Orbital / spin correlation and doping effects of disordered impurities

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U.S. DEPARTMENT OF ENERGY

Outlines

- Spin and orbital: Ferro-orbital correlation & C-type AF spin correlation
- More spin structures: unified magnetic structures (C-, E-, and X-type)
- Importance of the right symmetry: 1-Fe vs 2-Fe description
- Effects of disordered impurities:
  - Substitution of Fe: doping or not?
  - Fe vacancy: “violation” of Luttinger theorem
  - Ru substitution: realization of superdiffusion

Acknowledgement

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Current and former group members

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Collaborators within DOE CMCSN

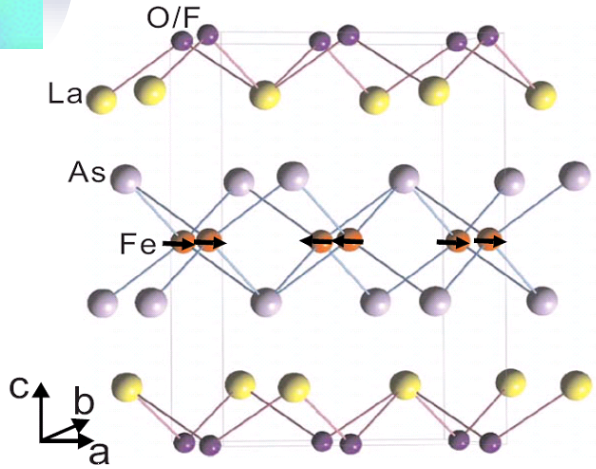
M. Jarrell, P. Hirschfeld, H.-P. Chen, D. Johnson, W. Shelton

Spin & orbital: Ferro-orbital order & anisotropic magnetic structure in 1111 (&122)

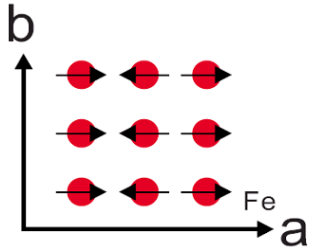
Chi-Cheng Lee, Wei-Guo Yin & Wei Ku

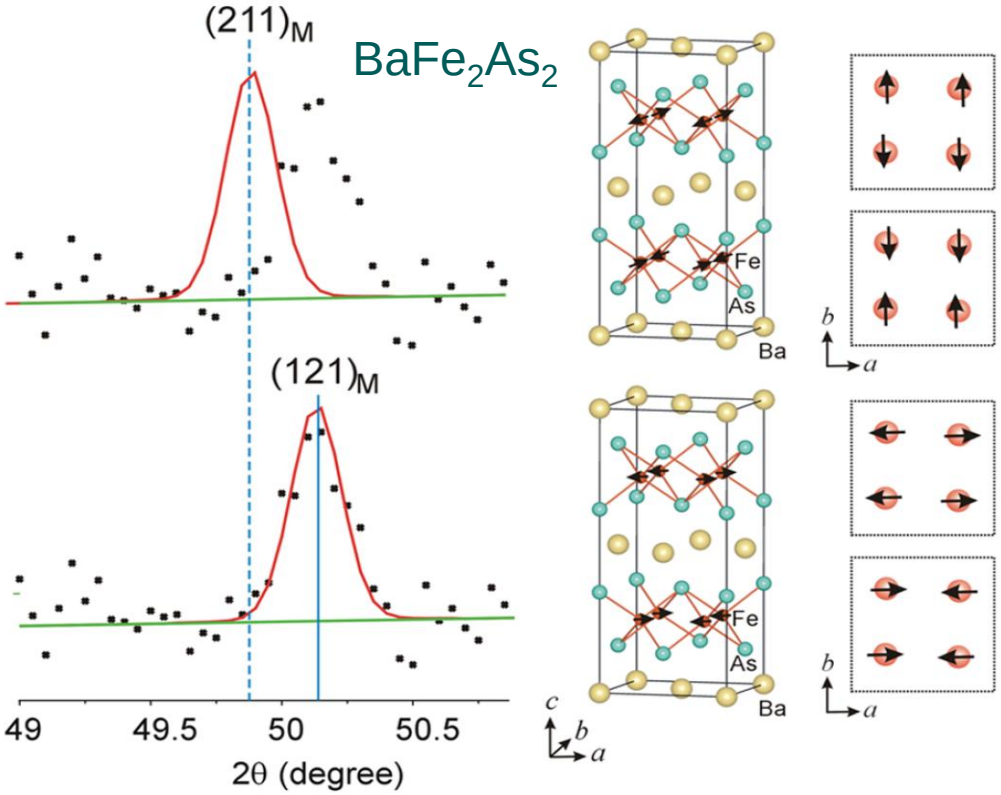
Phys. Rev. Lett. **103**, 267001 (2009)

Stripy magnetic and lattice structure



Phys. Rev. B **78**, 054529 (2008)

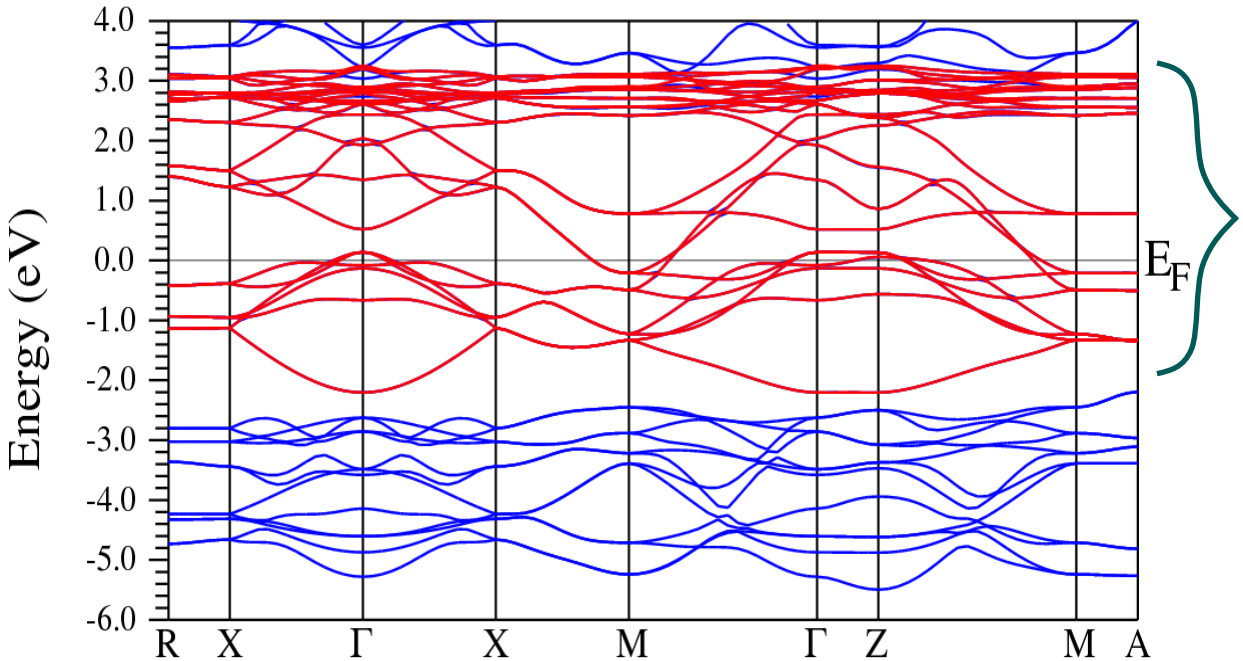




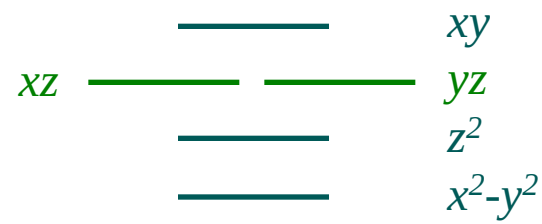
Q. Huang et al., PRL **101**, 257003 (2008)

- Structure transition at 155k; Stripy AFM order at 137K (AF bond longer?)
- What drives the magnetic transition?
  Fermi surface instability? (SDW due to nesting?)
- What drives the structural transition?
  Transition temperature so close to magnetic T_N : related?
- Implications to electronic structure and superconductivity?

Energy resolved, symmetry respecting Wannier function

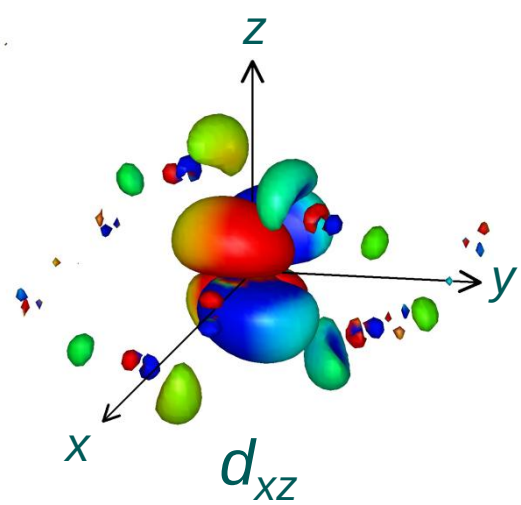


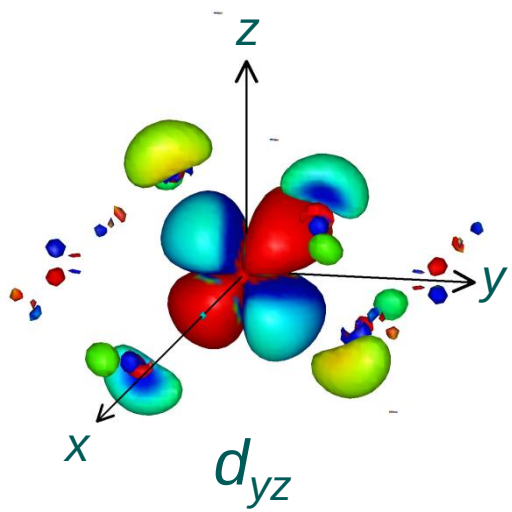
$$|\vec{R}n\rangle = \sum_{\vec{k}m}^{(\text{energy window})} |\vec{k}m\rangle\langle\vec{k}m|\vec{R}n\rangle$$
$$= \frac{1}{\sqrt{N_{cell}}}\sum_{\vec{k}m}|\vec{k}m\rangle e^{-i\vec{k}\cdot\vec{R}}U_{mn}^{(\vec{k})}$$
$$= \frac{1}{\sqrt{N_{cell}}}\sum_{\vec{k}}\left(\sum_{m}U_{mn}^{(\vec{k})}|\vec{k}m\rangle\right)e^{-i\vec{k}\cdot\vec{R}}$$



NM onsite energy (eV)

z^2	-0.03
x^2-y^2	-0.20
yz	0.10
xz	0.10
xy	0.34



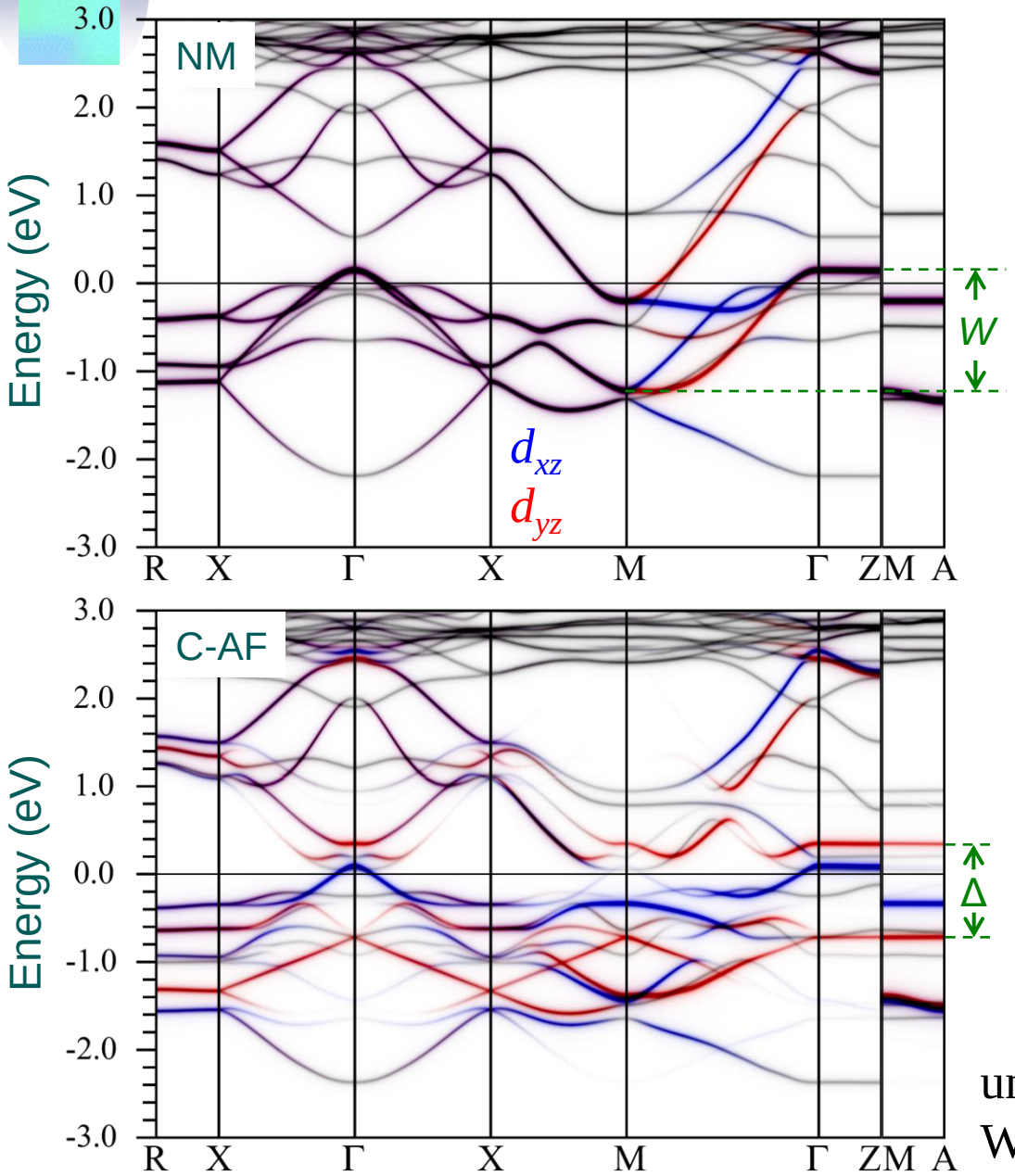


- small crystal field splitting
- degenerate *xz* and *yz*

→ orbital freedom !

methods see: W. Ku et al., PRL **89**, 167204 (2002); W. Yin et al., PRL **96**, 116405 (2006)

Comparing LDA band structures



- in NM 1st-BZ
- d_{xz} & d_{yz} most relevant to the low-E
- Only d_{yz} splits strongly near E_F
- d_{yz} more spin polarized ~0.34μ_B than d_{xz} (~0.15μ_B)
- more different with U=2eV
  0.58 vs. 0.23μ_B

→ orbital symmetry broken

- $\Delta \sim W$

→ large (ω,**k**)-space involved

→ local picture more suitable

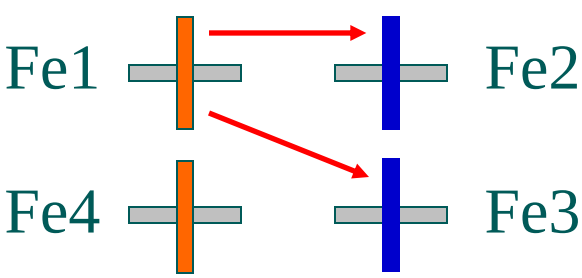
→ Fermi surface nesting not essential

→ SDW less convenient

unfolding methods see:
Wei Ku *et al.*, PRL **104**, 216401 (2010)

