca_{1-x}La_xFe_2As_2$ under pressure

SAMPLE 2: ***La12%, hydrostatic (He) cell***

Scanning Q = (0,0,4) vs P



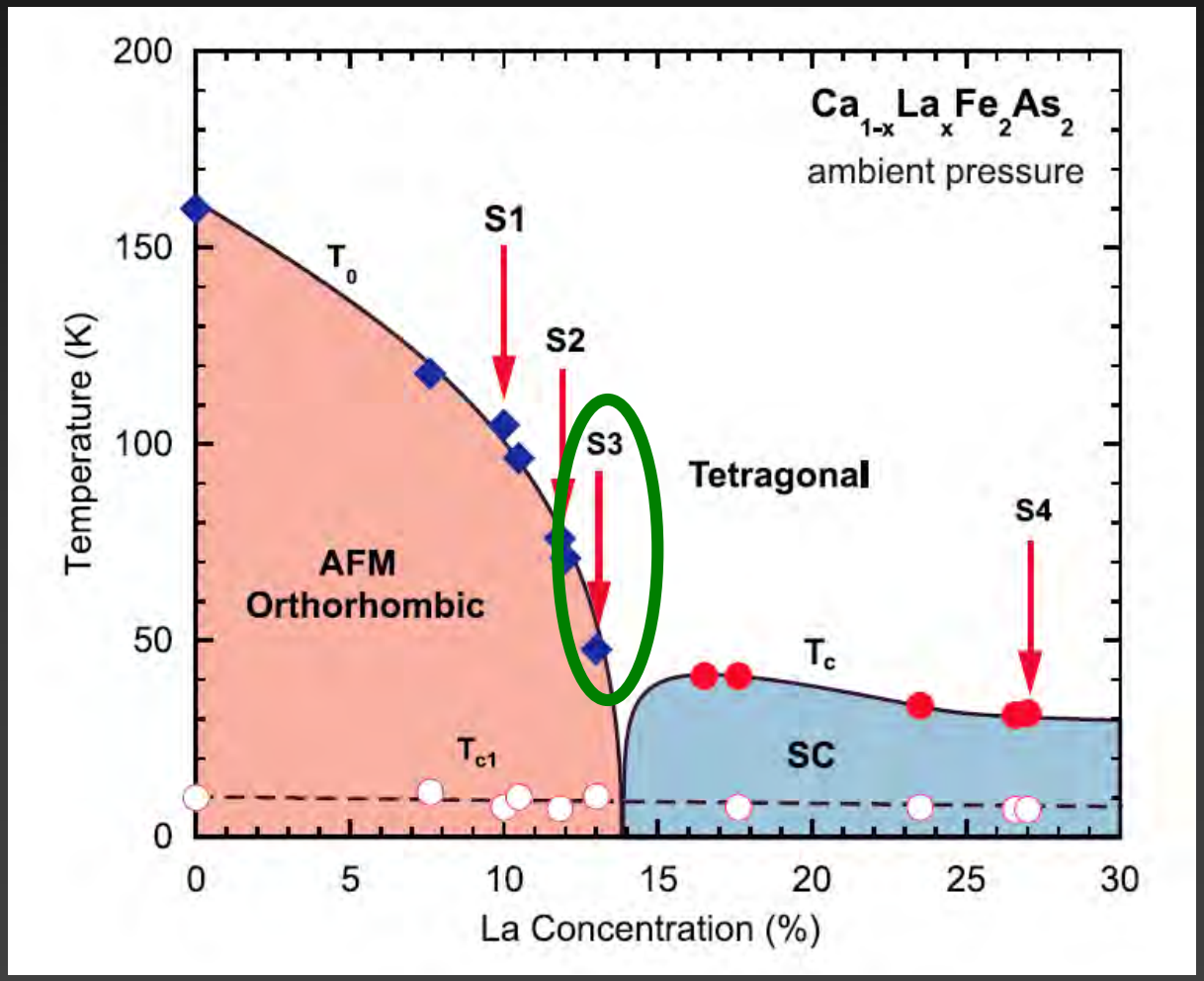
***c*-axis vs pressure**



- **No trace of collapse phase**

S.R. Saha *et al*, preprint

$Ca_{1-x}La_xFe_2As_2$ under pressure



S1. Clamp cell (UMD)

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resistivity

S2. helium cell (NIST)

0 – 4 kbar

neutron scattering

S3. helium cell (McMaster)

0 – 4 kbar

resistivity

S4. Anvil cell (Cambridge)

