Electron-phonon coupling and correlation in alkali-doped fullerenes

Olle Gunnarsson

1. Metal-insulator transition.

   Factors: a) El.-ph. coupl. b) lattice struct. c) orbital deg. d) filling

   New exp. makes it possible to disentangle factors.

   Model parameters from exp. and theory.

2. Superconductivity.

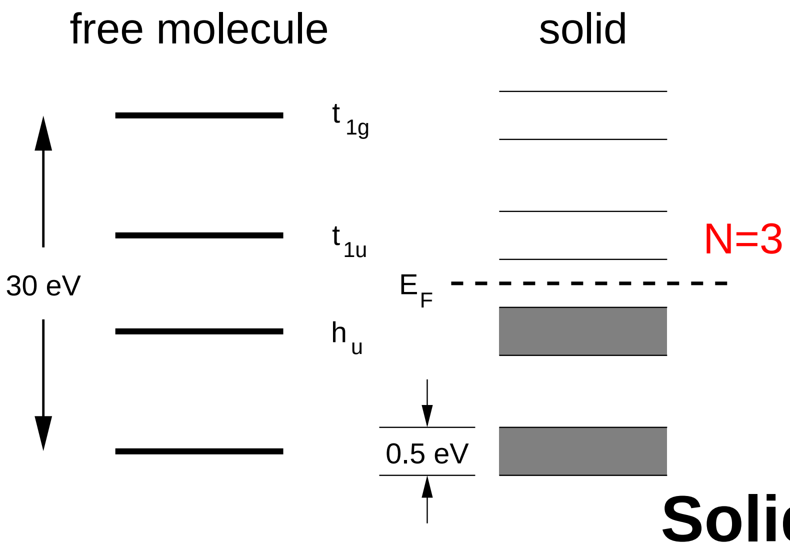
   What drives superconductivity?

   Same parameters for supercond. and metal-insulator transition?

Cooperation: Jong Han and Erik Koch.

Max-Planck Institut, Stuttgart, Germany

Solid C_{60}



Molecular levels broaden to sub bands.

Width only $W \sim 1/2$ eV, due to weak C_{60}-C_{60} interaction.

Solid A_nC_{60} (A=K, Rb)

Each alkali atom gives off one electron. Partly filled t_{1u} band.

1. A_3C_{60} is metal but A_4C_{60} is insulator.

2. A_3C_{60} superconductors with large T_c (up to 38 K).

Strong correlation and electron-phonon coupling

U can be deduced from Auger measurement for (surface of) bulk C_{60}.

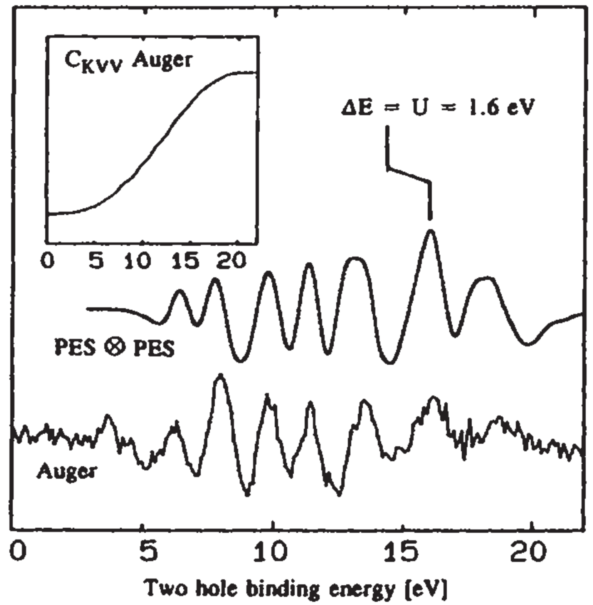
$U \approx 1.6$ eV. $\Rightarrow U/W \sim 1.5 - 2.5$

Strong correlation effects.

A_4C_{60} could be a Mott insulator.

But U/W similar for A_3C_{60} and A_4C_{60}

Why is then A_3C_{60} a metal?



Lof, van Veenendaal, Koopmans, Jonkman, and Sawatzky, PRL **68**, 3924.

Strong coupling to Jahn-Teller (H_g) phonons.

Weaker coupling to A_g phonons.

Varma, Zaanen, Raghavachari, Science **254**, 989.

Mazin, Rashkeev, Antropov, Jepsen, Liechtenstein, Andersen, PRB **45** 5114.

Strong Hund's rule coupling.

Factors determining metal insulator transition

Metal-insulator transition determined by competition between hopping and Coulomb energies.

Hopping usually measured by the band width W, but a) lattice structure, b) orbital degeneracy and c) filling are also important.

Coupling to Jahn-Teller phonons favors insulators.
Depends strongly on filling.

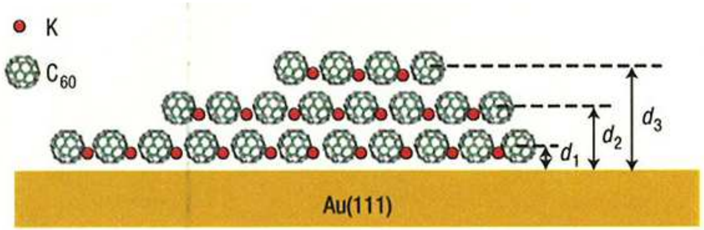
Taking these factors into account, we can explain the difference between A_3C_{60} and A_4C_{60}.

Many competing factors. Can we isolate effects of individual factors?

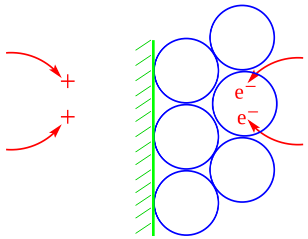
Tuning parameters

Study layers of doped C_{60} on an Au surface in STM. Measure band gap. Doping and number of layers can be varied.

Wang, Yamachika, Wachowiak, Grobis, Crommie, Nature Materials **7**, 194.



1. U is reduced by image charges. Variation of number of layers leads to variation of U.



2. Electron-phonon int. (EPI) more important for filling $n=$4 than $n=$3 and for $n=$3 than $n=5$. Varying n changes imp. of EPI.

3. Electron hopping more important for filling 3 than 5. Tune importance of electron hopping by comparing $n=$3 and 5.

O. Gunnarsson, Nature Materials **7**, 176.

K_3C_{60}, Na_4C_{60} and K_4C_{60}

In Crommie's STM measurement no clear change in lattice structure (hexagonal) with doping observed (for 2 and 3 layers).

