Absorção de raios-X aplicada ao estudo da Supercondutividade a altas temperaturas nos Pnictídeos de Fe

Eduardo Granado

SUMÁRIO

I. O SISTEMA – Os supercondutores à base de Fe

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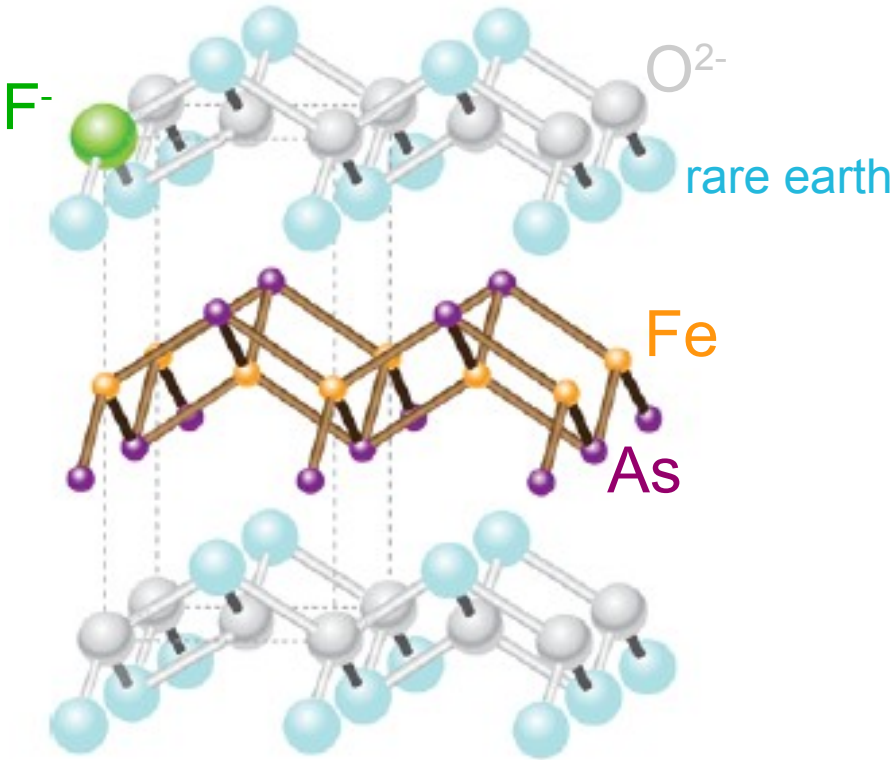
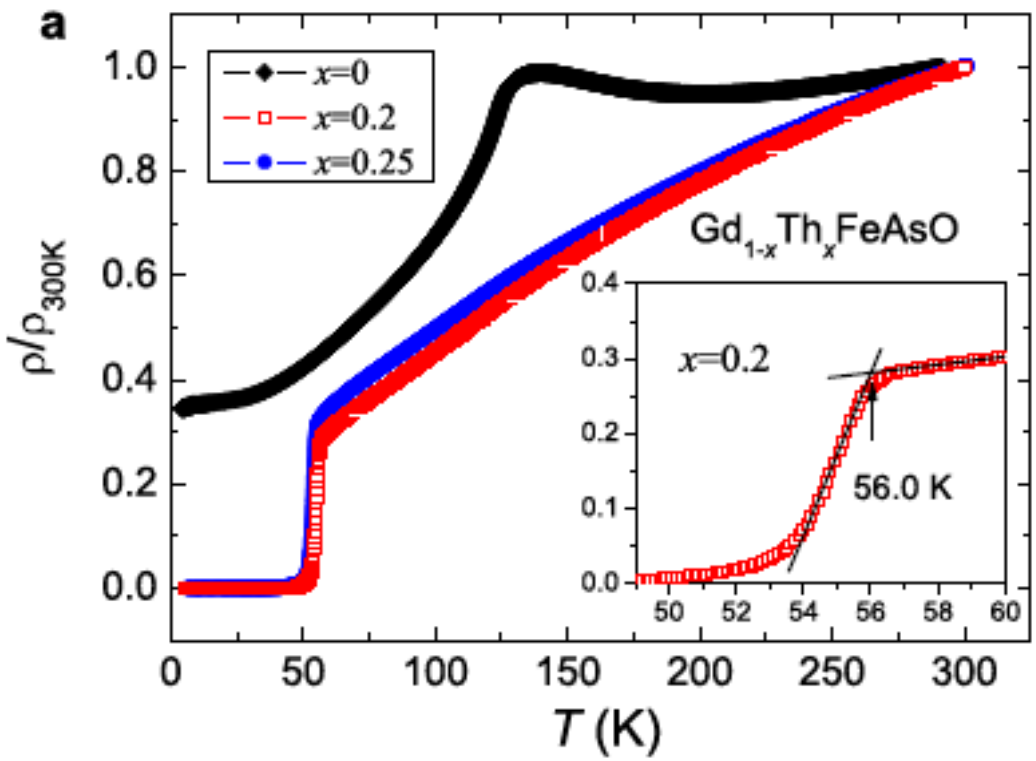
- Introdução ao LNLS

III. Estudo da estrutura atômica local de $BaFe_2As_2$

IV. Natureza da dopagem de Co no sítio de Fe em $BaFe_{2-x}Co_xAs_2$

High-Tc superconductivity in Fe-based oxypnictides





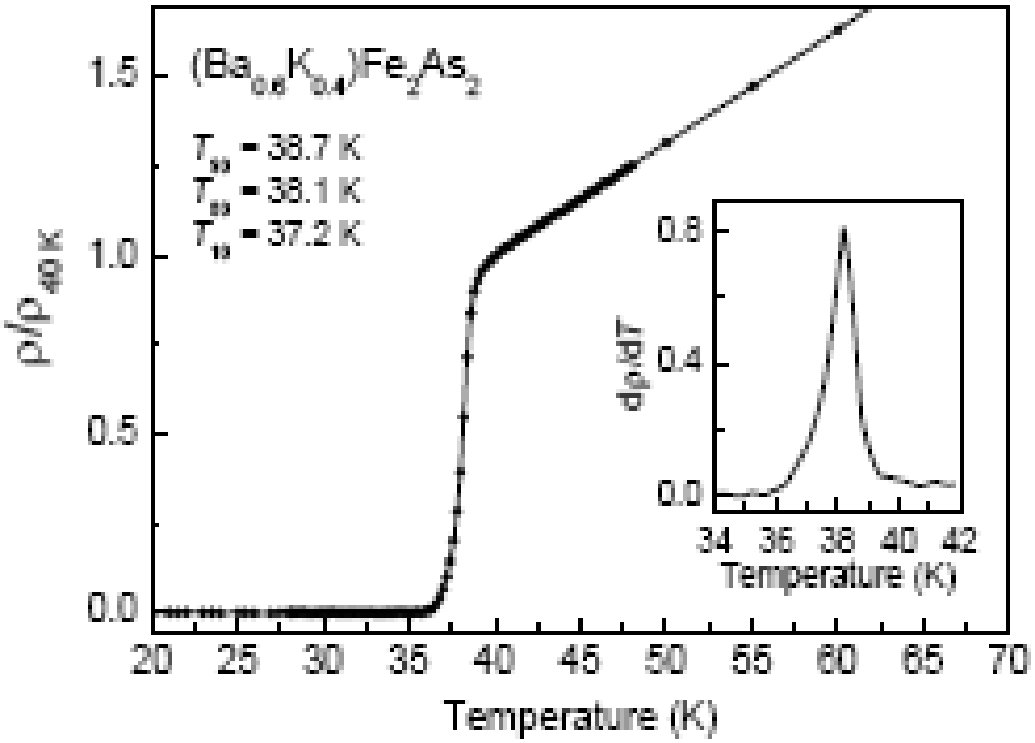
C. Wang *et al.*, Europhys. Lett. **83**, 67006 (2008).

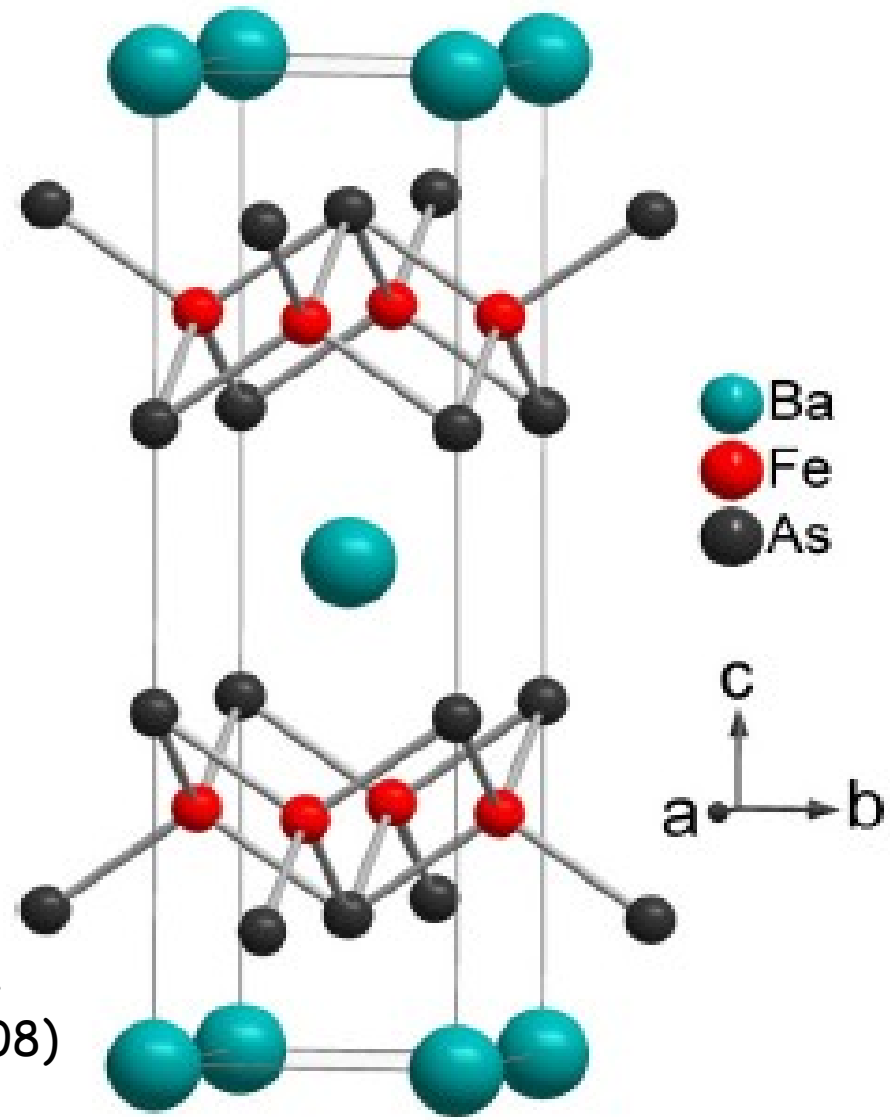
Initial discovery: T_c = 28 K in

F-doped LaOFeAs

Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).

$BaFe_2As_2$ - "hole doping"