0 – 50 kbar

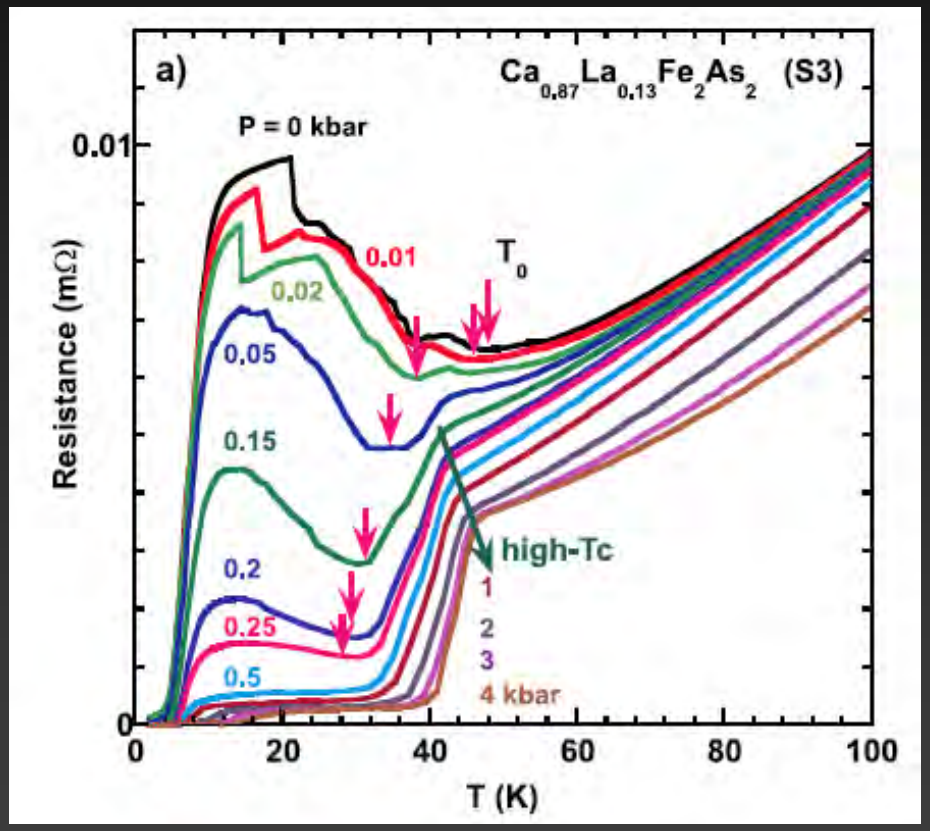
resistivity and TDO

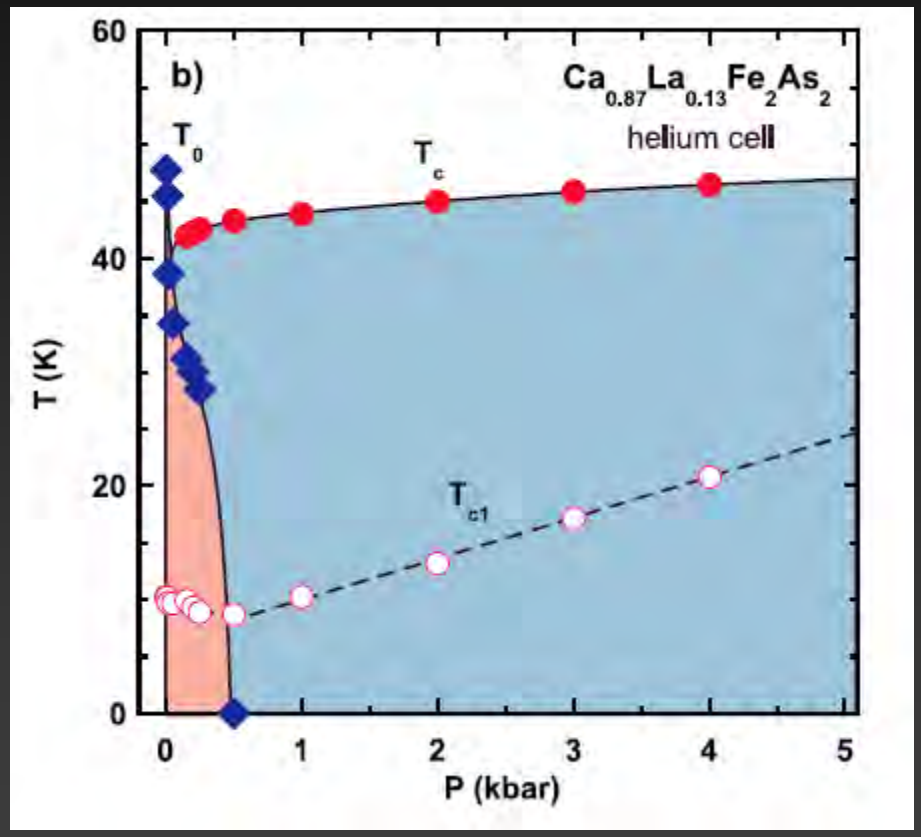
S.R. Saha *et al*, preprint

$Ca_{1-x}La_xFe_2As_2$ under pressure

McMaster University

SAMPLE 3: ***La13%, hydrostatic (He) cell***

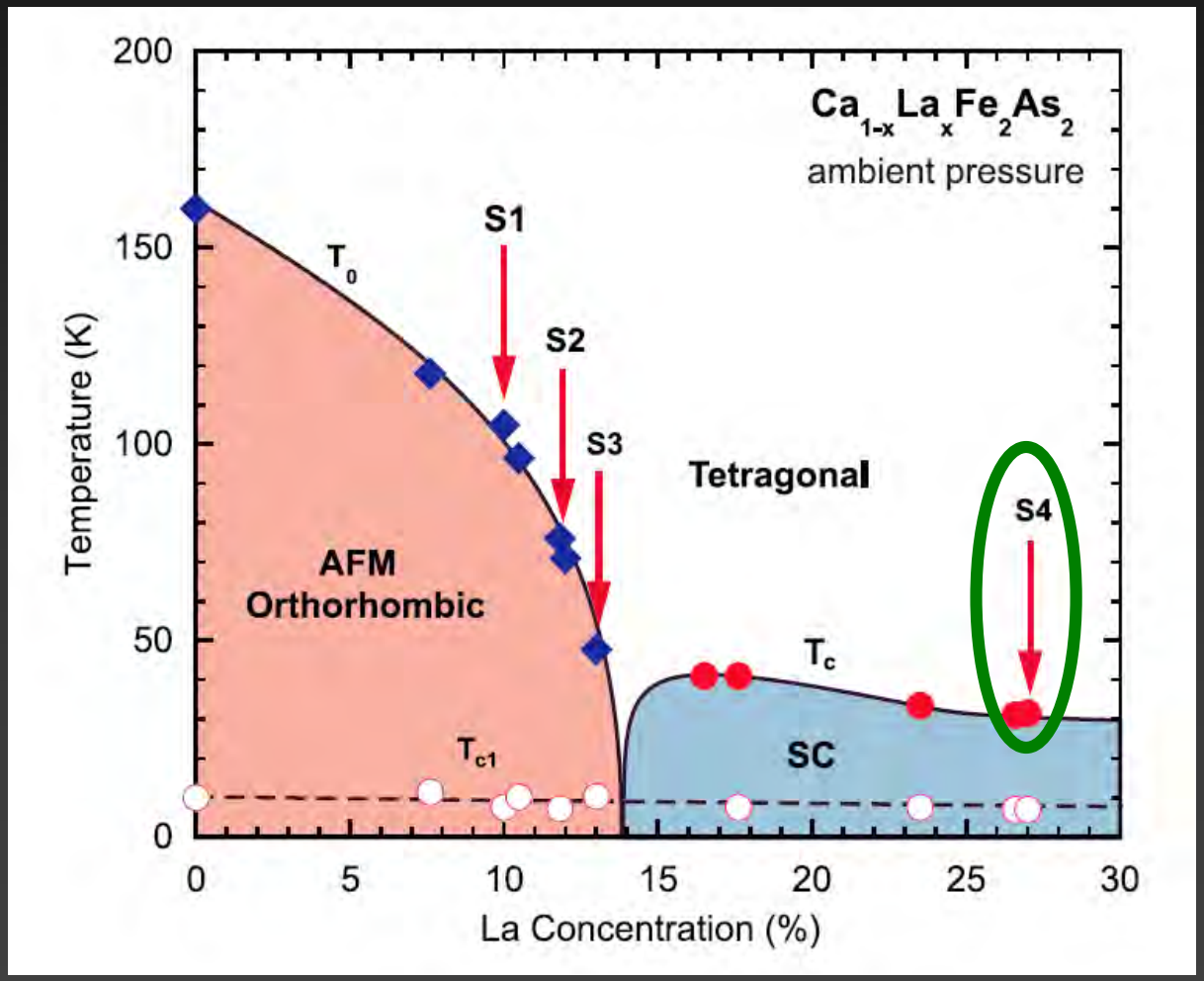




- **Only 50 bar required to reveal SC for T_N=50 K sample**
- **Completely reversible**

