Higher-T_c Superconductivity from Density Functional Calculations

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Program on the Physics of Higher-Tc superconductivity, KITP, Santa Barbara, 13/08/2009

Higher Tc superconductivity, General Questions:

? What is the Physics of high-Tc superconductors?

Can we understand SC pairing and the phase diagram ?

? What is the Chemistry of high-Tc superconductors?

What makes higher-Tc superconductor special ?

? How can we improve existing materials?

What can we learn from DFT?

! Normal-state properties can be calculated *ab-initio:*
Is standard LDA enough or do we need to go beyond ?

! Understand the electronic structure of HTSC

! Tune material properties via simulation.

Outline:

Higher Tc superconductivity, when DFT works…

Electron-Phonon (BCS) superconductors: the pairing mechanism is understood, but how can we improve the materials?

A simple example, doping graphite…

And when it doesn't work…

Exotic Superconductors: role of strong local (U) and non-local (HF) correlations, dynamic fluctuations…

A recent example, iron pnictides…

Can we still learn something, and how do we go beyond?

When DFT works: Electron-Phonon SC …

The SC pairing is well understood (**Migdal-Eliashberg Theory**):

AND

The **Eliashberg spectral function** can be calculated from **first-principles** using **Density Functional Perturbation Theory:**

$$\alpha^2 F(\Omega) = \frac{1}{N(0)} \sum_{kk',\alpha} \delta(\varepsilon_k)\delta(\varepsilon_{k'}) \mid g^{\alpha}_{kk'} \mid^2 \delta(\Omega - \omega_{k-k'})$$

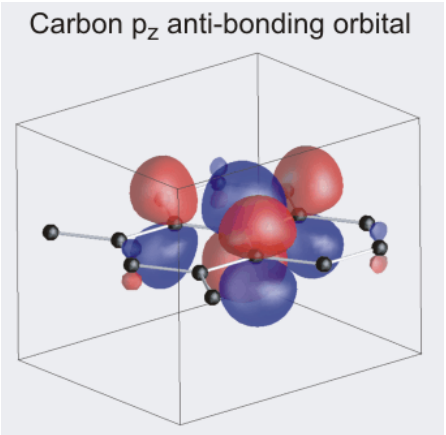
Electronic structure | **E-ph Matrix Elements** | **Phonon Spectra**

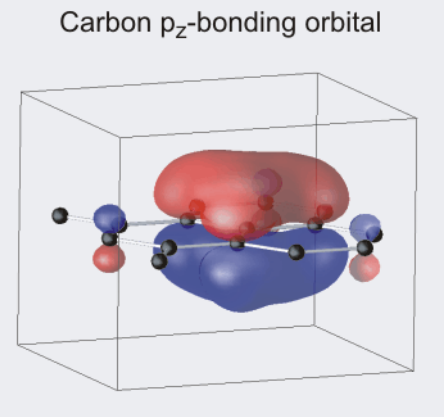
Can we use DFT to understand and predict new SC?

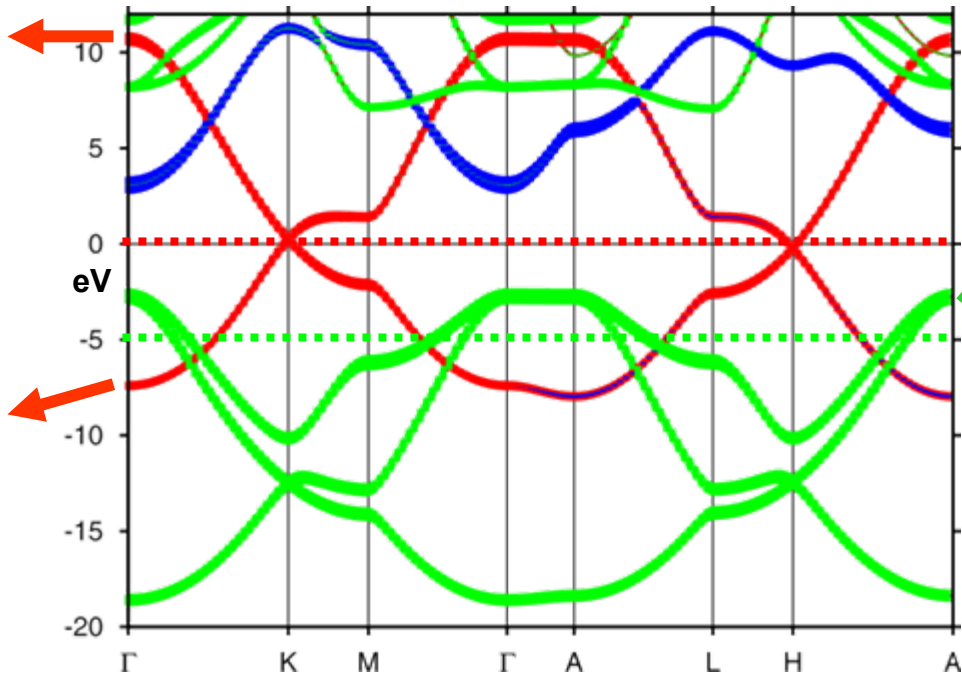
(See also ICMR school talk from Warren Pickett)

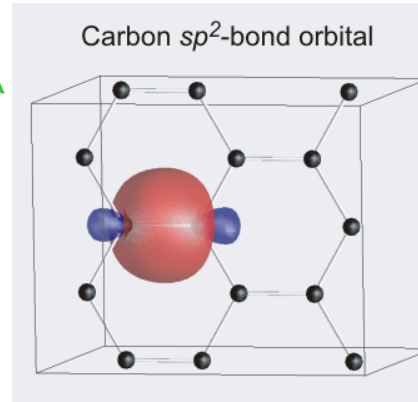
Graphite:

a simple system with many surprises!