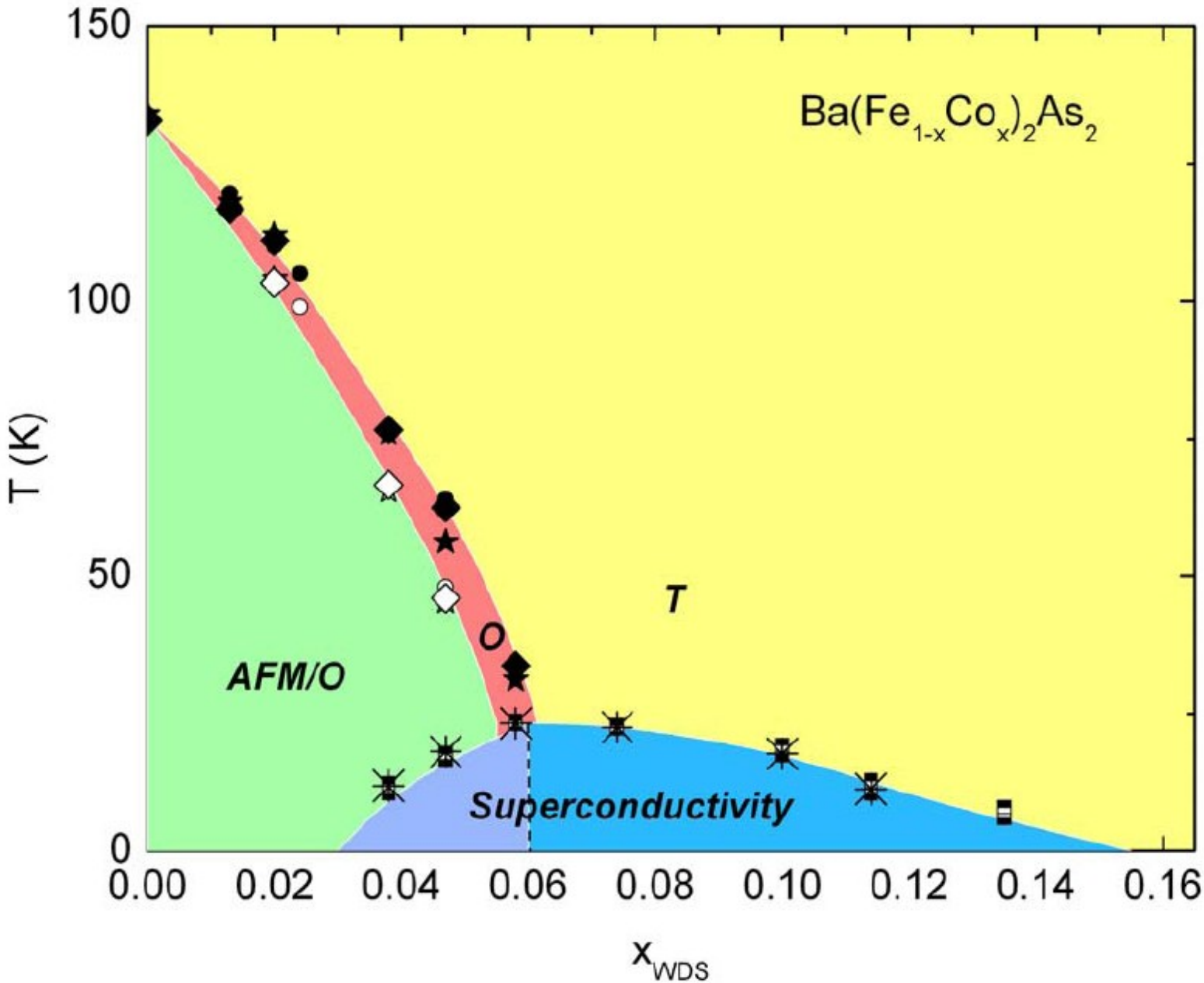




Rotter *et al.*, Phys. Rev. Lett. **101**, 107006 (2008)
G.F. Chen *et al.*, Chin, Phys. Lett. **25**, 3403 (2008).
K. Sasmal *et al.*, Phys. Rev. Lett. **101**, 107007 (2008)
G. Wu *et al.*, Europhys. Lett. **84**, 27010 (2008).

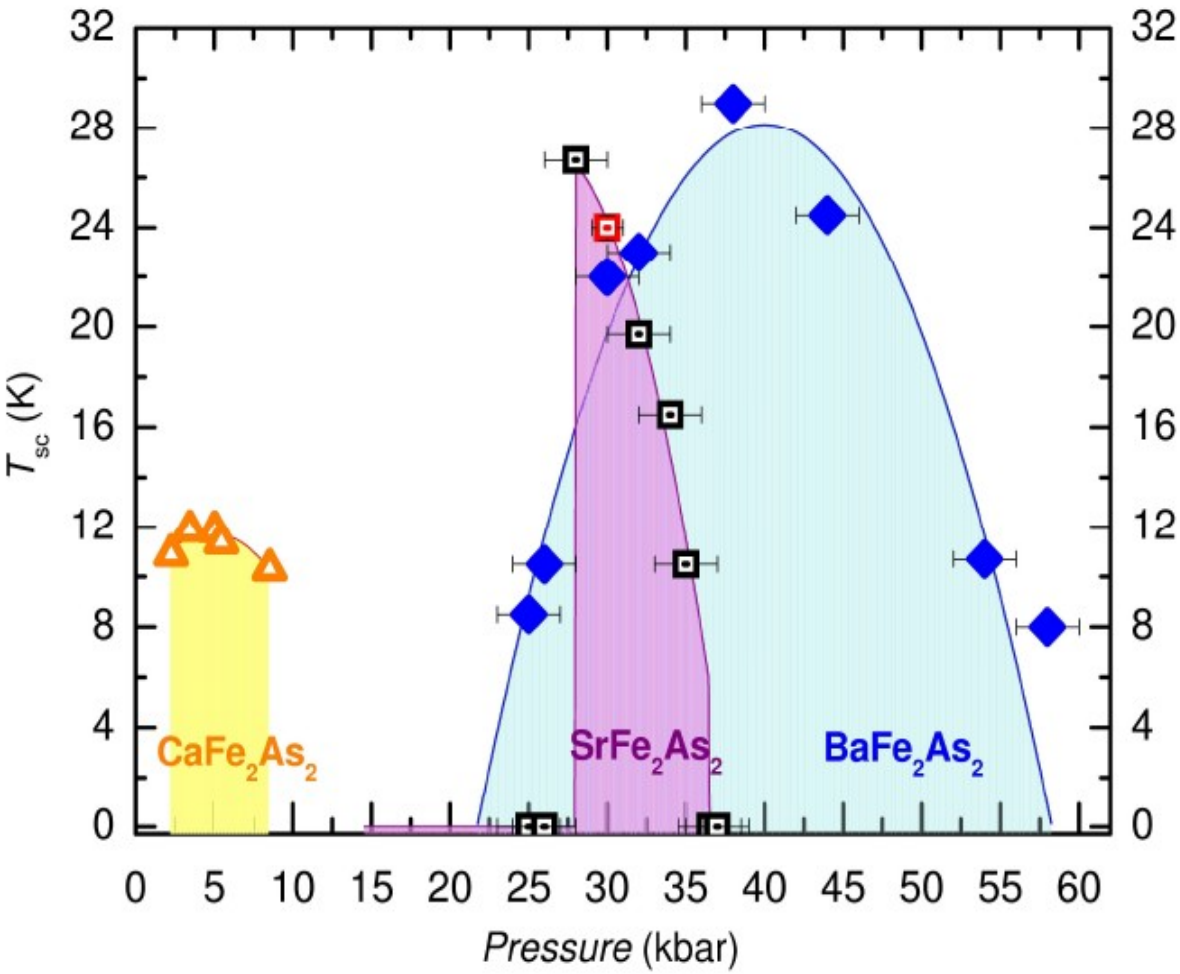
Single crystals !!

$BaFe_2As_2$ - "electron doping"



P.C. Canfield and S.L. Bud'ko, cond-mat 1002.0850

Pressure-induced superconductivity in undoped compounds !!



- M. S. Torikachvili, S.L. Bud´ko, N. Ni, and P.C. Canfield, Phys. Rev. Lett. **101**, 057006 (2008);
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- P. Alireza *et al.*, J. Phys.: Condens. Matter **21**, 012208 (2009).
- T. Park *et al.*, J. Phys..: Condens. Matter **20**, 322204 (2008).
- H. Fukasawa *et al.*, condmat/ 0808.0718.
- A. Mani *et al.*, cond-mat/ 0903.4236.
- E. Colombier, S.L. Bud´ko, N. Ni, and P.C. Canfield, condmat/ 0904.4488.

The million-dollars questions:

1 - Is there a common structural feature linking the "hole-doped", "electron-doped", and pressure-induced superconductivity in $BaFe_2As_2$?

2 – What is the nature of doping in this system in real space ? Is there an actual charge transfer to the Fe ions ?

nature materials

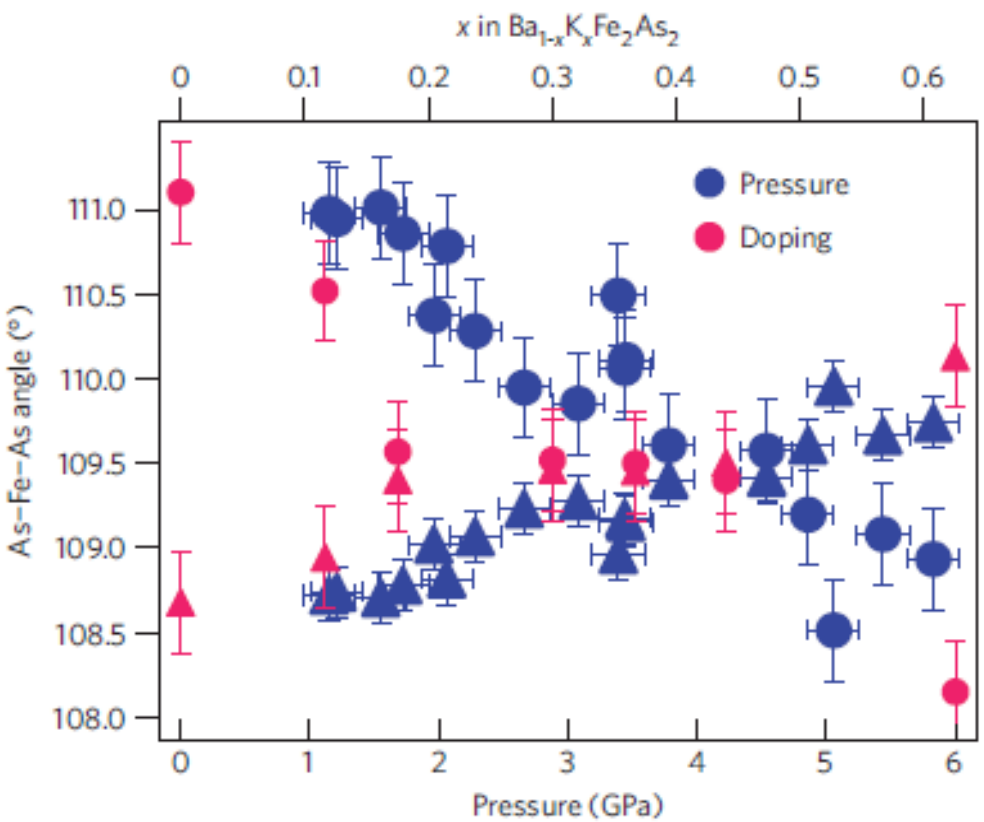
LETTERS

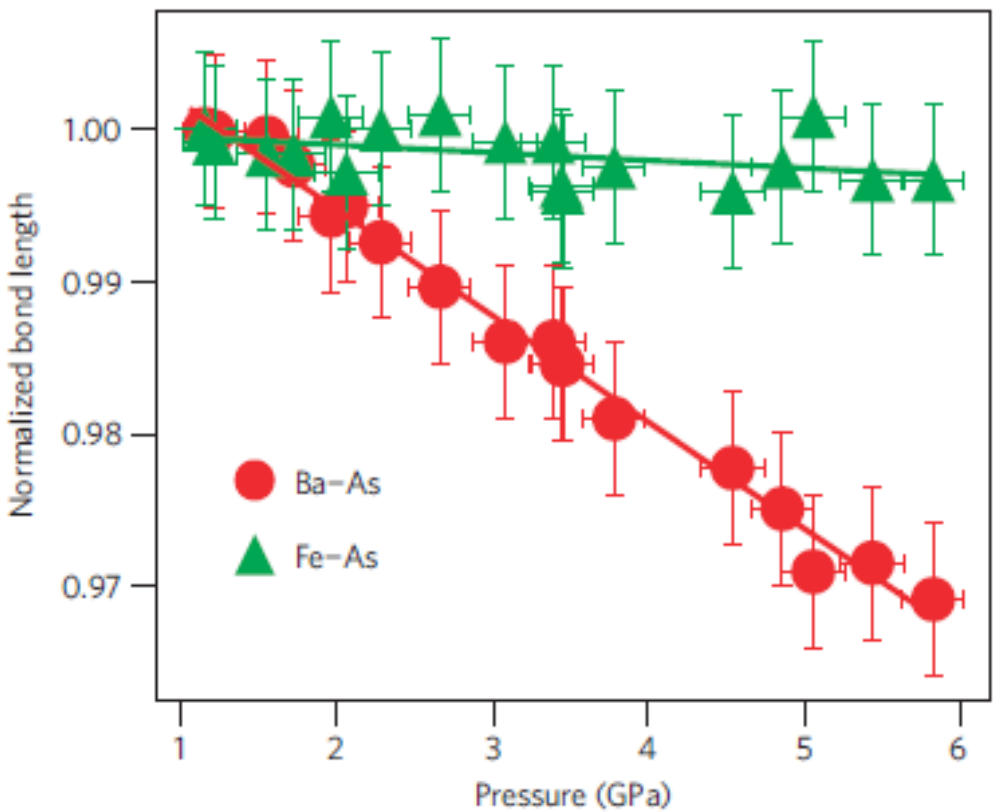
PUBLISHED ONLINE: 3 MAY 2009 | DOI: 10.1038/NMAT2443

Similarities between structural distortions under pressure and chemical doping in superconducting $BaFe_2As_2$

Simon A. J. Kimber[1]*, Andreas Kreyssig[2,3], Yu-Zhong Zhang[4], Harald O. Jeschke[4], Roser Valentí[4], Fabiano Yokaichiya[1], Estelle Colombier[2], Jiaqiang Yan[2], Thomas C. Hansen[5], Tapan Chatterji[6], Robert J. McQueeney[2,3], Paul C. Canfield[2,3], Alan I. Goldman[2,3] and Dimitri N. Argyriou[1]*

