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金属内包フラーレンの紫外光電子分光

ー内包金属とフラーレンケージの相互作用ー

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- Introductory
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  - **アルカリメタル･フラーレン錯体**
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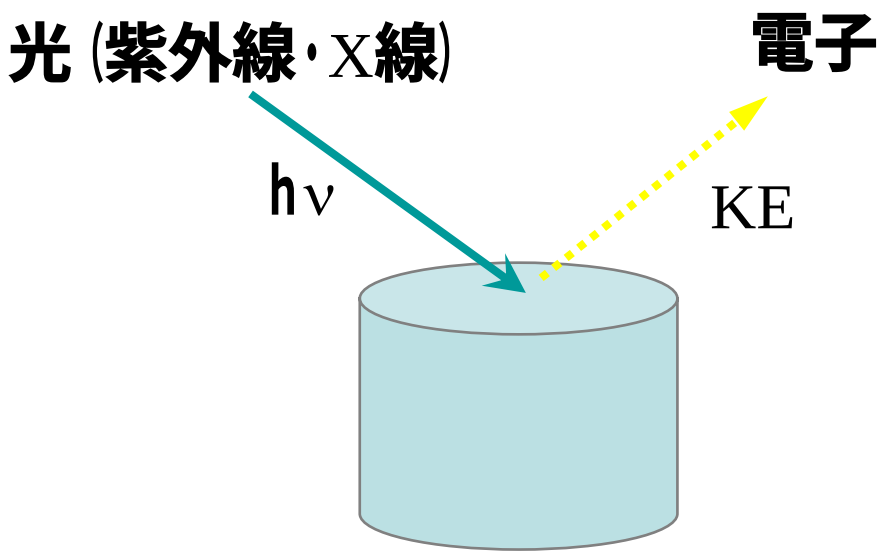
- **単原子内包フラーレン**
  - M@C_{82}
- **多原子内包フラーレン**
  - C_{82} cage
  - C_{78} cage
- **まとめ**

