What is going on in $K_xFe_ySe_2$ and FeSe monolayers?

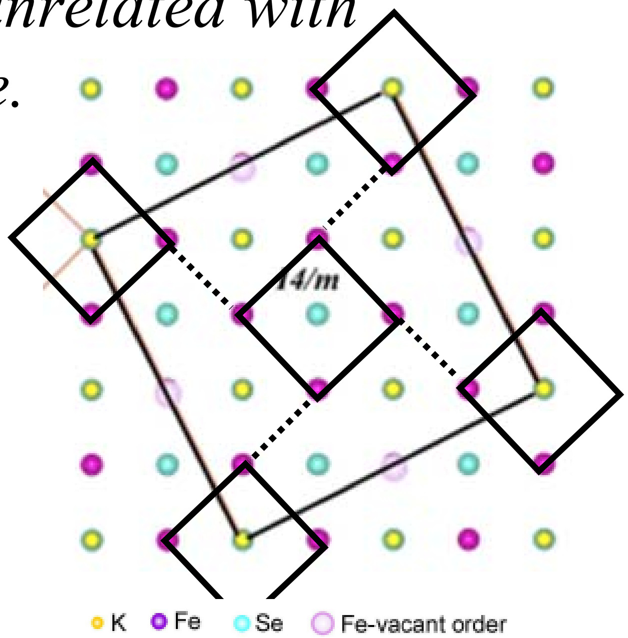
Igor Mazin, Naval Research Laboratory, Washington D. C.

- **Basic facts**
  1. Crystallography
  2. ARPES
  2. Band structure calculations
  3. Morphology
  4. Superconductivity (ARPES, INS)
- **Theoretical problems**
  1. Why DFT calculations so much disagree with ARPES?
  2. Why superconductivity in monolayers is so fragile?
  3. If we trust INS, where is the sign change?

Crystallography

$K_xFe_ySe_2$

- Magnetic phase at x=0.4, y=0.8 ($K_2Fe_4Se_5$). Fe vacancies ordered as √5x√5. Exchange-driven band insulator. *Most likely completely unrelated with the s/c phase.* Zero doping



FeSe monolayers

- Insulating as-made, probably magnetic. Become s/c upon annealing under very special prerequisites.

Crystallography

$K_xFe_ySe_2$

- s/c phase (doping always close to n=0.15e/Fe). Most common composition suggestions: $K_{0.3}Fe_2Se_2$, $K_{0.7}Fe_{1.8}Se_2$. The latter can be approximated as $K_{2+\delta}Fe_7Se_8$ (δ=0.8, n=0.1). Fe vacancies ordered as √10x√8. Stripe AFM metal (similar to pnictides) in the calculation. *Possibly the parent phase for s/c.*

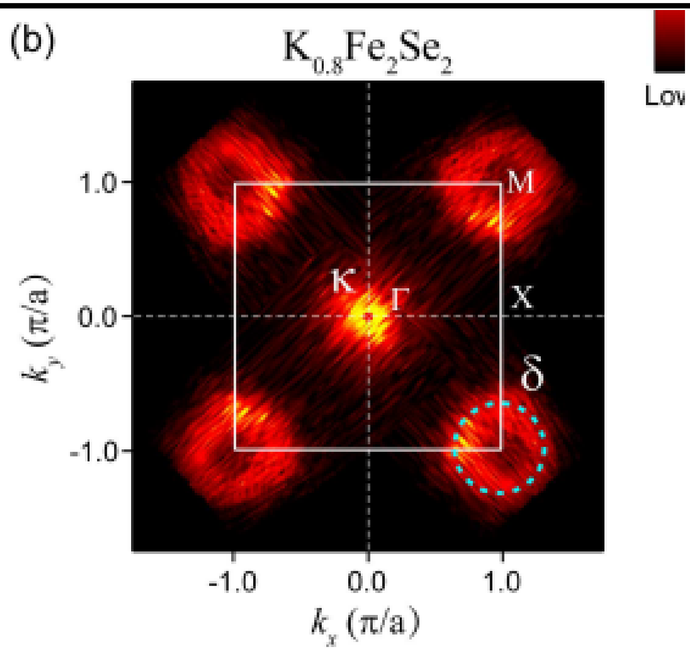
Haihu Wen's group

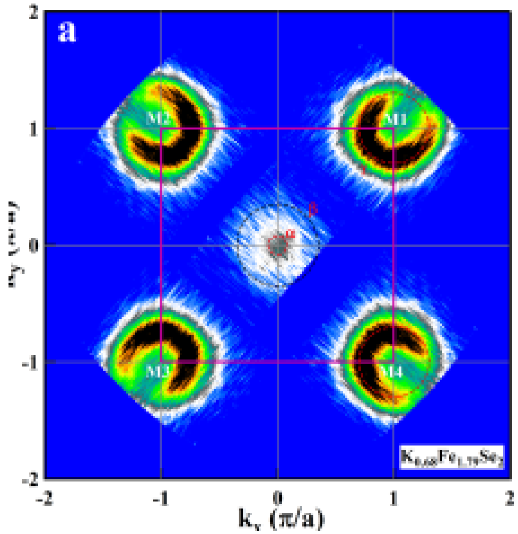
FeSe monolayers

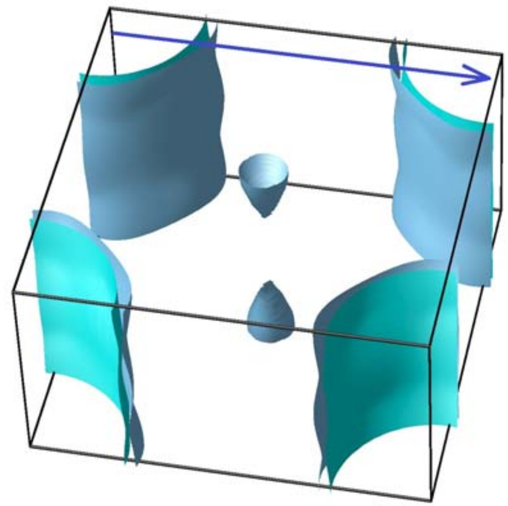
- Deposited on graphene: nonmetallic, not s/c. Deposited on $SrTiO_3$: nonmetallic, not s/c. Deposited on $SrTiO_3$ previously bombarded with Se, and then annealed: s/c at T~60 K