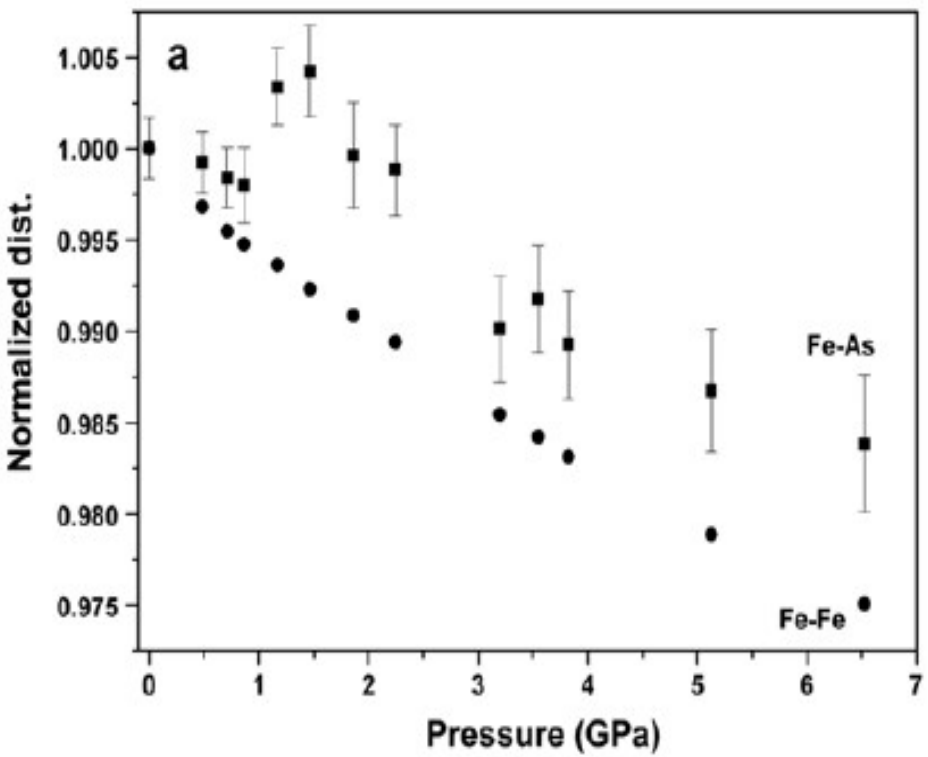
Neutron diffraction indicates Fe-As bond is rigid and superconductivity is apparently regulated by a tuning of the As-Fe-As angle

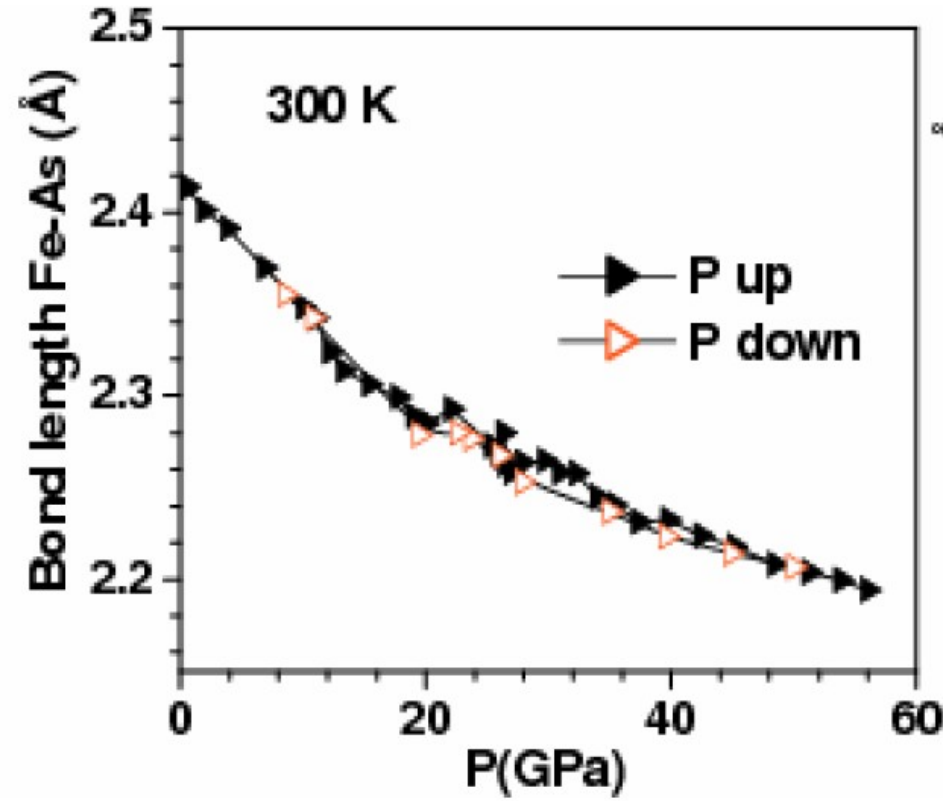




Nature Mater. **8**, 471 (2009).

However, synchrotron x-ray diffraction yield different results...



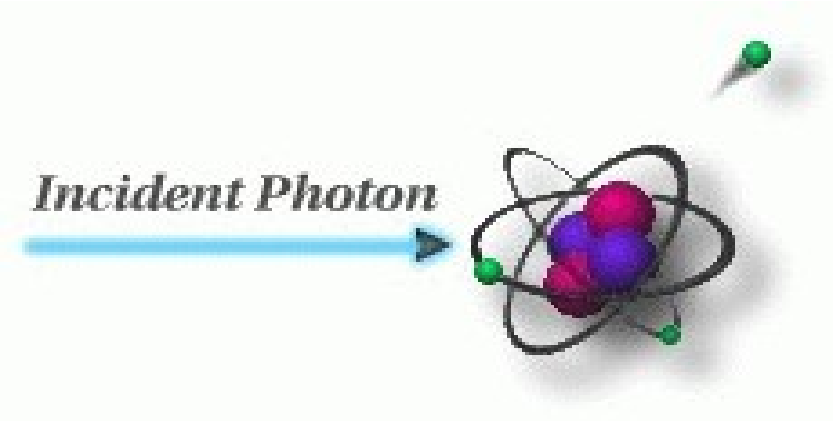


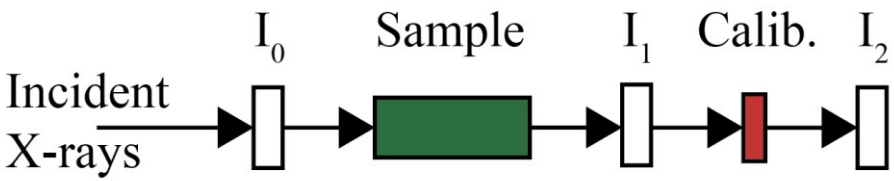
Jorgensen & Hansen, Eur. Phys. J. B 78, 411 (2010).

Mittal et al., cond-mat 1007.2320

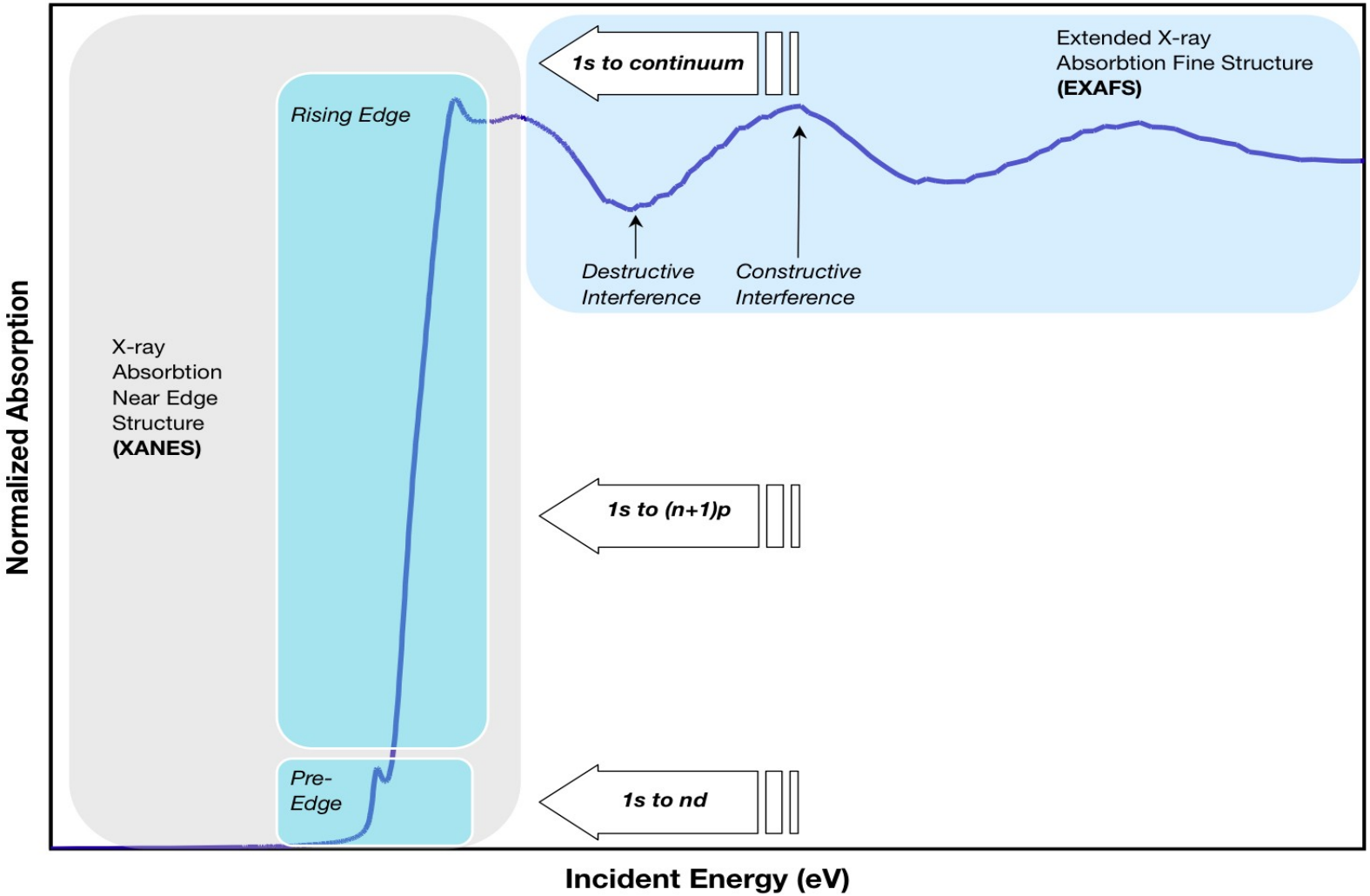
Also, the "electron-doped" Co-substituted system shows maximum Tc at As-Fe-As angles far away of the ideal tetrahedral value of 109.5°

Espectroscopia de Absorção de Raios-X





$$I_1 = I_o e^{-\mu t}$$



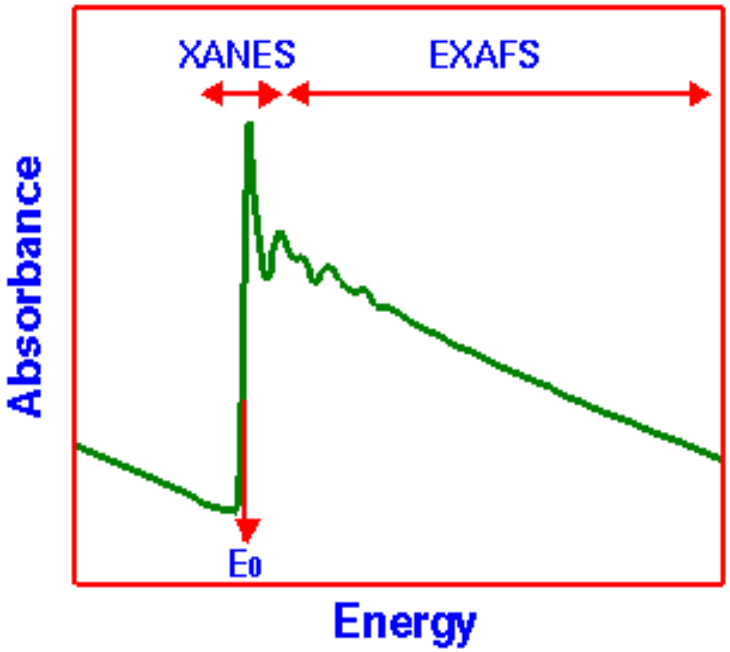
O coeficiente de absorção é proporcional à probabilidade do campo eletromagnético da luz (uma perturbação) induzir uma transição eletrônica. O cálculo é feito com teoria de perturbação dependente do tempo, com o resultado:

