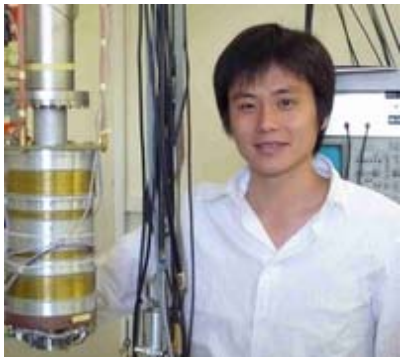
# NMR study of the pressure induced Mott transition to SC in the newly discovered $Cs_3C_{60}$ isomeric compounds



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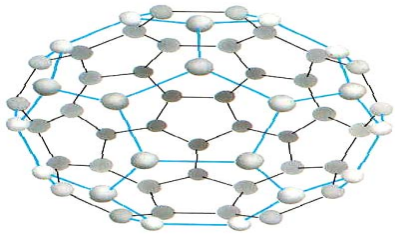
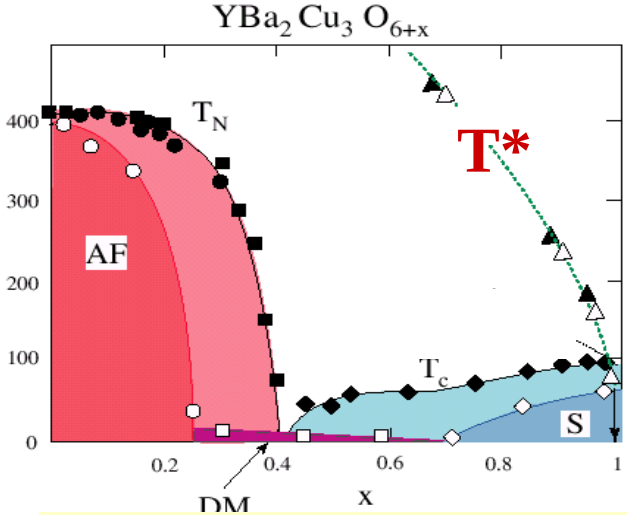
V. Brouet

*PRL, **104**,256402 (2010).*
*EPL **94**, 37007 (2011)*
*PRL **112**, 066401 (2014).*

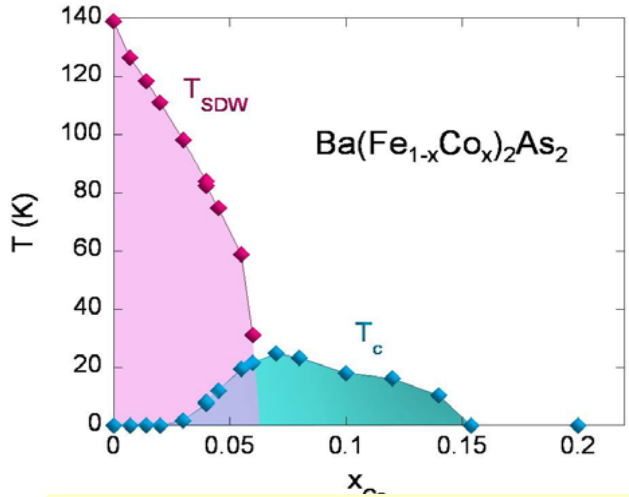


V. Brouet, H. Alloul *et al*
*PRL, **82**,2131 (1999); **86**,4680(2001);*
*PR **B**, **66**, 155122 , 15123, 15124(2002).*

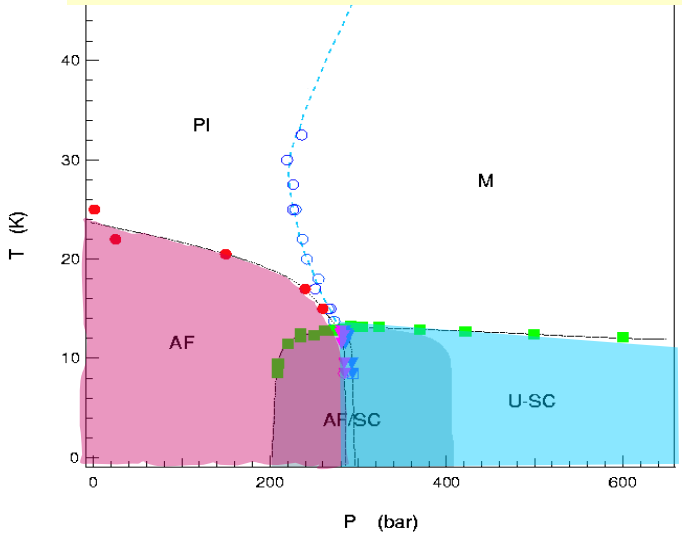
# Phase diagrams of superconducting correlated systems



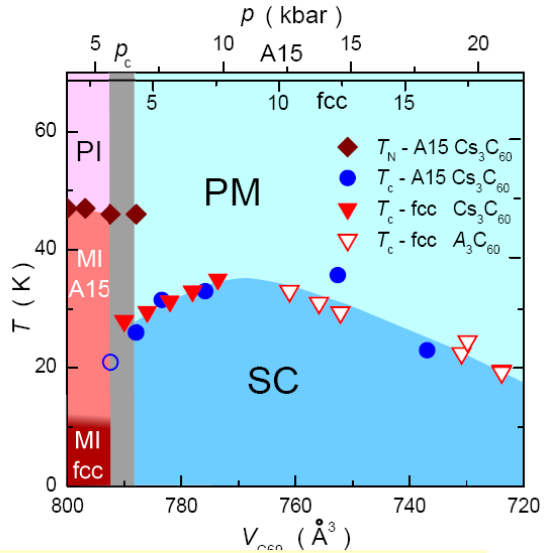

YBCO Hole doped cuprate




FeAs 122 electron doped




$\kappa$-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$
pressure induced IMT




$Cs_3C_{60}$
pressure induced IMT

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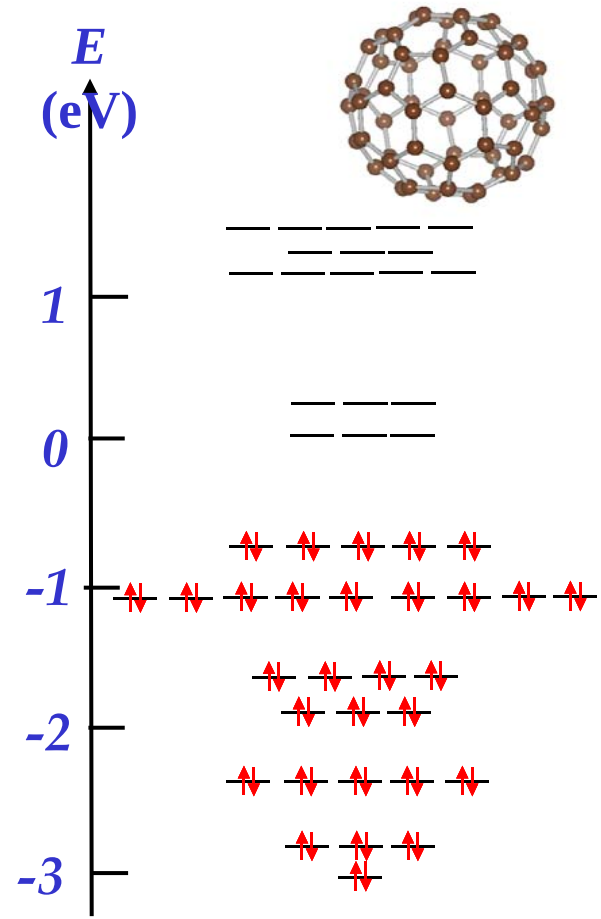
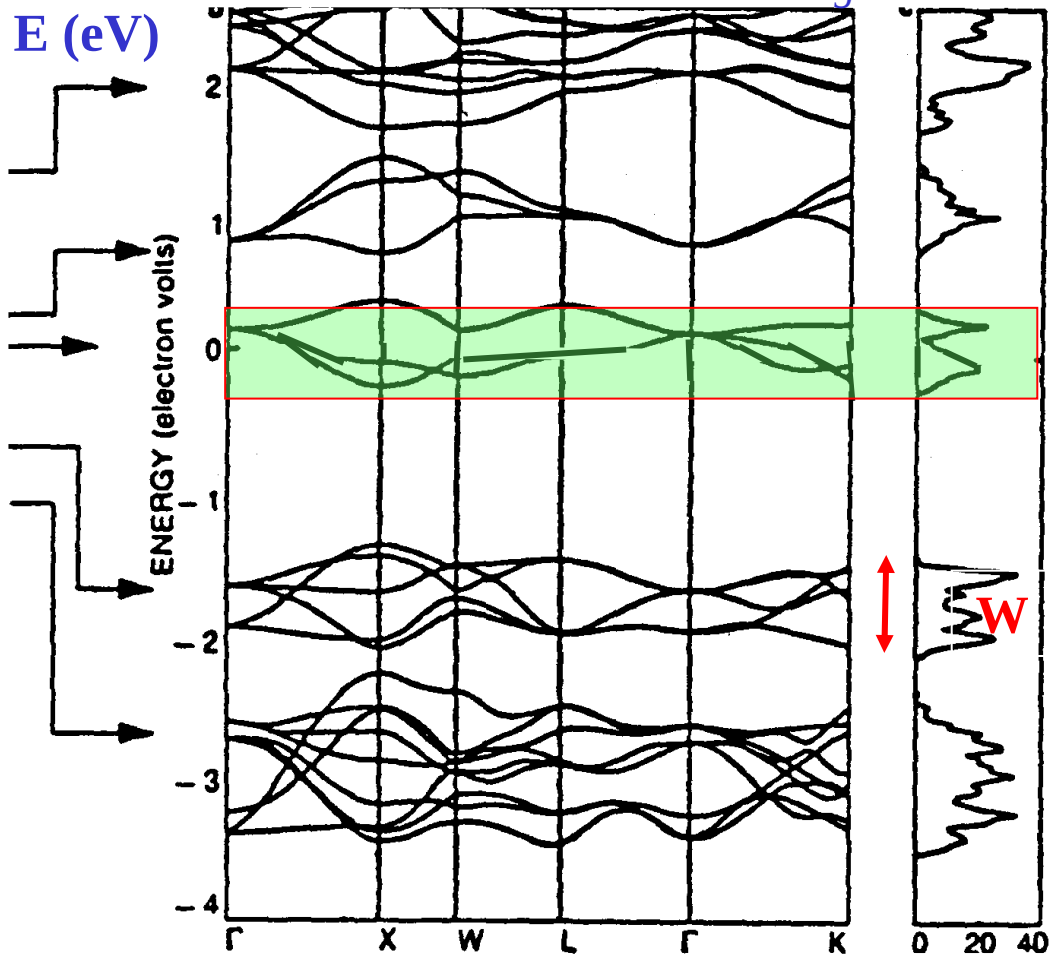
- **Summary**

# Electronic structure of doped fullerides

*C. H. Pennington RMP 1995.*




$C_{60}$ molecule




$C_{60}$ solid

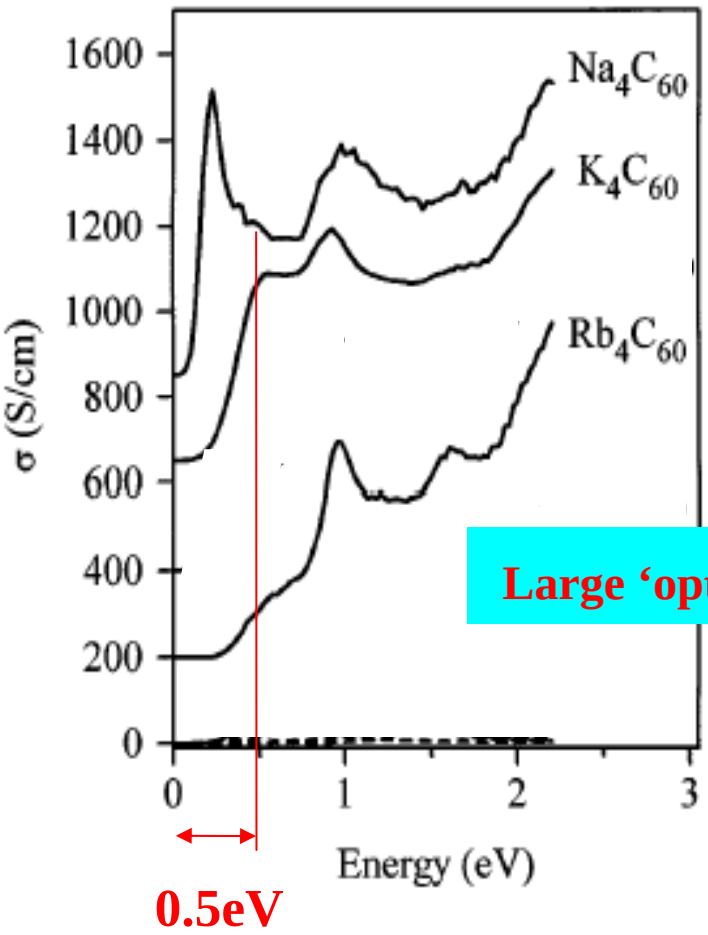
U~ 1 eV

W= 0.5 eV

**$A_nC_{60}$ should be metallic for any doping 0<n<6**

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

## Optical conductivity extracted by EELS



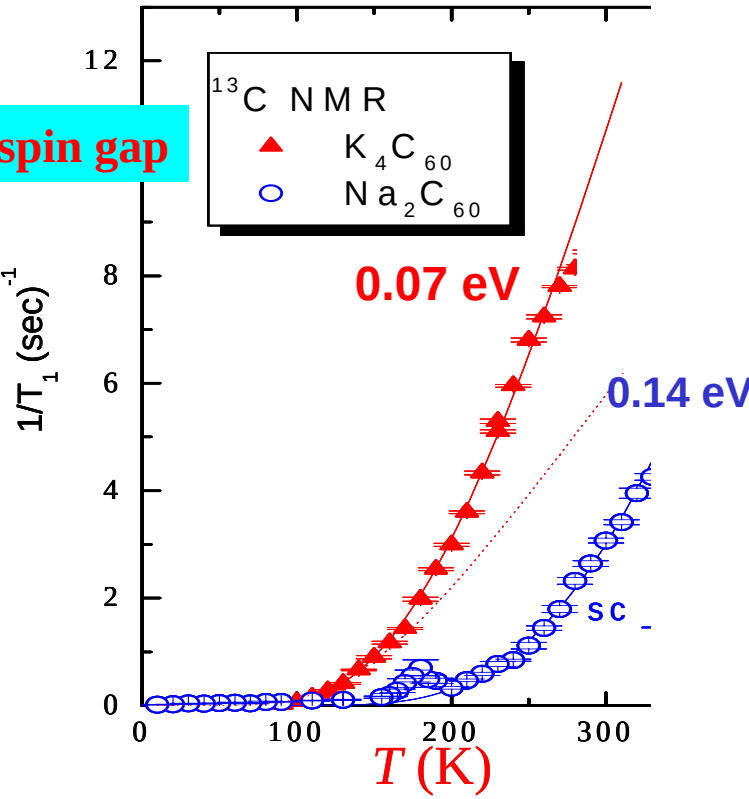

**0.5eV**

**Large 'optical' gap**

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

## NMR $1/T_1$

**Small spin gap**




*$K_4C_{60}$: G. Zimmer et al EPL (1994),*
*V. Brouet et al , PRB 66 155122 (2002).*
*$Na_2C_{60}$, F. Rachdi et al, PRB 1997,*
*V. Brouet et al PRL 2001, PRB 2002*