Xingjiang Zhou's group

ARPES





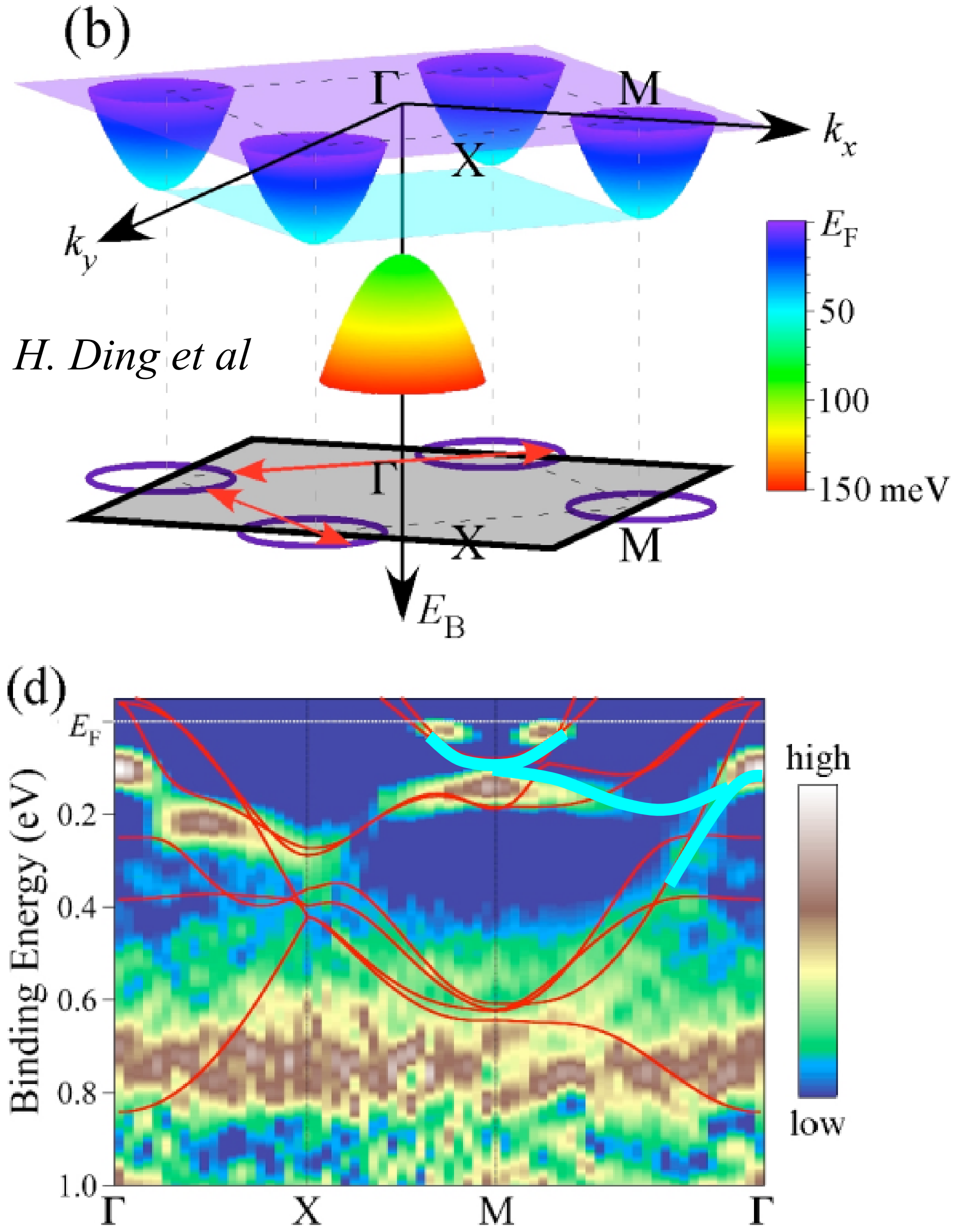


Fudan U.

IOP Beijing

ARPES is topologically consistent with ***stoichiometric*** LDA calculations (for KFe_2Se_2), n=0.5.

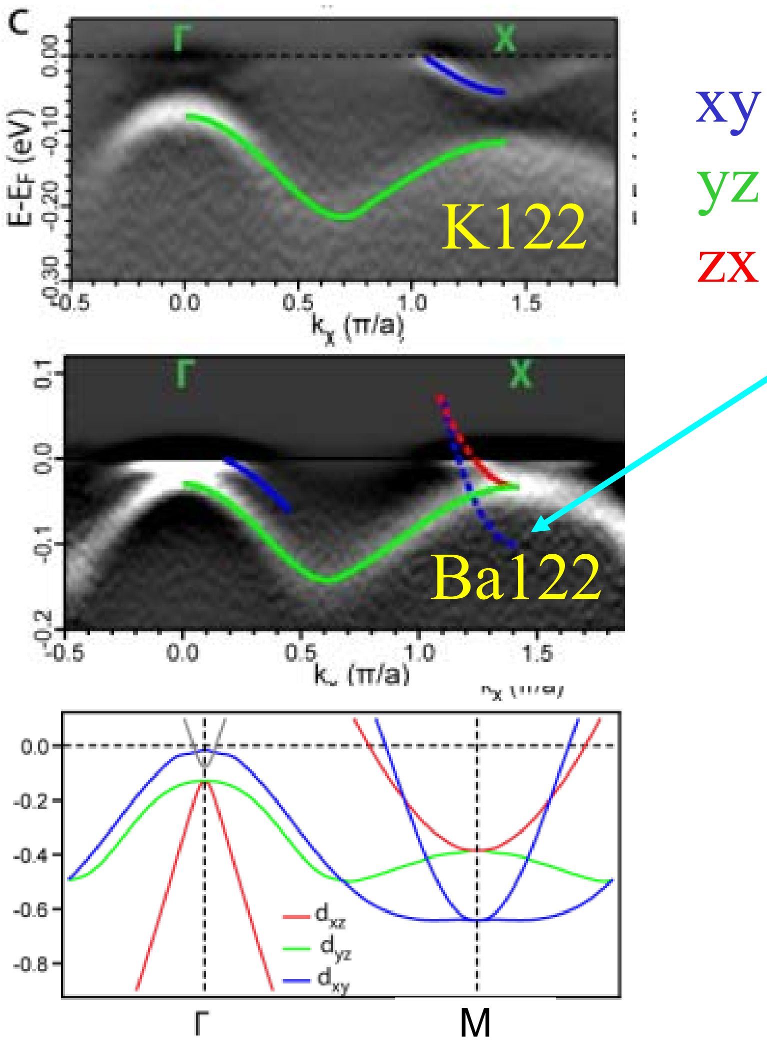
More ARPES



Allegedly $K_{0.8}Fe_{1.7}Se_2$ (0.1 *e* per Fe doping) and consistent with the Luttinger count.

Calculated band structure: enormously renormalized (170 meV shift claimed, in reality more like 250), with an implied dramatic topological transition between with doping (0<n<0.1)

More ARPES



blue: d_{xy}; red: d_{xz}; green: d_{yz}.