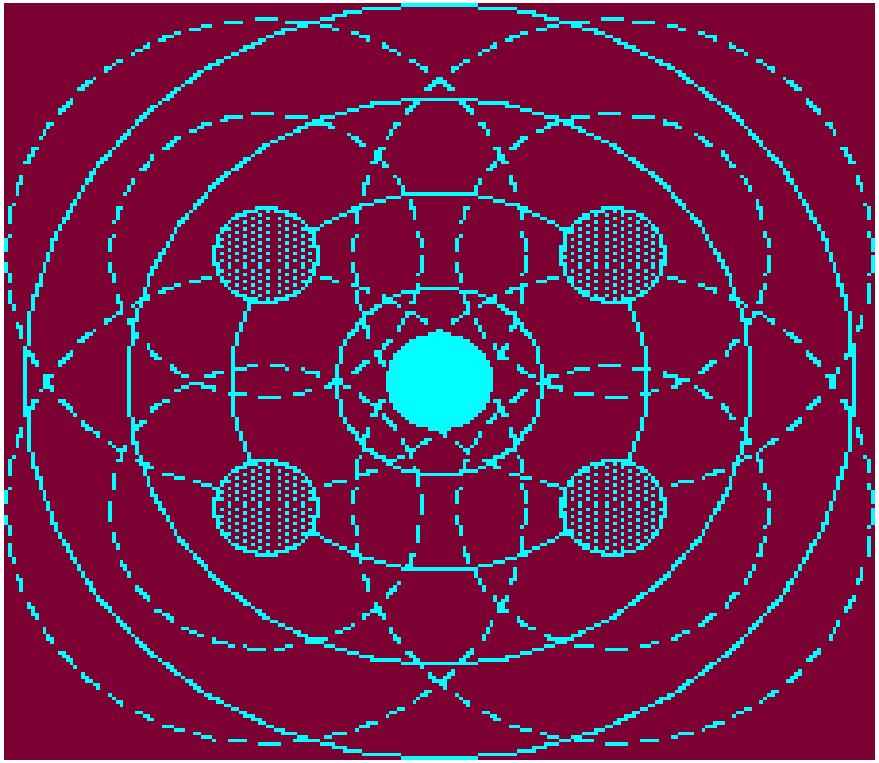
$$\mu = 4N_0\pi^2 e^2(\omega/c)|\langle f|H|i\rangle|^2 \rho(E_f)$$

$$|\langle f|H|i\rangle|^2 \longrightarrow \text{EXAFS}$$

$$\rho(E_f) \longrightarrow \text{XANES}$$

EXAFS:





Debye-Waller term

$\sigma^2 = \sigma_{stat}^2 + \sigma_{vib}^2$

$\sigma < 0.10$ Å

n_X = # of X atoms in shell

amplitude function

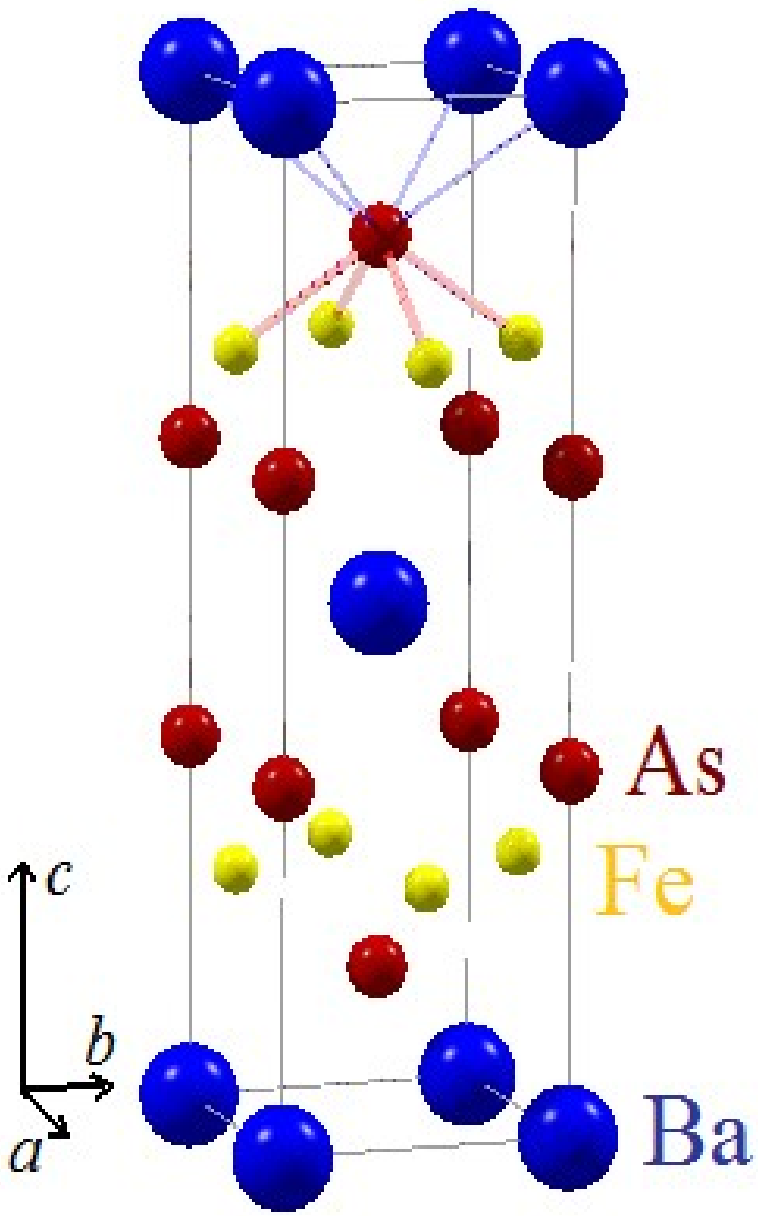
phase function

$$\chi = \sum_{shells} \frac{n_X \cdot S_0^2 \cdot f_X(k)\, e^{-2k^2\sigma^2}}{k \cdot r^2} \sin\left(2kr + \alpha_{MX}(k)\right)$$

amplitude reduction factor

r = (average) MX distance

EXAFS in the $BaFe_2As_2$ system



- The Fe-As bond distance controls the chemical pressure on Fe, and should be sensitive to the Fe valency and spin state.

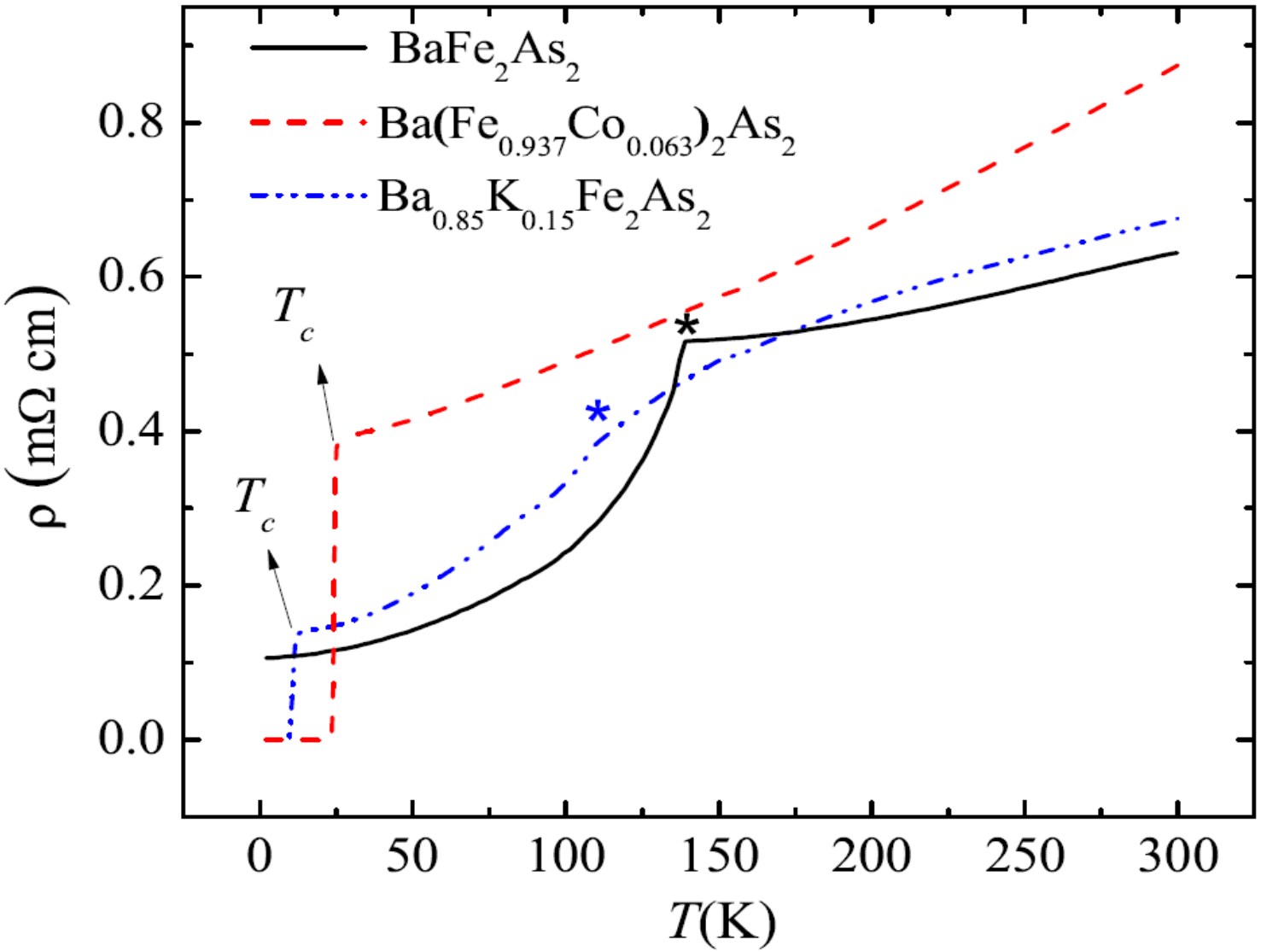
- EXAFS in the As K-edge is an ideally suited technique to investigate the Fe-As bond.

- As-Fe first shell widely separated from the As-Ba second shell.

- As K-edge: 11.865 keV → transmission experiments in thin single crystals possible.

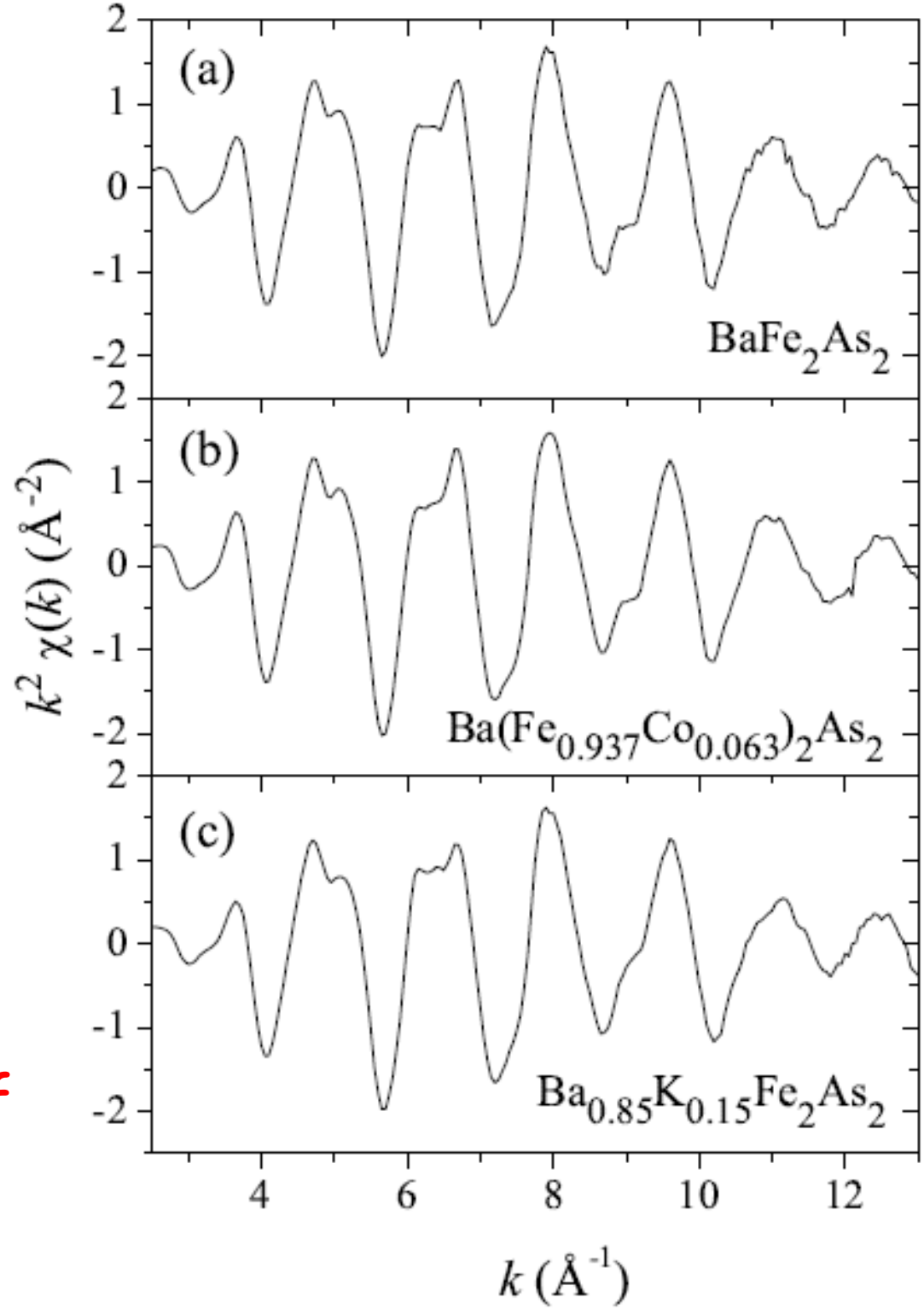
- Local structure may deviate from the crystal structure for doped samples.

