

放射光X線で視えてきたもの

—物理と化学の狭間で—

名古屋大学大学院 工学研究科 澤 博

1989. 4	青山学院大学 理工学部 助手
1990. 3	理学博士(青山学院大学)
1991. 4	東京大学物性研究所 X線測定室 助手
1996. 4	千葉大学 理学部物理学科 助教授
2001.10	高エネルギー加速器研究機構 物質構造科学研究所 助教授
2005. 5	同機構 教授に昇任
2008. 4	名古屋大学大学院 工学研究科

最終講義恒例？

昔を振り返る

- 青学 時代 (～1991) 銅酸化物超伝導体の世界的お祭り騒ぎ
- 物性研 時代 (～1995) 粉末から単結晶へ、酸化物から分子性結晶へ
- 千葉大 時代 (～2001) **【世の中の新しい仕組みへの取り組み】**
- KEK PF 時代 (～2008) 全国共同利用スタッフとしてのお役割
- 名大 時代 (2008～) そして、更にこれから …

本日の講演に入れられなかった名大での主たる成果

軌道液体の可能性 … 中辻、Broholm、片山、*etc.*
鉄系新超伝導体の発見 … 片山、野原、*etc.*
新蛍光体の発見 … 大長、中埜、細野、*etc.*
励起子絶縁体の可能性 … 中埜、鬼頭、片山、*etc.*

アーサー・C・クラークの三法則

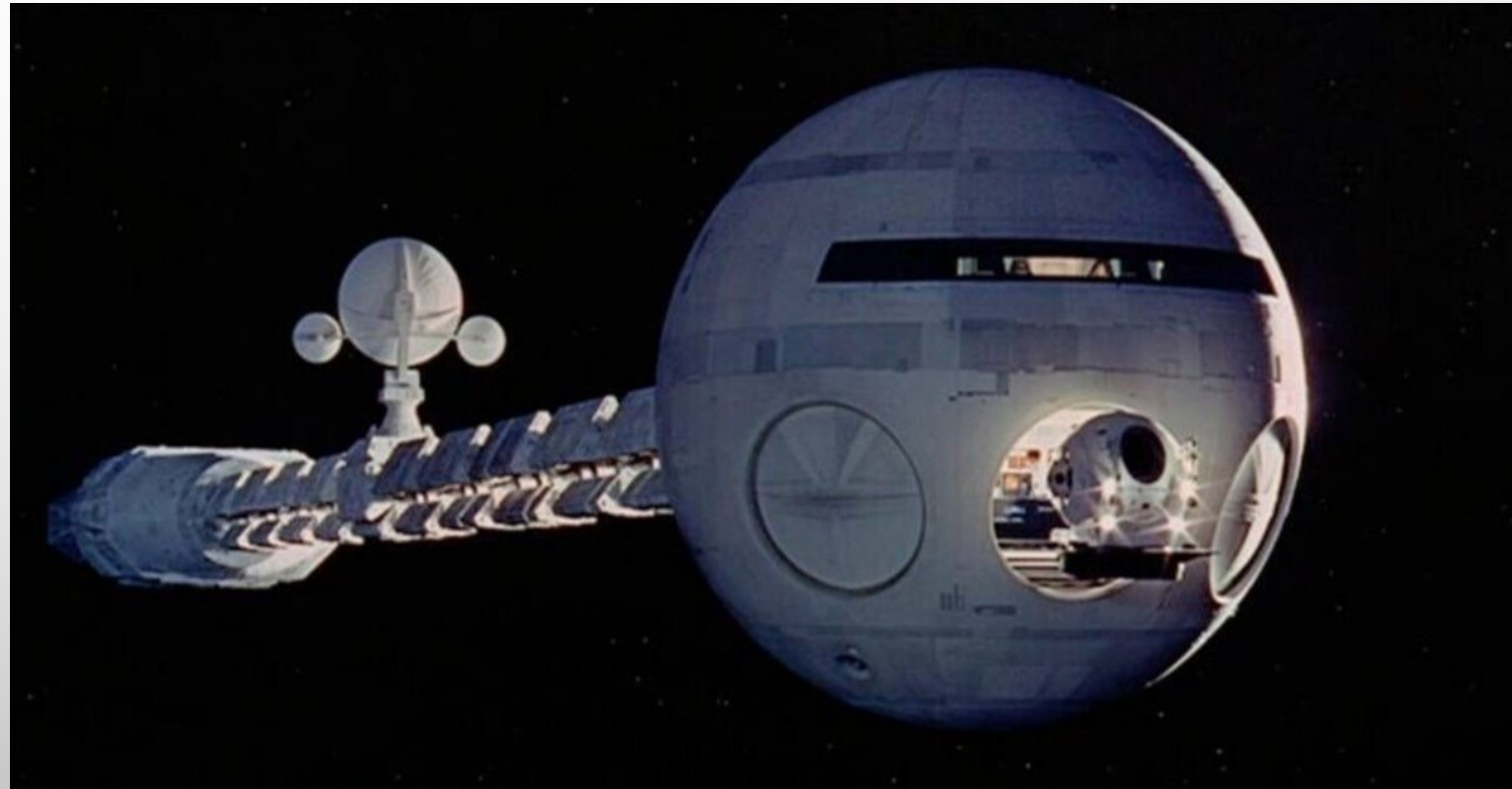


Wikipediaより

アーサー・C・クラークの三法則



WikiPediaより



2001年宇宙の旅

<https://note.com/nenkandokusyojin/n/n4fed44c6566b>

アーサー・C・クラークの三法則

1. When a distinguished but elderly scientist states that something is possible, he is almost certainly right. When he states that something is impossible, he is very probably wrong.
2. The only way of discovering the limits of the possible is to venture a little way past them into the impossible.
3. Any sufficiently advanced technology is indistinguishable from magic.

十分に発達した科学技術は、魔法と見分けがつかない

自己同一性 (identity)

「自分は何者か？」という問いに対する意識や確信のこと
自分の価値観、信念、経験、役割などを統合し、
一貫した自己像を持つことを指す

巨視的な系は「自己同一性」を持つ

素粒子は区別できない … 量子力学的波動性を持つ

- ✓ 「重ね合わせの原理」では、粒子は複数の状態を同時に持ち、観測されるまで確定しない
- ✓ 「量子もつれ（エンタングルメント）」により、離れた粒子同士が相互に影響を及ぼし合う

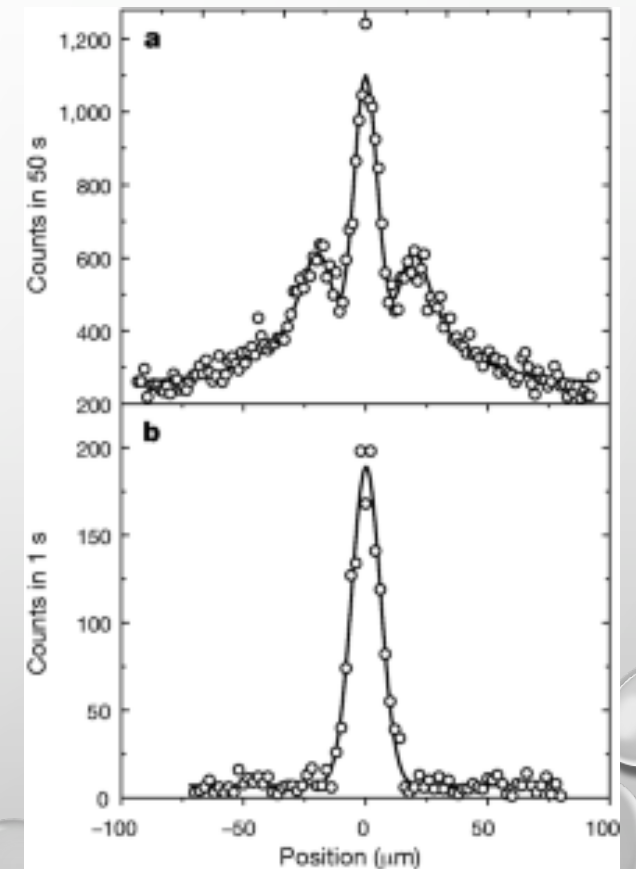
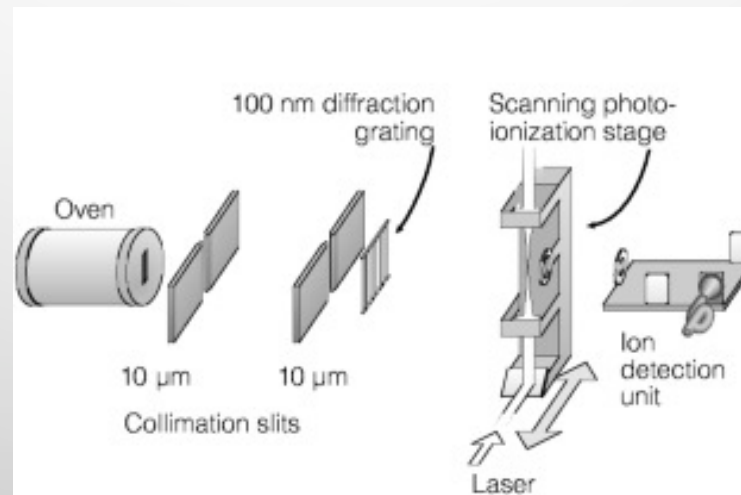
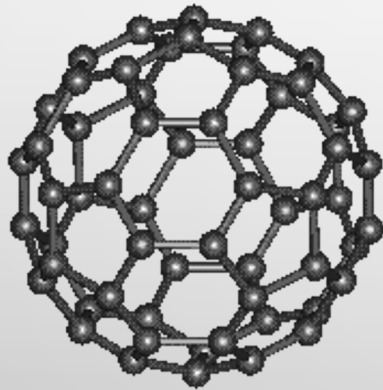
⇒ 波動性を持つ粒子は自己同一性を持たない!?