Anti-intuitive hopping parameters

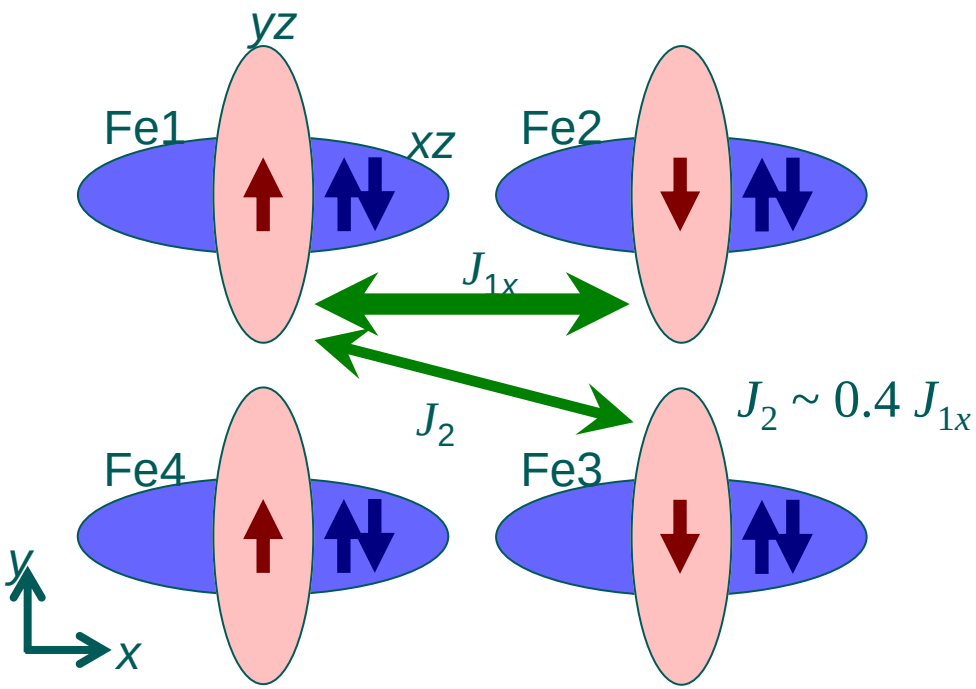
<WFs|H|WFs>	Fe1 z^2	x^2-y^2	yz	xz	xy
Fe2 (Fe4) z^2	0.13	0.31 (-0.31)	-0.10 (0.00)	0.00 (0.10)	0.00
x^2-y^2	0.31 (-0.31)	-0.32	0.42 (0.00)	0.00 (0.42)	0.00
yz	-0.10 (0.00)	0.42 (0.00)	-0.40 (-0.13)	0.00	0.00 (0.23)
xz	0.00 (0.10)	0.00 (0.42)	0.00	-0.13 (-0.40)	-0.23 (0.00)
xy	0.00	0.00	0.00 (0.23)	-0.23 (0.00)	-0.30
Fe3 z^2	0.06	0.00	-0.08	0.08	0.26
x^2-y^2	0.00	-0.10	0.12	0.12	0.00
yz	0.08	-0.12	0.25	-0.07	-0.05
xz	-0.08	-0.12	-0.07	0.25	0.05
xy	0.26	0.00	0.05	-0.05	0.16

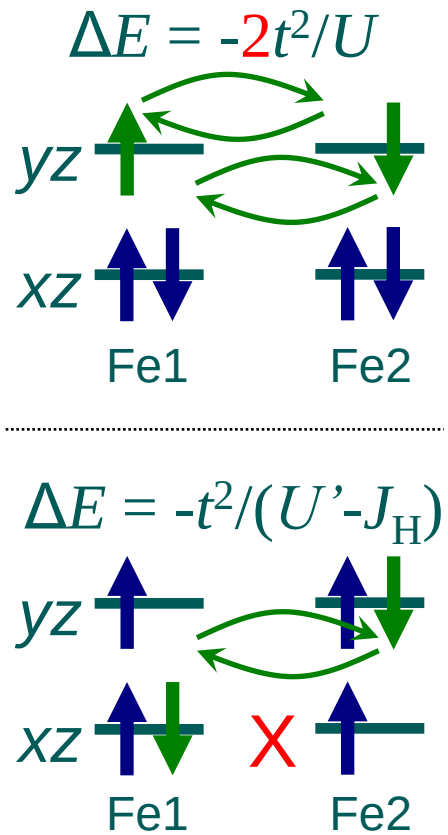


- Unusual coupling direction
- Cubic symmetry broken seriously by As
  → Fe-As phonon modes important
- Perpendicular hopping direction!

Chi-Cheng Lee *et al.*, PRL **103**, 267001 (2009)

C-AF magnetic structure and ferro-orbital order





- Strongly anisotropic super-exchange: $J_{1x} > J_2 >> J_{1y}$
  - → no competition with G-AF at all ! $J_1 \sim 2J_2$ irrelevant !
  - → Heisenberg model inadequate
- Orbital polarization and ferro-orbital correlation important

  Unusual coupling direction and strong anisotropic hoppings !
  - → *a* > *b*: AF across long bond (rare)
  - → strong in-plane nematic-like anisotropic response

    transport, optical, and lattice properties

Chi-Cheng Lee *et al.*, PRL **103**, 267001 (2009)

Treating materials with disordered impurities

T. Berlijn, D. Volja, and Wei Ku, PRL **106**, 077005 (2011)

For various applications, see

T.S. Herng, *et al*., *Phys. Rev. Lett.* **105**, 207201 (2010)

Tom Berlijn, *et al*., *Phys. Rev. Lett.* **108**, 207003 (2012)

Tom Berlijn, *et al*., *Phys. Rev. Lett.* **109**, 147003 (2012)

L.-M. Wang, *et al*., to appear in *Phys. Rev. Lett.*

First-principles methods for disorder

Relevance

- Defects, vacancy, chemical substitution, doping & intercalation
- Thermal/quantum fluctuation induced spatial inhomogeneity
- Paramagnetic phase with disordered local moment

Different approaches

- Mean-field potential: virtual crystal approximation
- Mean-field scattering: coherent potential approximation
- Perturbation: diagrammatic summation
- Non-perturbed direct method: configuration average over super cells

