2357-22

Innovations in Strongly Correlated Electronic Systems: School and Workshop

6 - 17 August 2012

When Mott meets BCS:
Molecular Conductors and the Search for High-Tc Superconductivity

Massimo CAPONE

CNR IOM and SISSA, Via Bonomea 265
Trieste
ITALY

Strada Costiera, 11 - 34151 - Trieste - Italy • Tel. +39 0402240111 • Fax. +39 040224163 • sci_info@ictp.it • www.ictp.it
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ICTP2012: Innovations in Strongly Correlated Electron Systems: School and Workshop

WHEN MOTT MEETS BCS: MOLECULAR CONDUCTORS AND THE SEARCH FOR HIGH-TC SUPERCONDUCTIVITY

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DEMOCRITOS
DEmocritos MOdeling Center for Research In aTOmistic Simulation
IOM

COWORKERS AND FUNDING

G. Giovannetti

erc

M. Fabrizio (Trieste)
C. Castellani (Rome)
E. Tosatti (Trieste)

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ma per seguir virtute e canoscenza
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SUPERBAD
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http://www.lemsuper.eu

http://superbadproject.wordpress.com

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FRAMEWORK

SUPERCONDUCTIVITY after the cuprate revolution

Conventional

- Phonon-mediated "BCS"
- **Weak correlations**
- s-wave
- low T_c

Unconventional

- "Electronic Mechanism"
- **Strong Correlations**
- d-wave (nodes)
- high T_c

Standard, conventional, boring… Exotic, unconventional, interesting, beautiful…

- New pieces in the puzzle (organics, iron-based, MgB_2, aromatics)
- Where do the iron-based SC belong ?
- Electron-phonon superconductors which benefit from correlations

"the other high-T_cs"

Cs_3C_{60}, K_3C_{60}, .. : M.C., M. Fabrizio, C. Castellani and E. Tosatti

$Ba_{1-x}K_xBiO_3$ β-HfNCl Z. P. Yin, A. Kutepov, G. Kotliar

Aromatics?

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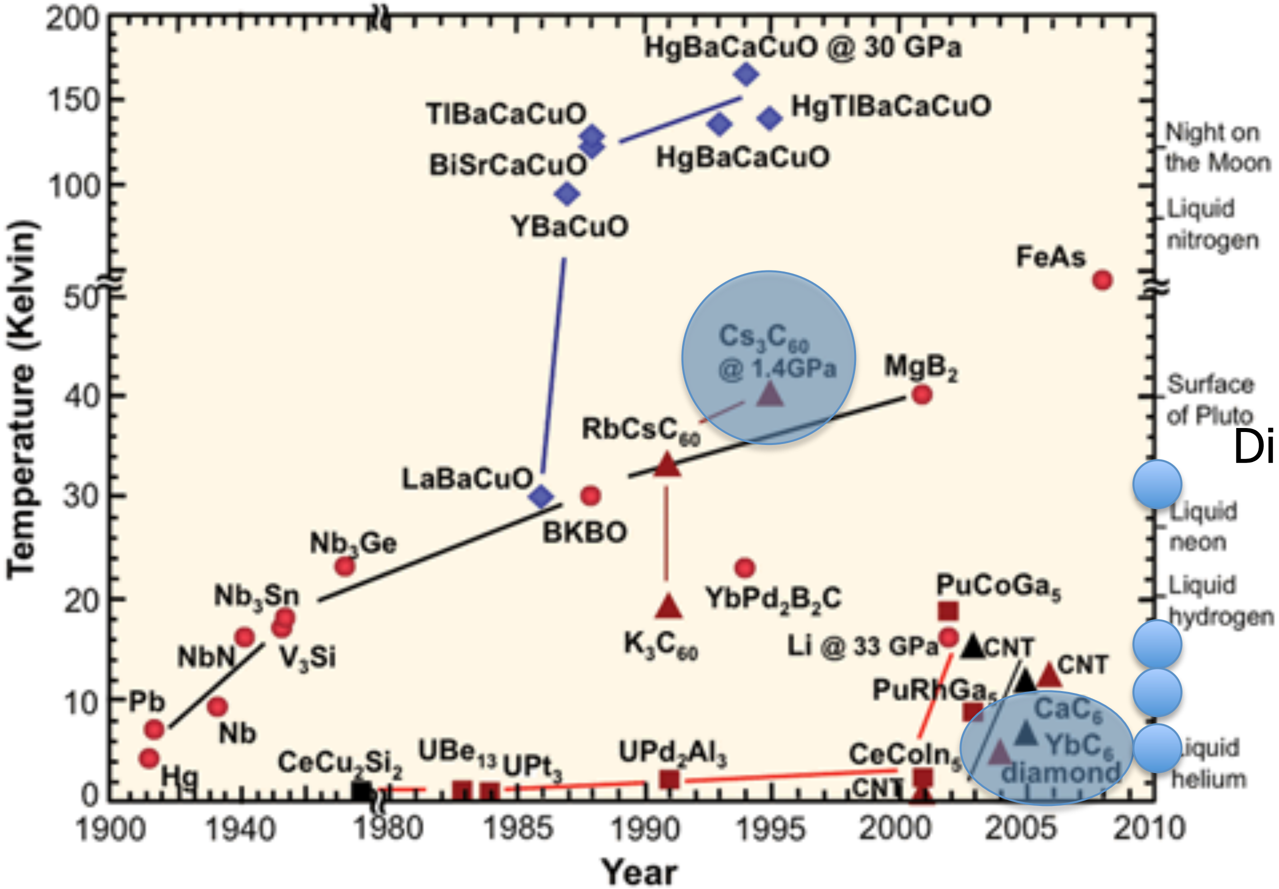
CARBON SUPERCONDUCTORS



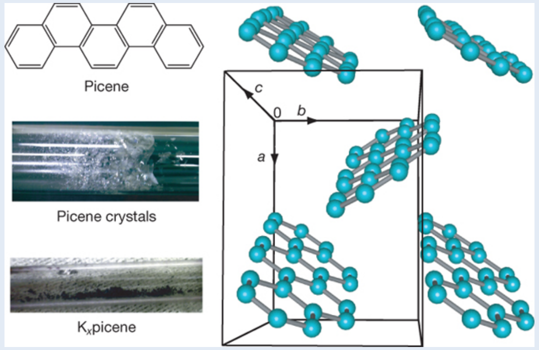
Dibenzopentacene

Picene

Coronene

Phenanthrene

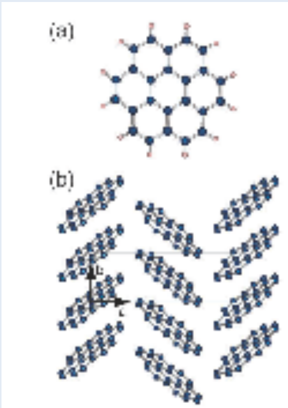
AROMATIC SUPERCONDUCTORS



K_x-picene

$2.7 < x < 3.3$ $T_c = 18K$

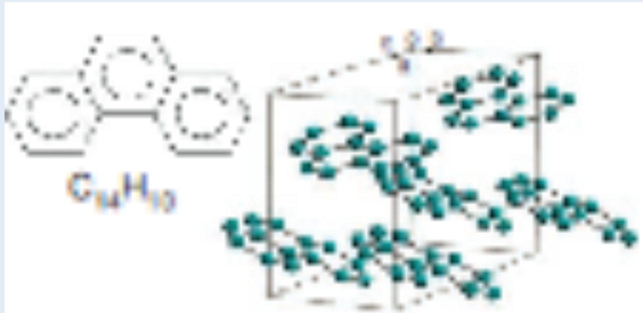
R. Mitsuhashi et al. Nature 464, 76 (2010)