電子は区別できない … と、量子力学で習う
原子は区別できるのか … ヘリウムの超流動とか？
分子は区別できるのか？ … サイズに依存？ 物質波とかいうし

フラーレン C_{60} 分子のド・ブロイ波干渉の観測

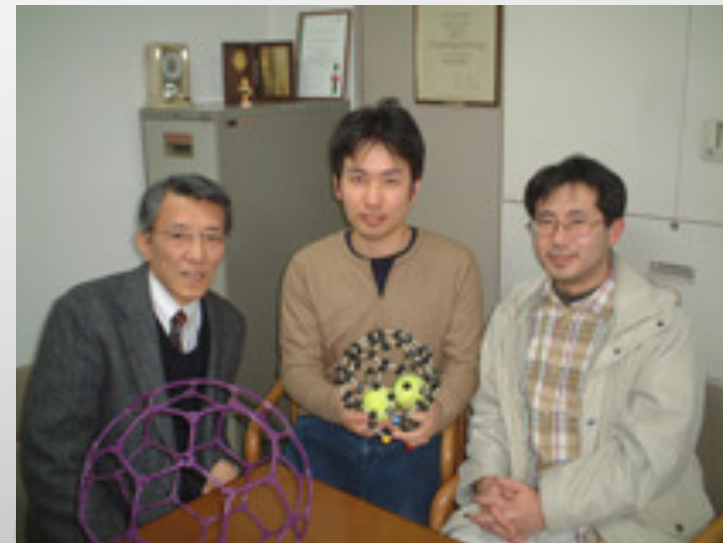
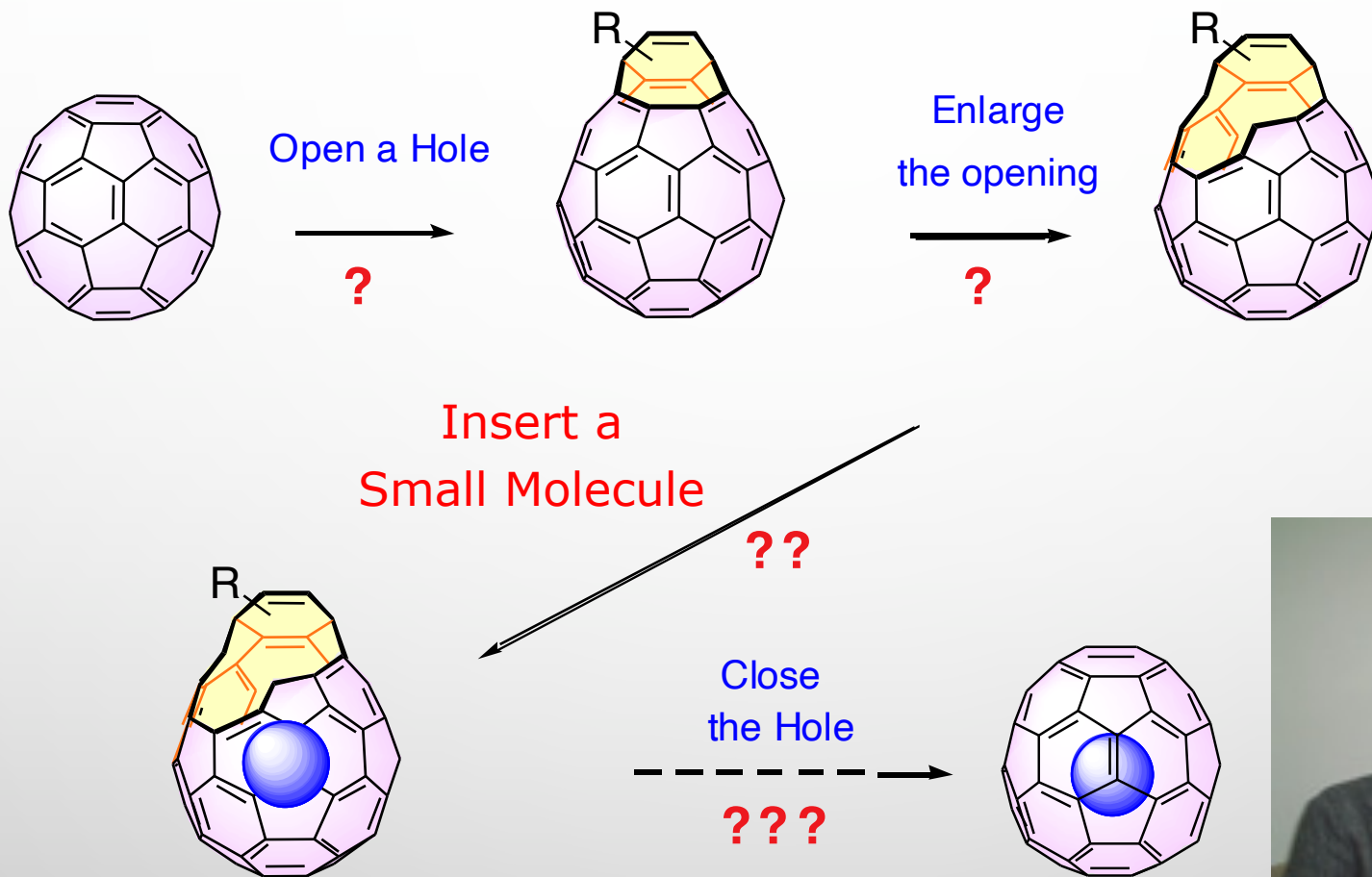
Wave-particle duality of C_{60} molecules

Nature 401 (1999) 680–682

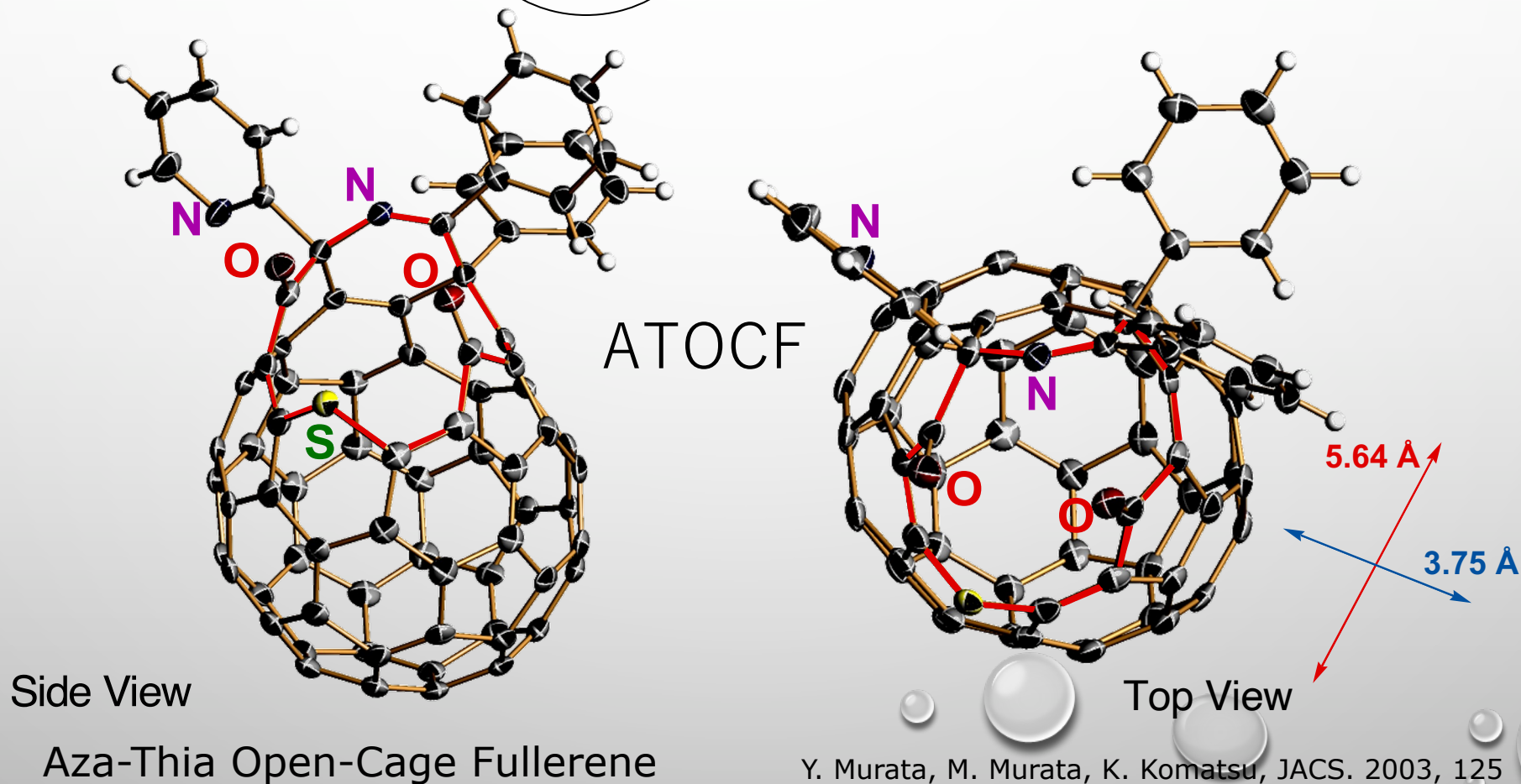
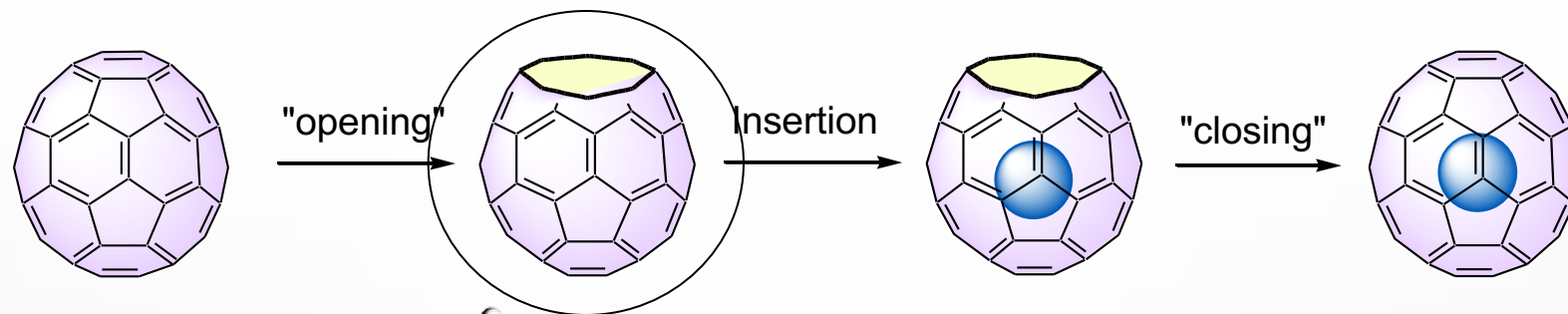


C_{60} で作る世界最小のカプセル

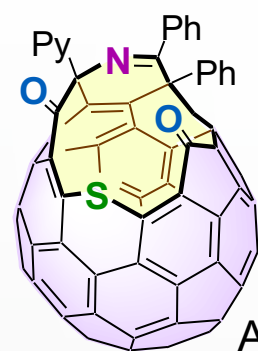
京都大学 化学研究所 小松研究グループ



化学的に合成された内包フラーレン



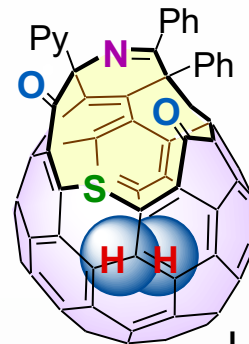
水素分子をかごの中に閉じ込める



800気圧
560気圧
水素 180気圧

200 °C, 8 h

ATO CF (Solid)