ZX Shen's group

In the geometry used, the band is extinct (Wei Ku, V. Brouet).

xz and yz bands non-degenerate at M? Note that x/y symmetry can be broken by breaking z/-z symmetry (xz/y,-z)

Wrong crystallography? Defects?

DFT calculations

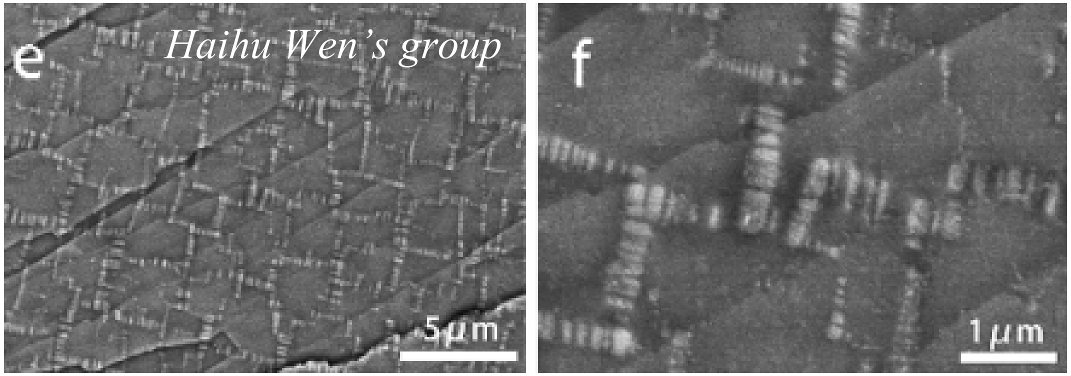
1. DFT successfully predicts:
   - *Magnetic and crystal structure of the 245 phase* *X.W. Yang et al, Renmin U.*
   - *Insulating properties of 245 (should be more correlated than 278!)*
   - *Crystal structure of 278* *IIM, unpublished.*
   - *Fermi surface of 11 (should be at least as correlated as 278)*
2. Why the relative positions of two bands with the same orbital character are so poorly predicted in 278?
3. Why the parent 278 (with different FS topology) never forms, only 10-15% doped version does?

Are we dealing with bulk properties? →

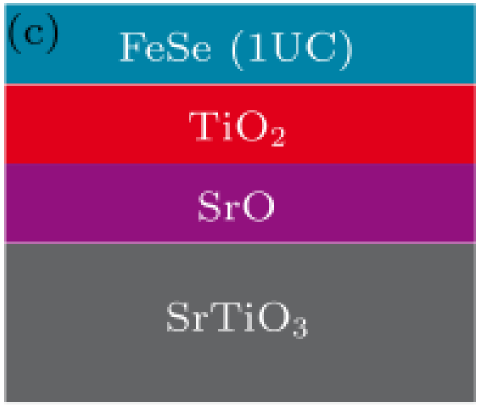
Morphology

"Spider web in 278"

Filamentary phase embedded in a nonsuperconducting matrix

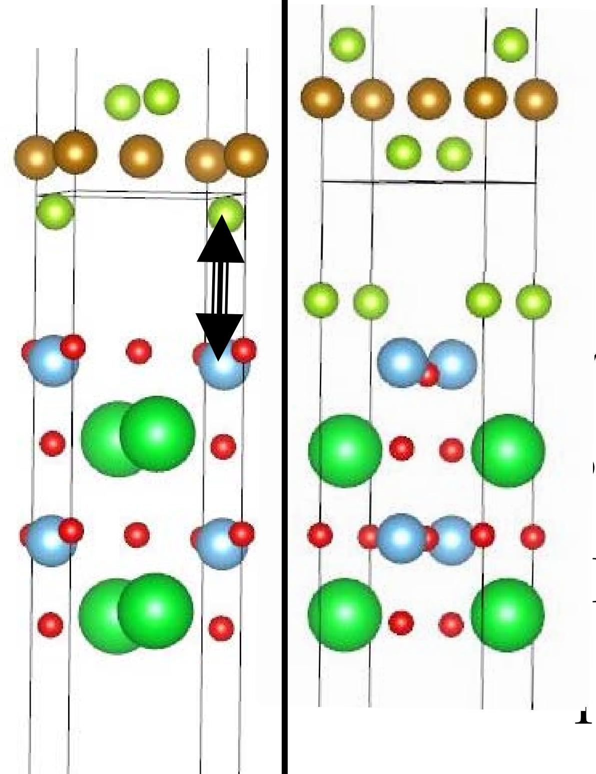


FeSe monolayer



1. Why Se etching is needed?
2. Where the doping (the same 0.15e!) is coming from?
3. Are (1) and (2) related?

DFT calculations



SP structural optimization with consequent WIEN verification.
, unpublished.

. TiO_2 layer and Se layer do not bind (3.34 A!)

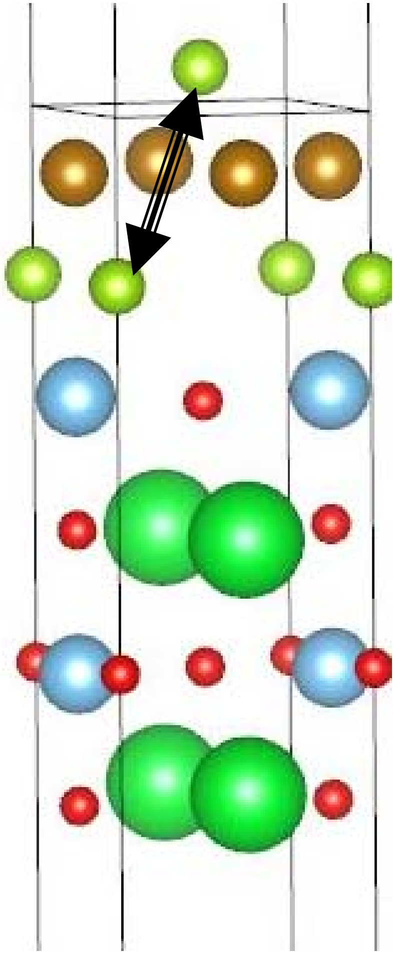
. No detectable charge transfer

. No change in the Fermi surface

But this is not what works in the experiment!