光電子分光法とは？

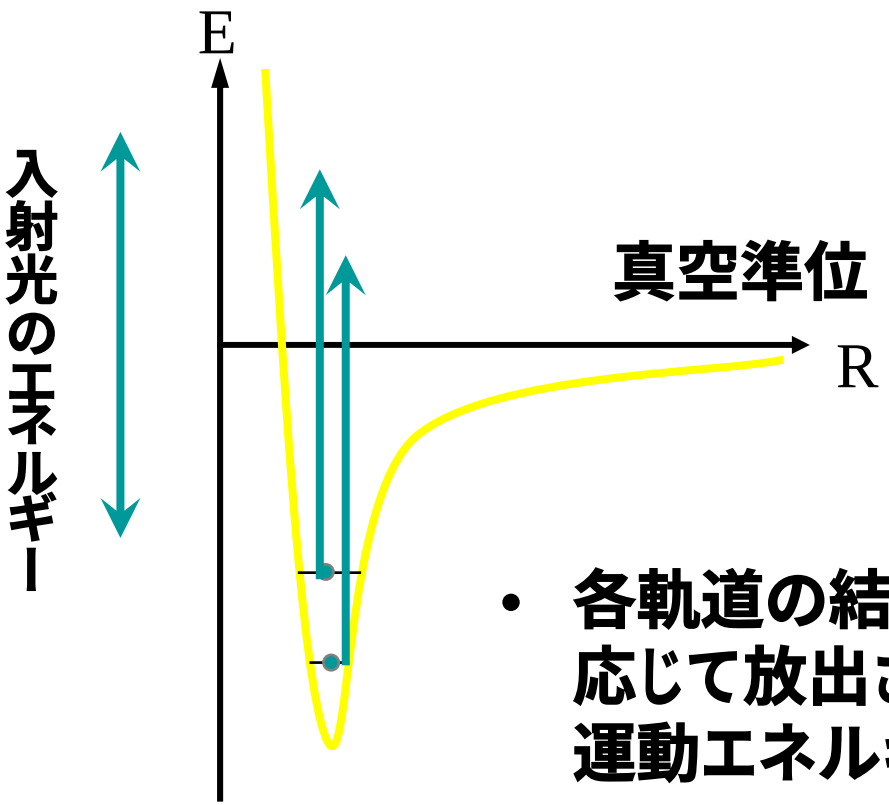
- **原理は**Einstein**の光電効果（１９０５）**



$$KE = h\nu - BE$$

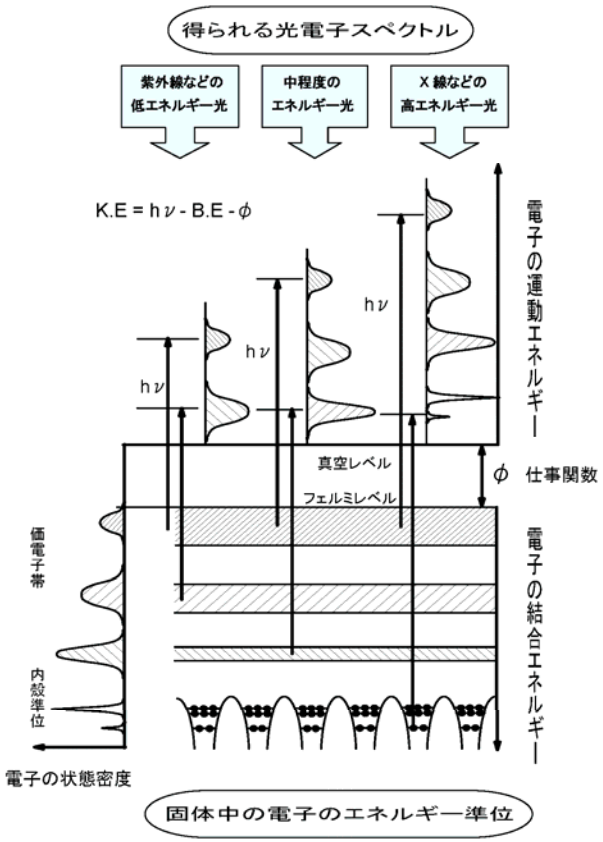
BE **は電子の結合エネルギー**

自由原子･分子からの光電子放出



- 各軌道の結合エネルギーに応じて放出される電子の運動エネルギーが異なる

固体からの光電子放出



原則的には
気体からの
光電子放出と同じ

ただし、
エネルギーの基準点は
Fermi Level

固体からの光電子分光で分かること

- 電子状態
  - 内殻準位の結合エネルギー
  - 価電子帯の電子の状態密度
- さらに. . .
  - 金属･半導体の判定

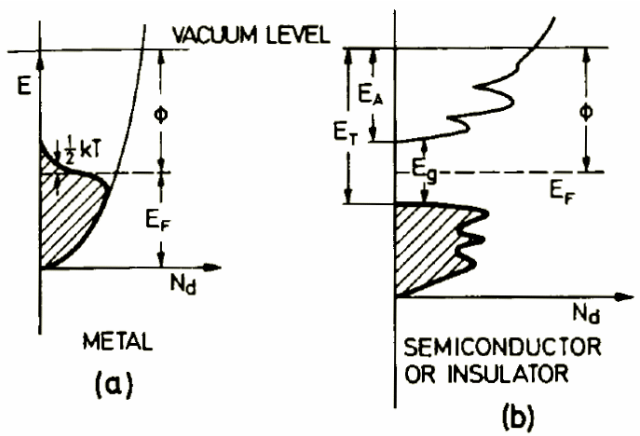
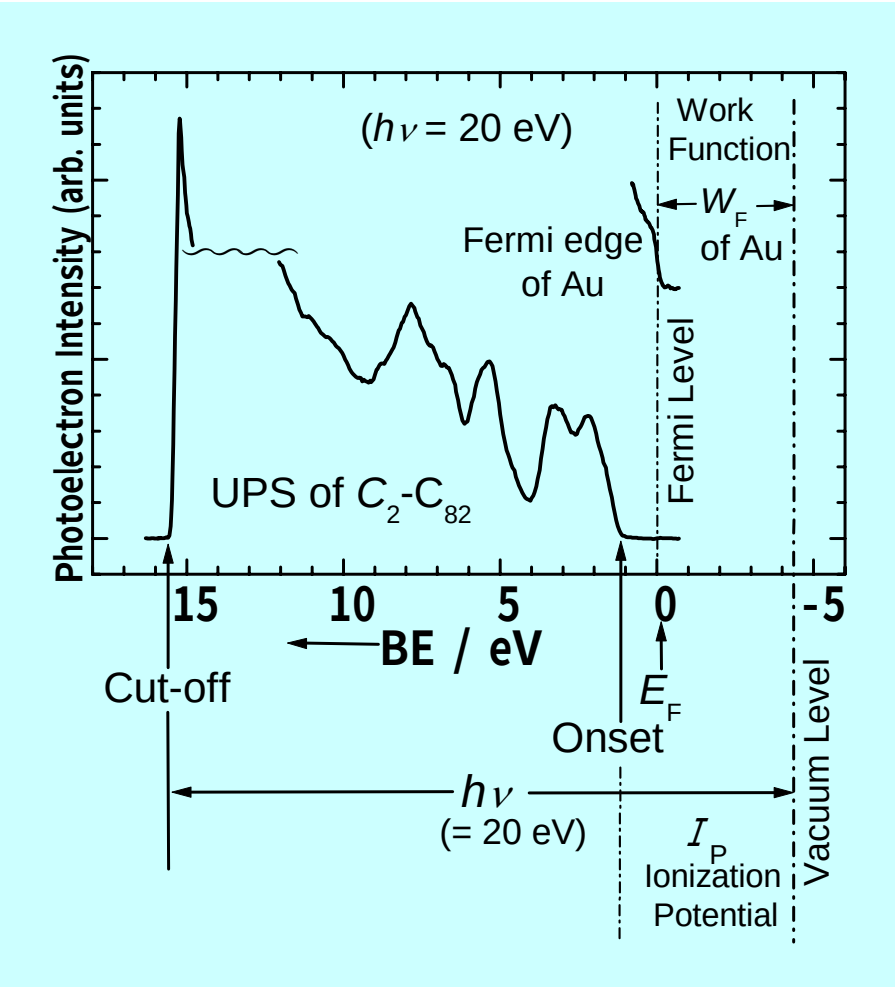


Fig. 1.9a and b. Density of occupied and empty states in (a) a metal and (b) in a semiconductor or insulator. Also, definition of the Fermi level E_F, the work function ϕ, the electron affinity E_A, the photoelectric threshold E_T, and the fundamental gap E_g. For a metal $E_T = \phi$