K_3C_{60}: fcc structure. K_4C_{60}: bct structure.

Since Na atoms are small, films (1000 Å) of Na_4C_{60} can be produced in the fcc structure. EELS in transmission + KK-analysis.
Electronically essentially bulk properties.

1. $K_3C_{60} \longrightarrow Na_4C_{60}$: Change of filling.

2. $Na_4C_{60} \longrightarrow K_4C_{60}$: Change of lattice structure.

Knupfer and Fink, PRL **79**, 2714.

See also fcc Na_2C_{60}.

Brouet, Alloul, Le, Garaj and Forro, PRL **86**, 4680.

1. General results for band gaps.

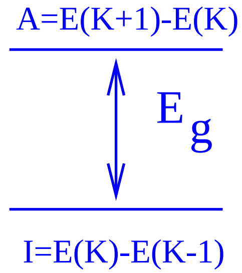
2. Model and parameters.

3. Comparison with experiment.

Band gap

K sites. No orbital deg. Half-filling:

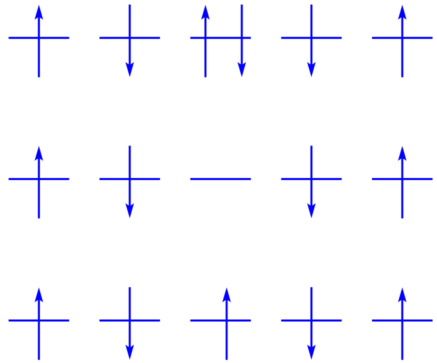
$E_g = A - I = E(K+1) + E(K-1) - 2E(K)$



Large U

$E_g \sim U - W$

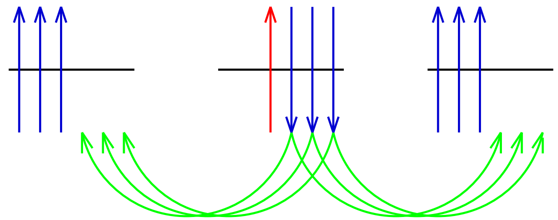
$(U - E_g)/W \sim 1$



Orbital degeneracy N

(Hopping energy)/W increased by orbital deg.

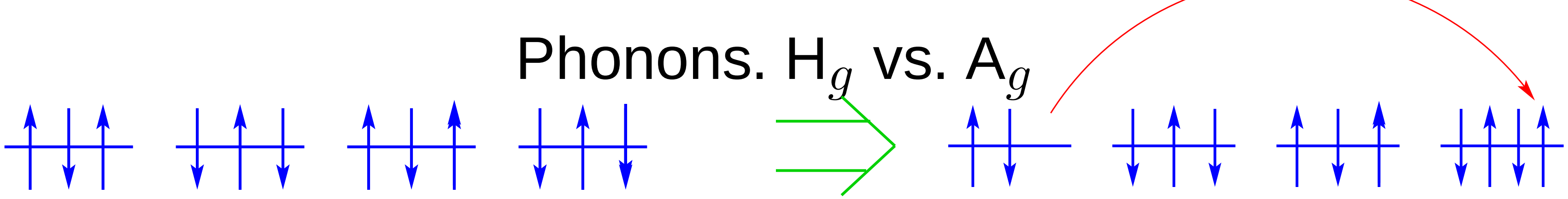
$(U - E_g)/W > 1.$



Crucial for A_3C_{60} being a metal.

Gunnarsson, Koch, Martin: PRB **54**, R11026.

Phonons. H_g vs. A_g



E_g=$E(K$+$1)$+$E(K$-$1)$-$2E(K)$. Limit: $g \ll \omega_{ph} \ll W \ll U$.

A_g phonons: (Coupling to charge fluctuations).

Neutral state: Charge fluctuations suppressed. Little coupling.

Charged states: Coupling to electron and hole.

Gap reduced. Critical U_c increased.

H_g (Jahn-Teller) phonons: (Coupling to internal degrees of freedom).

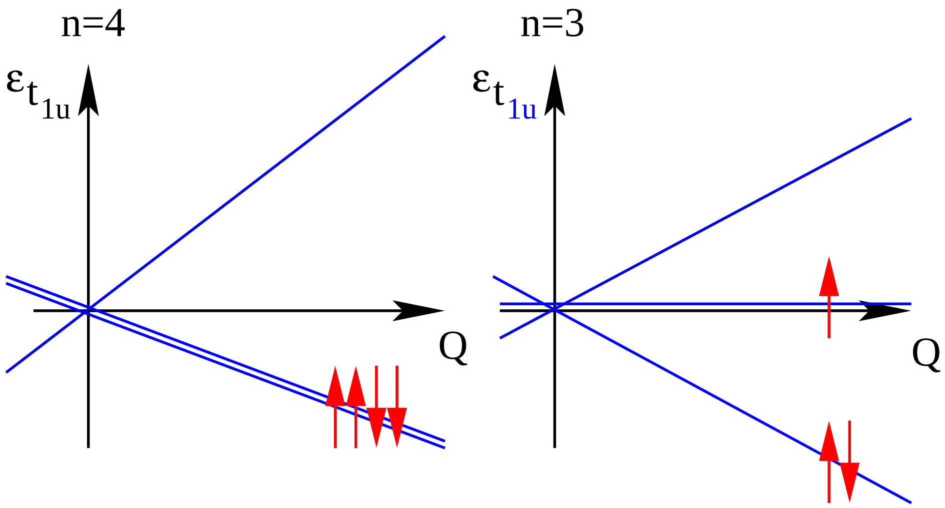
Neutral state: Strong coupling.

Charged states: Coupling to phonons interfere with hopping.

Gap increased. Critical U_c reduced.

Han, Koch, Gunnarsson, PRL **84**, 1276.