K_x-coronene

$T_c = 15K$

Y. Kubuzono et al.



Phenanthrene $T_c = 5K$

X.F. Wang et al. Nat. Comm.

and 1,2:8,9-dibenzopentacene with T_c=33K

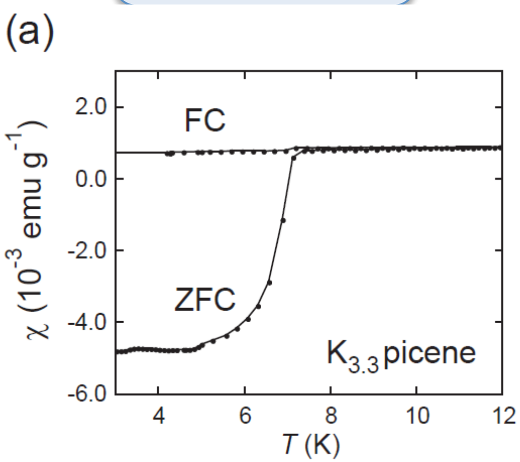
M. Xue et al. Scientific Report

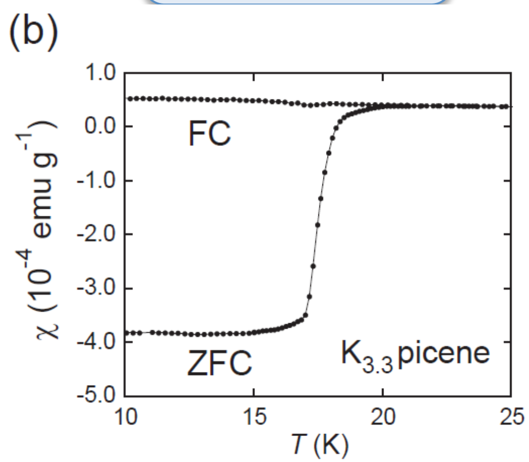
A FEW EXAMPLES: THREE IS THE MAGIC NUMBER

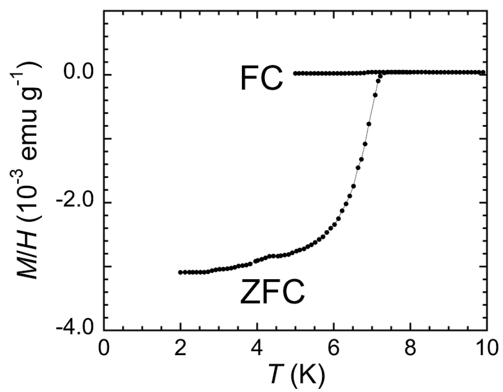
$K_{2.9}$picene
7K

$K_{3.3}$picene
18K

Rb_3picene
7K



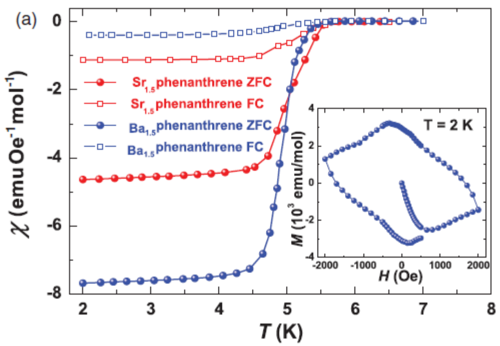


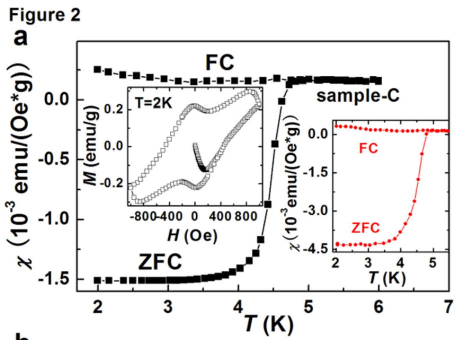


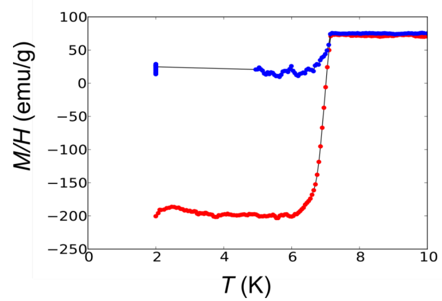
$Sr_{1.5}$phenanthrene
5.6K

K_3-phenanthrene
4.5K

K_3-coronene
4.5K

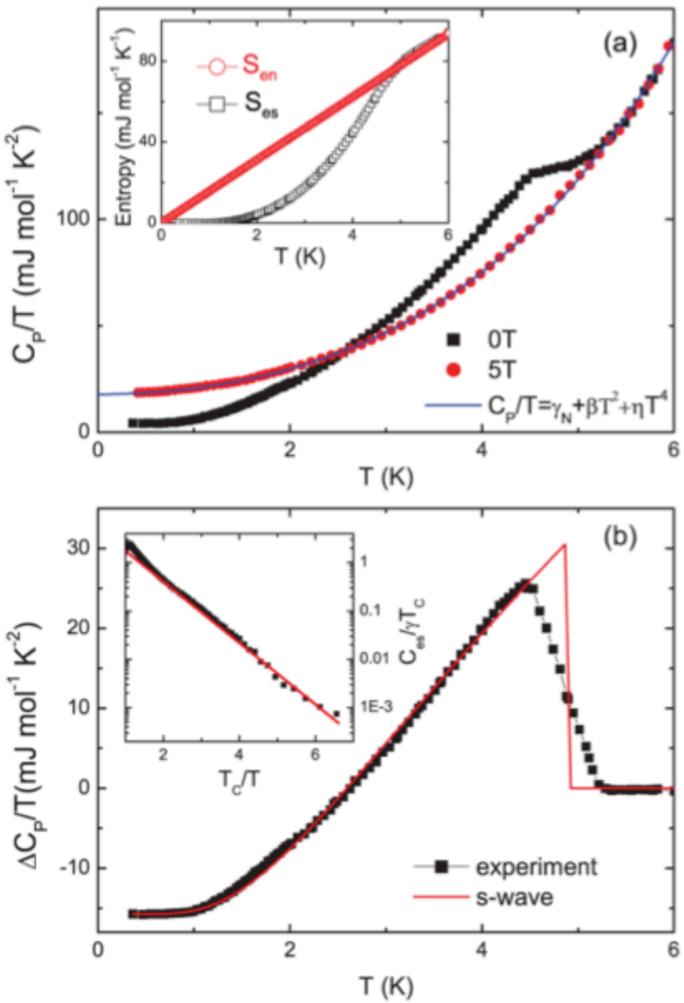






Y. Kubozono *et al*. Phys. Chem. Chem. Phys. (Perspective) 13 , 16476-16493 (2011)

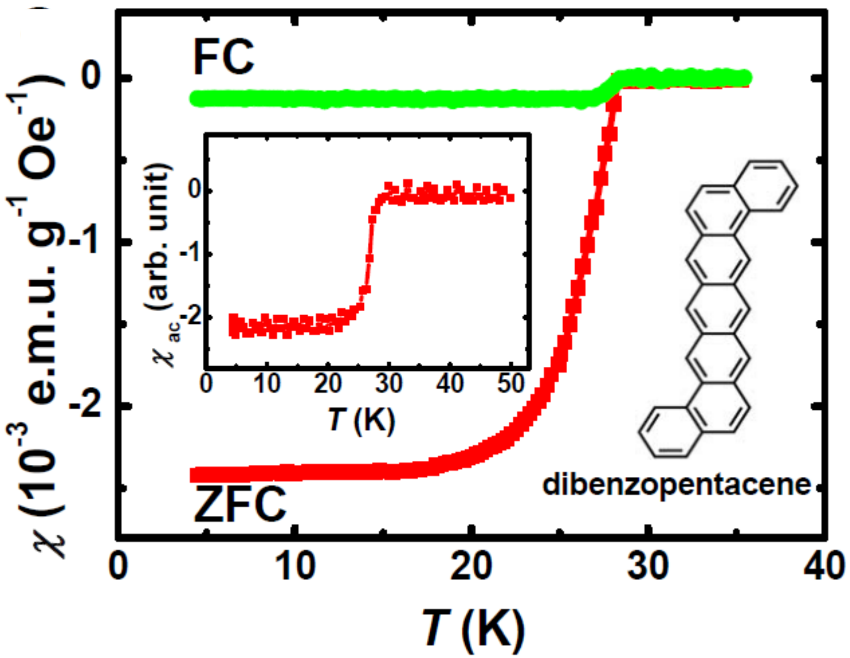
SPECIFIC HEAT ($Ba_{1.5}$-PHENANTHRENE)