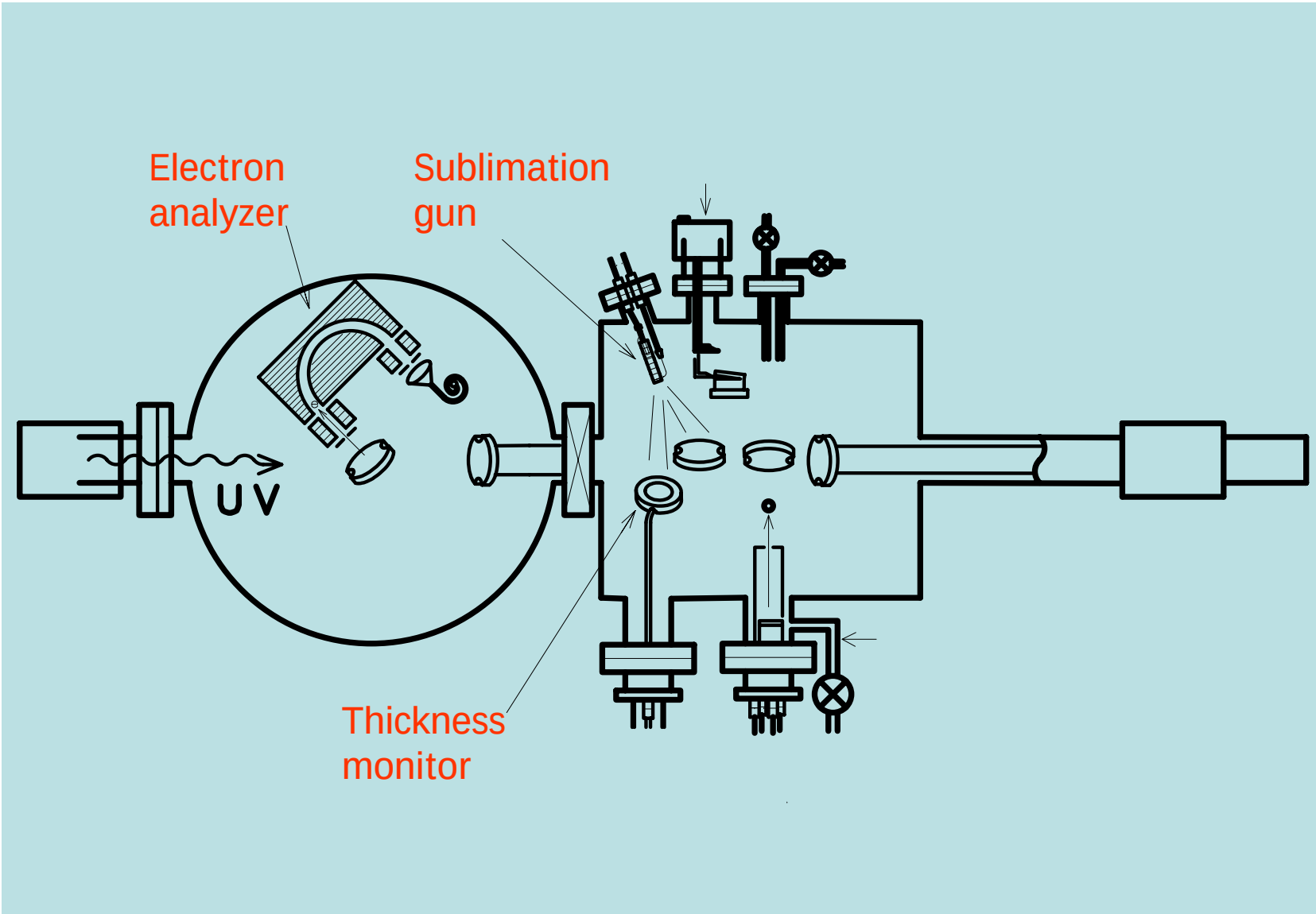
紫外光電子スペクトルの見方

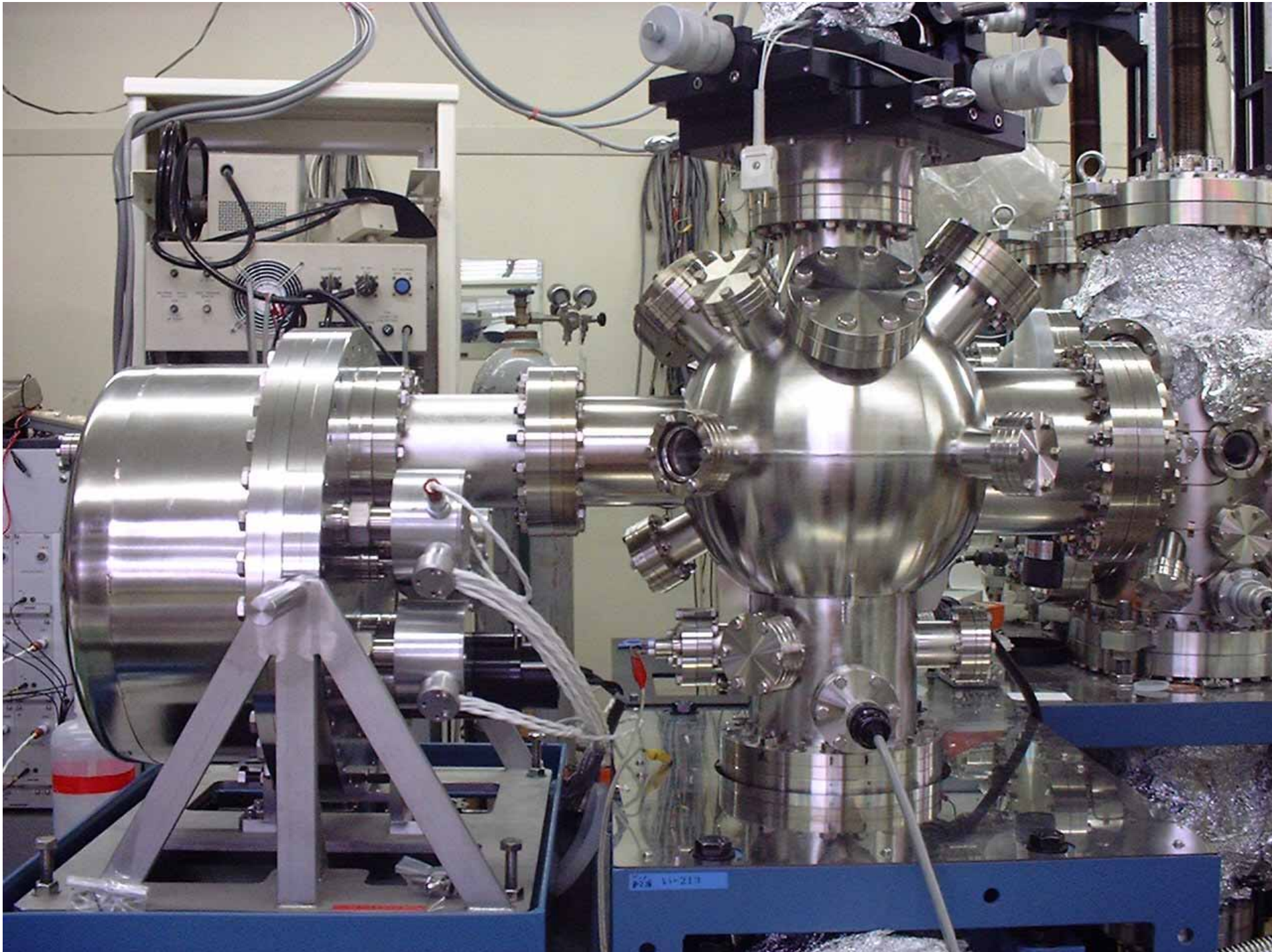


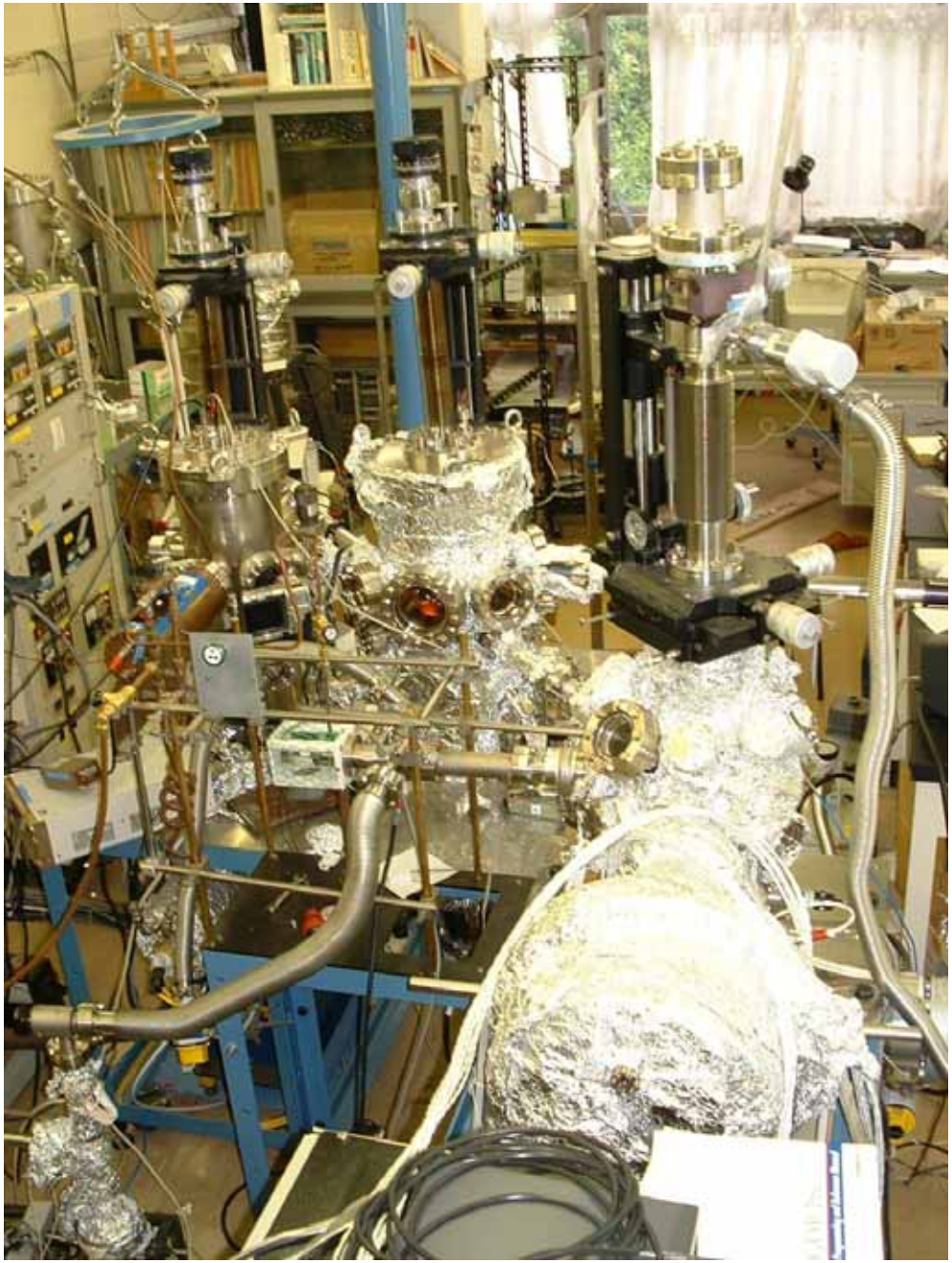
まず、金のスペクトルを測定して
Fermi levelを決める

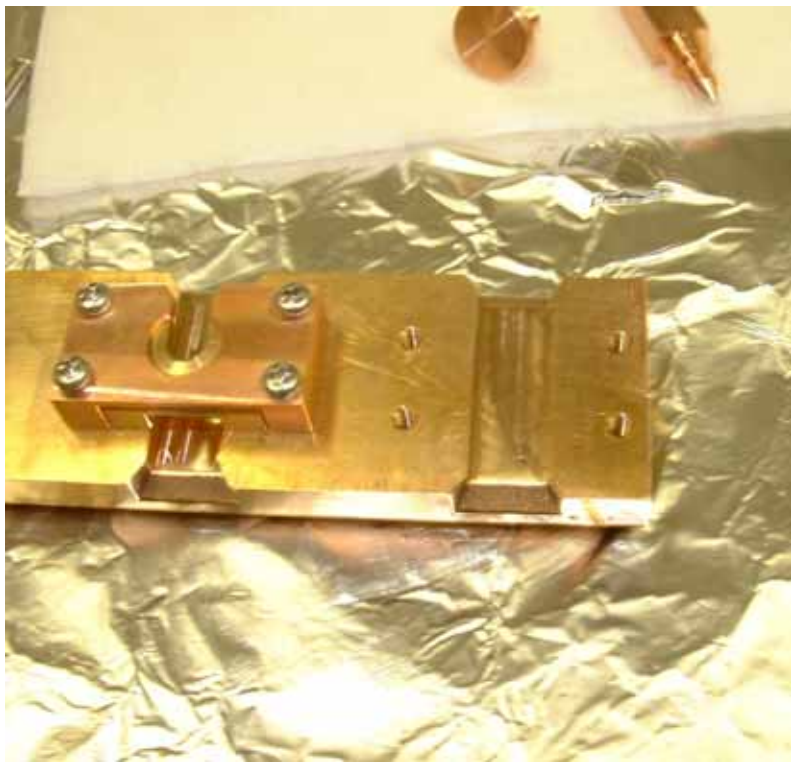
次に試料を蒸着して測定

光電子分光装置の概要









- Superconductivity in alkali metal – C_{60} complex

Superconductivity at 18 K in potassium-doped C_{60}

A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez & A. R. Kortan

AT&T Bell Laboratories, Murray Hill, New Jersey 07974-2070, USA

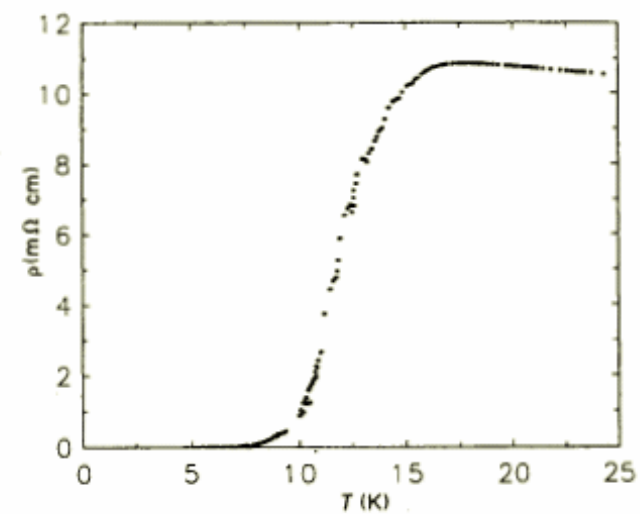


FIG. 2 Temperature dependence of the electrical resistivity of a 960-Å-thick film of K_xC_{60}.

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From 18 K (K_3C_{60}) to 33K (Cs_2RbC_{60})

expectation of high temperature superconductor

on higher fullerenes

As for A_xC_{60},

Stable phases : A_1C_{60}, A_3C_{60}, A_4C_{60}, A_6C_{60}

