The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization
IAEA

2157-1

Workshop on Principles and Design of Strongly Correlated Electronic Systems

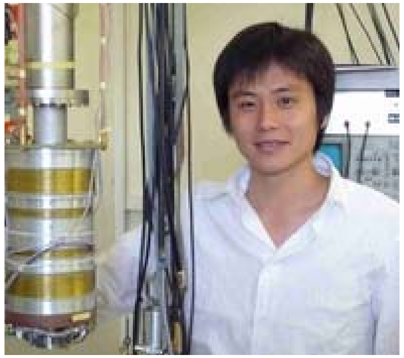
2 - 13 August 2010

NMR Study of the Pressure Induced Mott Transition to Superconductivity in the Two Phases of Cs3C60

Henri ALLOUL

Universite de Paris XI (Paris-Sud)
Lab.de Physique des Solides Batiment 510
F-91405 Orsay cedex
FRANCE

NMR study of the pressure induced Mott transition to superconductivity in the two phases of Cs_3C_{60}



Y. Ihara H. Alloul P. Wzietek

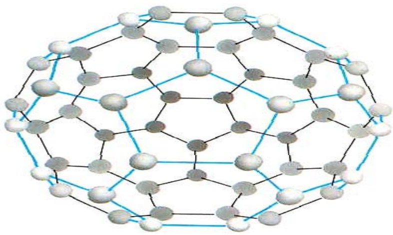
Laboratoire de Physique des Solides, Université Paris XI, Orsay, France.

Daniele Pontiroli, Marcello Mazzani, Mauro Riccò.

CNISM and Dipartimento di Fisica, Universita di Parma

V.Brouet

*PRL, **104**,256402 (2010).*



V. Brouet, H. Alloul *et al*

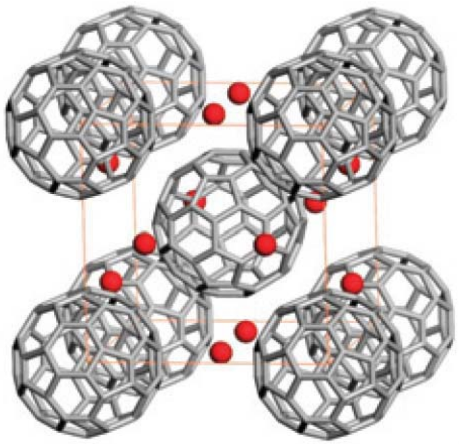
*PRL, **82**,2131 (1999); **86**,4680(2001);*

*PR **B**, **66**, 155122 , 15123, 15124(2002).*

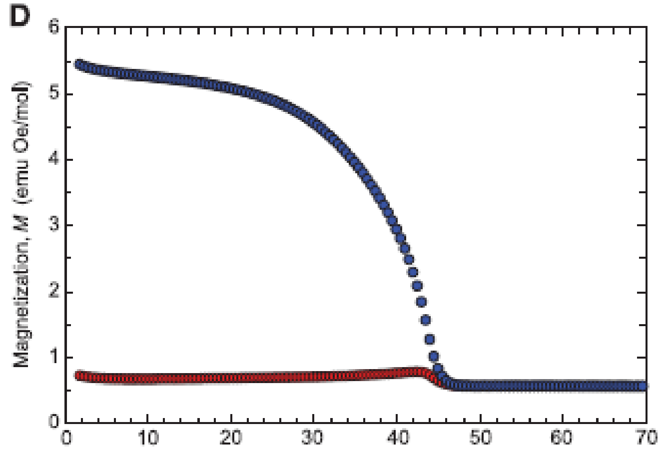
TRIANGLE DE LA PHYSIQUE

LPS ORSAY

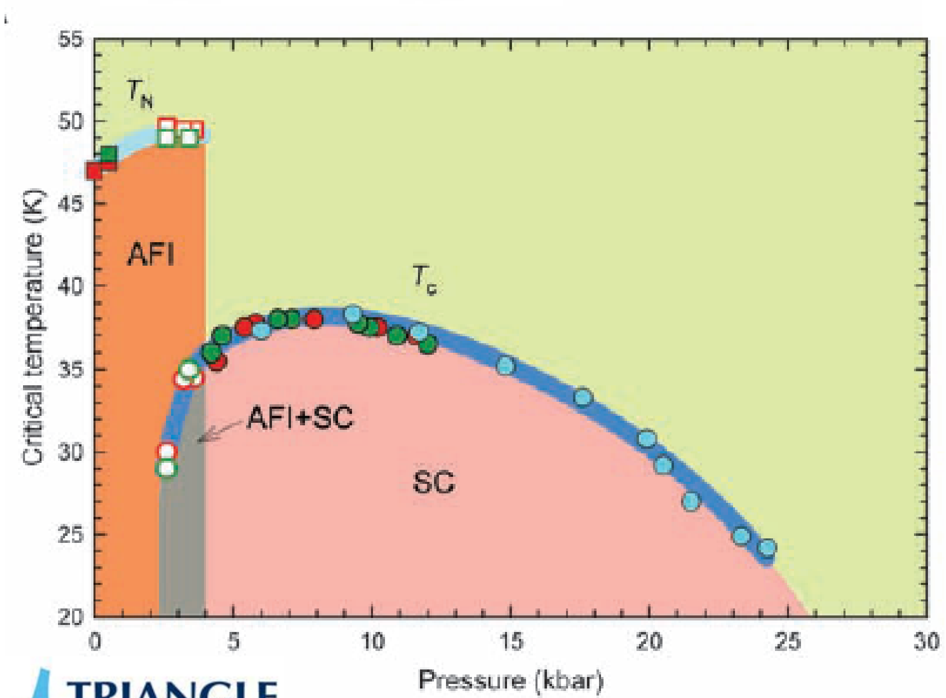
A15 Cs_3C_{60} : magnetic at ambiant pressure



M



T



SC induced by pressure
Proximity of magnetism and SC.

Palstra et al. Sol. Stat. Commun. 93 327 (1995).

A Ganin et al Nature Materials, April 2008

Takabayashi et al , Science 2009

TRIANGLE DE LA PHYSIQUE

LPS ORSAY

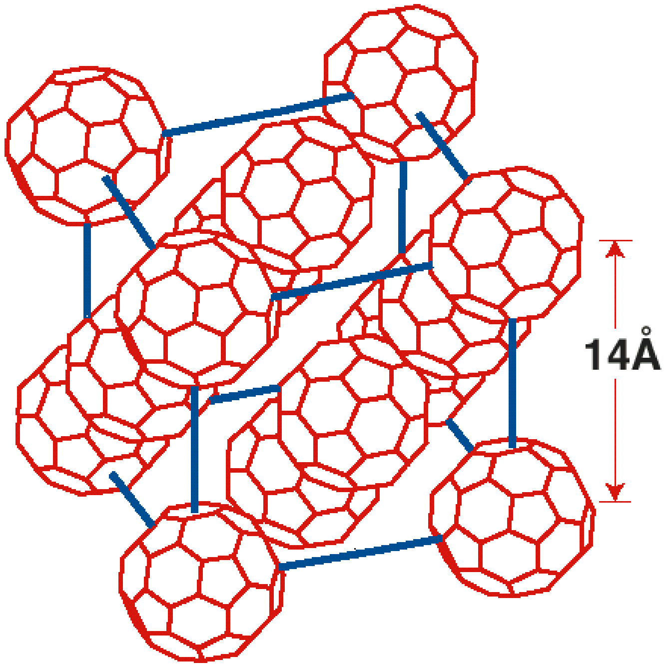
NMR study of the pressure induced Mott transition to superconductivity in the two phases of Cs_3C_{60}

- **Introduction: A_3C_{60} and their superconductivity**
  - **LDA Electronic structure**
  - **BCS SC :** Coupling of electrons with molecular phonons
  - **Electronic correlations?** Study Other stochiometries!
- **Electronic correlations and Jahn Teller distorsions**
  - **Na_2C_{60} and A_4C_{60} : Mott Jahn-Teller insulators**
    Electronic interactions mediated by JTD
  - **$A_1 C_{60}$ Mott insulator?**
    Low *T* charge segregation
- **Expanded magnetic compounds and Cs_3C_{60} phases**
  - **AF phases for large lattice spacings**
  - **Magnetism in A15 and fcc phases of Cs_3C_{60}**
  - **Pressure induced superconductivity**
- **Conclusion: phase diagram for the A_3C_{60} phases**

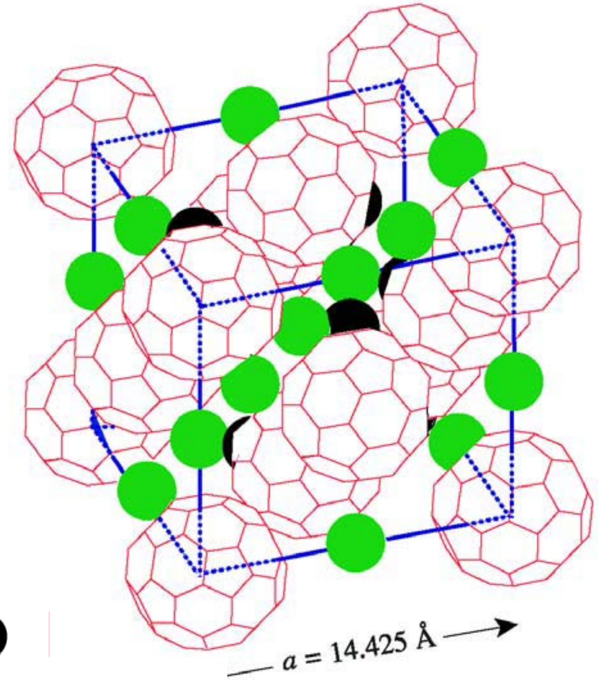
TRIANGLE DE LA PHYSIQUE

LPS ORSAY

sc and fcc phases of fullerides



Solid C_{60}



tetrahedral A site

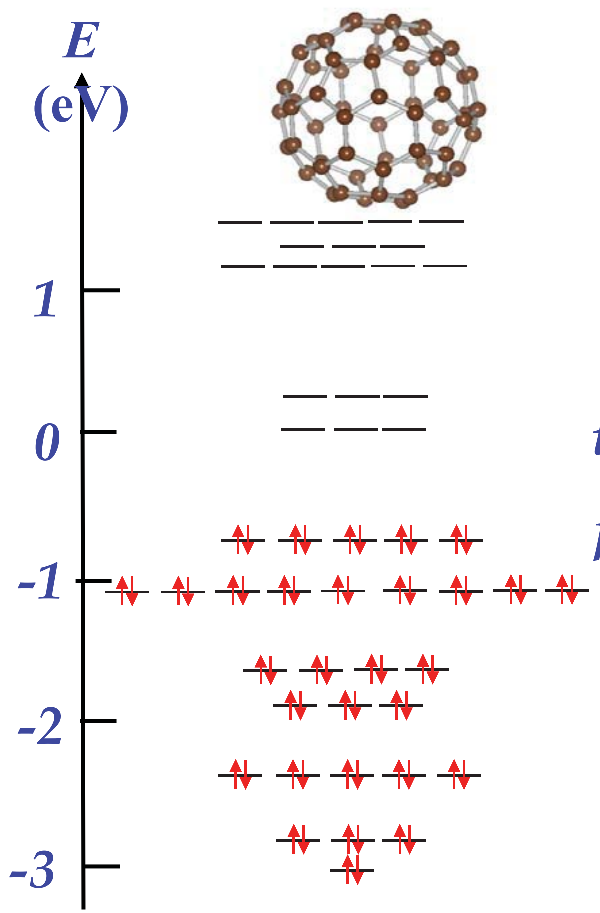
octahedral A site

A_3C_{60}
(A= K , Rb, Cs)

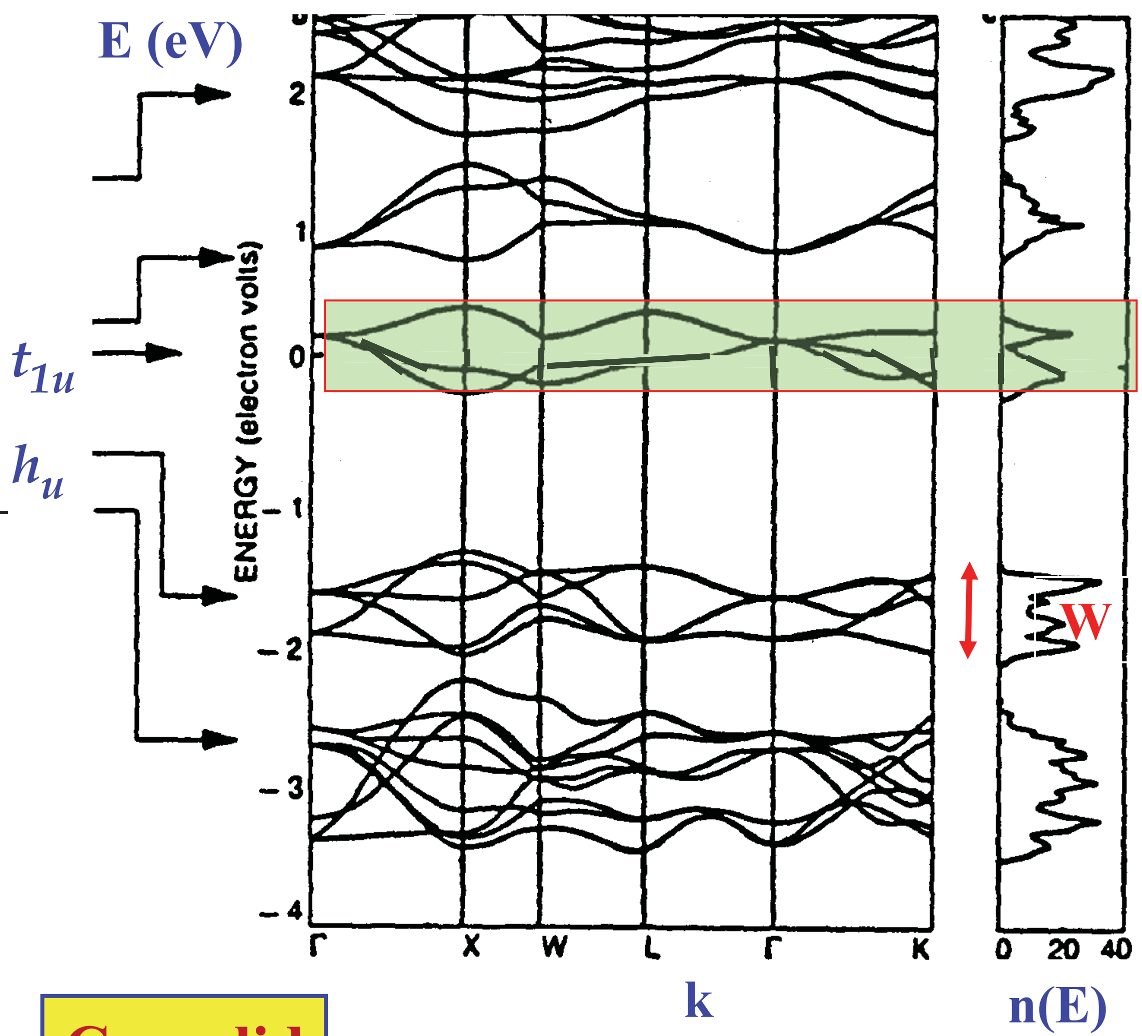
High T_c superconductors

Electronic structure of doped fullerides

C. H. Pennington RMP 1995.



C_{60} molecule



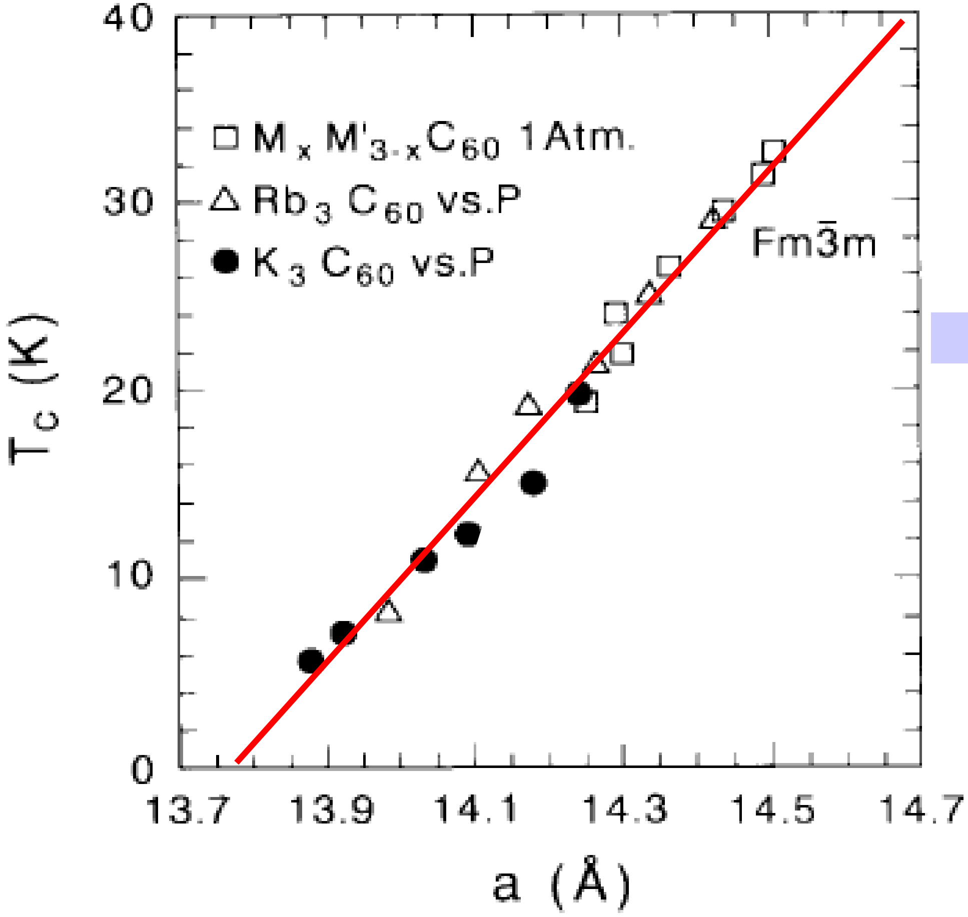
C_{60} solid

W= 0.5 eV

TRIANGLE DE LA PHYSIQUE

LPS ORSAY

Superconductivity in A_3C_{60}



$$k_B T_c = 1.14\hbar\omega_D \exp\left[-\frac{1}{V_0\, n(E_F)}\right]$$

T_c depends only on $n(E_F)$

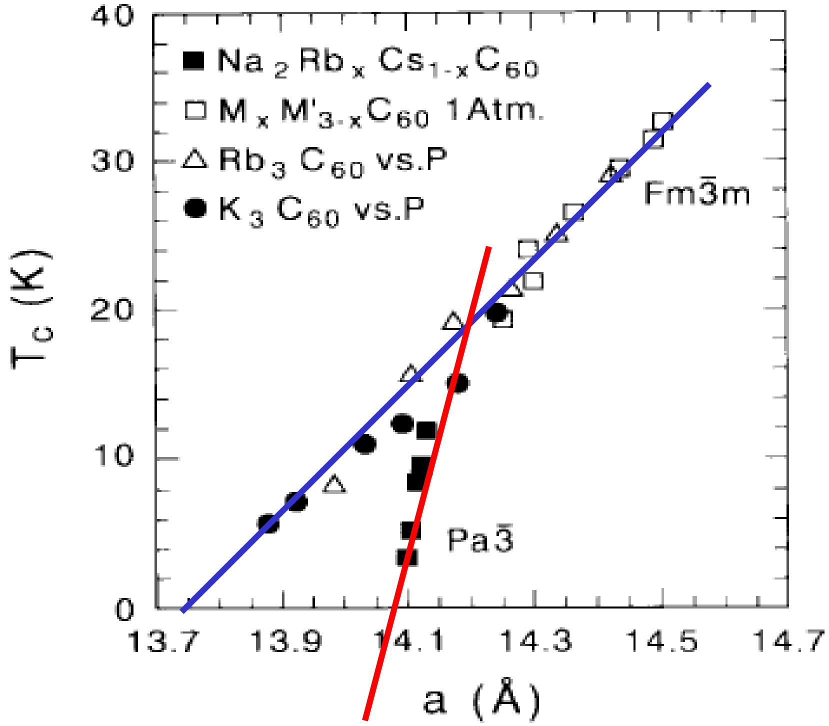
$\hbar\omega_D$ **and** V_0

are molecular properties

Only C_{60} phonons are involved

The scaling between T_c and the lattice parameter is assumed to support a BCS-like mechanism