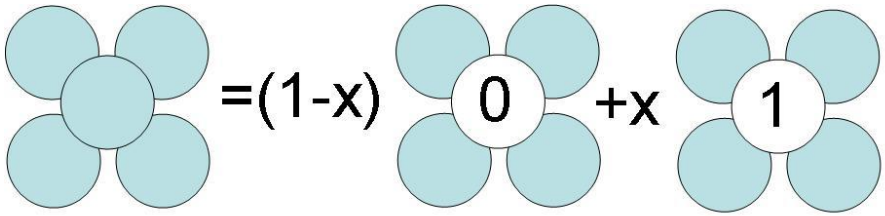
Mean-field approaches

VCA: Virtual Crystal Approximation

$$V_{\text{virtual crystal}} = (1-x)\ V_0 + x\ V_1$$

no scattering

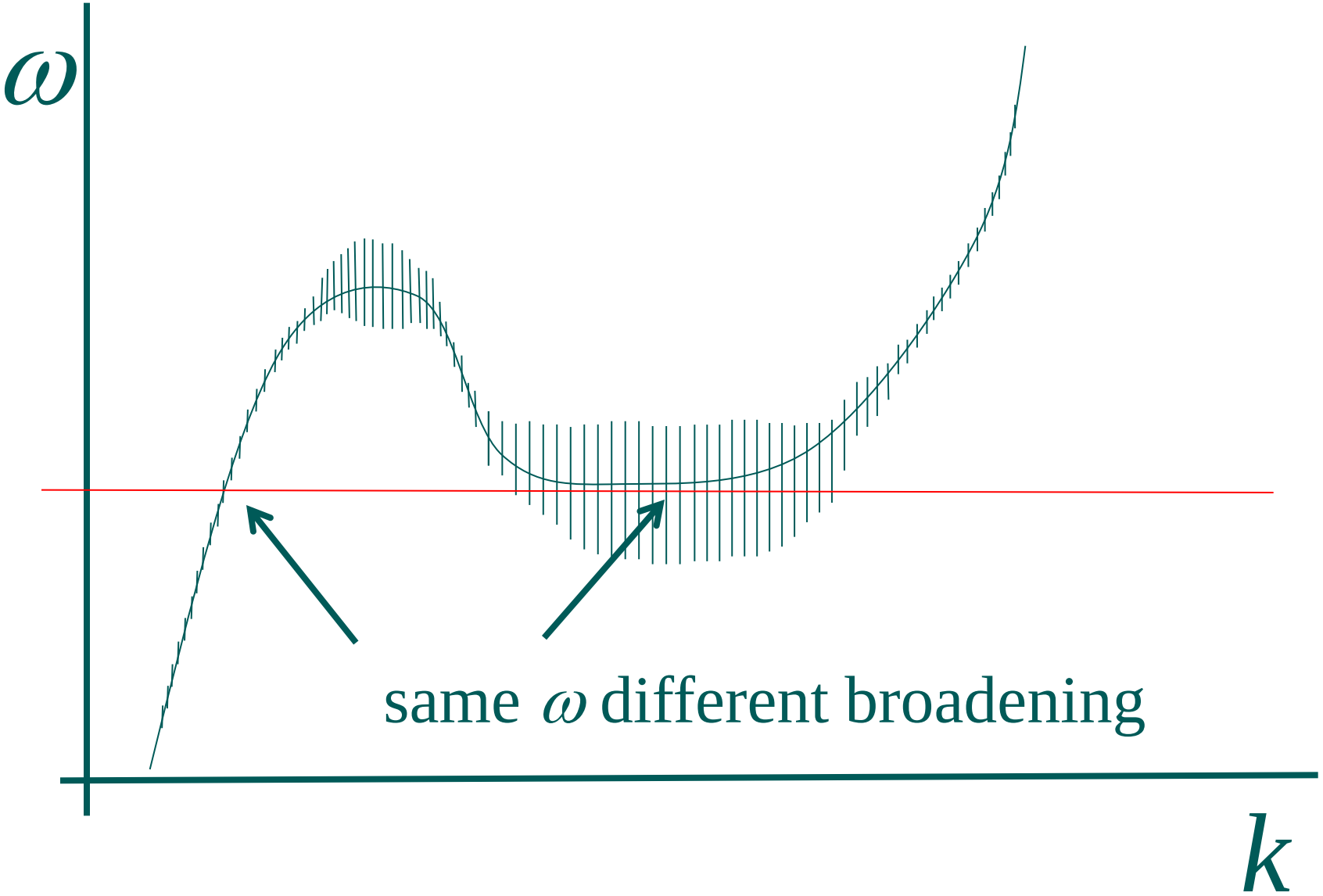
CPA: Coherent Potential Approximation



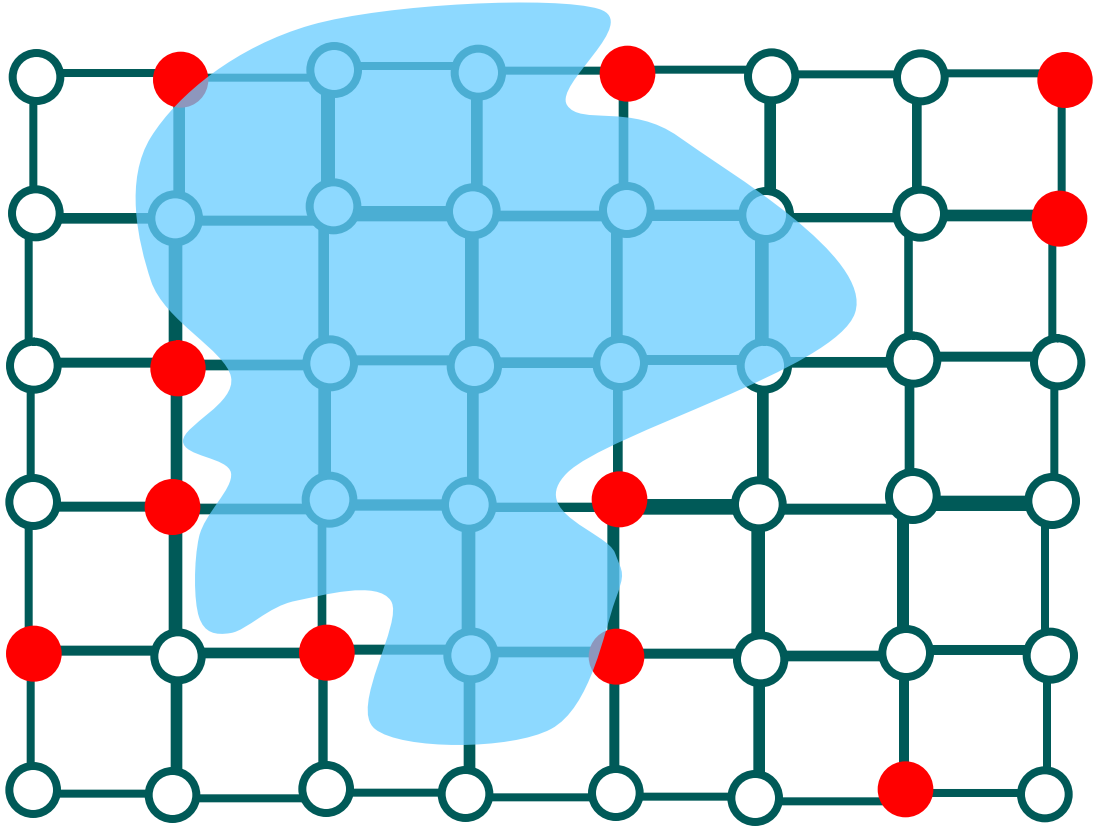
lack cluster-scattering

A. Gonis, “Green functions for ordered and disordered systems” (1992)

Non-local physics: *k*-dependent broadening

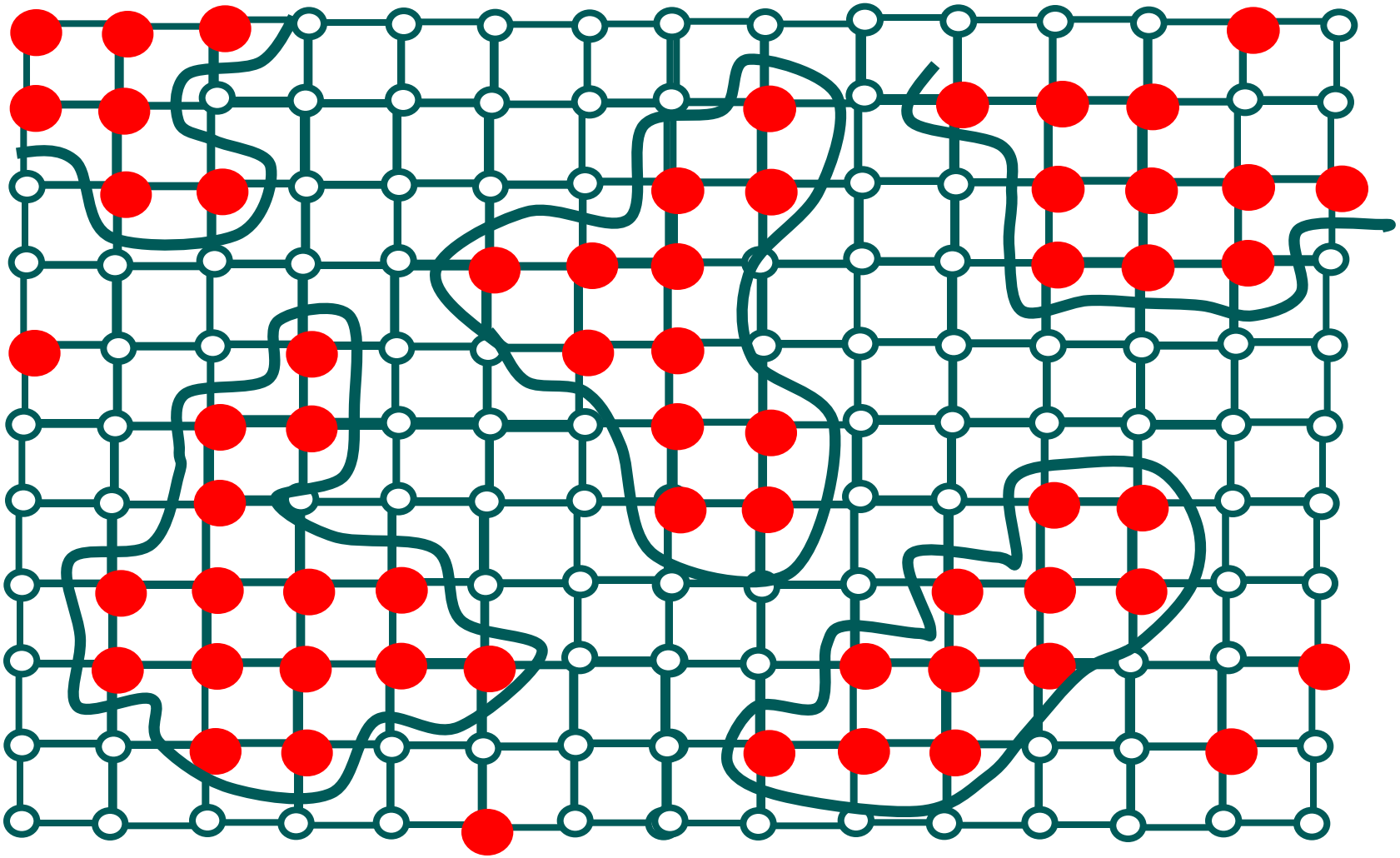


Non-local physics: large-sized impurity states

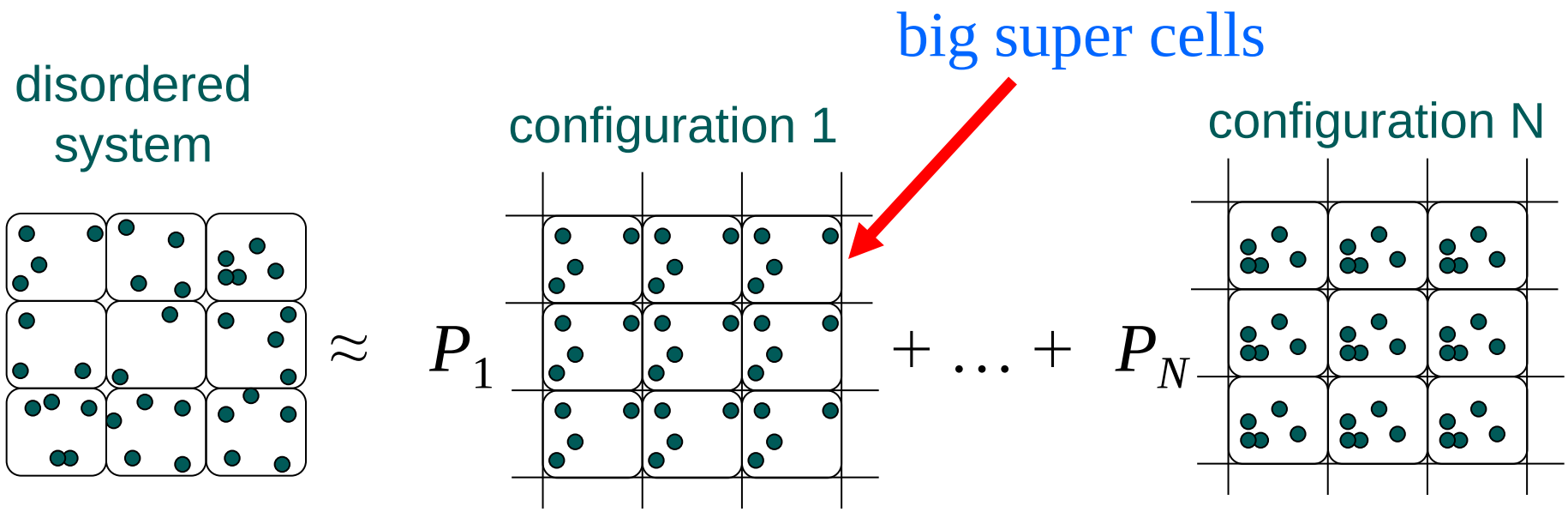


Anderson localization, multiple scattering required

Non-local physics: short-range order



Configuration average over super cell

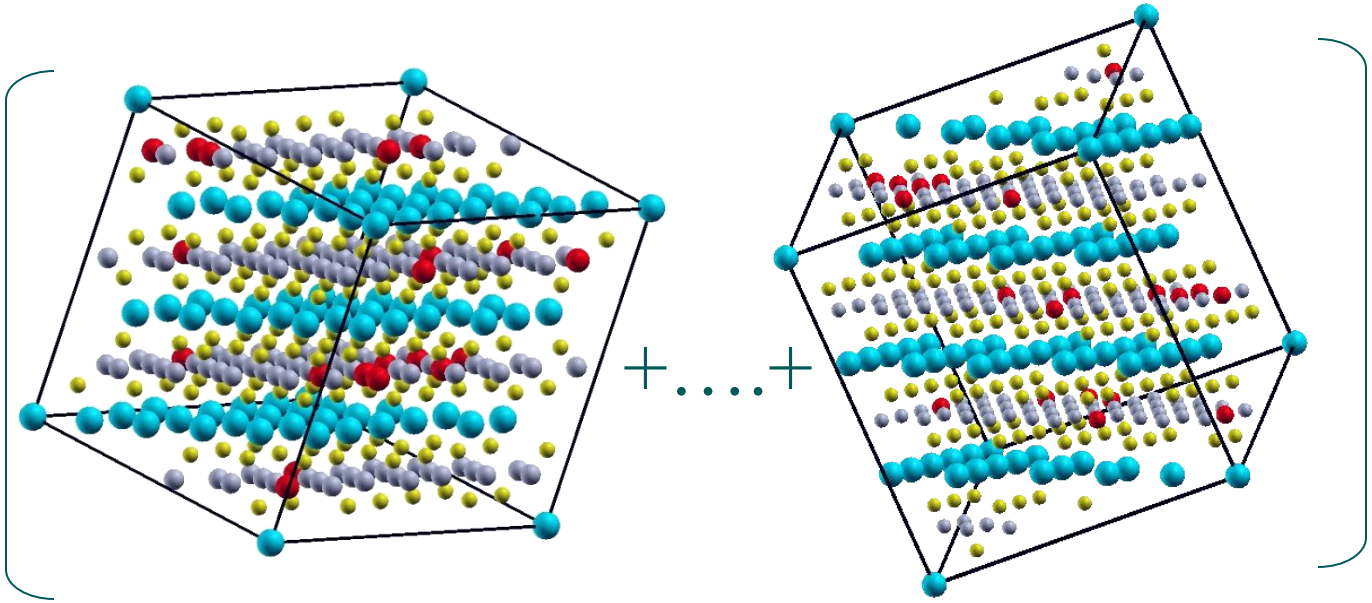


$$\langle G \rangle \approx P_1 G_1 + \ldots + P_N G_N$$

Challenge: solving many Hamiltonians with big super cells

Configuration average over super cell

big super cells (100 ~ 1000 of atoms)



$$\langle G \rangle \approx P_1 G_1 + \ldots + P_N G_N$$

Challenge: solving many Hamiltonians with big super cells

Constructing small and accurate effective H

Consider H from influence of impurities at $x_1, \ldots, x_N$

$$H^{(x_1,\ldots,x_N)} = H^0 + \sum_{i=1}^{N} \Delta^{(x_i)} + \sum_{i>j=1}^{N} \Delta^{(x_i,x_j)} + \ldots$$

1. Calculate $H^0, H^{(x_i)}$ & $H^{(x_i,x_j)}$ in same Wannier basis from DFT
2. Calculate Δ by taking difference of H^{DFT} in Wannier basis

$$\Delta^{(x_i)} = H^{(x_i)} - H^0; \quad \Delta^{(x_i,x_j)} = H^{(x_i,x_j)} - H^0 - \Delta^{(x_i)} - \Delta^{(x_i)}$$

3. Assemble H_c for each disorder configuration

$$\left\langle r'n' \middle| H^{((r_1,m_1),\ldots,(r_N,m_N))} \middle| r''n'' \right\rangle =$$

$$\left\langle r'-r'', n' \middle| H^0 \middle| 0n'' \right\rangle + \sum_{i=1}^{N} \left\langle r'-r_i, n' \middle| \Delta^{(m_i)} \middle| r''-r_i, n'' \right\rangle + \ldots$$

4. Solve H and unfold $A(k, \omega)$ to the normal cell unit
5. Average over configurations with different size & shape

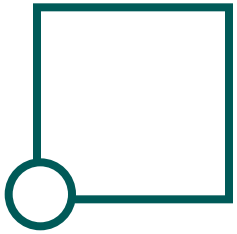
$$\langle A(k,w) \rangle = \sum_c P_c A_c(k,w)$$

T. Berlijn, D. Volja, and Wei Ku, PRL **106**, 077005 (2011)

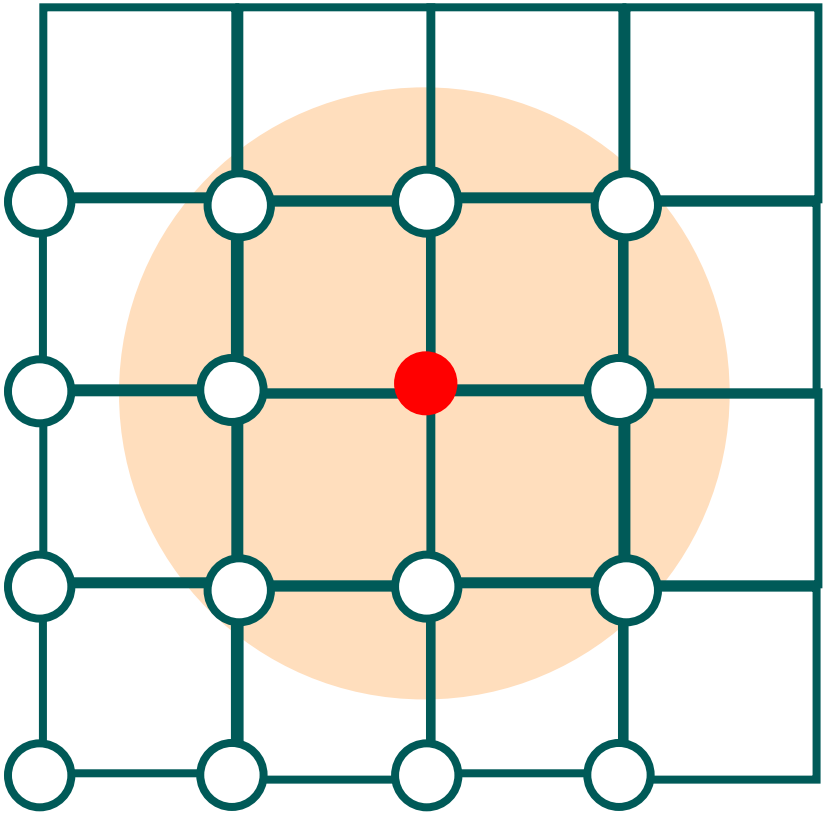
Including Effects in Density Functional Theory

two DFT Calculations

undoped normal cell

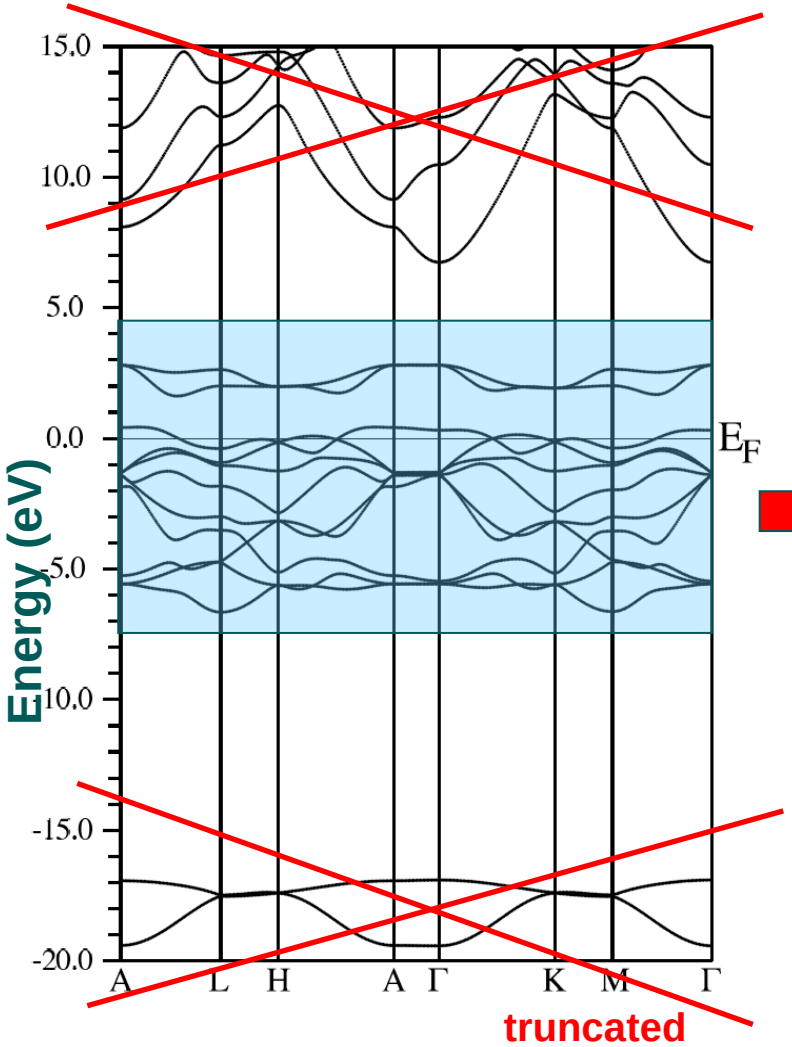


1 impurity in large super cell

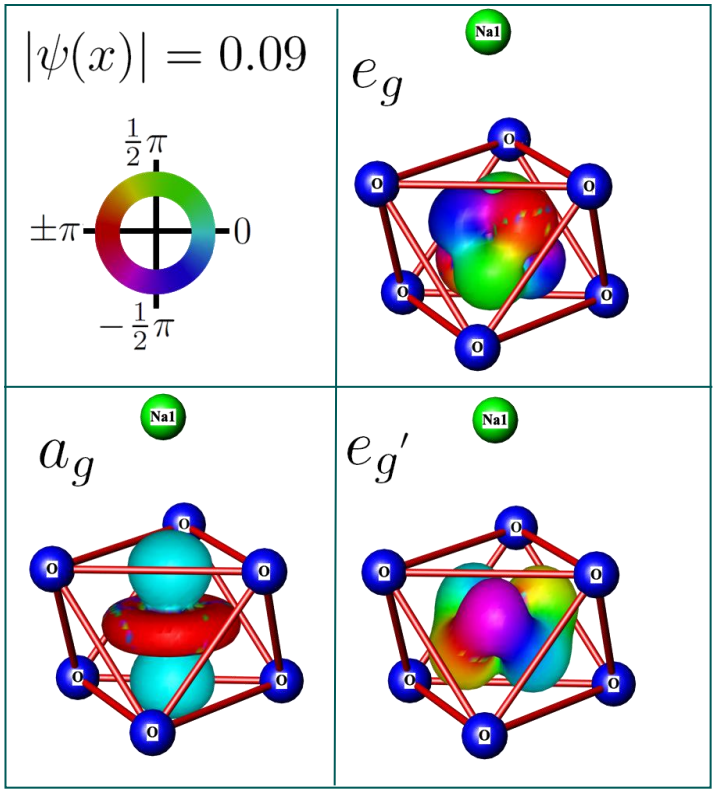


Reducing Hilbert Space via Wannier Transformation

DFT CoO_2

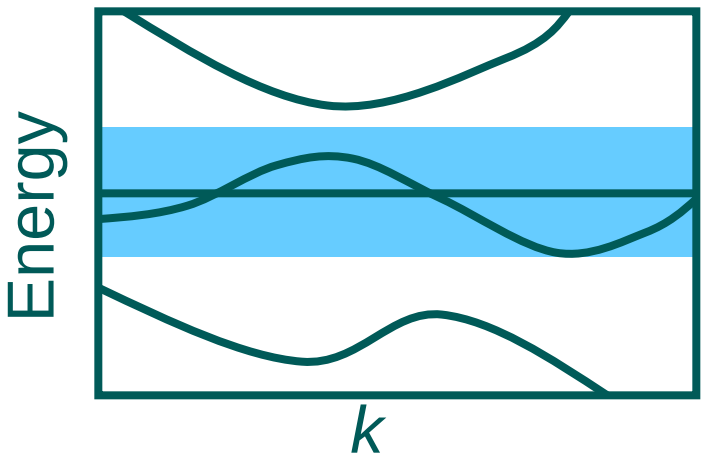


Wannier functions

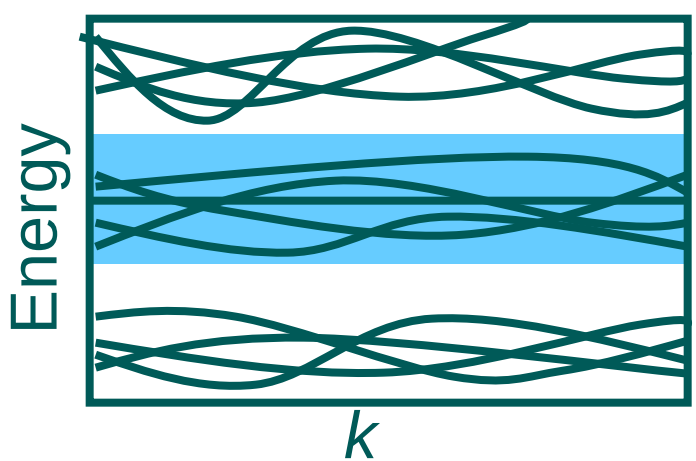


Obtain Effects of Impurities on H^{DFT}

DFT undoped



DFT 1 impurity



2 Wannier transformations

$$|\mathbf{Rn}> = \sum_{\mathbf{k},\mathbf{j}} \mathbf{e}^{-\mathbf{ik}\cdot\mathbf{R}} \mathbf{U}_{\mathbf{nj}}(\mathbf{k}) |\mathbf{kj}>$$