S.R. Saha *et al*, preprint

$Ca_{1-x}La_xFe_2As_2$ under pressure



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resistivity

S4. Anvil cell (Cambridge)

0 – 50 kbar

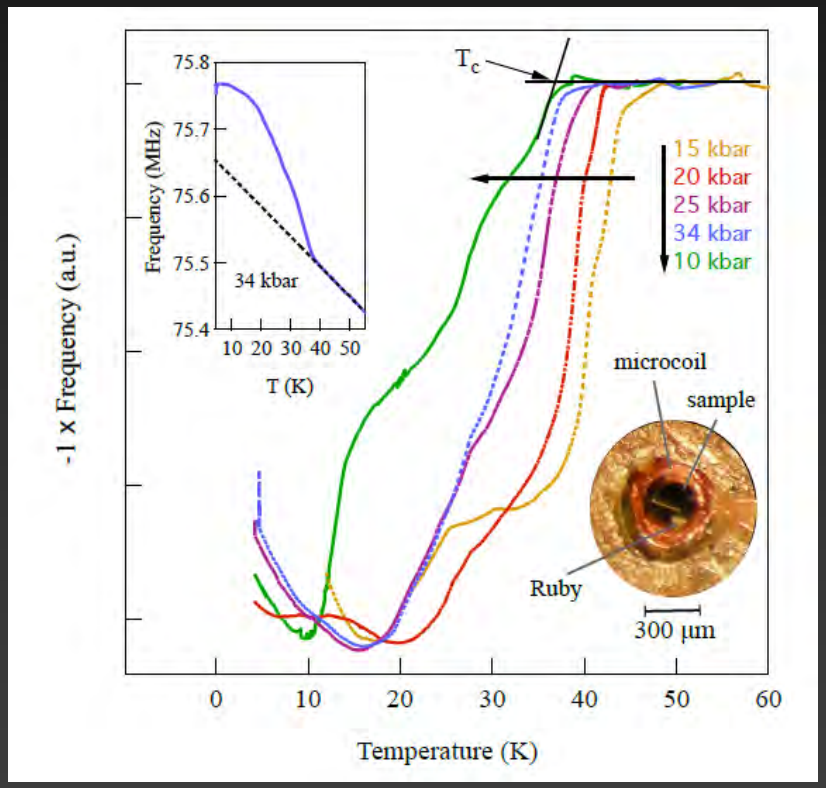
resistivity and TDO

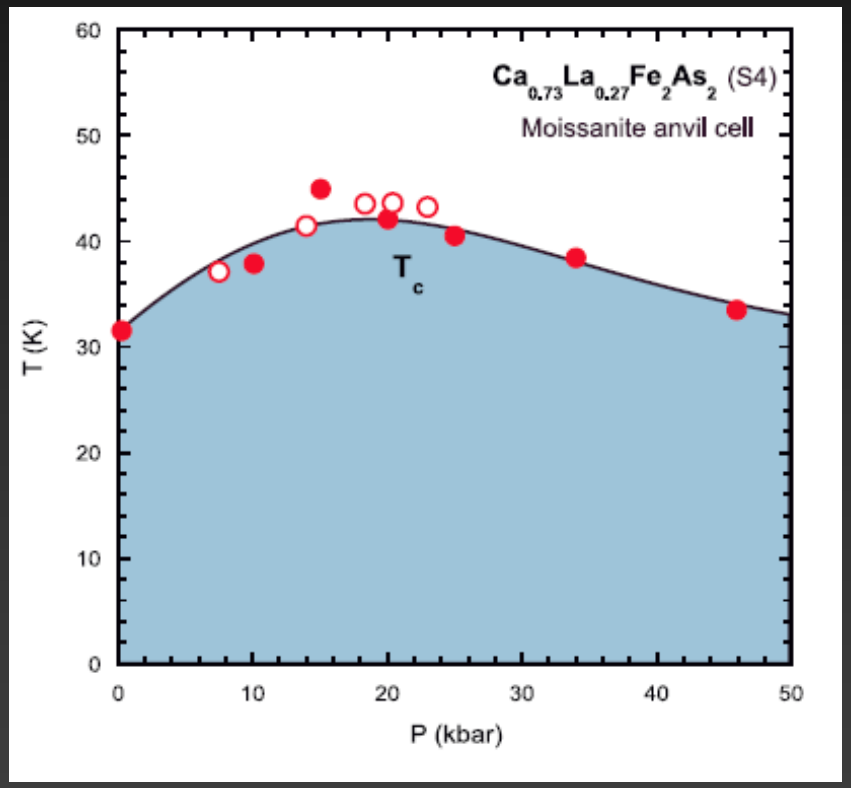
S.R. Saha *et al*, preprint

$Ca_{1-x}La_xFe_2As_2$ under pressure

UNIVERSITY OF CAMBRIDGE

SAMPLE 4: ***La27%, Moissanite anvil cell***



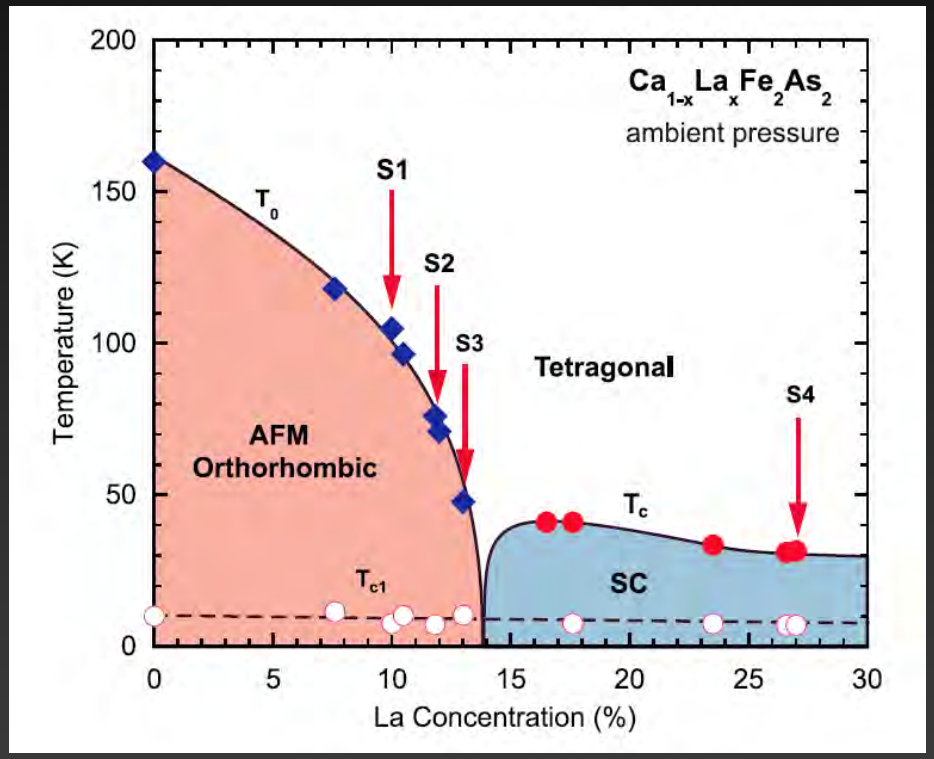