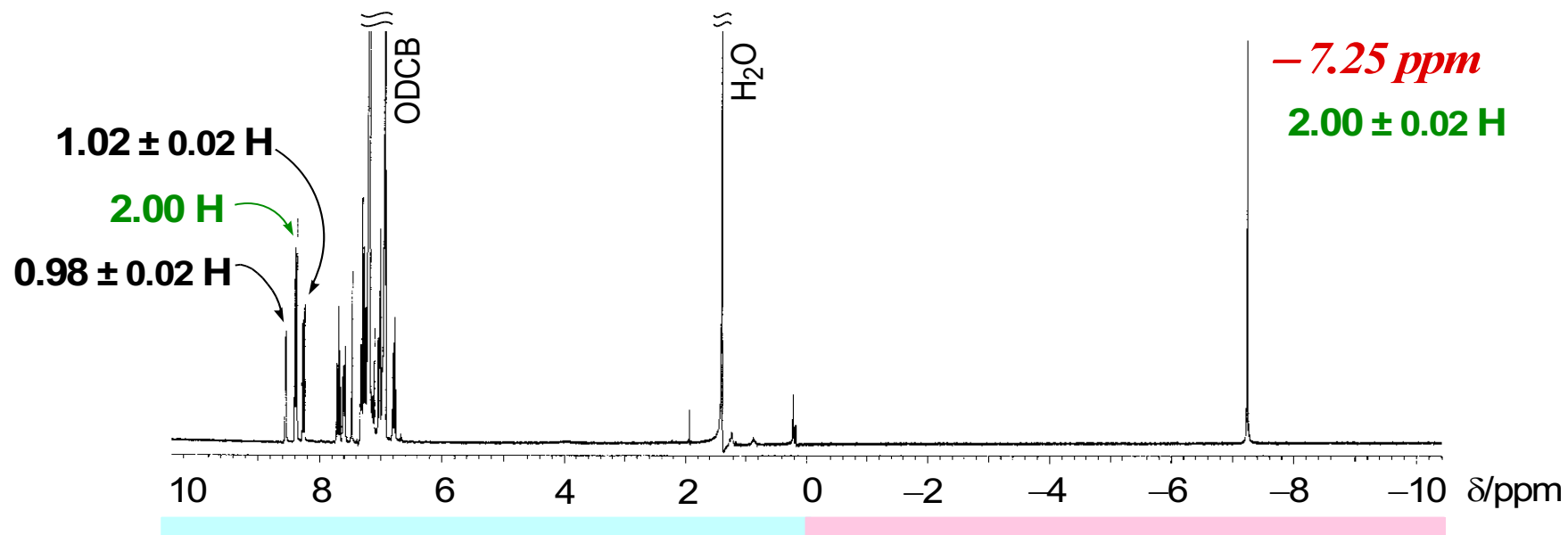
H₂@ ATOCF

100%
90%

水素の内包量 51%

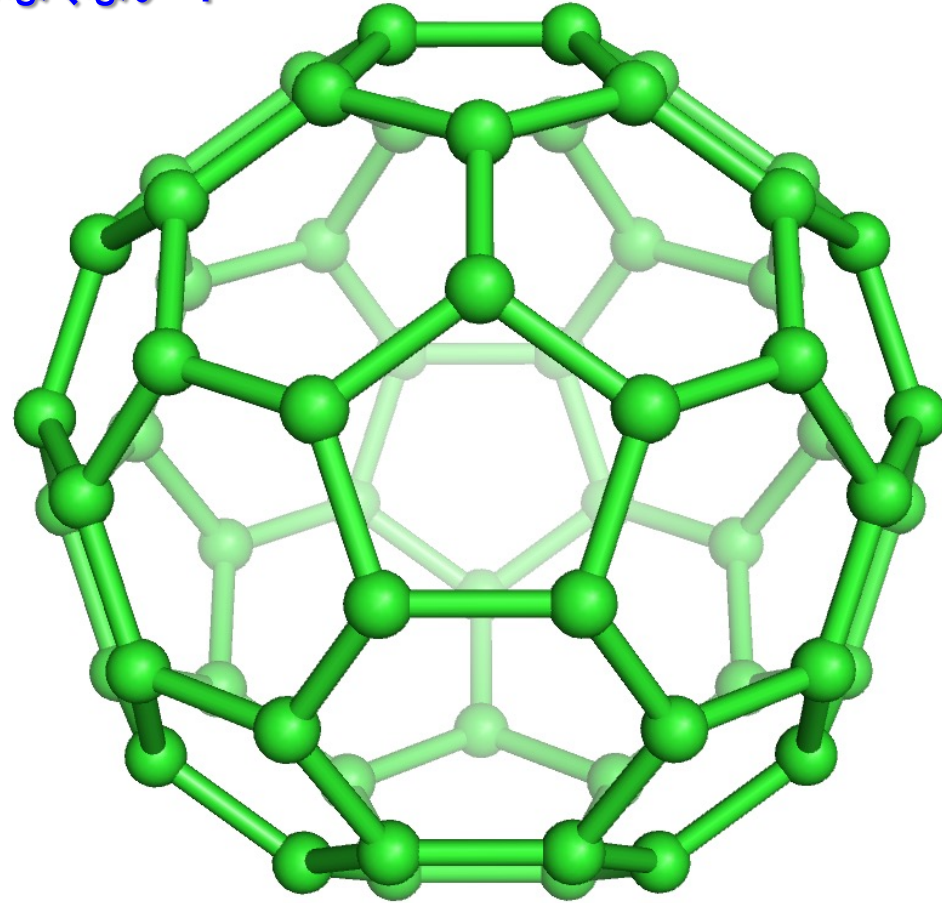
[HR MS m/z 1069.1040 (M+1)⁺
calculated 1069.1011]

¹H NMR (300 MHz, ODCB-*d*₄)