Reduced Hilbert space

2 Tight Binding Hamiltonians

undoped	1 impurity
$\mathbf{H}^{\mathbf{0}}_{\mathrm{DFT}}$	$\mathbf{H}^{\mathbf{1}}_{\mathrm{DFT}}$

$$\Delta^{(x_i)} = H^{(x_i)} - H^0$$

Constructing small and accurate effective H

Consider H from influence of impurities at $x_1, \ldots, x_N$

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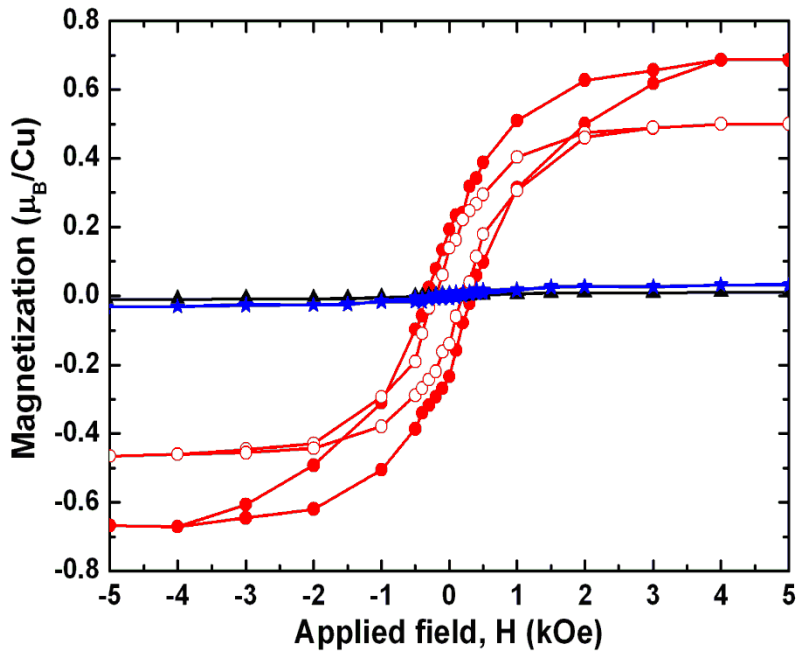
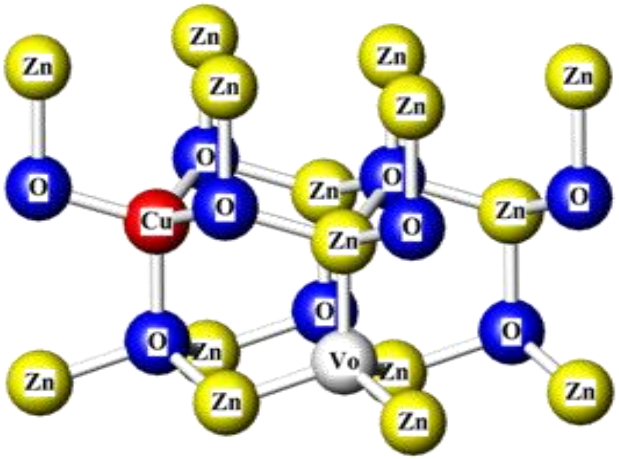
T. Berlijn, D. Volja, and Wei Ku, PRL **106**, 077005 (2011)

Substitution & vacancies: $Zn_{1-x}Cu_xO_{1-y}$

SQUID



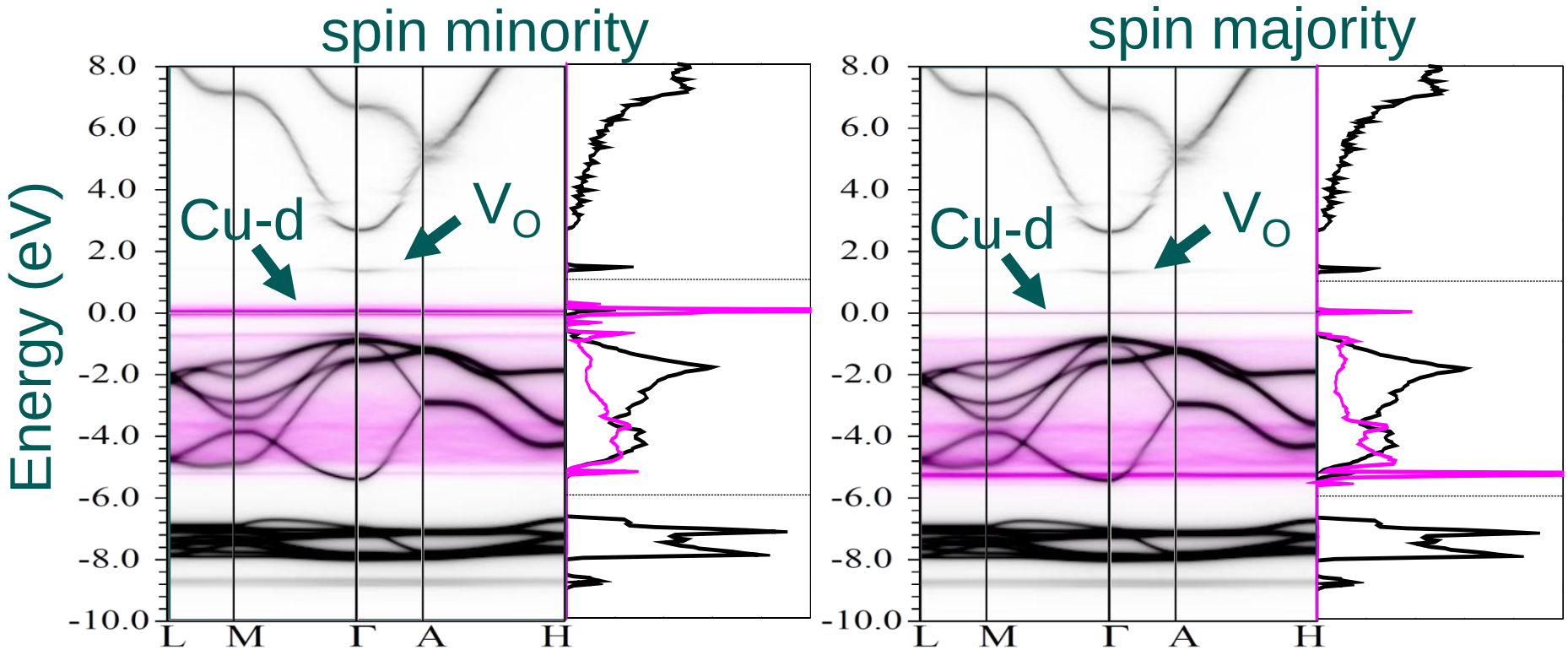
ZnO @ 300K (O-poor)
ZnO:Cu @ 300K (O-rich)
ZnO:Cu @ 5K (O-poor)
ZnO:Cu @ 300K (O-poor)



Q1) Where do the doped electrons reside?

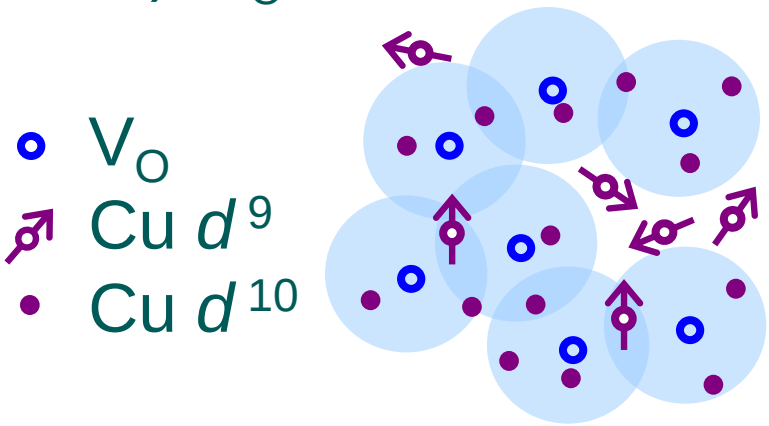
Q2) What is the role of oxygen vacancy?

T. S. Herng, *et. al*, PRL **105**, 207201 (2010)



A1) Doped electrons reside in Cu orbitals

A2) V_O mediates Cu moments



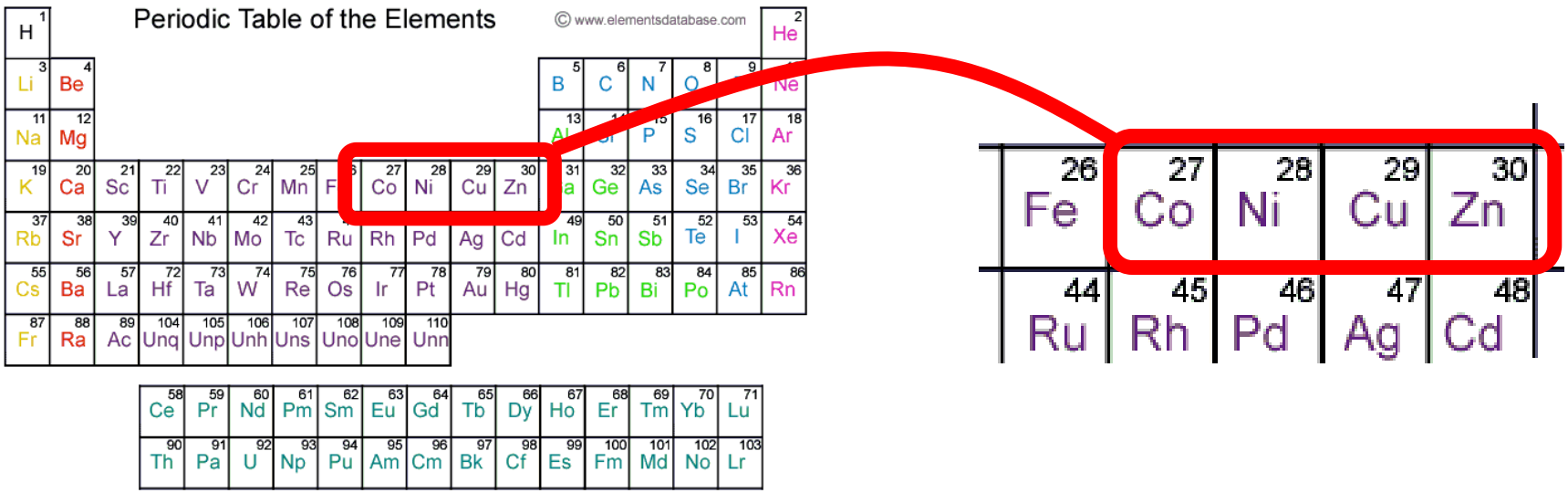
T. S. Herng, *et. al*, PRL **105**, 207201 (2010)

Do transition metal substitution dope carriers in Fe-based superconductors

T. Berlijn & Wei Ku

PRL **108**, 207003 (2012)

Do TM substitutions dope carriers in Fe-SC?



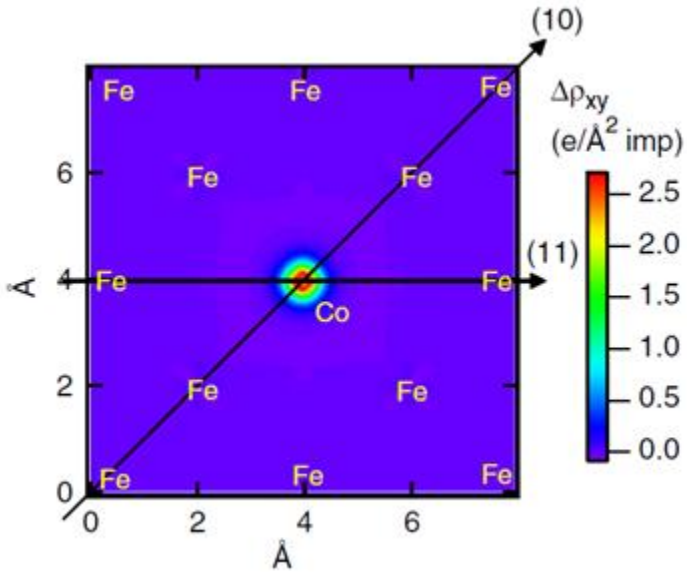
more valence electrons than Fe → expect electron doping

Additional Charge Residing in the Substituted Atoms in Fe-SC

Theory

DFT (density)

Co:122

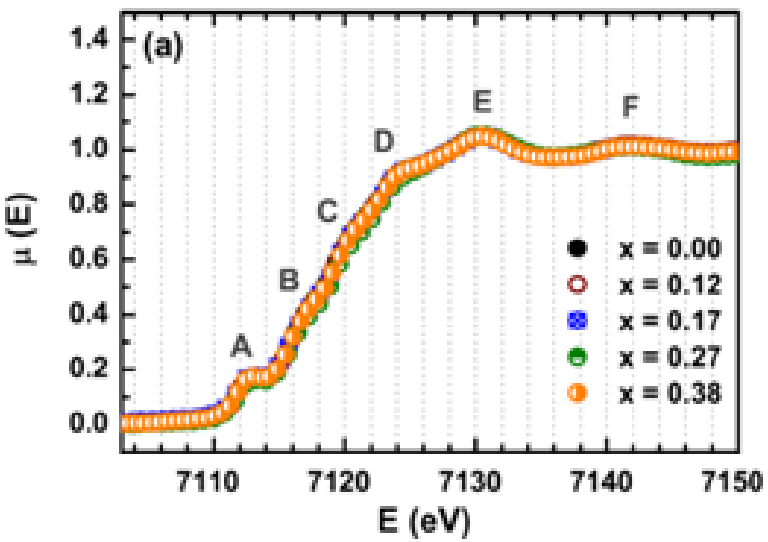


H. Wadati *et al*, PRL **105** (2010)

Experiment

XANES

Co:122



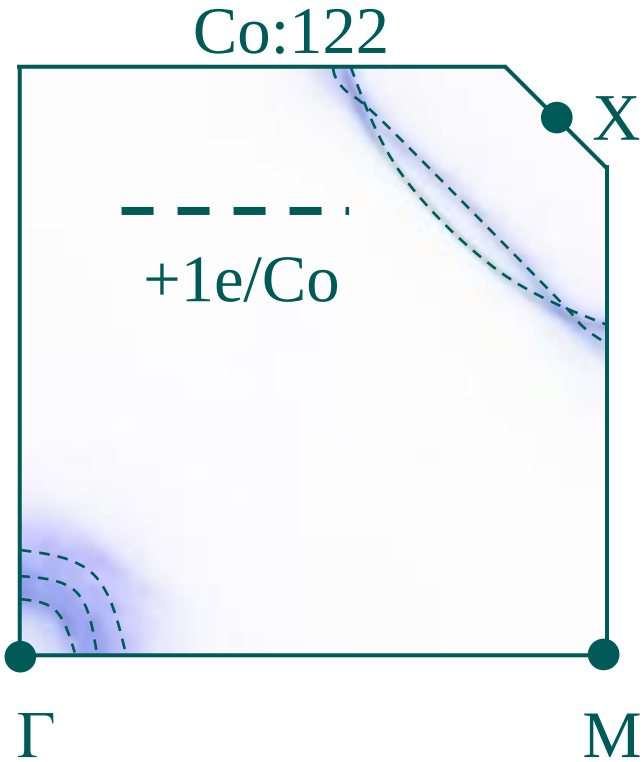
E. M. Bittar *et al*, PRL **107** (2011)

- Substitution does not dope the system (?)