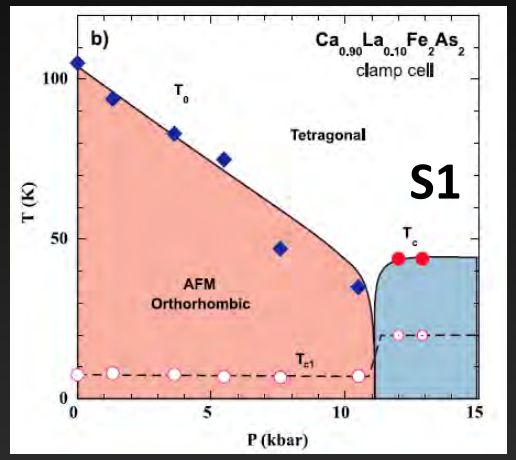
- **TDO measurement: T_c increase to max value for La**

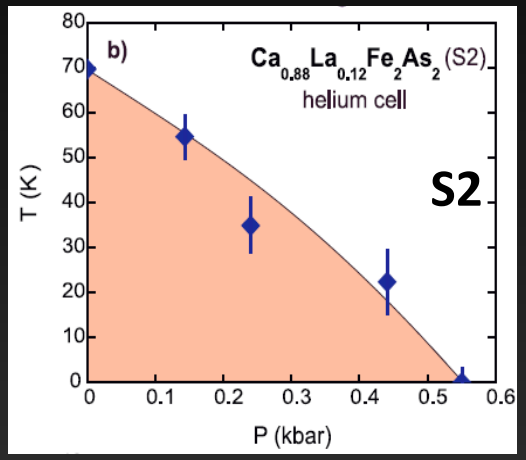
S.R. Saha *et al*, preprint

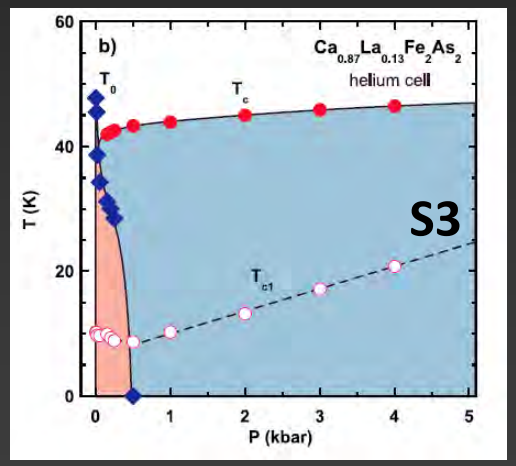
$Ca_{1-x}La_xFe_2As_2$ under pressure

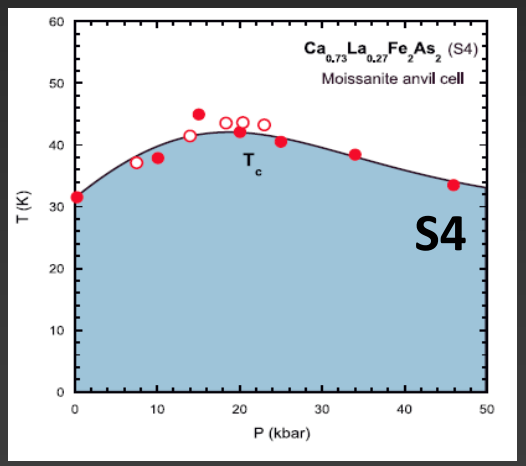
Four Samples







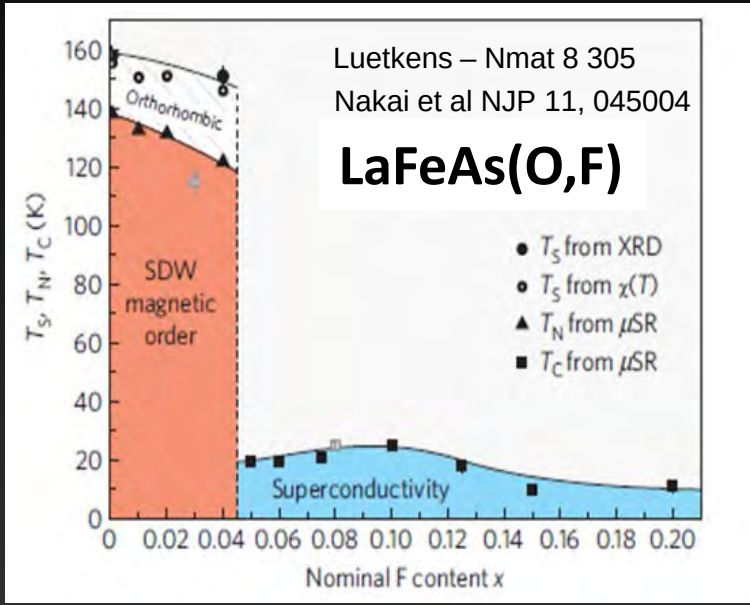


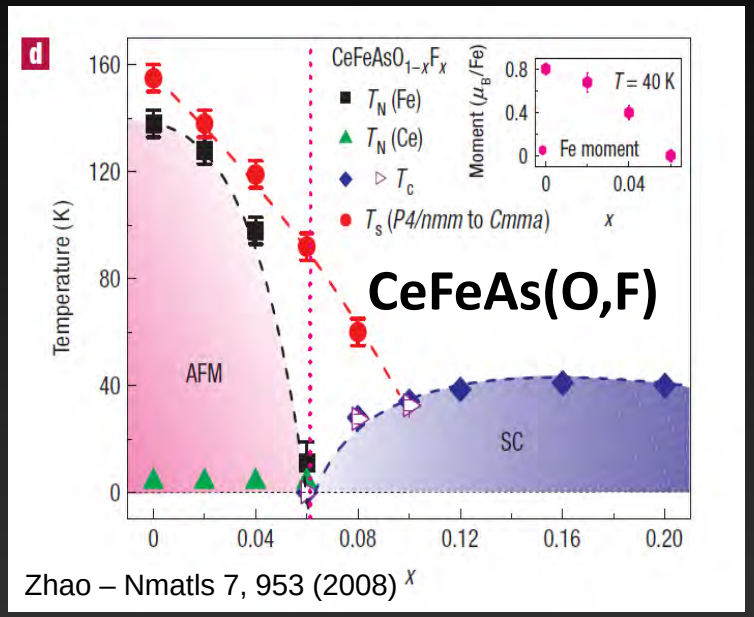


- **Lack of coexistence vs doping and pressure (<0.5 kbar)**
- **Similar to "1111" phase diagrams?**