**Insulating non magnetic ground state**

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

Two electrons on a ball costs an energy ***U=1eV***

Hund's $J_H$ should favor high spin (S=1)

Experimental situation

- **Non magnetic ground state**
- **2 different gaps**

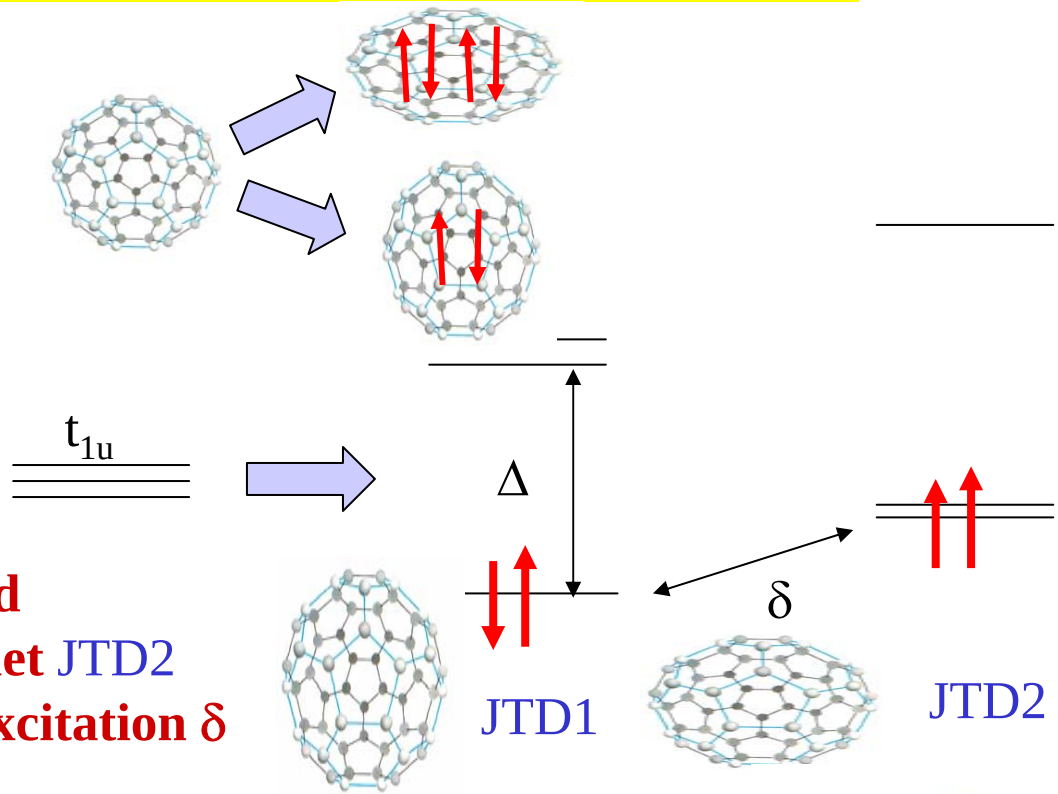
So there is an energy gain which opposes to $J_H$ and stabilizes singlets

For a charged molecule

The degeneracy of the $t_{1u}$ level

is lifted by a **Jahn Teller distortion**

*Fabrizio, Tosatti PRB97*




-In the **fundamental** JTD1 state

**Hund's rule is not obeyed**

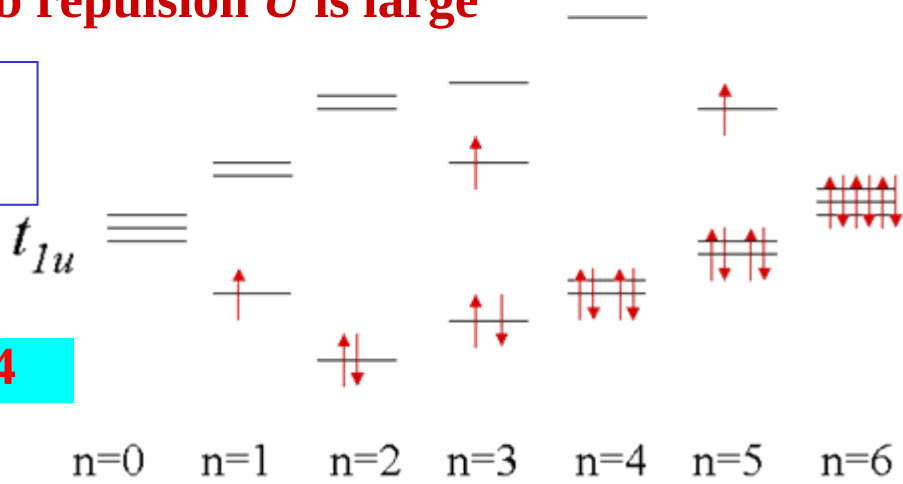
- **Excited state** corresponds to a **triplet** JTD2
- NMR detects the **Singlet Triplet excitation δ**

NMR detects the Singlet Triplet excitation

# Strong electronic correlations induce the insulating behaviour

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

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

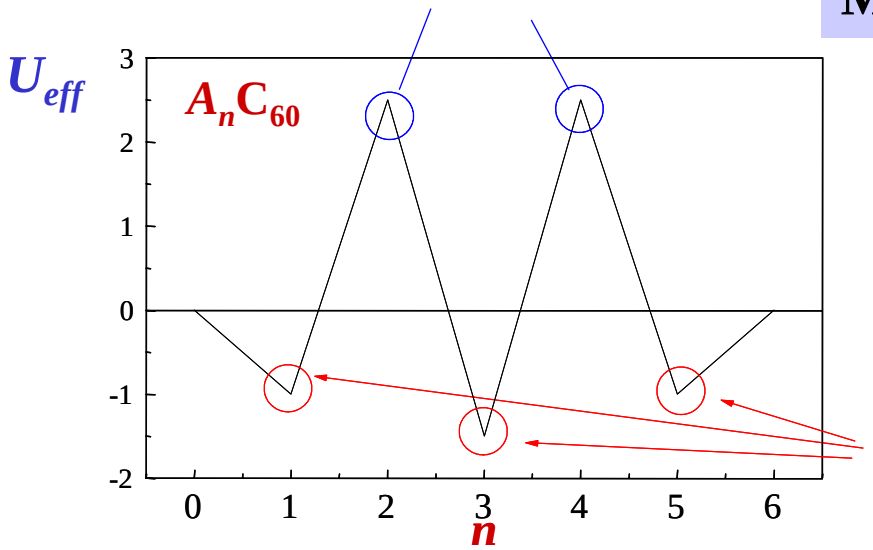



**Jahn-Teller adds a contribution $U_{eff}$ to $U$**

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

**$U_{eff}$ adds to $U$ for even $n$**

**Correlated insulators**




**Mott Jahn-Teller insulators**

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

**$U_{eff}$ reduces $U$ for odd $n$**

**Metals correlated : weak or strong?**

**Interplay of electronic interactions and JTD**

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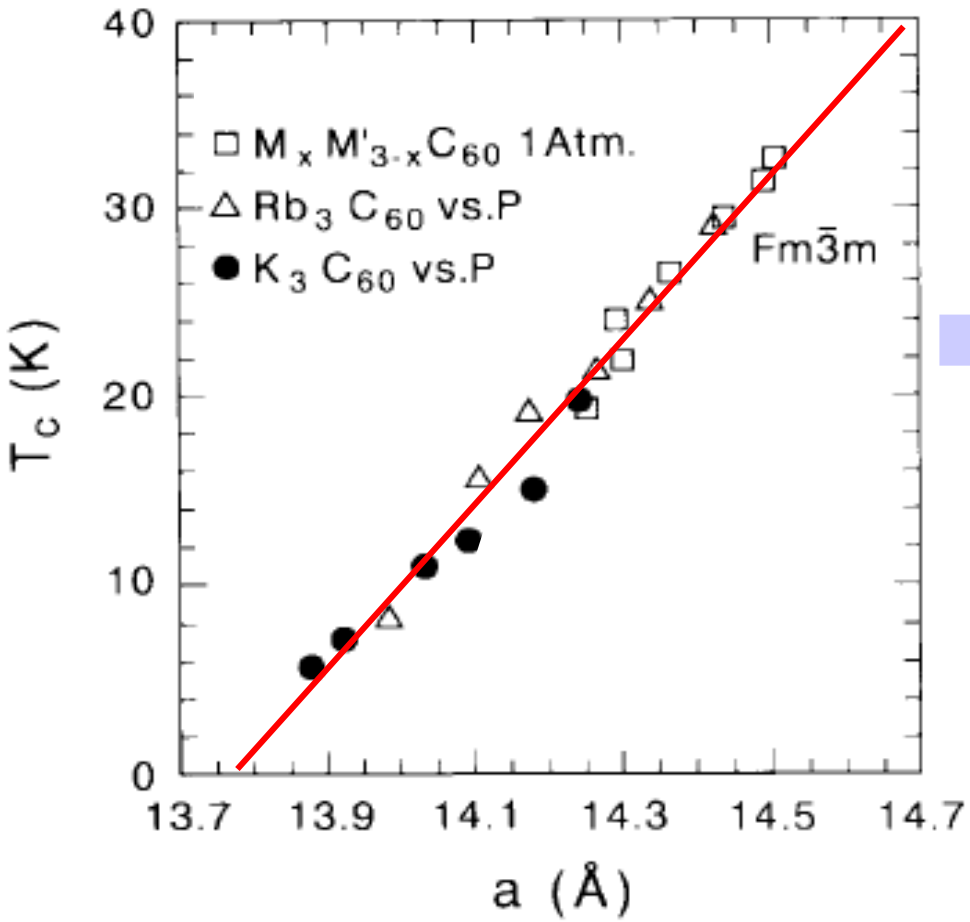
# Superconductivity in $A_3C_{60}$