Difference between Na_2AC_{60} and the other A_3C_{60}



Yildirim et al. MRS proceedings 359 273 (1995).

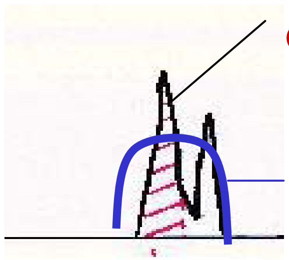
Na_2AC_{60} sc Pa3 structure

other A_3C_{60} are fcc

-Different slope for sc phases ?

- Different variation of $n(E_F)$?

- Alkali plays a role after all ?



What happens then for other *n* values ?

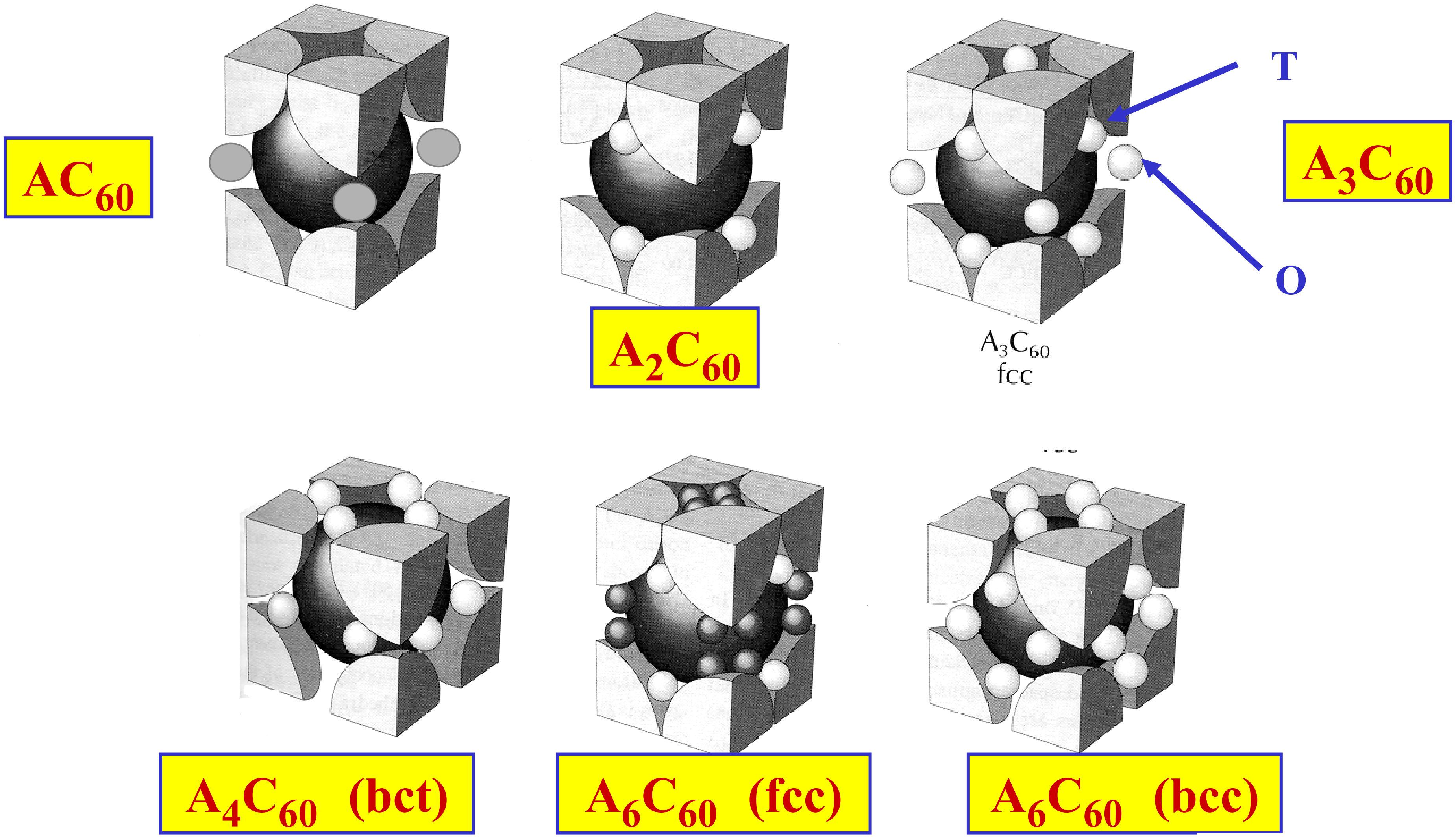
NMR study of the pressure induced Mott transition to superconductivity in the two phases of Cs_3C_{60}

- **Introduction: A_3C_{60} and their superconductivity**
  - **LDA Electronic structure**
  - **BCS SC :** Coupling of electrons with molecular phonons
  - **Electronic correlations?** Study Other stochiometries!
- **Electronic correlations and Jahn Teller distortions**
  - **Na_2C_{60} and A_4C_{60} : Mott Jahn-Teller insulators**
    Electronic interactions mediated by JTD
  - **$A_1 C_{60}$ Mott insulator?**
    Low *T* charge segregation
- **Expanded magnetic compounds and Cs_3C_{60} phases**
  - **AF phases for large lattice spacings**
  - **Magnetism in A15 and fcc phases of Cs_3C_{60}**
  - **Pressure induced superconductivity**
- **Conclusion: phase diagram for the A_3C_{60} phases**

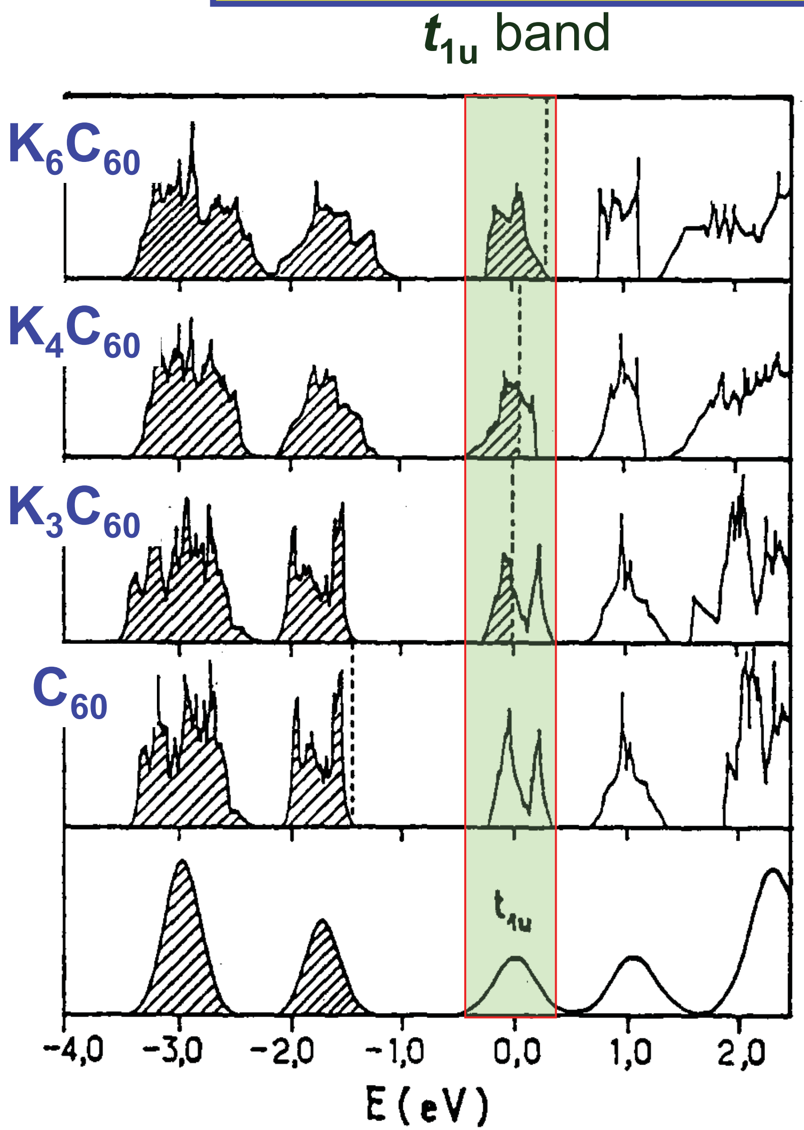
TRIANGLE DE LA PHYSIQUE

LPS ORSAY

The various cubic alkali A_nC_{60} phases



The anomalous properties of A_nC_{60} compounds



Electronic doping of triply degenerate t_{1u} orbitals

All compounds with n<6 should be metallic.

But…

x = 4 : Insulator (bct)

K_4C_{60}, G. Zimmer EPL 1994, V. Brouet PRB 2002.

***x* = 3 : Superconductor** (fcc, cubic)

x = 2 : Insulator (cubic)

Na_2C_{60}, F. Rachdi PRB 1997, V. Brouet PRL 2001, PRB 2002.

x = 1 : Mott-Insulator or metal?

polymer-Cs_1C_{60}, V. Brouet PRL 1996, B. Simovic Synth. Met. 1999.

cubic--Cs1C60, V. Brouet PRL 1999.

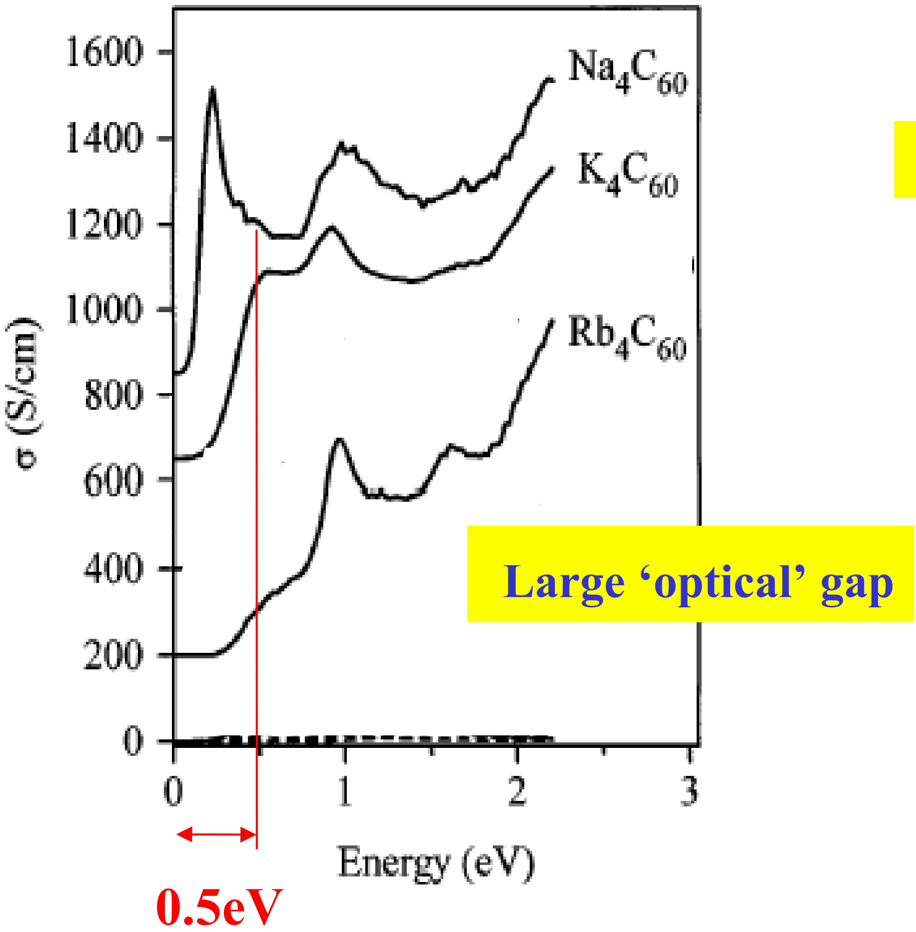
TRIANGLE DE LA PHYSIQUE

Strong correlations and Jahn-Teller distortions (JTD)

LPS ORSAY

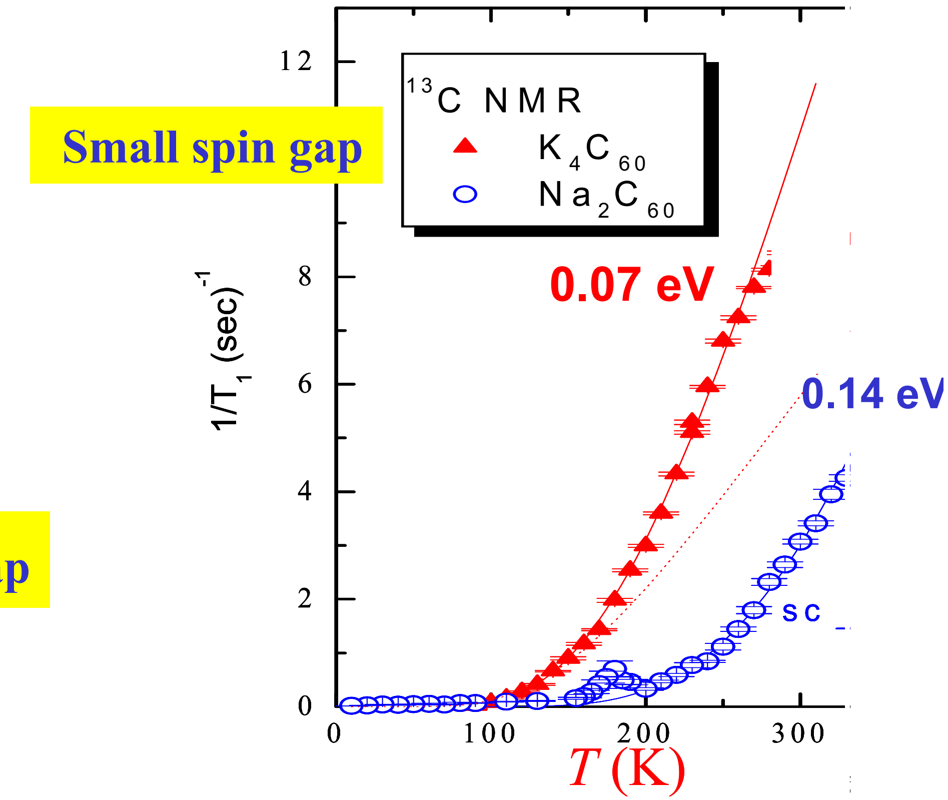
Electronic properties of A_4C_{60} (bct) and Na_2C_{60} (cubic)

Optical conductivity σ extracted by EELS



M. Knupfer et al, PRL **79**, 2714 (1997).

NMR $1/T_1$



K4C60: G. Zimmer et al EPL (1994), V. Brouet et al , PRB 66 155122 (2002).Na2C60, F. Rachdi et al, PRB 1997, V. Brouet et al PRL 2001, PRB 2002