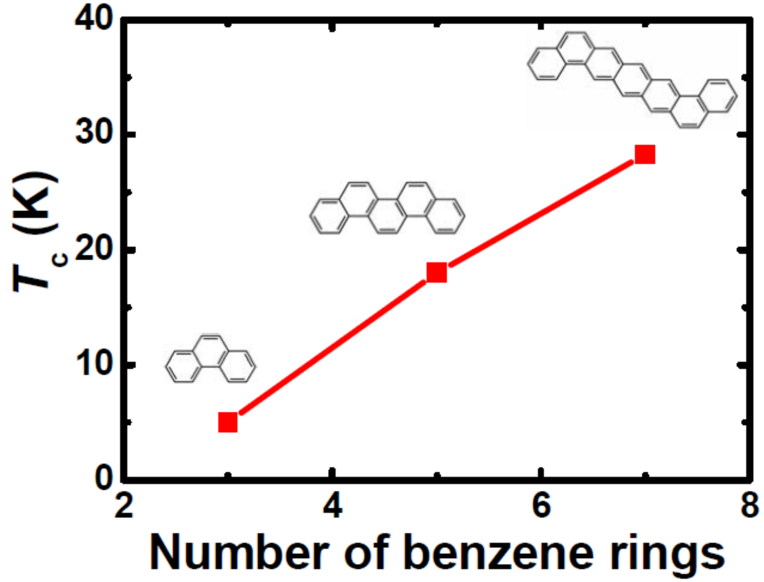


$\Delta(0)/k_BT_c = 1.95$

Intermediate coupling
s-wave with single gap

T_c INCREASES, MORE PIECES OF THE PUZZLE





$K_{3.17}DBP$ T_c = 28.2 K

$K_{3.4}DBP$ T_c = 33.1 K

M. Xue et al. Scientific Report, 2, 389 (2012)

AROMATIC SUPERCONDUCTORS: WHAT DO WE KNOW?

- 3 electron seems a magic number
- Possibly s-wave
- Molecular character (orbitals)
- Electron-phonon interaction?
- Correlations?

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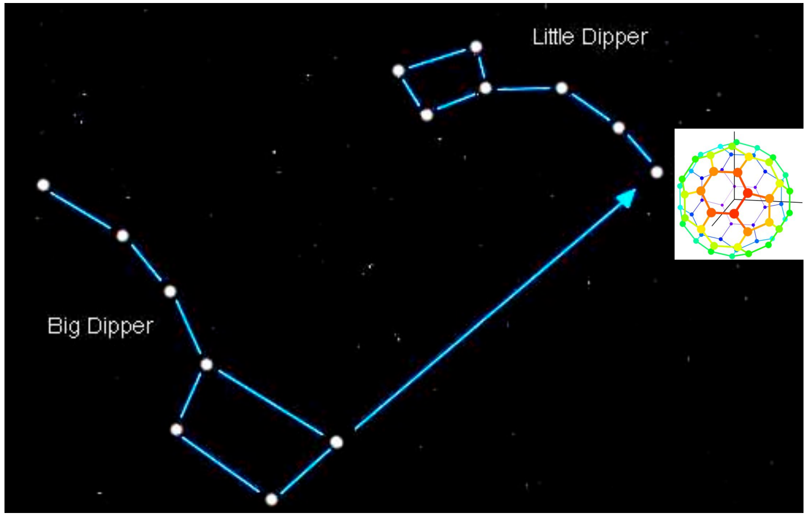
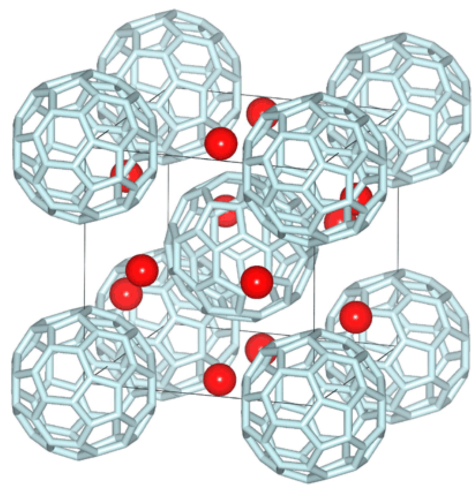
OUR NORTH STAR: THE FULLERIDES





- Solid C_{60} forms a molecular crystal
- Undoped Band insulator with a 3-fold degenerate (t_{1u}, like p) LUMO

A_3C_{60}: alkali-metal atoms donate electrons to C_{60} bands

A = K, Rb, Cs

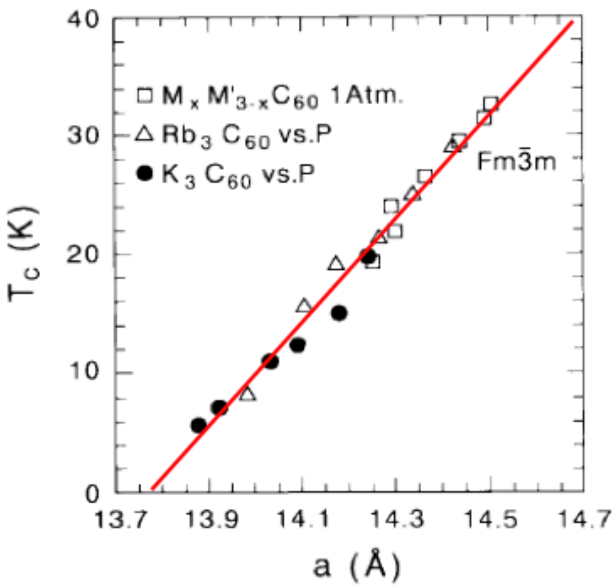
- A=K, Rb s-wave superconductor
- A=Cs AFM insulator
- SC with T_c=38K at 5 kbar

THE FIRST ANSWER: ELECTRON-PHONON

“old” (90s) compounds (K_3C_{60}, Rb_3C_{60})

- Carbon Isotope effect on T_c
- Regular Specific heat jump at T_c
- Increase of T_c and DOS with lattice spacing

⇒ Ordinary “BCS” Superconductors with “moderate” effective mass enhancement



$$T_C \cong 1.14\omega_D e^{-\frac{1}{VN(E_F)}}$$

O. Gunnarsson, Rev. Mod. Phys. 69, 575 (1997)

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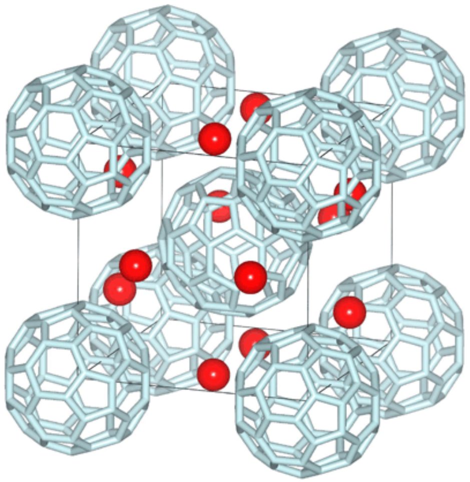
A "NEW" ENTRY: Cs_3C_{60}