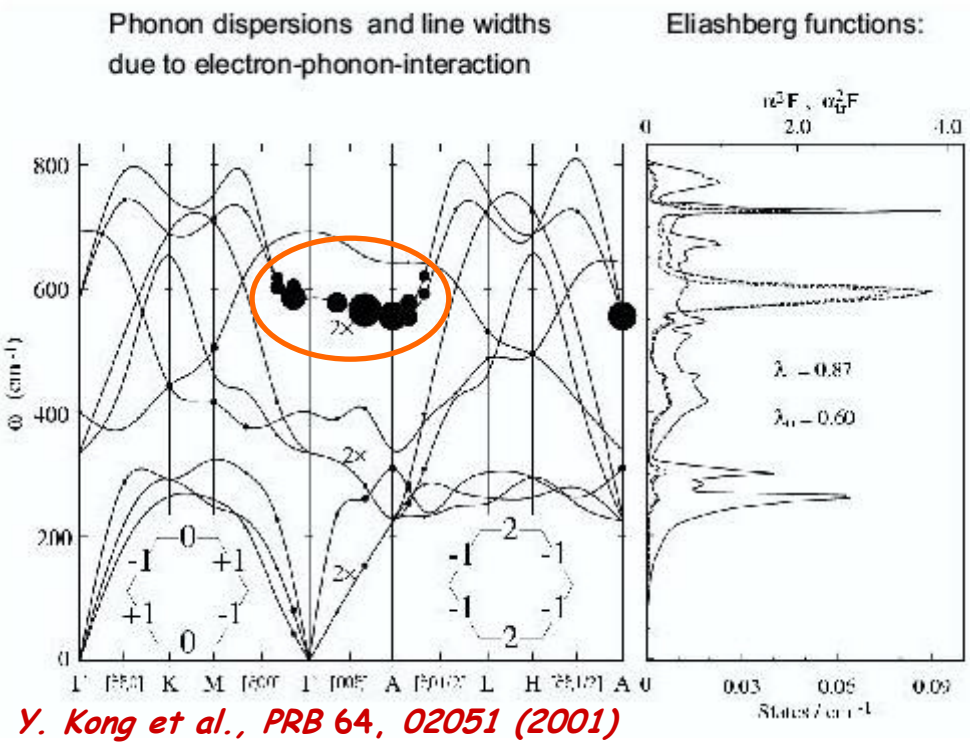




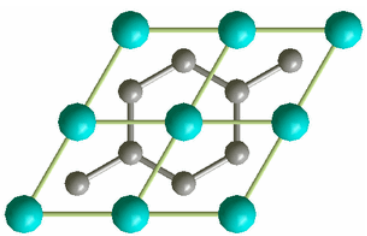
Undoped: EF is at the **Dirac point** -> semimetal, no sc.

Hole Doping (MgB_2): EF sits in the **σ bands** -> Strong coupling to bond-stretching phonons -> Tc=40 K!

Hole Doping: MgB_2



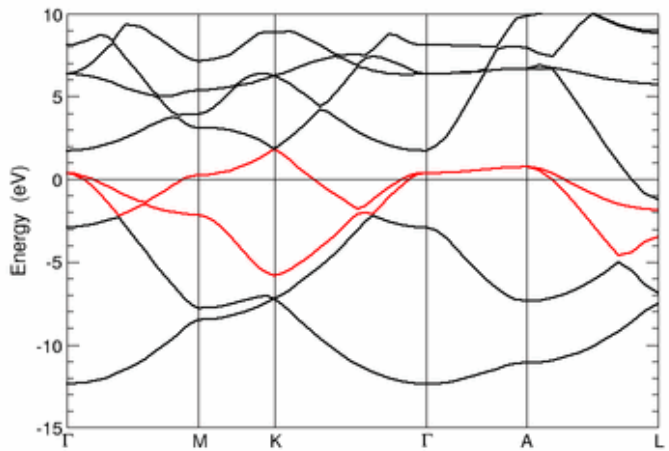
Y. Kong et al., PRB 64, 02051 (2001)



Strong geometrical coupling between bond-stretching modes and stiff σ bonds!

• Total e-ph interaction λ=0.8-0.9: concentrated in a doubly-degenerate Bond-stretching mode <- graphite!