水素分子はどこに？

見てみないとわからない？

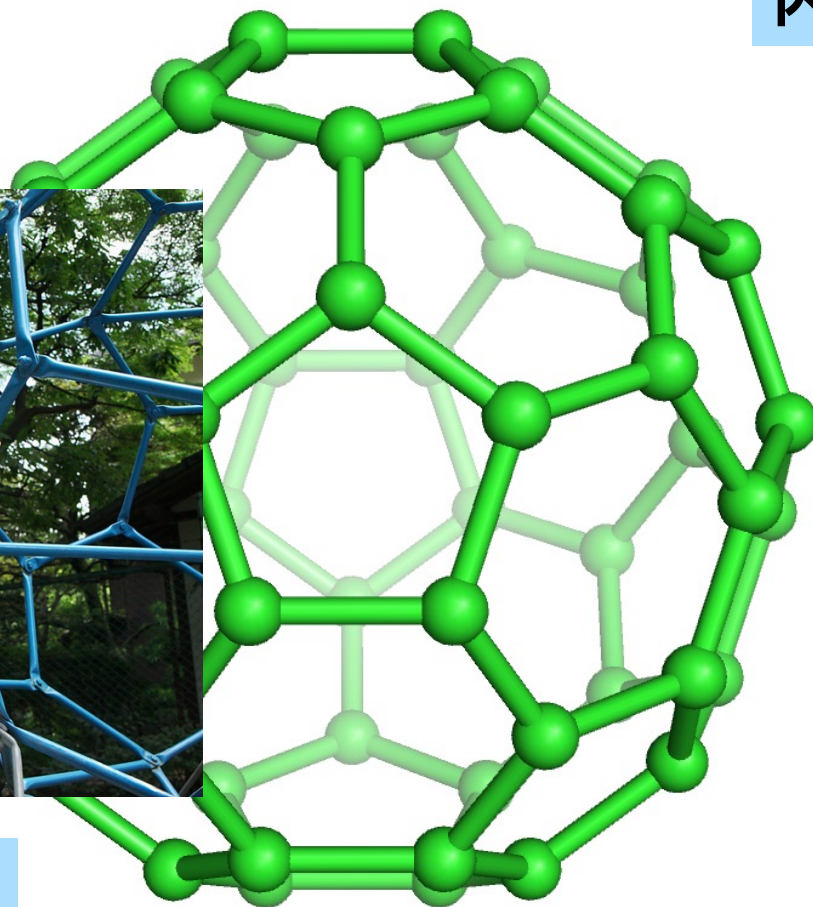


水素分子はどこに？

内包している？



外部に付着？



水素分子はどこに？

見てみないとわからない？

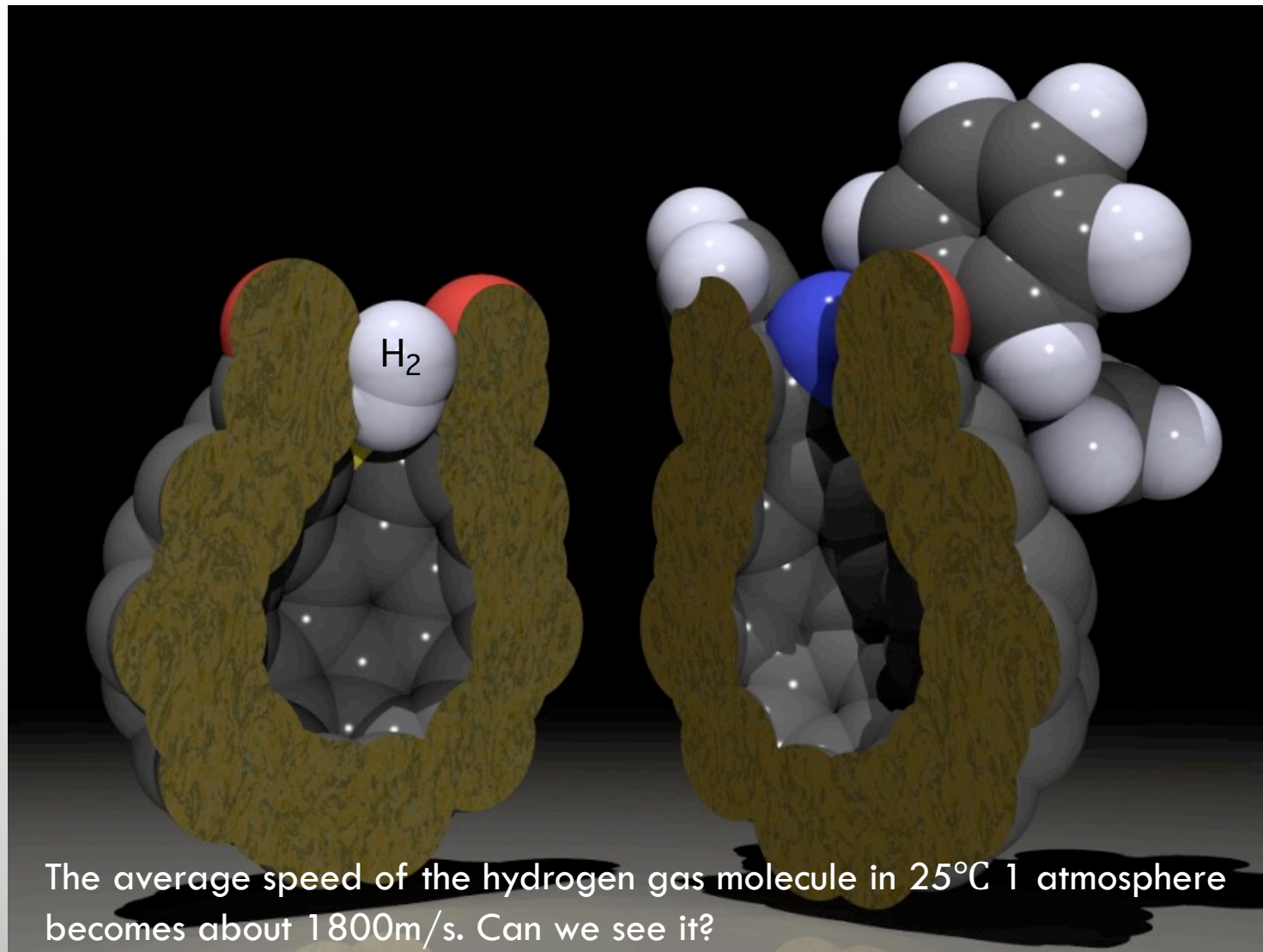
内包している？



外部に付着？



Transition State for H_2 Insertion



軽い元素や精密な原子配列を見るために…

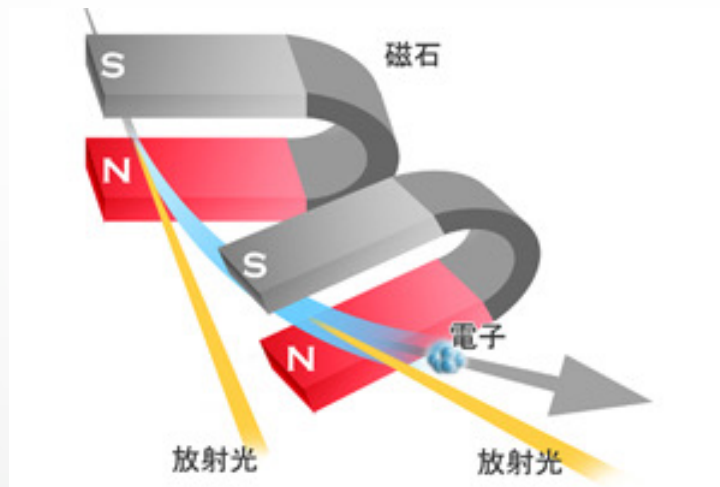


非常に明るい光を使う

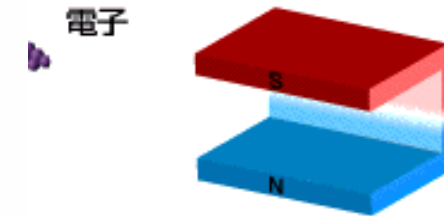


放射光 X 線による精密解析の技

放射光の発生

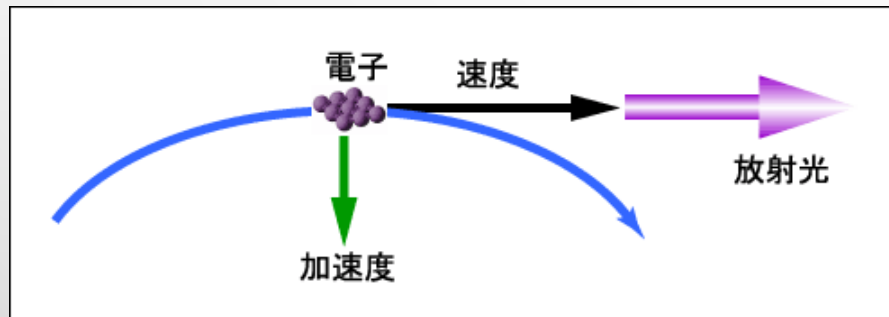


<https://hayabusa.kek.jp/SynchrotronLight/index.html>

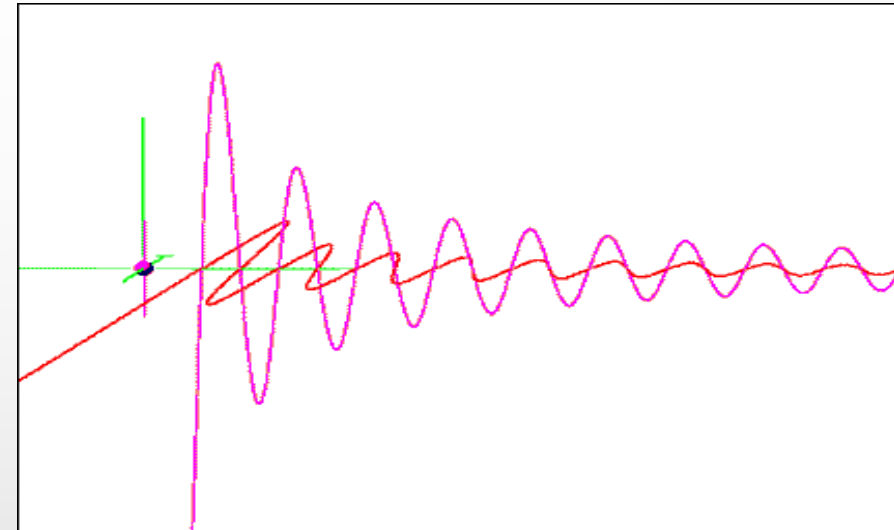


▲偏向電磁石からの放射光

http://www.spring8.or.jp/ja/about_us/whats_sp8/whats_sr/generation_sr/



http://www.spring8.or.jp/ja/about_us/whats_sp8/whats_sr/generation_sr/



放射光発生のおくみ

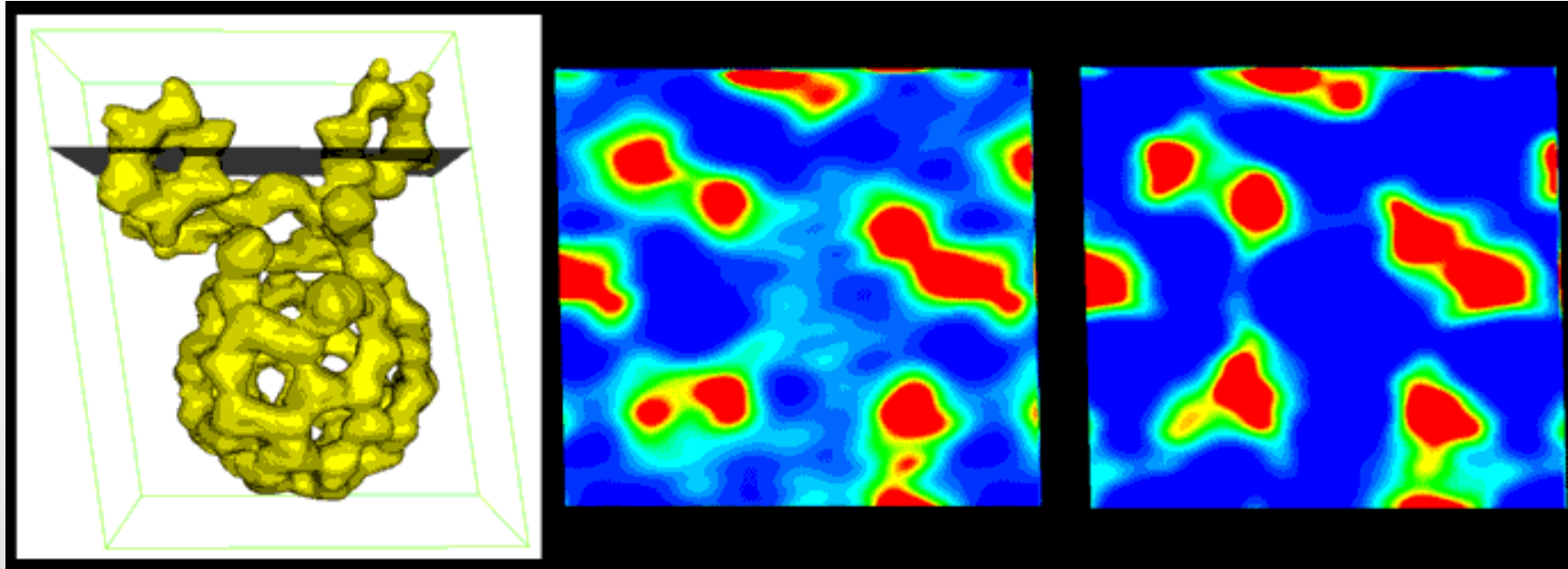
ほぼ光速で進む電子を磁場で曲げると、接線方向に放射光が放出される。

断層写真

ATOCF 分子

水素内包 C_{60}

空の C_{60}

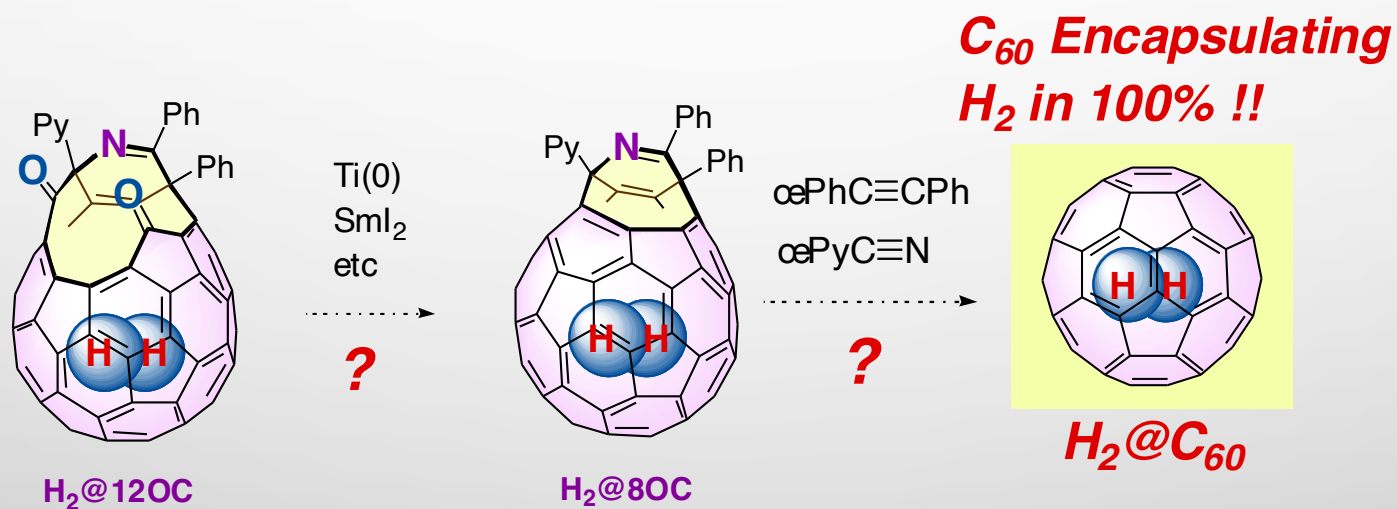


水素内包 C_{60} : 水素の電子が C_{60} ケージの中心に浮いている！
空っぽの C_{60} : ケージ中には何もない！

Encapsulation of Molecular Hydrogen in Fullerene C_{60} by Organic Synthesis

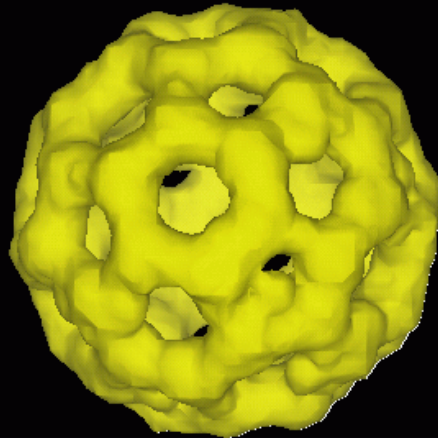
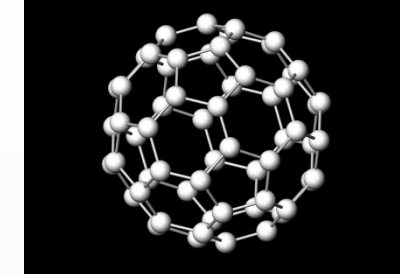
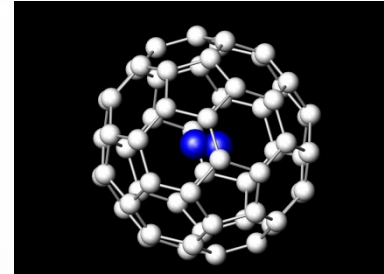
Koichi Komatsu,* Michihisa Murata, Yasujiro Murata

14 JANUARY 2005 VOL 307 SCIENCE



$H_2@C_{60}$ と C_{60} の断層写真 SPring-8 にて

C_{60} に閉じ込められた
水素分子一つの観測に成功！

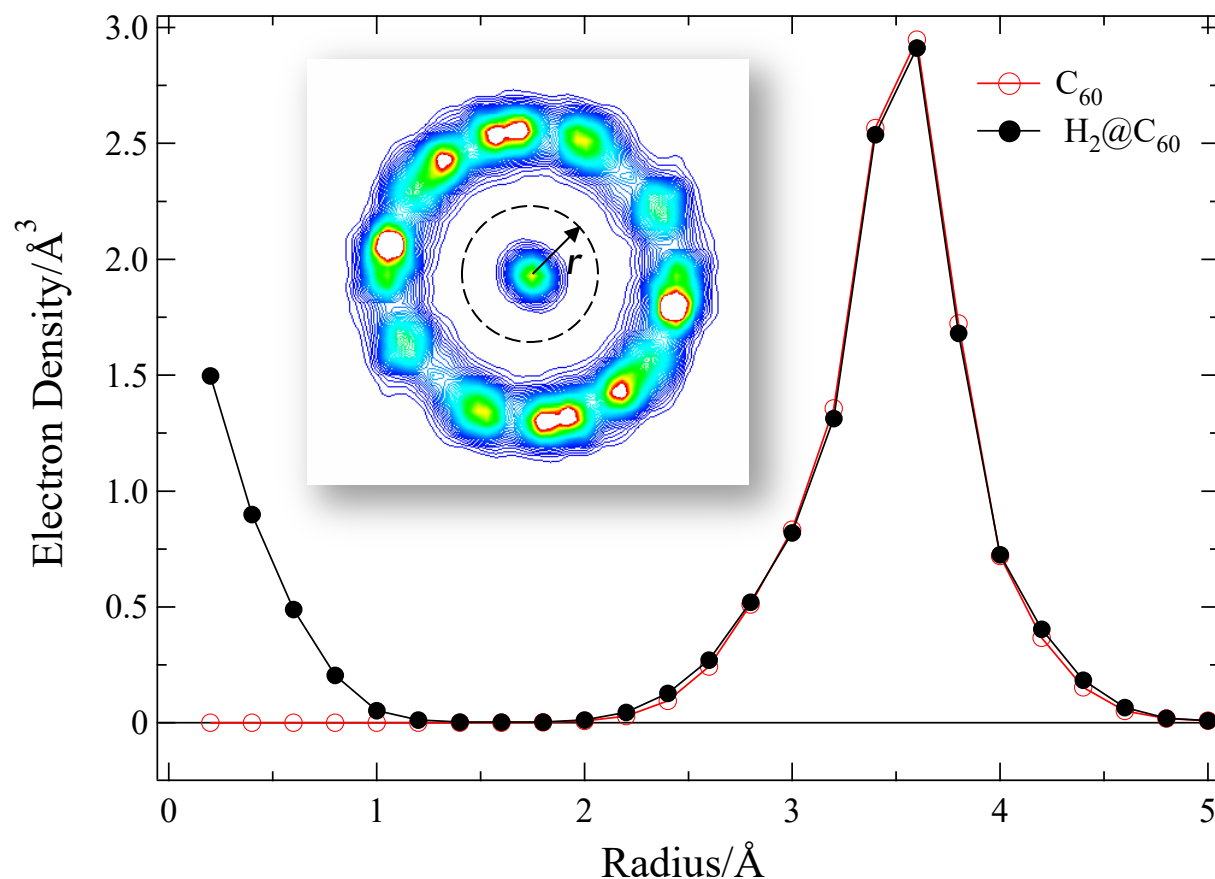


$H_2@C_{60}$

C_{60}

Charge Density and Electron Number

Ideal Electron number: $360(\text{C}_{60}) + 2(\text{H}_2)$



No. of el. of $\text{H}_2@\text{C}_{60}$
 $r \leq 2\text{\AA}$ 1.9(4)
 $r \leq 5\text{\AA}$ 361.8(5)