Our samples:

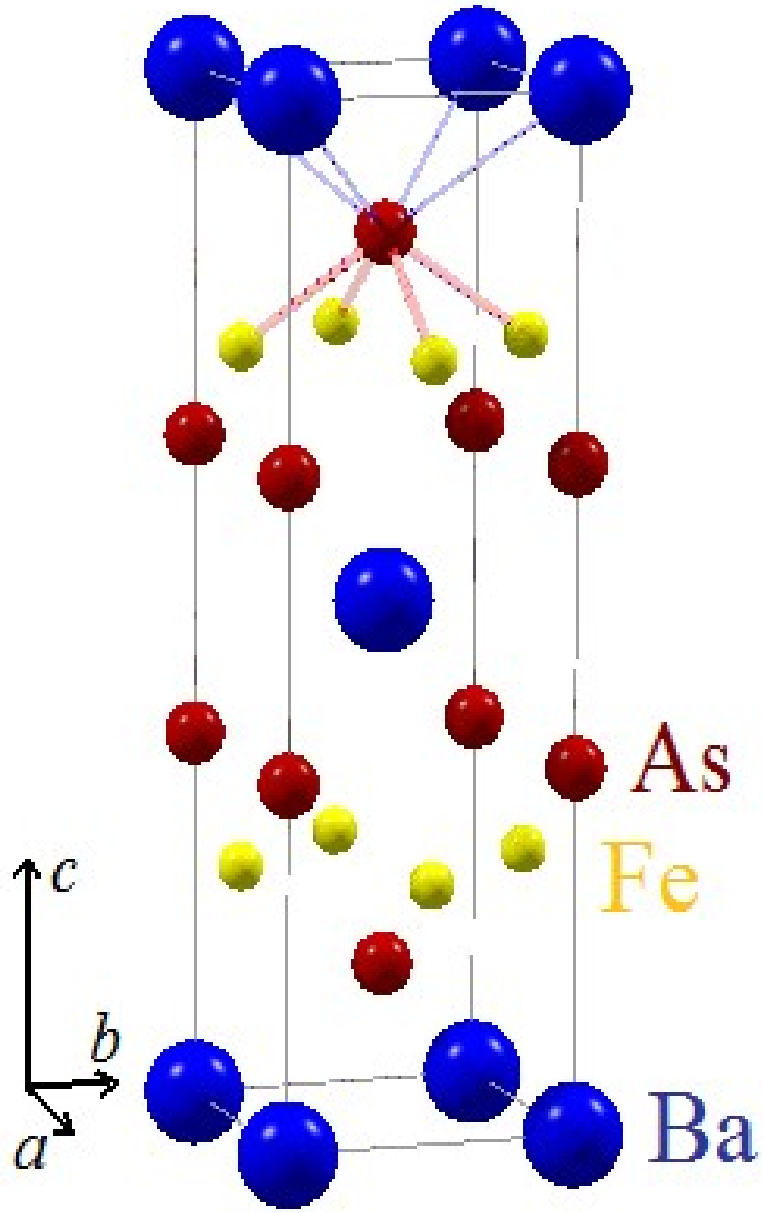


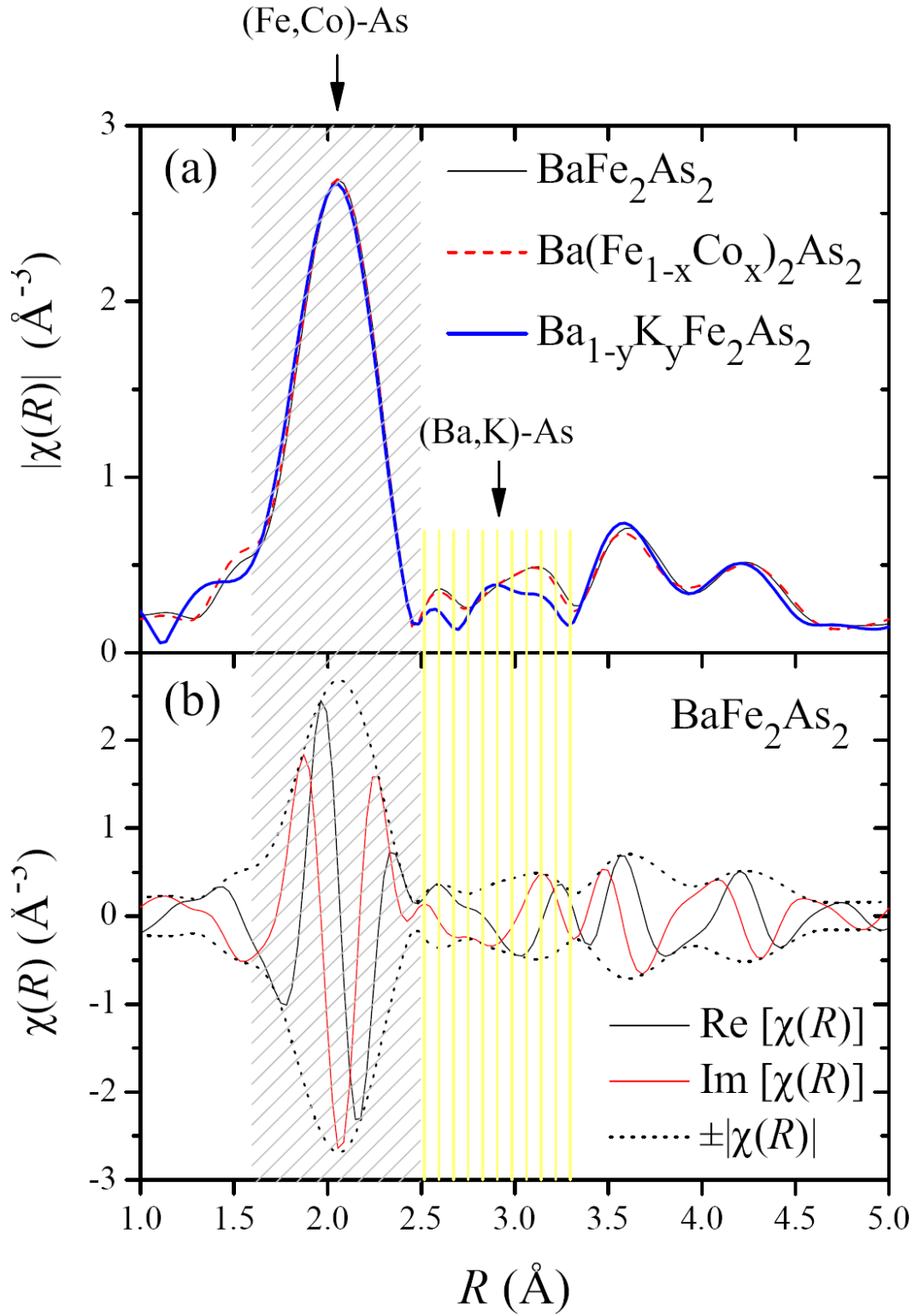
- Thin (~10 microns) single Xtals grown by the In-flux technique.

Raw EXAFS data:



XAFS-2 Beamline of LNLS


As
Fe
Ba
c
b
a


(Fe,Co)-As
(a)
BaFe2As2
Ba(Fe1-xCox)2As2
Ba1-yKyFe2As2
(Ba,K)-As
|χ(R)| (Å-3)
(b)
BaFe2As2
Re [χ(R)]
Im [χ(R)]
±|χ(R)|
χ(R) (Å-3)
R (Å)

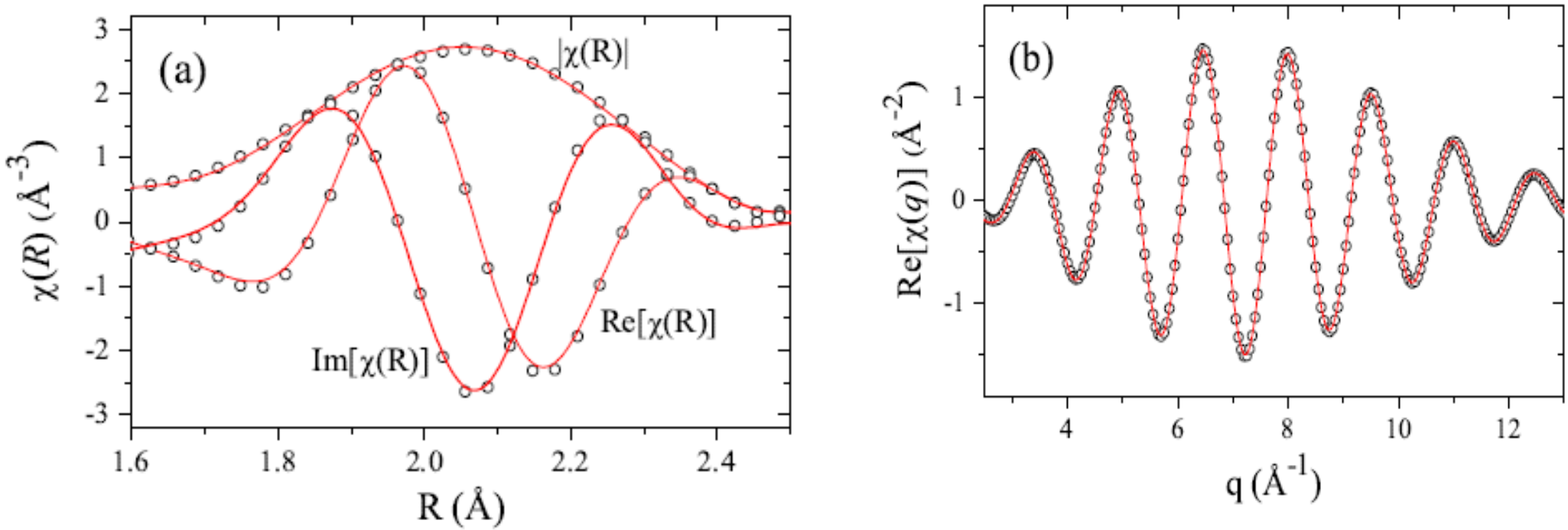
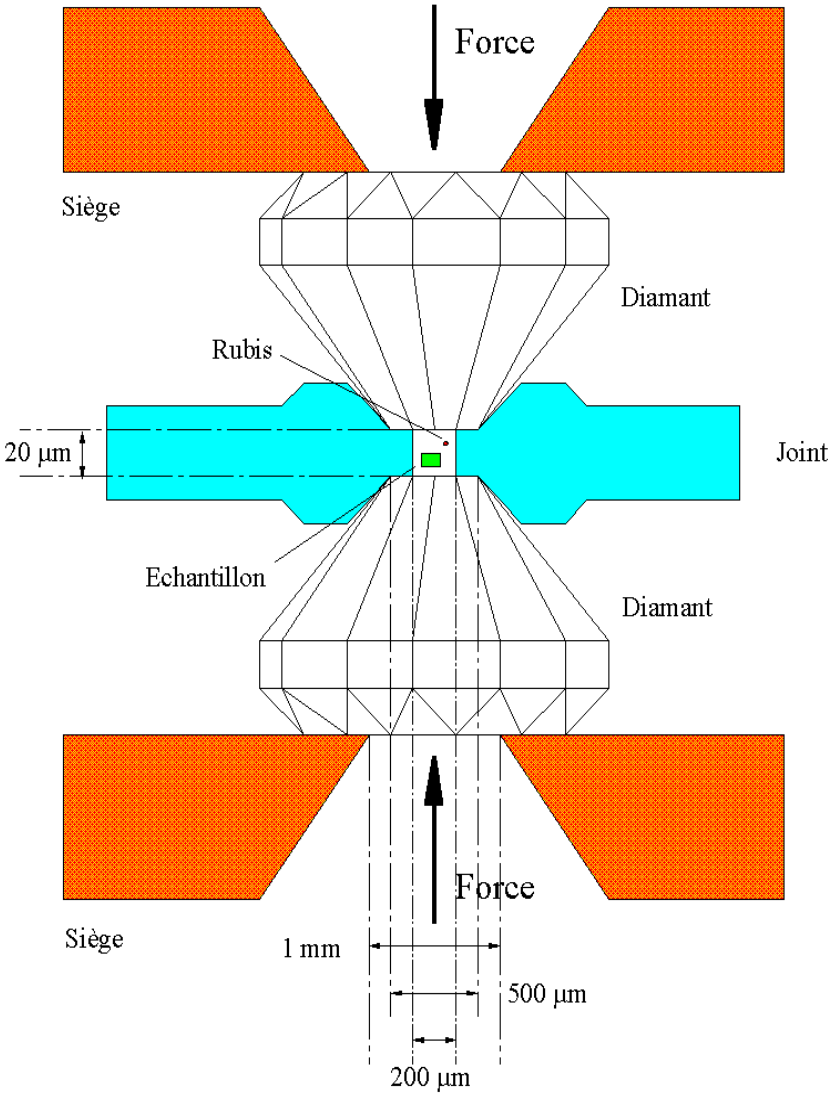
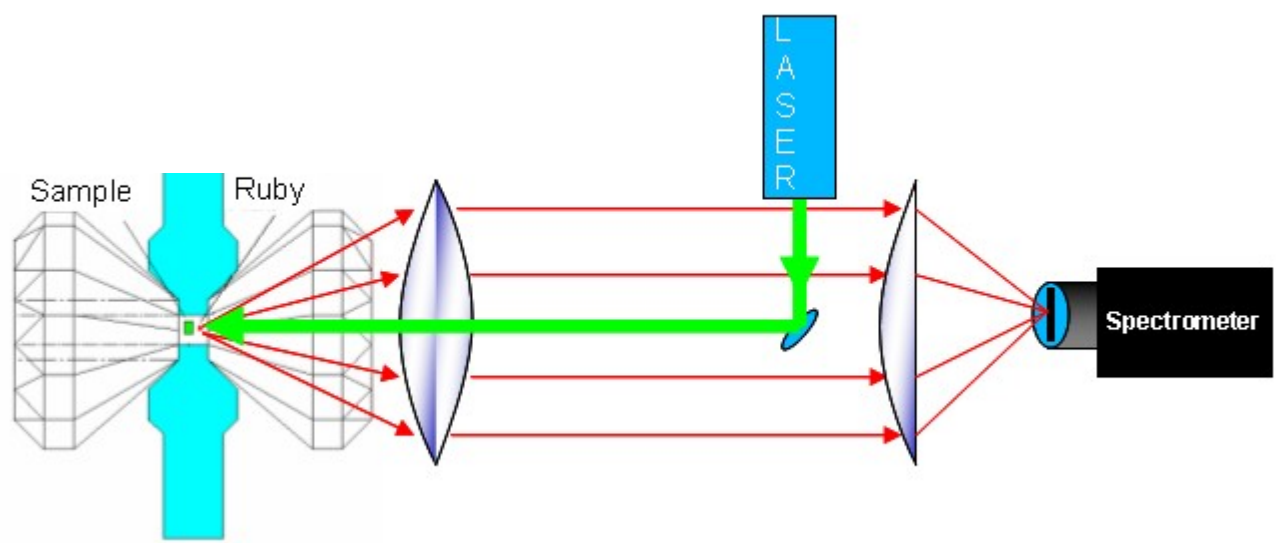