$$D = \left.\frac{d\varepsilon_k}{du}\right|_{E_F} = 12 eV/A$$



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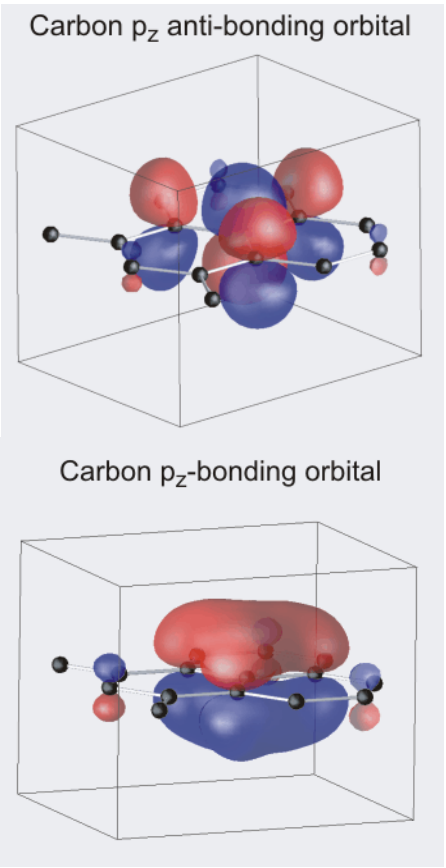
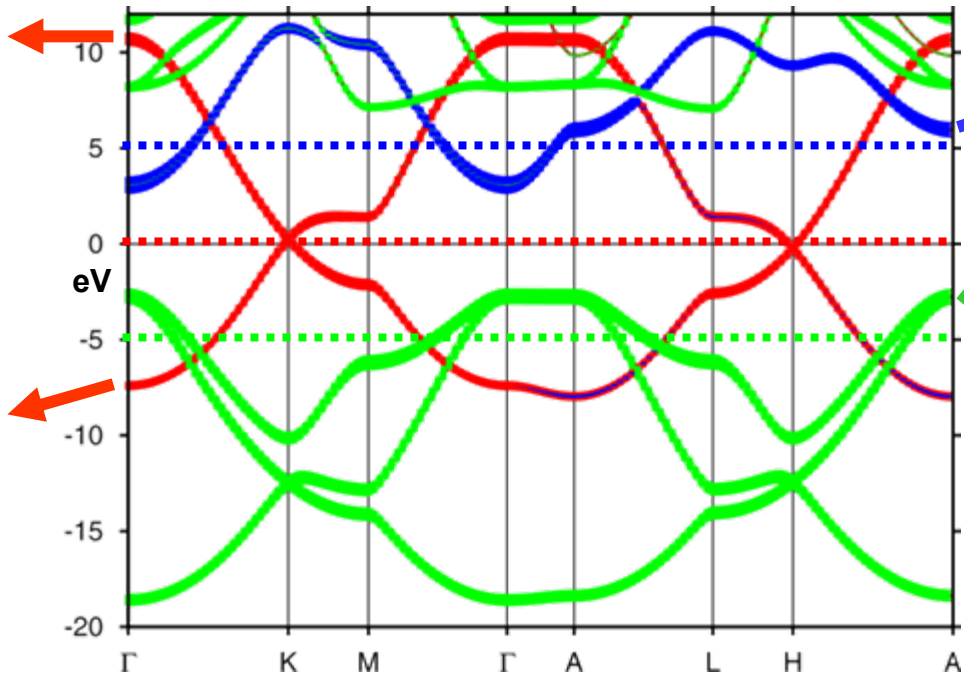
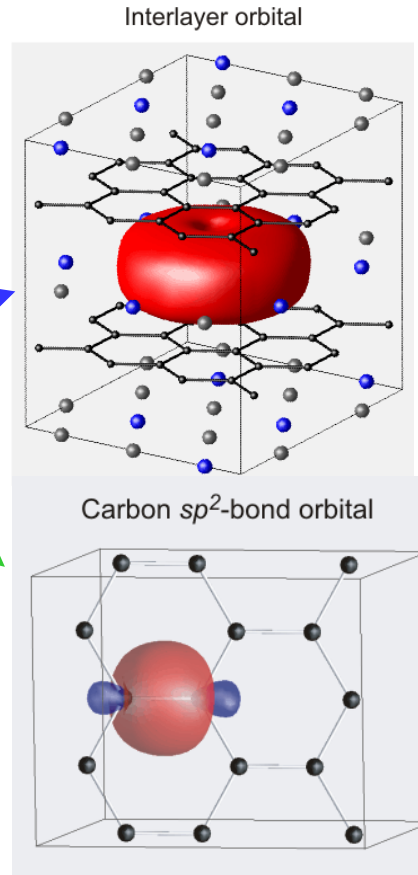
a simple system with many surprises!







Undoped: EF is at the **Dirac point** -> semimetal, no sc.

Hole Doping (MgB_2): EF sits in the **σ bands** -> Tc=40 K!

T.E. Weller, et al., Nature Physics 1, 39 (2005).

Electron Doping (CaC_6): EF sits in the **IL + π* bands** -> Tc ≤ 15 K!

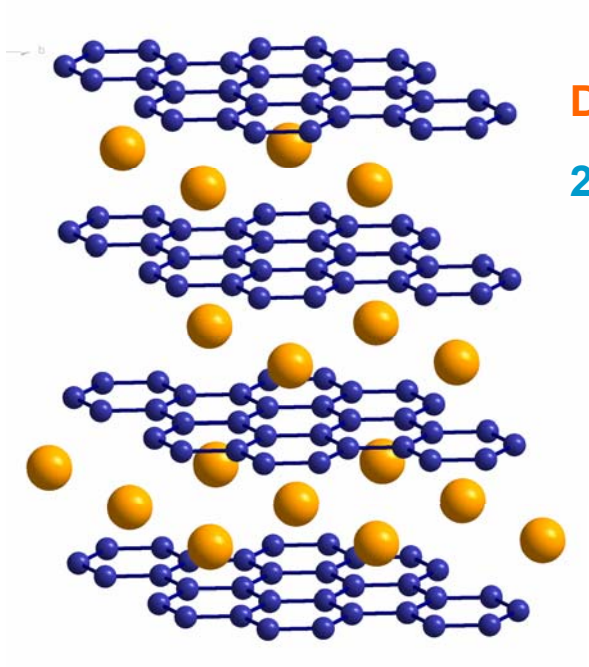
T.E. Weller, et al., Nature Physics 1, 39 (2005).

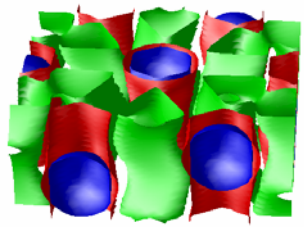
Plasmons or electron-phonon?

! In all graphite intercalation compounds which are superconducting the interlayer band is full…

The IL electrons behave like free electrons…

Plasmon-mediated superconductivity?





NO!