12.5% Co Substituted $BaFe_2As_2$

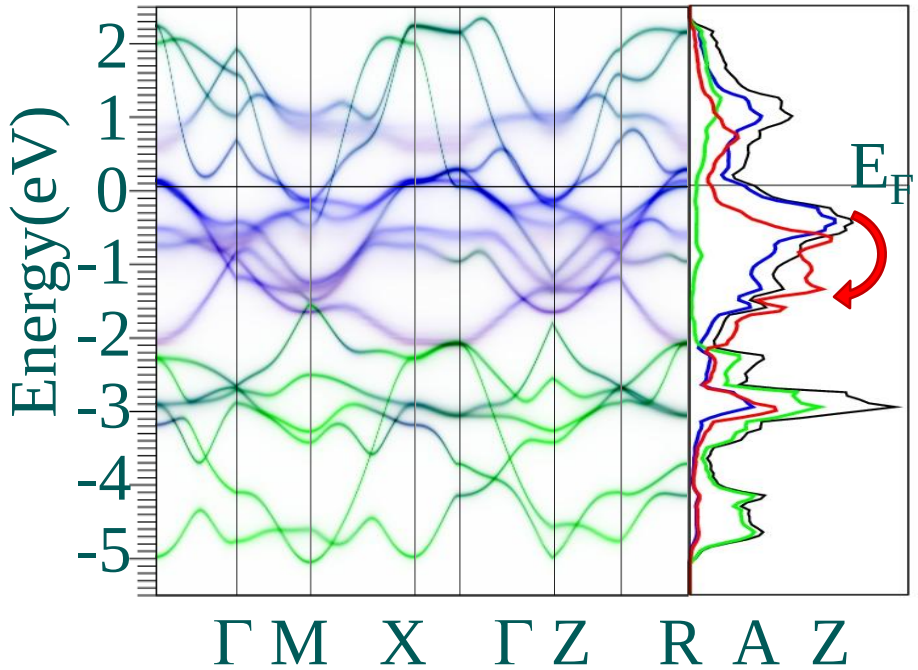
	α	$\sum_{n\in\alpha}\int_{BZ} d^3k \int^{E_F} d\omega \langle A_n(k,\omega)\rangle$
122	Fe	7.22
Co:122	Fe	7.19 x 7/8
Co:122	Co	8.40 x 1/8

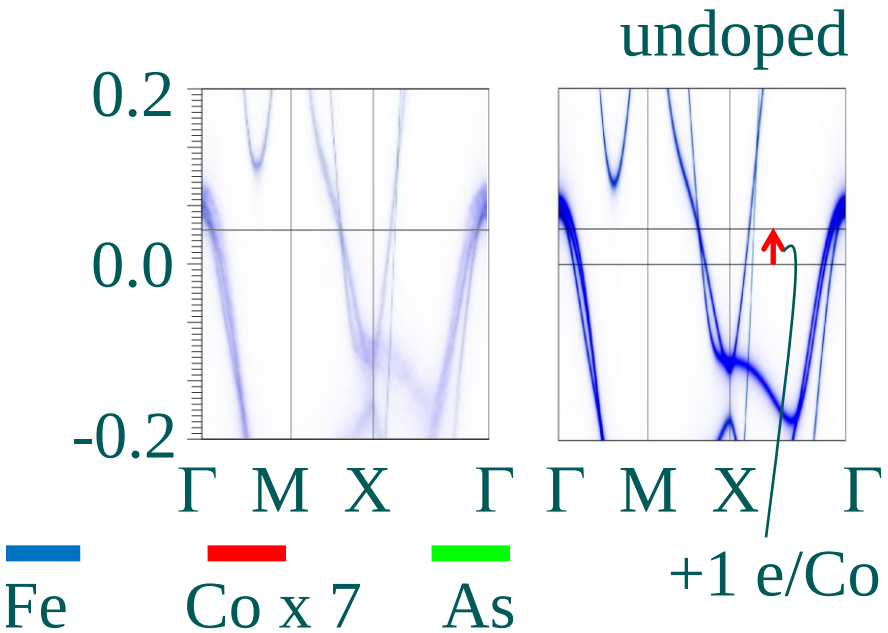
$$\langle A(k,\omega = E_F)\rangle$$



- Change of density in substituted atoms → not doping ?
- Enlarged Fermi surfaces & shift of chemical potential → doping?

Example: Does Co/Zn substitution dope Fe-SC?





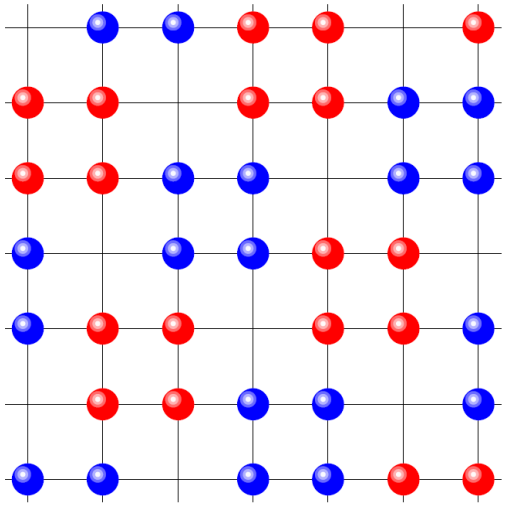
Most definitely yes, in the simplest manner,
but some carriers lose coherence!

Tom Berlijn, *et al.*, PRL **108**, 207003 (2012)

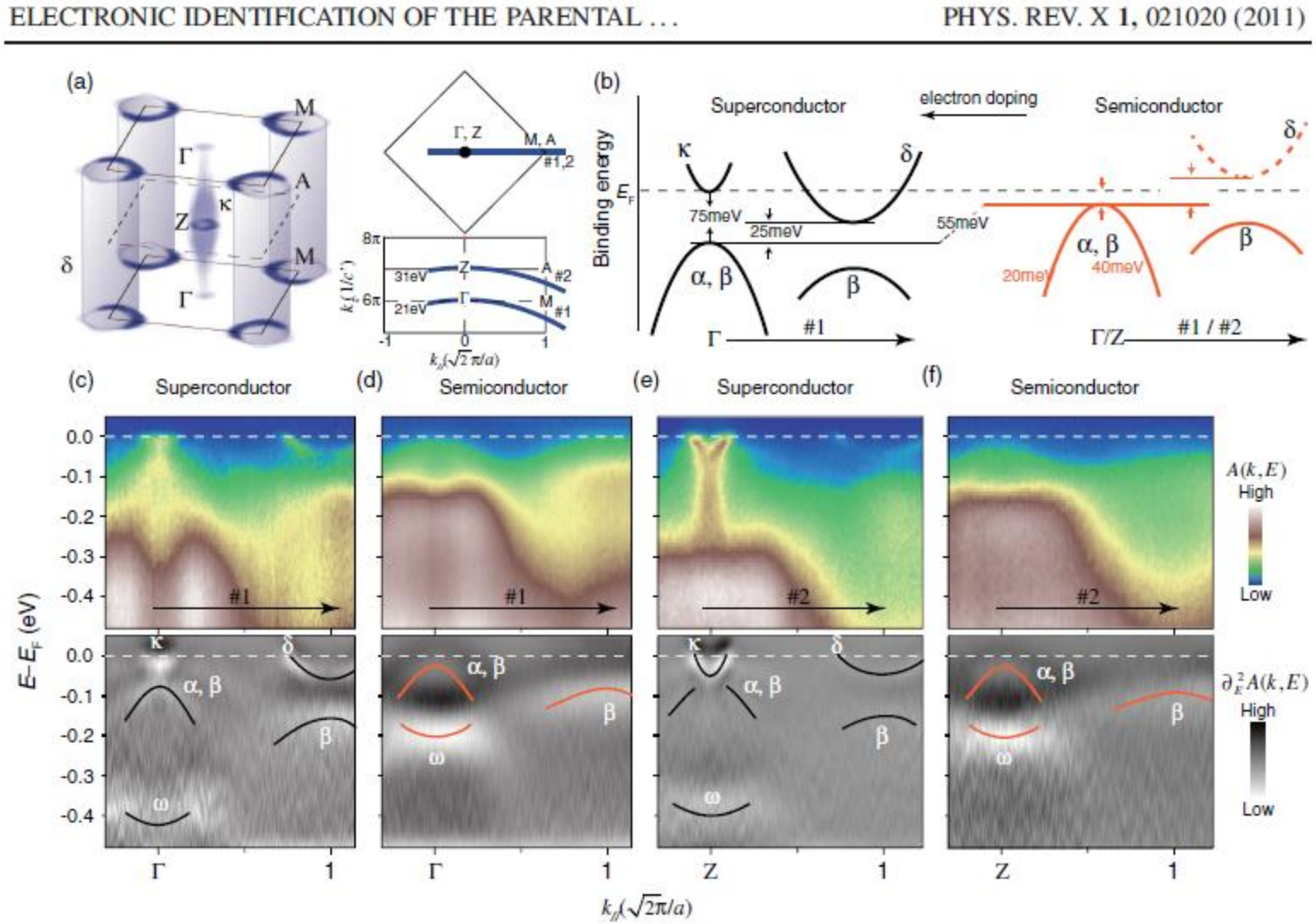
Fe vacancy in $K_2Fe_4Se_5$

T. Berlijn, P. Hirschfeld, & Wei Ku

PRL **109**, 147003 (2012)

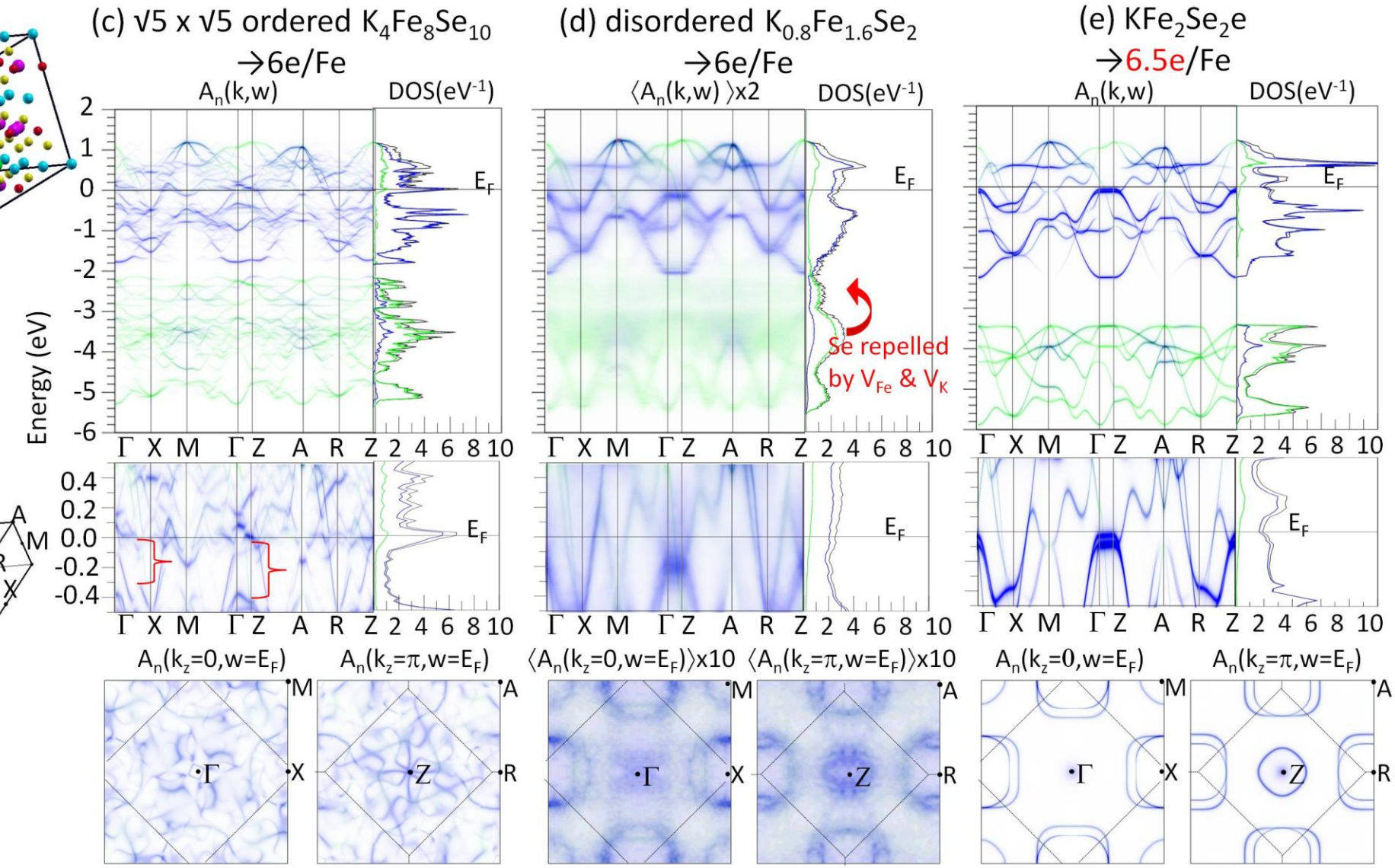


A heavily electron doped system?



F. Chen et al. Phys. Rev. X **1**, 021020 (2011)

Effective "doping" with Fe vacancy: Luttinger theorem?