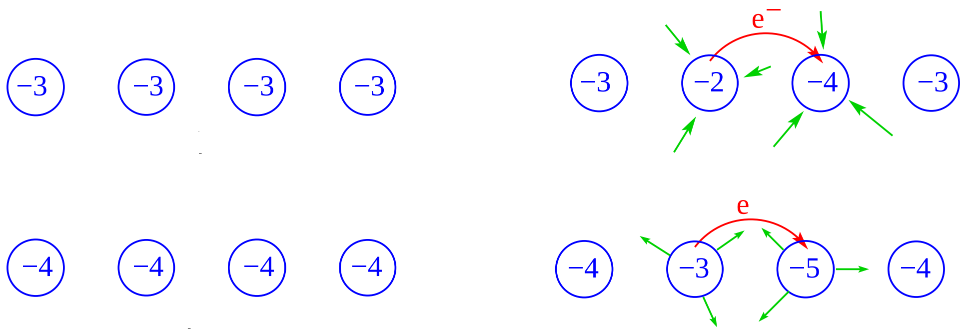
Filling n =3 vs. 4



Stronger Jahn-Teller coupling for n =4 than for n =3.

Favors insulator more for A_4C_{60} than A_3C_{60}.

Effective U?



U_{eff} reduced

U_{eff} increased

Transfer an electron from one molecule to another.

Assume phonons can relax completely to new charge distribution.

(Anti-adiabatic approximation).

Phonons couple more strongly to charge 2 and 4 than to 3 and 5.

$\Rightarrow$ H_g phonons favor metal for A_3C_{60} and insulator for A_4C_{60}.

Auerbach, Manini and Tosatti, PRB **49**, 12998; Gunnarsson, PRB **51**, 3493.

But, H_g phonons favor insul. for both A_3C_{60} (less) and A_4C_{60} (more).

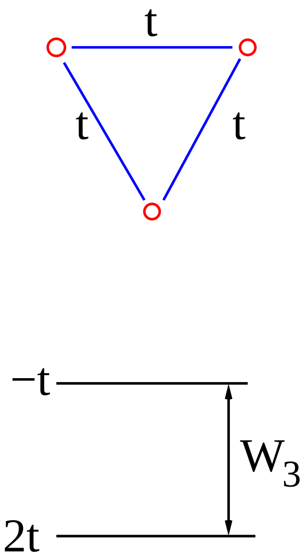
Anti-adiabatic approximation leads to incorrect conclusions!

Han, Gunnarsson, Physica **292**, 196.

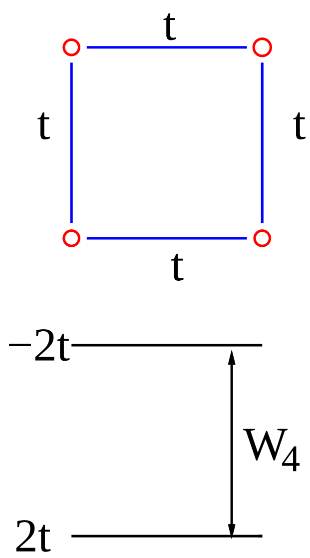
Lattice structure. Geometrical frustration

fcc lattice: Hopping over triangle possible.

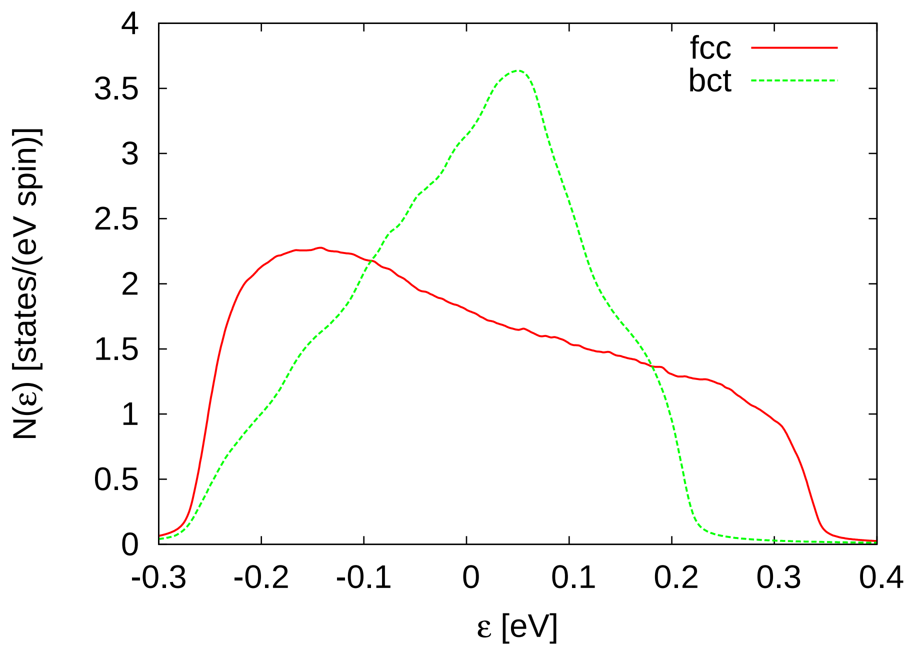
bct lattice: Only hopping over square (nearest neighbor hopping).



$$|t| = \frac{W_3}{3}$$



$$|t| = \frac{W_4}{4}$$



Typically U/W considered. 2nd moment better measure of hopping.

For given U/W, bct (A_4C_{60}) lattice favors insulator over fcc (A_3C_{60}).

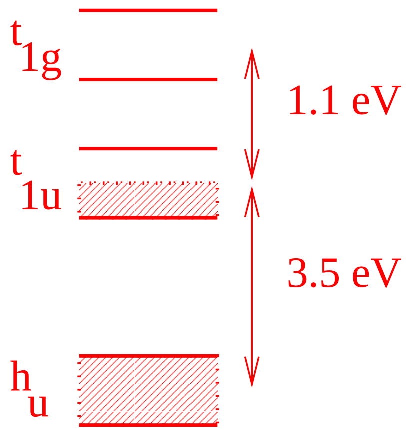
Han, Koch, Gunnarsson, PRL **84**, 1276.

Model

$$H=\sum_{ij\sigma mm'} t_{im,jm'} c^\dagger_{im\sigma} c_{jm'\sigma} + U \sum_i \sum_{(m\sigma)<(m'\sigma')} n_{im\sigma} n_{im'\sigma'}$$

$$+\omega_{ph} \sum_{i\nu} b^\dagger_{i\nu} b_{i\nu} + \frac{g}{2} \sum_{i\sigma\nu mm'} V^{(\nu)}_{mm'} c^\dagger_{im\sigma} c_{im'\sigma} (b_{i\nu} + b^\dagger_{i\nu}).$$

$V^{(\nu)}_{mm'}$ is determined by symmetry and includes the Jahn-Teller effect for H_g phonons. Coupling to net charge for A_g phonons.