1) **Interlayer** electrons have a 3D dispersion

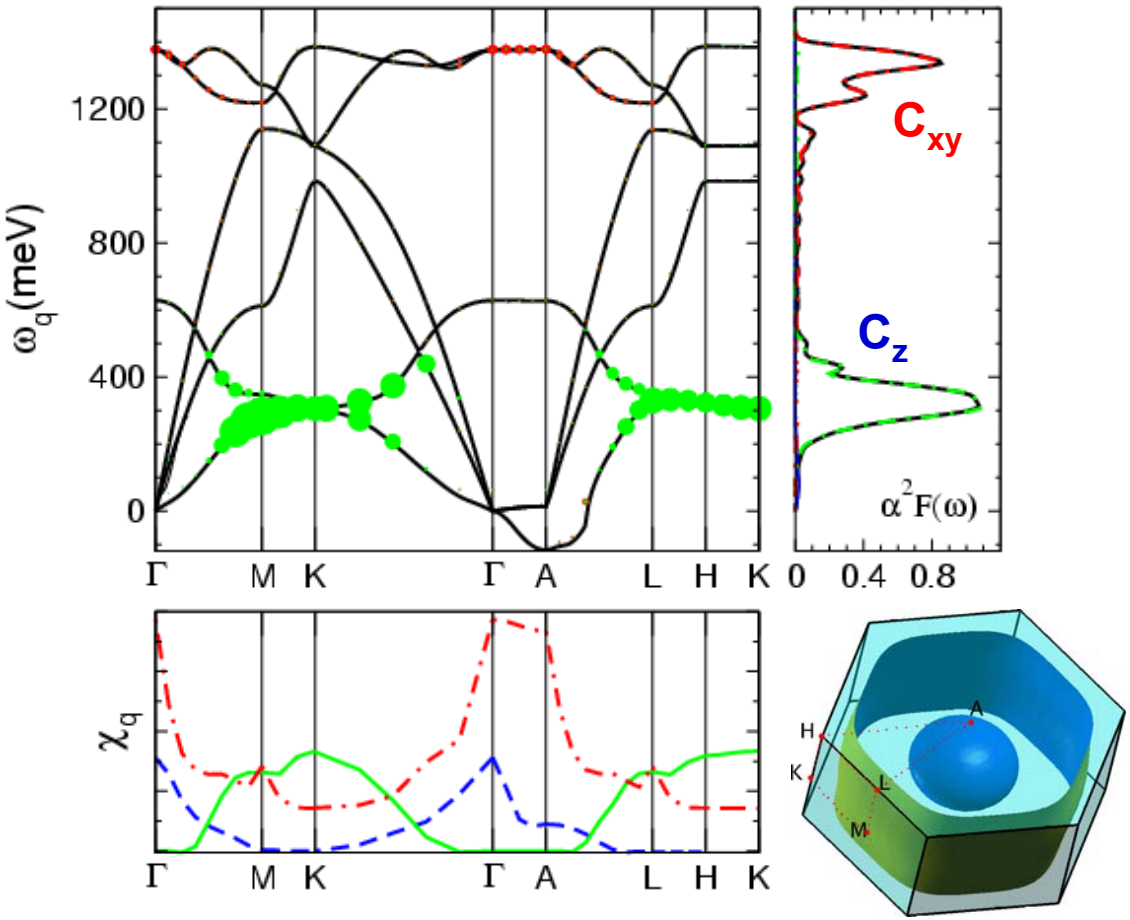
2) Interlayer electrons can interact with graphite phonons even without an intercalant!

G.Csànyi, et al., Nature Phys.**1**,42(2005).

Where does the electron-phonon coupling come from?

? What happens if we dope pure graphite (i.e. without intercalants ?)

! Replacing the intercalant with jellium (2/3 e- for every C atom), we can feel the interlayer band. 2 types of bands at EF: interlayer +π*



2 peaks in $\alpha^2F(\omega)$!!!

80% of λ from C(z) modes

$$\lambda_{tot} = 1.01$$

In this case we exploit the dormant interaction between π* states and interlayer band!!

L. Boeri, G.B. Bachelet, M. Giantomassi, O.K. Andersen, PRB 2007.

In summary…

In BCS-like superconductors, where the superconducting pairing is understood and electronic correlations are negligible, ab-initio calculations represent a valuable tool to search for new superconductors…

Graphite: High Tc occurs when dormant electron-phonon interactions are awakened by the appropriate band filling…

DOPE INTO STRONG COVALENT BONDS!

The search for new materials can be driven by **chemical/empirical** methods…

…or completely *ab-initio*:

Predicting Crystal Structures by

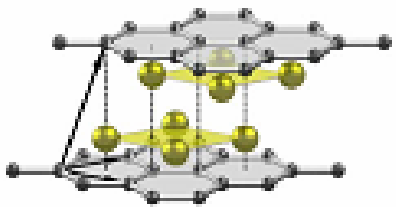
Random Searching (C. Pickard)

Genetic Algorithms (A. Oganov)

Data Mining of Quantum Computations (Cedered, Curtarolo)

PHYSICAL REVIEW B **73**, 180501(R) (2006)

Prediction of different crystal structure phases in metal borides: A lithium monoboride analog to MgB_2



b) MS1

Aleksey N. Kolmogorov and Stefano Curtarolo
1 Engineering and Materials Science, Duke University, Durham, North Carolina 27708, USA
(Received 2 March 2006; published 5 May 2006)

When DFT doesn't work: what can we learn?

A case study, Fe pnictides (and chalchogenides)

EXP: Broad class of compounds, containing SC Fe(As) layers. Tc up to 55 K. Rich phase diagram: SC, magnetism and structural transitions.