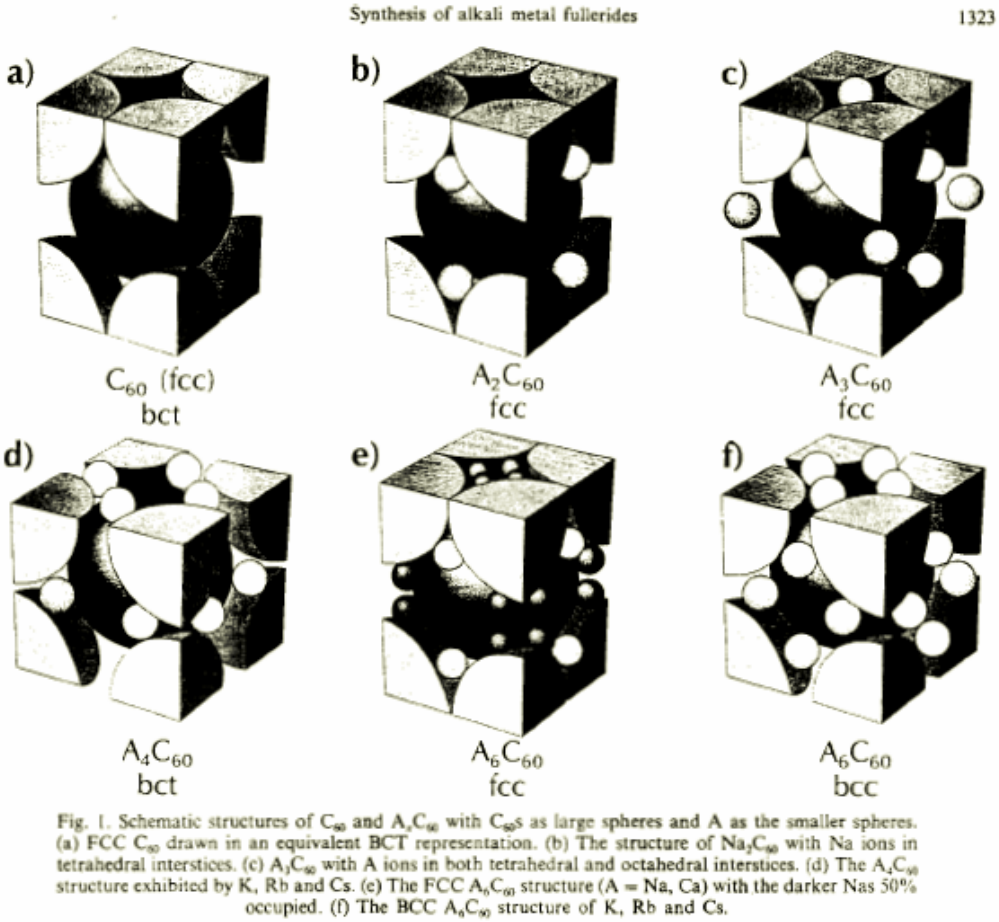

Fig. 1. Schematic structures of C_{60} and A_xC_{60} with C_{60}s as large spheres and A as the smaller spheres. (a) FCC C_{60} drawn in an equivalent BCT representation. (b) The structure of Na_2C_{60} with Na ions in tetrahedral interstices. (c) A_3C_{60} with A ions in both tetrahedral and octahedral interstices. (d) The A_4C_{60} structure exhibited by K, Rb and Cs. (e) The FCC A_6C_{60} structure (A = Na, Ca) with the darker Nas 50% occupied. (f) The BCC A_6C_{60} structure of K, Rb and Cs.

Metallic A_xC_{60} complexes
A = K, Rb, Cs

Semiconductive A_xC_{60} complex
A = Li, Na, Mg

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- Alkali (alkali earth) metal C_{60} complexes
  - Metallic (superconducting*) phase :

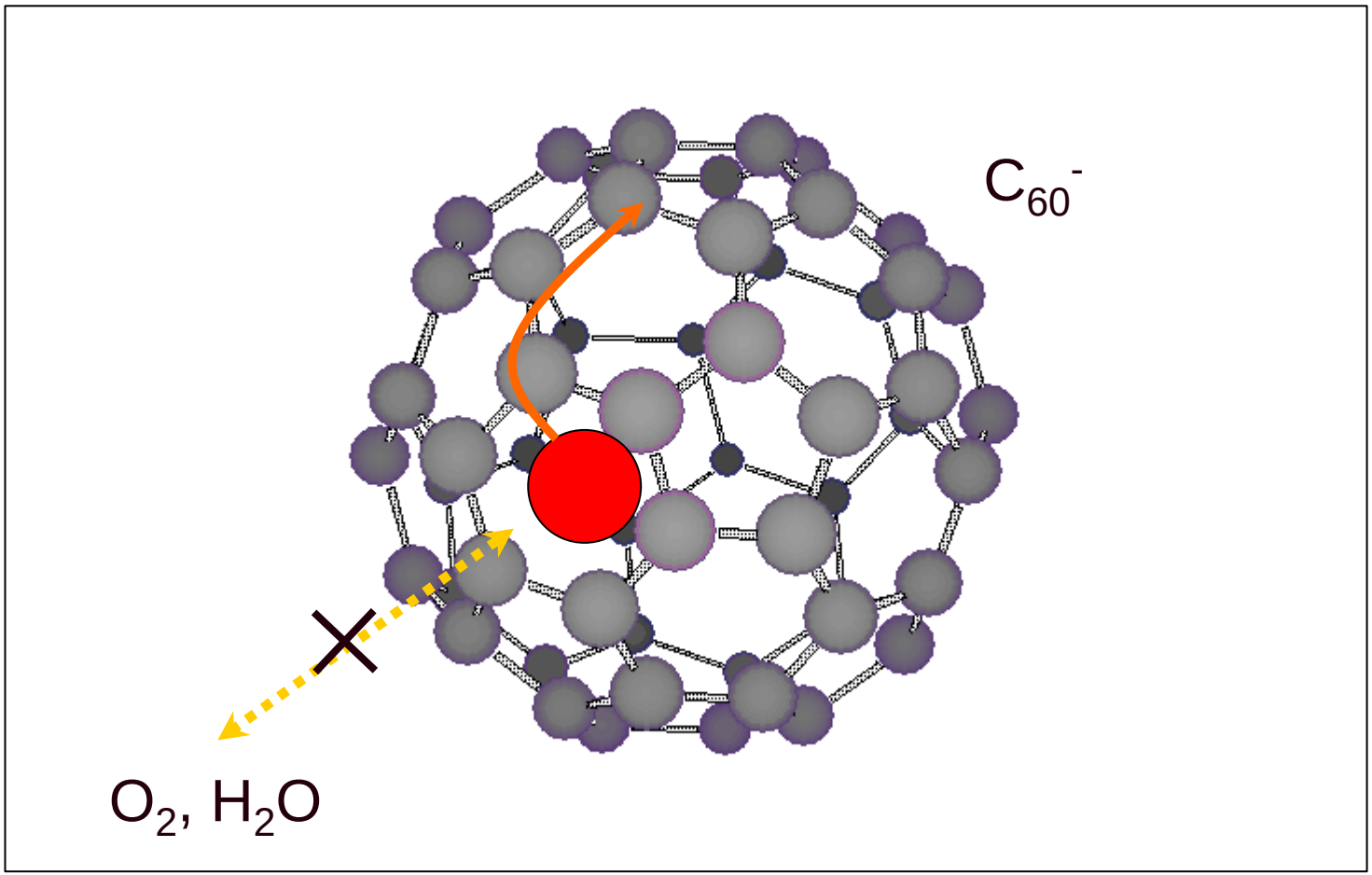
    A_1C_{60}, A_3C_{60}* (A = K, Rb, Cs)