Insulating non magnetic ground state

Stabilization of the singlets

Why singlets? Two electrons on a ball costs an energy ***U***

So there is an energy gain which opposes to *U*

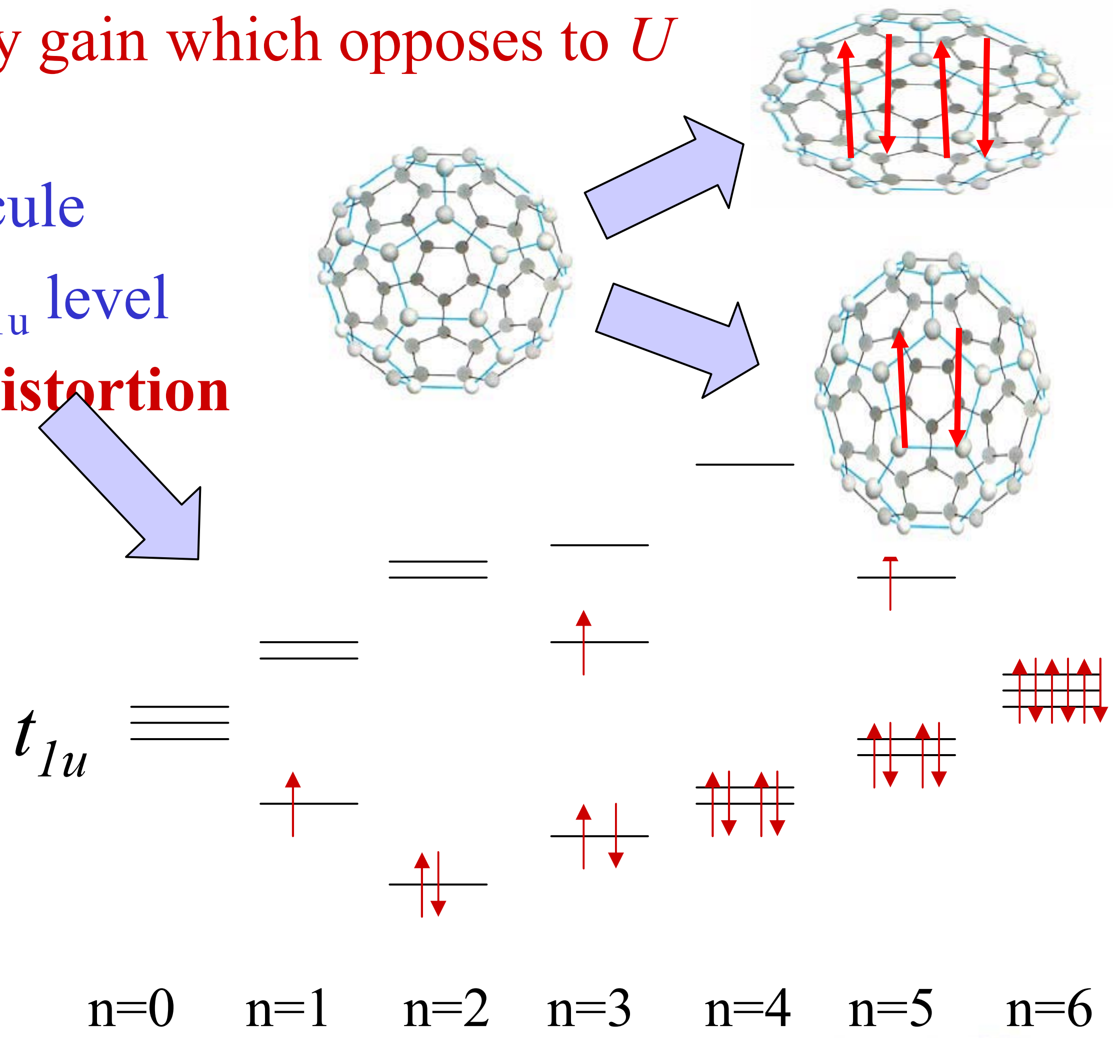
For a charged molecule

The degeneracy of the t_{1u} level

is lifted by a **Jahn Teller distortion**

The Jahn-Teller splitting of the t_{1u} level depends on the C_{60} charge

Manini, Tosatti PRB94



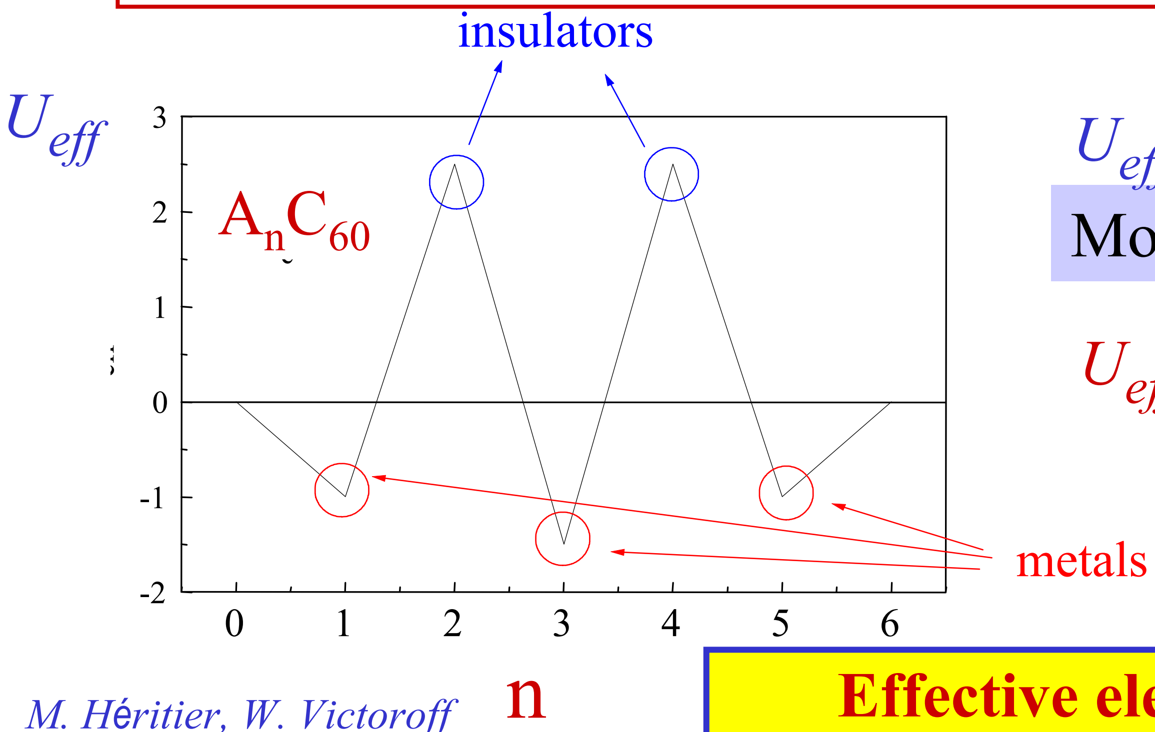
The larger gain per electron is for n=2 or 4

Strong electronic correlations induce the insulating behaviour

In all A_nC_{60} the coulomb repulsion U is large

The Jahn-Teller distortion adds a contribution U_{eff} to U

Yields a S=0 ground state rather than S=1 for n =2 or 4



U_{eff} adds to U for even n

Mott Jahn-Teller insulators

U_{eff} reduces U for odd $\boldsymbol{n}$

M. Héritier, W. Victoroff
O. Gunnarson
M. Fabrizio, E. Tosatti

Effective electronic interactions mediated by Jahn-Teller distortions

TRIANGLE DE LA PHYSIQUE

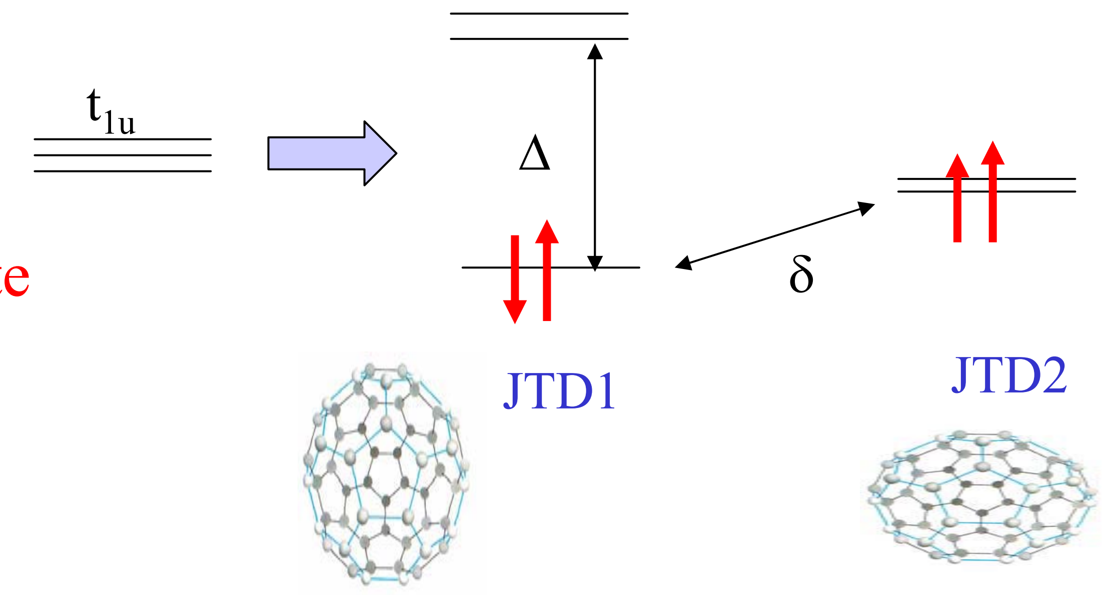
LPS ORSAY

Insulating states of A_4C_{60} and Na_2C_{60}

Fabrizio, Tosatti PRB97

Experimental situation

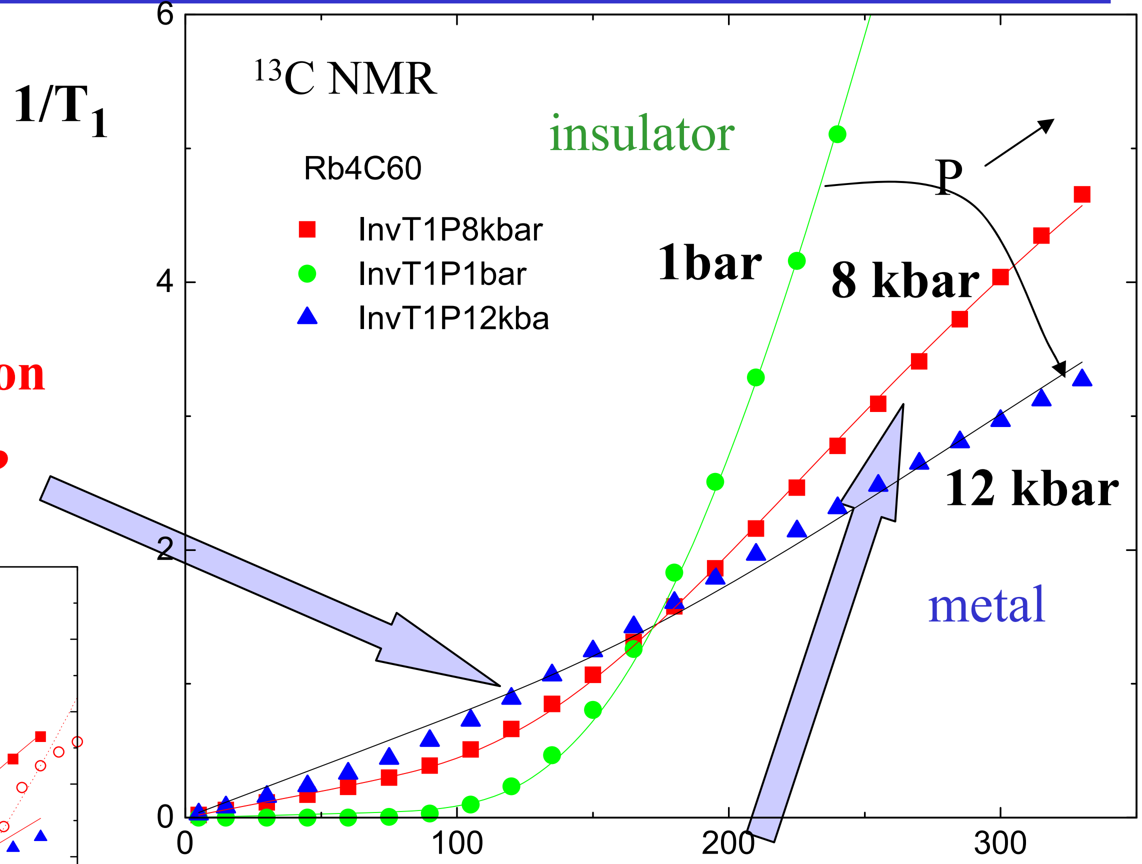
- Non magnetic ground state
- 2 different gaps



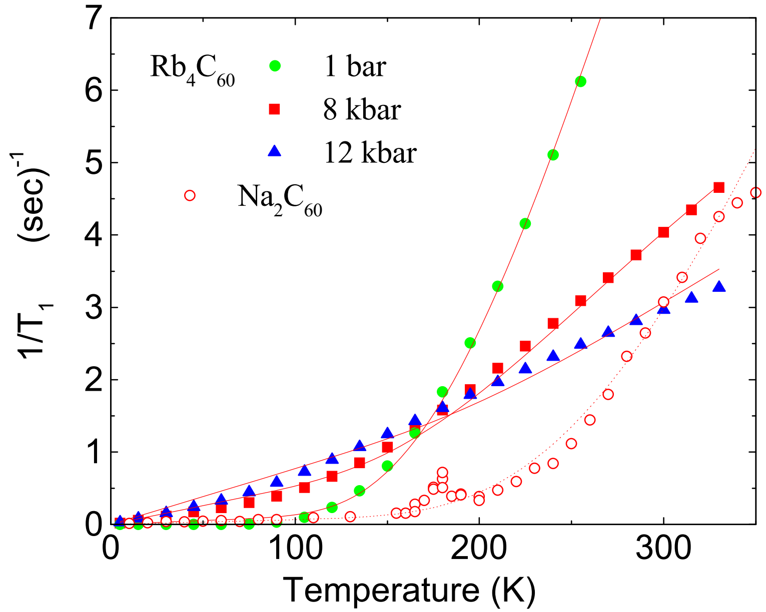
- **Hund's rule is not obeyed** in the fundamental JTD1 state
- **Excited state is triplet** and corresponds to a different JTD2
- NMR detects the **Singlet Triplet excitation δ**

Pressure induced insulator to metal transition in Rb_4C_{60}

R. Kerkoud, D. Jerome et al.



A low *T* metallic contribution appears with increasing *P*



Coexistence of metallic and molecular excitations for intermediate pressures

Kondo like resonance peak near a MIT?

TRIANGLE DE LA PHYSIQUE

LPS ORSAY

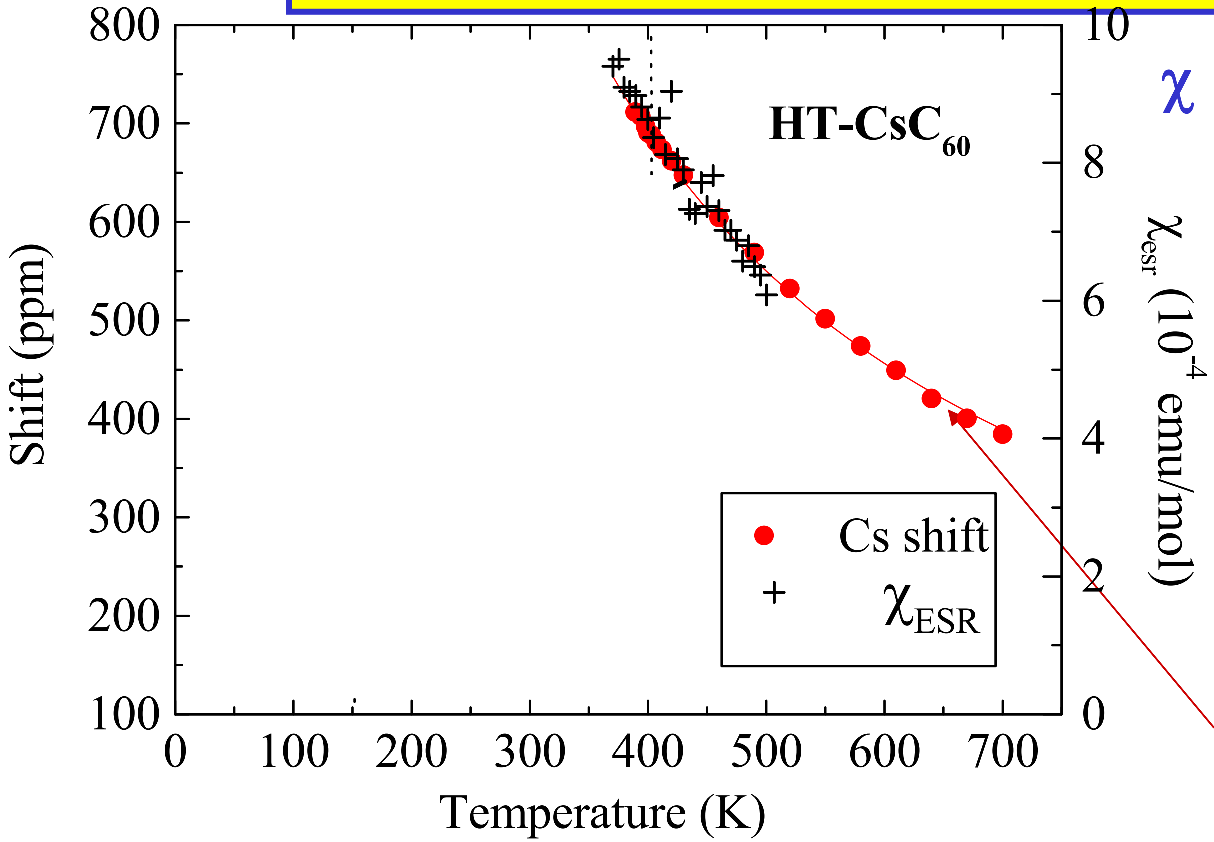
NMR study of the pressure induced Mott transition to superconductivity in the two phases of Cs_3C_{60}

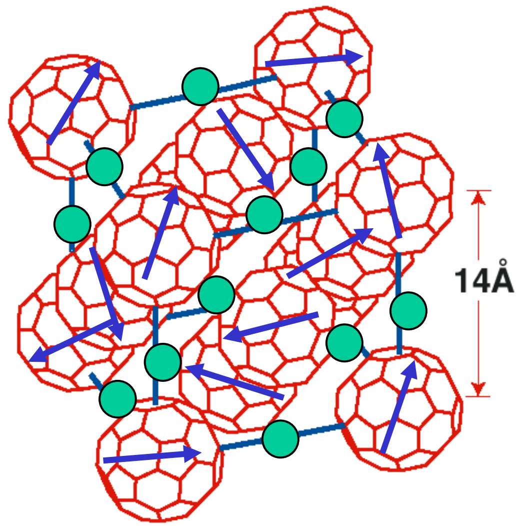
- **Introduction: A_3C_{60} and their superconductivity**
  - **LDA Electronic structure**
  - **BCS SC :** Coupling of electrons with molecular phonons
  - **Electronic correlations?** Study Other stochiometries!
- **Electronic correlations and Jahn Teller distorsions**
  - **Na_2C_{60} and A_4C_{60} : Mott Jahn-Teller insulators**
    Electronic interactions mediated by JTD
  - **$A_1 C_{60}$ Mott insulator?**
    Low *T* charge segregation
- **Expanded magnetic compounds and Cs_3C_{60} phases**
  - **AF phases for large lattice spacings**
  - **Magnetism in A15 and fcc phases of Cs_3C_{60}**
  - **Pressure induced superconductivity**
- **Conclusion: phase diagram for the A_3C_{60} phases**

TRIANGLE DE LA PHYSIQUE

LPS ORSAY

The special case of the cubic phase of CsC_{60}





$$\chi_P = \frac{g^2 \mu_B S(S+1)}{3k_B(T+\theta)}$$

with S=1/2 and θ<5K

Strong correlations for A_3C_{60} as well ?