Early DFT Results: Basic Electronic Structure, E-ph Coupling, Nesting, Magnetism and Structural Transitions

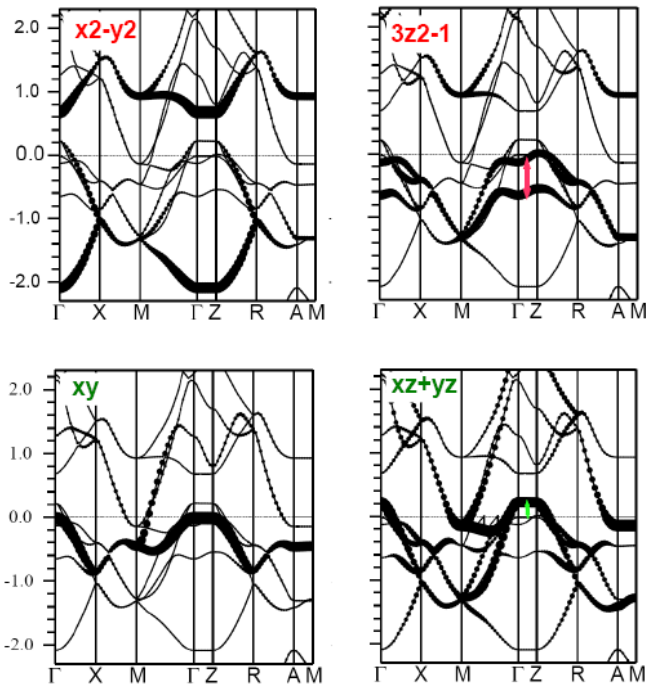
BUT

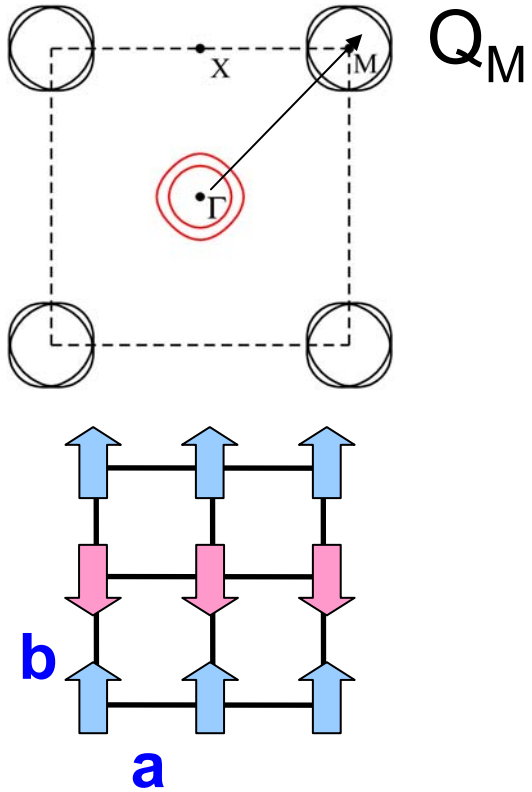
Problems in reconciling DFT with experiment…

WHY?

How do we go beyond?

Fe pnictides, basic electronic structure:

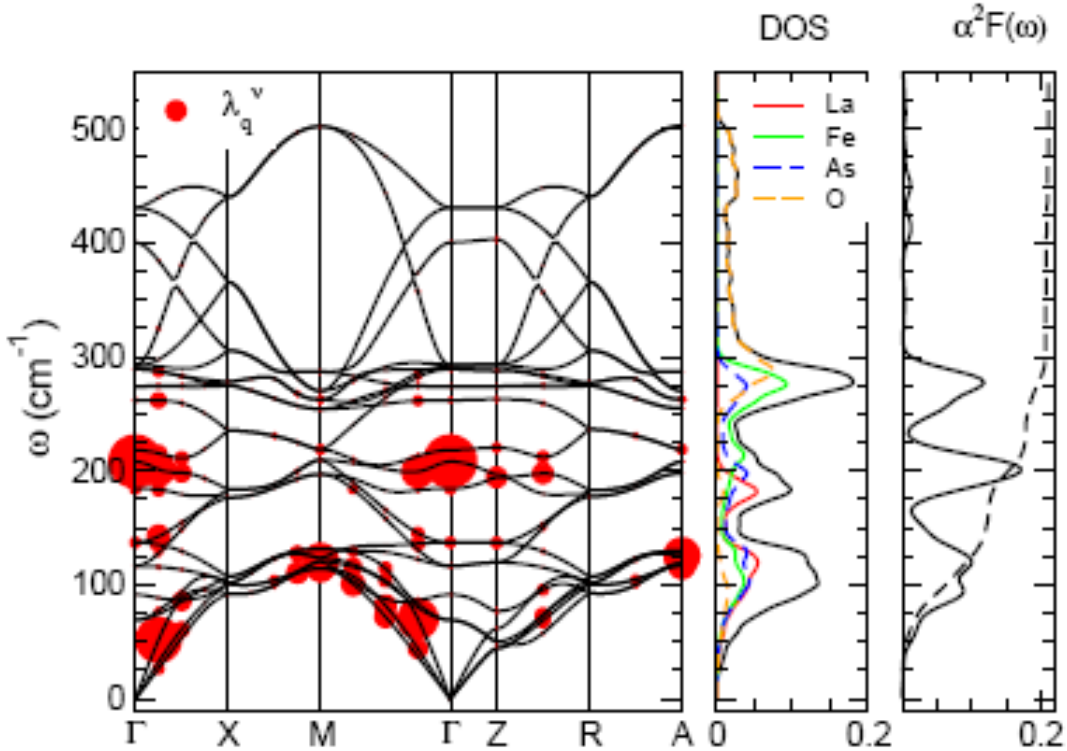




- The 10 bands around EF are derived by the 2x5 Fe-d orbitals
- No clear separation between e_g and t_{2g} bands (tetrahedral splitting).
- Strong modulation of the bands with Fe-As hoppings.
- 2 holes + 2 electron Fermi surfaces; ~ perfect nesting!
- Ground state is an AFM striped metal, with m=2 μ_B

See D.J. Singh's, P. Hirschfeld's and O.K. Andersen's talks

Can e-ph interaction explain Tc in FeAs compounds?c



$$\lambda = 0.21$$

$$\omega_{\log} = 206K$$

$$T_c^{ME}(\mu^* = 0) = 0.5K$$

NO!

- E-ph interaction: λ~0.2 is too small to account for T_c
- Doping can only decrease λ.
- N(0) is large, λ is small because of **small e-ph matrix elements**.