1. Suppose Se bombardment creates O → Se substitution?
2. Se puckers up by as much as 1.4 A
3. …which makes binding even worth
4. But if Se is shared … (O vacancy)

DFT calculations



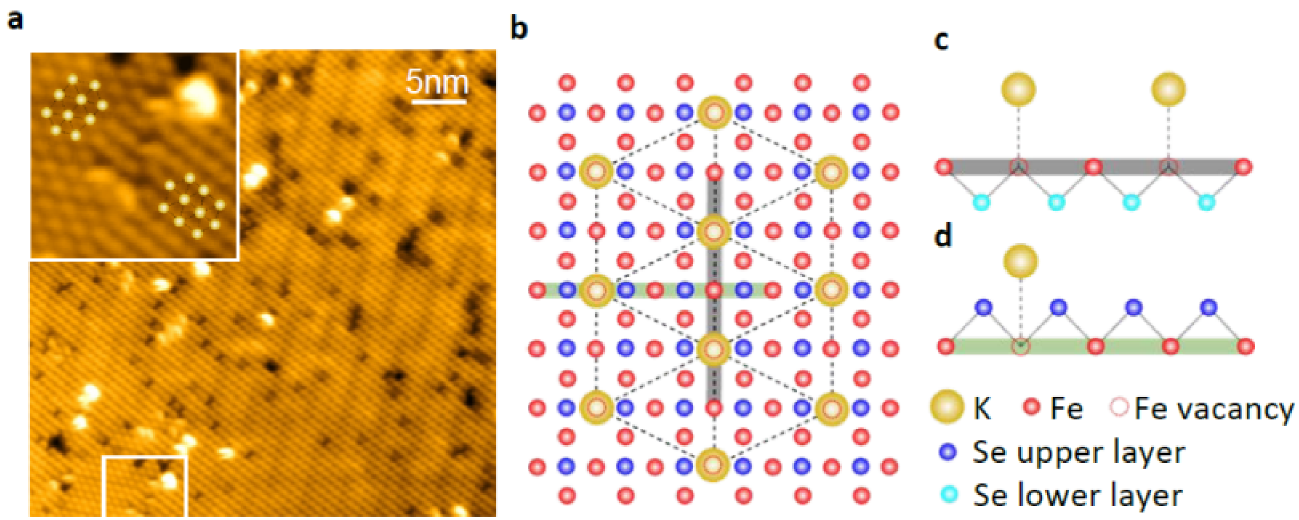
Corrolaries:

- Charge transfer (2e per each shared Se)
- Broken xz/-yz symmetry
- Explains why Se "etching" is essential

Is this the whole message? Of course not.

The message is that crystallography at the phase boundary is important

The 278 phase



Xiaxin Ding ... Hai-Hu Wen, cond-mat, 2013

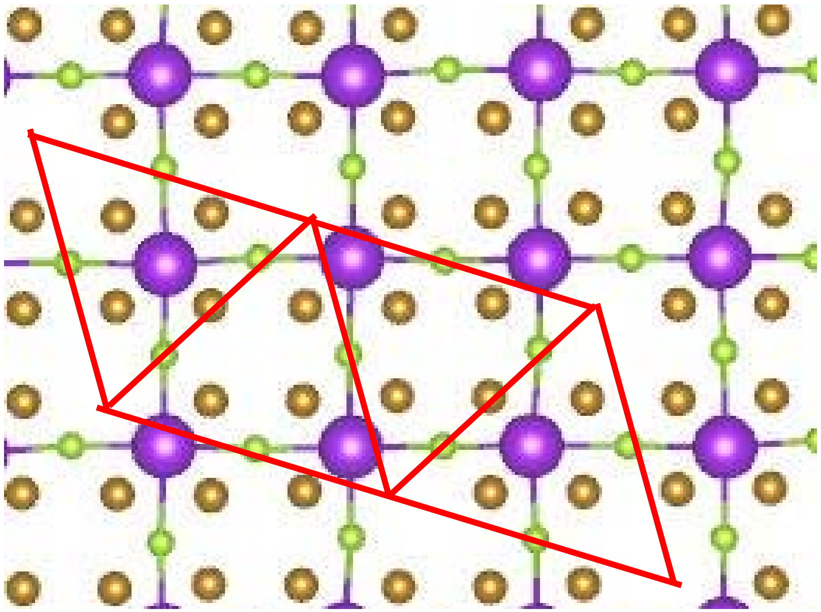
Substantial energy gain from vacancy ordering

(IIM, unpb.)

Figure 5 | Atomically resolved topography and the sketch of the 1/8 Fe-vacancy $\sqrt{8}\times\sqrt{10}$

- Both Fe vacancies and K form a nearly triangular ($\sqrt{10}\times\sqrt{8}$) lattice.
- Only possible at the surface [N(K)=N(vac)]!
- Different structure forms in the bulk:

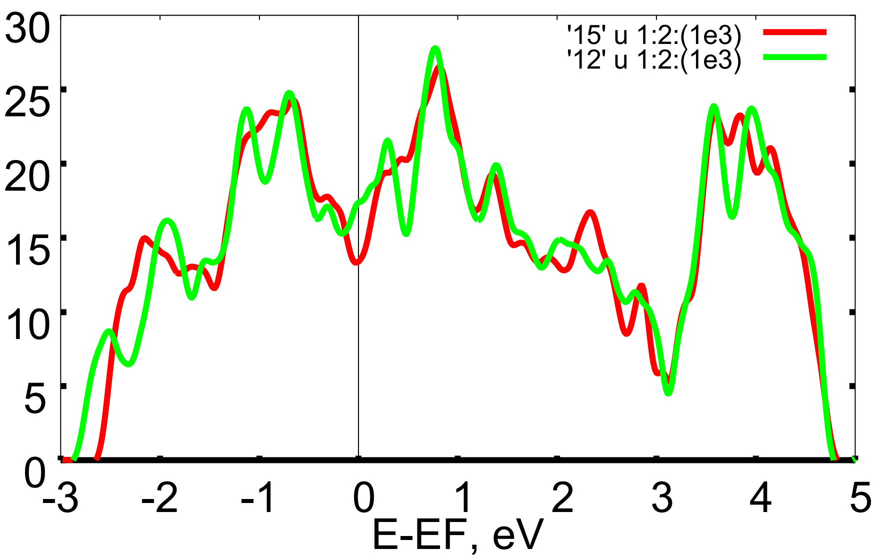
The 278 phase



•Both Fe vacancies and K form a nearly triangular ($10\times\sqrt{8}$) lattice.
•Only possible at the surface [N(K)=N(vac)]!
•Different structure forms in the bulk ($K_4Fe_{14}Se_8$): Ks form a square lattice.

•Substantial energy gain from K ordering – 50 meV/K!