No. of el. of C_{60}
 $r \leq 2\text{\AA}$ 0
 $r \leq 5\text{\AA}$ 359.99(5)

$\text{H}_2@C_{60}$ の比熱測定

PRL 103, 073001 (2009)

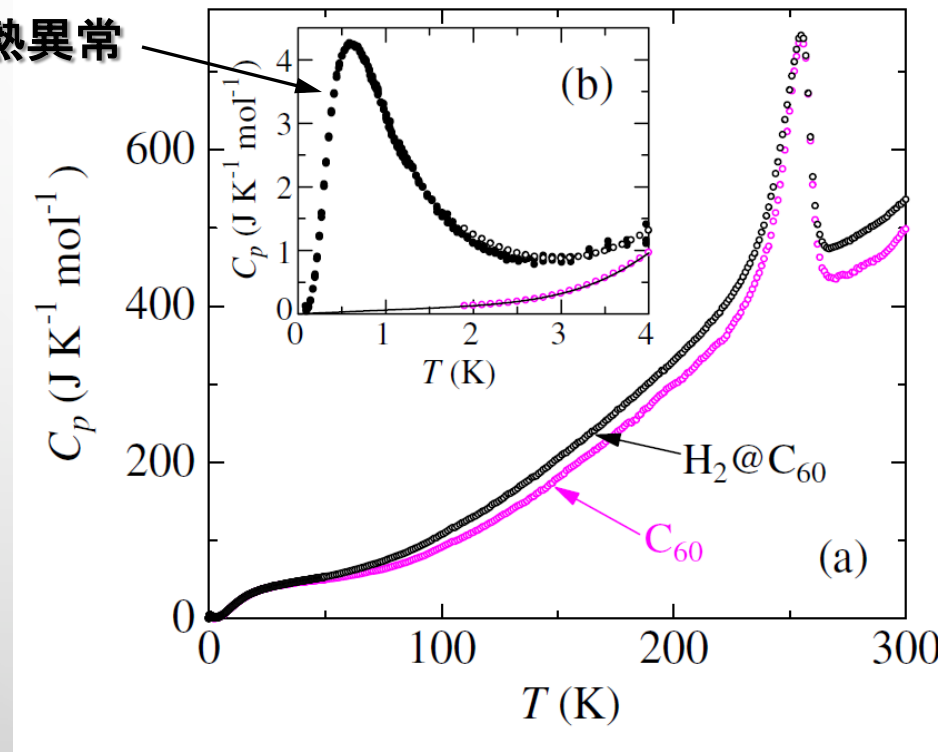
PHYSICAL REVIEW LETTERS

week ending
14 AUGUST 2009

Rotational Sublevels of an Ortho-Hydrogen Molecule Encapsulated in an Isotropic C_{60} Cage

Yoshimitsu Kohama,^{1,*} Takeshi Rachi,² Ju Jing,² Zhaofei Li,² Jun Tang,² Ryotaro Kumashiro,² Satoru Izumisawa,¹
Hitoshi Kawaji,¹ Tooru Atake,¹ Hiroshi Sawa,³ Yasujiro Murata,⁴ Koichi Komatsu,⁵ and Katsumi Tanigaki^{2,†}

極低温での比熱異常



H_2 内包による際立った物性の変化は観測されていない。

H₂@C₆₀の比熱測定

PRL 103, 073001 (2009)

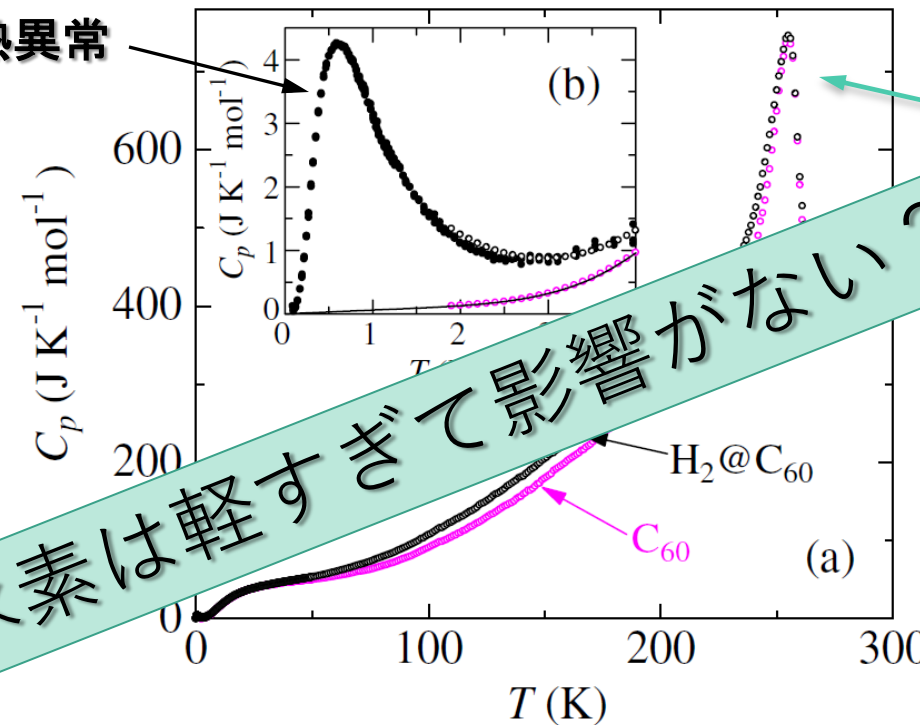
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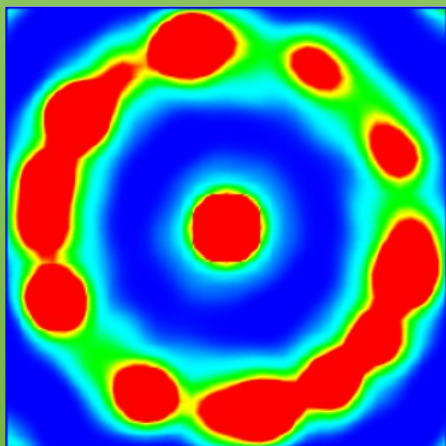
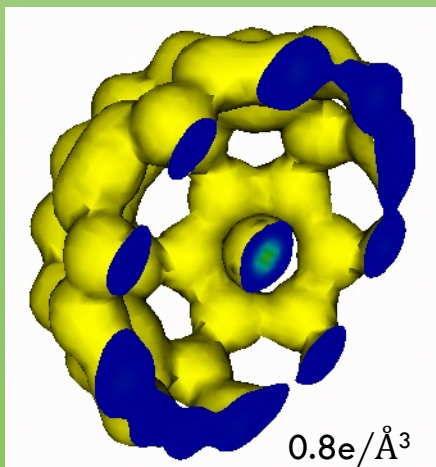


分子回転の秩序化

H₂内包による際立った物性の変化は観測されていない。

もっと重たいアルゴンガス分子を内包すると？

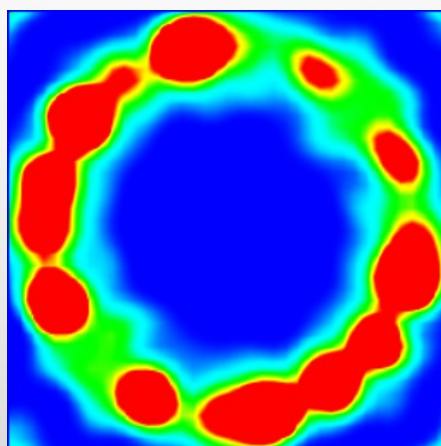
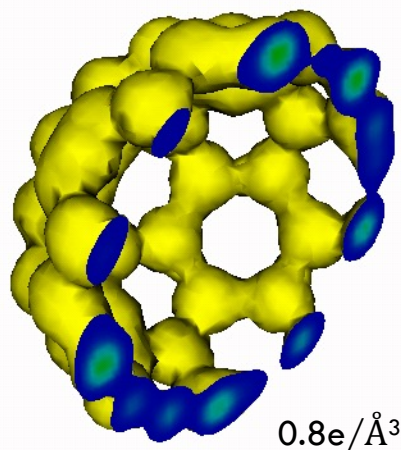
Ar@C₆₀



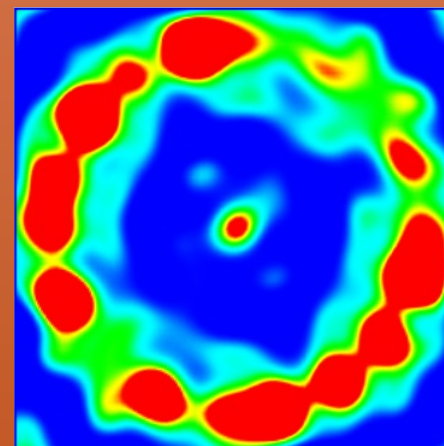
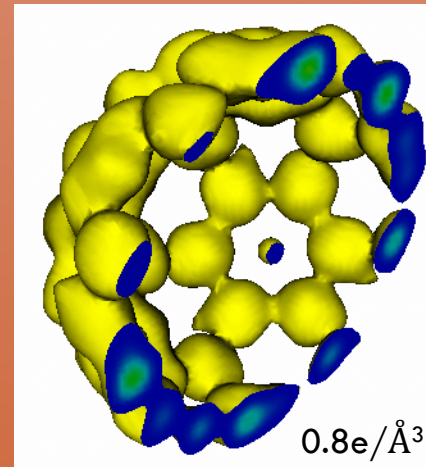
東大 高木グループ

Chem. Commun.(2006) 912-914

C₆₀



H₂@C₆₀



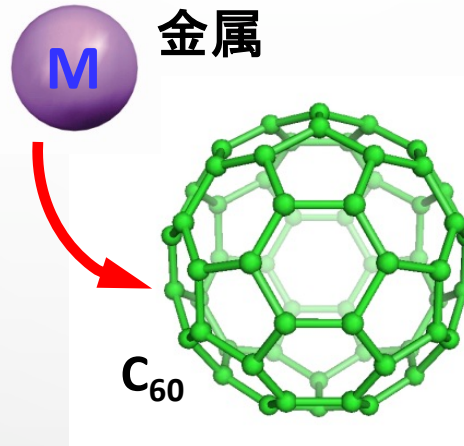
京大 小松グループ

Phys. Rev. Lett. (2009)

金属内包C₆₀フラーレン

ガス分子(H₂, He, Ar)内包フラーレン: 内包による際立った物性変化なし

金属(Li, Sc, La, ...)内包フラーレン: 太陽電池、FET、分子メモリ、分子スイッチなど、幅広い応用の可能性



1985年 J. R. Heathらが報告 (La@C₆₀)

1996年 E. E. B. Campbellらが報告(Li@C₆₀)

Li@C₆₀: 単離できない...