Both NMR and ESR indicate a paramagnetic Curie law for fcc AC_{60}

So CsC_{60} is a Mott insulator

TRIANGLE DE LA PHYSIQUE

LPS ORSAY

Phase diagram for AC_{60}

CsC_{60}

High T cubic phase

310K

Polymer

200K Quench

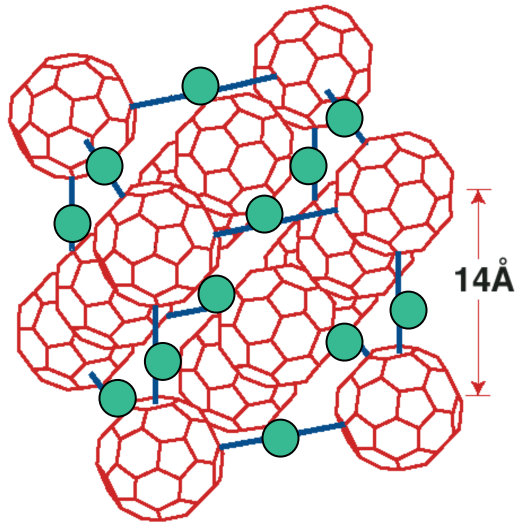
Dimer phase

77K Quench

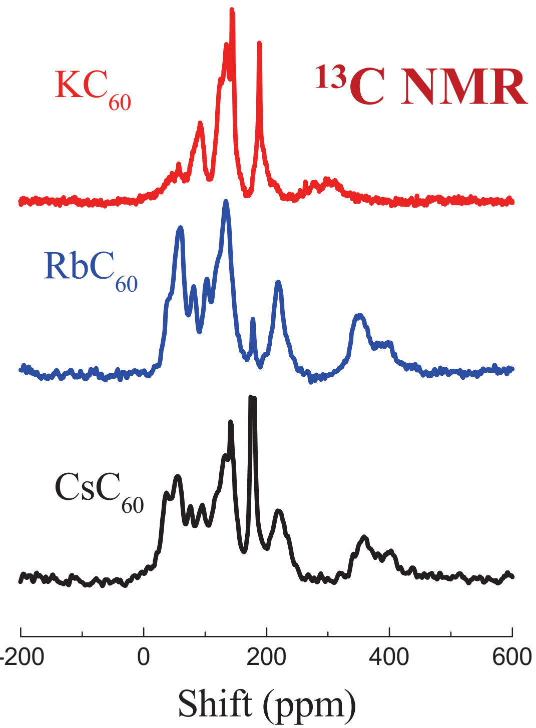
Quenched cubic phase

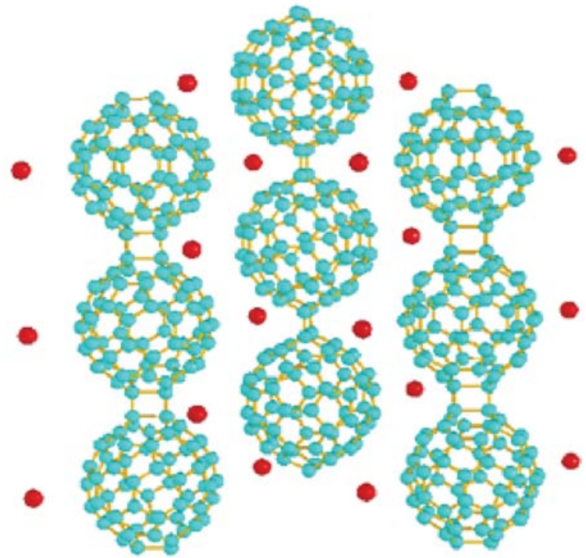
300 K, MAS 18 kHz

cubic phase



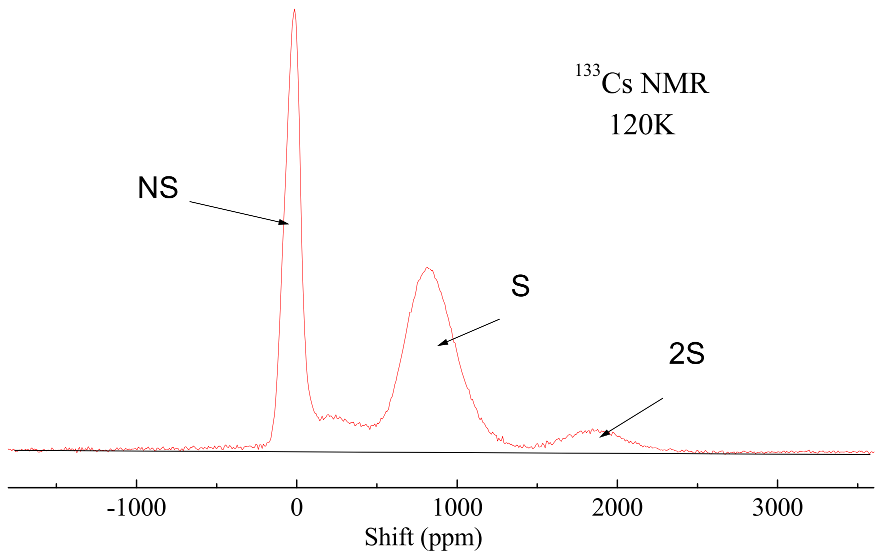
Polymer phase



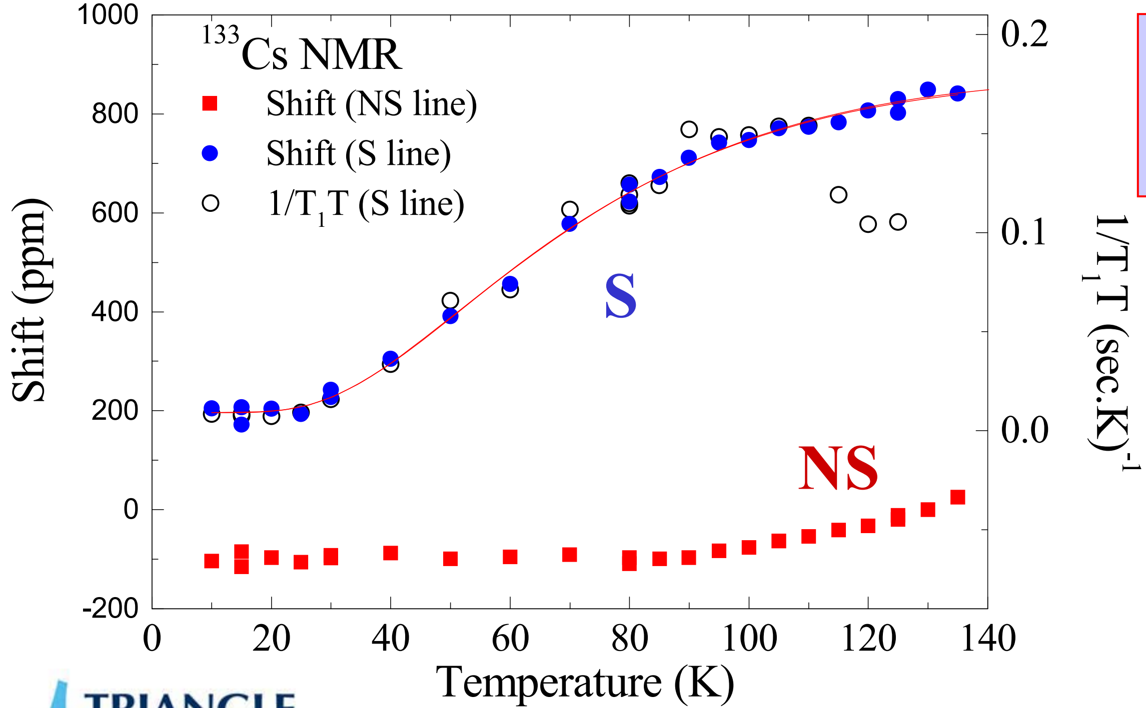


Cs NMR in CQ-CsC_{60}

Three Cs lines for one Cs site?



χ

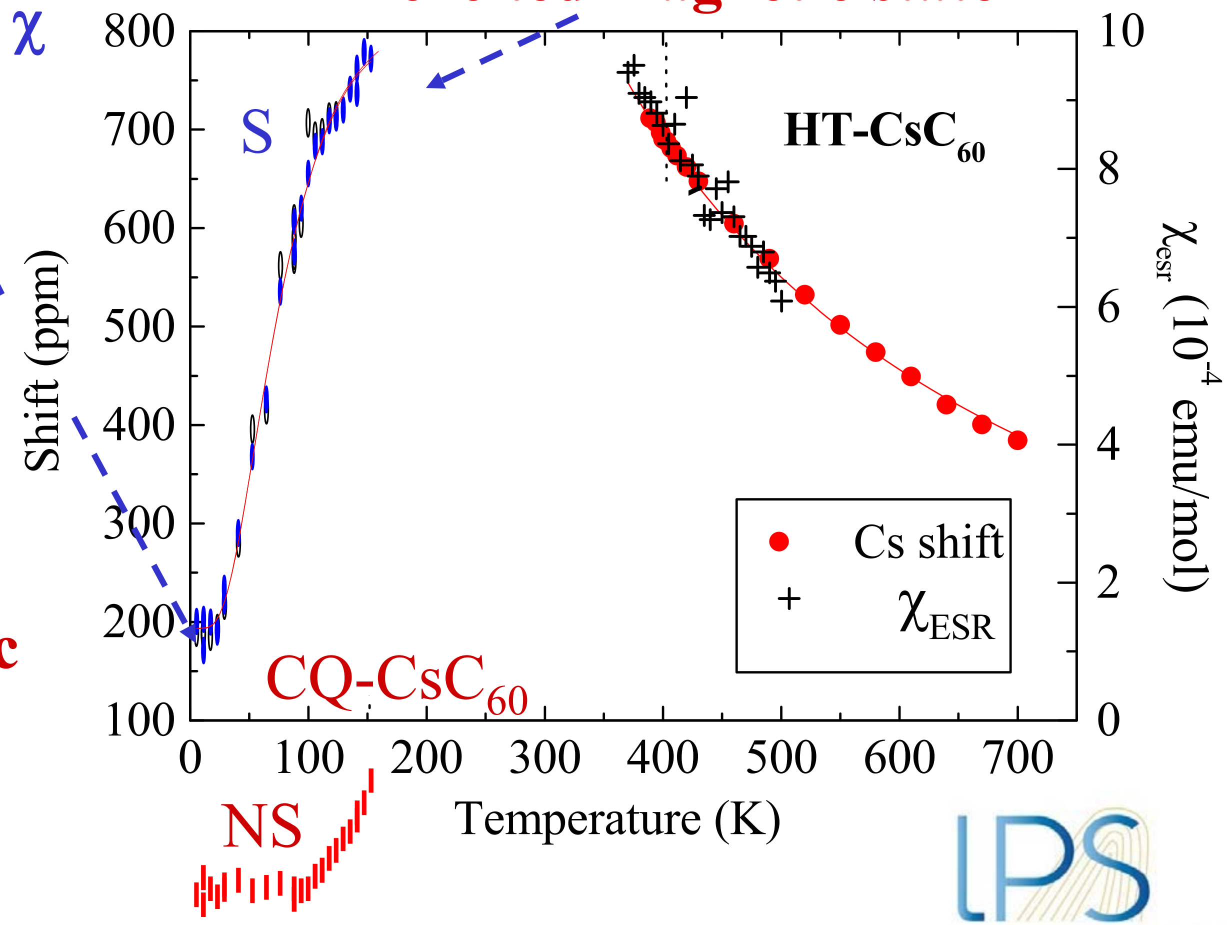


Sites with different electronic environments

Comparison of Cs NMR in QC- CsC_{60} and HT- CsC_{60}

Very different from HT cubic phase

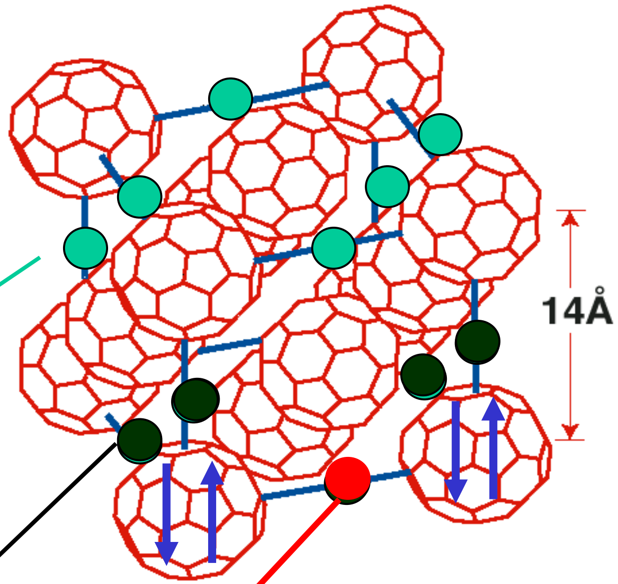
S (and 2S) sense a transition from a **local non-magnetic ground state** …… towards an **excited magnetic state**



NS has a non magnetic *T* dependence

H. Alloul, ICTP Trieste, 05/08/2010

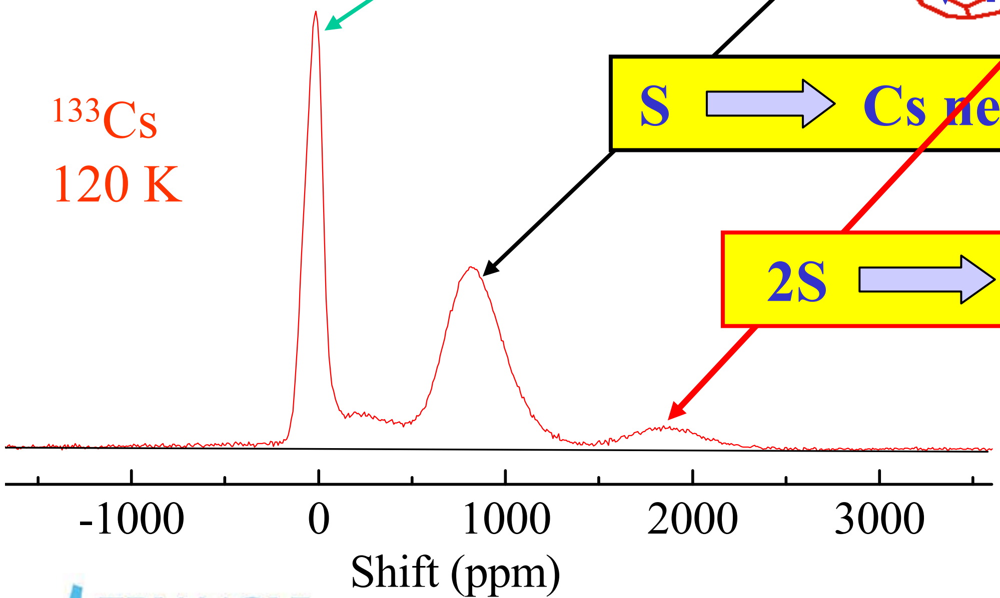
Evidence for charge segregation: singlet states