•Substantial effect on electronic structure (surprising!) *(IIM, unpb.)*



Superconductivity

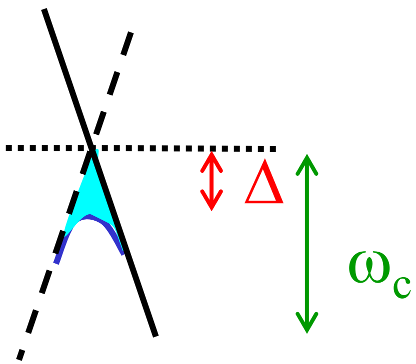
1. *Questions as posed in two years ago:*
   - Coexistence or phase separation?
   - d-wave or s-wave?
2. *Answers from two years ago*:
   - Fe_4 plackets represent rigid supermoments of 13 μ_B, exchange field ~40000 T. Coherence length ~10 lattice parameters. Thus, the average misalignment per 100 sites of 0.05^o exceeds the paramagnetic limit. Coexistence is *impossible.*
   - Nodeless d-wave is incompatible with crystal symmetry

Superconductivity: proposed models (historically)

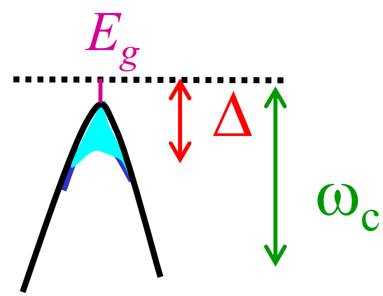
1. S++ (incipient S± state)

e.g., D.H. Lee, Chubukov & IIM (unpubl)

Metal pairing



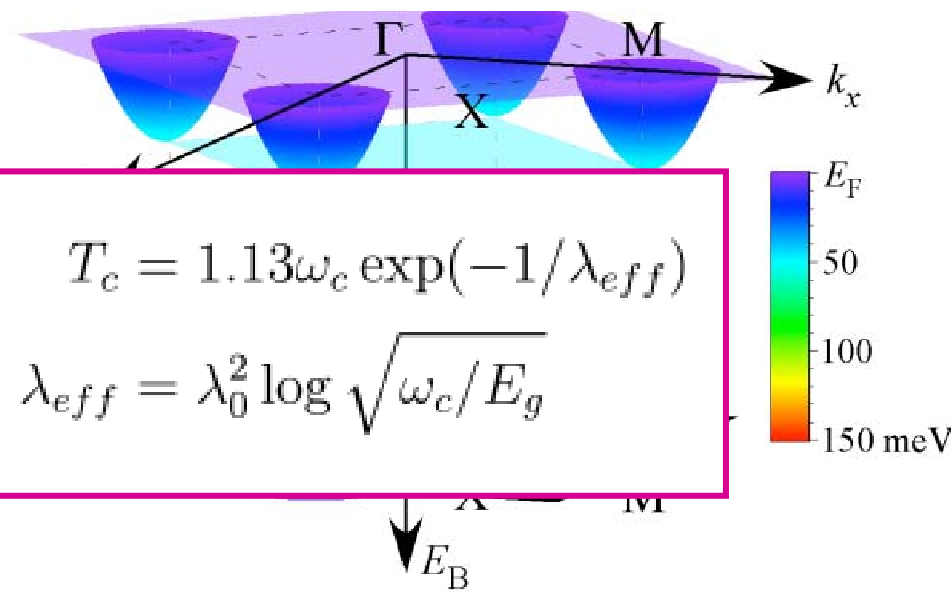
Semiconducting pairing



$$\Delta_1 = -\frac{V}{2}\int_{-\omega_c}^{-E_g} d\varepsilon \frac{n_2\Delta_2}{|\varepsilon|}\tanh\left(\frac{|\varepsilon|}{2T}\right)$$

$$\Delta_2 = -\frac{V}{2}\int_{-\omega_c}^{\omega_c} d\varepsilon \frac{n_1\Delta_1}{|\varepsilon|}\tanh\left(\frac{|\varepsilon|}{2T}\right)$$

$$Det\begin{vmatrix} 1 & -\frac{Vn_2}{2}\log(\omega_c/E_g) \\ -Vn_1\log(1.13\omega_c/T_c) & 1 \end{vmatrix} = 0$$



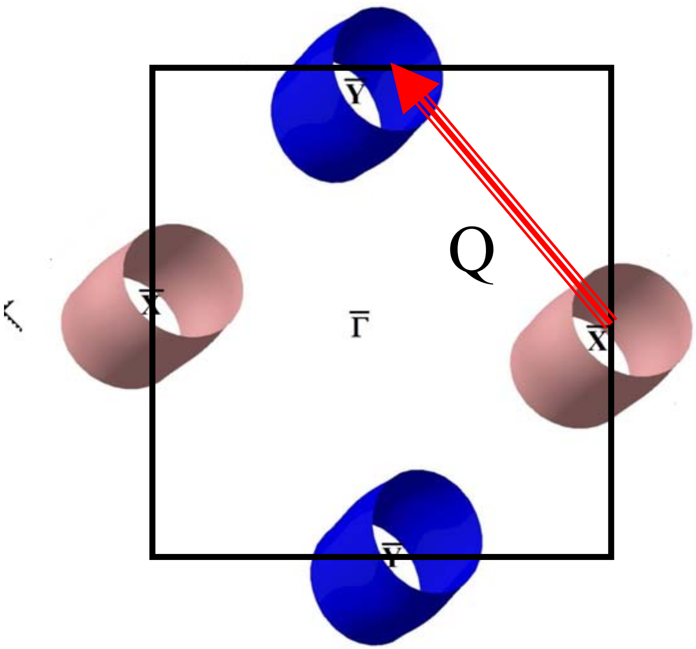
$$T_c = 1.13\omega_c \exp(-1/\lambda_{eff})$$

$$\lambda_{eff} = \lambda_0^2 \log\sqrt{\omega_c/E_g}$$

2. Nodeless d;

e.g., Hirschfeld et al, D.H. Lee et al

We start with the unfolded BZ



d-wave is:

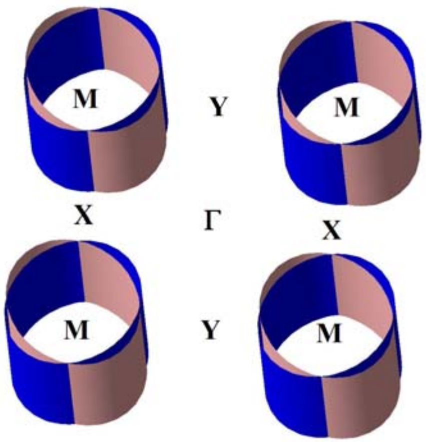
(a) Possible (modulo the fact that e-e nesting is weaker than e-h one)