H₂: 電子数2

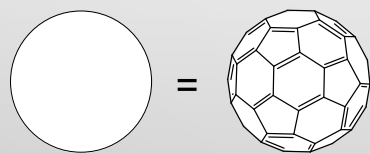
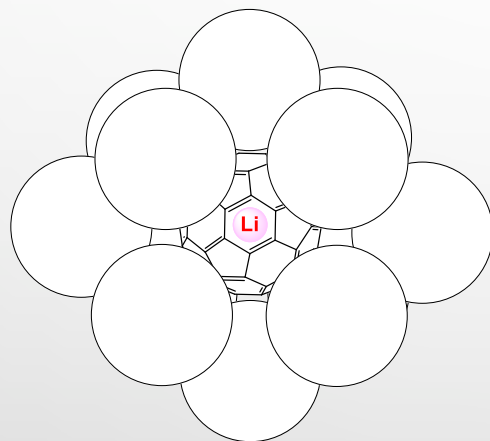
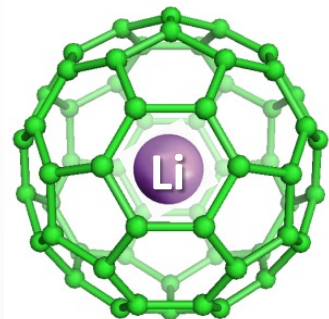
Li⁺: 電子数2

	1A	2A	3A	4A	5A	6A	7A	8	1B	2B	3B	4B	5B	6B	7B	0		
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	Zn	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

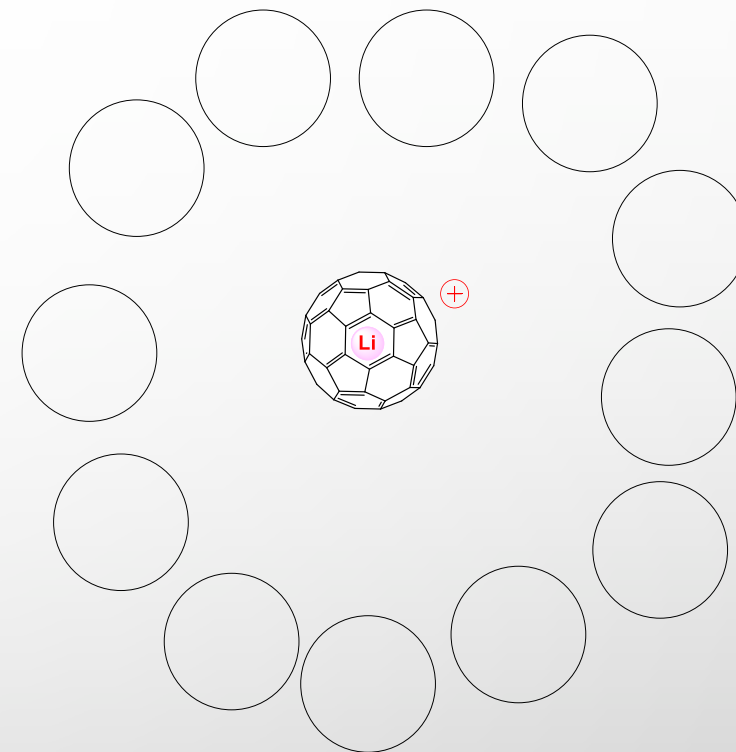
[Li@C₆₀]を取り出すには…？



名大理化
篠原久典 教授



酸化
電子



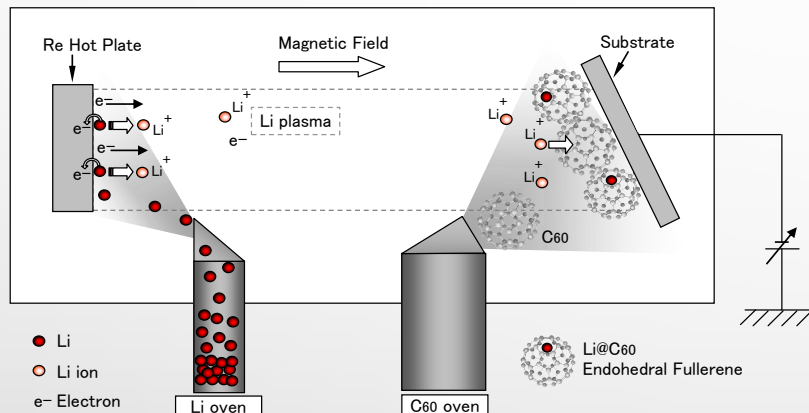
電子を取り去ってやれば(酸化)
[Li@C₆₀]だけ取り出せるかも？

金属内包C₆₀フラーレン

ガス分子(H₂, He, Ar)内包フラーレン: 内包による際立った物性変化なし

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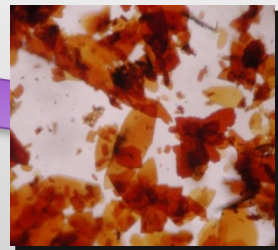
リチウム内包(?)フラーレンLi@C₆₀の大量合成(株イデアルスター)



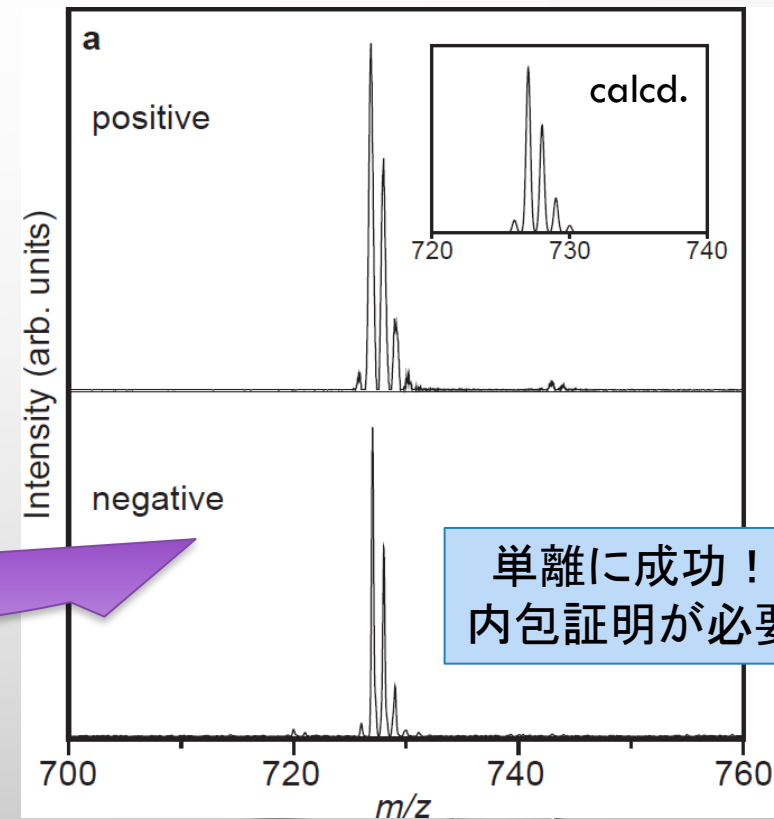
プラズマシャワー法



酸化
抽出
再結晶



[Li@C₆₀](SbCl₆)



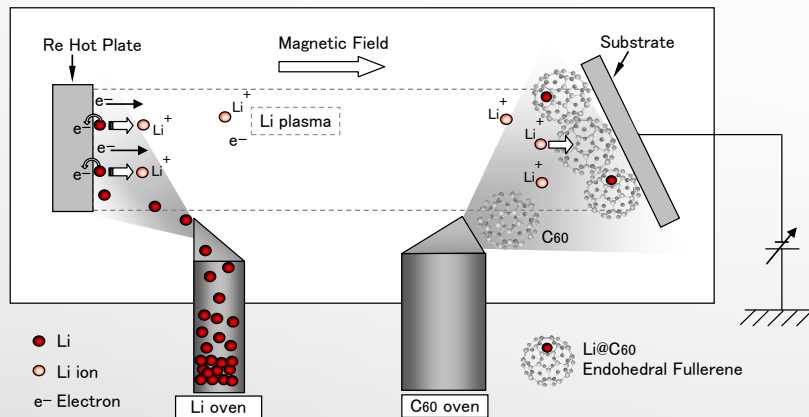
単離に成功！
内包証明が必要

金属内包C₆₀フラーレン

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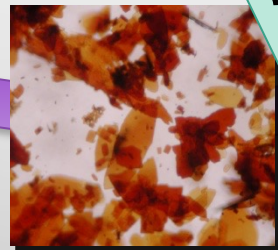
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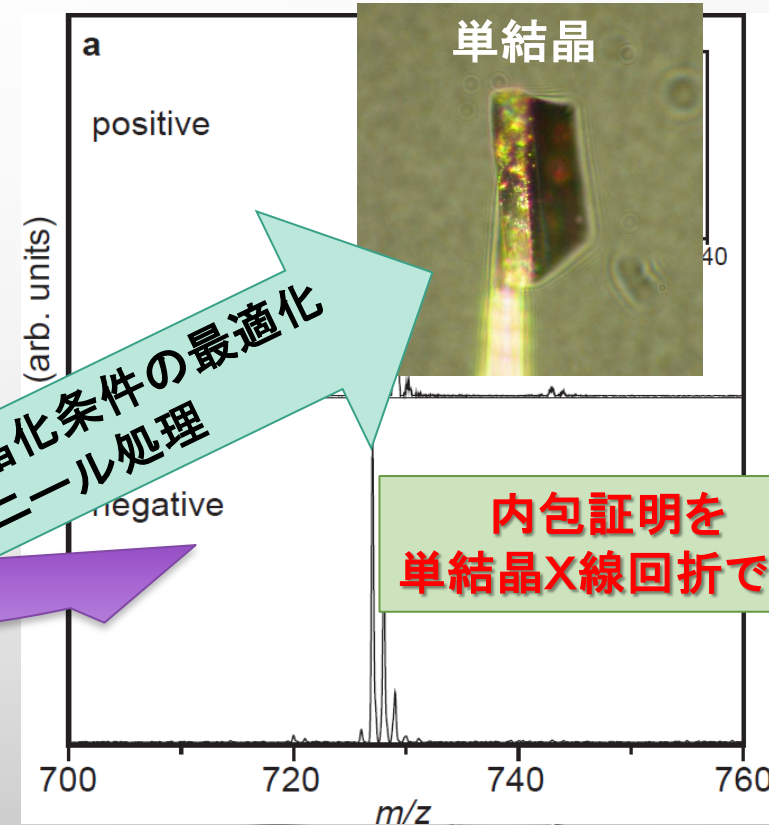
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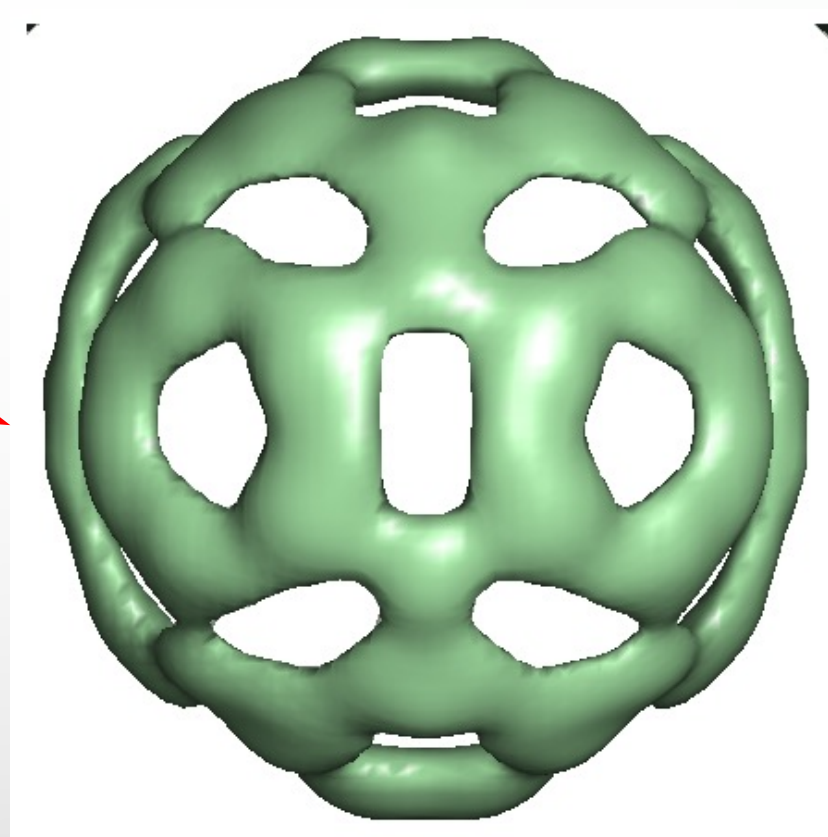
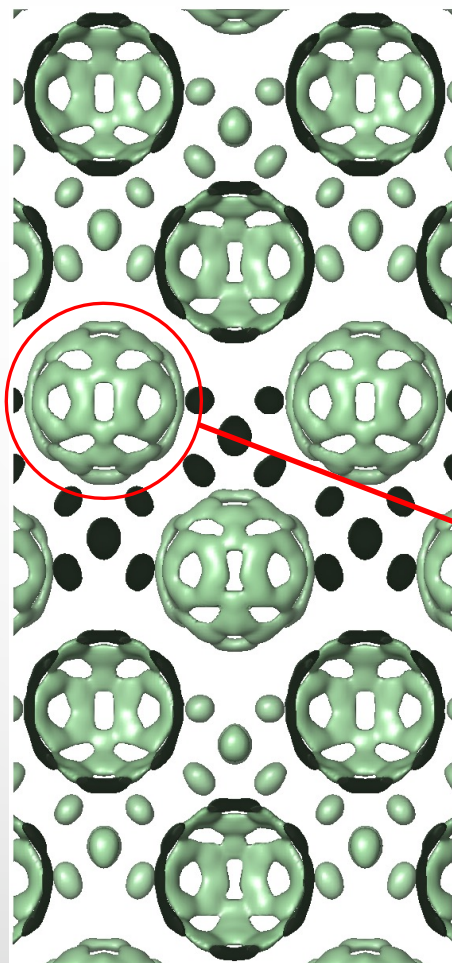
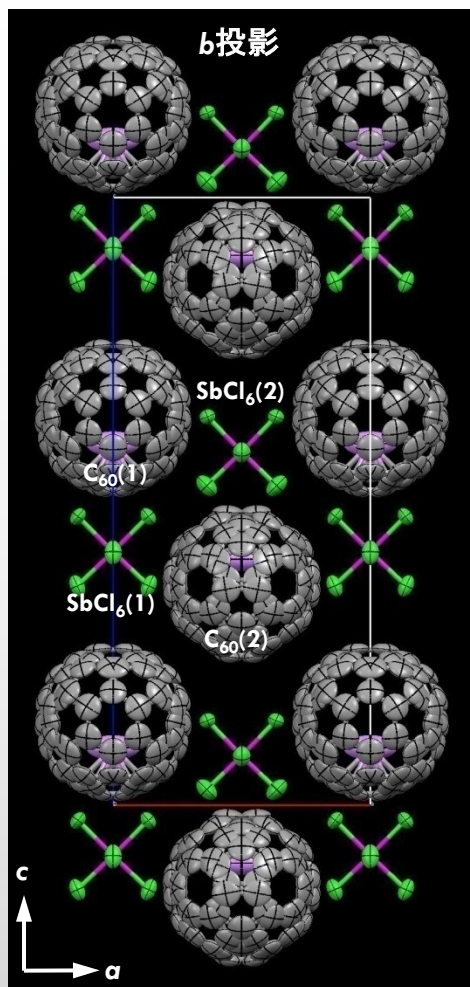