TABLE I: Refined As-M (M =Fe,Co) distances and Debye-Waller factors obtained from the fits of x-ray absorption fine structure data at the As $K-$edge at ambient pressure. Errors given in parentheses are statistical only, and are defined as the standard deviation of the results obtained from repeated measurements under identical conditions.

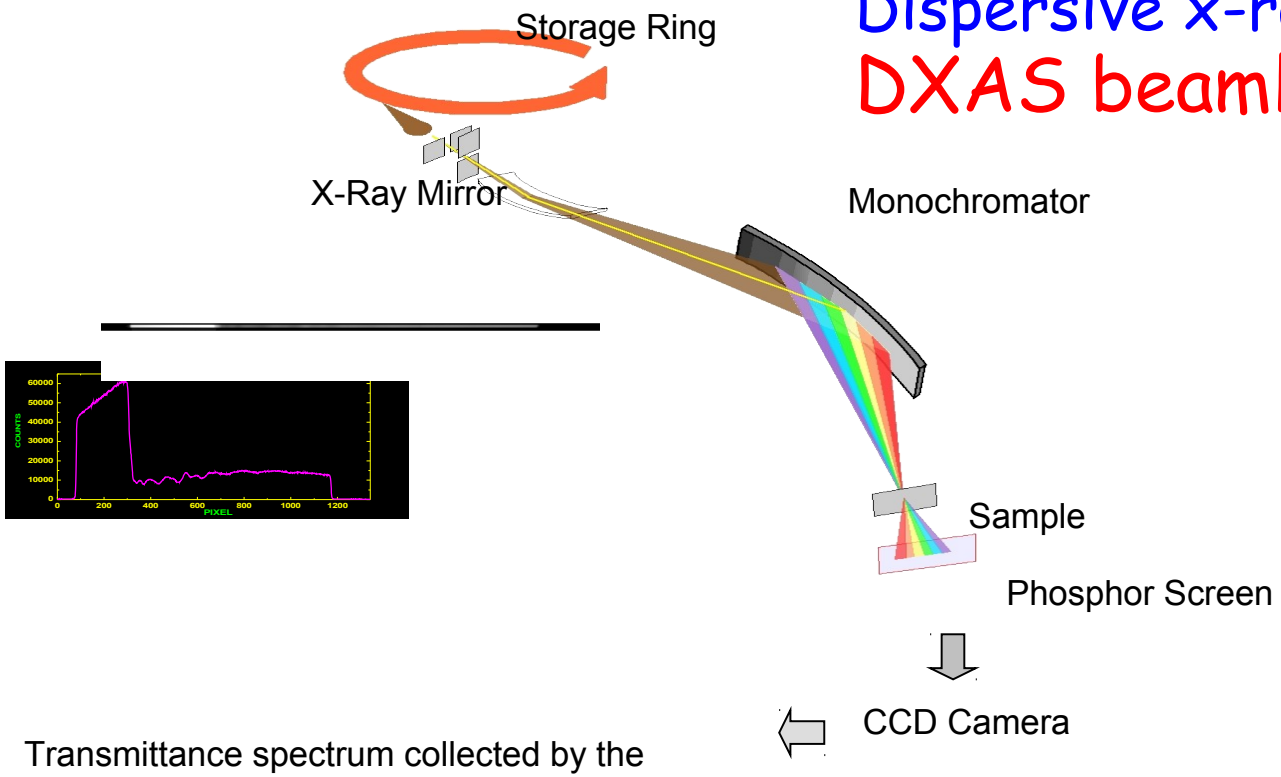
	$T = 2$ K	$T = 30$ K	$T = 298$K
$BaFe_2As_2$			
d(As-Fe) (Å)	2.3915(12)	2.3914(7)	2.3985(14)
σ^2 (Å ^{2})	0.00266(12)	0.00250 (7)	0.00465(11)
$Ba[Fe_{0.937}Co_{0.063}]_2As_2$			
d[As-(Fe,Co)] (Å)	2.3833(12)	2.3838(9)	2.3951(12)
σ^2 (Å ^{2})	0.00262(12)	0.00268(9)	0.00466(9)
$Ba_{0.85}K_{0.15}Fe_2As_2$			
d(As-Fe) (Å)	2.3865(15)	2.3900(12)	2.3955(9)
σ^2 (Å ^{2})	0.00242(15)	0.0248(12)	0.00466(7)

Diamond anvil cell

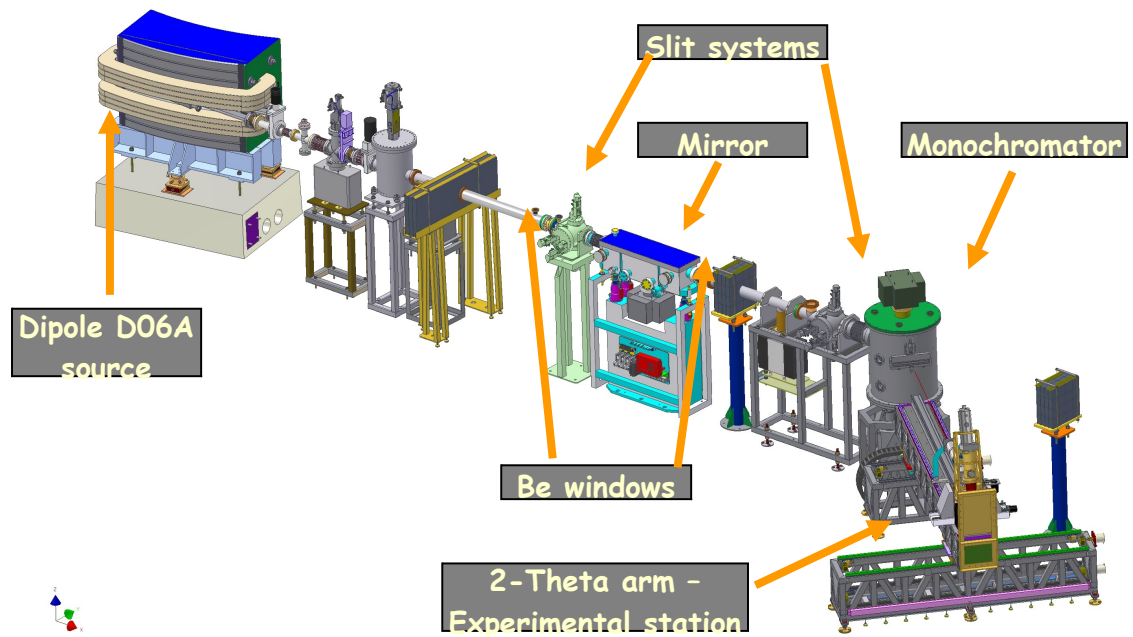




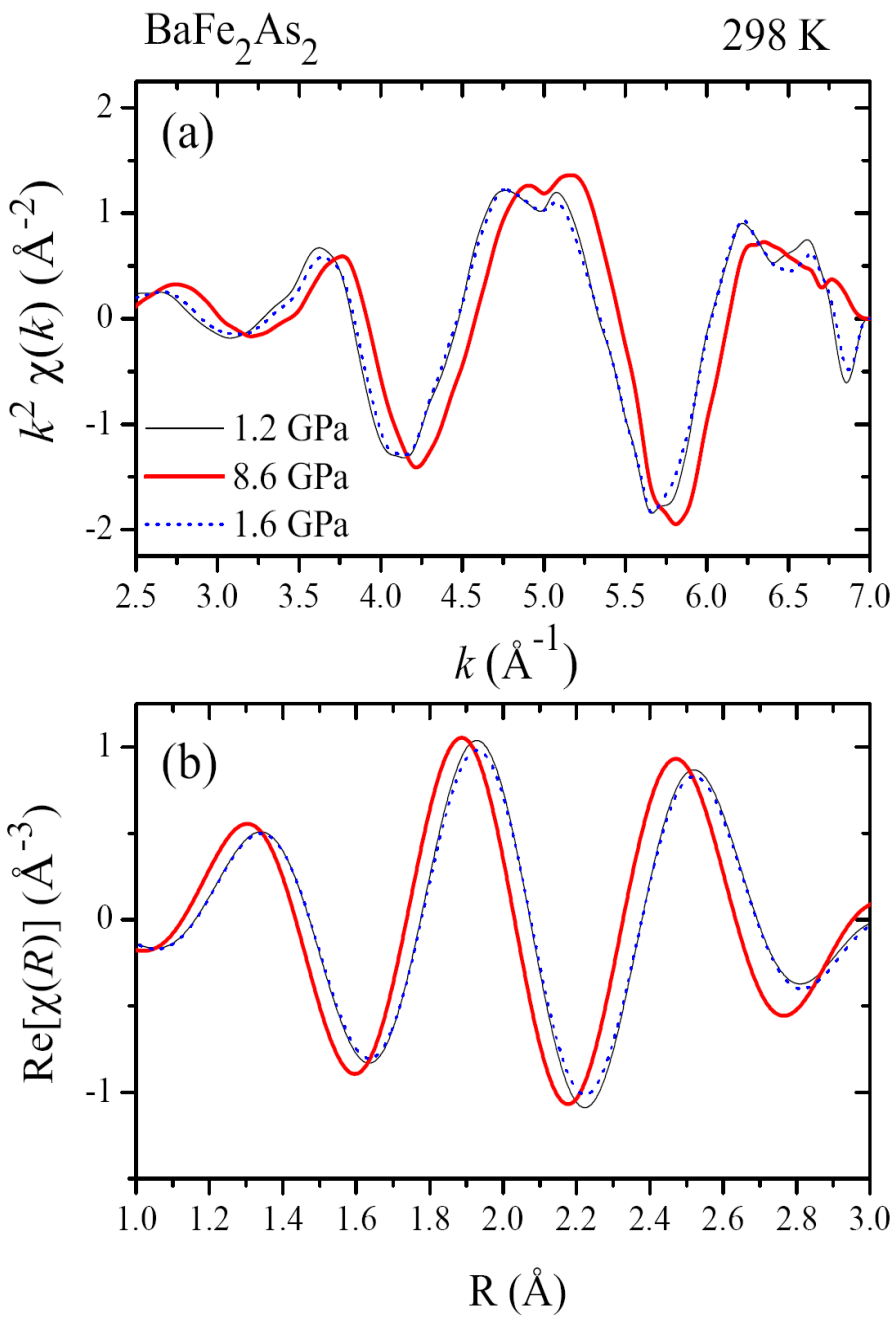
Dispersive x-ray absorption experiment
DXAS beamline