L. Boeri, O.V. Dolgov, A.A. Golubov, Phys. Rev. Lett. 101, 026403 (2008).

LDA gives a reasonable description of the normal state properties of Fe SC…

BUT

PHYSICAL REVIEW B 78, 085104 (2008)

Problems with reconciling density functional theory calculations with experiment in ferropnictides

Magnetic moments predicted by DFT are **too large compared with experiment**

Magnetic moments depend sizably on the **crystal structure**

Optimization of the crystal structure in the non magnetic phase is **wrong**

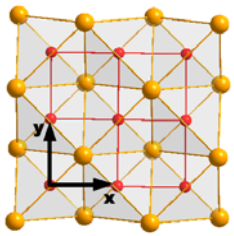
What is DFT telling us?

In order to explain Tc, we need to understand the superconducting mechanism…

How can we go beyond?

A critical look at the electronic structure: what are the crucial details? (see also Ole Andersen's talk)

1) Crystal Structure and chemistry:



Two details are crucial: presence of Fe(Pn/Ch) planes + band filling (d^6); the magnetic/SC properties of other MPn compounds can be basically understood in a rigid band picture.

Electronic and magnetic properties of Mn, Fe, Co, Ni and Zn in LaTPnO

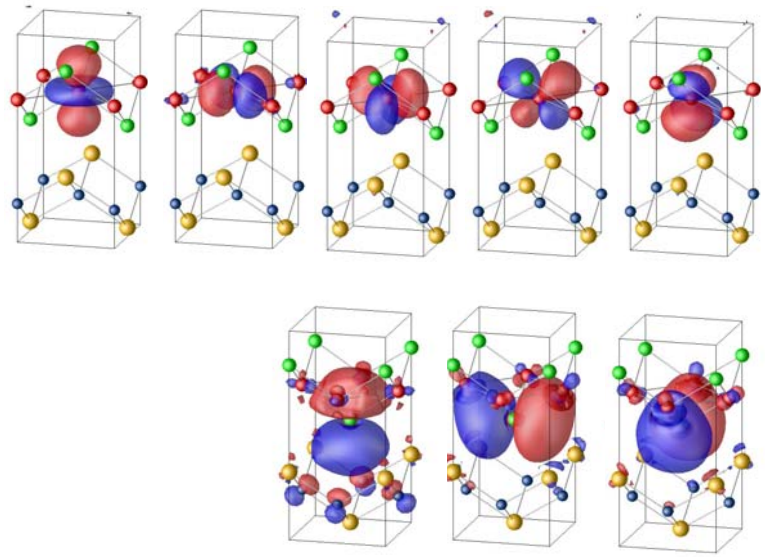
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr

TM	Mn		Fe		Co		Ni		(Cu)	Zn	
Pn	P	As	P	As	P	As	P	As		P	As
Elect. Prop.	Mott Insulator		Superconductor		Metal		Superconductor		—	Semiconductor	
Magnetism	AFM				FM				—	Non-magnetic	
E_g	~1 eV		—		—		—		—	~1.5 eV	
T_c (SC) $T_{N,C}$(Mag.)	> 400 K		Undoped: 4 K	F-doped: 26 K	43 K	66 K	Undoped: 3 K	Undoped: 2.4 K		—	
Ref.	Yanagi et al JAP (submitted)		Kamihara et al. JACS(2006), Kamihara et al. JACS (2008)		Yanagi et al. PRB (2008)		Watanabe et al. IC (2007), Watanabe et al. JSSC (2007)		—	Kayanuma et al. PRB (2007), Kayanuma et al. TSF (2008)	

Fig. 10. Electromagnetic and optical properties elucidated in LaT_xPnO.

2) Bonding:

As orbitals are extended and long-ranged: strong Fe-As hybridization + long range of the hoppings.