- Carbon Isotope effect on $T_c$
- Regular Specific heat jump at $T_c$

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

$T_c$ depends only on $n(E_F)$

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

are molecular properties

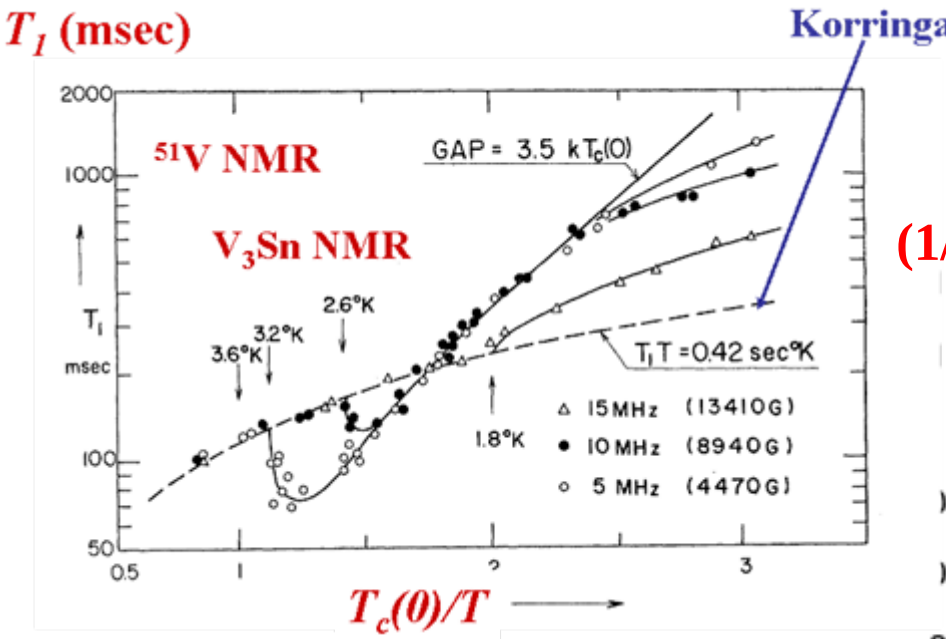
**Only $C_{60}$ phonons are involved**

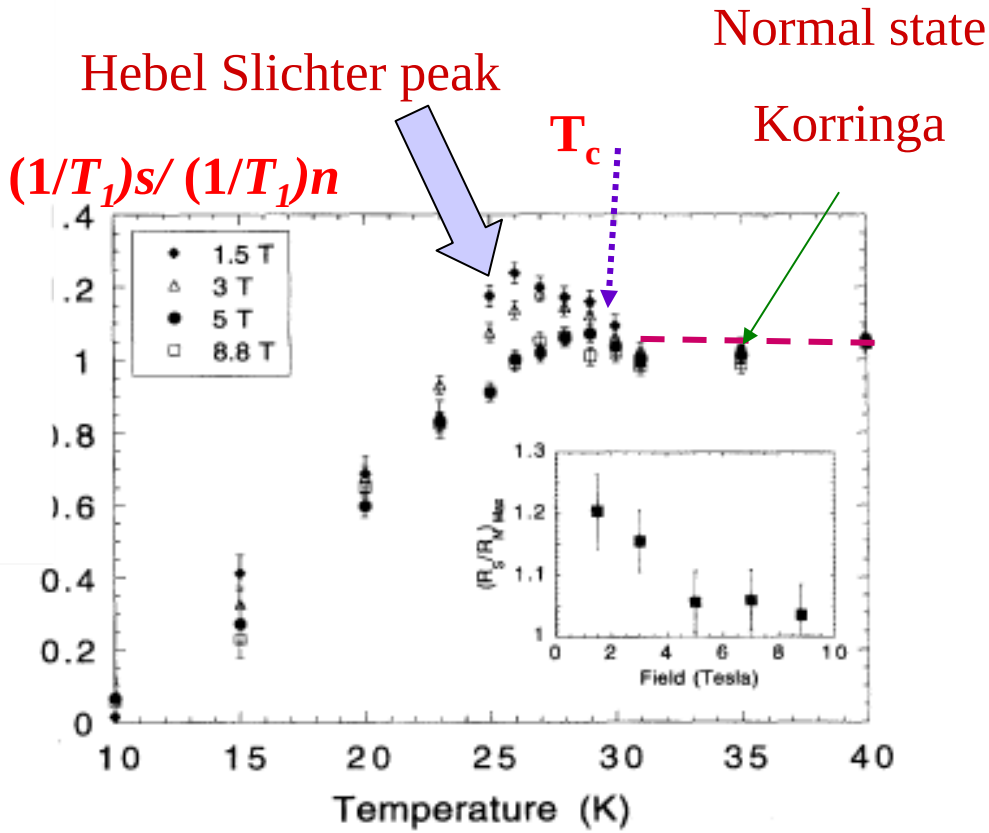
**The scaling between $T_c$ and the lattice parameter has been assumed to support a phonon BCS-like mechanism**

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

# Superconductivity in $Rb_2CsC_{60}$

NMR spin lattice relaxation rate




**The Hebel Slichter peak is characteristic of BCS SC**

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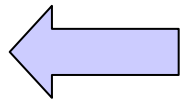
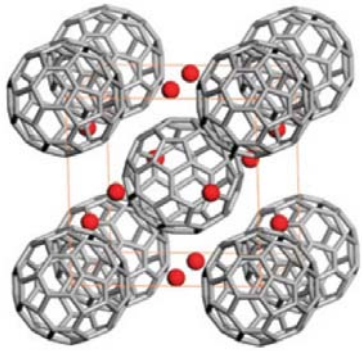
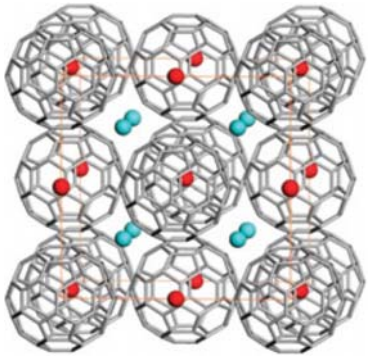


# Multiple phases in the samples: $^{133}$Cs NMR is very helpful



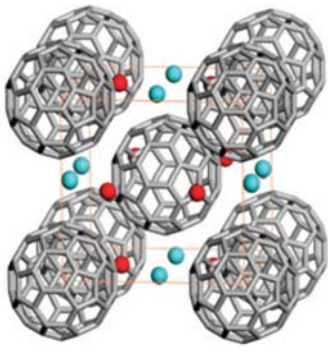
## A15 $Cs_3C_{60}$

A single Cs site
with non cubic
local symmetry



## fcc $Cs_3C_{60}$

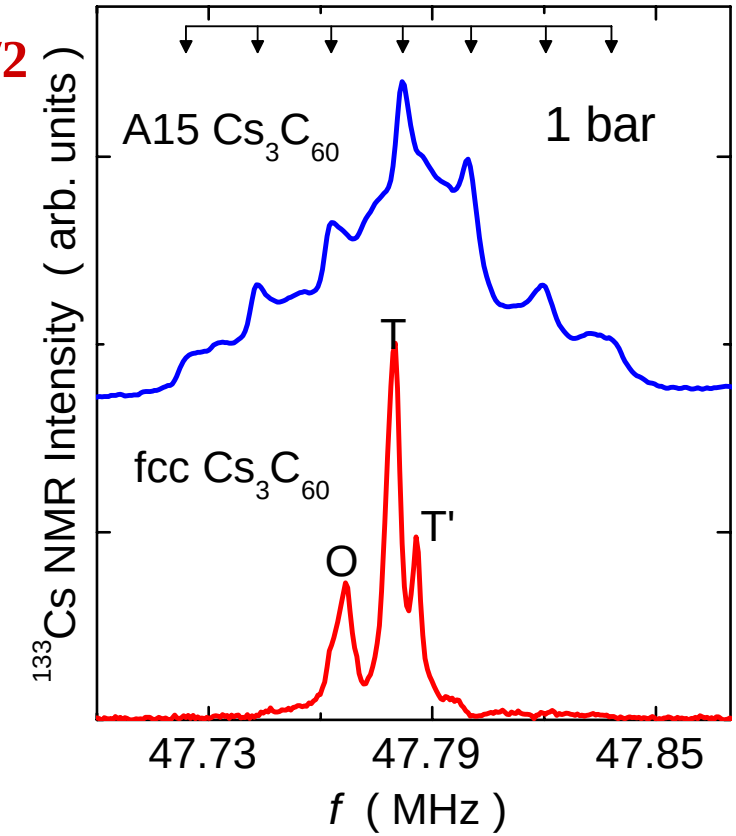
Well known: two Cs sites
O and T = 1 : 2
With cubic local symmetry
T splits at low T
Merohedral disorder of the $C_{60}$



## $Cs_4C_{60}$

Insulating phase
Eliminated by its very long $T_1$

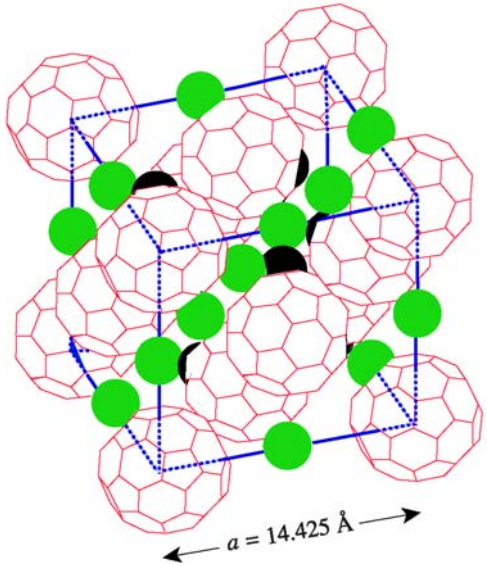
## $^{133}$Cs $I$=7/2




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

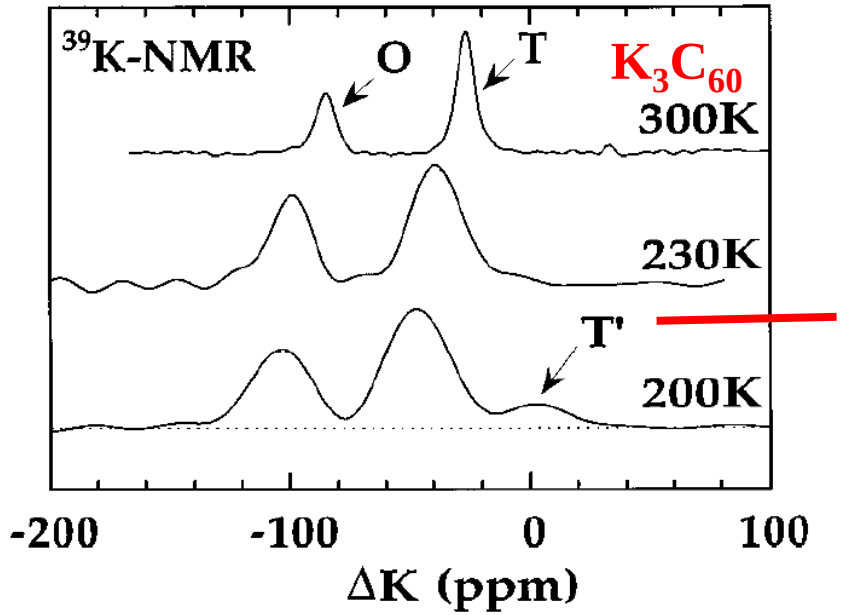
**Differences allow selective NMR experiments**

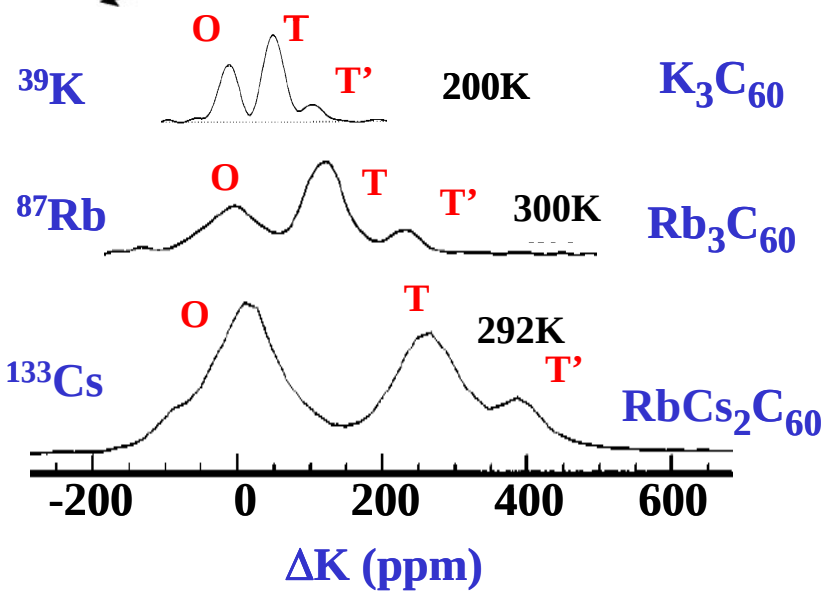
# Defects in $A_3C_{60}$ compounds: the T' NMR line problem