(b) Natural

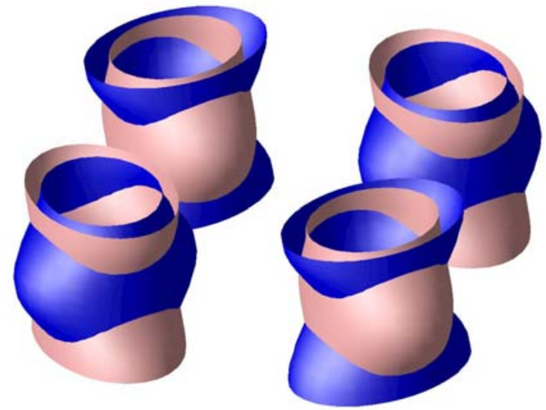
(c) Nodeless

Folding down the "nodeless" d-wave

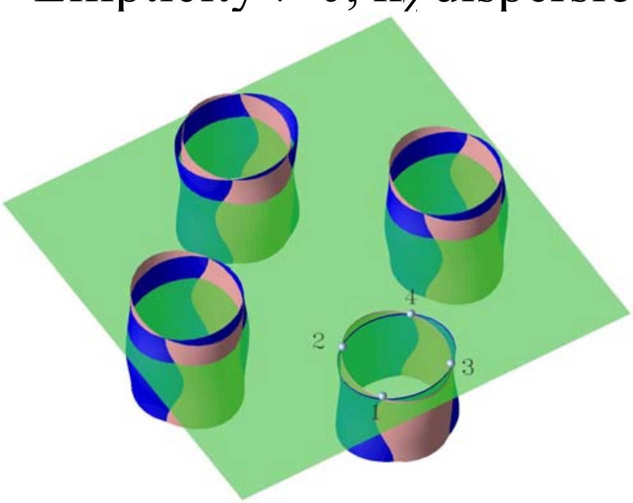
Ellipticity ≠ 0, k_z dispersion = 0



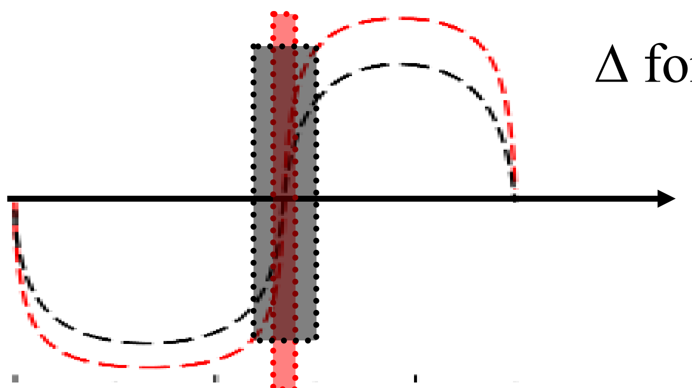
Ellipticity ≠ 0, k_z dispersion very large



Ellipticity ≠ 0, k_z dispersion ≠ 0



In 1111 or 11 (or in 122 without k_z dispersion) the nodal lines are infinitely (up to spin-orbit) thin



Δ for V/E_F=1/6, 1/12

3. bonding-antibonding S± ;

e.g., IIM, Khodas & Chubukov

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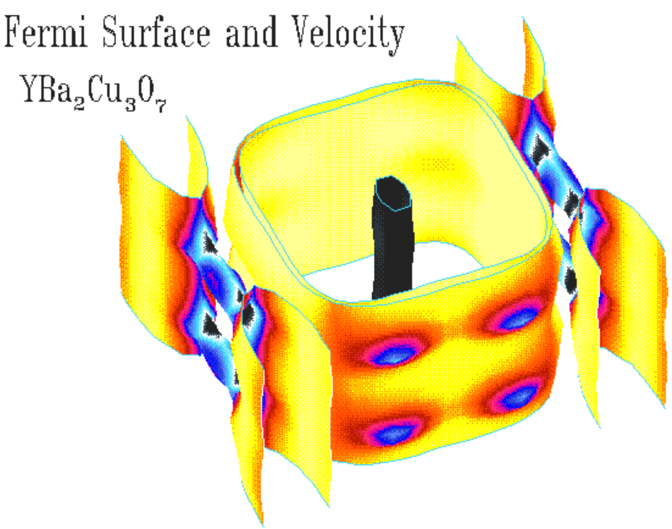
s-Wave Superconductivity from an Antiferromagnetic Spin-Fluctuation Model for Bilayer Materials

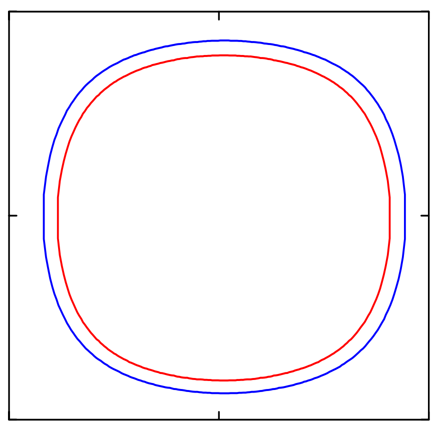
A. I. Liechtenstein,[1] I. I. Mazin,[1,2] and O. K. Andersen[1]

PHYSICAL REVIEW B VOLUME 45, NUMBER 10 1 MARCH 1992-II

Nodeless d-wave pairing in a two-layer Hubbard model

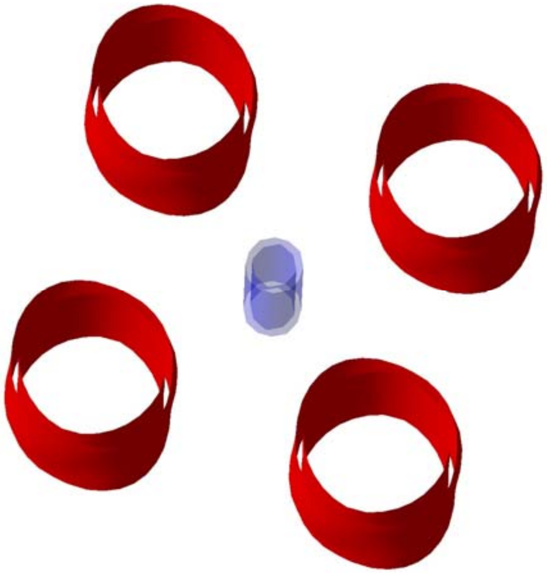
Nejat Bulut and Douglas J. Scalapino
Richard T. Scalettar