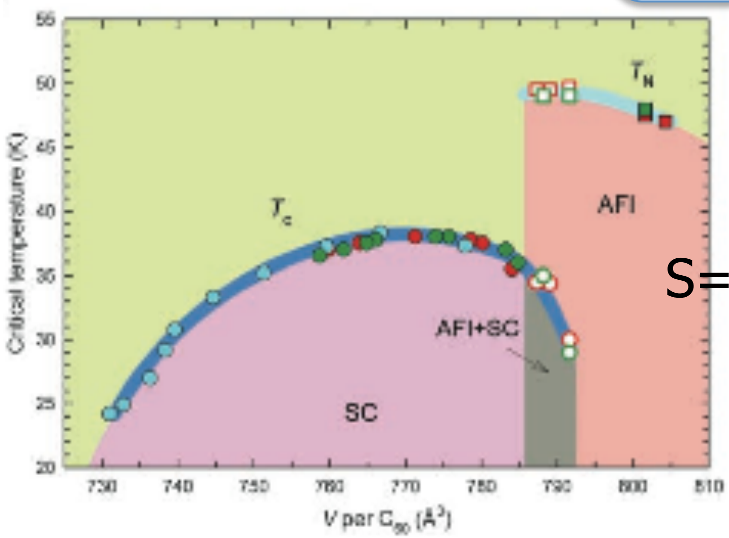


A_3C_{60}: alkali-metal atoms donate electrons to C_{60} bands

A = K, Rb, Cs

- A=K, Rb s-wave superconductor

- A=Cs S=1/2 AFM insulator
- SC with T_c=38K at 5 kbar



A "correlated" phase diagram!

S=1/2 "low spin"

A. Y. Ganin et al. Nature Materials 7, 367 (2008)

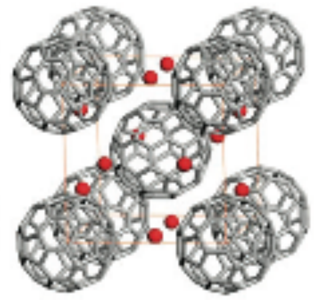
Y. Takabayashi et al., Science 323, 1585 (2009)

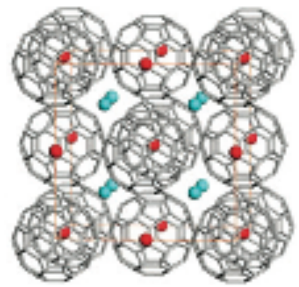
V per C_{60} or U/W

Larger lattice spacing implies a smaller W

A NEW ENTRY: A15 Cs_3C_{60}

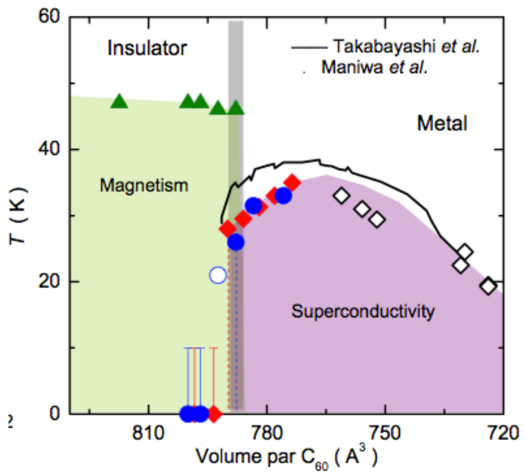
Comparison between A15 (bcc) and fcc Cs_3C_{60}

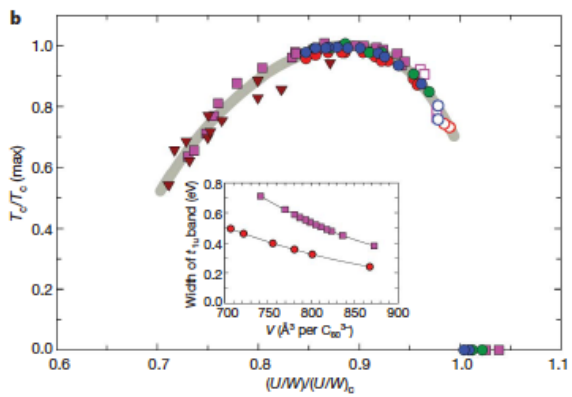




- Frustration reduces T_N by an order of magnitude
- T_c and the dome are essentially identical

The SC dome comes close to Mott



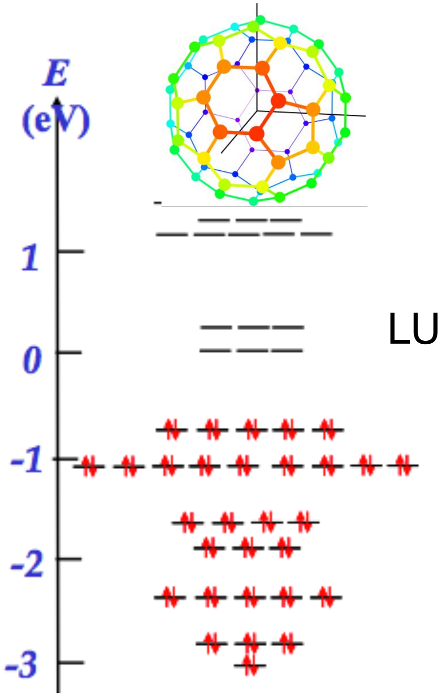


A. Y. Ganin et al. Nature 466, 221 (2010)

Y. Ihara et al. Phys. Rev. Lett. 104 256402 (2010)

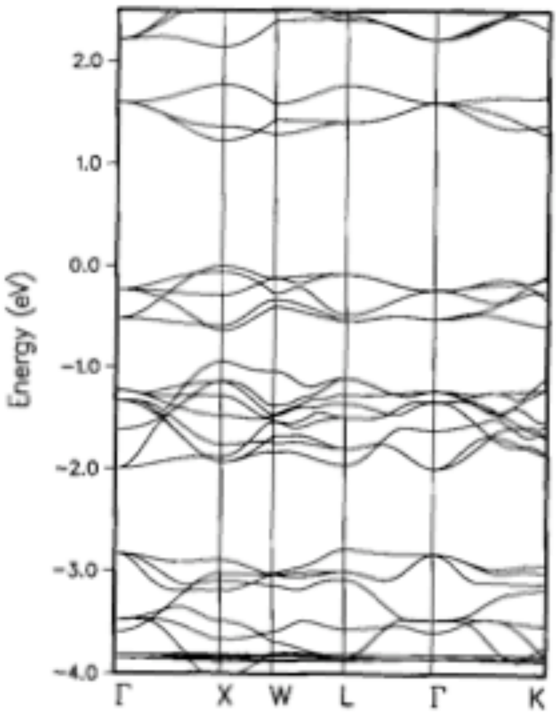
BACK TO THE QUESTION: ELECTRON-PHONON OR NOT ?