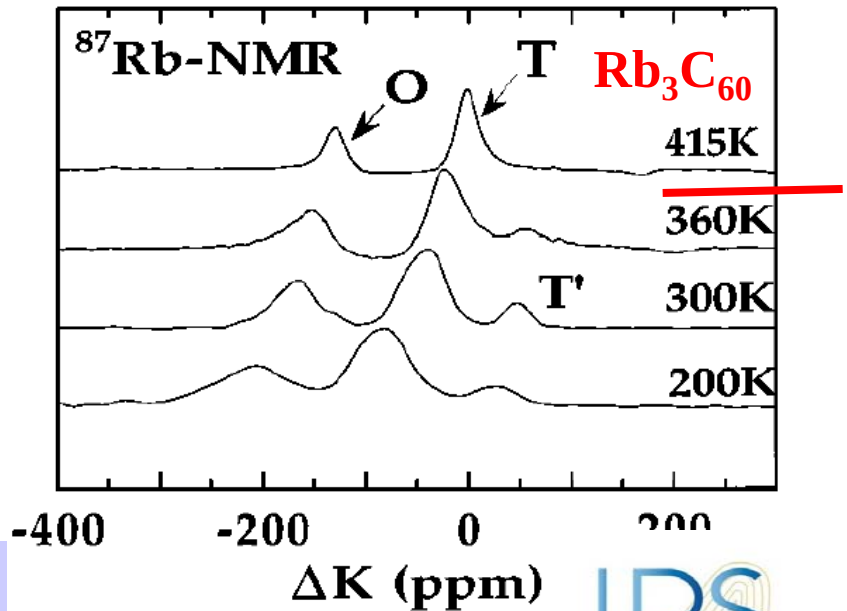



tetrahedral A site

octahedral A site

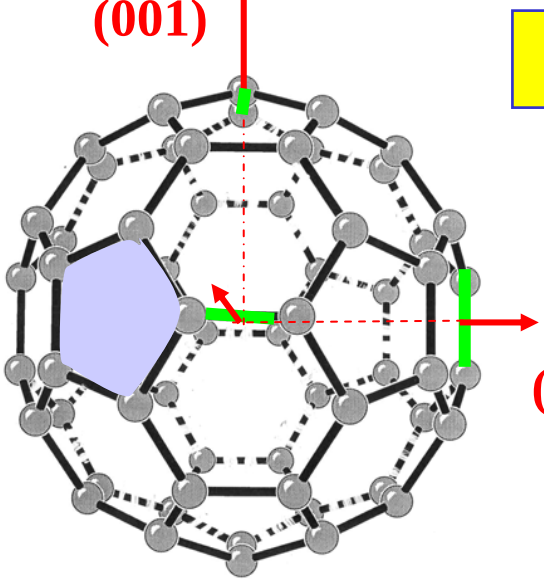


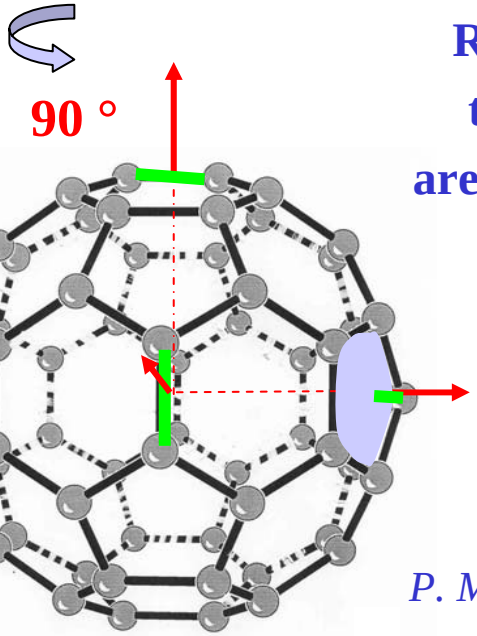



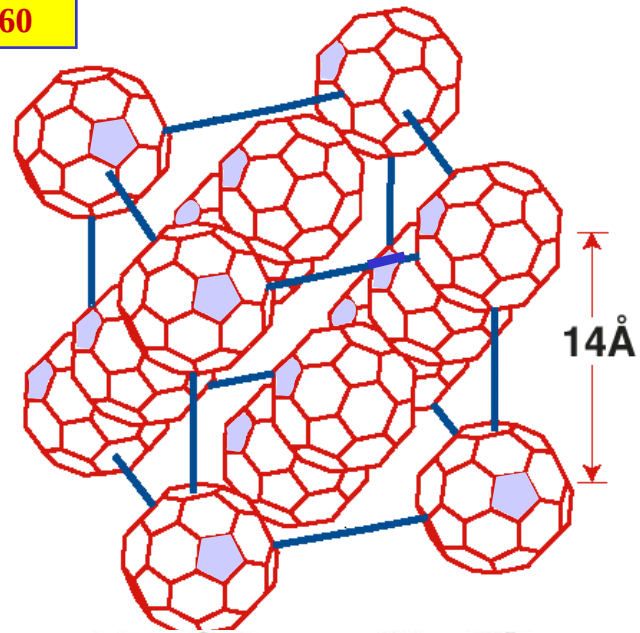




**Fraction of T' sites is ~ 15%**

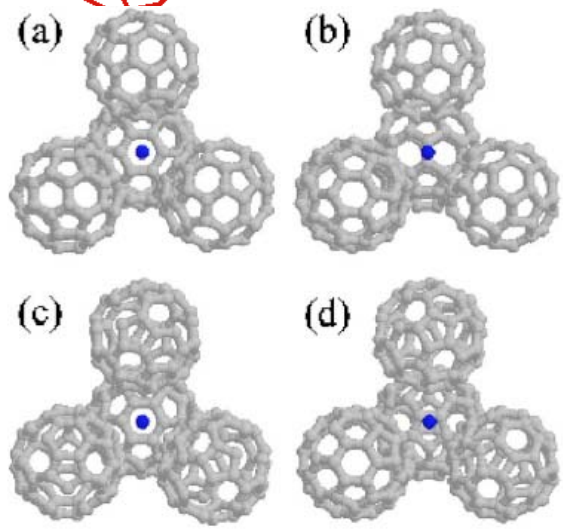
# Merohedral disorder in $A_3C_{60}$




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

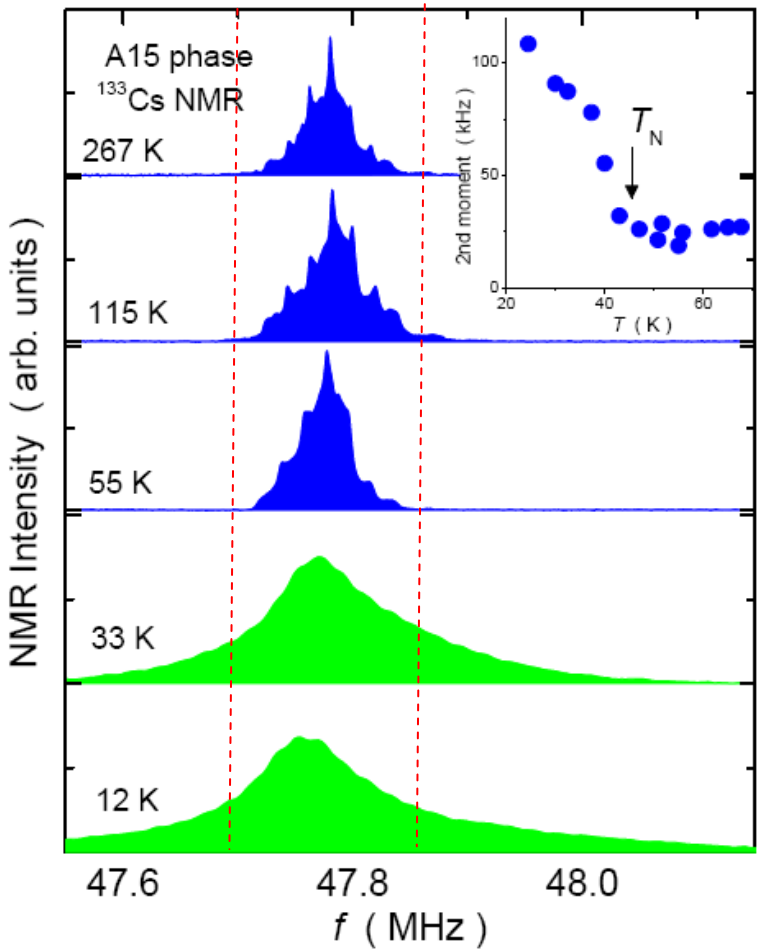


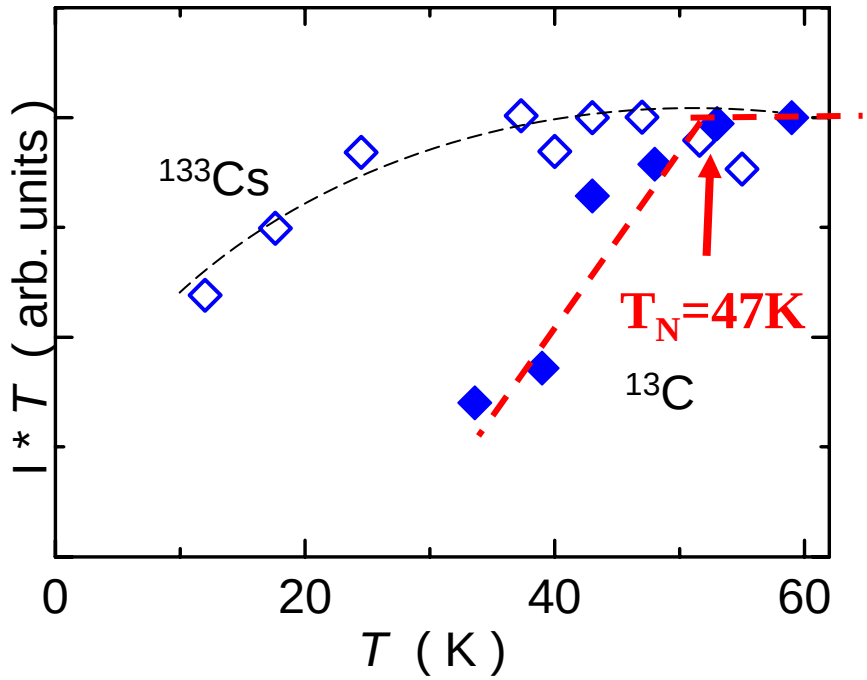

*P. Matus, Phys. Rev.* ***B 74****, 214509 (2006)*

**A15 rich**

# Magnetic transition in the A15 phase

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



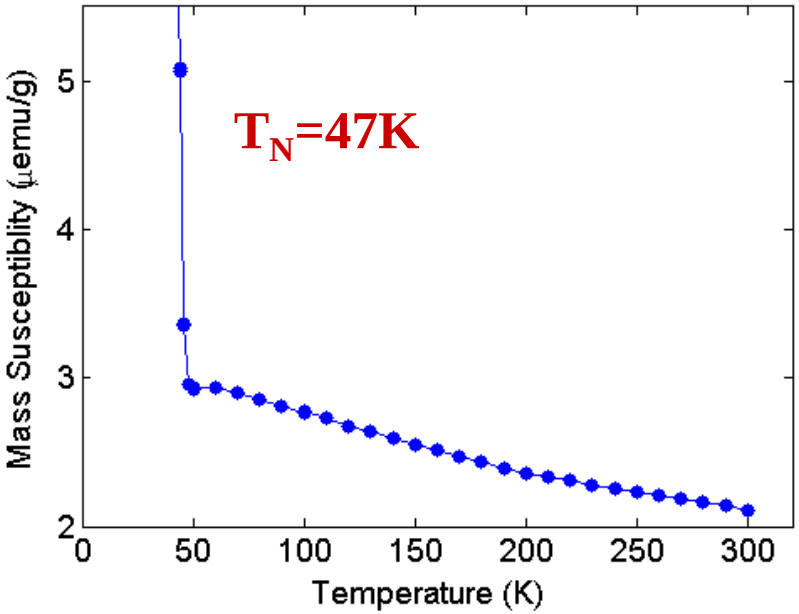



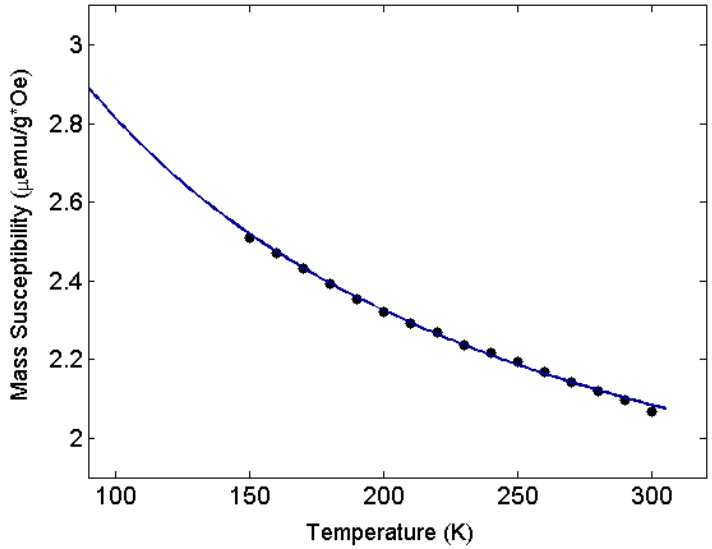

**Small field on Cs site**
**Large on C site**
**Néel AF**

**Spectral broadening : static internal magnetic field.**

# Paramagnetic state SQUID susceptibility data

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




**High T Curie-Weiss behavior**

**Weiss temperature**: $\theta \sim 100\ K$

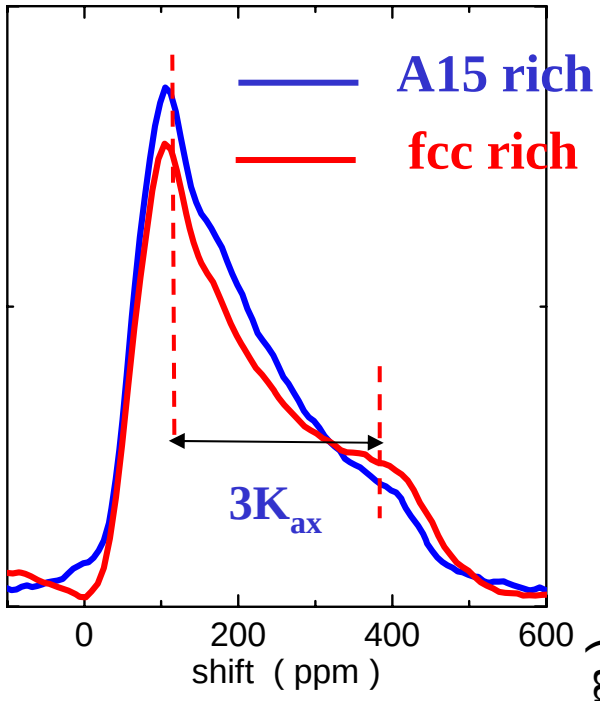
**Effective moment** : $p_{eff} \sim 1.70\ \mu_B$