Appears to be heavily doped ~ 0.5 e / Fe with disordered Fe vacancy

Tom Berlijn, Peter Hirschfeld, and Wei Ku, **109**, 147003 (2012)

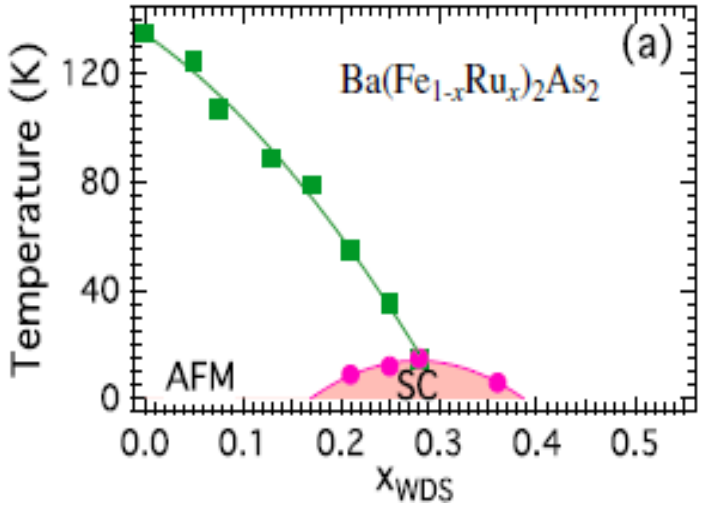
Ru substitution of $BaFe_2As_2$

Limin Wang, Tom Berlijn, Chia-Hui Lin, Yan Wang, Peter Hirschfeld,

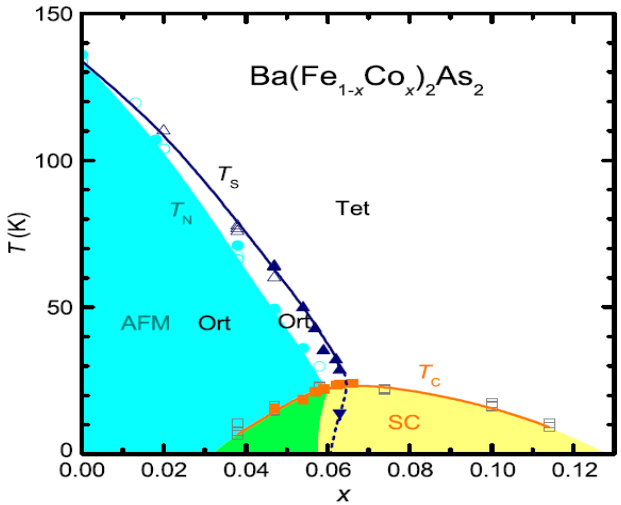
Wei Ku

PRL **110**, 037001 (2013)

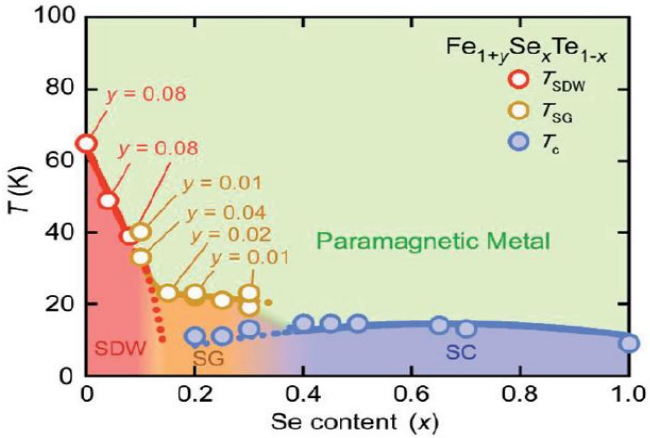
Temperature-composition phase diagram



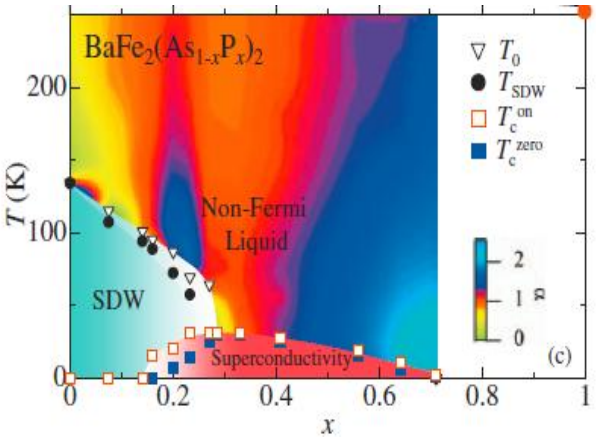
[R. S. Dhaka *et al*, PRL 107, 267002]



S. Nandi et al, PRL 104, 057006



[N. Katayama, et al , JPSJ 79,113702]



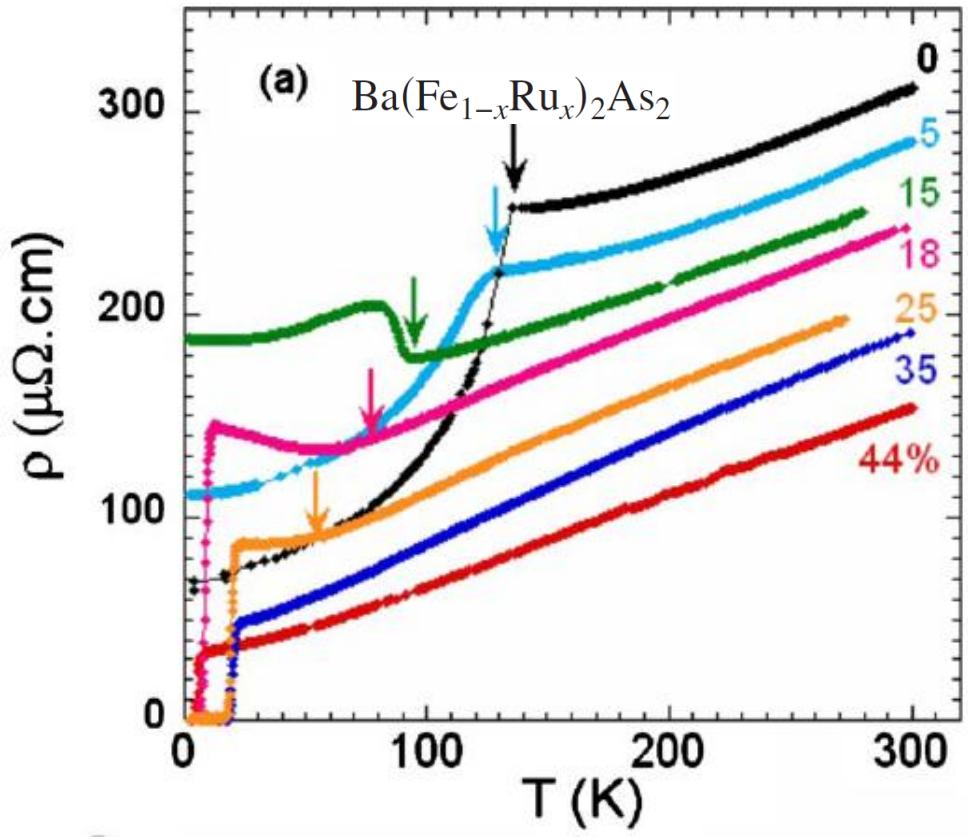
[S. Kasahara, et al , PRB 81 184519]

Ru/Co atoms replace the most essential Fe atom.

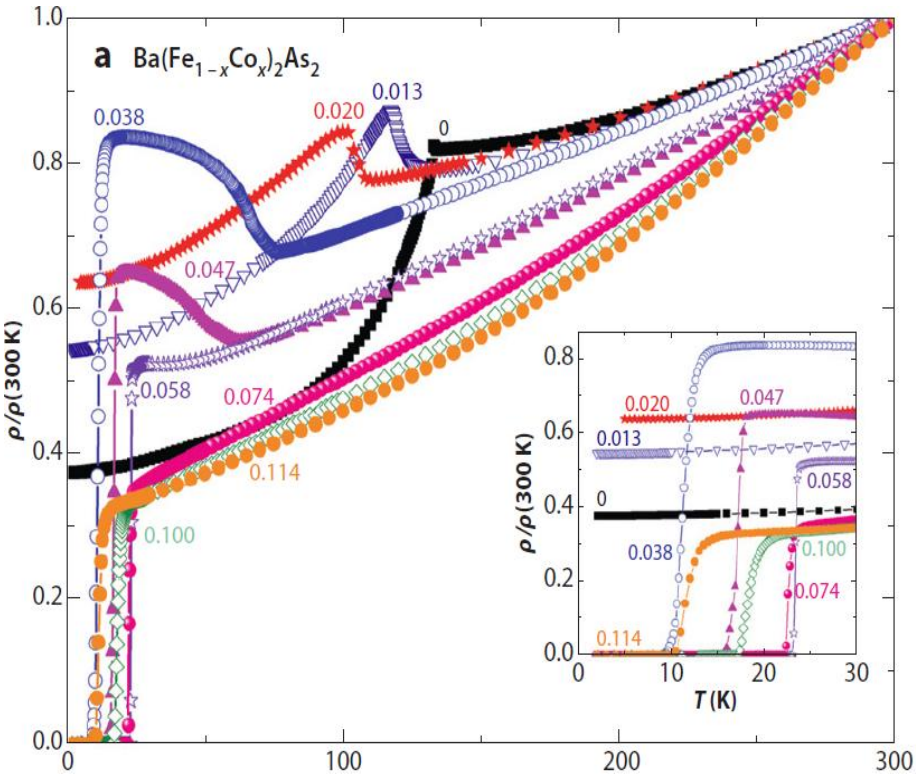
Superconductivity can survive even with 40% Ru substitution

Transport property

[F. Rullier-Albenque et al., PRB 81, 224503 (2010)]



[P. C. Canfield et al., Annu. Rev. Cond. Matt. 27 (2010)]

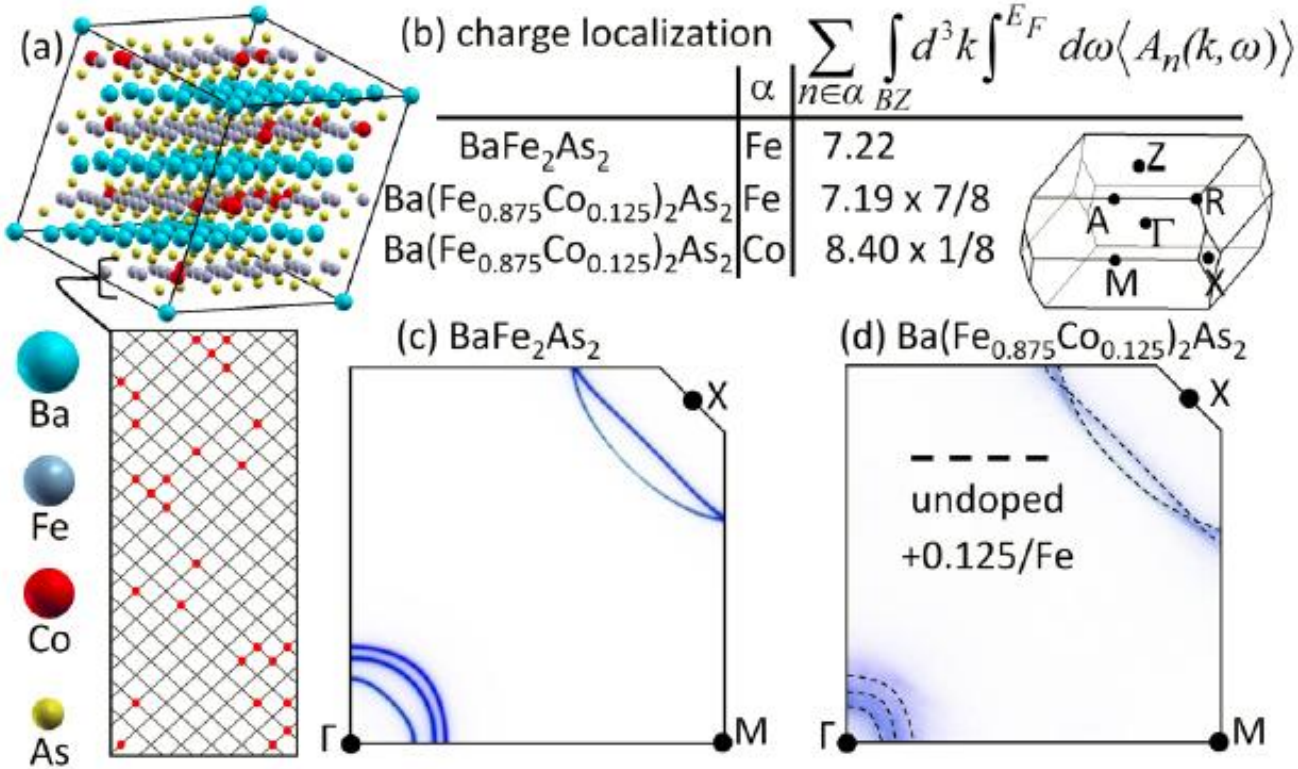


T(K)

Ru substituted samples exhibit a residual resistivity comparable to 8% C substituted system at a much higher 35% substitution level

Suppression of the long-range order

For Co substitution (additional doped carrier, PRL 108, 207003)



For Ru substitution

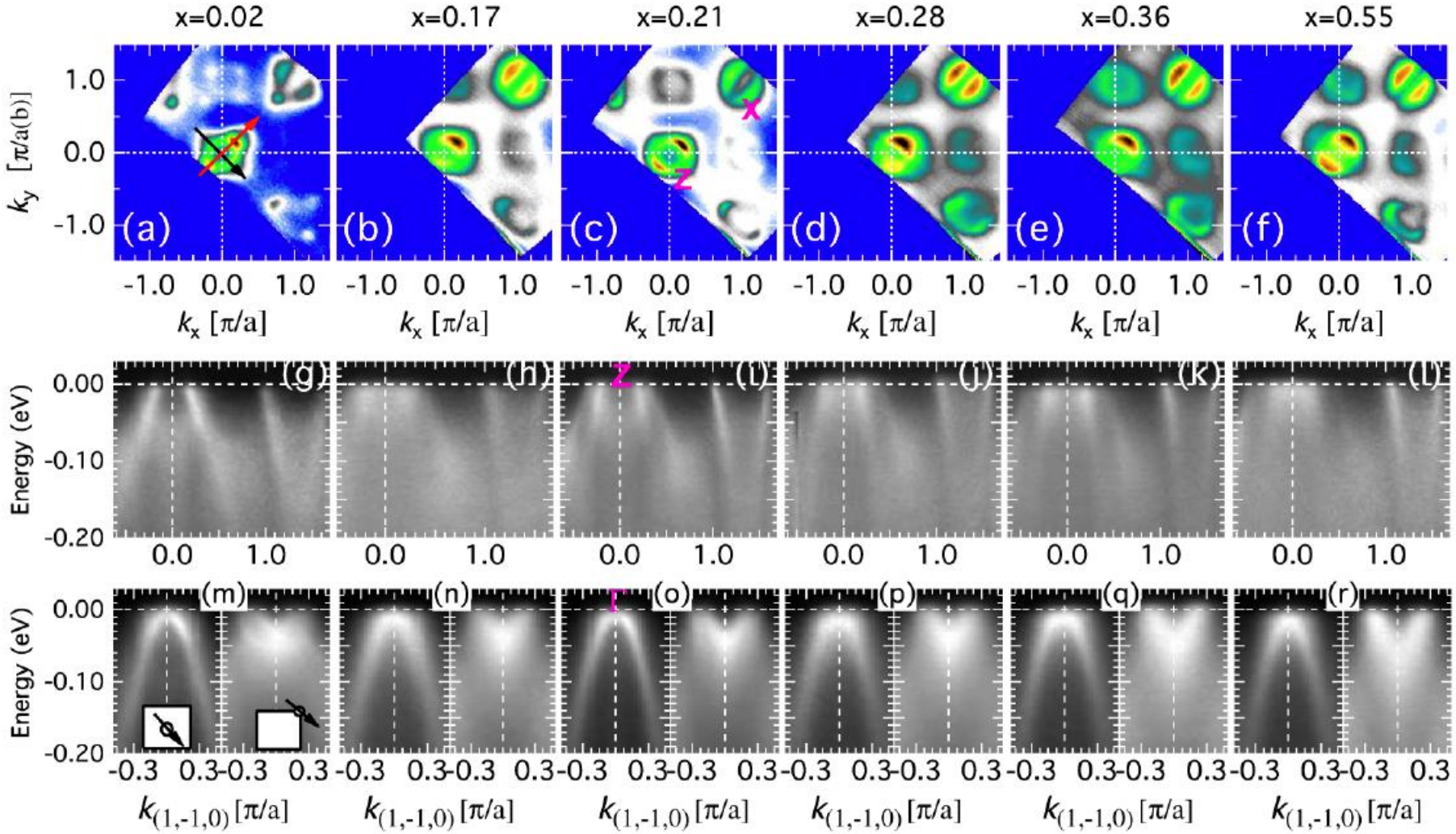
The size of the electron and hole pockets should remain balance.