    Ca_5C_{60}*, Ba_6C_{60}*
- Not all electron accepting fullerenes become metallic or superconducting.

- Electron donation to C_{60} is the key.

- They are unstable to the ambient air !

Enclosure of donor in the cage



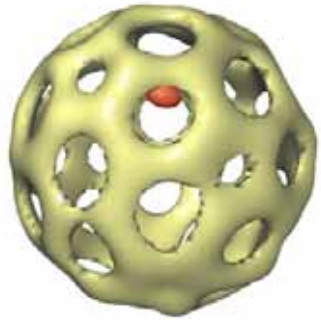
Encapsulation of electron donating atom(s) prohibits degrading of donor

Metallofullerenes synthesized so far

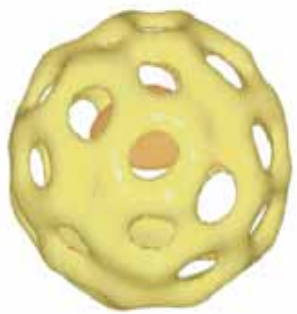
$M^{2+}@C_{2n}^{2-}$、$M^{3+}@C_{2n}^{3-}$、$M^{4+}@C_{2n}^{4-}$

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zu	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac															

Lanthanoid Series	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinoid Series	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

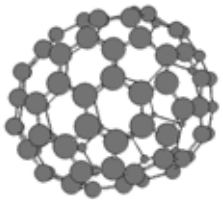


$Sc@C_{82}$

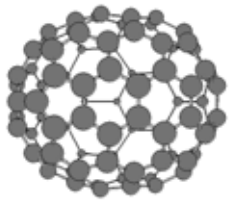


La@C82

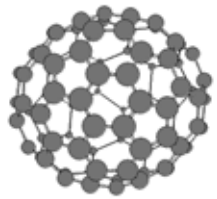
Isolated pentagon rule (IPR) satisfying C_{82} cages



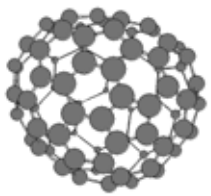
No.1 C_2(b)



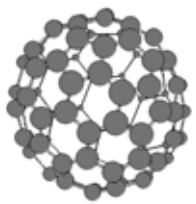
No.2 C_s(b)



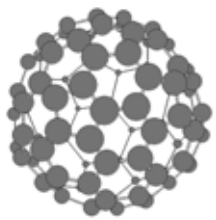
No.3 C_2(a)



No.4 C_s(c)

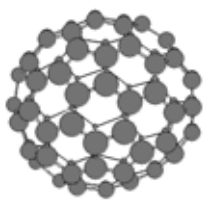


No.5 C_2(c)



No.6 C_s(a)

No.7 C_{3v}



No.8 C_{3v}

No.9 C_{2v}

$M^{3+}@C_{82}^{3-}$
C_{2v} (major),
C_s

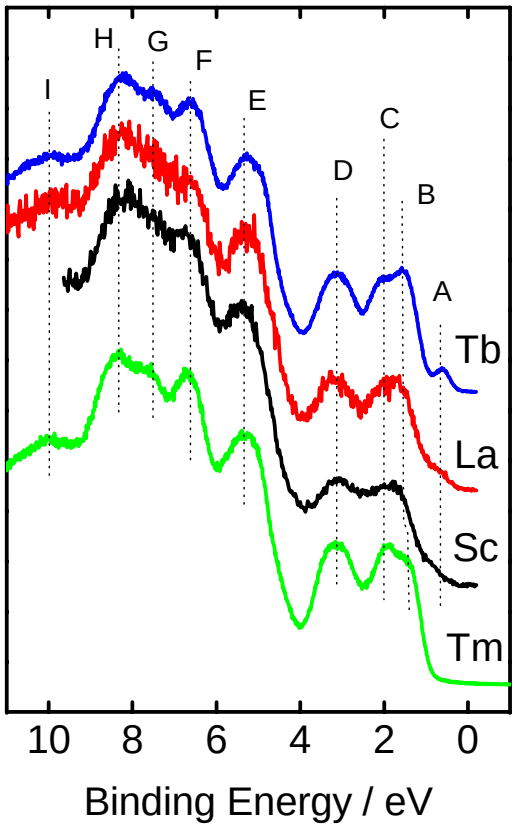
$M^{2+}@C_{82}^{2-}$
C_{2v}, C_2
C_s, C_{3v}

C_2 ×3
C_s ×3
C_{3v} ×2

One of the issues on $M@C_{82}$

- **電子状態を決めているものはなにか?**
  - **ケージ構造？　内包原子種？**
- **決定方法**
  - **内包原子種を変える**
  - **ケージ構造を変化させる**

Summary of Mono-metal atom entrapped C_{82}



Principally metallofullerenes with the same C_{2v} cage give essentially the same spectra.

That is,

Small or no interaction between the fullerene cage and the entrapped atom

Difference only in upper band due to the difference in the amount of electrons transferred

Multiple atoms encapsulated metallofullerenes

Examples ;

$Er_2@C_{82}$,

$La_2@C_{78}$, $La_2@C80$, $La_2@C_{84}$

$Sc@C_{66}$,$Sc_3@C_{82}$, $Sc_3N@C_{82}$, $Sc_2@C_{82}(Sc_2@C_{84})$, $Sc_2C_2@C_{84}$

$Ti_2C_2@C_{78}(Ti_2@C_{80})$, $Ti_2@C_{82}$, $Ti_2C_2@C_{82}$

$Y_2@C_{82}$, $Y_2C_2@C_{82}$ etc. etc….

Issues

Any special difference from $M@C_{82}$?

Entrapped atoms play differently or not?