結晶化条件の最適化
アニール処理

内包証明を
単結晶X線回折で!

単結晶

[Li@C₆₀](SbCl₆)の結晶構造 (370 K)



$R1 = 4.69\%$ ($> 4\sigma$, $> 0.8\text{\AA}$)

配向A : 配向B

= 42 : 58 (C₆₀(1))

= 58 : 42 (C₆₀(2))

$d > 0.8\text{\AA}$

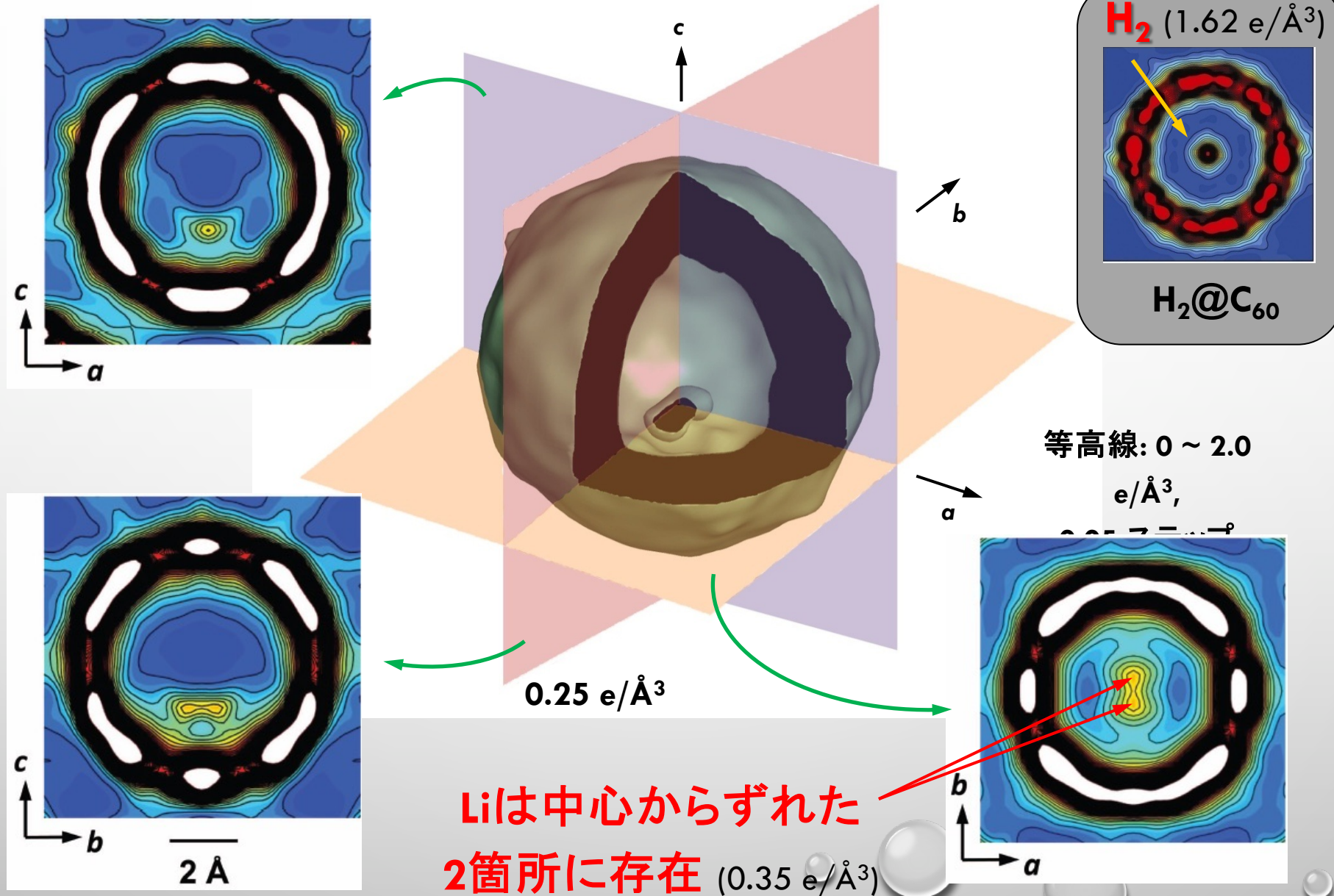
$R_{\text{MEM}} = 3.74\%$

$C = 1.0$

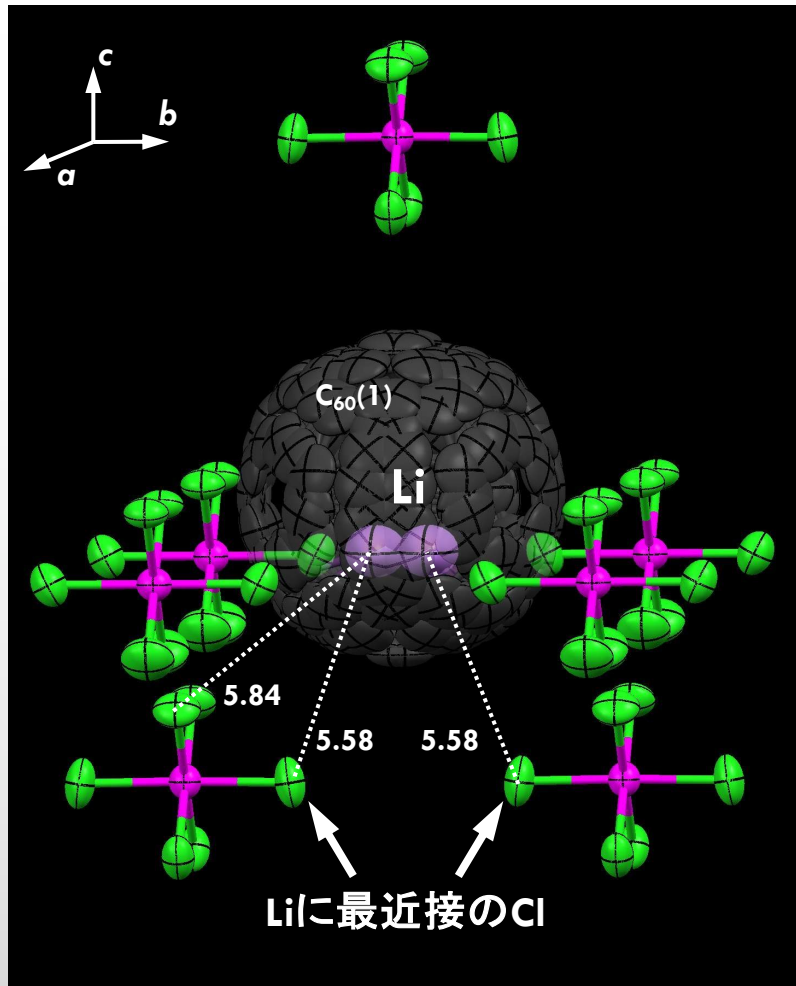
等電子密度面: $2\text{ e}/\text{\AA}^3$

$0.25\text{ e}/\text{\AA}^3$

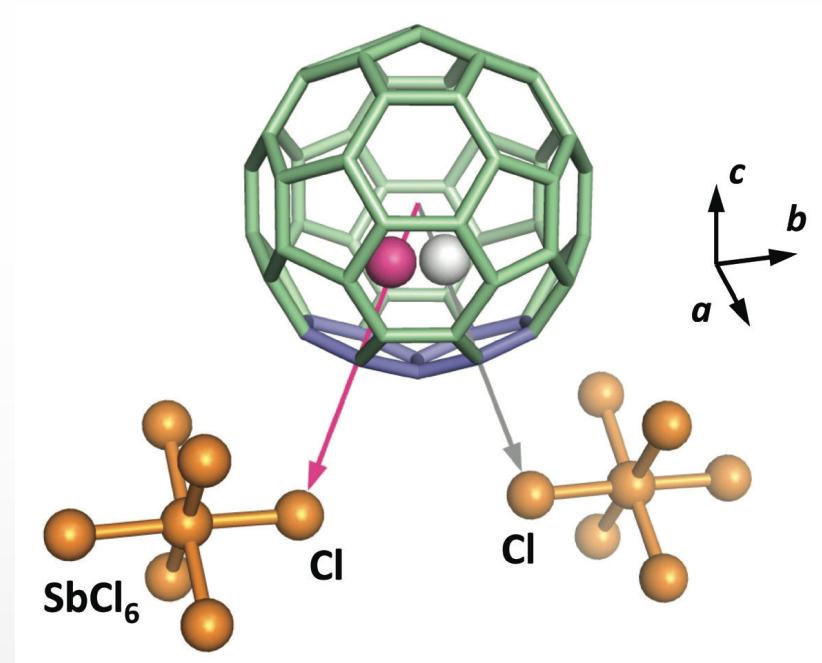
Li@C₆₀の電子密度分布



Liの占有位置と SbCl_6 との関係



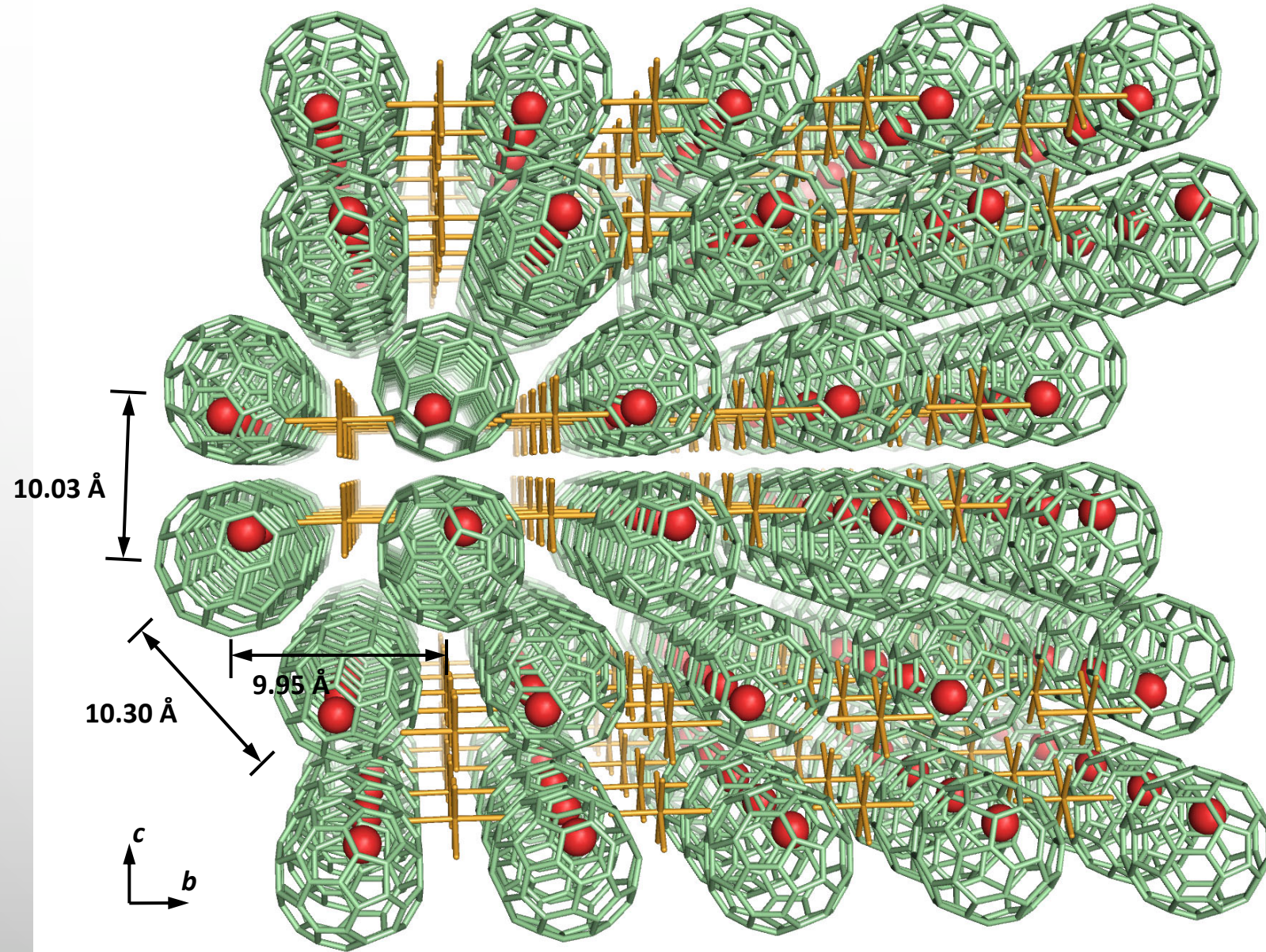
Li@C_{60} : 7つの SbCl_6 が配位
LiはClが多い方向に局在



Cl^- の静電場の引力

$[\text{Li@C}_{60}]^+$: 電気分極を持ち
外場でスイッチング可能

$[\text{Li}@\text{C}_{60}](\text{SbCl}_6)$ の層状構造



[Li@C₆₀](SbCl₆)の層状構造

日本経済新聞

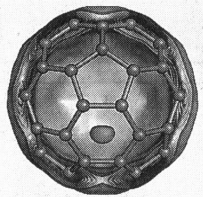
2010年(平成22年)6月21日(月)

11面

名古屋大学と東北大学などは、サッカーボールの形をした直径1ナノ(ナノは10億分の1)の球状炭素分子「C₆₀」の中に金属原子が入った物質を合成した。太陽電池や記録媒体に活用が期待できる。成果は21日付の英科学誌「ネイチャー・ケミストリー」(電子版)で発表する。

球状炭素分子の内部にリチウム

名古屋大など合成
開発には名大の澤博教授と東北大の飛田博実教授に加え、新素材ベンチ

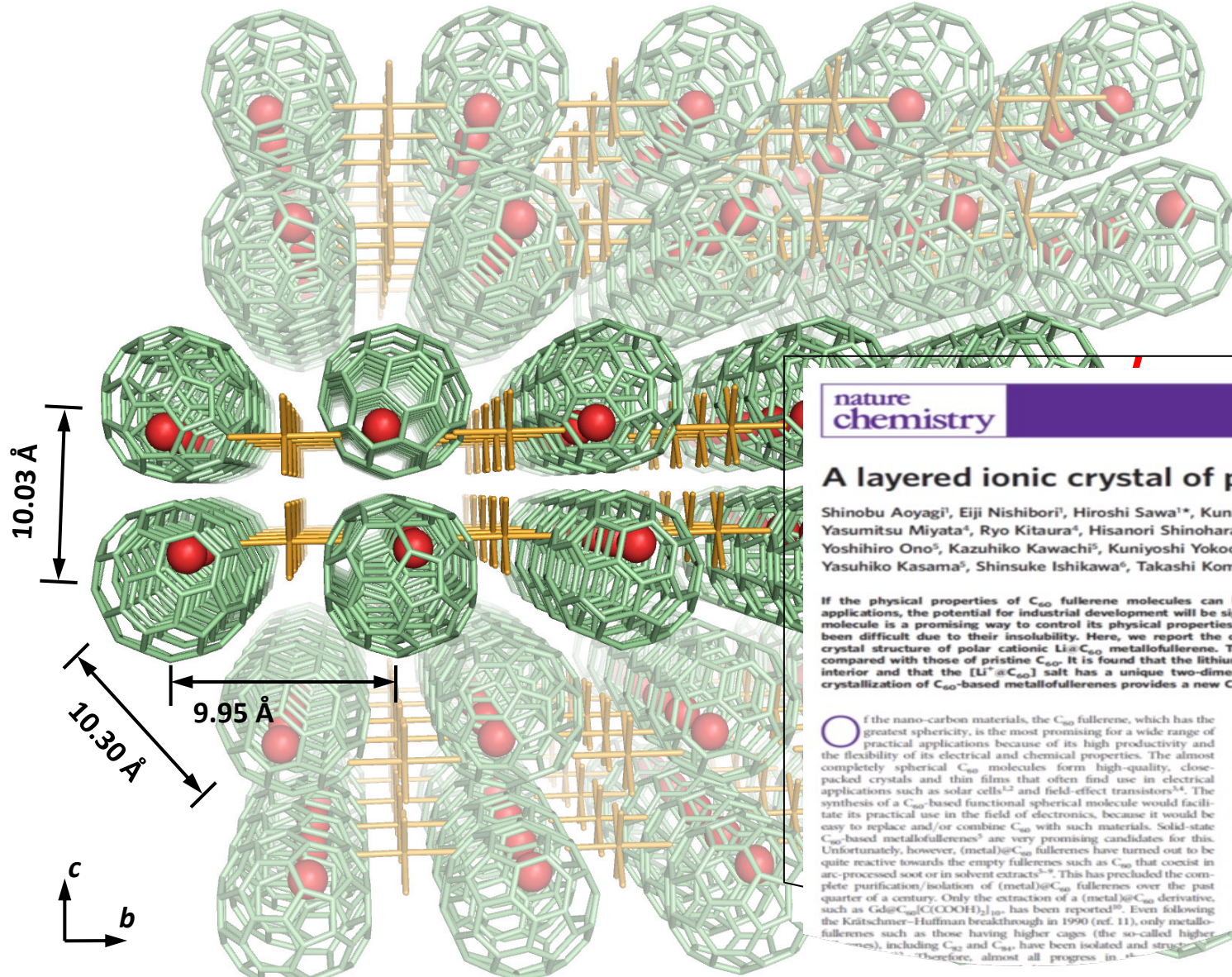


太陽電池に応用

C₆₀にリチウム原子(中央下)が入っている「ボール」の形ははじめて画像、名古屋大学提供

大型放射光施設「SPring-8」のエック線で確認した。

ヤーのイデアアルスター(仙台市)、高輝度光科学研究センター、理化学研究所が参加した。独自の合成技術でC₆₀の中に金属原子のリチウムを入れた。C₆₀に金属原子を入れたのは初めて。記録ができるようになるという。



nature
chemistry

ARTICLES

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A layered ionic crystal of polar Li@C₆₀ superatoms

Shinobu Aoyagi¹, Eiji Nishibori¹, Hiroshi Sawa^{1*}, Kuniyoshi Sugimoto^{2,3}, Masaki Takata^{2,3}, Yasumitsu Miyata⁴, Ryo Kitaura⁴, Hisanori Shinohara⁴, Hiroshi Okada⁵, Takeshi Sakai⁵, Yoshihiro Ono⁵, Kazuhiko Kawachi⁵, Kuniyoshi Yokoo⁵, Shoichi Ono⁵, Kenji Omote⁵, Yasuhiko Kasama⁵, Shinsuke Ishikawa⁶, Takashi Komuro⁶ and Hiromi Tobita^{6*}

If the physical properties of C₆₀ fullerene molecules can be controlled in C₆₀ products already in use in various applications, the potential for industrial development will be significant. Encapsulation of a metal atom in the C₆₀ fullerene molecule is a promising way to control its physical properties. However, the isolation of C₆₀-based metallofullerenes has been difficult due to their insolubility. Here, we report the complete isolation and determination of the molecular and crystal structure of polar cationic Li@C₆₀ metallofullerene. The physical and chemical properties of Li@C₆₀ cation are compared with those of pristine C₆₀. It is found that the lithium cation is located at off-centre positions in the C₆₀-like cage interior and that the [Li⁺@C₆₀]⁺ salt has a unique two-dimensional structure. The present method of purification and crystallization of C₆₀-based metallofullerenes provides a new C₆₀ fullerene material that contains a metal atom.