What substitution-dependent features in the electronic structure suppress the long-range order in this case?

Experimental (ARPES) controversy

- Nearly substitution-independent FS

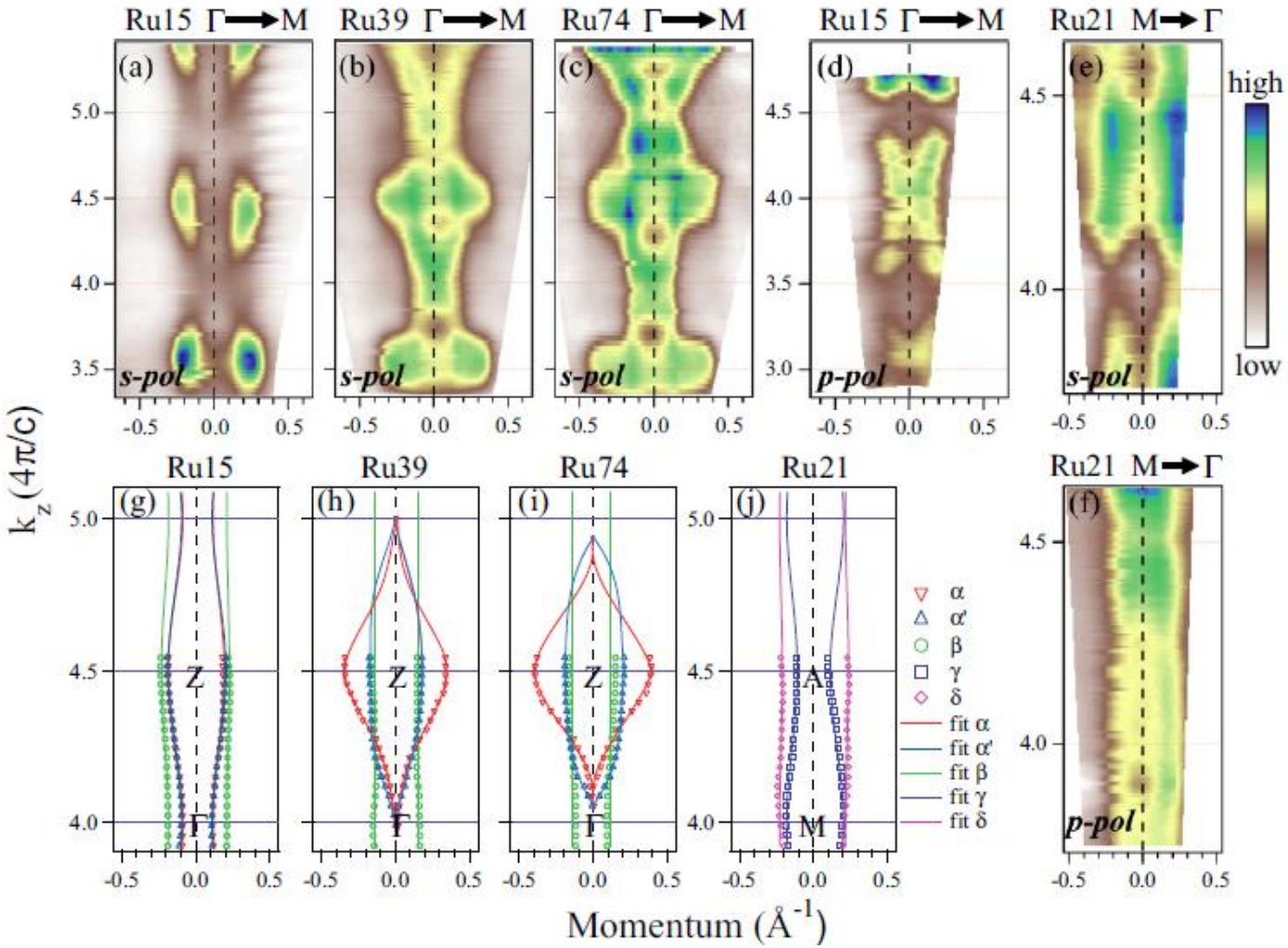
[R. S. Dhaka *et al*, PRL 107, 267002(2011)



Experimental (ARPES) controversy

- A crossover from two-dimensional to three dimensional structure

[N. Xu et al, PRB 86, 064505]



Physical puzzles in Ru 122

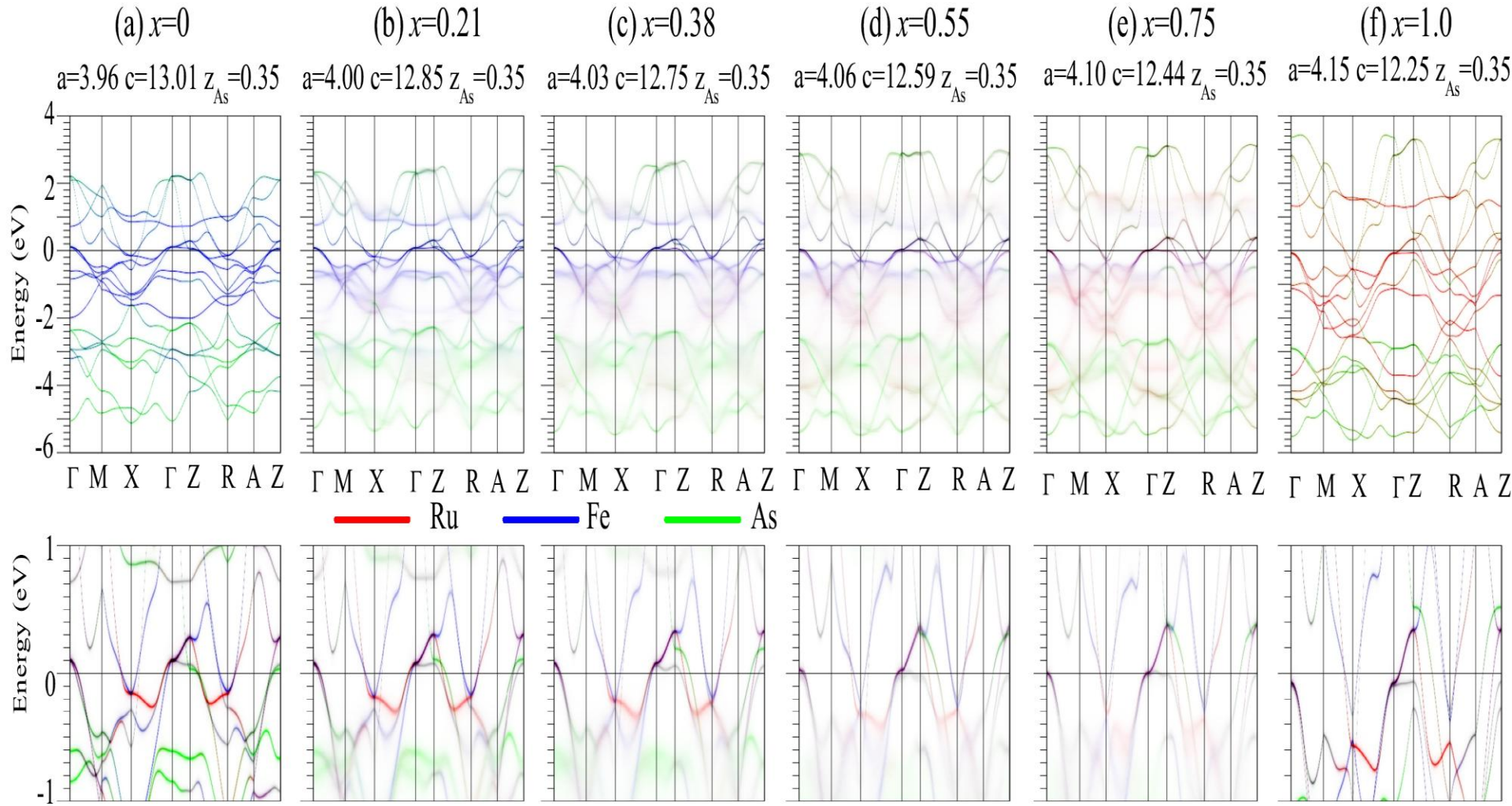
- How does the superconductivity in Ru122 survive up to 40% doping level.

- What substitution-dependent features in the electronic structure suppress the long-range order in Ru122?

Contradictory experimental and theoretical electronic structure ?

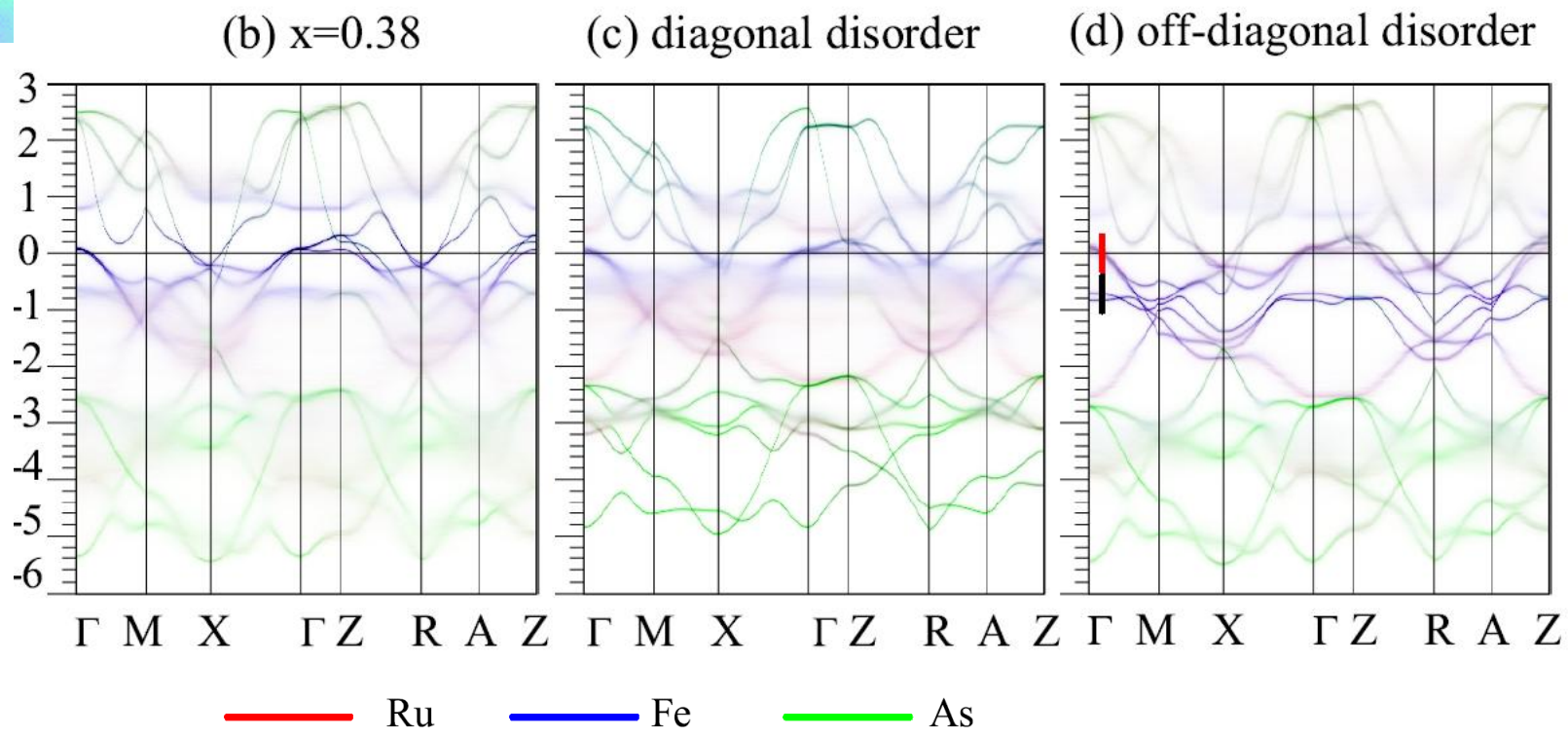
It is timely to investigate the substitution-dependence of the electronic structure of Ru122 with a proper account of the disorder effects.

Band structure for different Ru substitution



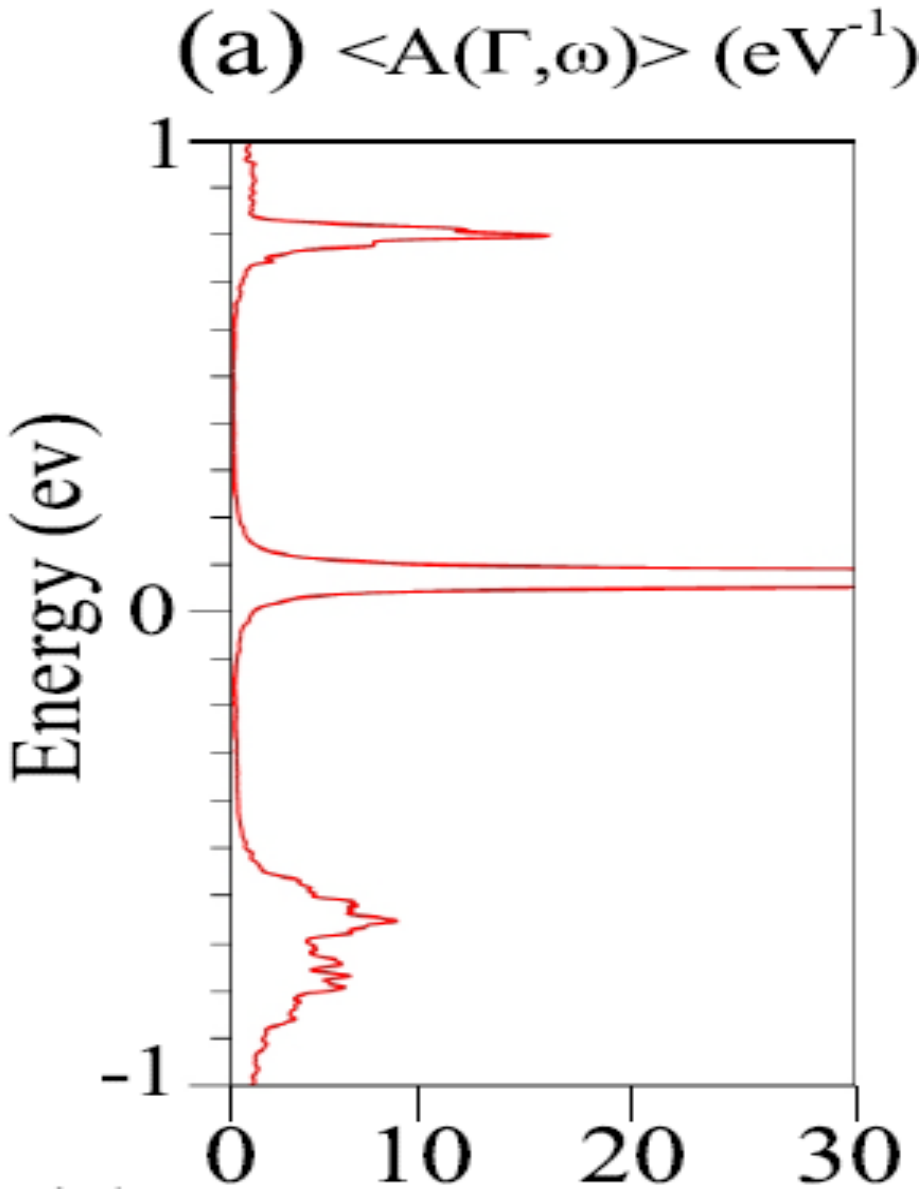
- The bands are heavily smeared.(-0.8ev)
- x=0.55 is the most disordered one.
- Fe bands around the Fermi level remain very sharp.