Cage structure of three isomers : (I) $C_s(6)$, (II) $C_{2v}(9)$, (III) $C_{3v}(8?)$

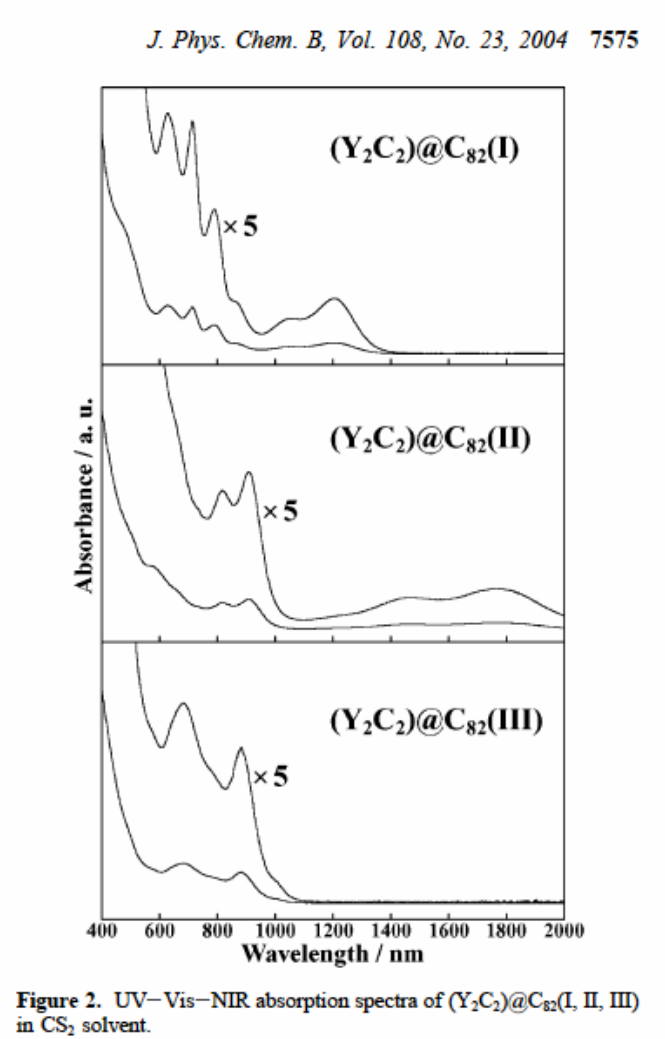


Figure 2. UV−Vis−NIR absorption spectra of $(Y_2C_2)@C_{82}$(I, II, III) in CS_2 solvent.

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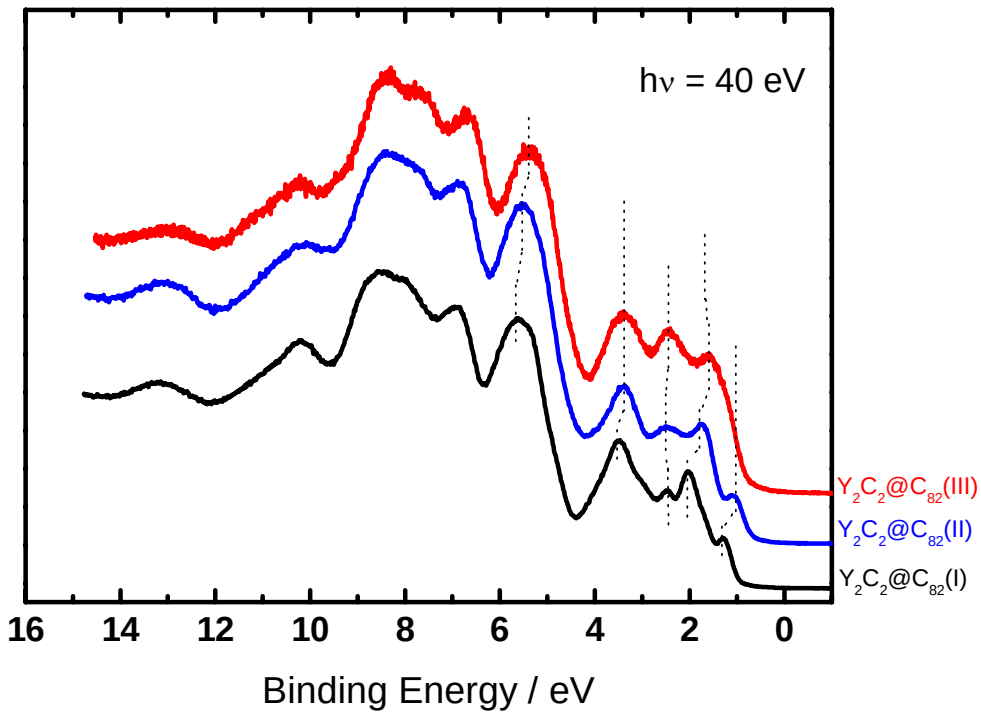


Different electronic structure, particularly in upper valence band region

C_{82} cage also contains metal atoms without carbon atoms.

$Y_2C_2@C_{82}$ and $Y_2@C_{82}$ give analogous absorption and have the same C_{3v} cage structure

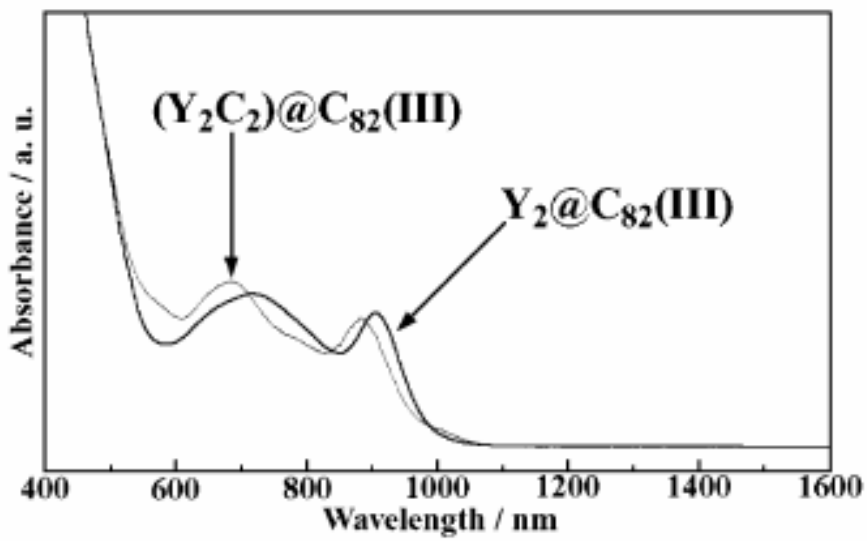
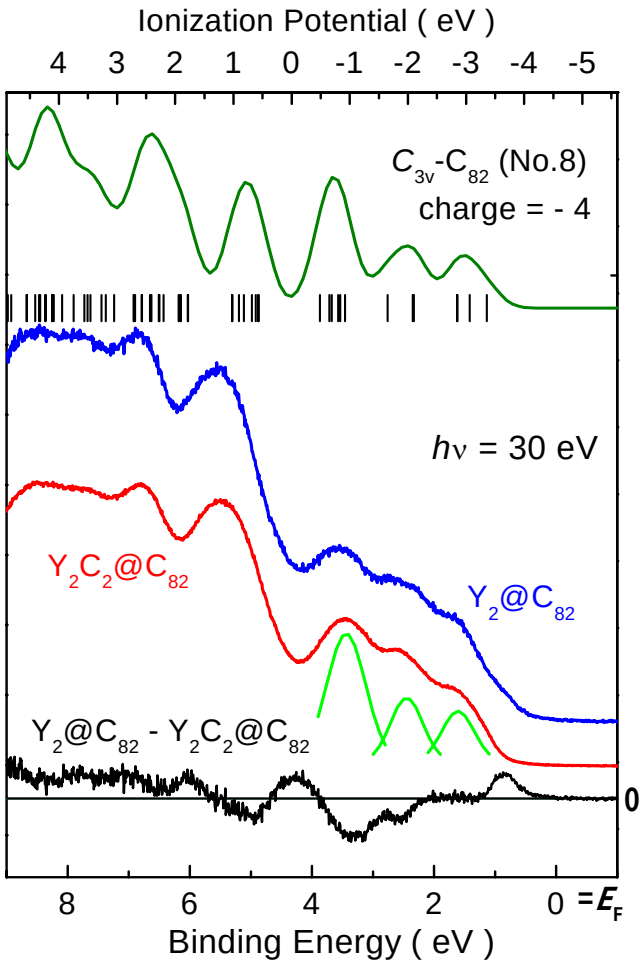


Figure 4. UV−Vis−NIR absorption spectra of $(Y_2C_2)@C_{82}$(III) and $Y_2@C_{82}$(III) in CS_2 solvent.

Do they have analogous electronic structure ?

Comparison of $Y_2@C_{82}$ and $Y_2C_2@C_{82}$ (III)
the same cage structure and entrapped metal atoms
difference is additional two carbon atoms.