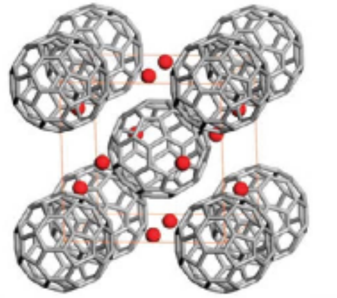
C_{60} molecule MOs



LUMO t_{1u}

Solid C_{60} bands





3 degenerate LUMO bands

Molecular Crystal: the bands are formed by molecular orbitals

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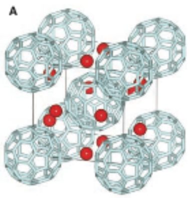
MODELING A_nC_{60}



One C60 per lattice site
Alkali only donate their s electrons

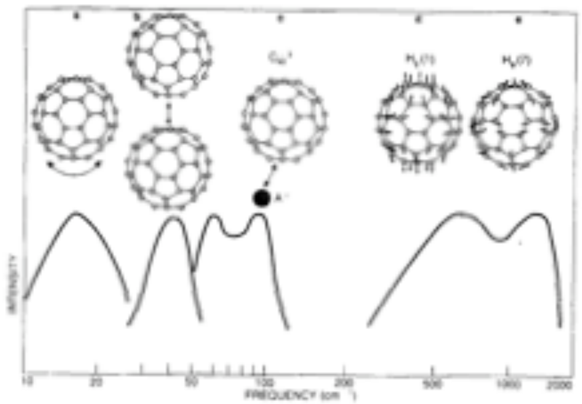
$$-t\sum_{<ija>} c^{+}_{ia\sigma} c_{ja\sigma}$$ hopping Term → 3 bands
W ~ 0.5-0.6 eV

$$+\frac{U}{2}\sum_{i}(n_i - 1)^2$$ Coulomb Repulsion U ~ 1/1.5 eV

A correlated system (even the "old" K, Rb guys)!

MODELING A_nC_{60} Chap. 2 - ELECTRON-PHONON

Electron-phonon interaction
t_{1u} coupled to H_{1g} phonons
(deformations of the ball)



The interaction lives on a single molecule

$$-J_H(2S_i^2 + \frac{1}{2}L_i^2) - \frac{5}{6}J_H(n_i - 3)^2$$

Hund's rule
(F_2 Slater integral)

$$J = -J_H + J_{el-ph}$$

$$J_{el-ph} \approx 0.1eV$$

$$J_H \approx 0.07eV$$

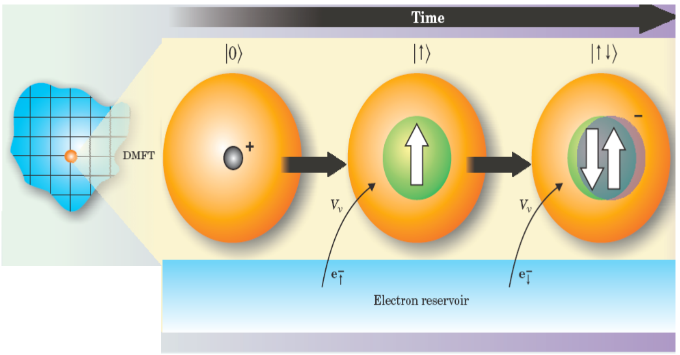
J > 0 favors minimum S e L (inverted Hund's rule)

HOW DO WE SOLVE THE MODEL?

Several competing Energy scales

Local (on-ball) Interaction Terms

DYNAMICAL MEAN-FIELD THEORY



An atom in a self-consistent medium

Anderson Impurity model

A. Georges, G. Kotliar, W. Krauth, M.J. Rozenberg. Rev. Mod. Phys. 68, 13 (1996)

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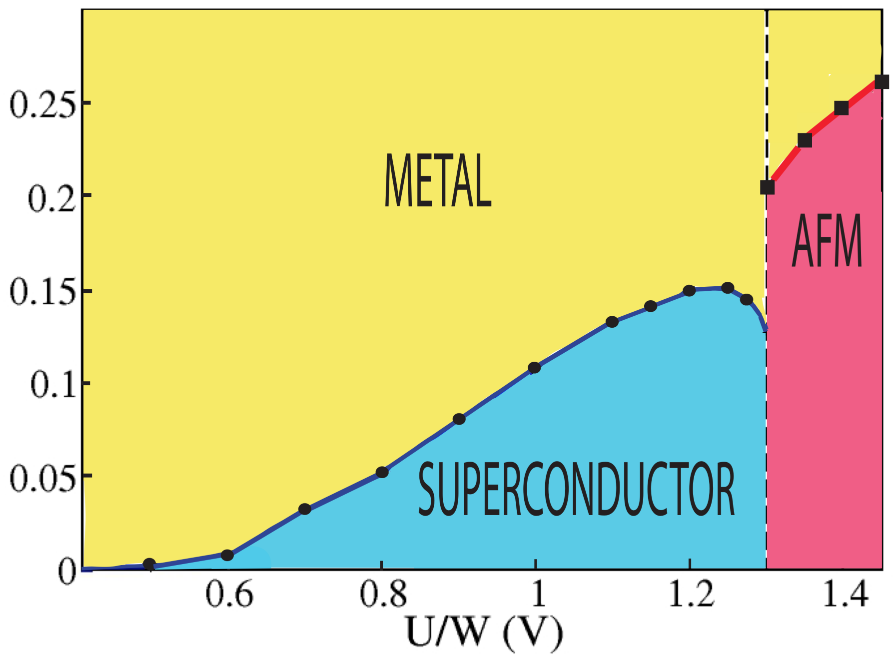
DMFT PHASE DIAGRAM



- Orbital Degeneracy (3 t1u orbitals)
- Jahn-Teller coupling
- Strong Correlation

- s-wave superconductors
- S=1/2 AFM Mott
- First-order transition

Superconductivity close to a Mott state is enhanced by correlations

M. C., M. Fabrizio, C. Castellani, and E. Tosatti, Rev. Mod. Phys. 81, 943 (2009)
[before the experiment in Cs_3C_{60}]
M. C. and G. Giovannetti, arXiv1204.0253

WHY?

Active Phonons are coupled with Spin/Orbital Degrees of Freedom
still active when charge fluctuations are frozen by correlations
even in the Mott state the singlet energy gain is J

$W \longrightarrow ZW$

$Z << 1$

$U \longrightarrow ZU$

Coulomb Repulsion

$J \longrightarrow J$

Electron-phonon

Enhanced Superconductivity

Take-home message: coupling to molecular phonons can be enhanced by Coulomb repulsion

M.C., M. Fabrizio, C. Castellani, and E. Tosatti, Science 296, 2364 (2002)

WHAT DOESN'T KILL YOU MAKES YOU STRONGER

$$T_c = \omega_0 e^{-\frac{1}{\lambda - \mu^*}}$$

$\boxed{\lambda = \rho V}$ → Attractive Potential → Density of States

Electron-electron Correlations ⇨ Quasiparticles with Reduced bandwidth

$W \longrightarrow ZW$

$Z << 1$

$$\rho \propto \frac{1}{W}$$ ⇨ $\rho \longrightarrow \rho/\mathbf{Z}$

Repulsion enhances T_c!