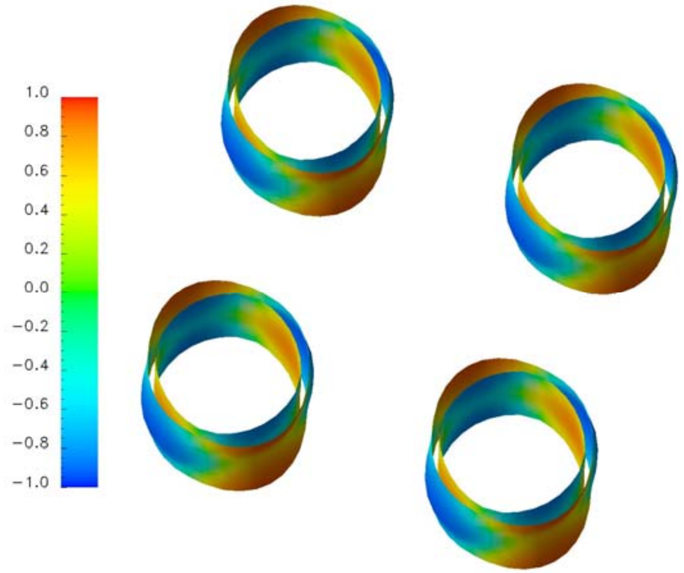


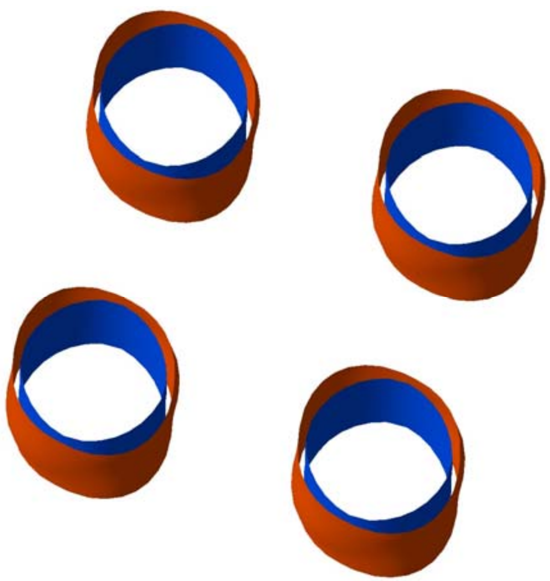


If SF are perfectly AF correlated between the two layers, only bonding-antibonding SF scattering is allowed. Naturally leads a nodeless bonding-antibonding $s_{\pm}$ superconductivity

Three states (summary)

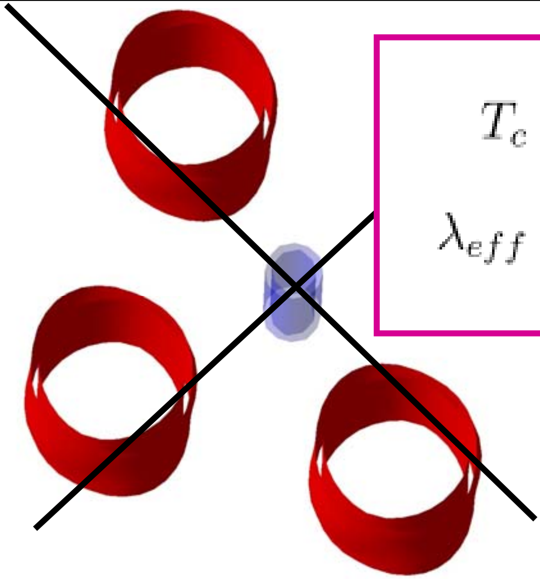






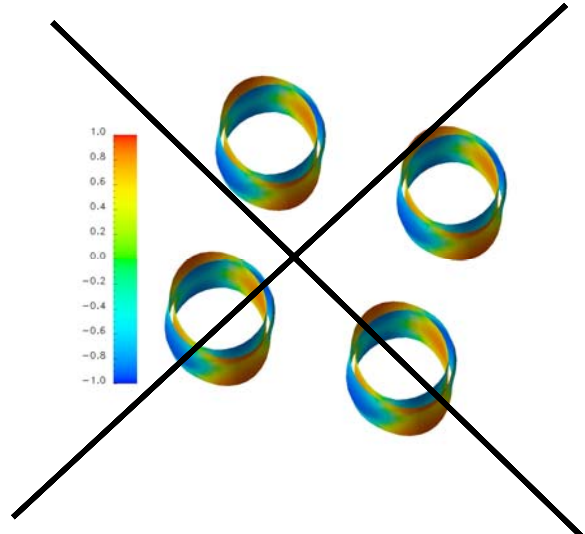
…and, of course, regular S++

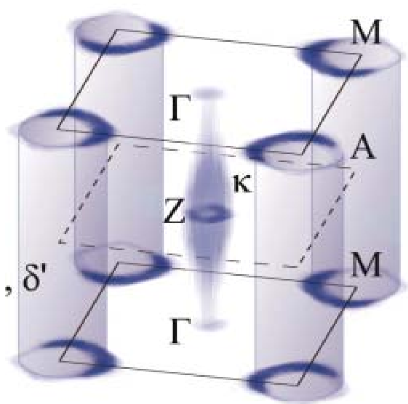
Experimental verification

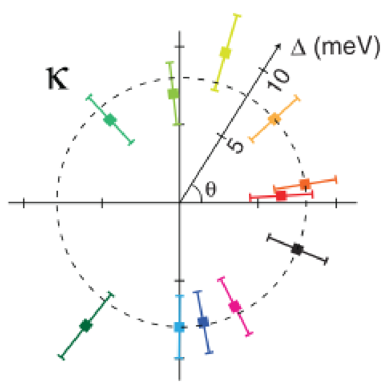


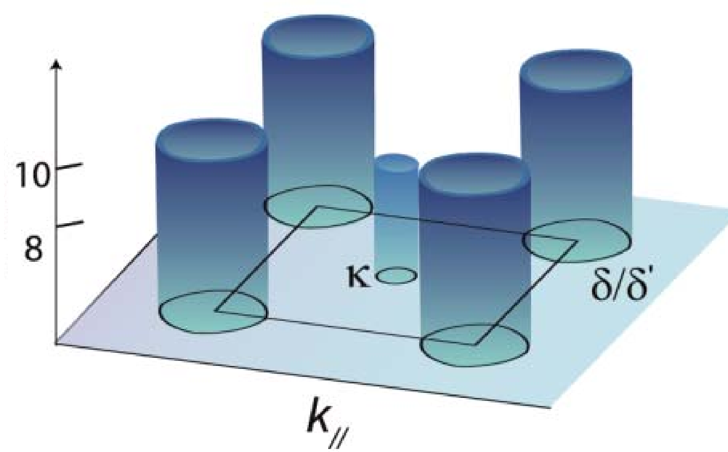
$$T_c = 1.13\omega_c \exp(-1/\lambda_{eff})$$
$$\lambda_{eff} = \lambda_0^2 \log \sqrt{\omega_c/E_g}$$