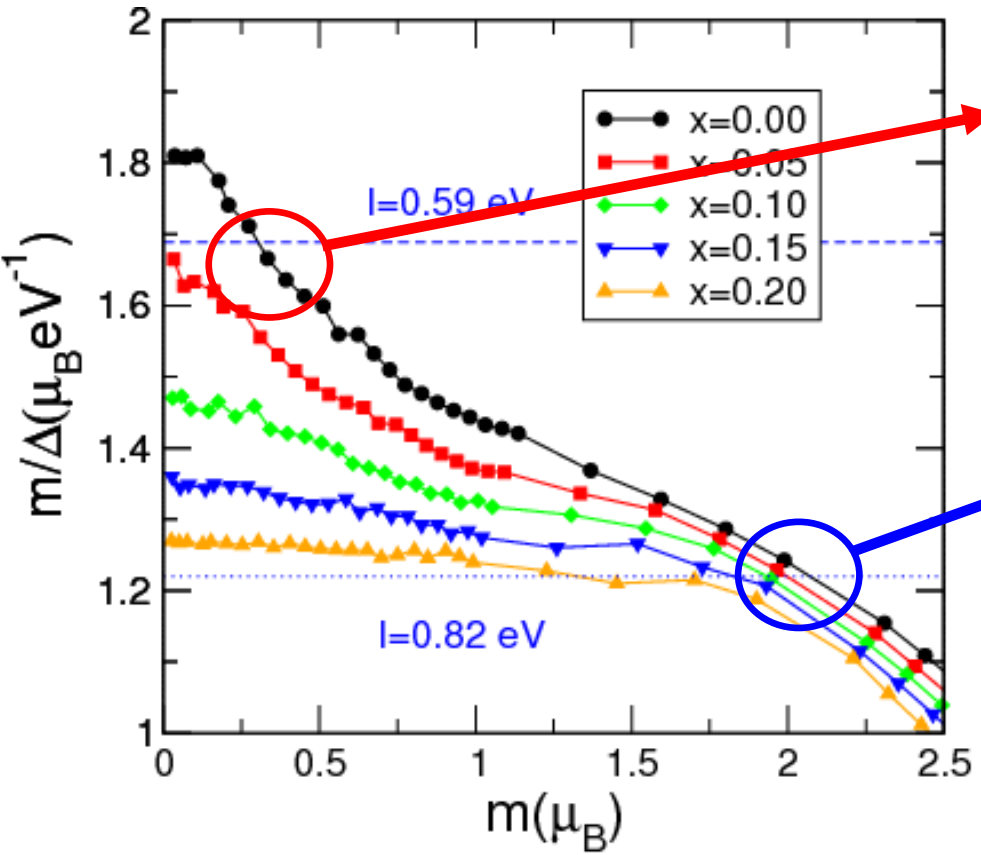


Fe-As hybridization is large: Polarizability model, based on the picture of "tightly bound Fe 3d electrons propagating in a lattice of rather isolated As negative ions" probably does not apply.

Long-range hoppings -> free-electron like masses
Electrons are strongly delocalized -> itinerant rather than local picture.

3) Magnetism, weak or strong coupling?

Band structure susceptibility (stripe order) of La 1111; the exchange splitting is a free parameter.

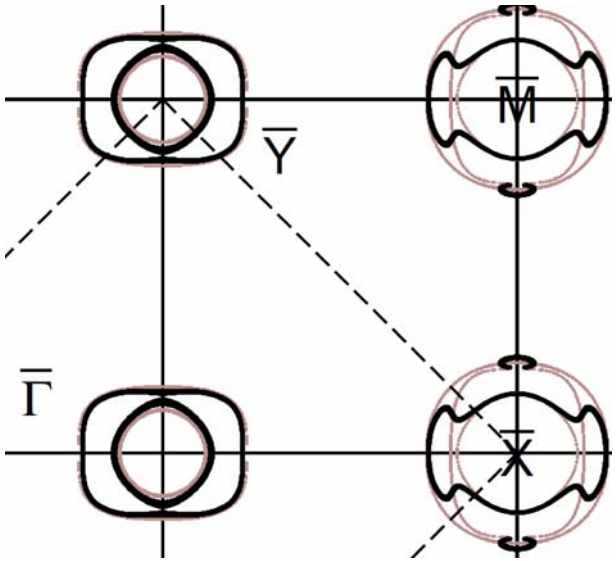


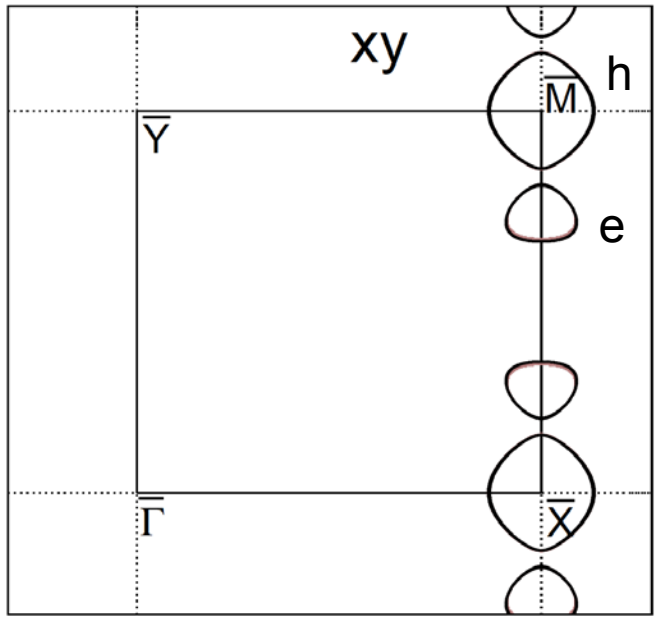
Small moment (EXP):
Nesting regime

Large Moment (DFT):
Strong coupling

Possible reasons for disagreement: LDA is overestimating the Stoner parameter, or fluctuations suppress the effective magnetic moment.

3) Magnetism, weak or strong coupling?