1. Three-fold deg. t_{1u}-level on each molecule.
2. Hopping.
3. Coulomb interaction.
4. Hund's rule coupling included implicitly.
5. One Einstein mode per molecule (H_g or A_g sym.)

Hopping parameters

Band width K_3C_{60}: LDA $\Rightarrow W = 0.61$ eV
(Erwin, Bruder, Physics B **199-200**, 600).

GW $\Rightarrow$ LDA W of undoped C_{60} increased by 30 %.
(Shirley and Louie, PRL **71**, 133).

$\Rightarrow W = 0.79$ eV. Adjust tight-binding parameters.

Other structures: Use the same tight-binding parameters (with distance dependence from LDA).

Surface layers: C_{60} orientation not known:
Assume semi-elliptic DOS. $W = 0.56$ eV.

Unclear how good these parameters are.

Coulomb interaction for a free C$_{60}$ molecule

Calculate U_0 for a free molecule using LDA: $U = \delta^2 E(n)/\delta n^2$,

where n is the number of t_{1u} electrons.

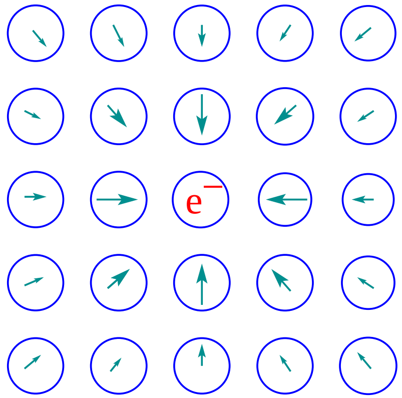
U_0=2.7 eV (Antropov, Gunnarsson, Jepsen, PRB **46**, 13647).

Other LDA calculations U_0=3.0 eV (Pederson, Quong, PRB, **49**, 13584).

Experiment: $U_0 = I_p(C_{60}^-) - A(C_{60}^-)$.

$I_p(C_{60}^-) = 2.7$ eV. $A(C_{60}^-) \approx 0$ $\Rightarrow U_0 \approx 2.7$ eV.

Coulomb interaction in solid C_{60}



Estimate polarizability of a molecule from exp. dielectric function of C_{60}.

Put a polarizability on each molecule. Self-consistently screen charge on central molecule.

$U = U_0 - \delta U$.

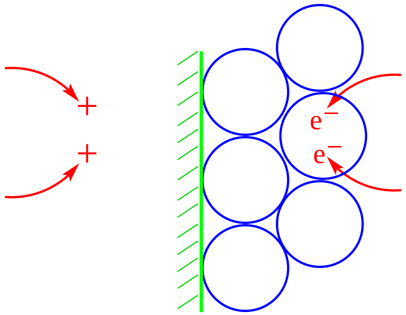
C_{60} surface. Theory: $U = 1.3$ eV for the t_{1u} level.

C_{60} surface. Exp.: $U = 1.4$ eV for the h_u level.

1.6 eV averaged over occ. levels..

Antropov, Gunnarsson, Jepsen, PRB **46**, 13647.

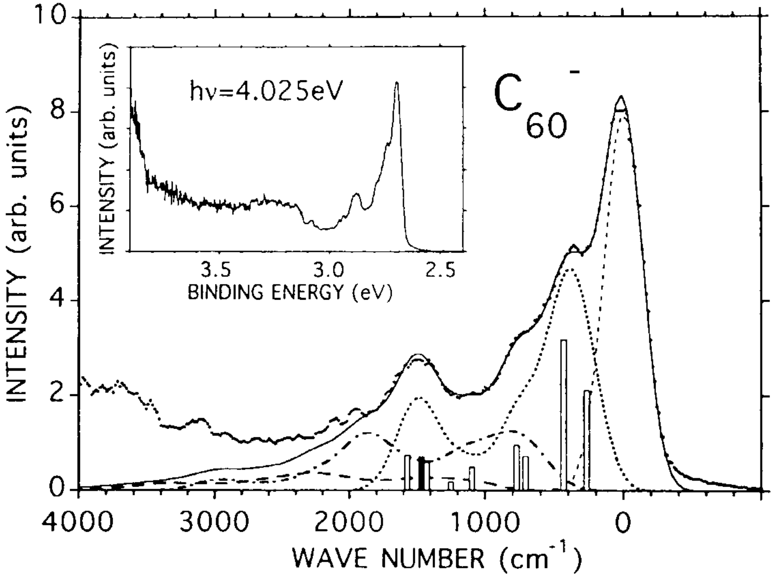
For C_{60} layers on a metal:
Introduce image charges.

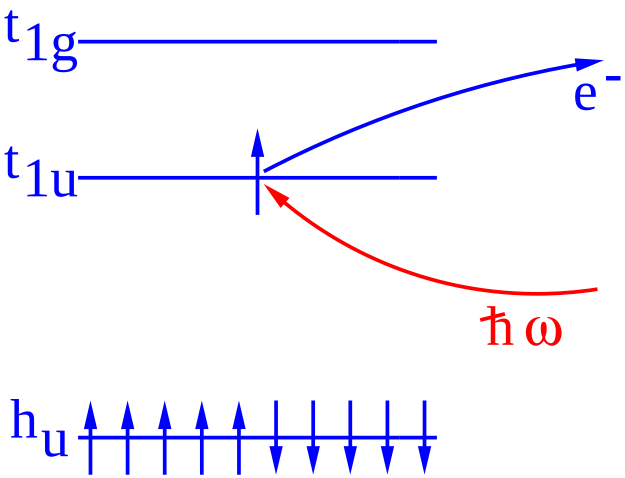


Hesper, Tjeng, Sawatzky, Europhys. Lett. **40**,177.

How strong is the electron-phonon coupling?

Photoemission from free C_{60}^{-} molecule.





As the t_{1u} electron is removed, phonons are excited.

These excitations show up as satellites. Final states very simple.

The weight of satellites give information about electron-phonon coupling. $\Rightarrow \lambda \approx 1$.