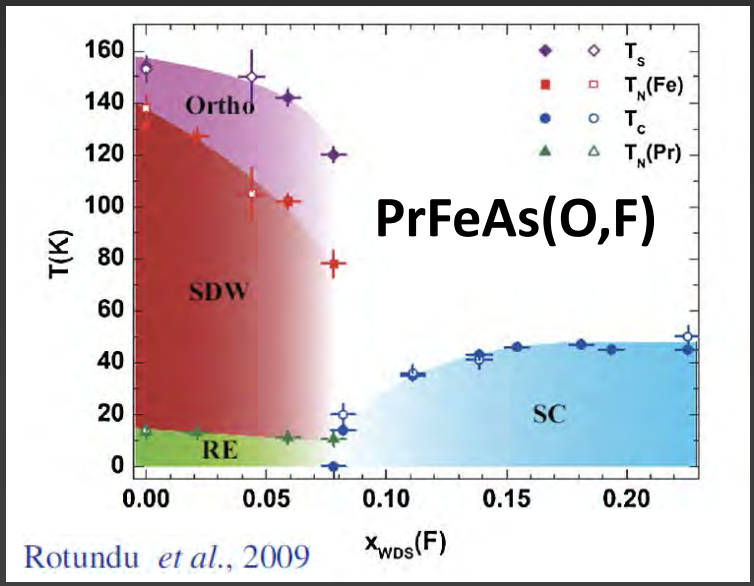
S.R. Saha *et al*, preprint

$Ca_{1-x}La_xFe_2As_2$ under pressure

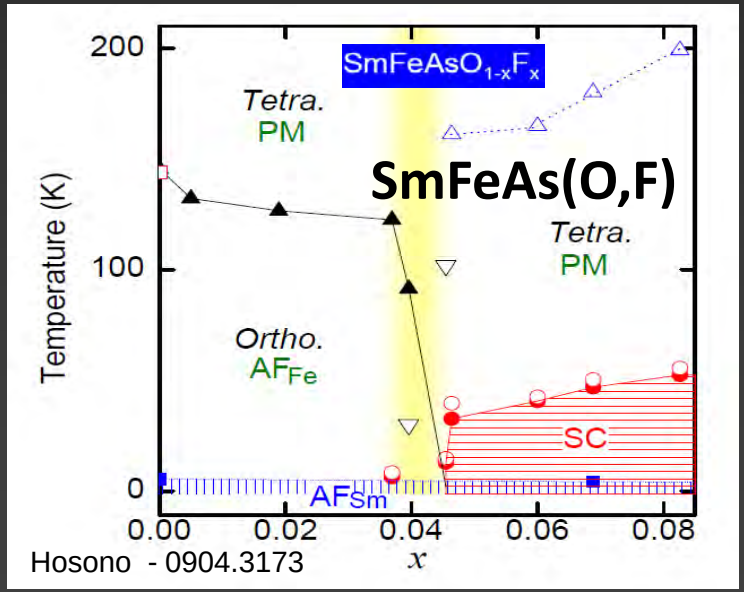




Zhao – Nmatls 7, 953 (2008)