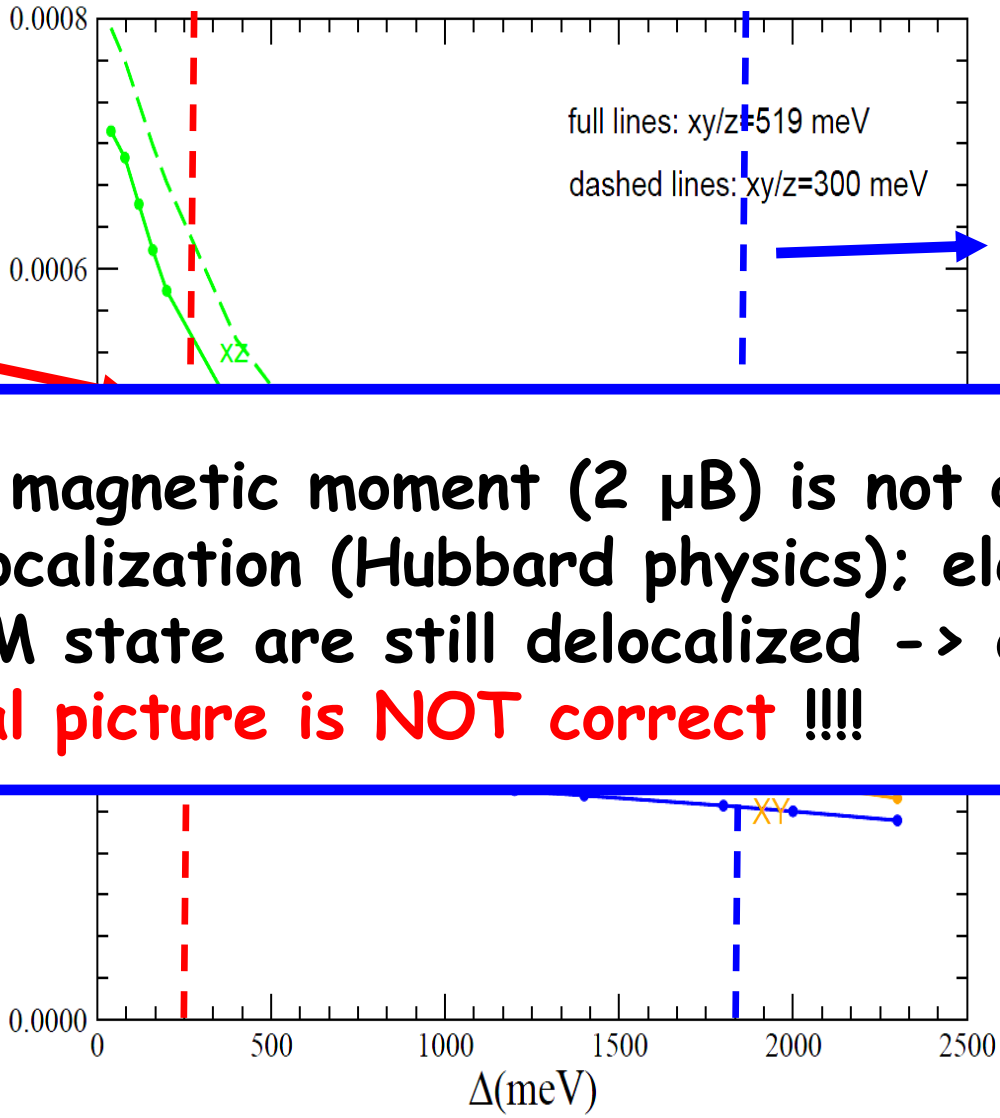


Small moment: Partial reconstruction of the FS (nesting)

Large moment: Total reconstruction of the FS; states at EF have different orbital character.

3) Origin of the magnetic moment:

Partial Band structure susceptibility (stripe order) of La 1111.



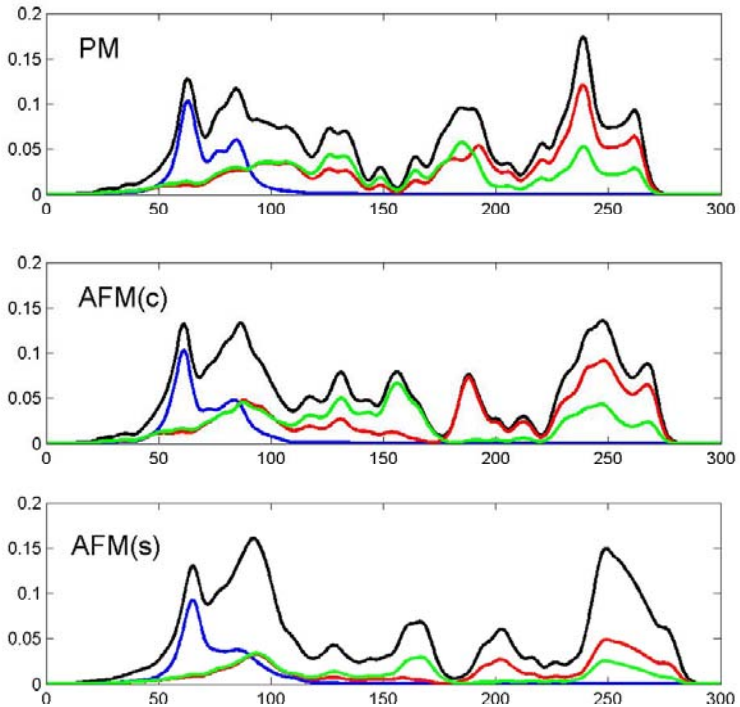
Small moment:

Large moment: There is a more or less uniform

The large magnetic moment (2 μB) is not due to electron localization (Hubbard physics); electrons in the AFM state are still delocalized -> once more, local picture is NOT correct !!!!

3) Magnetism and lattice (effect of Fe-As hybridization);

Inclusion of the magnetic moment in the calculations is crucial to lead the correct structure (tetragonal distortion + Fe-As distance)



AND

Improves the agreement between theory and experiment for phonon properties -> mainly affect Fe and As modes.

Ba-122, effect of magnetism on phonon DOS.

In summary…

In Fe pnictides DFT calculations cannot explain SC…

BUT

They impose important constraints on the microscopic models:

Strong Fe-As hybridization
+ long-range hopping

⇩

Lattice structure and dynamics seem to suggest a large magnetic moment suppressed by fluctuations…

Even for large magnetic moments local picture is not correct…

Search for higher Tc superconductors:

Electron-Phonon (BCS) superconductors: Current DFT methods work fine, the big challenge is optimize the material properties -> ab-initio prediction of new compounds?

Exotic Superconductors: Current DFT methods seem to fail for different reasons:

BKBO: non-local exchange; negative U due to large e-ph interaction?

Cuprates: lack of Hubbard physics (large local Coulomb repulsion).

Pnictides: delocalized electrons with large magnetic moment, suppressed by fluctuations -> dynamic effects?

THANK YOU!!!

And also thanks to…

Theory:

- G.B. Bachelet, *Università la Sapienza, Roma, Italy*
- J. Kortus, *TU Bergakademie Freiberg*
- M. Giantomassi, *Université Catholique de Louvain, Belgium*
- O.V. Dolgov, *MPI-FKF,*
- A.A. Golubov, *Univ. Twente, the Netherlands.*
- M. Johannes, I.I. Mazin, *NRL Washington, USA*
- O.K. Andersen, *MPI-FKF, Stuttgart*
- M. Calandra (Paris)

Experiment:

J.S. Kim, R.K. Kremer, *MPI-FKF, Stuttgart;* F.S. Razaavi, *Brock Univ., Canada*