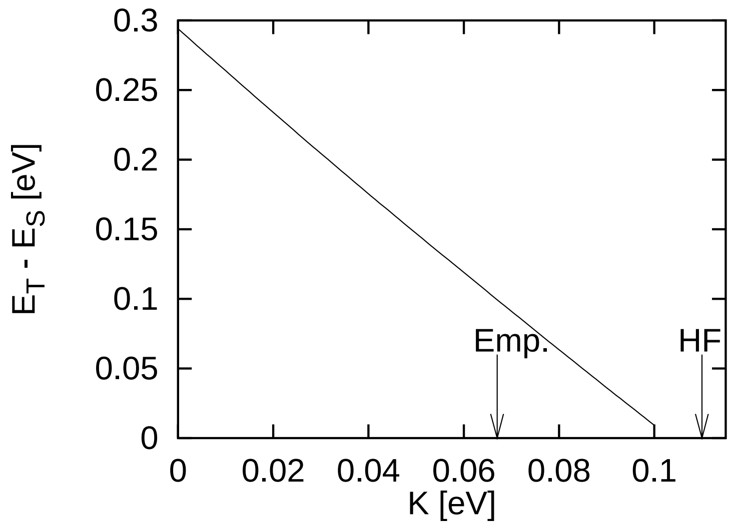
Gunnarsson, Handschuh, Bechthold, Kessler, Ganteför, and Eberhardt, PRL **74**, 1875.

Hund's rule coupling

From NMR meas. for K_4C_{60}, Na_2C_{60}: Triplet $\sim$0.1 eV above singlet.

Calculate singlet-triplet splitting using PES electron-phonon coupling and multiplet integral K.

Experimental splitting for $K \approx 0.07$ eV (64 $\%$ of Coulomb integral. Similar but somewhat larger than reduction for atoms).



Han, Koch, Gunnarsson, PRL **84**, 1276.

Neglecting Hund's rule $\Rightarrow$ Singlet-triplet splitting factor 3 too large.

In the following: Neglect Hund's rule and reduce λ by factor 3.

K_3C_{60}: Use $\lambda = 0.3$. Adjust λ for other systems according to DOS.

Unclear how accurate this estimate is.

Dynamical mean-field theory

Assume that self-energy $\Sigma(\mathbf{k},\omega) \equiv \Sigma(\omega)$ is $\mathbf{k}$ independent.

The full lattice problem mapped onto an impurity problem in a self-consistently determined host.

Impurity problem solved using a Quantum Monte-Carlo (Hirsch-Fye).

Metal-Insulator transition:

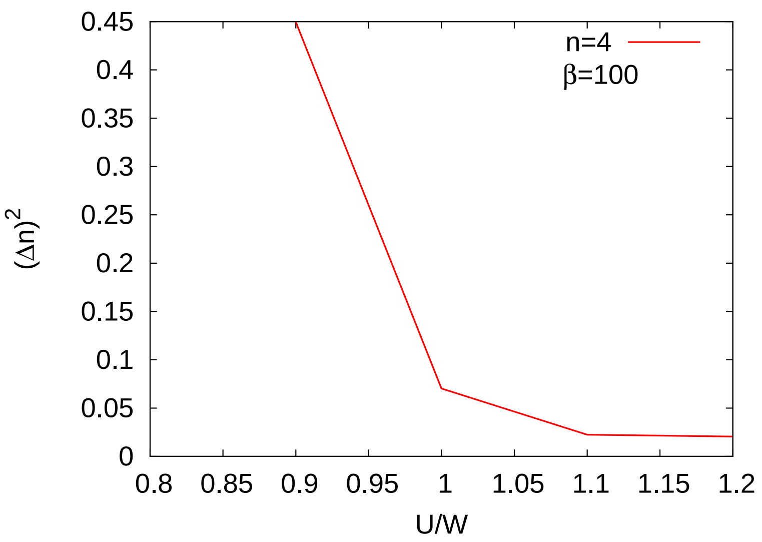
Study charge fluctuation

$$(\Delta n)^2 = \langle (n_i - \langle n_i \rangle)^2 \rangle.$$

Rozenberg, Chitra, and Kotliar, PRL **83**, 3498.

Filling 4: $U_c/W \approx 1$

(el-phon coupl. included).



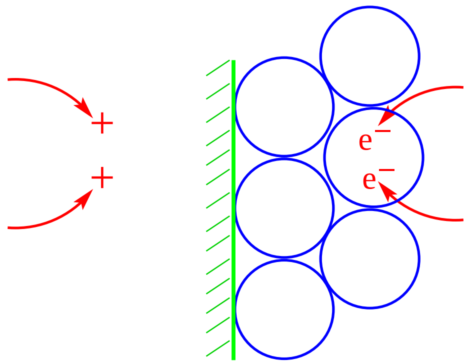
Dependence of U on layer index. K_4C_{60}

δU: Screening of charge on surface molecule due to other molecules and metal substrate.

$U = U_0 - \delta U$

$U_0 = 2.7$ eV is U for free molecule.

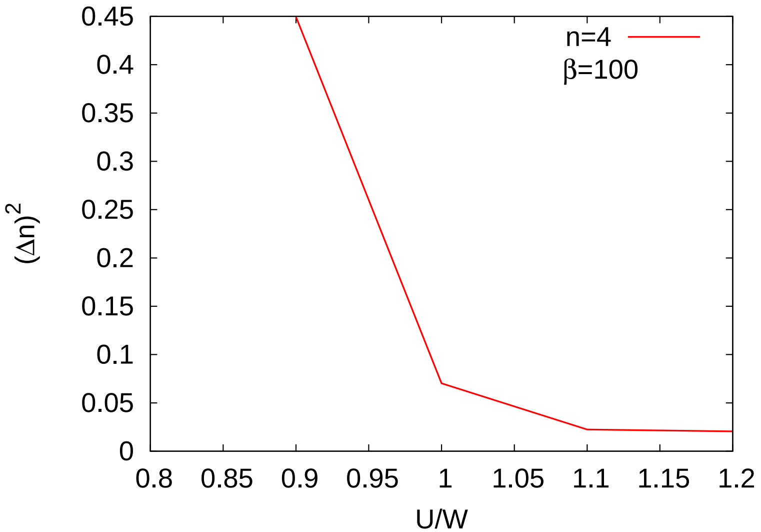
Layer	δU	$U_0 - \delta U$	$U - W$	Exp. Gap
1	1.85	0.85	0.29	0.2
2	1.49	1.21	0.65	0.6
3	1.31	1.39	0.83	0.8



Use charge fluctuation to determine metal-insulator transition.