Exponentially small



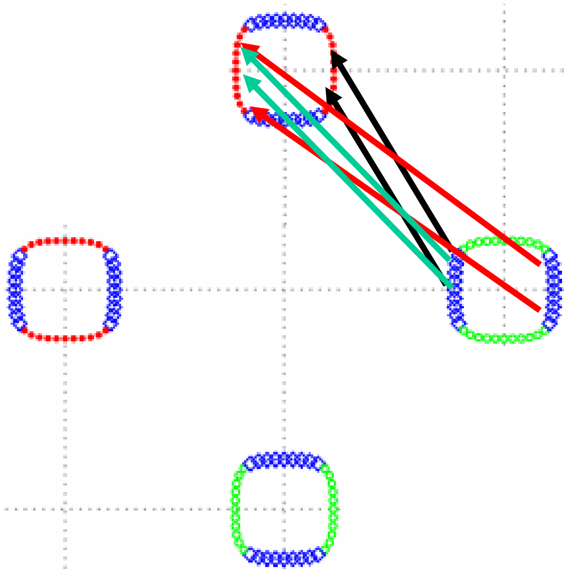




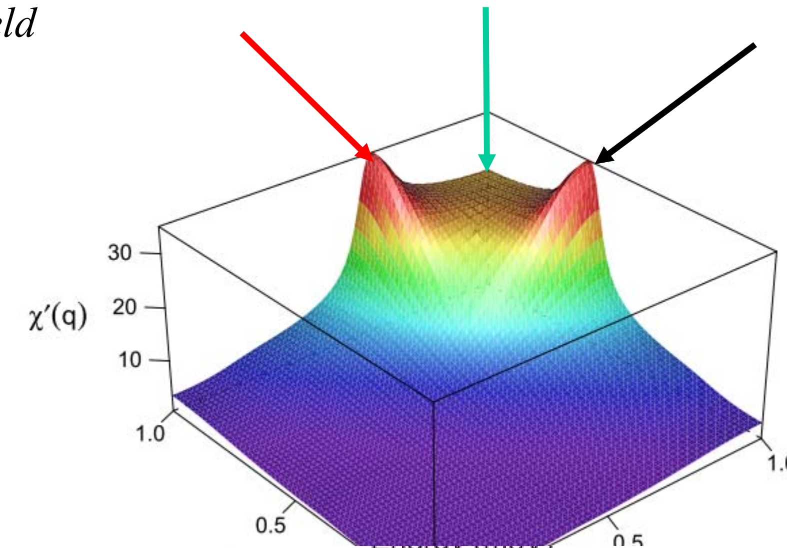


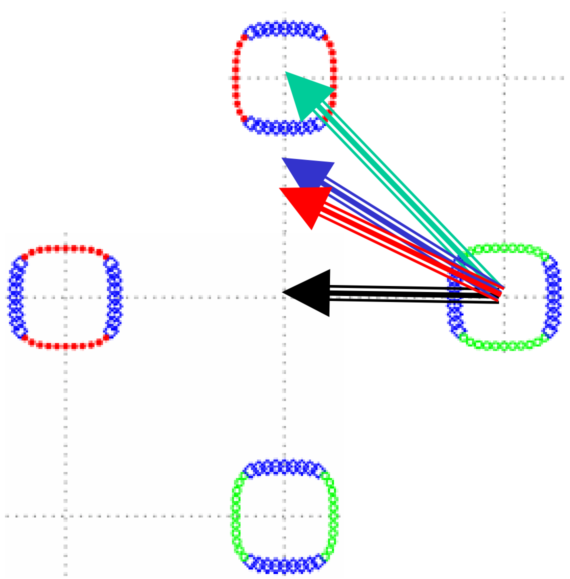
M. Xu et al, Fudan & Hefei

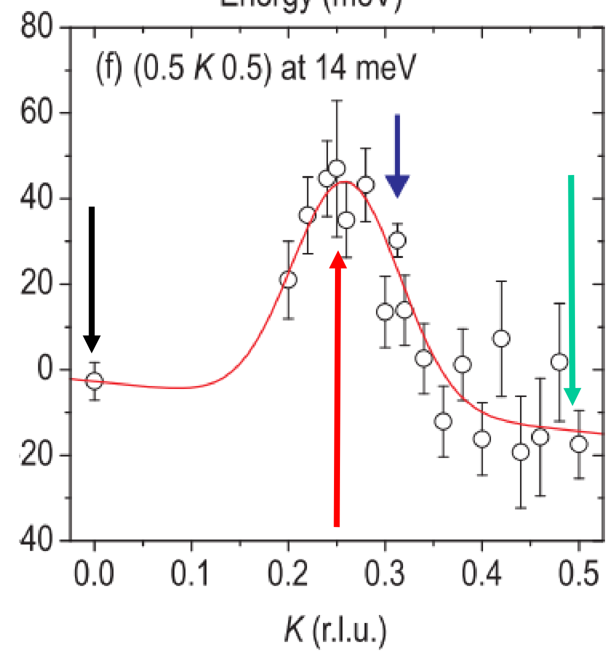
Neutron peak



Maier … Hirschfeld

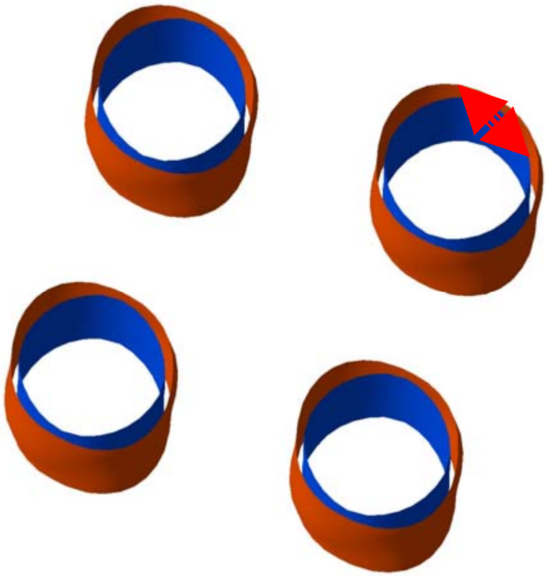






Park … Inosov

Bonding-antibonding S±



1. This state cannot be easily "unfolded" onto the one-Fe unit cell!
2. But, it allows for sign-changing scattering at q~Q
3. This state is only possible if ellipticity and k_z dispersion are very small (as in DFT calculations)
4. Pairing involves both "intraband" $(k\uparrow|-k\downarrow)$ and "interband" $(k\uparrow|Q-k\downarrow)$ pairs
5. **But what can be the pairing interaction in this case?**

Conclusions (no conclusions)

THE MAIN CONCLUSION: WE KNOW TOO LITTLE TO MAKE CONCLUSIONS!

1. Superconductivity and measured band structure is likely a surface/interfacial phenomenon. Main indications to that point:
   a) Similarity between the $K_xFe_ySe_2$ and FeSe monolayers (but only some)
   b) Incompatibility of measured ARPES with the 122 bulk symmetry
2. All models have problems:
   a) "Incipient s±" is exponentially weak, while Tc is rather large
   b) Bonding-Antibonding s± (ABS): microscopic mechanism not confirmed by model calculations and neutron resonance is suppressed by symmetry.
   c) d-wave implies nodes on both M and Γ pockets, and there are neither
3. Sign change of the order parameter is likely. Main indications to that point:
   a) Proximity to (very strong) magnetism
   b) Neutron resonance