"Typically"
V is also renormalized

$V \longrightarrow V\mathbf{Z}^2$ ⇨ $\lambda \longrightarrow \lambda \mathbf{Z} << \lambda$

$\boxed{T_c \downarrow}$

Correlation can enhance Tc when the attraction is not renormalized

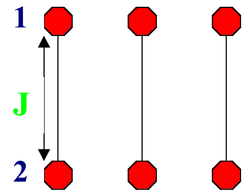
A SIMPLER MODEL FOR SCS

Two-Orbital Hubbard model with inverted J

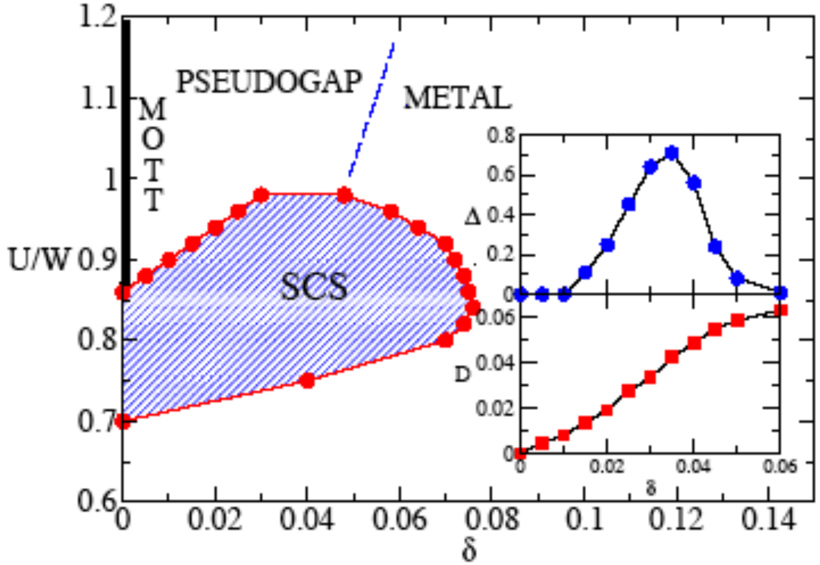
$$H = H_{hopping} + H_{Hubbard} - J\sum_i (l_x^2 + l_z^2)$$

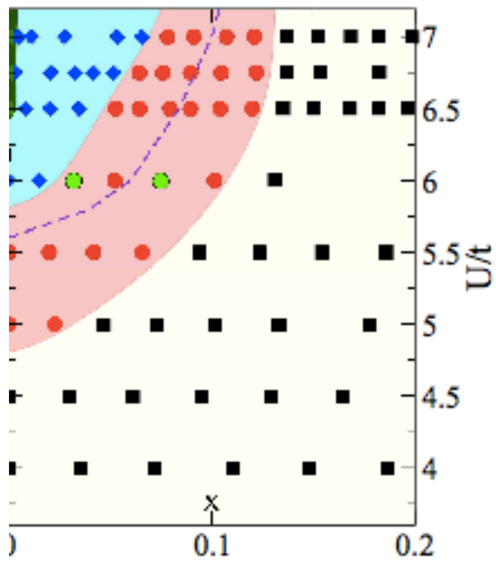
$$l_x = \sum_\sigma c^+_{1\sigma} c_{2\sigma} + c^+_{2\sigma} c_{1\sigma}$$

$$l_z = n_1 - n_2$$



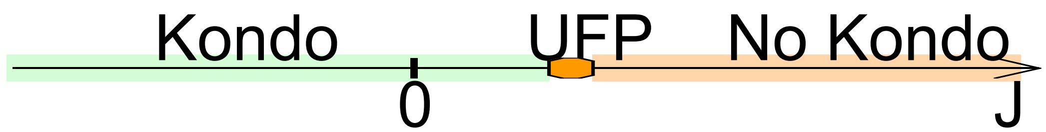
Bridge with the Cuprates: The pairs of molecular orbitals are local “bonds”





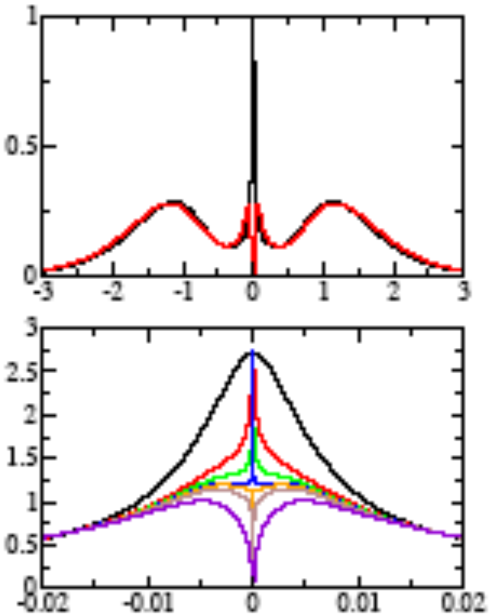
Same of diagram of 2d Hubbard model in cluster DMFT
E. Gull, O. Parcollet and A. Millis, arXiv:1207.2490

LESSONS FROM THE IMPURITY MODEL



Competition between ordinary Kondo screening leading to a Fermi liquid and J which forms local singlets (for two electrons)

$$\rho_{\pm}(\omega) = \frac{\rho_0}{2}\left(\frac{T_+^2}{\omega^2+T_+^2} \pm \frac{T_-^2}{\omega^2+T_-^2}\right)$$



- In the screened phase we obtain the FL Kondo resonance on top of a broader resonance
- In the unscreened phase the narrow peak becomes a Pseudogap
- At the Fixed Point only the broad resonance survives
- Superconductivity is the leading instability: it “cures” the critical point

L. De Leo and M. Fabrizio, Phys. Rev. B. 69, 245114 (2004)

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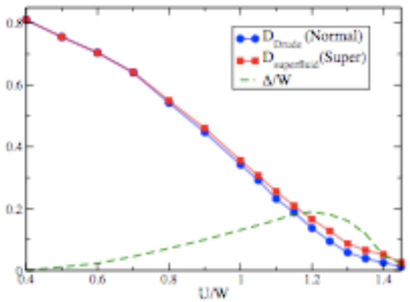
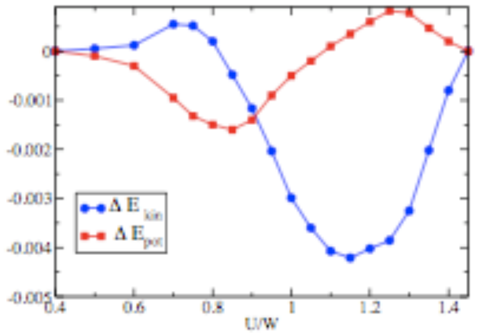
WHATEVER DOES NOT KILL YOU SIMPLY MAKES YOU STRANGER

SUPERCONDUCTIVITY "HEALS" THE ANOMALOUS METAL CLOSE TO THE CRITICAL POINT

Superfluid delta-function in optical conductivity larger than the Drude Weight of the metal





a kinetic energy gain stabilizes the SC Anti-BCS

(as it happens in u.d. cuprates)

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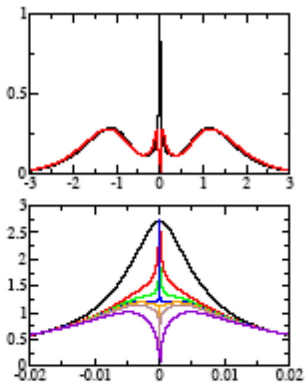
SPECIFIC HEAT JUMP