$E_g \approx U - W$ (for K_4C_{60}).

$W = 0.56$ eV is band width of surface layer.



Preliminary data

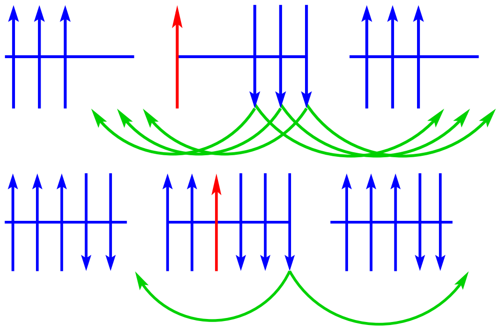
Exp: Wang, Yamachika, Wachowiak, Grobis, Crommie, Nature Materials **7**, 194 (2008).

Han and Gunnarsson (to be publ.)

Hopping. Filling dependence

n=3:

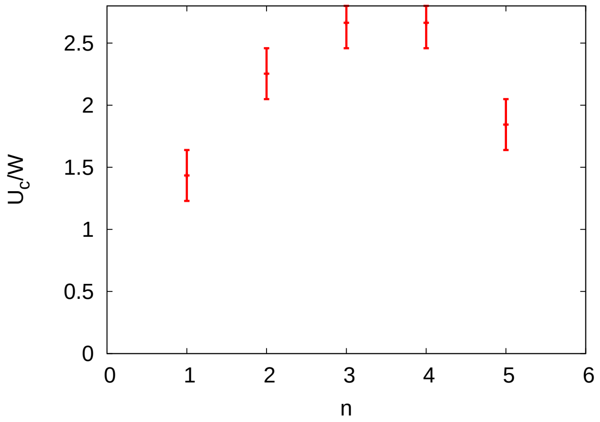
n=5:



Tends to make gap larger for n=5.

Electron-phonon coupling more effective for $n=3$ than $n=5$.

This tends to make gap larger for $n=3$ than $n=5$.



Fixed-node diffusion Monte Carlo. No el.-ph. coupl.

Koch, Gunnarsson, Martin, PRB **60**, 15714.

Kotliar and Kajueter, PRB **54**, R14221.

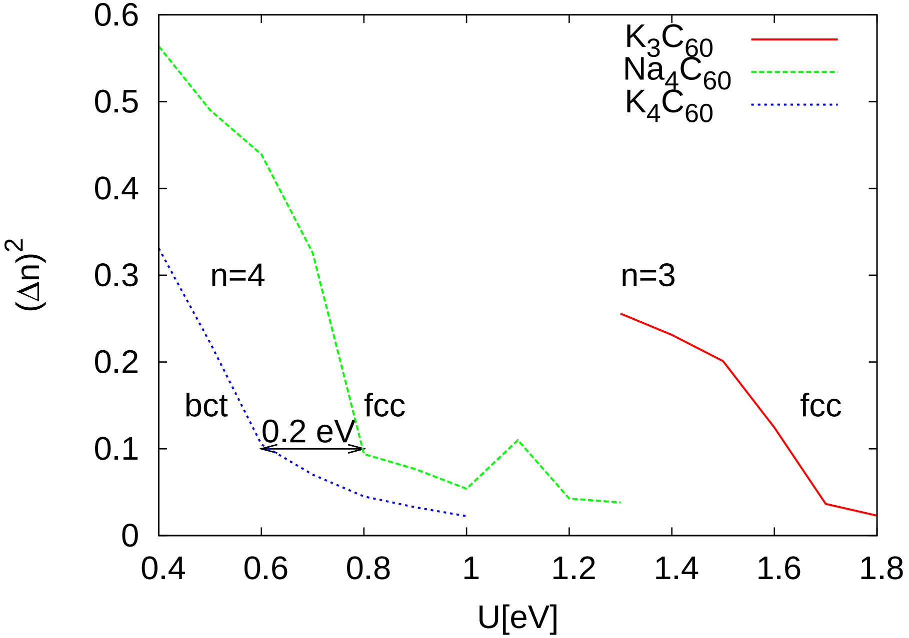
	K_3C_{60}	K_4C_{60}	K_5C_{60}
Exp.	0.2	0.8	0.4

Wang, Yamachika, Wachowiak, Grobis, Crommie, Nature Materials **7**, 194.

But gap larger for n=5 than n=3.

Hopping less efficient for $n=5$.

Metal-insulator transition



	fcc K_3C_{60}	fcc Na_4C_{60}	bct K_4C_{60}
U	1.04	1.07	1.10
U_c	1.7	0.8	0.6
Gap Theory	-0.7	0.3	0.5
Gap Exp	metal	0.25	0.50

Preliminary data

Determine U_c and put $E_g = U - U_c$.

Difference K_3C_{60} to K_4C_{60} mainly due to filling (efficiency of Jahn-Teller coupling), but also due to weaker hopping for K_4C_{60}.

Han and Gunnarsson (to be publ.)

Character of metal

1. Stoichiometric A_3C_{60} is an insulator but exp. A_3C_{60} is a metal because of deviations from stoichiometry (doped Mott insulator).

2. Stoichiometric A_3C_{60} is a metal but close to a Mott insulator.

I. 3rd layer of K_3C_{60} on Au: Small exp. gap (0.2 eV).

Bulk K_3C_{60}: W (0.79 vs. 0.56 eV) and U smaller (1.04 vs. 1.39 eV).
$\Rightarrow$ Metal.

II. Na_4C_{60}: Small exp. gap (.25 eV)

K_3C_{60}: Substantial reduction predicted (weaker effects of Jahn-Teller).
$\Rightarrow$ Metal.

Han and Gunnarsson (to be publ.)

Superconductivity

Conventional superconductors: $\omega_{\rm ph} \ll E_F$.

Retardation believed to reduce effects of U.

A_3C_{60}: $\omega_{\rm ph} \sim E_F$. Retardation effects small.

U is large.

What drives superconductivity?