NS far from singlets$^-$

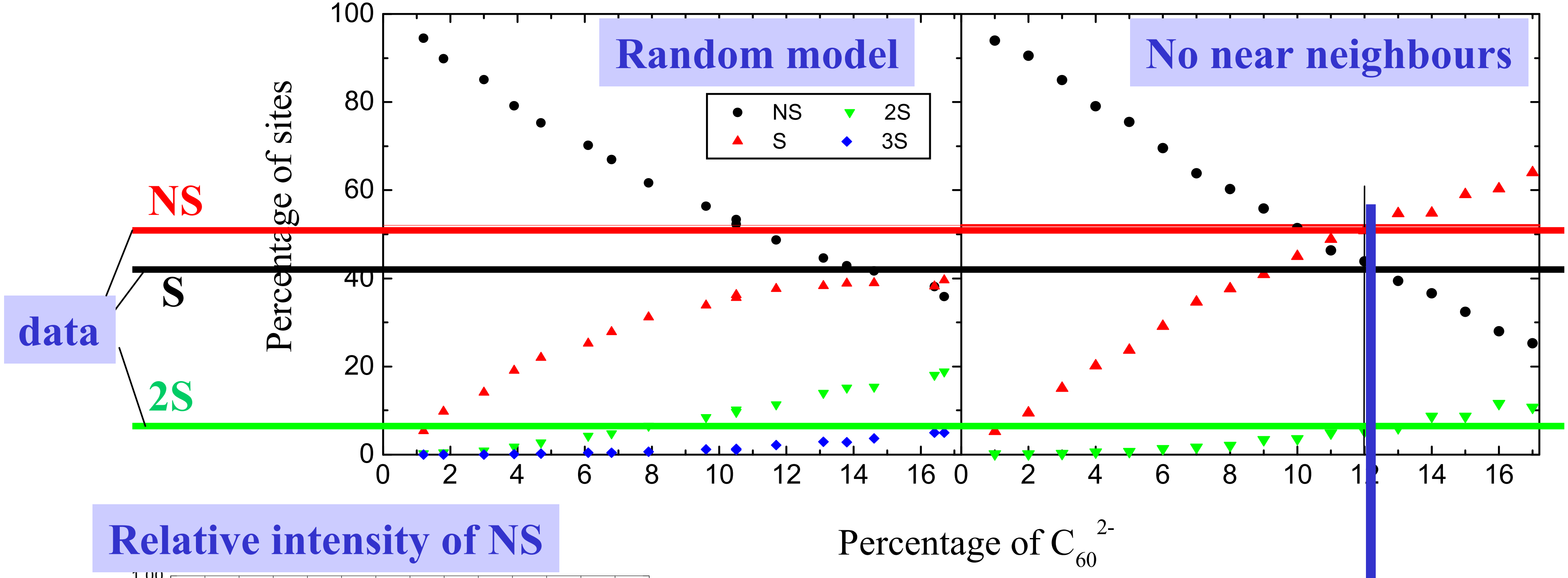
S ⇨ Cs neighbors of one localized C_{60}^{2-}

2S ⇨ Cs neighbors of two localized C_{60}^{2-}



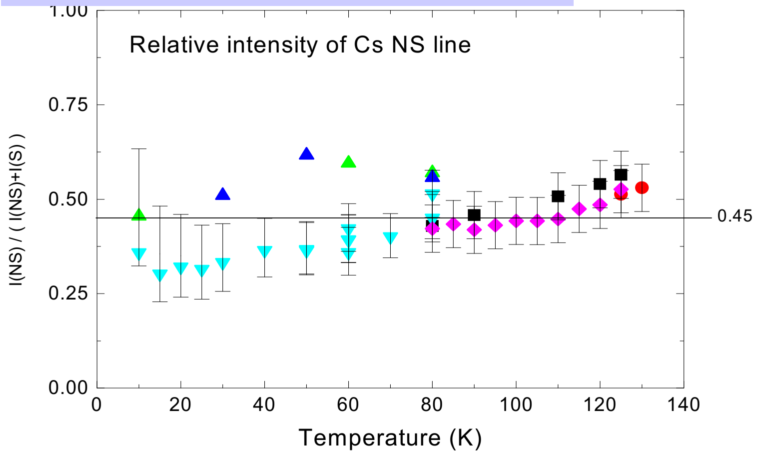
V. Brouet et al , PRL 1999.

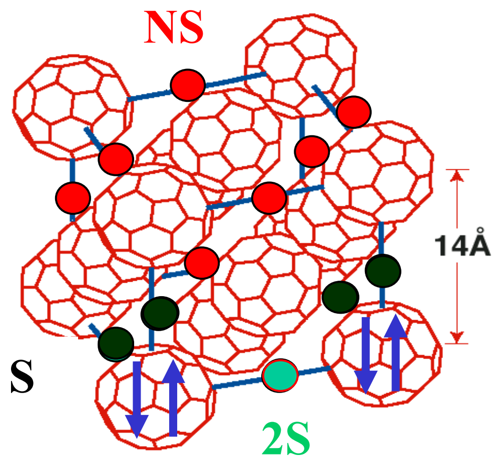
Intensity analysis of trapped C_{60}^{2-}



12% of singlets

Relative intensity of NS





No first *n.n.*

H. Alloul, ICTP Trieste, 05/08/2010

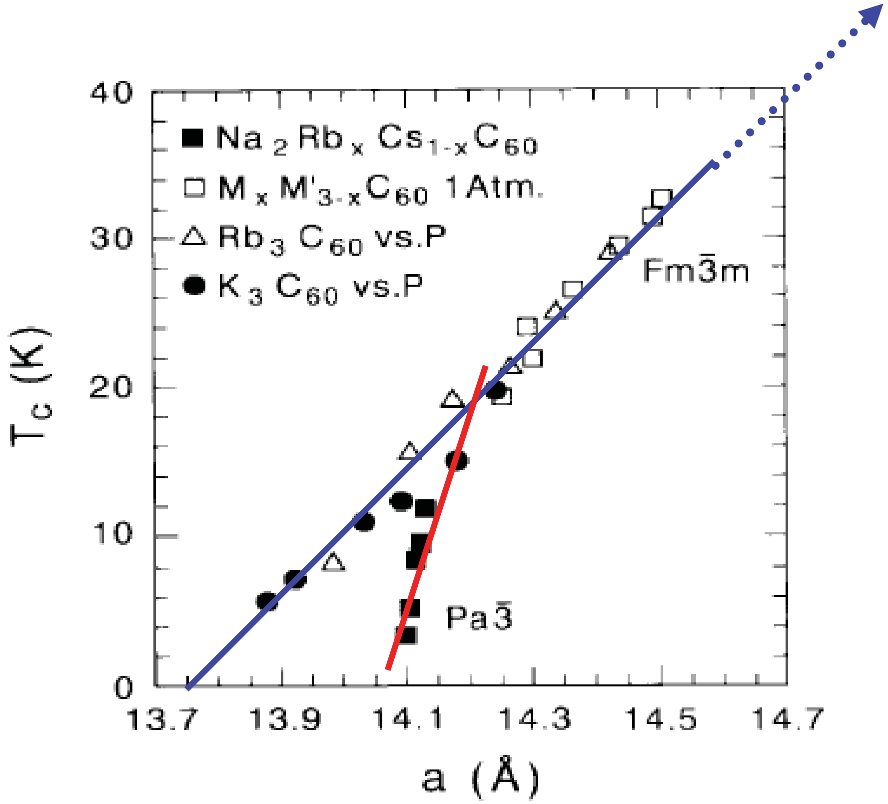
NMR study of the pressure induced Mott transition to superconductivity in the two phases of Cs_3C_{60}

- **Introduction:** A_3C_{60} **and their superconductivity**
  - **LDA Electronic structure**
  - **BCS SC :** Coupling of electrons with molecular phonons
  - **Electronic correlations?** Study Other stochiometries!
- **Electronic correlations and Jahn Teller distorsions**
  - **Na_2C_{60} and A_4C_{60} : Mott Jahn-Teller insulators**
    Electronic interactions mediated by JTD
  - **A_1C_{60} Mott insulator?**
    Low *T* charge segregation
- **Expanded magnetic compounds and Cs_3C_{60} phases** ⇐
  - **AF phases for large lattice spacings**
  - **Magnetism in A15 and fcc phases of Cs_3C_{60}**
  - **Pressure induced superconductivity**
- **Conclusion: phase diagram for the A_3C_{60} phases**

TRIANGLE DE LA PHYSIQUE

LPS ORSAY

Superconductivity in A_3C_{60}



Higher Tc?

Mott transition?

Alkali Ionic radius

Li
Na
K
Rb
Cs
Fr

Cs_3C_{60}

Expanded Mott state in K_3C_{60} expanded by NH_3 molecules

$(NH_3)_xK_3C_{60}$ a = 14.971 Å (bct)

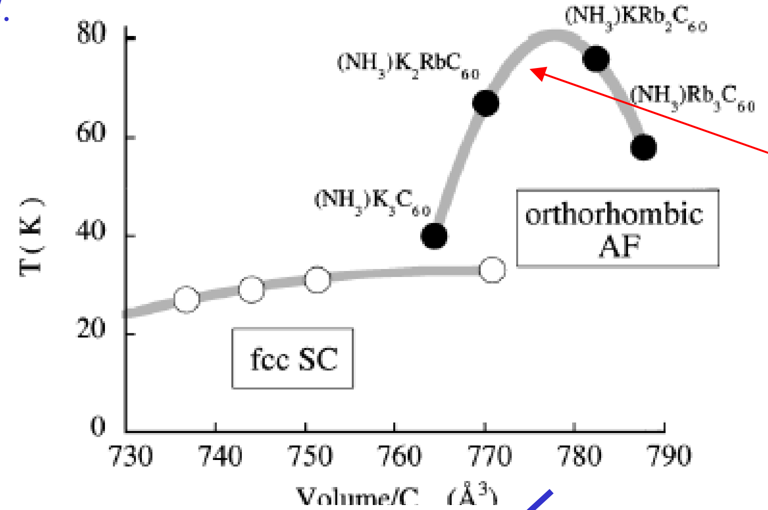
Rosseinsky Nature 364 425 (1993).

TRIANGLE DE LA PHYSIQUE

LPS ORSAY

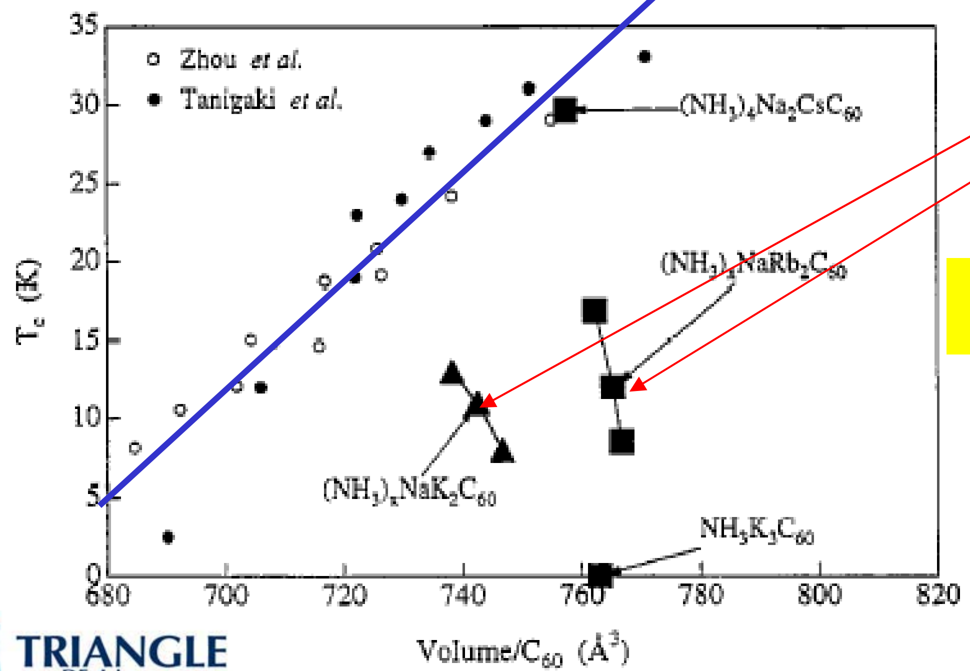
Metal-insulator transition in expanded A_3C_{60}

Iwasa et al.
PRL2000



For large lattice spacings:

the system becomes AF.



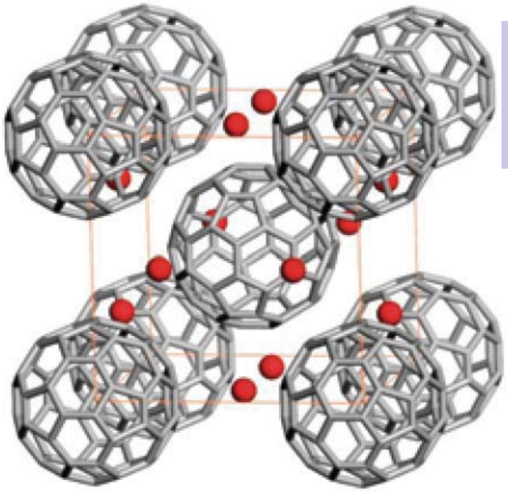
But:

structural distortions also induce magnetism

Lowering of the degeneracy?

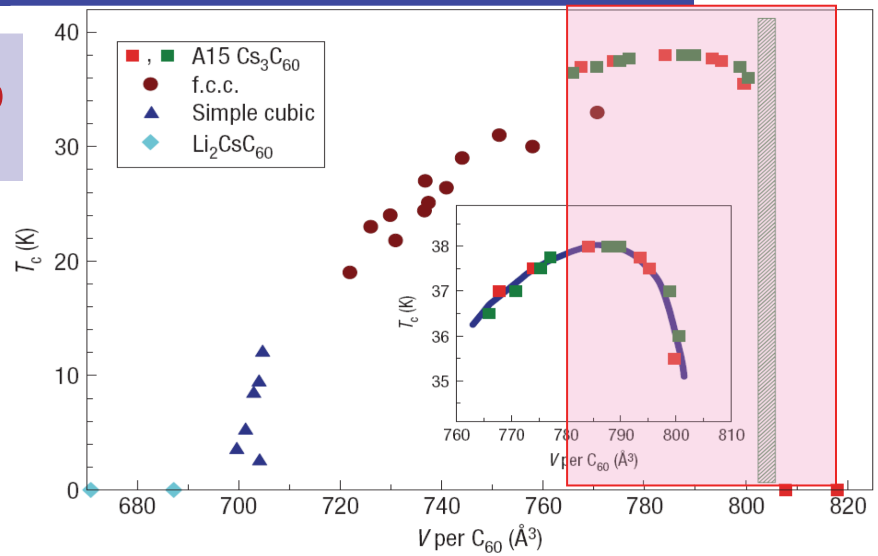
Rosseinsky, Maniwa, Iwasa , Prassides

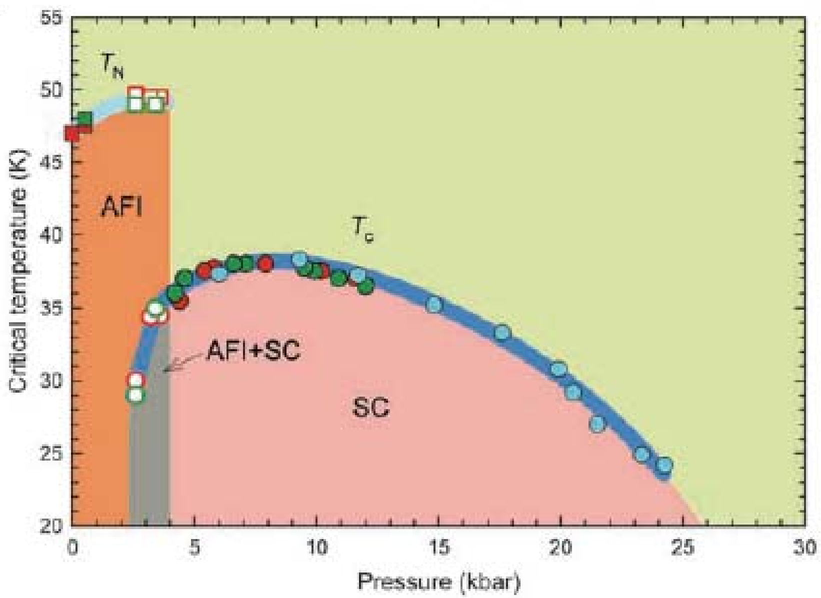
A15 Cs_3C_{60} pressure induced superconductivity



New phase of Cs_3C_{60} with A15 structure

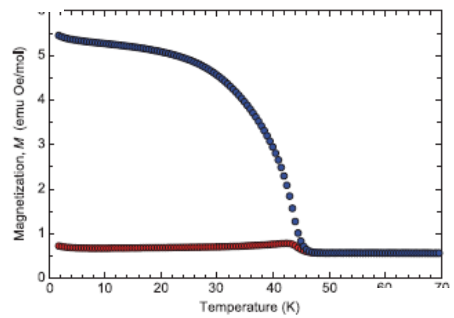
A. Ganin et al
Nature Materials , 2008





Takabayashi et al , Science 2009

M



T

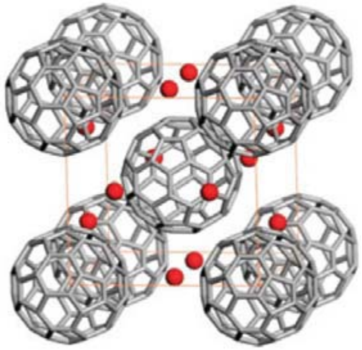
Magnetic at ambient pressure

SC and Mott transition

TRIANGLE DE LA PHYSIQUE

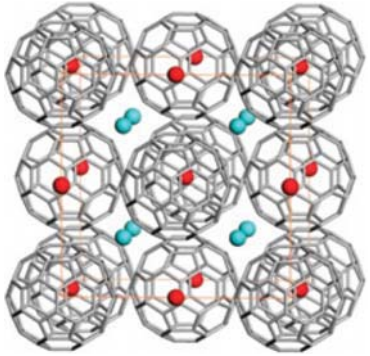
LPS ORSAY

Multiple phases in the samples: ^{133}Cs NMR is very helpful



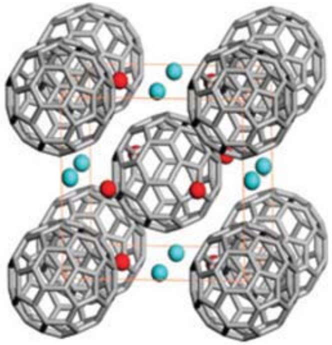
A15 Cs_3C_{60}

A single Cs site
with non cubic
local symmetry



fcc Cs_3C_{60}

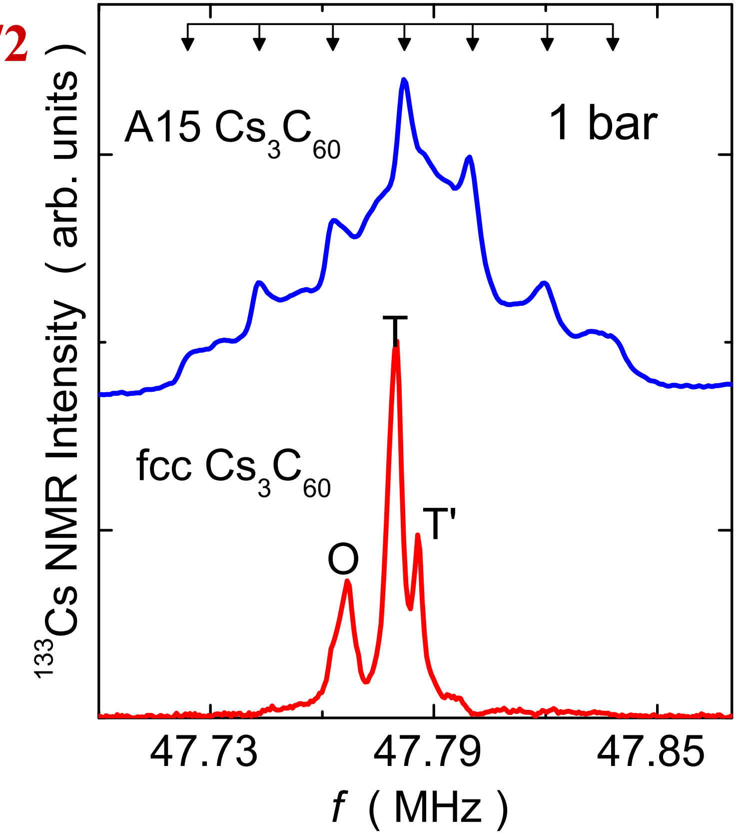
Well known: two Cs sites
O and T = 1 : 2
With cubic local symmetry
T splits at low T
Merohedral disorder of the C_{60}