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

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

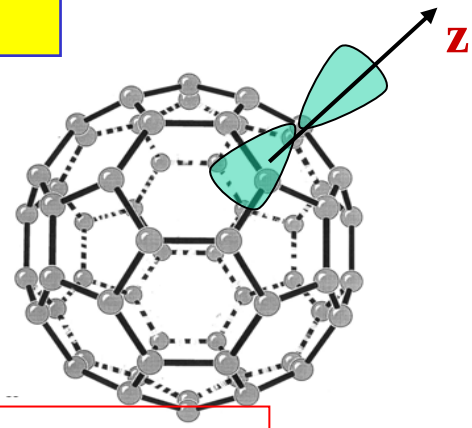
# $^{13}$C NMR

## Paramagnetic state NMR shifts $^{13}$C

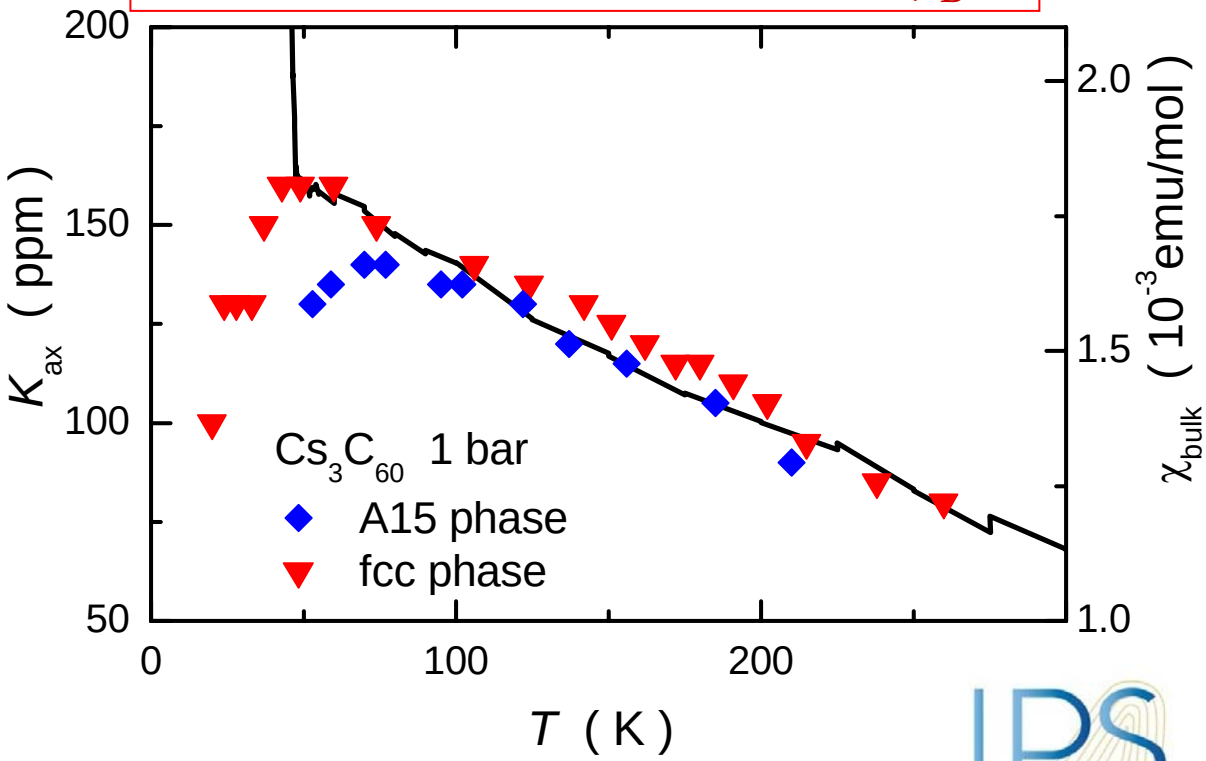



Molecular orbitals:
constructed from $p_z$ orbitals

Anisotropic hyperfine coupling
for $p_z$ orbitals $K_{ax} = A \ \chi_s$

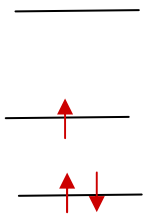



Here A is dipolar $A_{exp} \sim 700$ Oe/$\mu_B$
Calculated value : $A = 640$ Oe/$\mu_B$




**Local moment is indeed on the $C_{60}$ balls!**
**Low spin state (JTD)**

$S = 1/2$



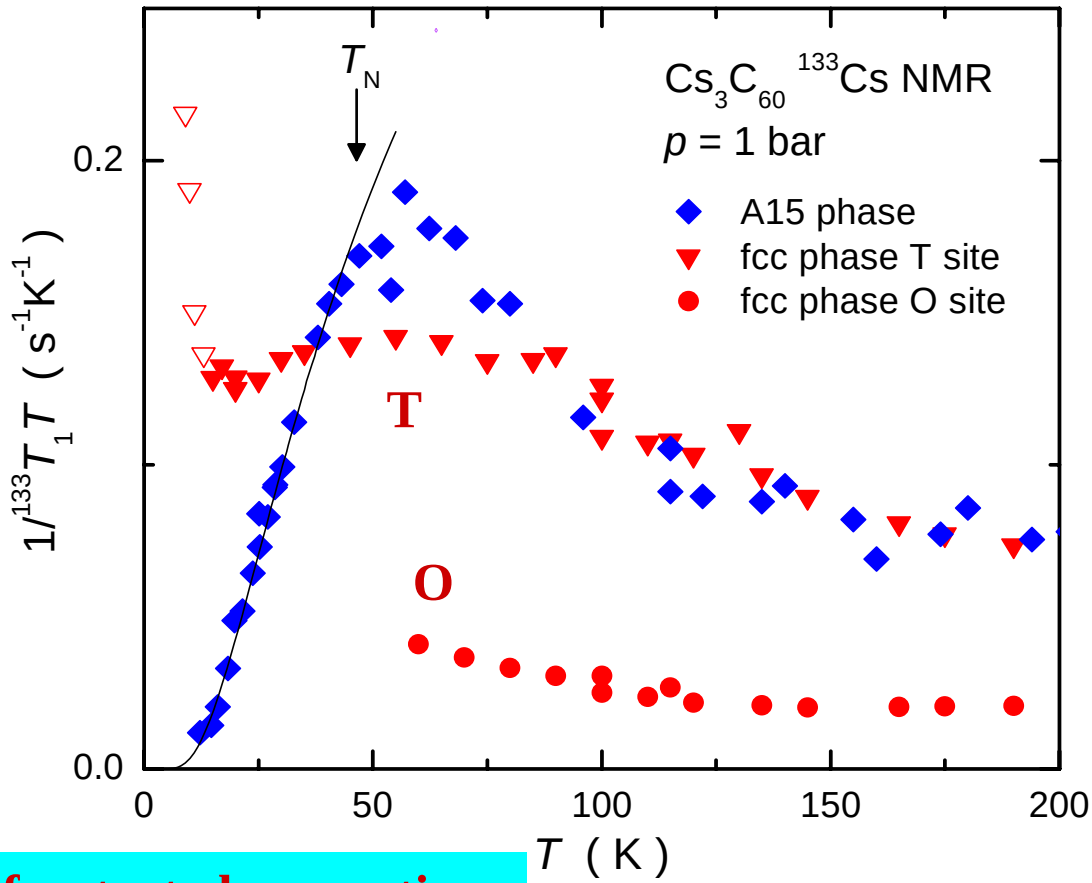
# Spin dynamics and crystal structure

$^{133}$Cs NMR $T_1$

**Both phases**
**Enhanced magnetic fluctuations in the paramagnetic state.**

**A15 phase**
**magnetic gap**
**$\Delta$ ~ 50 K**

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

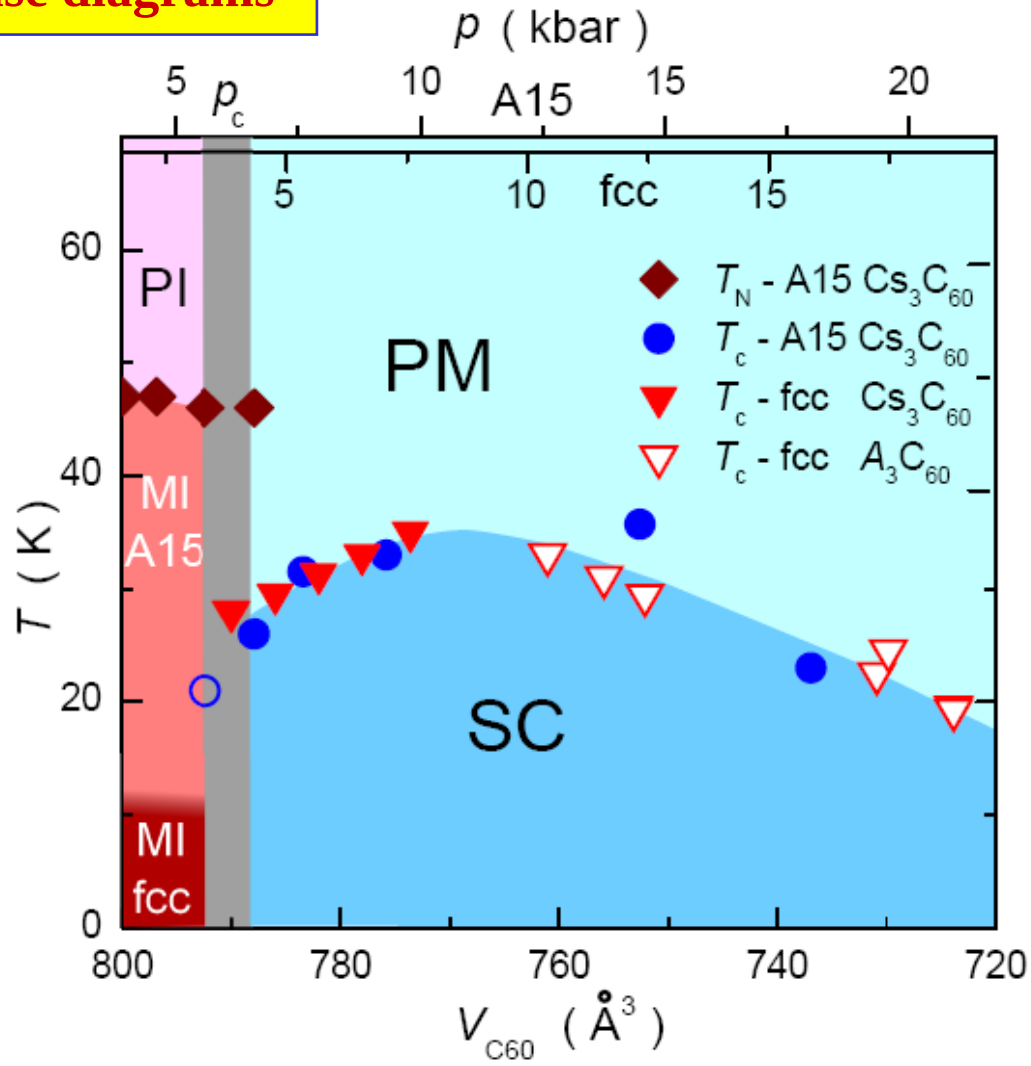



O site has twice smaller coupling constant than that for T site.

**Ordered versus frustrated magnetism (fcc not bipartite)**

# Phase diagrams

**Phase diagram of the two phases plotted versus volume per $C_{60}$ in the unit cell**




**Crystal structure has no incidence on the SC side**

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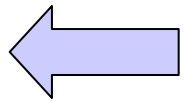
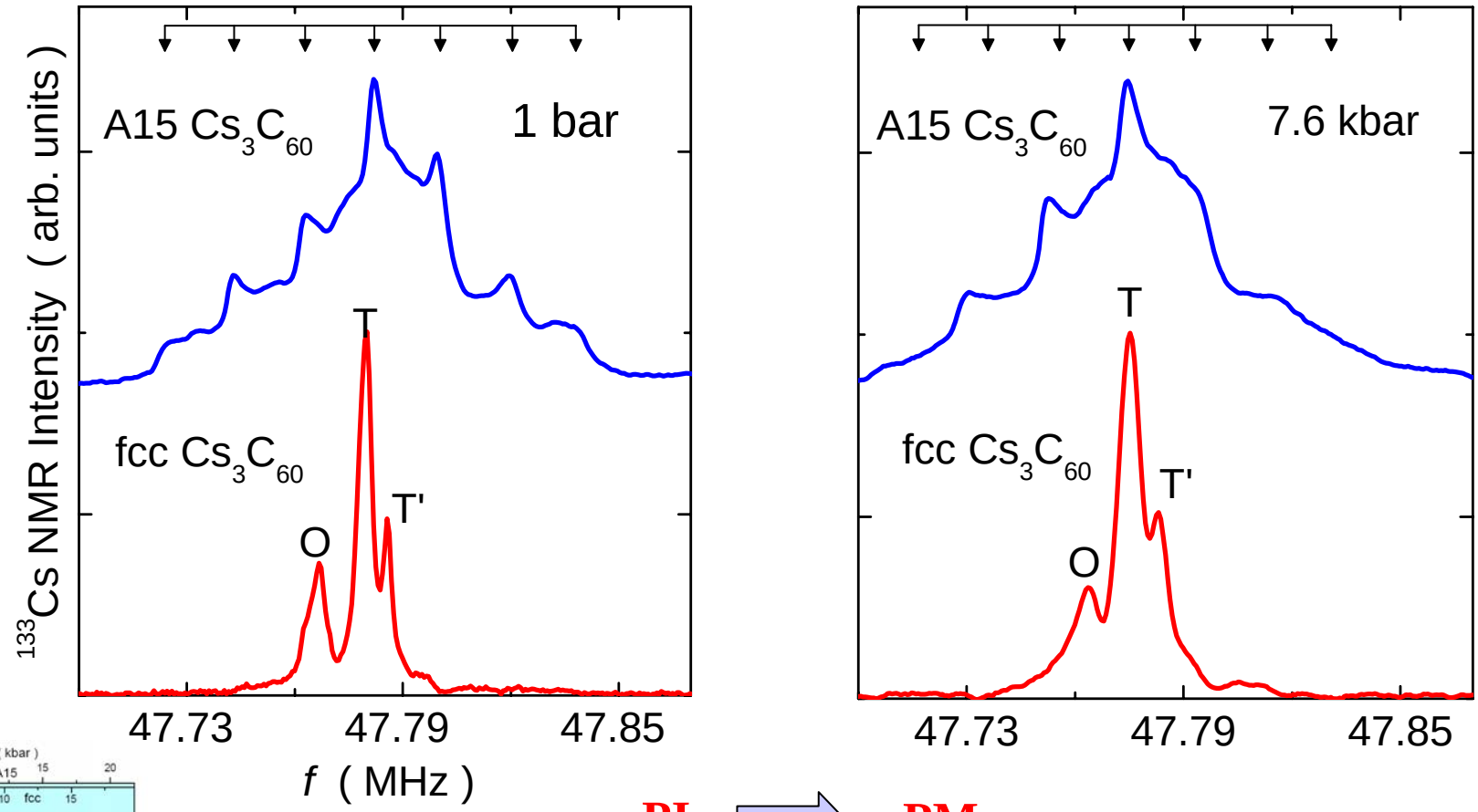
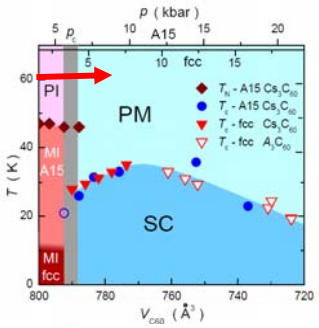