For a BCS superconductor

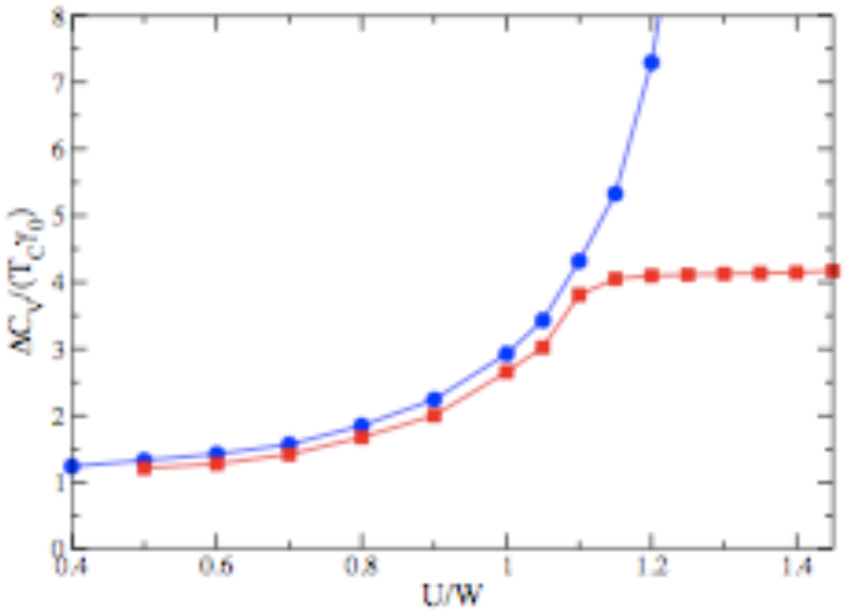
$$\boxed{\frac{\Delta C}{T_C} \cong 1.5\gamma \propto m^* = \frac{1}{Z}}$$



Why? Z vanishes, but a broad resonance of width J survives

Experiments (K_3C_{60})

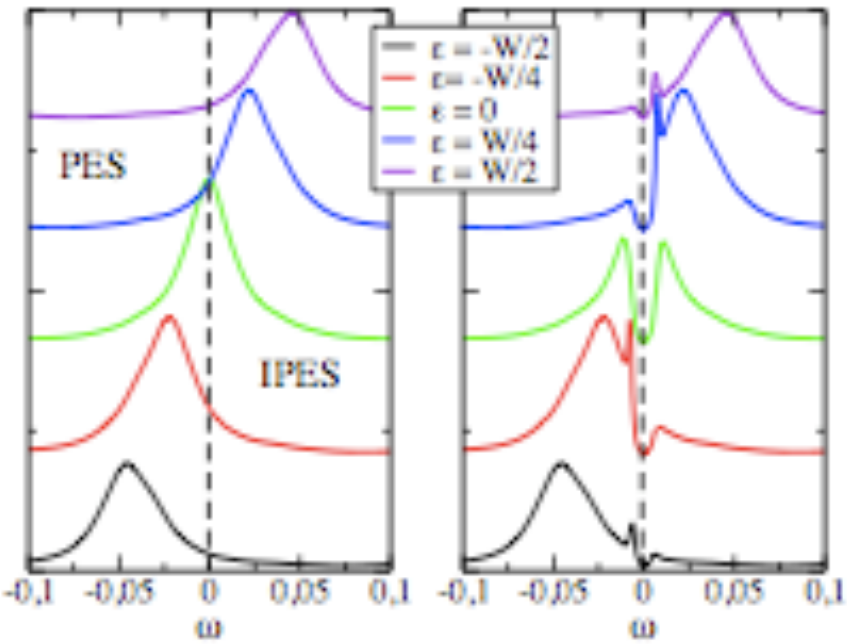
$$\gamma \cong 3\gamma_0$$



Y. Kasahara et al. confirms the prediction

PHOTOEMISSION SPECTRA

Unexpanded Expanded



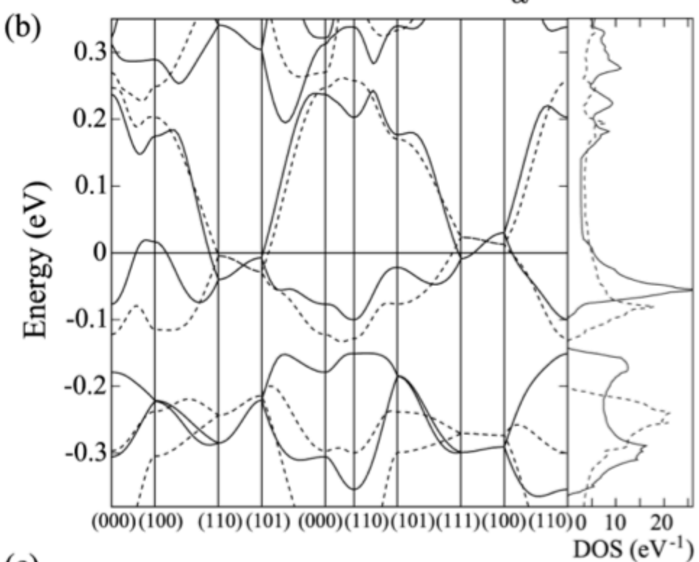
$$\rho(\varepsilon,\omega) = -\frac{1}{\pi}\mathrm{Im}G(\varepsilon,\omega)$$

- No pseudogap in the "overdoped" side (small lattice spacing, K_3C_{60})
- Pseudogap in the "underdoped" side (expanded, Cs_3C_{60})

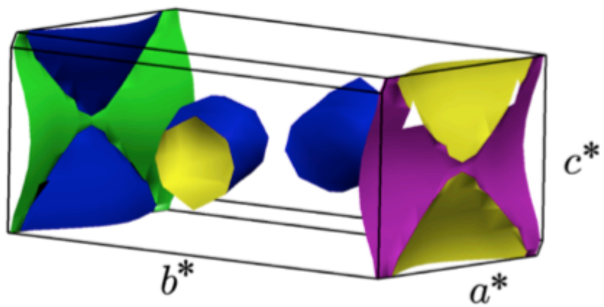
BACK TO K-PICENE

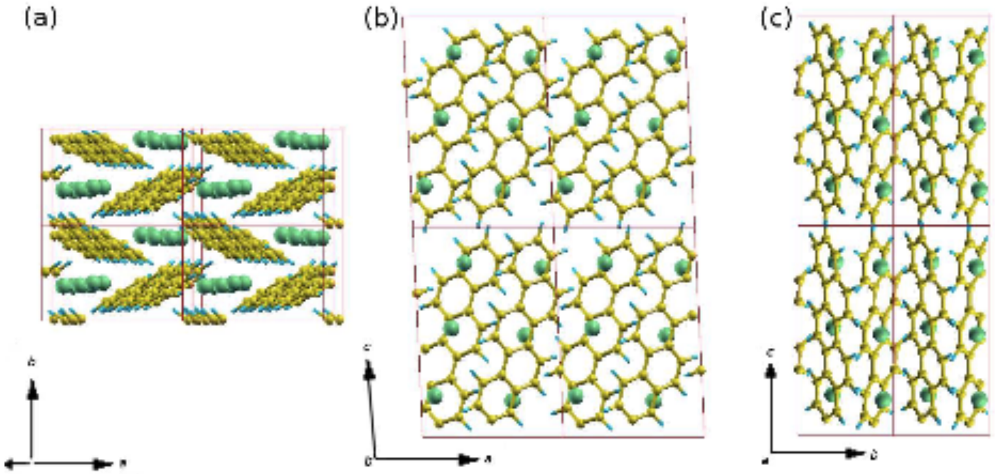
$C_{22}H_{14}$

(b)



(c)