Cs_4C_{60}

Insulating phase
Eliminated by its very long T_1

^{133}Cs I=7/2



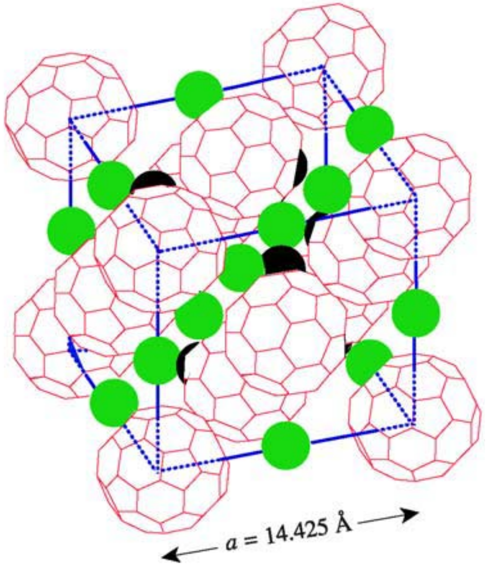
A15-rich sample		fcc-ri ch sample	
A15 :	**58.4 %**	A15 :	34 %
FCC :	12 %	FCC :	**55 %**
Cs_4C_{60} :	29.5 %	Cs_4C_{60} :	11 %

TRIANGLE DE LA PHYSIQUE

Differences allow selective NMR experiments

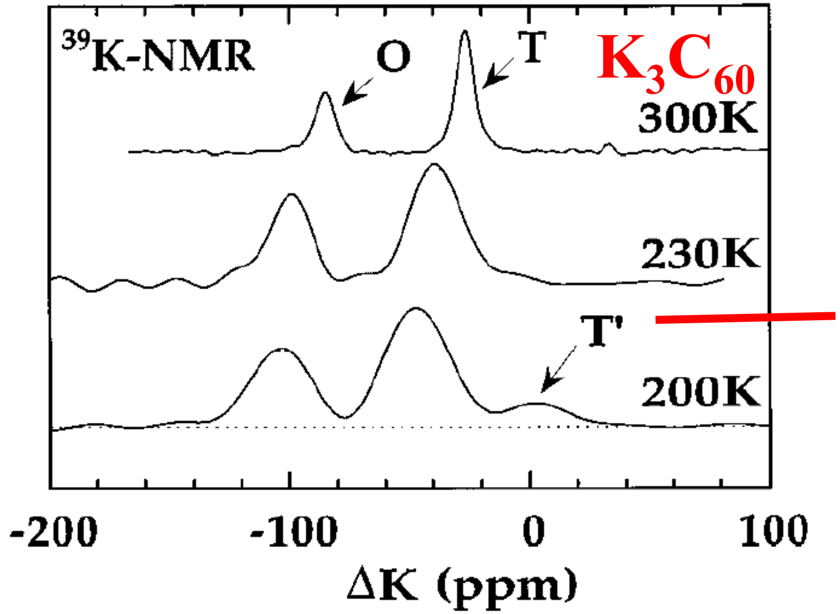
LPS ORSAY

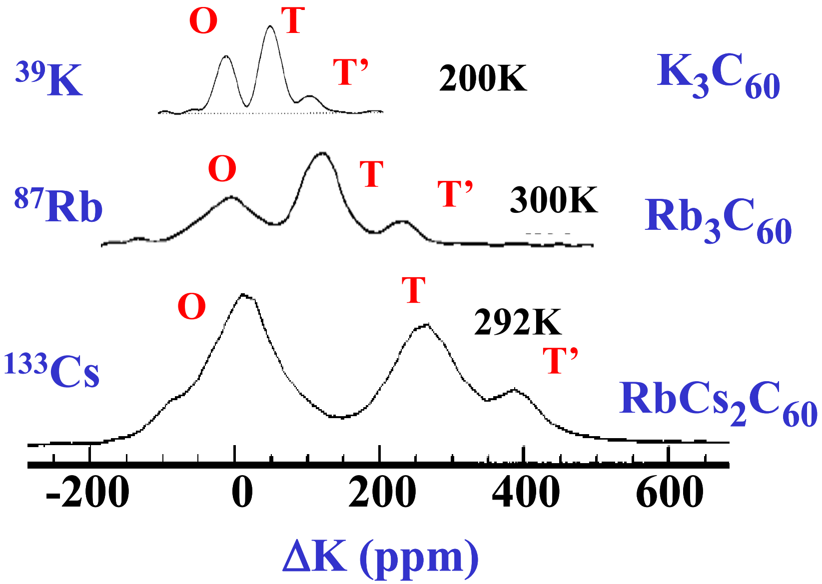
Defects in A_3C_{60} compounds: the T' NMR line problem

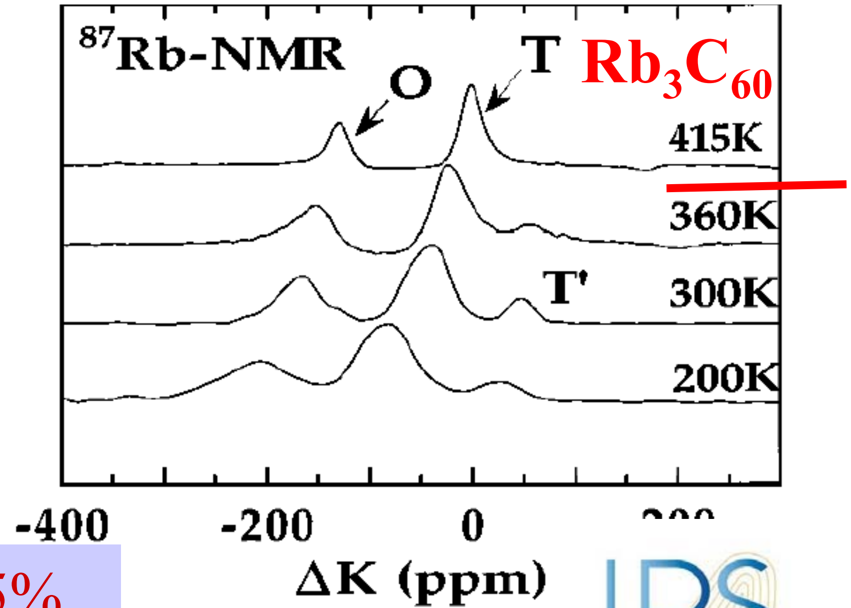


tetrahedral A site

octahedral A site

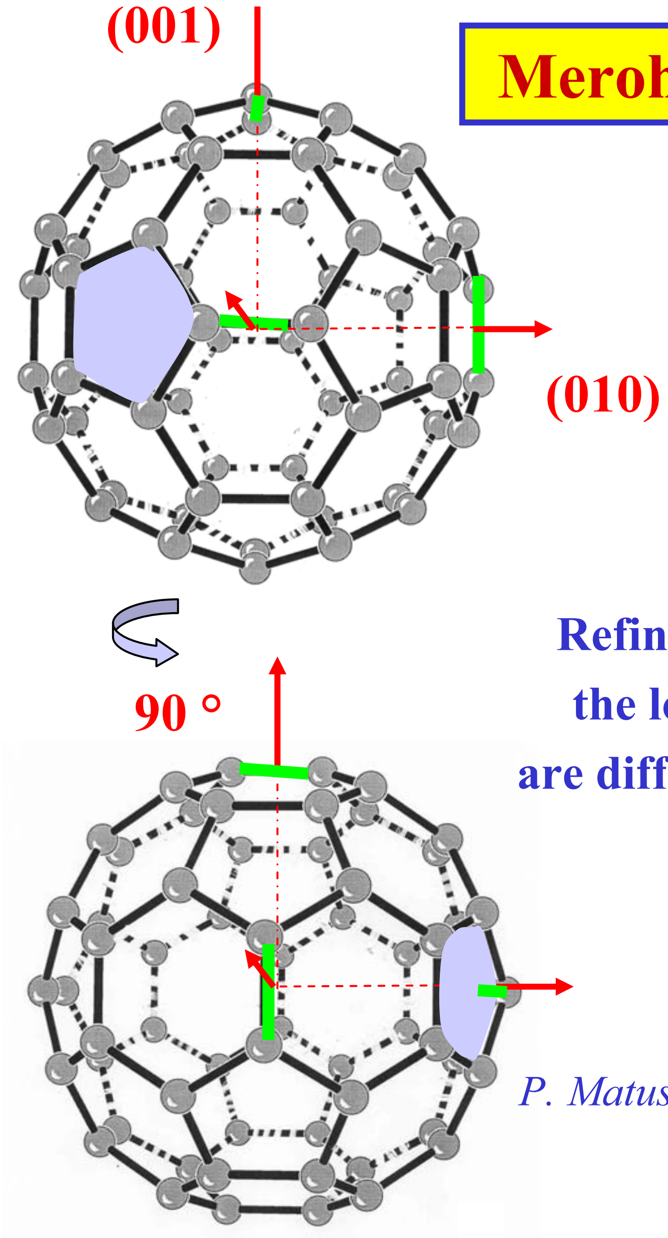


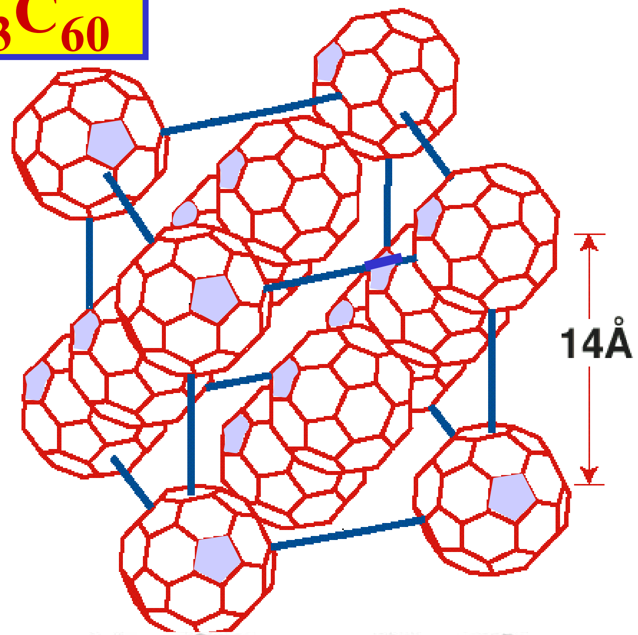




Fraction of T' sites is ~ 15%

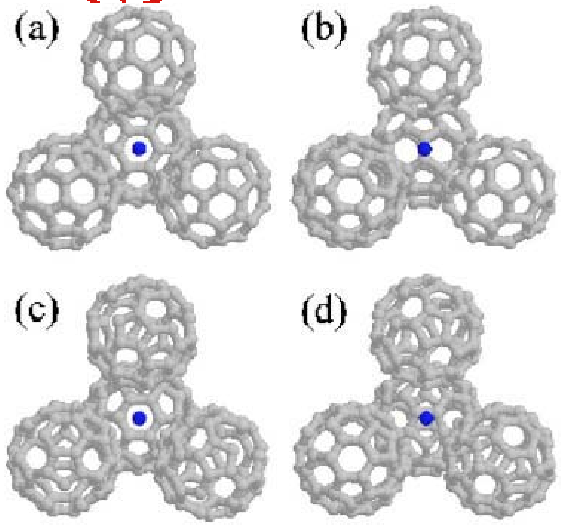
Merohedral disorder in A_3C_{60}





Refined experiments show that the local ordering of C_{60} balls are different around T and T' sites

P. Matus, Phys. Rev. ***B 74****, 214509 (2006)*

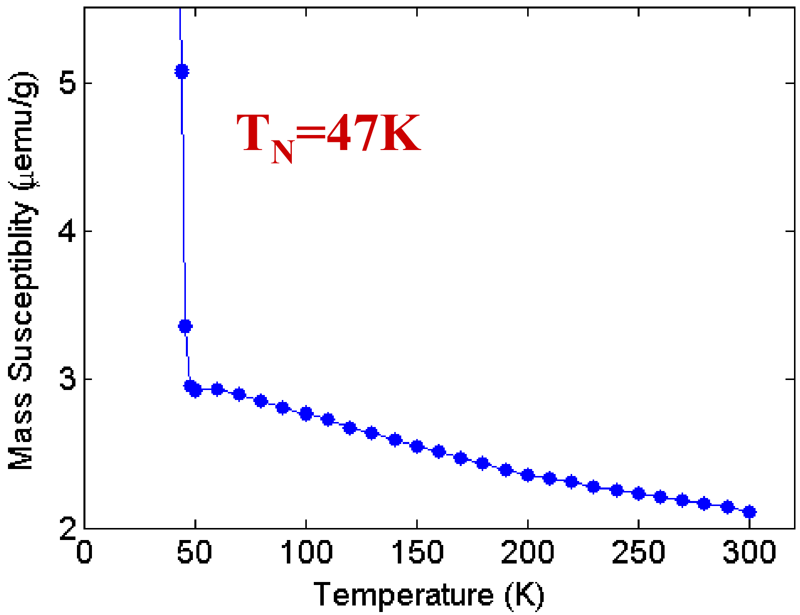


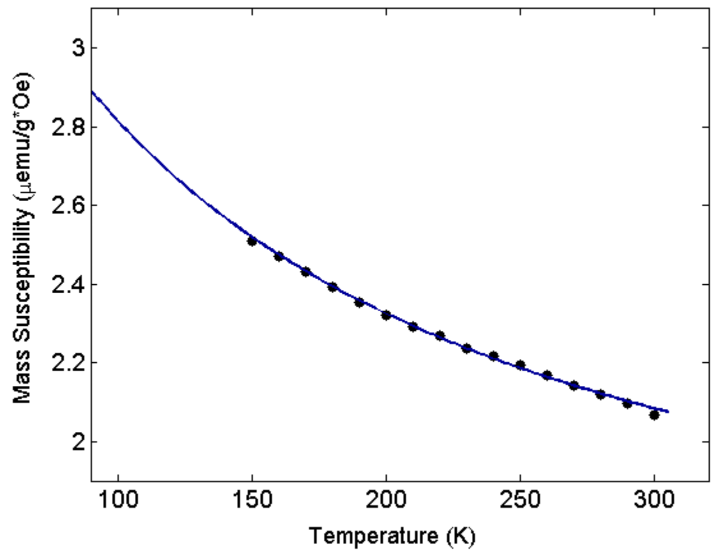
TRIANGLE DE LA PHYSIQUE

LPS ORSAY

Paramagnetic state susceptibility

(30.9% Cs_3C_{60} FCC,   53.6% Cs_3C_{60} A15, 15.5% Cs_4C_{60})





High T Curie-Weiss behavior

Weiss temperature: $\theta \sim 100$ K

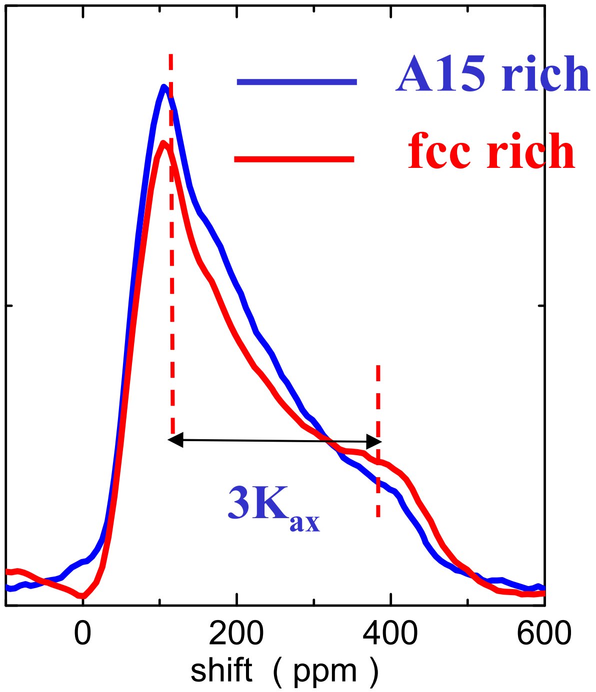
Effective moment : $p_{eff} \sim 1.70\ \mu_B$