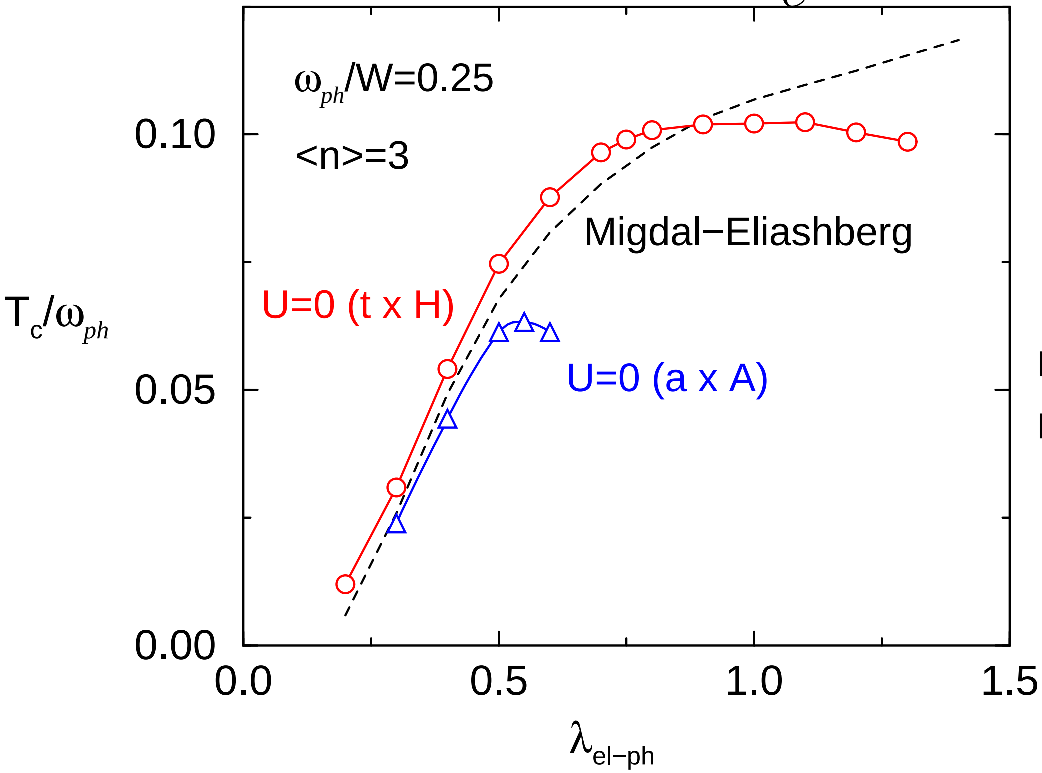
Syst.	Θ_D	E_F	Θ_D/E_F
Al	0.034	11.2	0.003
Ga	0.020	11.8	0.002
Mo	0.033	7.3	0.005
Cd	0.010	9.5	0.001
Pb	0.008	12.4	0.001
A_3C_{60}	0.1	0.3	0.3

Capone, Fabrizio, Castellani, Tosatti, Science **296**, 2364.

Capone, Fabrizio, Castellani, Tosatti, Rev. Mod. Phys. **81**, 943

Han, Gunnarsson, Crespi, PRL **90**, 167006.

T_c for $U = 0$.



Han, Gunnarsson, Crespi, PRL **90**, 167006.

DMFT.

Small and intermediate λ:

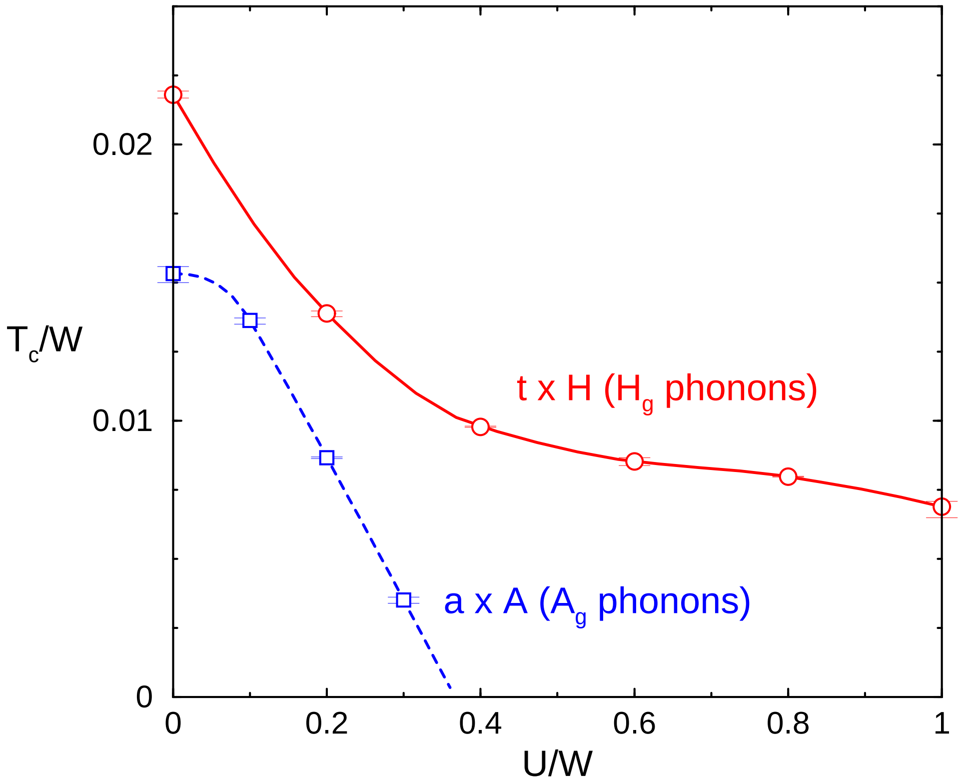
$t \times H$, $a \times A$ models $\Rightarrow$ Similar T_c.

Migdal-Eliashberg rather accurate although $\omega_{ph}/W = \frac{1}{4}$.

Large values of λ:

Close to metal-insulator transition. T_c. suppressed.

T_c for finite U



$\lambda = 0.6, \omega_{ph}/W = 0.25.$

Han, Gunnarsson, Crespi,

PRL **90**, 167006.

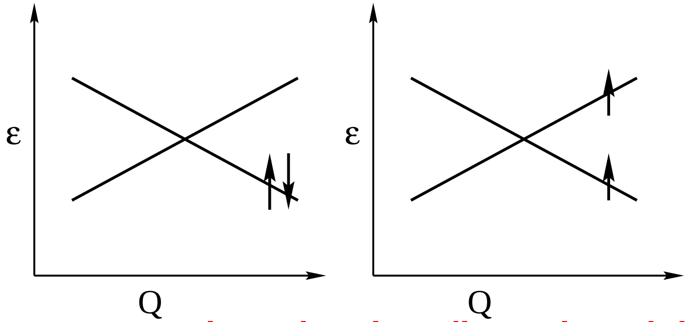
DMFT.