Origin of the superdiffusion around the Fermi level



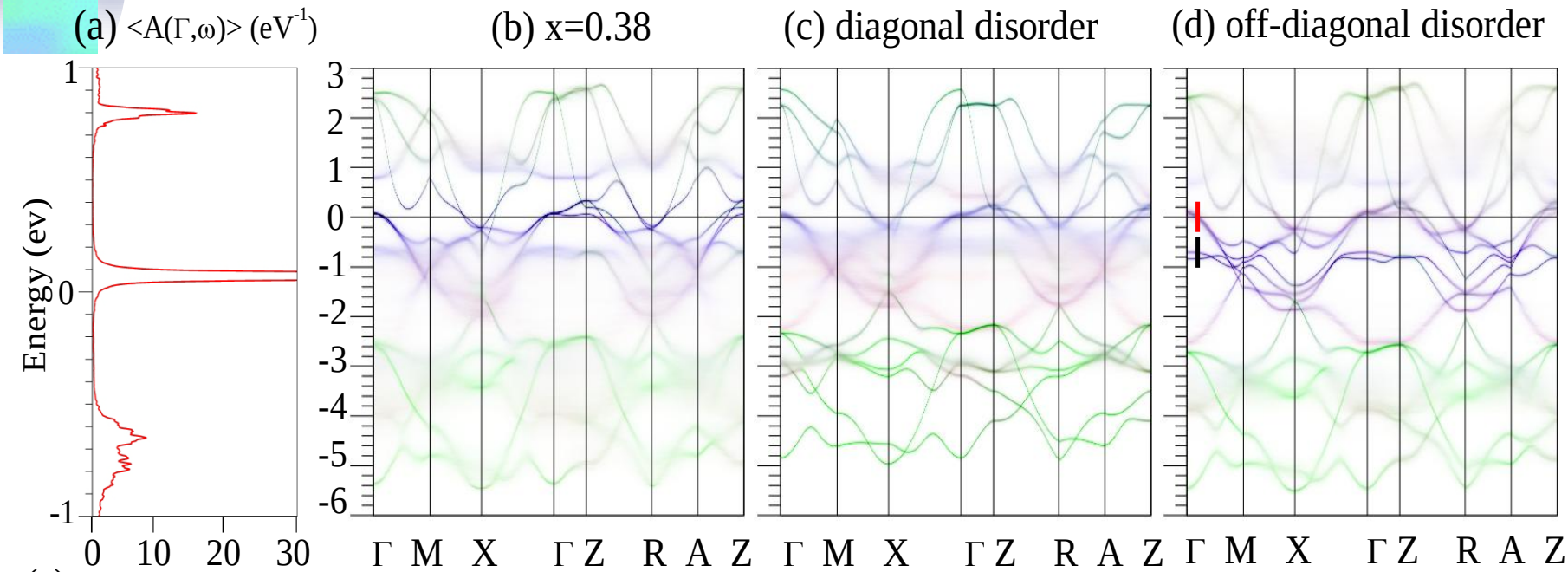
- For diagonal disorder, a strong smearing of the entire d-band.
- For off-diagonal disorder, the impurity scattering diminishes near the center of the d-band.
- Upon combining, the energy rang with weak impurity scattering moves up.

Configuration-averaged spectral function



- A very sharp peak around the Fermi level.
- A much broader peak around ~1 ev.
- Lack of net impurity scattering for states near the Fermi level.

Origin of the superdiffusion around the Fermi level



(e)

k	j	k'	j'	$\langle kj\|\Delta\|k'j'\rangle$	$\langle kj\|\Delta_D\|k'j'\rangle$	$\langle kj\|\Delta_{OD}\|k'j'\rangle$
Γ	9	0.3ΓM	10	-0.0578	-0.3023	0.2445
Γ	8	0.3ΓM	7	-0.2938	-0.3316	0.0378

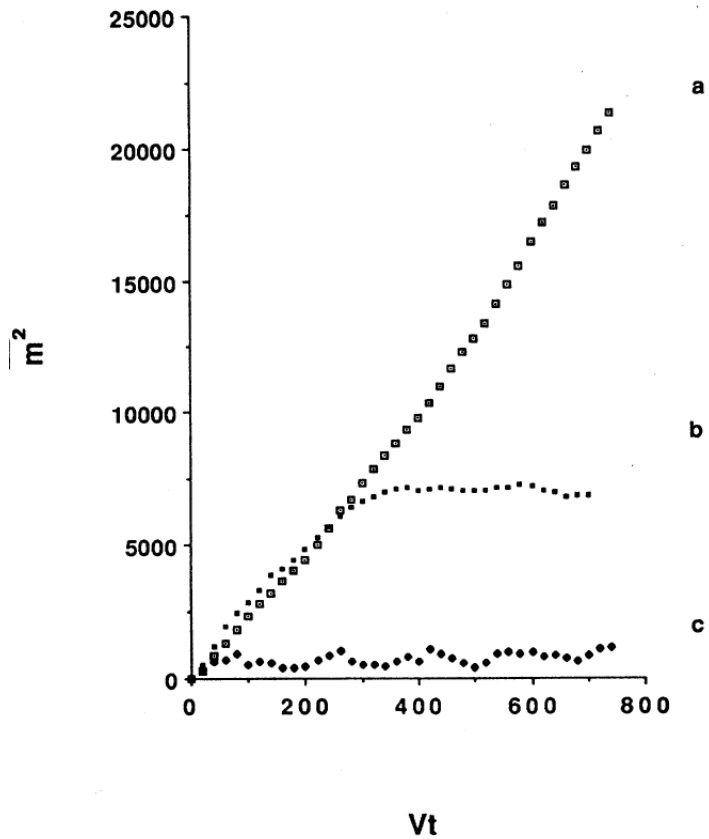
- This insensitivity here originates from a coherent interference between on-site and off-site impurity effects.

Superdiffusion in 1D model

[D. H. Dunlap, K. Kundu, and P. Phillips, PRB 40, 10999 (1989)]

Single-particle Hamiltonian

$$H = H_{\text{lattice}} + \sum_{\mathbf{k}} \varepsilon_0 a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_{\mathbf{k},\mu} 2V_{\mu} \cos(\phi_{\mu} - k_{\mu}) a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}}$$
$$+ \sum_{\mathbf{k},\mathbf{q},\mu} 2i[\gamma_{\mu} \sin(k_{\mu} - \theta_{\mu}) - \gamma_{\mu} \sin(k_{\mu} - q_{\mu} - \theta_{\mu})$$
$$- G_{\mu} \sin(q_{\mu})] x_q^{\mu} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k} - \hat{\mu} q_{\mu}} , \qquad (1.2)$$



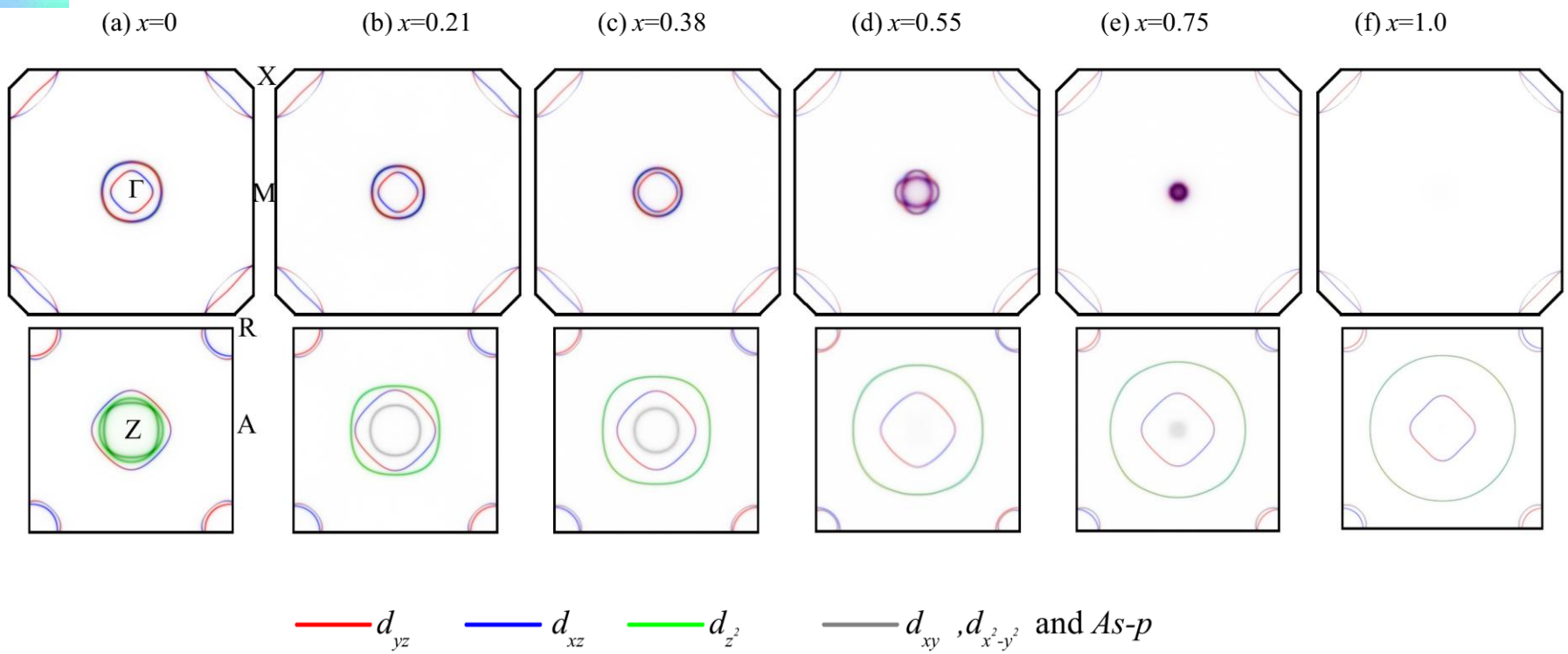
a correlated disorder ($\gamma = G$)

b site-diagonal disorder.

c site-off diagonal disorder.

- Correlations between site and off-diagonal disorder give rise superdiffusion transport.

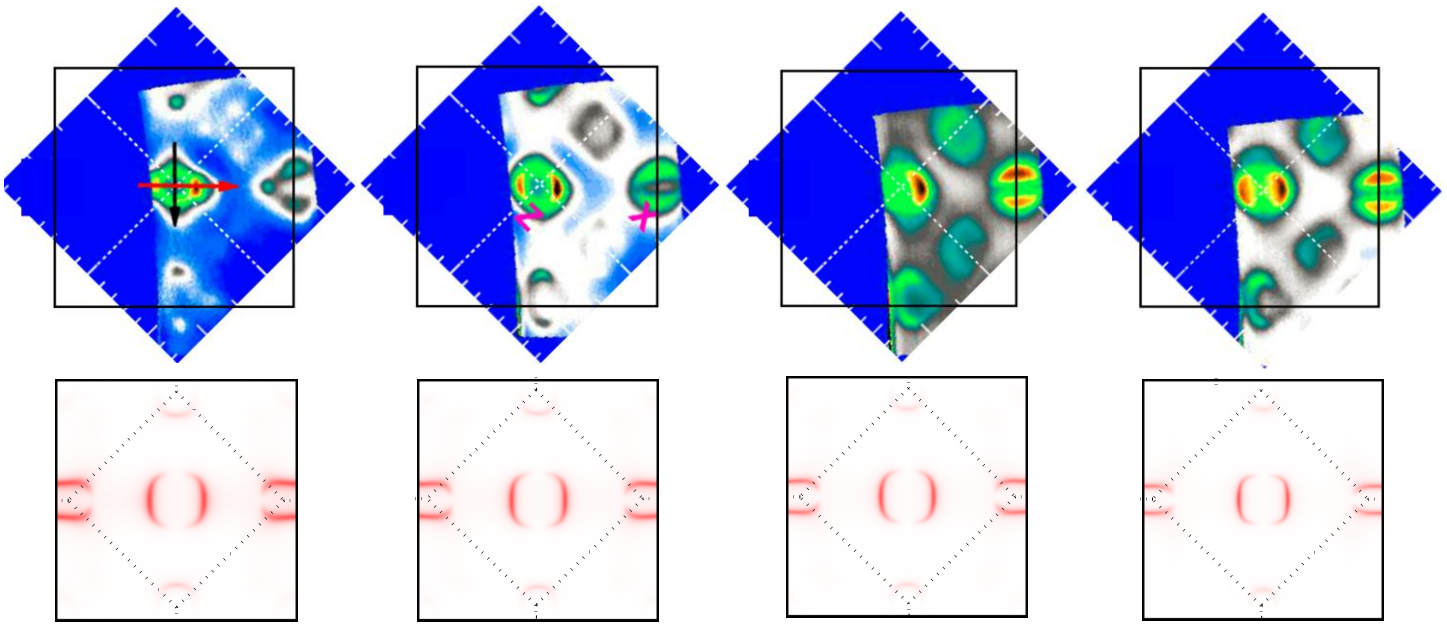
Fermi surface (2Fe) for different Ru substitution



- The hole pockets become more three dimensional
- The electron pockets show a slight substitution dependence.

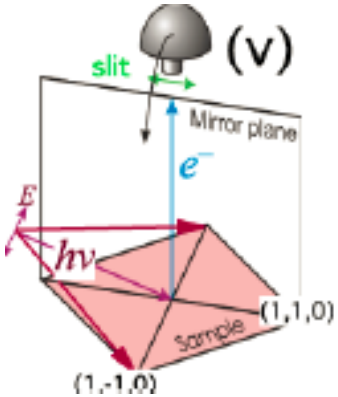
Resolution of the ARPES controversy

(a) x=0.02 (b) x=0.21 (c) x=0.36 (d) x=0.55



[R. S. Dhaka *et al*, PRL 107, 267002]

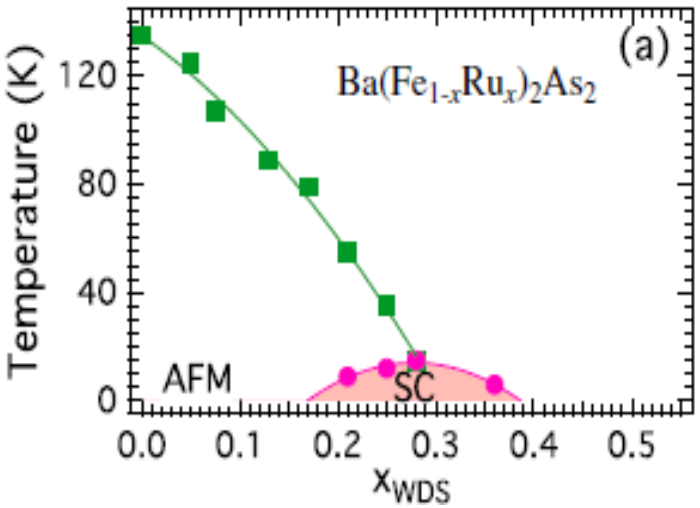
1Fe zone



- The photon polarization couples mostly to the yz.
- The yz character of our unfolded BS also show a little change.

Suppression of the long-range order

	x=0	x=0.21	x=0.38	x=0.55	x=0.75	x=
$e/Fe = h/Fe$	0.162	0.151	0.142	0.127	0.123	0.120
$DOS(E_F)$	2.393	2.024	1.775	1.458	1.299	0.868



[R. S. Dhaka *et al*, PRL 107, 267002]

- carrier reduction originate from a larger splitting between the conduction and valence bands.
- The reduced DOS and enhanced 3D tend to suppress the long-range orbital/ magnetic order

Conclusions

- Symmetry-respecting Wannier function
  - Simple, flexible and efficient basis to describe physics
  - Intuitive microscopic picture + quantitative realism
- Unfolding 1st-principles band structures
  - Visualizing each band's coupling to the order parameters and other symmetry breakers
  - Useful for the study of extrinsic (doping, intercalation, vacancy, substitution, & defects) and intrinsic (CDW, SDW, OO, & structure distortion) effects on the electronic structure
  - Direct comparison with ARPES spectrum, built-in matrix elements effects
- A non-perturbative beyond-mean-field first-principles method for materials with disordered impurities
  - Defects, vacancy, chemical substitution, doping & intercalation
  - Thermal/quantum fluctuation induced spatial inhomogeneity
  - Paramagnetic phase with disordered local moments