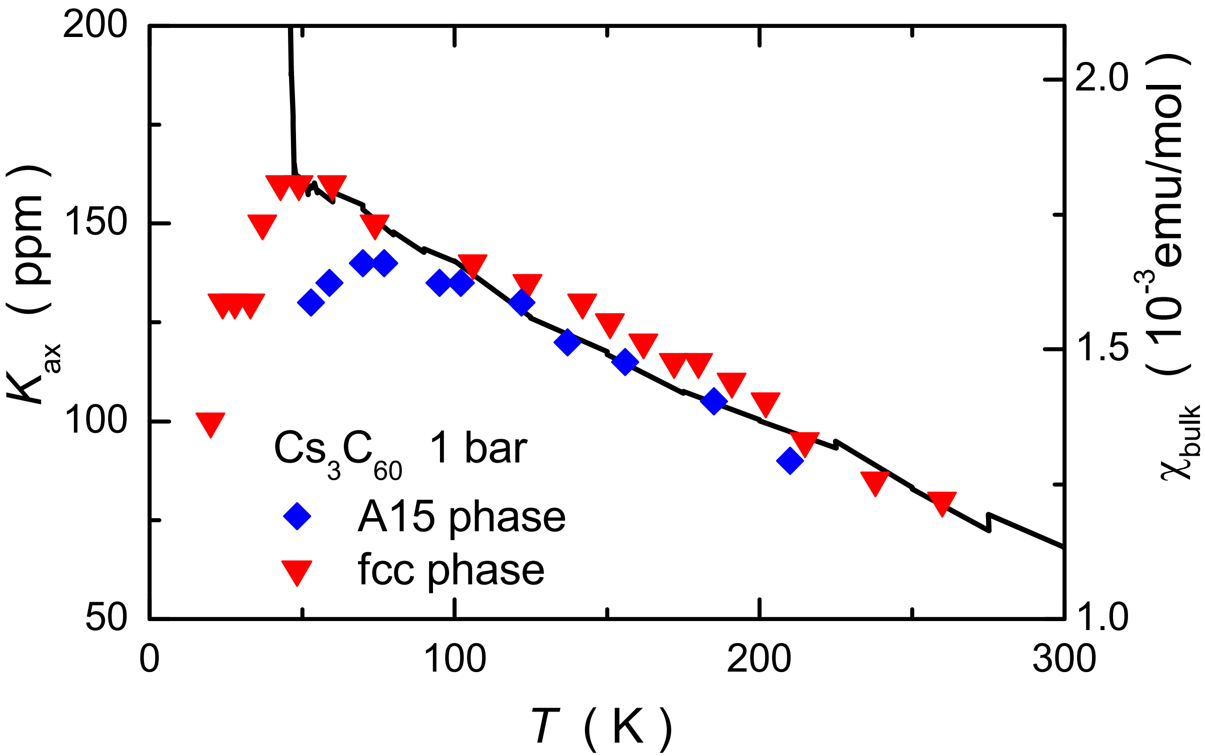
$$\chi^{-1} = p_{eff}^2/3k_B(T+\theta)$$

Local moment S ~ 1/2 on the C_{60} balls?

Paramagnetic state susceptibility

^{13}C NMR





Anisotropic hyperfine coupling

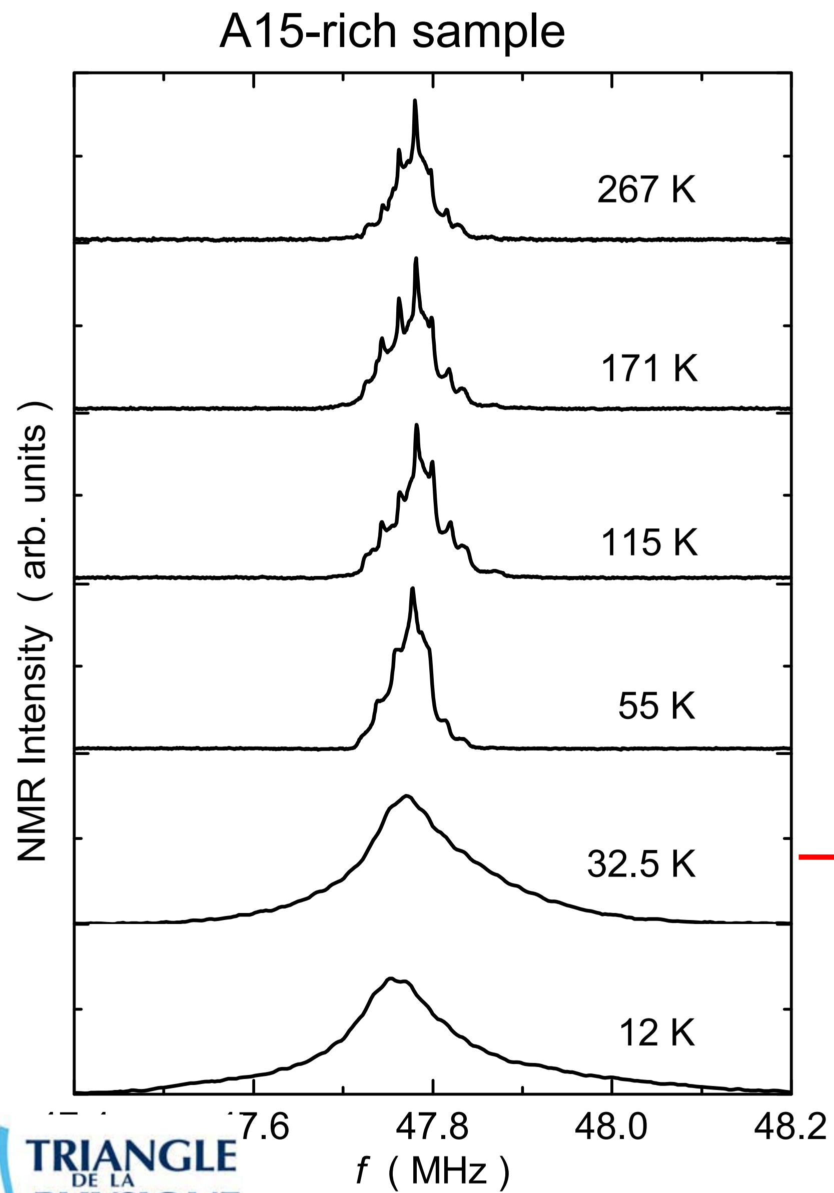
$K_{ax} = A \quad \chi_s$

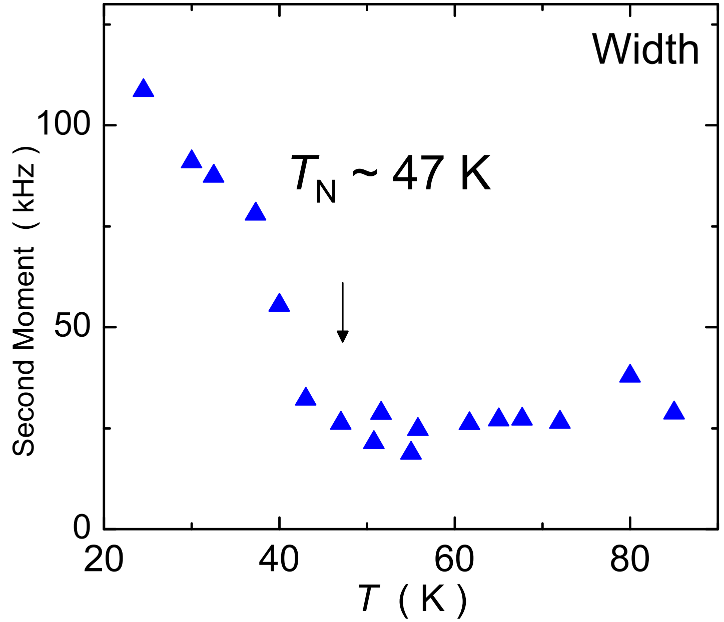
Here A is dipolar $A_{exp} \sim 700\ Oe/\mu_B$

Calculated value : $A = 640\ Oe/\mu_B$

Local moment is indeed on the C_{60} balls!

Magnetic transition in A15 phase





Spectral broadening :
static internal magnetic field.

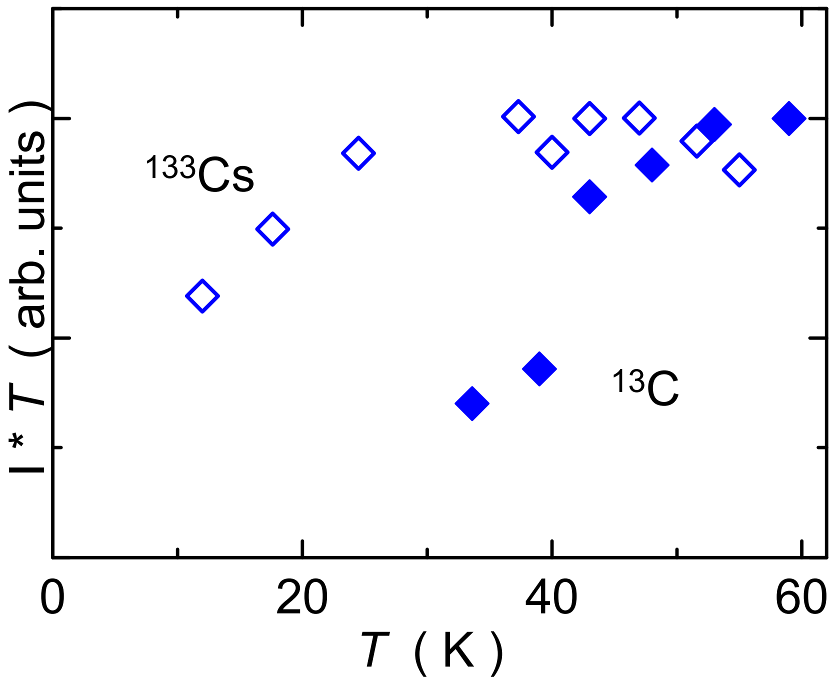
A15 phase shows magnetic order below T_N = 47 K at ambient *p*.

Takabaya

Magnetism and crystal structure

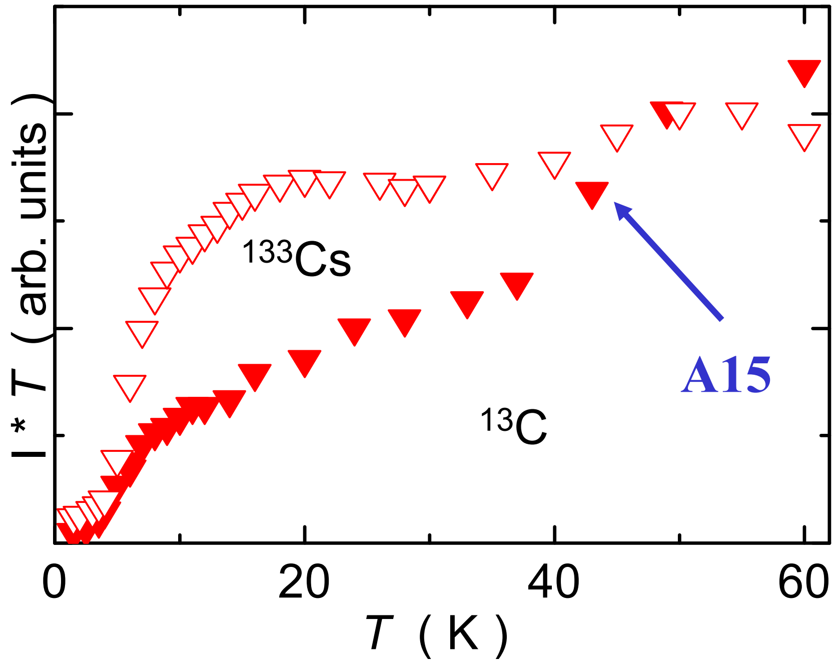
^{13}C and ^{133}Cs NMR intensities

A15 rich



T_N=47K

fcc rich



Gradual freezing below 10K ?

Geometrical frustration depresses the magnetic ordering (fcc not bipartite)

TRIANGLE DE LA PHYSIQUE

LPS ORSAY

Spin dynamics and crystal structure

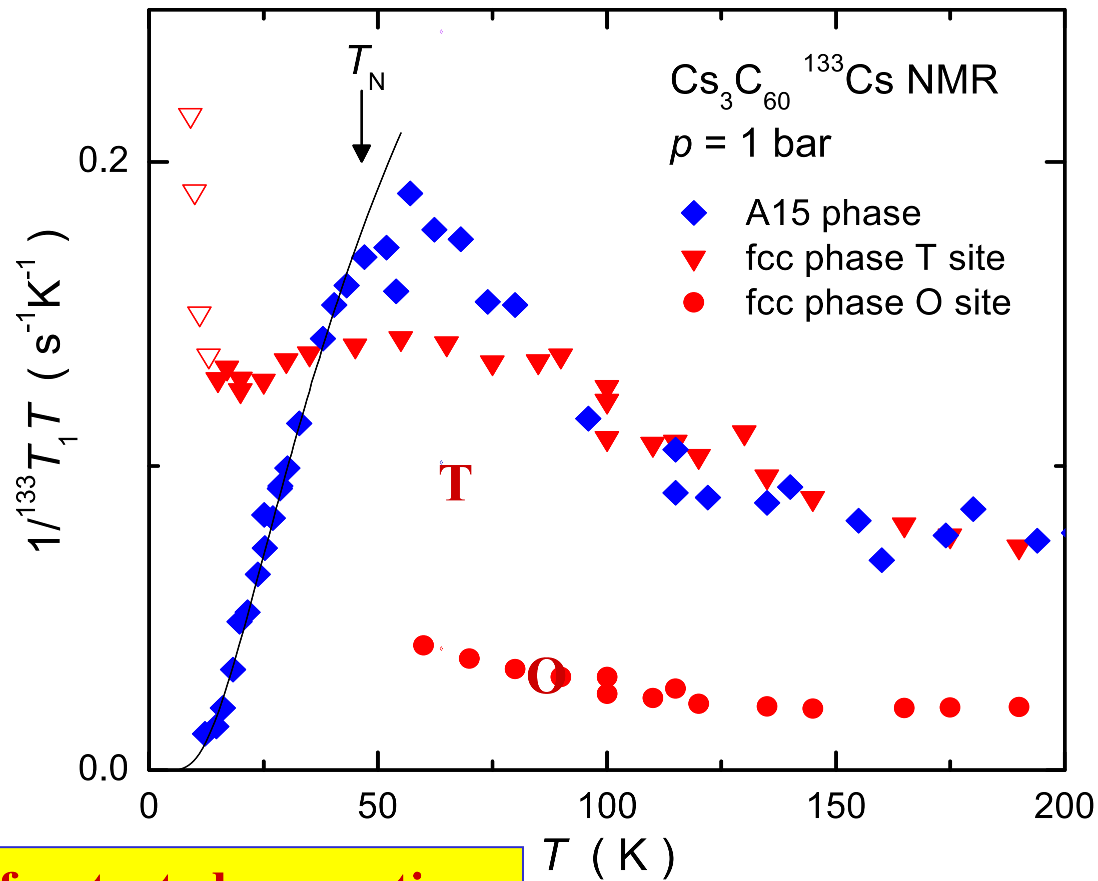
^{133}Cs NMR T_1

Both phases
Enhanced magnetic fluctuations in the paramagnetic state.

A15 phase
magnetic gap
$\underline{\Delta} \sim 50$ K

fcc phase
No magnetic gap.
Still some slow dynamics below 10 K.

O site has twice smaller coupling constant than that for T site.



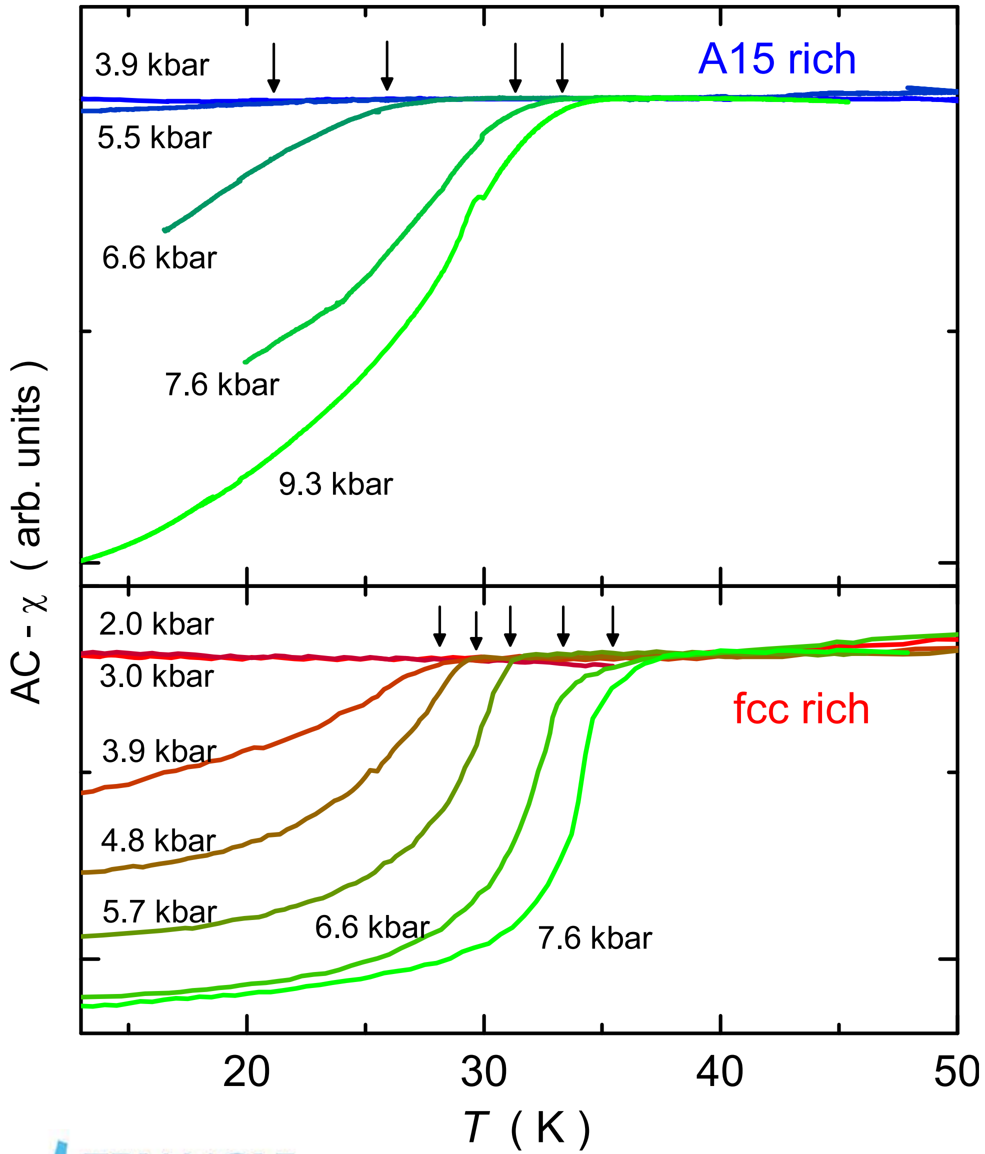
Ordered versus frustrated magnetism (fcc not bipartite)?