# Mott transitions to the metallic state in the two phases



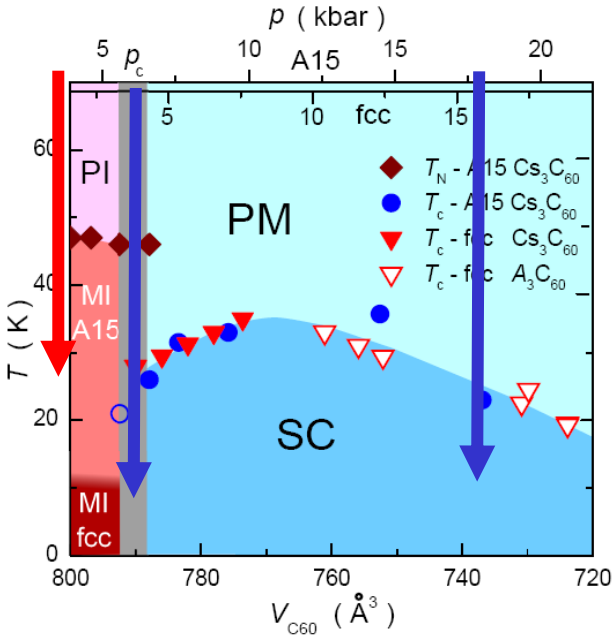

**PI** ⇨ **PM**

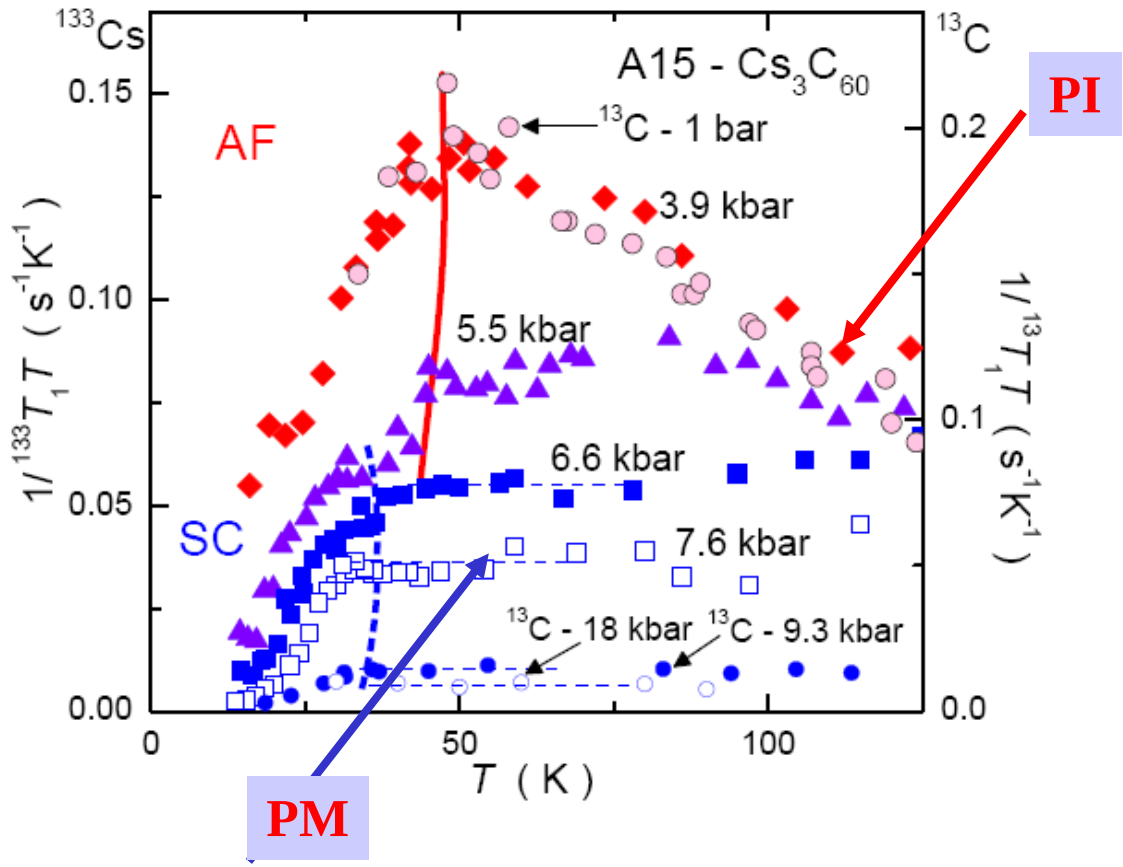
**No change of crystal structure across the transition**