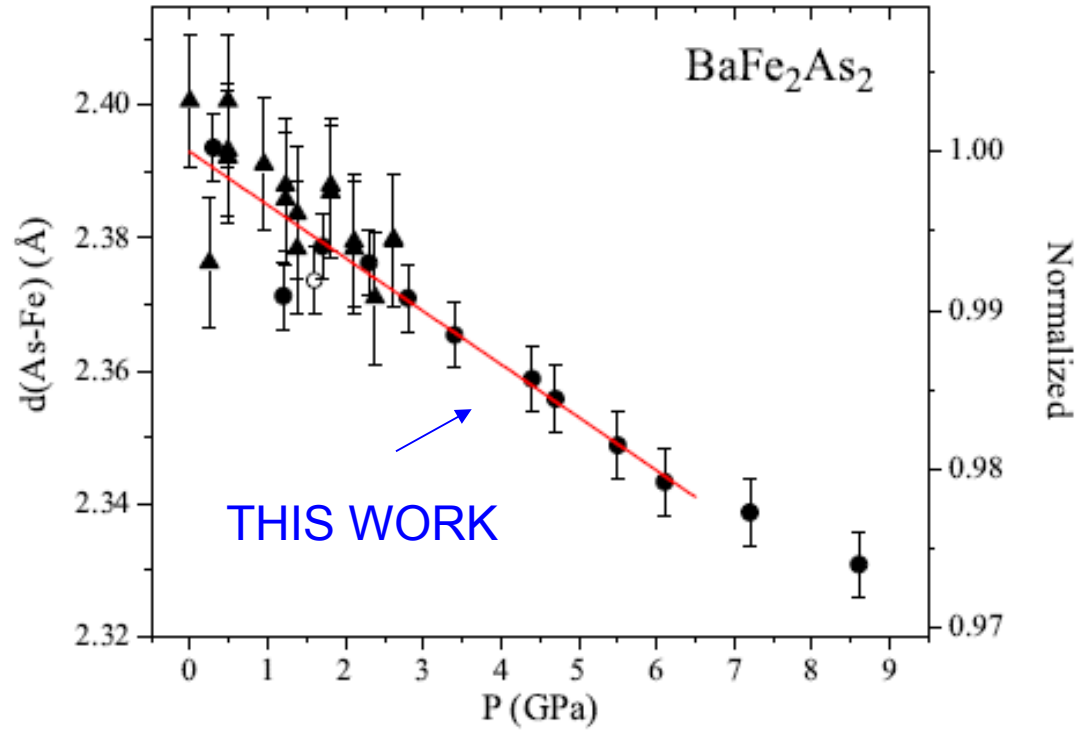


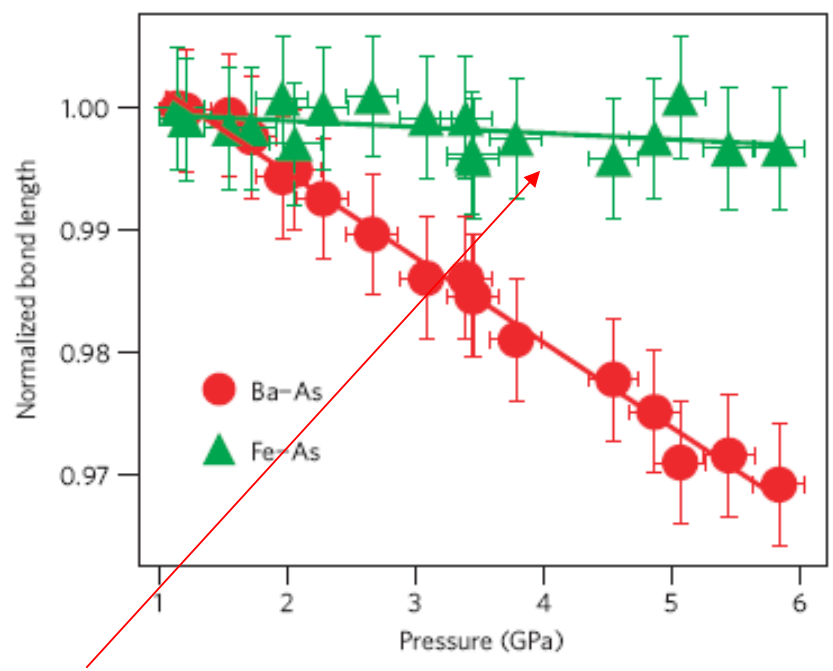
Transmittance spectrum collected by the CCD camera. The upper insert correspond to the beam image formed in the phosphor screen.



J.C. Cesar *et al.*, J. Synchrotron Rad. **17**, 93 (2010).







Neutrons, S.A.J. Kimber et al., Nature Mater. 8, 471 (2009).

PHYSICAL REVIEW B **83**, 184508 (2011)

Pressure and chemical substitution effects in the local atomic structure of $BaFe_2As_2$

E. Granado,[1,2,*] L. Mendonça-Ferreira,[3] F. Garcia,[2] G. de M. Azevedo,[4] G. Fabbris,[1,2] E. M. Bittar,[1,2] C. Adriano,[1] T. M. Garitezi,[1] P. F. S. Rosa,[1] L. F. Bufaiçal,[5] M. A. Avila,[6] H. Terashita,[1,2] and P. G. Pagliuso[1]

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(Received 2 February 2011; revised manuscript received 8 April 2011; published 17 May 2011)

Thus, Co-substitution, K-substitution, and applied pressures induce at least one common structural feature: a contraction of the Fe-As bond !!

Can it be related to the emergence of superconductivity ?

PHYSICAL REVIEW B **82**, 024527 (2010)

Effect of doping and pressure on magnetism and lattice structure of iron-based superconductors

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(Received 13 April 2010; revised manuscript received 13 July 2010; published 30 July 2010)

Using first-principles calculations, we analyze structural and magnetic trends as a function of charge doping and pressure in $BaFe_2As_2$, and compare to experimentally established facts. We find that density-functional theory, while accurately reproducing the structural and magnetic ordering at ambient pressure, fails to reproduce some structural trends as pressure is increased. Most notably, the Fe-As bond length which is a gauge of the magnitude of the magnetic moment, μ, is rigid in experiment but soft in calculation, indicating residual local Coulomb interactions. By calculating the magnitude of the magnetic ordering energy, we show that the disruption of magnetic order as a function of pressure or doping can be qualitatively reproduced but that in calculation, it is achieved through diminishment of $|\mu|$, and therefore likely does not reflect the same physics as detected in experiment. We also find that the strength of the stripe order as a function of doping is strongly site dependent: magnetism decreases monotonically with the number of electrons doped at the Fe site but increases monotonically with the number of electrons doped at the Ba site. Intraplanar magnetic ordering energy (the difference between checkerboard and stripe orderings) and interplanar coupling both follow a similar trend.

DOI: 10.1103/PhysRevB.82.024527 PACS number(s): 74.70.Xa, 74.62.Fj, 75.50.Ee

Thus...

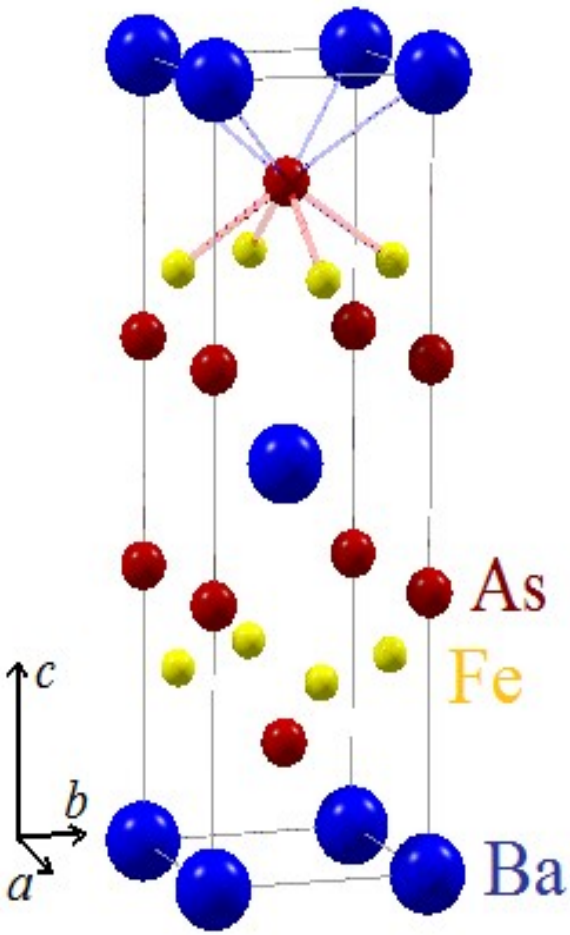
The observed contraction in the Fe-As distance upon doping and pressure is likely related to a reduction of the Fe local moments.

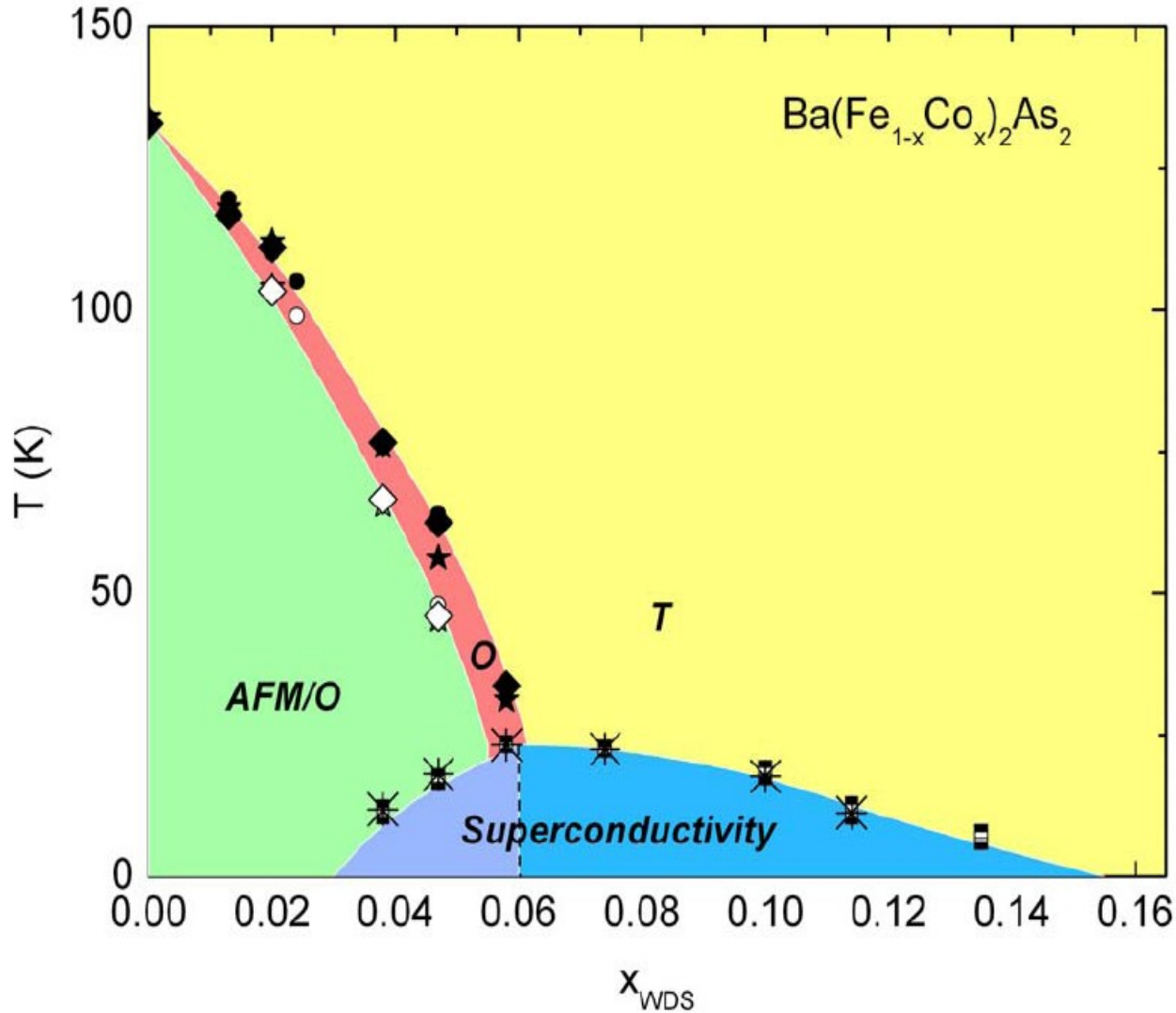
BTW, The local moments is not the same thing as the ordered AFM moments (extracted, e.g., by neutron diffraction).

Contraction weakens the antiferromagnetic ground state and alters the balance with respect to superconductivity, favoring the latter.

EXAFS may be the most accurate technique to access the Fe-As distances, and therefore the behavior of the Fe moments !

Besides bond distance control, is there "electronic tuning" ?





Common sense say "yes", but...

PRL **105,** 157004 (2010) PHYSICAL REVIEW LETTERS week ending 8 OCTOBER 2010

Where Are the Extra *d* Electrons in Transition-Metal-Substituted Iron Pnictides?

H. Wadati,[1,*] I. Elfimov,[2] and G. A. Sawatzky[1,†]

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(Received 12 March 2010; published 4 October 2010)

Transition-metal substitution in Fe pnictides leading to superconductivity is usually interpreted in terms of carrier doping to the system. We report on a density functional calculation of the local substitute electron density and demonstrate that substitutions like Co and Ni for Fe do not carrier dope but rather are isovalent to Fe. We find that the extra *d* electrons for Co and Ni are almost totally located within the muffin-tin sphere of the substituted site. We suggest that Co and Ni act more like random scatterers scrambling momentum space and washing out parts of the Fermi surface.