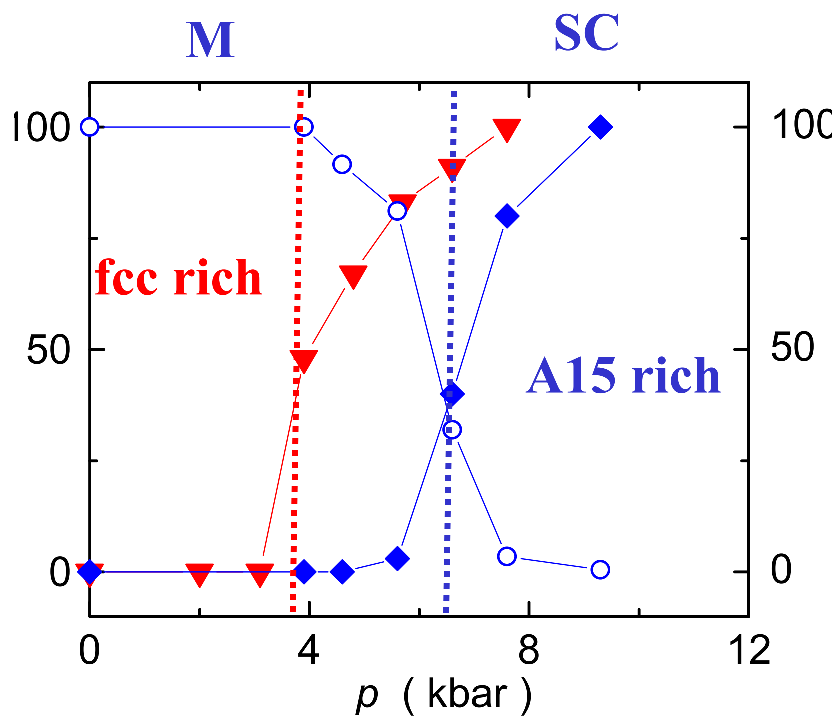
TRIANGLE DE LA PHYSIQUE

H. Alloul, ICTP Trieste, 05/08/2010

LPS ORSAY

Pressure induced superconductivity

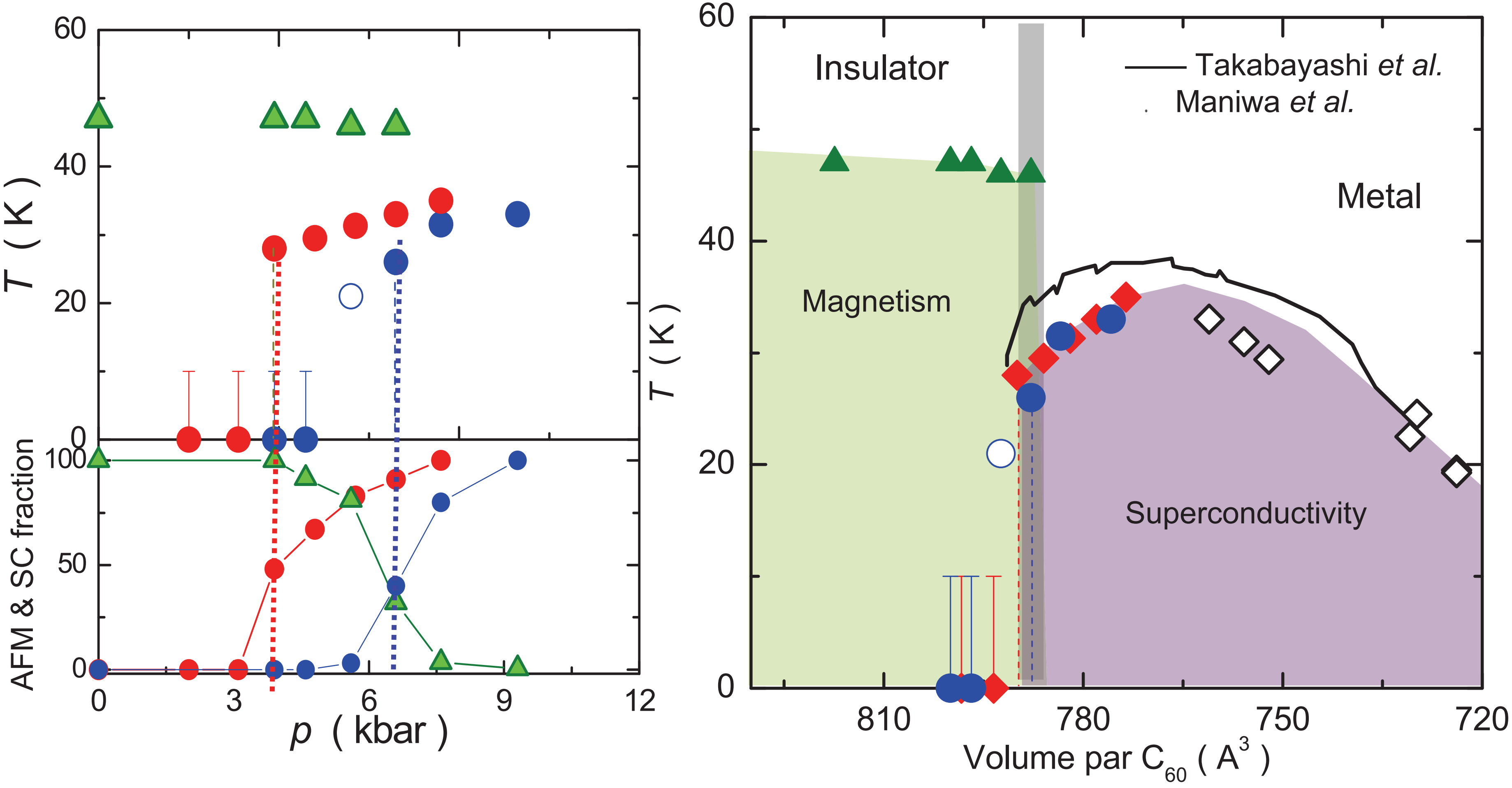




Distinct (*p*,*T*) phase diagrams for the two phases

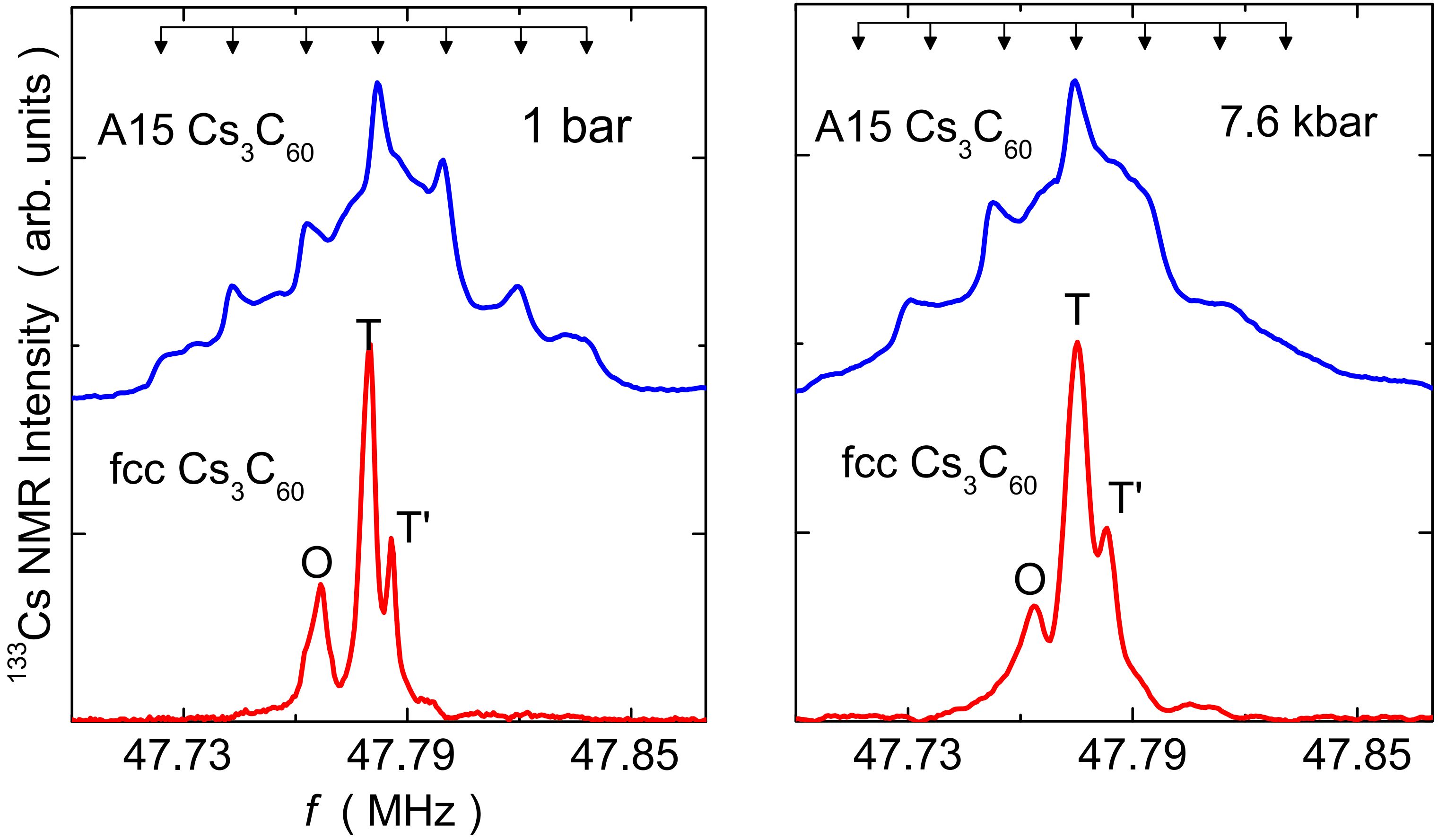
H. Alloul, ICTP Trieste, 05/08/2010

Phase diagrams



No difference with crystal structure on the SC side

Mott transitions to the metallic state in the A15 phase



p=1bar

p=7.6 kbar

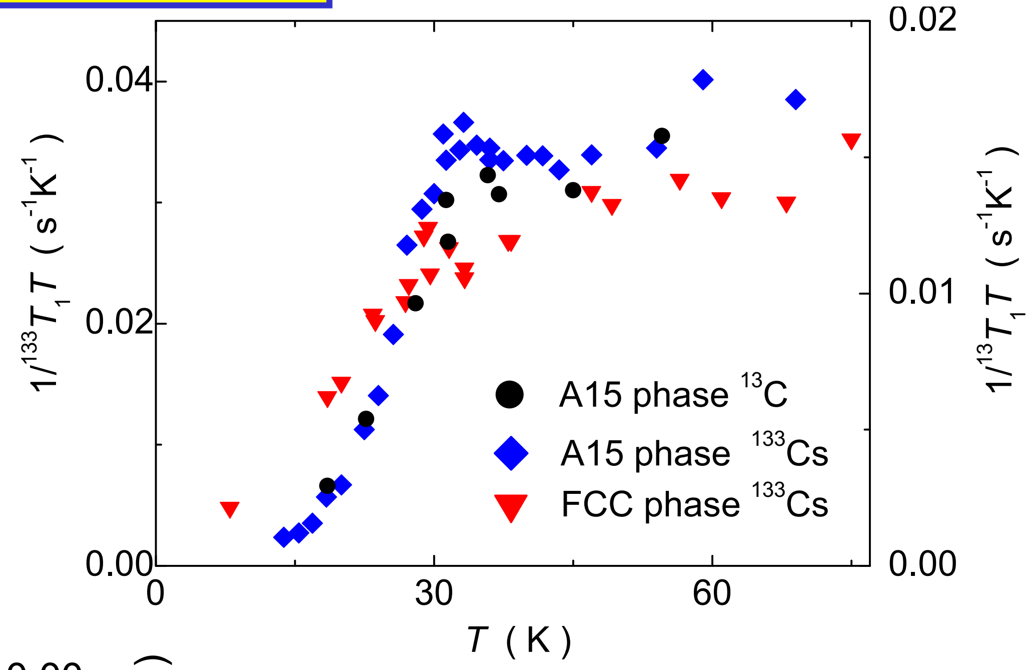
No change of crystal structures

TRIANGLE DE LA PHYSIQUE

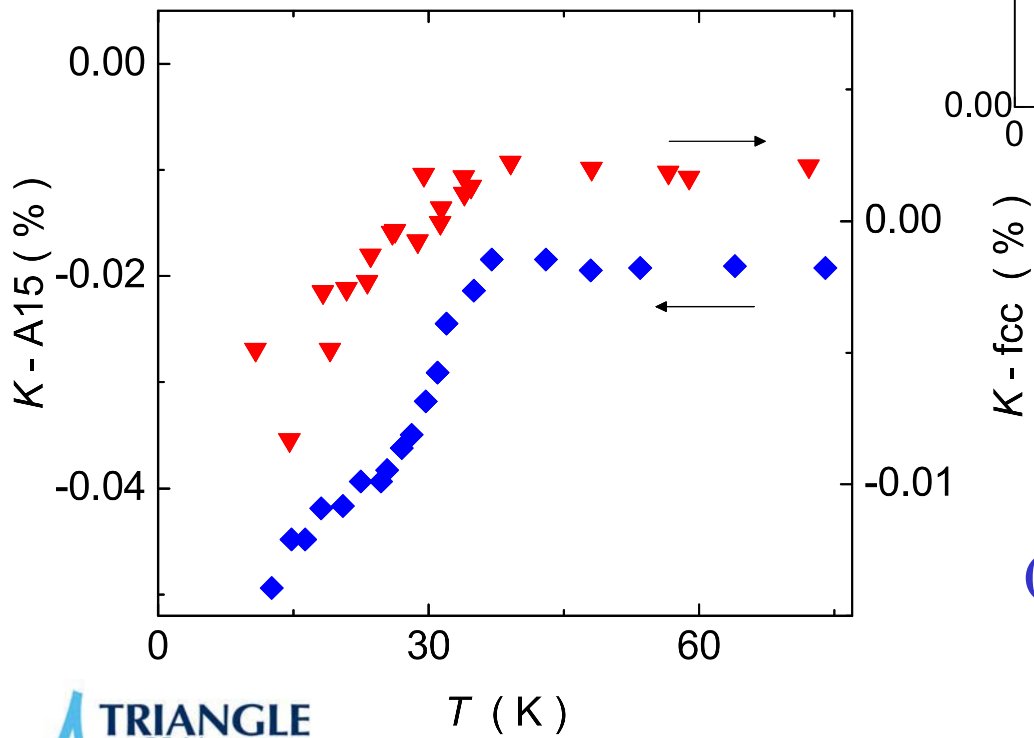
LPS ORSAY

Superconductivity

$p \gg p_c$

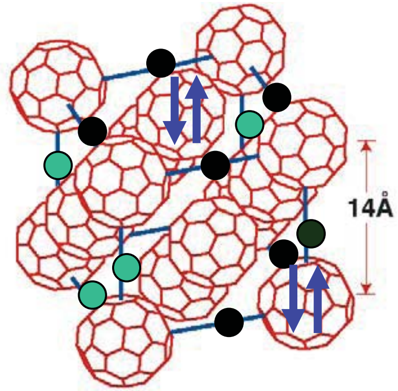


T_1 data

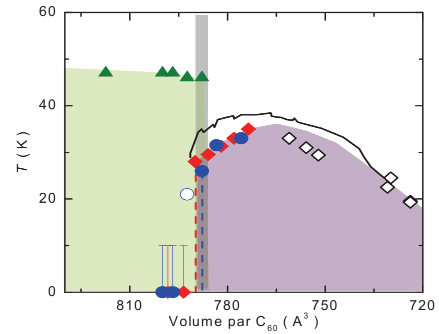


Knight shift (singlet pairing)

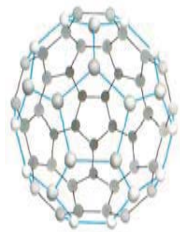
Summary



- Fulleride compounds are peculiar correlated electron systems
- Originalities asociated with their nanostructure
  - Icosaedric symmetry of the soccer ball.
  - Orientational disorder
  - Internal degrees of freedom of the molecule:
  - Phonons, Molecular Jahn-Teller distorsions
- They display many effects driven by correlations
  - Static charge segregation in Cs_1C_{60}
  - High Tc superconductivity near a MIT (Cs_3C_{60})
  - Molecular excitations survive in the solid.



- Those are strongly influenced by molecular Jahn Teller effects
  - Favor singlet formation in Cs_1C_{60}
  - Jahn Teller Mott insulating states in K_4C_{60} or Na_2C_{60}
  - Jahn-Teller effects explain why electronic correlations appear smaller in A_3C_{60} but remain sizable as Cs_3C_{60} is magnetic



- Excellent possibility to study multiorbital Mott transitions

TRIANGLE DE LA PHYSIQUE

LPS ORSAY