TRIANGLE DE LA PHYSIQUE

LPS ORSAY

# Metallic properties near the Mott transition



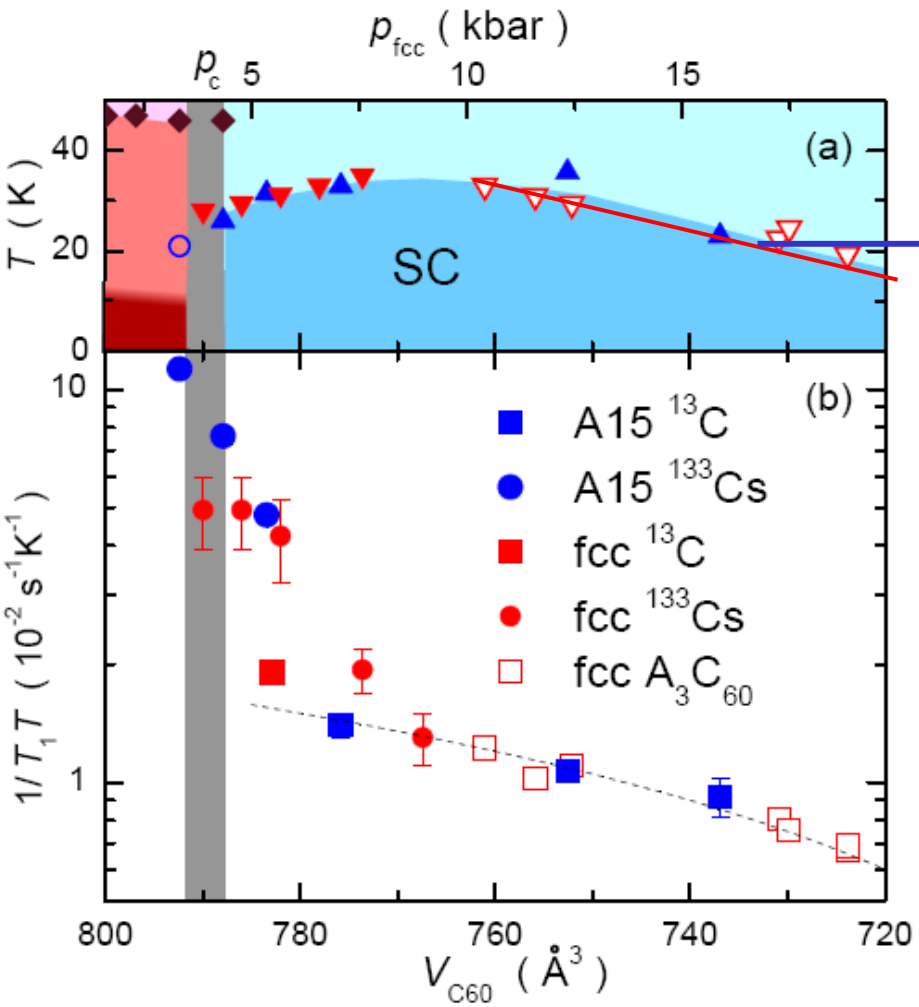



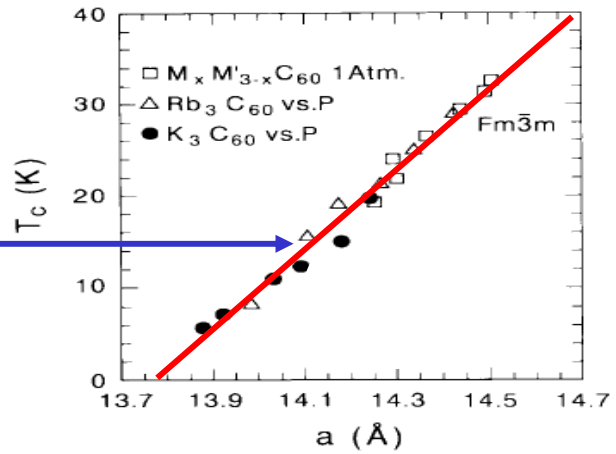

## Korringa constant near $T_c$

$$\frac{1}{T_1 T} = \frac{4\pi k_B}{\hbar} A_{\mathrm{hf}}^2 \rho(E_F)^2$$

**Large increase of $(T_1T)^{-1}$ with decreasing p towards $p_c$**

# Metallic properties near the Mott transition




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

$$(T_1T)^{-1} = \frac{4\pi k_B}{\hbar} A_{hyf}^2 \rho^2(E_F)$$

**Distinct behaviours near $p_c$**

**AF correlations dominate near $p_c$**

# Characteristics of the 3D Mott Transition

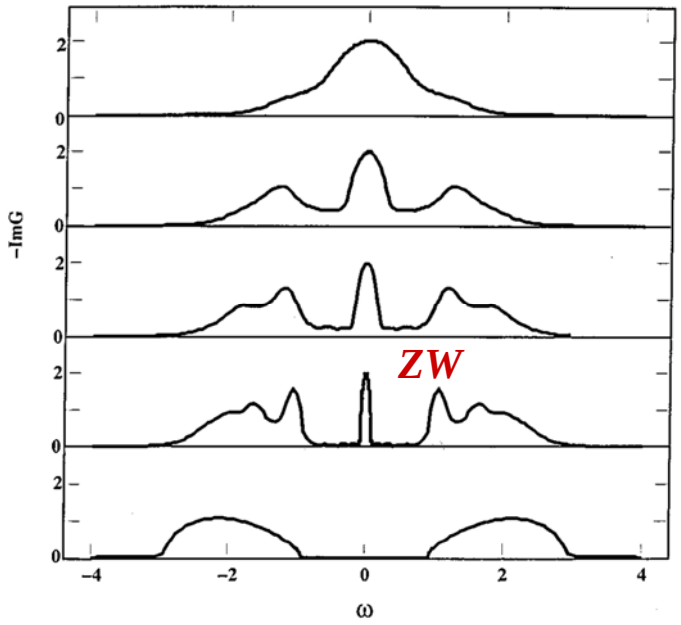
*A.. Georges and G. Kotliar*

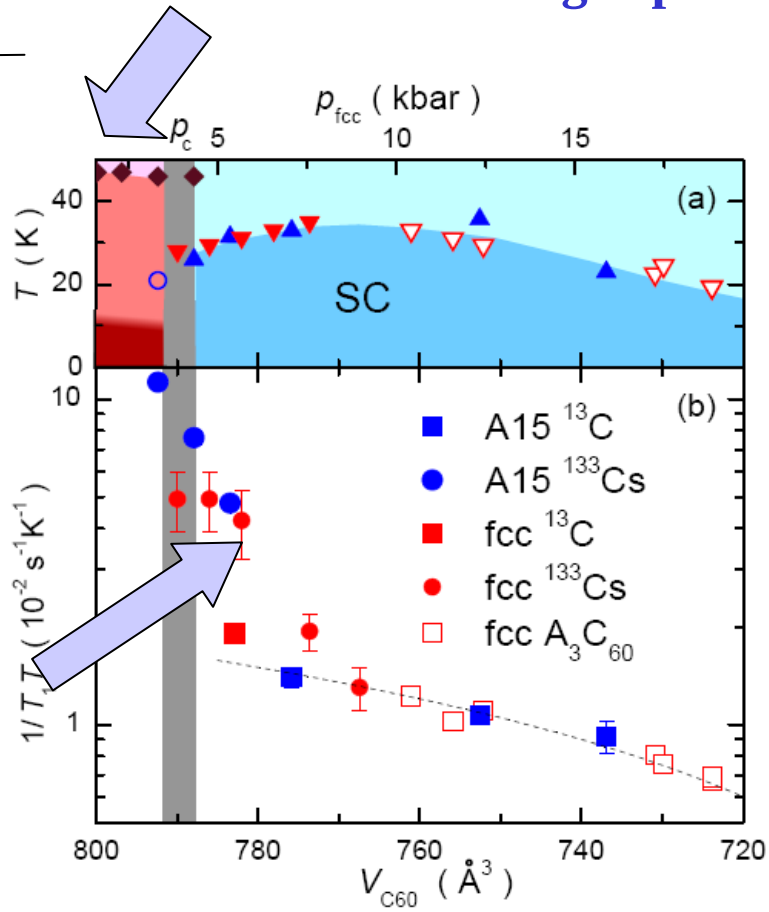
**S= 1/2**

**Multiorbital Mott transition**

**But no excitation to high spin state**

*U*

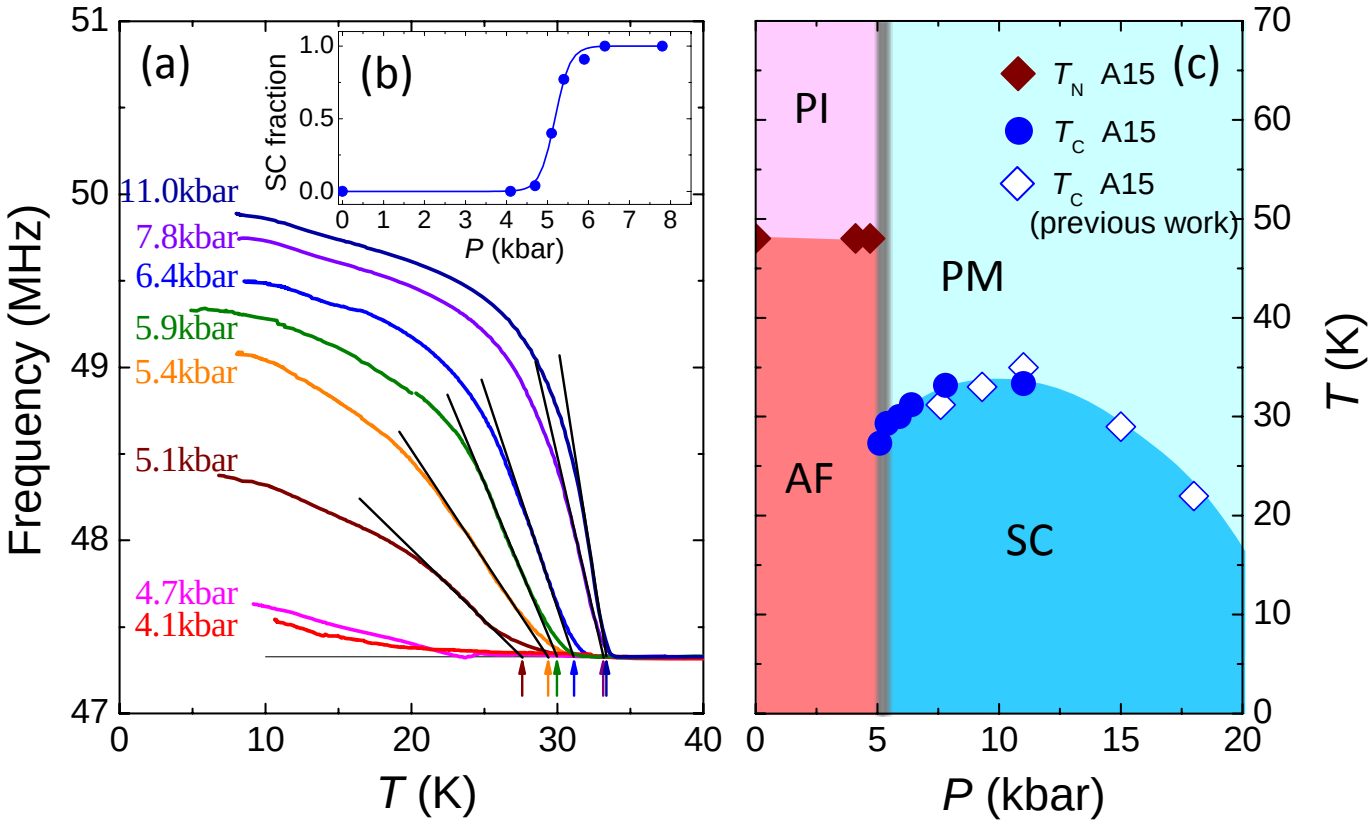



**AF correlations in the metallic state near $p_c$ while low quasiparticle weight is expected**

**SC favored in the correlated multiorbital state ?**

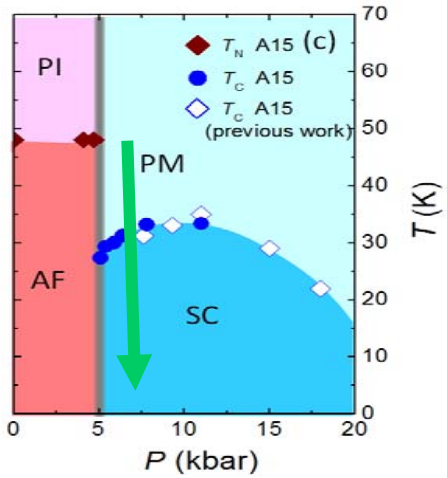
# Mott transition to the metallic state in a clean A15 sample