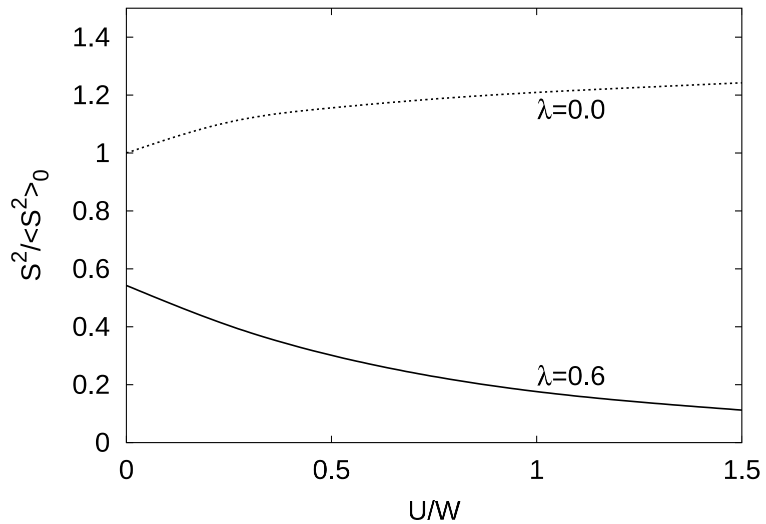
Completely different behavior for $t \times H$ and $a \times A$ models.

T_c drops rapidly with U for $a \times A$ but not for $t \times H$ model.

Slow drop with U crucial for A_3C_{60}.

Local pairing. Jahn-Teller phonons. $e \times E$





Free mol.: Singlet (local pairing) favorable.

No competition with Hubbard U.

$|0\rangle = \frac{1}{\sqrt{2}} \sum_m c^\dagger_{m\uparrow} c^\dagger_{m\downarrow} |\mathrm{vac}\rangle$.

Competition: Hopping $\leftrightarrow$ Jahn-Teller effect. Hopping tends to spread the electrons arbitrarily over the levels. $U = 0$: Hopping wins.

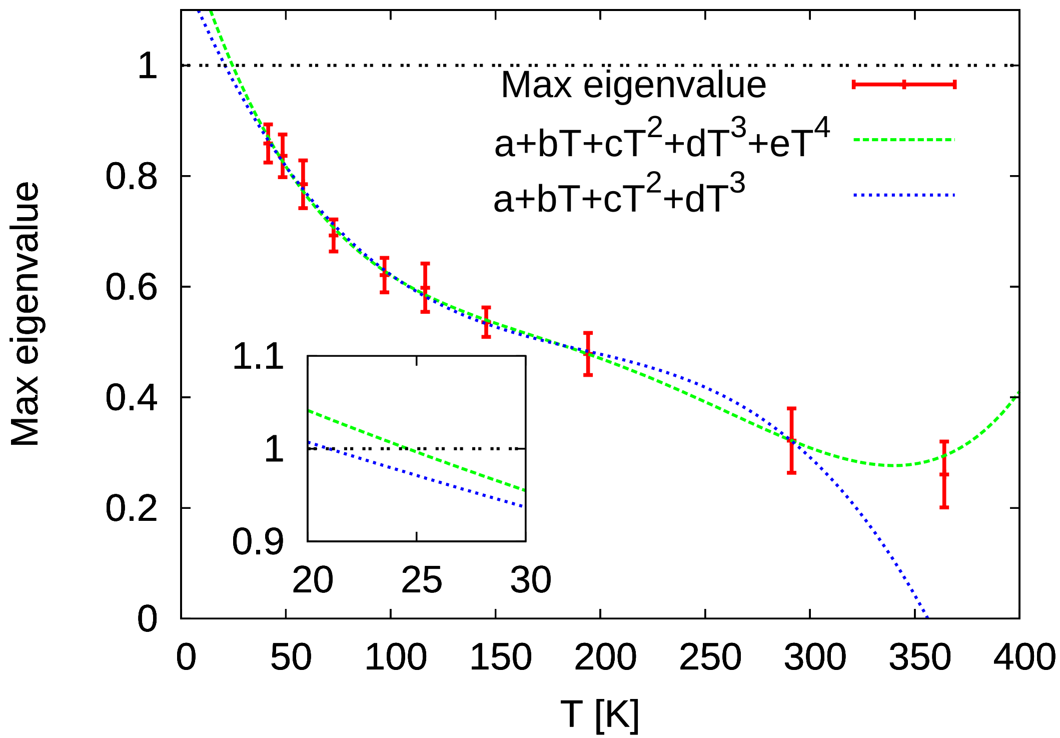
Competition: Hopping $\leftrightarrow$ Coulomb repulsion. Hopping reduced.

Local pairing becomes important. U *helps* local pairing.
Favors superconductivity. Sum rule $\Rightarrow$ Eff. attractive int.

But U disfavors formation of coherent state.

Present parameters: Superconductivity moderately hurt by U.

Absolute size of T_c for K_3C_{60}



$$\chi = (1 - \chi_0 \Gamma)^{-1} \chi_0.$$

Eigenvalues of $\chi_0 \Gamma$.

Preliminary data

Use parameters obtained earlier to calculate T_c.

K_3C_{60}: $T_c \sim 20 - 25$ K. Exp.: $T_c = 19$ K. Right order of magnitude!

Rb_3C_{60}: Probably insulator. Exp.: $T_c = 29$ K.

Han and Gunnarsson (to be publ.)

Summary

1. Phonon symmetry crucial:

   A. H$_g$(A$_g$) phonons reduce (increase) U_c for metal-insulator trans.

   B. Superconductivity: H$_g$ (but not A$_g$) phonons overcome U.

2. A$_4$C$_{60}$ (insulator) vs. A$_3$C$_{60}$ (metal):

   A. Factors: a) El.-ph. coupl. b) lattice struct. c) filling d) degeneracy

   B. Main diff.: Jahn-Teller phonons reduce U_c more for $n = 4$.

   C. U_c/W smaller for bct (A$_4$C$_{60}$) than fcc (A$_3$C$_{60}$) lattice.

3. Same param. describe metal-insulator trans. and supercond.