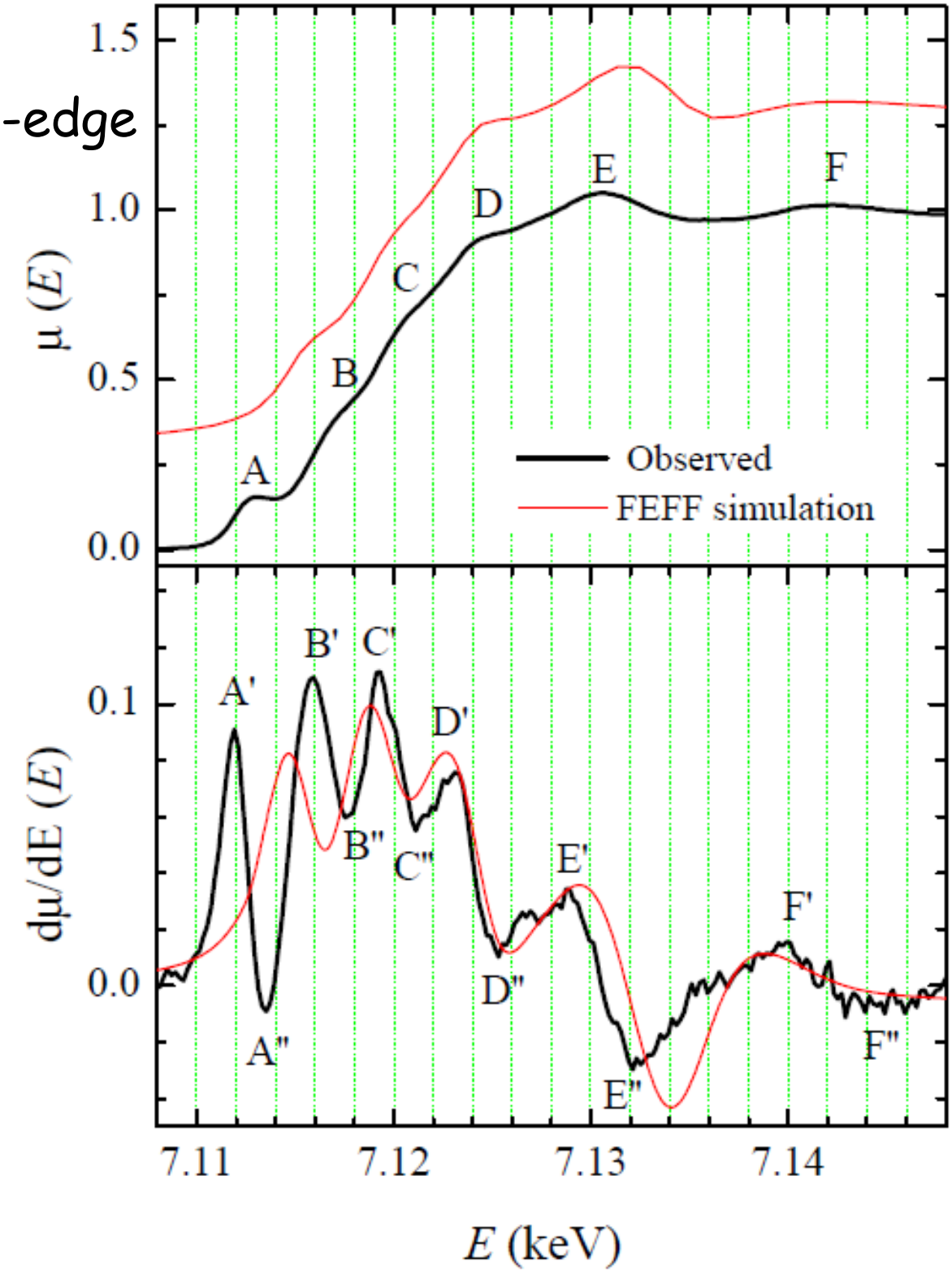
DOI: 10.1103/PhysRevLett.105.157004 PACS numbers: 74.70.Xa, 71.15.Mb, 74.25.Jb, 74.62.Dh

X-ray absorption near-edge Structure (XANES) of $BaFe_2As_2$

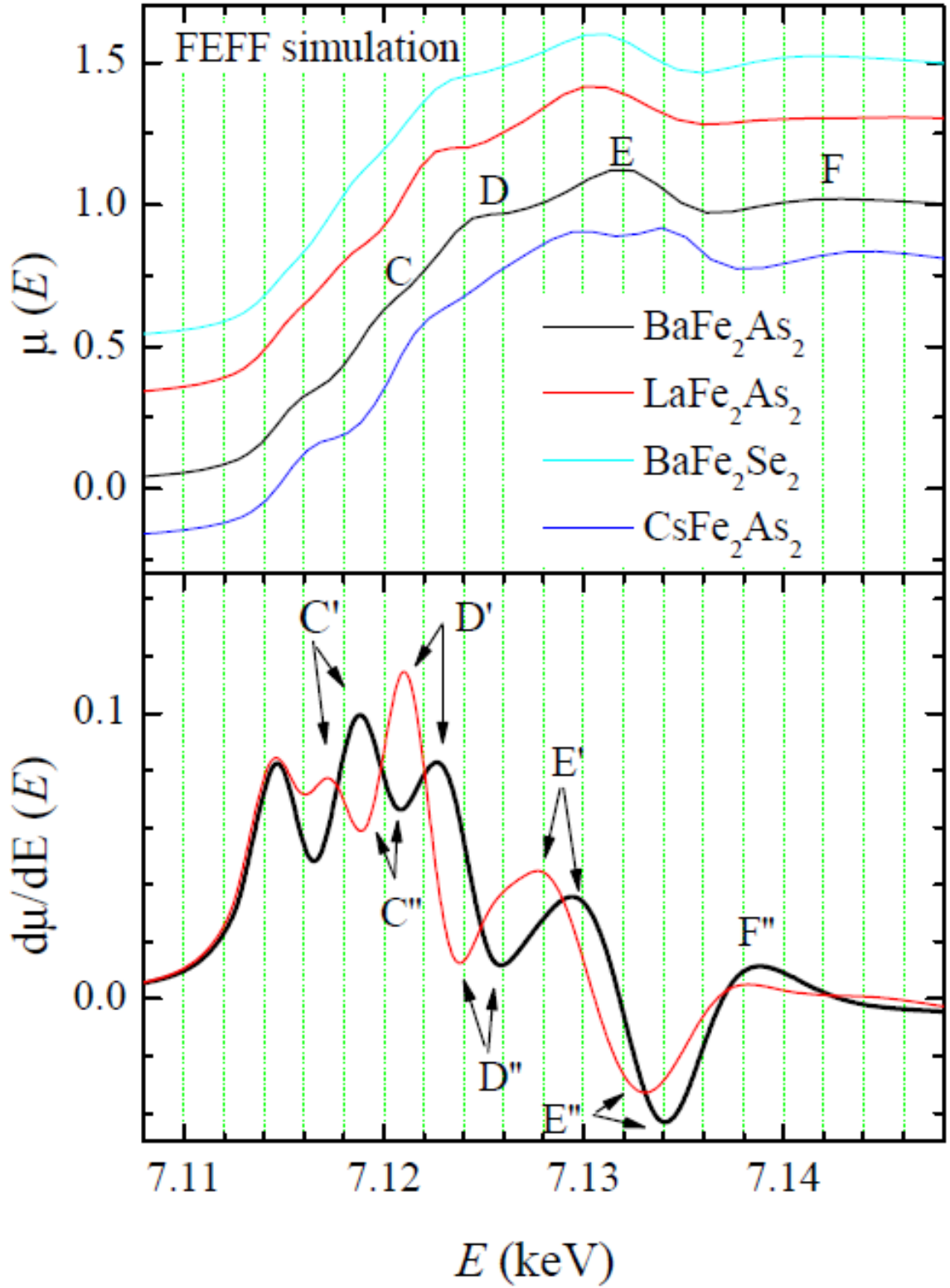
Fe K-edge

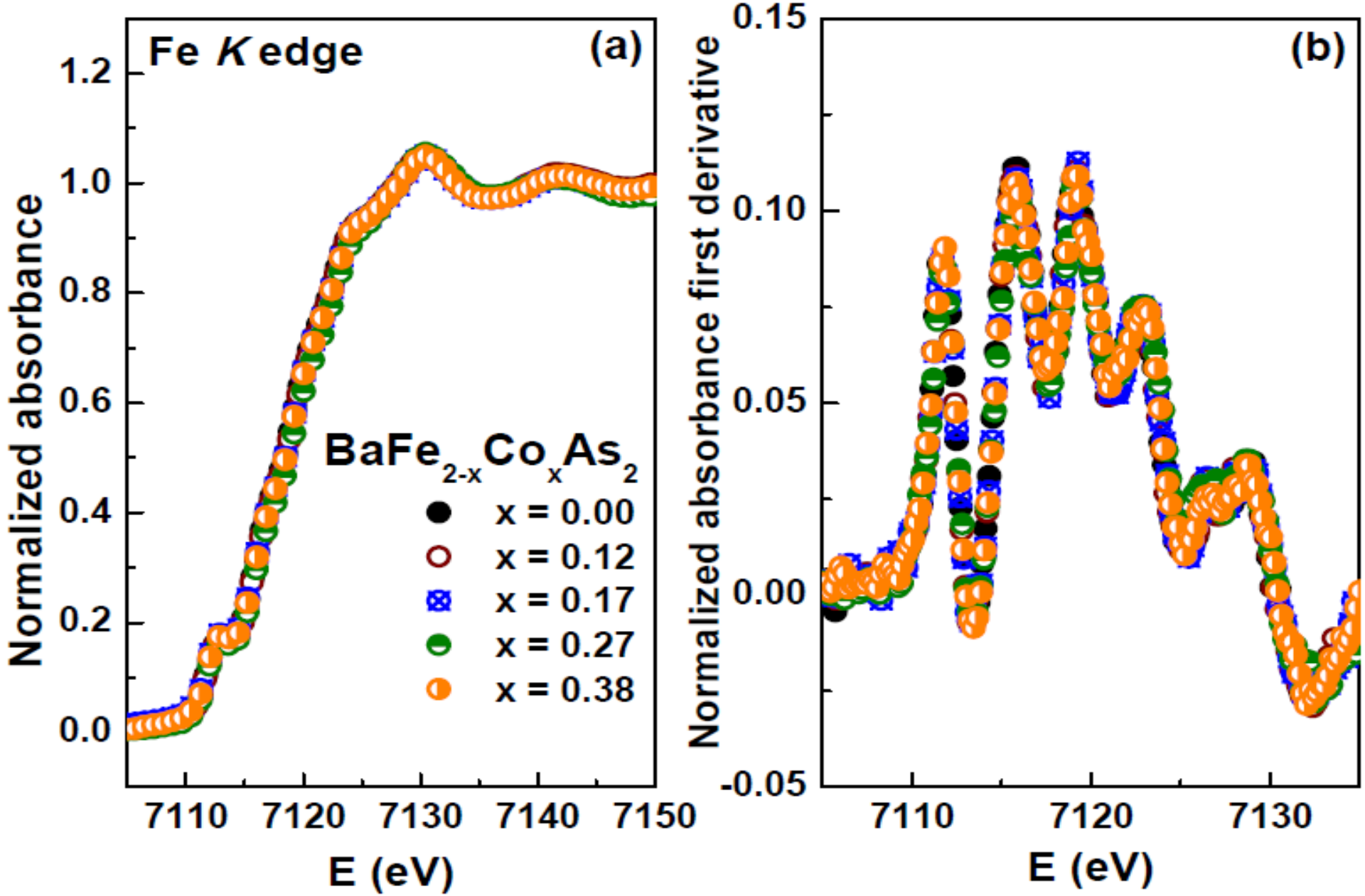
Probed transitions:
A,B: 1s → 3d
C,D,E,F: 1s → 4p

XANES is an element-specific probe of the electronic structure



Simulations indicate that electron doping of the FeAs layers should shift significantly the 1s → 4p peaks (C-F) to lower energies





No shift of any feature was observed by Co-substitution

NO ELECTRON DOPING !

Co-Substitution Effects on the Fe Valence in the $BaFe_2As_2$ Superconducting Compound: A Study of Hard X-Ray Absorption Spectroscopy

E. M. Bittar,[1,*] C. Adriano,[2] T. M. Garitezi,[2] P. F. S. Rosa,[2] L. Mendonça-Ferreira,[3] F. Garcia,[1] G. de M. Azevedo,[4] P. G. Pagliuso,[2,5] and E. Granado[2,1]

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[4]*Instituto de Física, Universidade Federal do Rio Grande do Sul (UFRGS), 91501-970, Porto Alegre, RS, Brazil*
[5]*Department of Physics and Astronomy, University of California Irvine, 92697-4575, Irvine, California, USA*
(Received 5 July 2011; published 20 December 2011)

Summary and conclusions

- Successful XAS measurements in $BaFe_2As_2$ at LNLS, under doping, temperature, pressure, in the XANES and EXAFS regions.
- Both K and Co doping induce a slight Fe-As bond compression.
- Significant Fe-As bond compressibility.
- Reduction of Fe-As bond distance likely related to a decrease of the Fe local moments, favoring superconductivity against magnetic order.
- Co-substitution does not promote charge tranfer to the Fe ions.

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