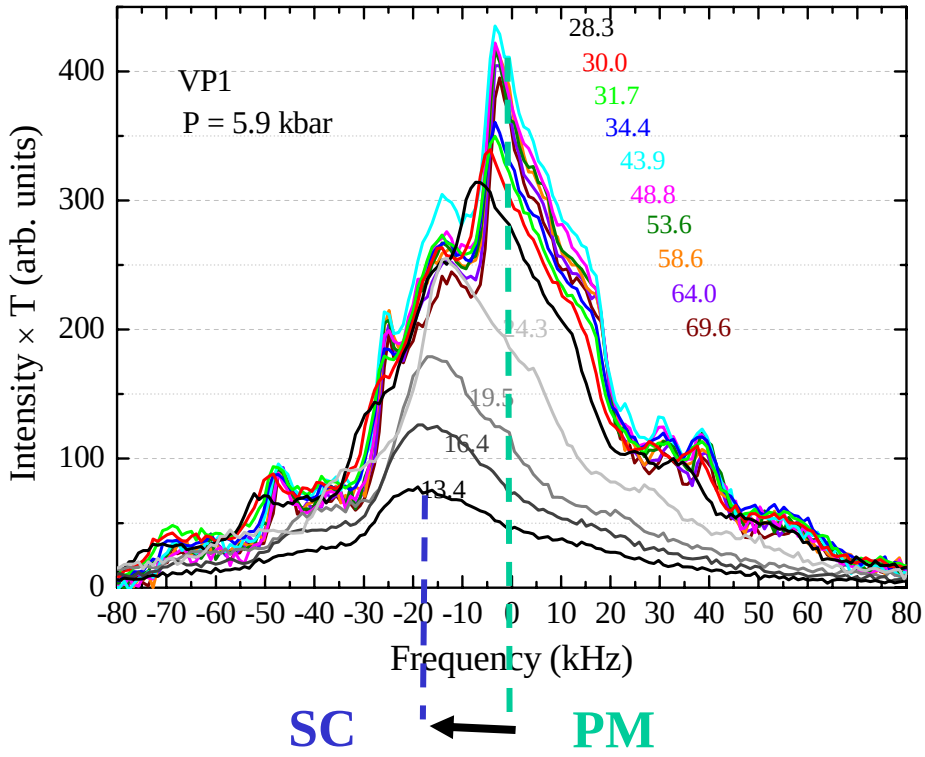

**Sharp first order Mott transition**

*P. Wzietek, et al, Phys. Rev. Lett.* ***112,*** *066401 (2014), arXiv1310.5529*

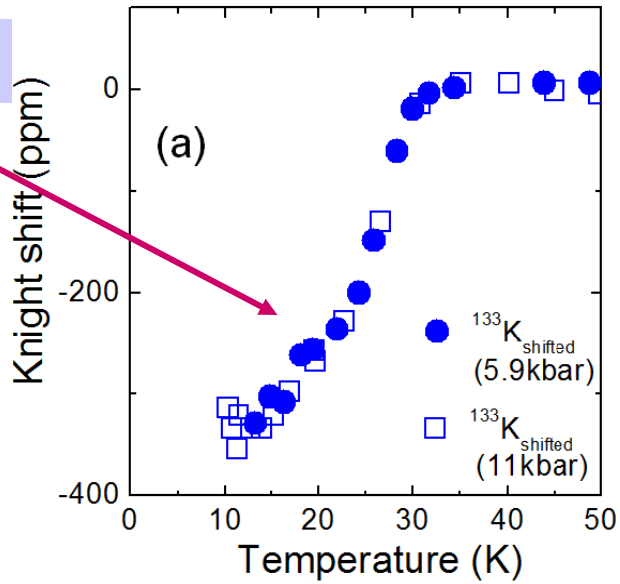
# Superconductivity : singlet behaviour




**p >> $p_c$**



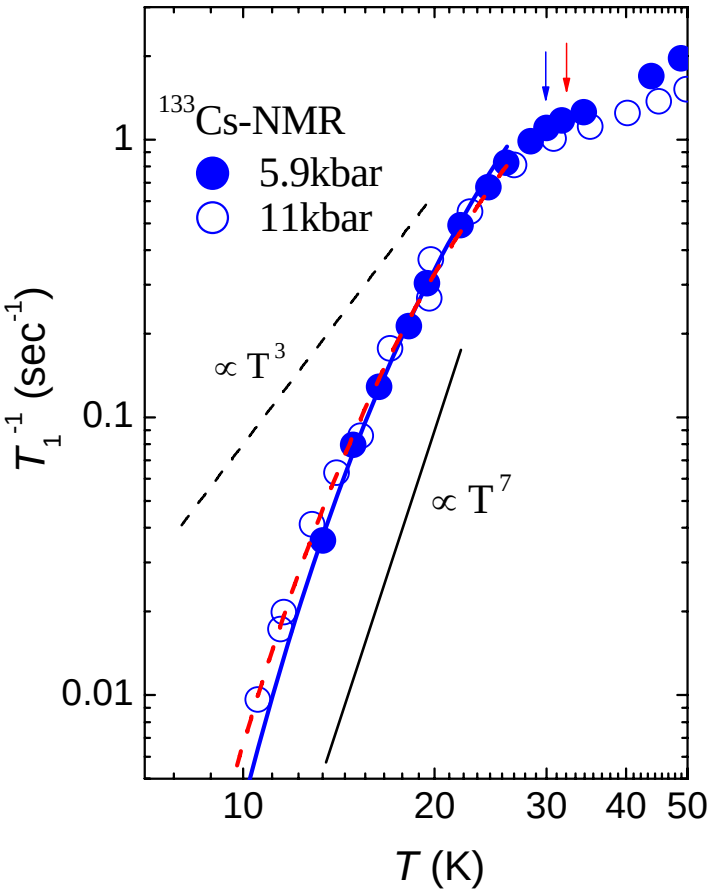

**SC gap**

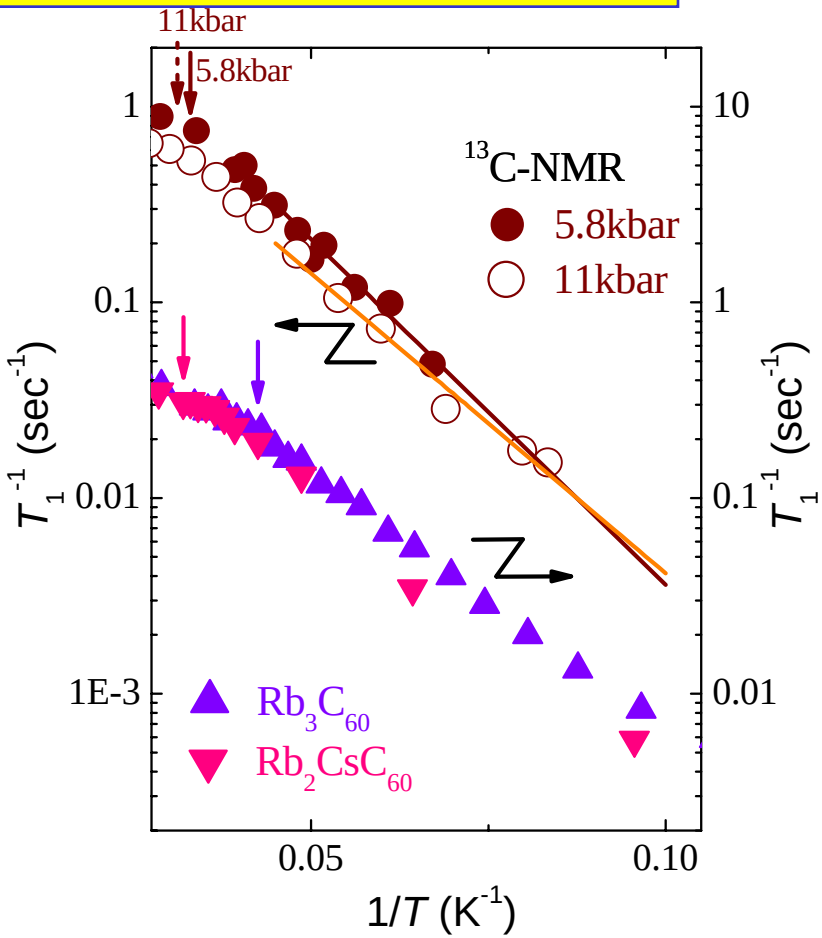



**Knight shift and $\chi_s$ drop below $T_c$ (singlet pairing)**

**s wave as $K_3C_{60}$ or $Rb_3C_{60}$**

# Superconducting gap variation near the Mott transition

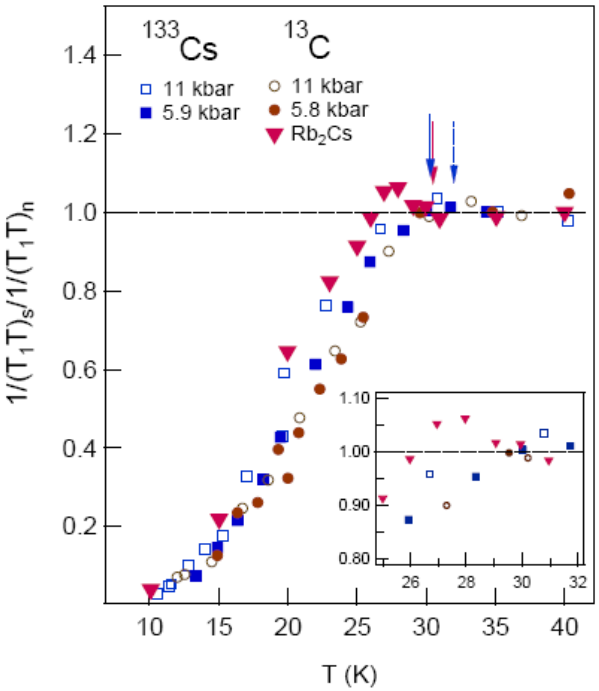


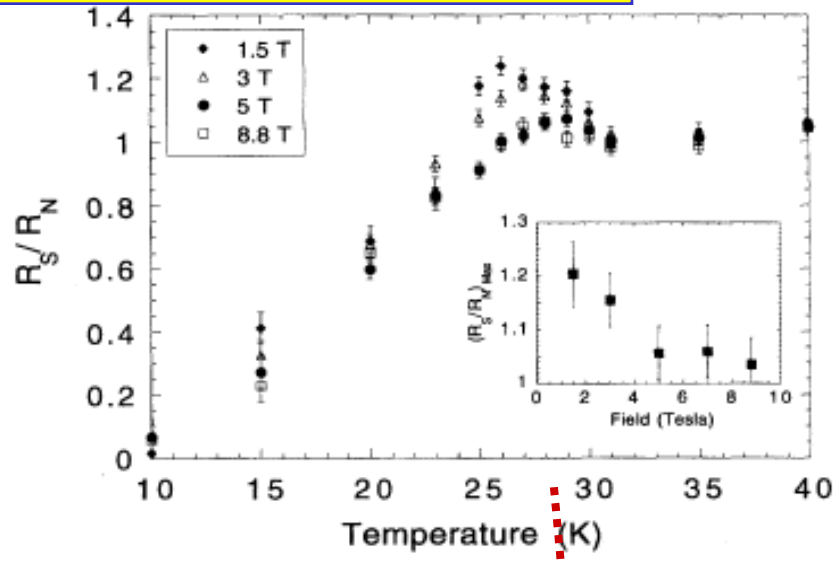



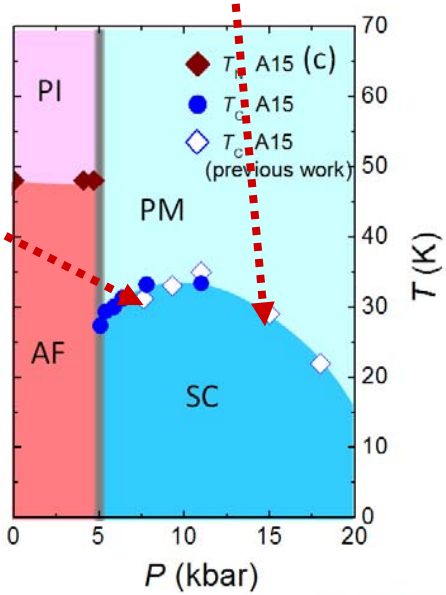

**Low T variation of $1/T_1$**
**Probes the SC excitations**
**$1/T_1 \alpha\ exp\ (-\Delta/k_BT)$**
**isotropic gap**

**Measurement of the gap**
**for various distances between $C_{60}$ balls**

# No Hebel Slichter peak near the Mott transition



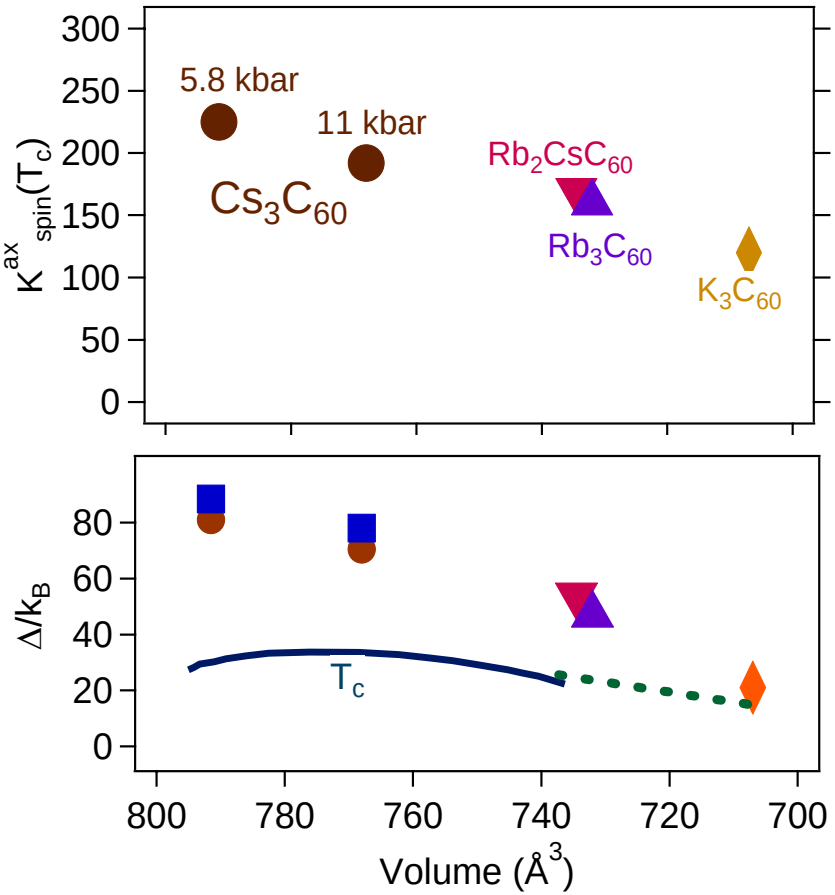



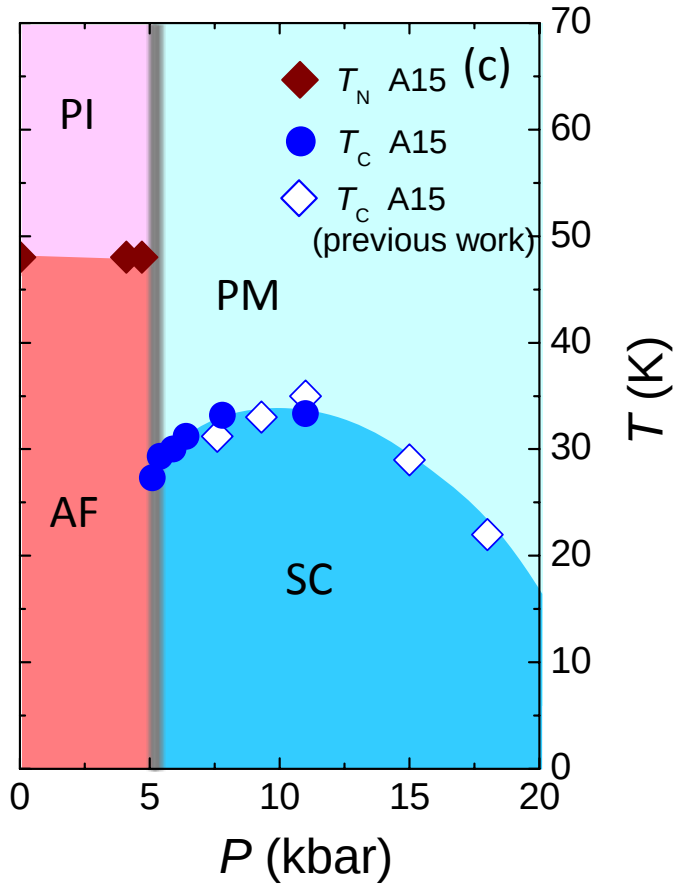




**Near $T_c$ no sign of Hebel Slichter**
**Different from the case of $Rb_2CsC_{60}$**

# Variation of the physical quantities with pressure near the Mott transition

**No pseudogap on $\chi$ nor on $1/T_1$**




**The SC gap increases up to the Mott transition**

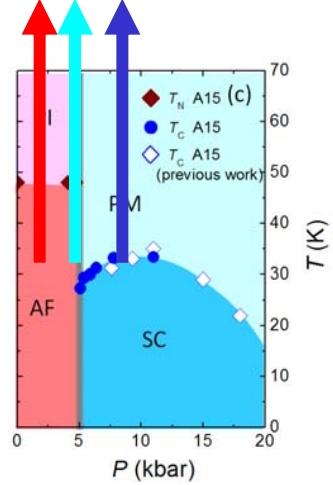
# Critical point of the high T Metal to Insulator transition?

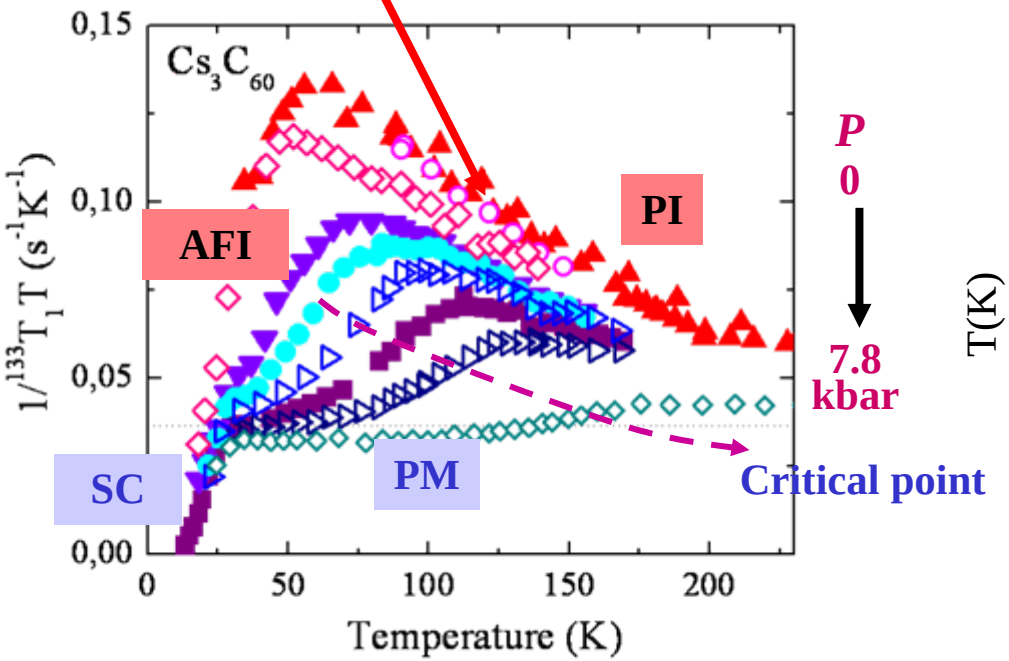
**A15 phase**

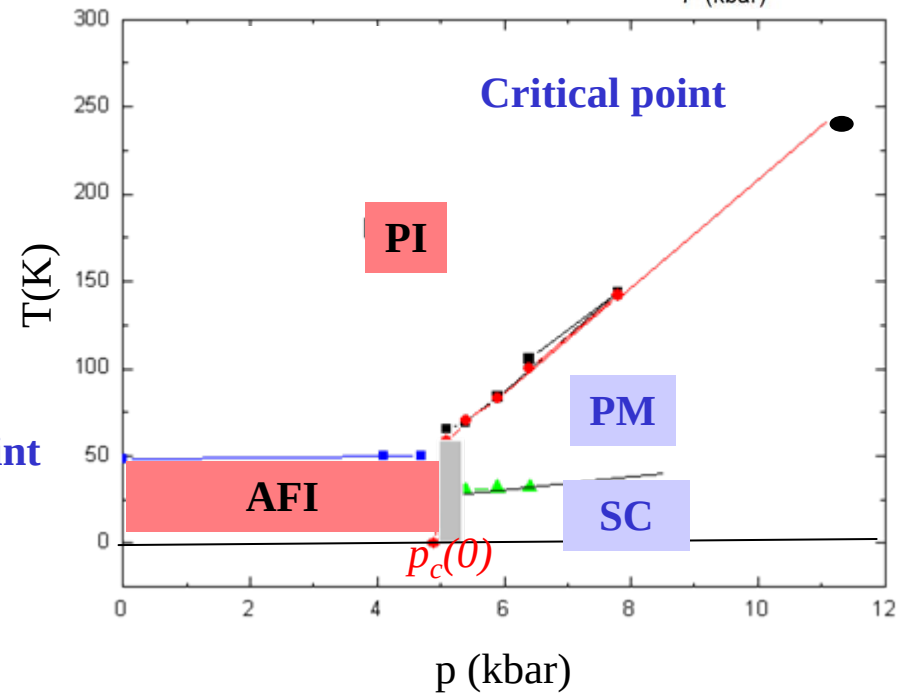
**Dense paramagnet phase well above $T_N$**

$$\frac{1}{T_1} = A_{hyf}^2 \frac{\sqrt{\pi S(S+1)/3}}{\gamma_e \mu_B k_B z J}$$

**The insulating phase is recovered with increasing T**



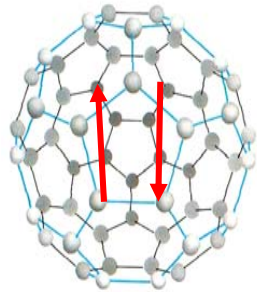




**Variation with lattice parameter that is *t /U* ?**

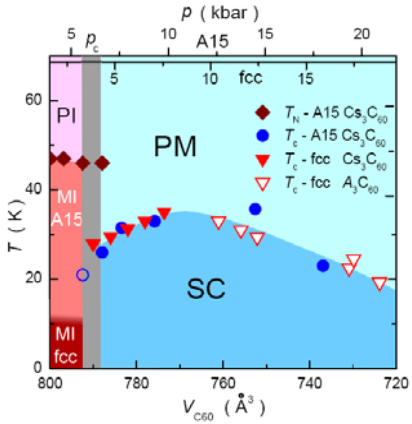
# Summary

- **Fullerides: originalities asociated with their nanostructure.**
  **Internal degrees of freedom of the molecule:**
  **Phonons, Molecular Jahn-Teller distorsions**



- **Peculiar correlated electron systems**
  **Interplay of Jahn-Teller effects and correlations**

- **$Cs_3C_{60}$ : IMT toward High $T_c$ superconductivity**
  - **Multiorbital Mott transition** ( no excitation to high spin)
  - **"Model" 3D MIT** ( no structural change detected so far )
  - **SC is at ease with electron correlations**
  - **Electron correlations strengthen phonon mediated SC??**
  - **DMFT calculations predicted SC dome above Mott**




M. Capone, M. Fabrizio, C. Castellani and E. Tossati RMP 2009

- **Ideal system for theoretical understanding of SC near MIT**