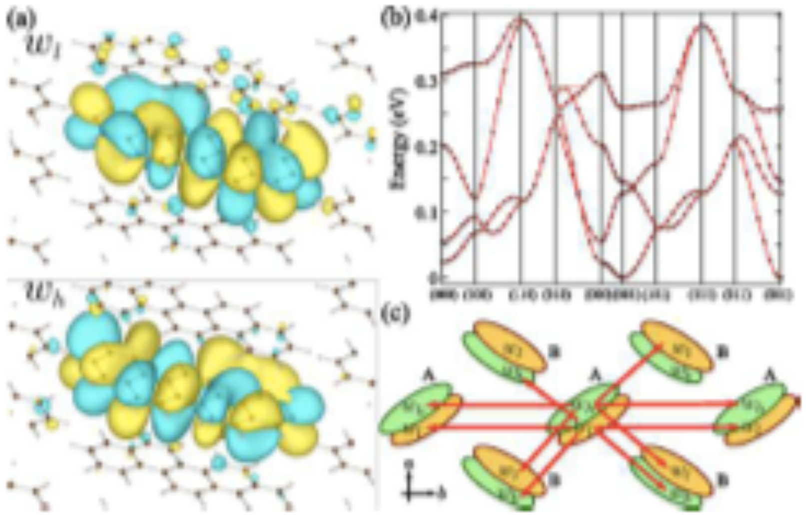
3d pockets +
1d surfaces

Conduction bands from LUMO and LUMO+1 nearly degenerate

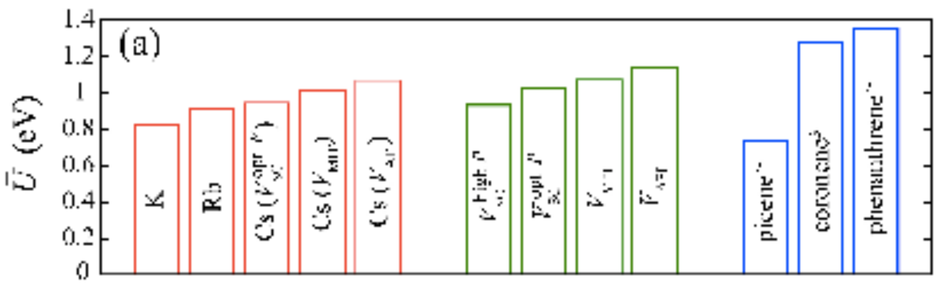
T. Kosugi et al.JPSJ 79, 044705 (2010)

MOLECULAR ORBITALS

$C_{22}H_{14}$



We build a lattice model and include the interactions



U is around 0.7 eV

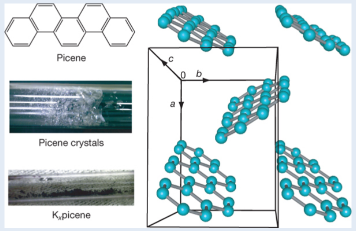
W < 0.6 eV

Y. Nomura, K. Nakamura and R. Arita, Phys. Rev. B 85, 155452 (2012)

CORRELATION EFFECTS IN K-PICENE

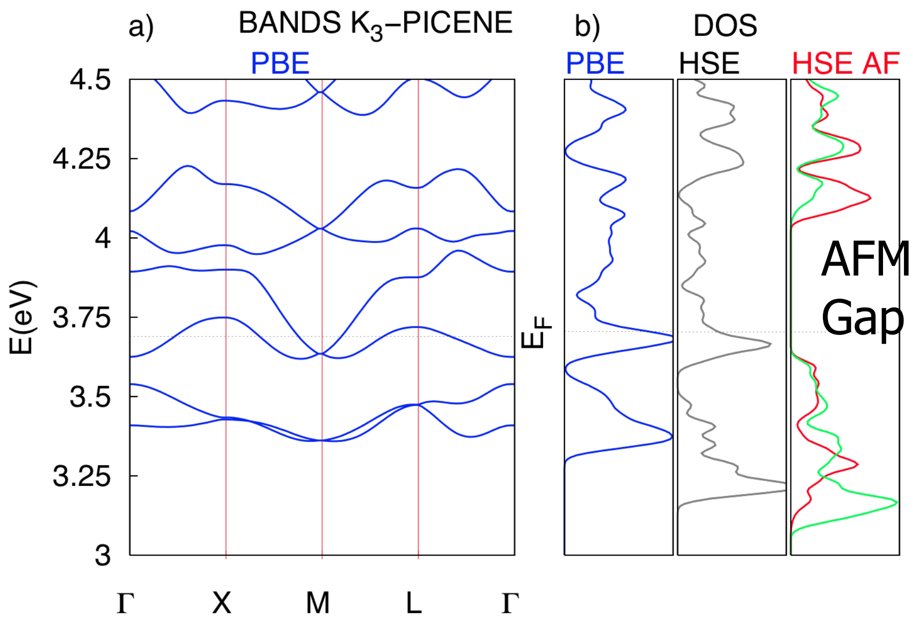
G. Giovannetti and M.C. Phys. Rev. B 83, 134508 (2011); M. Kim et al.

$C_{22}H_{14}$



Conduction bands from LUMO and LUMO+1 **nearly degenerate**

T. Kosugi et al.JPSJ 79, 044705 (2010)

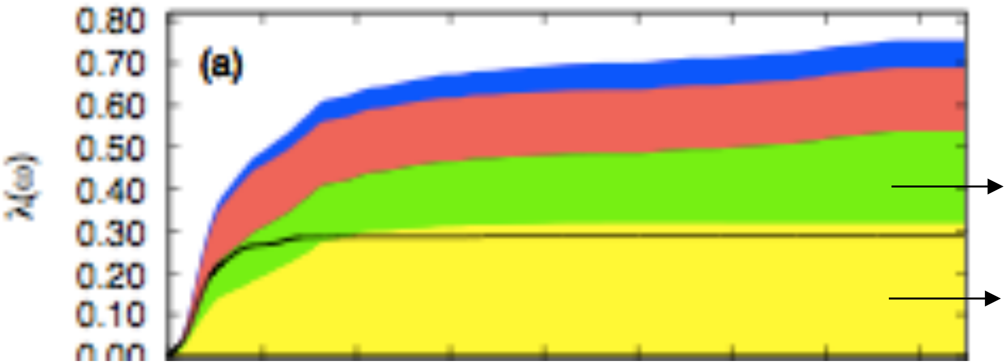


- Using HSE functional within DFT we find a low-spin AFM state
- No AFM using LDA, GGA – We need correlations
- AFM ordering competing with SC
- cRPA evaluation of U/W by Y. Nomura, K. Nakamura and R. Arita U/W > 1

Correlation effects are important

ELECTRON-PHONON AND CORRELATIONS

Cs_3C_{60}	K_3picene
Threefold degenerate orbitals	Nearly degenerate
U/W ~ 1.5	U/W ~ 1.2
Coupling Molecular Phonons	?



Casula et al. PRL 2011

Off-plane C

In-plane C

40% of the e-ph coupling comes from dopant+intermolecular modes

- The intramolecular phonons can behave like in fullerene
- The intermolecular and intercalant are expected to be depressed

ELECTRON-PHONON AND CORRELATIONS

Cs_3C_{60}	K_3picene
Threefold degenerate orbitals	Nearly degenerate
U/W ~ 2	U/W ~ 1.2
Coupling Molecular Phonons	Coupling to all sorts of phonons

A more subtle competition (wrt fullerene) whose result can depend on the specific aromatic molecule

Preliminary DMFT results for pure correlation effects

- We are on the verge of the Mott transition (confirming DFT)
- Electron-phonon interaction should reduce the effective U

G. Sangiovanni et al., Phys. Rev. Lett. 94, 026401 (2005), Phys. Rev. B 73, 165123 (2006)

CONCLUSIONS

- Electron-phonon interaction and Mott physics can live happily everafter
- Phononic Superconductivity favored by strong correlation if it involves internal degrees of freedom
- A general mechanism for superconductivity in correlated systems
- Cs_3C_{60} is a clear example: experimental phase diagram predicted on the basis of e-ph+e-e+multiorbital
- Aromatic Superconductors share many similarities, but the interplay between e-ph and e-e is more subtle

G. Giovannetti and M.C. Phys. Rev. B 83, 134508 (2011)

M. C., M. Fabrizio, C. Castellani, and E. Tosatti, Rev. Mod. Phys. 81, 943 (2009)