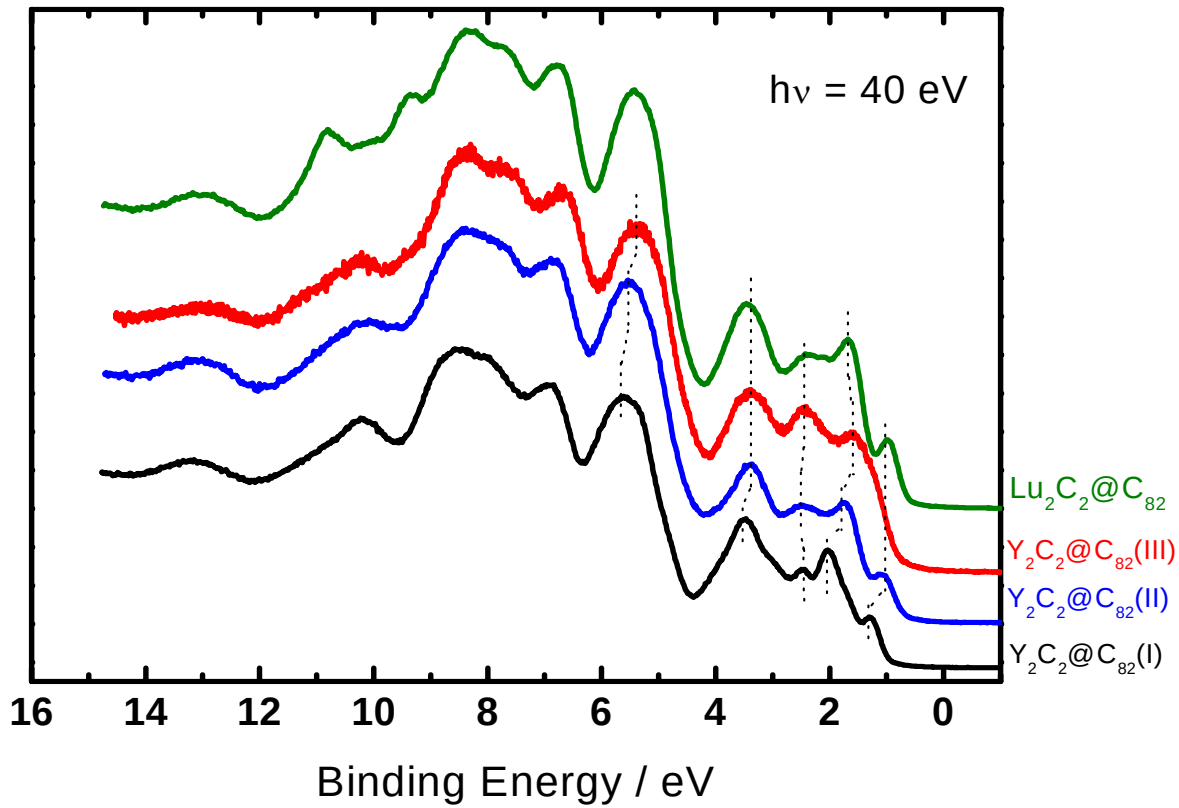
Cage symmetry seems to dominate
the electronic structure !

Difference spectrum indicates additional two electron transfer in $Y_2@C_{82}$

$(YC)_2^{4+}@C_{82}^{4-}$ and $Y^{3+}{}_2@C_{82}^{6-}$

Because Y^{3+} is the oxidation states of both fullerenes, carbon atoms accept two electrons or bonds is formed in $(Y_2C)_2@C_{82}$

when different species, Lu^{3+} and Y^{3+}, entrapped

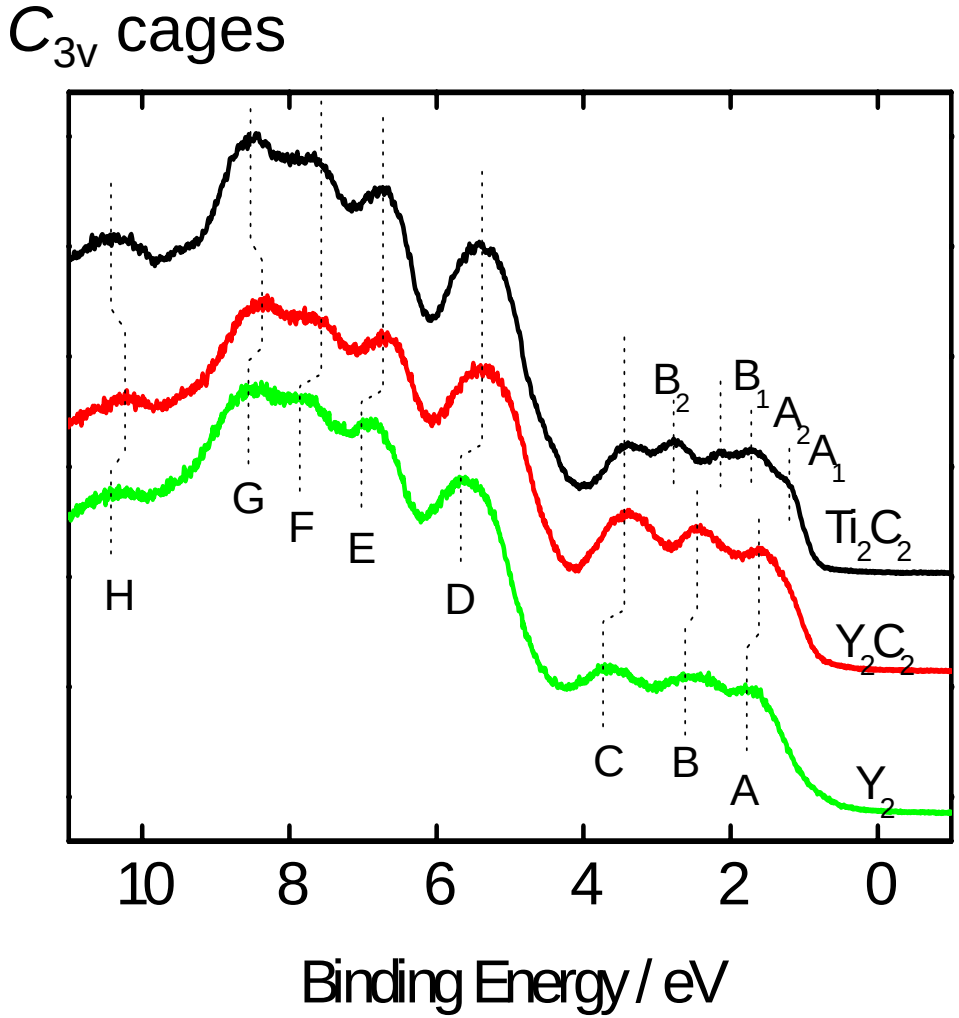


The UPS of the same C_{3v} (8) cages $Ti_2C_2@C_{82}$ and $Y_2C_2@C_{82}$ are not identical !

Oxidation state of Ti in $Ti_2C_2@C_{82}$ is +2,

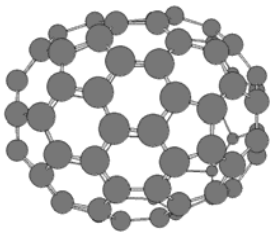
Y in $Y_2C_2@C_{82}$ is +3 !

Oxidation state of entrapped atoms seems to be the key !

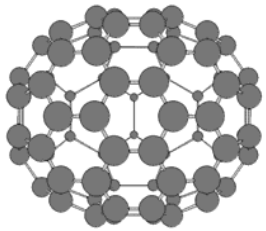


Electronic structure change might be introduced by strong interaction between the cage and entrapped species.