Rotundu *et al.*, 2009

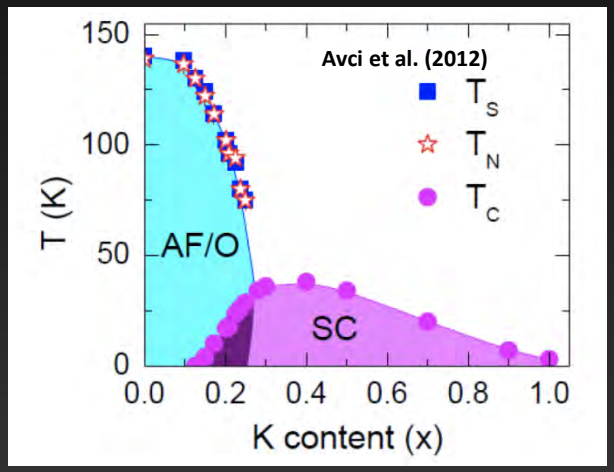


Hosono - 0904.3173

F,H-doped systems exhibit **NO** coexistence

$Ca_{1-x}La_xFe_2As_2$ under pressure

$Ba/Sr_{1-x}K_xFe_2As_2$



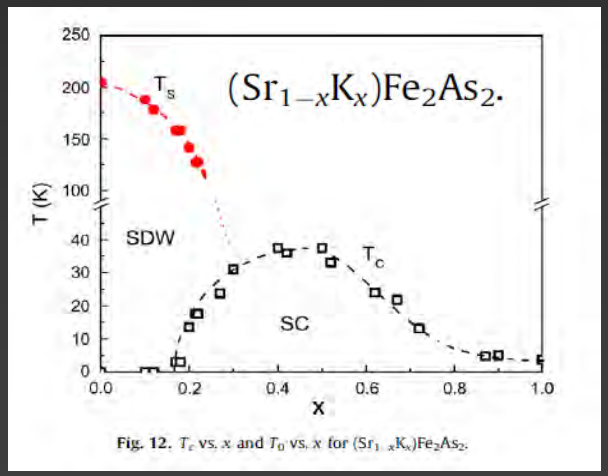
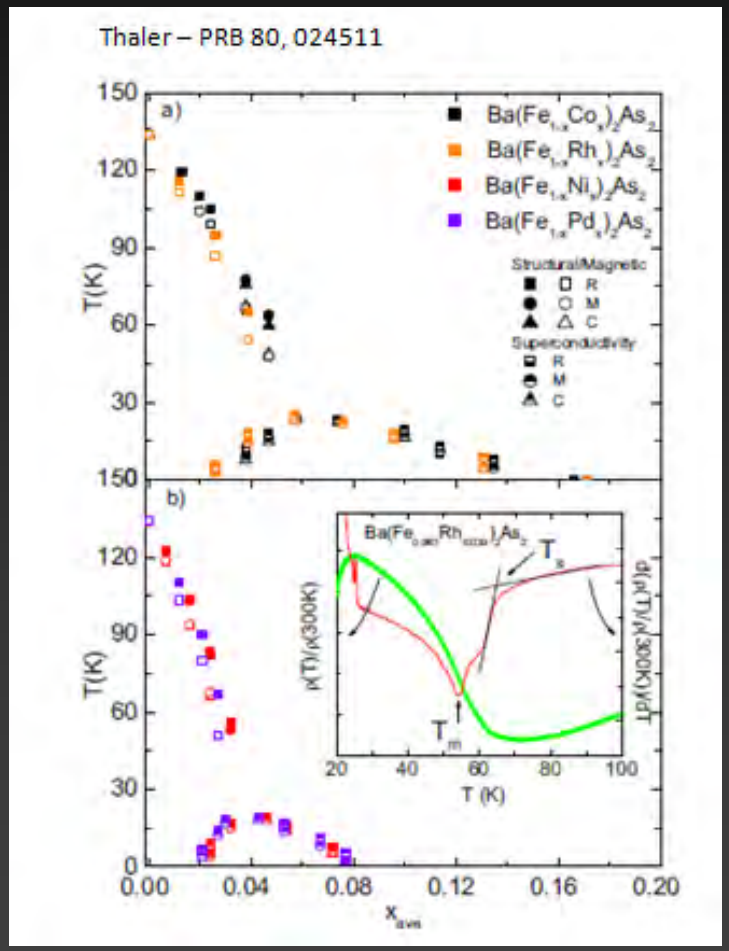
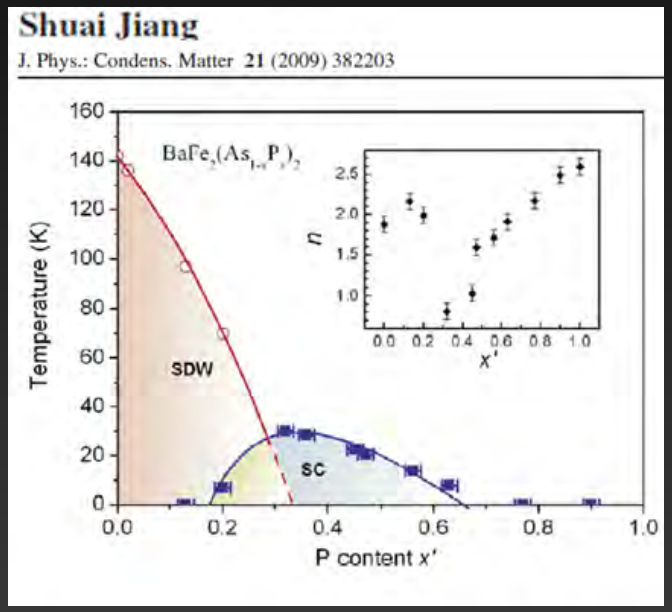


Fig. 12. T_c vs. x and T_0 vs. x for $(Sr_{1-x}K_x)Fe_2As_2$.

$BaFe_{2-x}T_xAs_2$



$BaFeAs_{2-x}P_x$



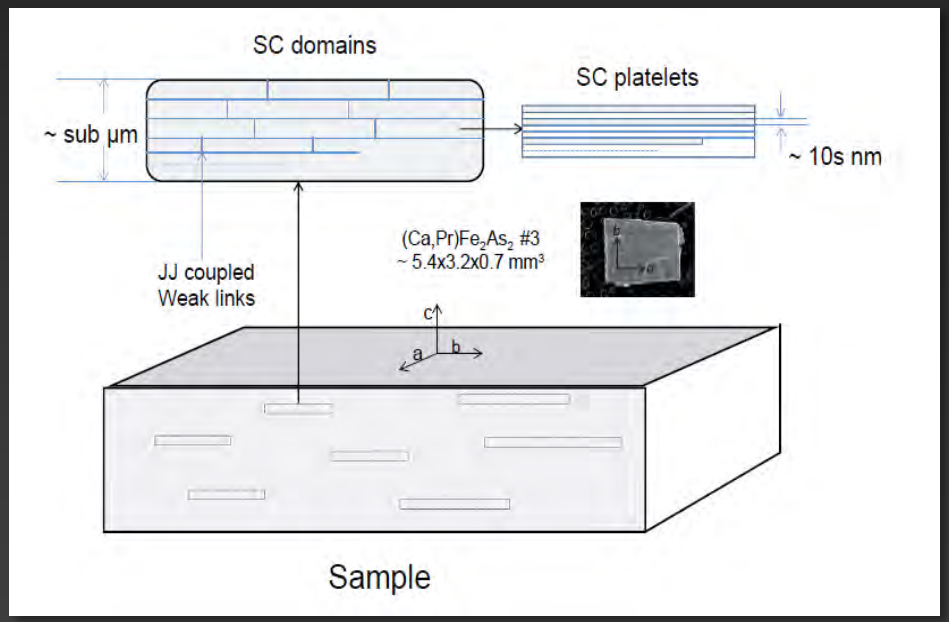
A-, T- and P-doped systems exhibit microscopic coexistence

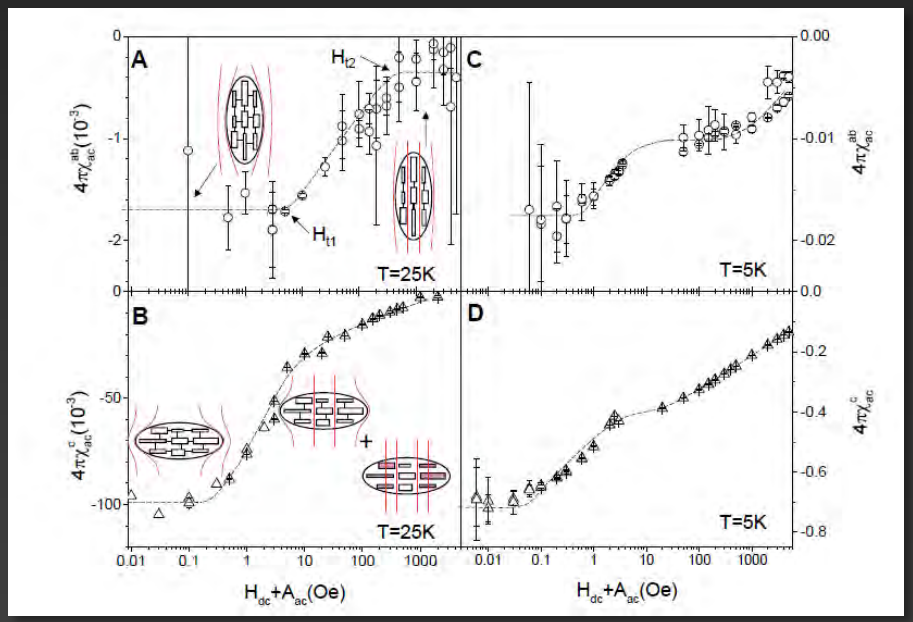
$Ca_{1-x}La_xFe_2As_2$ under pressure

- **We rule out defect/impurity-based origin of high-Tc phase**

Why is the superconducting T_c so high in rare-earth-doped $CaFe_2As_2$?