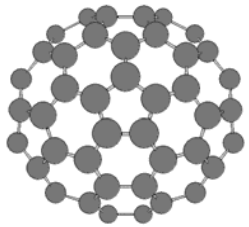
IPR satisfying C_{78} cages



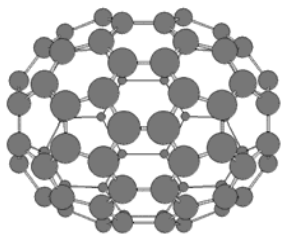
No.1-D_3



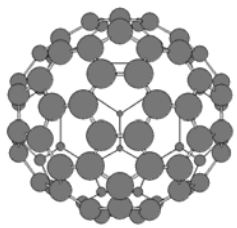
No.2-C_{2v}



No.3-C_{2v}



No.4-D_{3h}

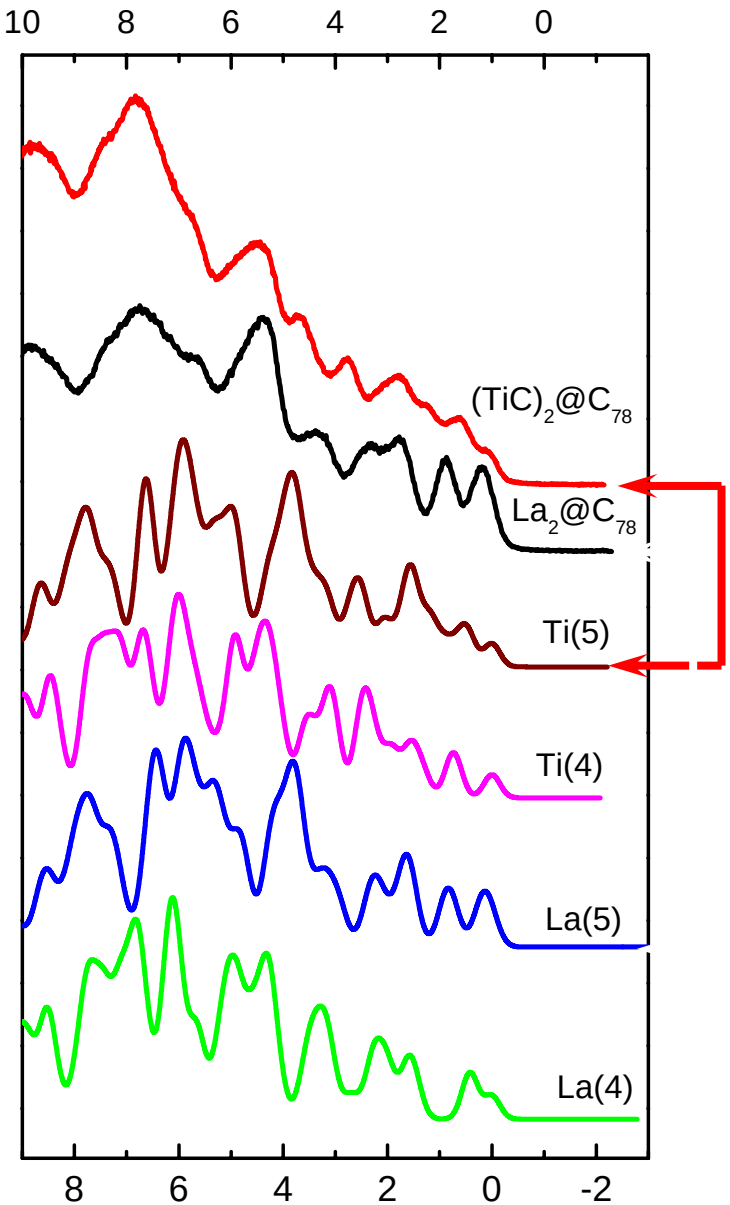


No.5-D_{3h}

One of the important Issues

There are two D_{3h} structures.

Are the structure of $(TiC)_2@C_{78}$ and $La@C_{78}$ the same or not ?



LDA-DFT calculation on *two* D_{3h} cage structures with encapsulated La_2 and $(TiC)_2$

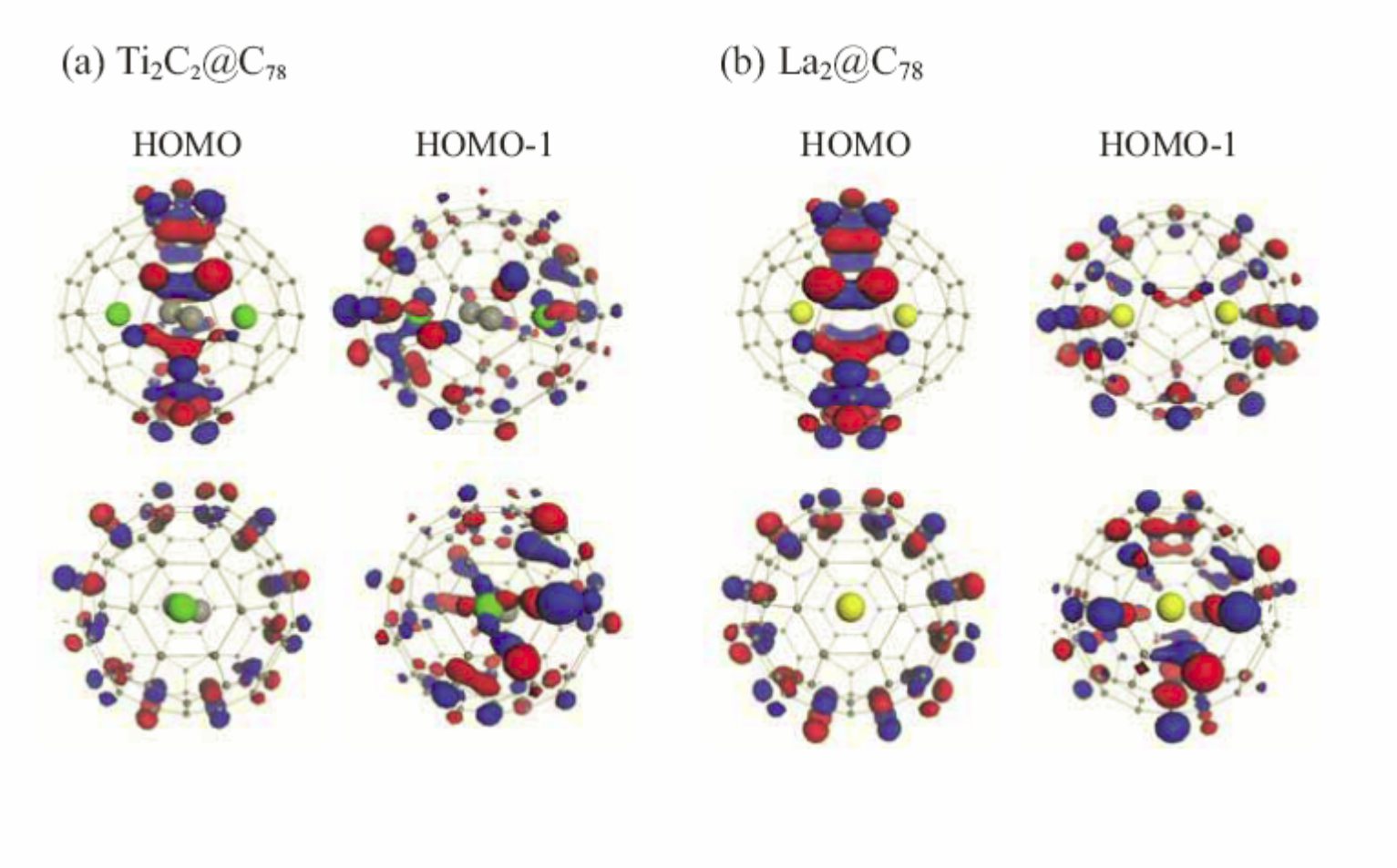
Good agreement on D_{3h} (5) cage structure

Although they have the same cage structure,

but have the different electronic structures

Oxidation states of entrapped atoms may be the key !

Wave function distribution



Hybridization is observed in HOMO-1 of $Ti_2C_2@C_{78}$

Summary
(as for the effect of entrapped atoms to the electronic structure of the cage)

- Mono metal atom encapsulated fullerenes
  - Cage dominate the electronic structure
  - Entrapped species have few influence
  - weak interaction between the cage and entrapped atom
- Multiple atoms encapsulated fullerenes
  - Fullerenes with metals of the same oxidation state and the same cage give analogous electronic structure
  - Upper π-valence band depends on different oxidation states of entrapped species
  - Strong interaction is expected thanks to narrow inner space of fullerenes