Authors: F. Y. Wei,[1] B. Lv,[1] L. Z. Deng,[1] J. K. Meen[2], Y. Y. Xue[1], J. E. Hoffman[3] and C. W. Chu[1,4,*]





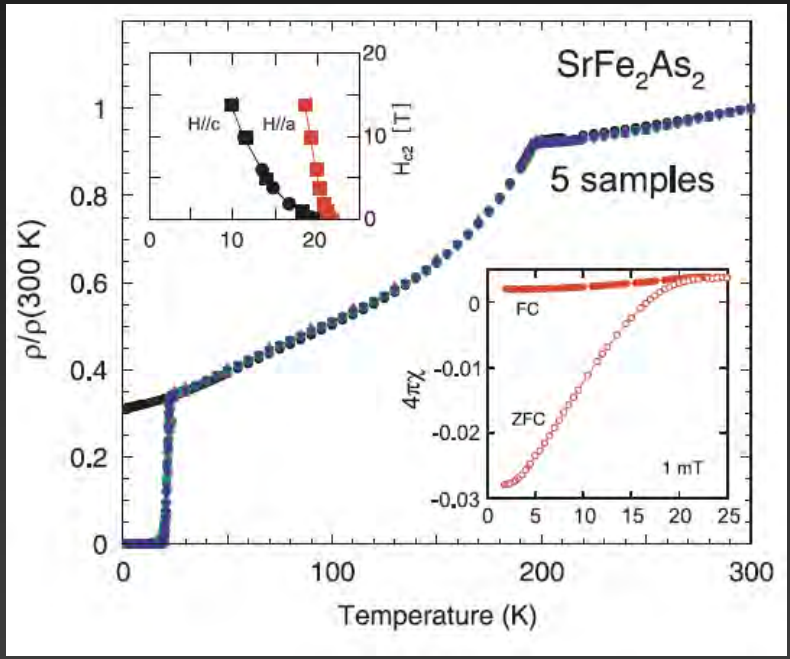
Wei/Chu et al, - 1309.0034

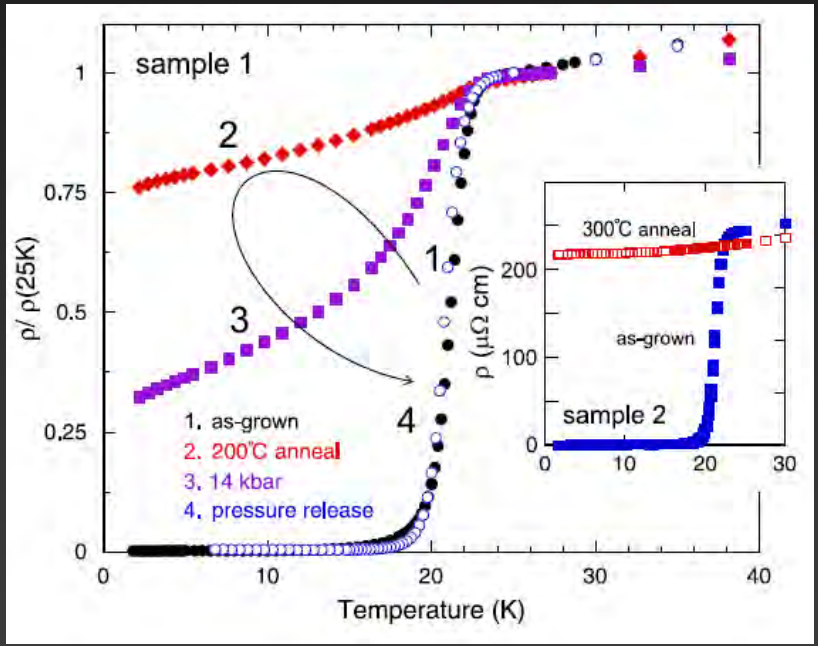
PRL **103,** 037005 (2009) PHYSICAL REVIEW LETTERS week ending 17 JULY 2009

Superconducting and Ferromagnetic Phases Induced by Lattice Distortions in Stoichiometric $SrFe_2As_2$ Single Crystals

S. R. Saha, N. P. Butch, K. Kirshenbaum, and Johnpierre Paglione*

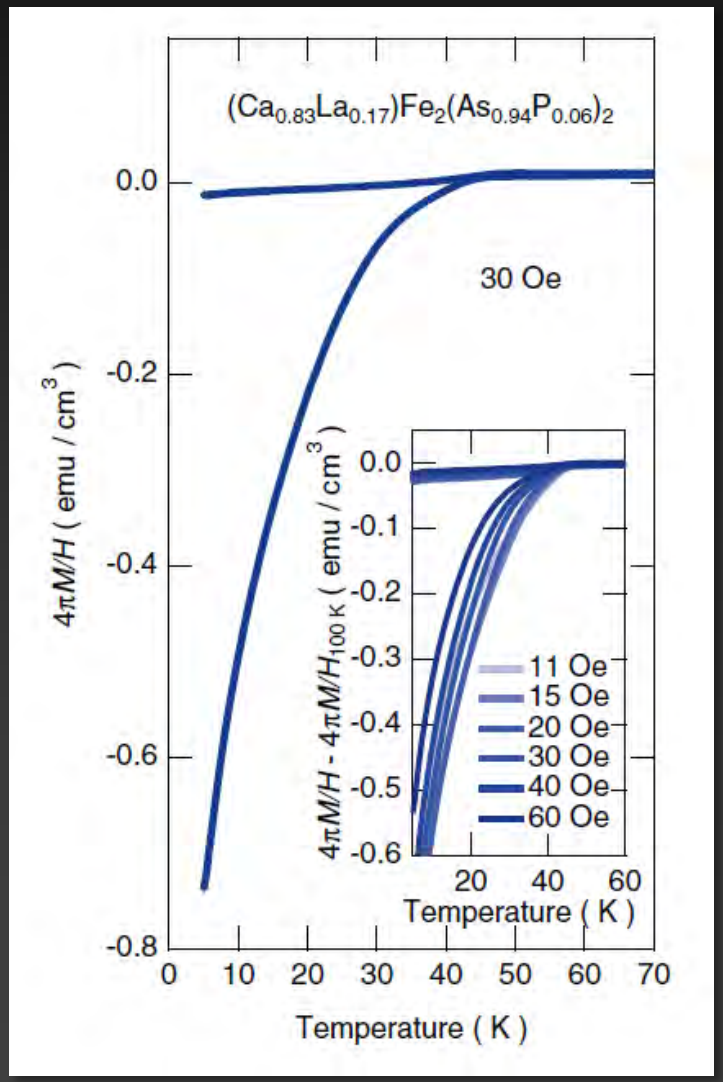
Center for Nanophysics and Advanced Materials, Department of Physics, University of Maryland, College Park, Maryland 20742, USA





$Ca_{1-x}La_xFe_2As_2$ under pressure

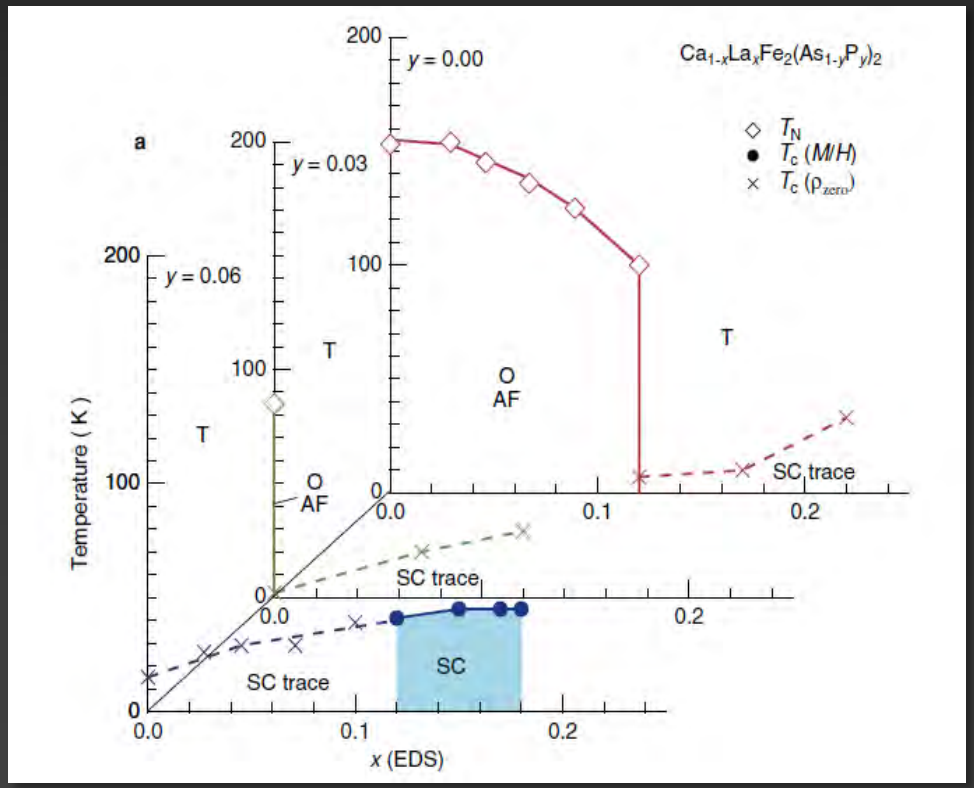
How do we get bulk phase???



SCIENTIFIC REPORTS | 3 : 1478 | DOI: 10.1038/srep01478

Emergence of superconductivity at 45 K by lanthanum and phosphorus co-doping of $CaFe_2As_2$

Kazutaka Kudo, Keita Iba, Masaya Takasuga, Yutaka Kitahama, Jun-ichi Matsumura, Masataka Danura, Yoshio Nogami & Minoru Nohara

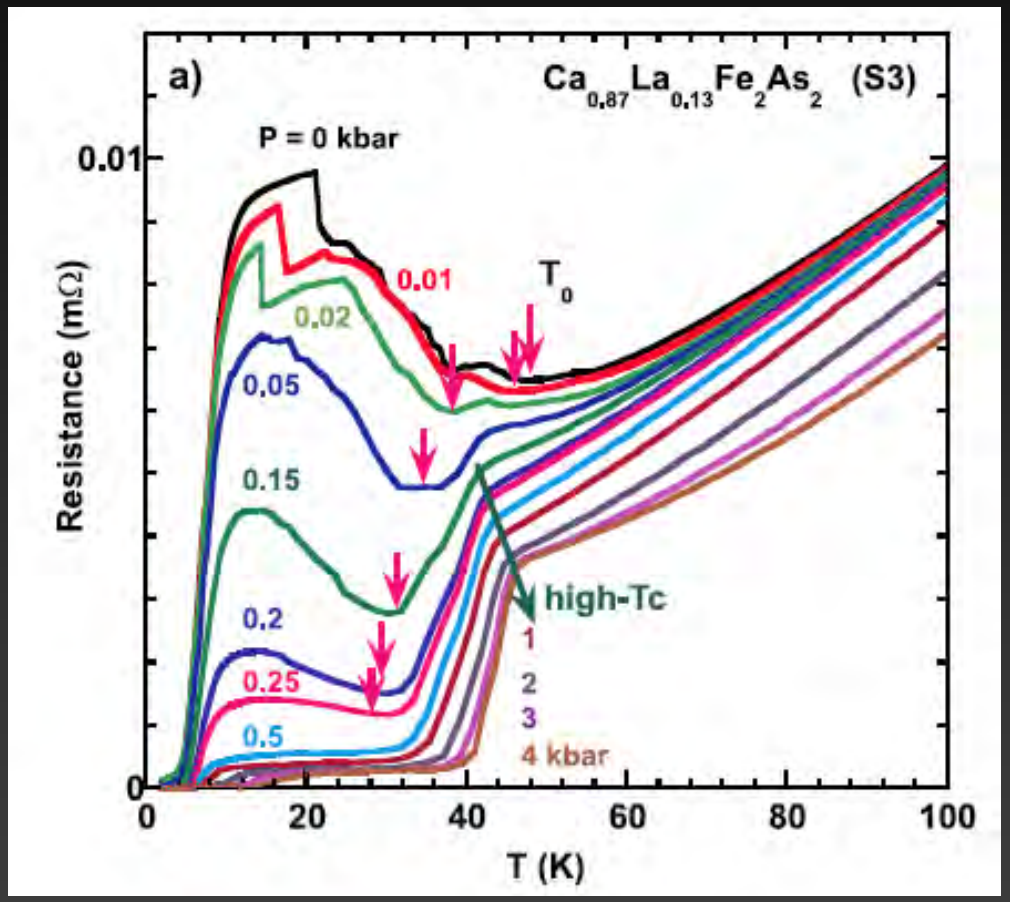


$Ca_{1-x}La_xFe_2As_2$ under pressure

center for nanophysics and advanced materials

Conclusions

- **Rare Earth Substitution in $CaFe_2As_2$**
  - Controllable structural collapse
  - La, Ce, Pr, Nd, Sm, Gd…
  - High-Tc superconductivity
- **La substitution under pressure**
  - Continuous tuning of AFM/SC
- **Separation of AFM/SC phases**
  - Consistency with Tc >40 K materials



S.R. Saha *et al*, PRB 85, 024525 (2012)
T. Drye *et al,* SST 25, 084014 (2012)
H. Gretarsson et al, PRL. 110, 047003 (2013)
L. Ma *et al,* CPB 22, 057401 (2013)

S.R. Saha *et al*, preprint (2013)