Of the nano-carbon materials, the C₆₀ fullerene, which has the greatest sphericity, is the most promising for a wide range of practical applications because of its high productivity and the flexibility of its electrical and chemical properties. The almost completely spherical C₆₀ molecules form high-quality, close-packed crystals and thin films that often find use in electrical applications such as solar cells^{1,2} and field-effect transistors^{3,4}. The synthesis of a C₆₀-based functional spherical molecule would facilitate its practical use in the field of electronics, because it would be easy to replace and/or combine C₆₀ with such materials. Solid-state C₆₀-based metallofullerenes⁵ are very promising candidates for this. Unfortunately, however, (metal)@C₆₀ fullerenes have turned out to be quite reactive towards the empty fullerenes such as C₆₀ that consist in arc-processed soot or in solvent extracts^{6–9}. This has precluded the complete purification/isolation of (metal)@C₆₀ fullerenes over the past quarter of a century. Only the extraction of a (metal)@C₆₀ derivative, such as Gd@C₆₀[C(COOH)]₁₀, has been reported¹⁰. Even following the Krätschmer–Huffman breakthrough in 1990 (ref. 11), only metallofullerenes such as those having higher cages (the so-called higher fullerenes), including C₇₀ and C₈₄, have been isolated and structurally characterized^{12–14}. Therefore, almost all progress in the

Here, we report the bulk synthesis of Li@C₆₀, its oxidation and the complete isolation of a [Li⁺@C₆₀]⁺ salt, together with the molecular and crystal structure determination of a [Li@C₆₀](SbCl₆) (1). Over the past decades since 1990, it has not been possible to separate Li@C₆₀ from the pristine C₆₀ due to a charge transfer interaction between them, but the present selective one-electron oxidation of Li@C₆₀ has led to the complete separation of Li@C₆₀ from C₆₀. We have, therefore, finally succeeded in growing single crystals of the [Li⁺@C₆₀]⁺ salt as a lithium endohedral fullerene. The endohedral nature and polar/ionic character of the Li@C₆₀ cation in the [Li@C₆₀](SbCl₆) crystal have been clearly demonstrated. An electrochemical study of [Li@C₆₀](SbCl₆) in solvents shows that it has a stronger electron-accepting property than pristine C₆₀. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of [Li@C₆₀](SbCl₆) have been determined to be the same as that of C₆₀. This result indicates that the Li@C₆₀ cation has been fully encapsulated in the C₆₀ cage.

Li@C₆₀分子配列の制御 → 強誘電分子薄膜が可能?

究極への挑戦！

- 水素分子、 Li^+ イオンは見える
- X線回折は原子の持つ電子を見ている
- X線＝電磁波・・・振動電場による電子の発振現象

⇒ 原子の電子状態を見ることは可能なのか？

アーサー・C・クラークの三法則

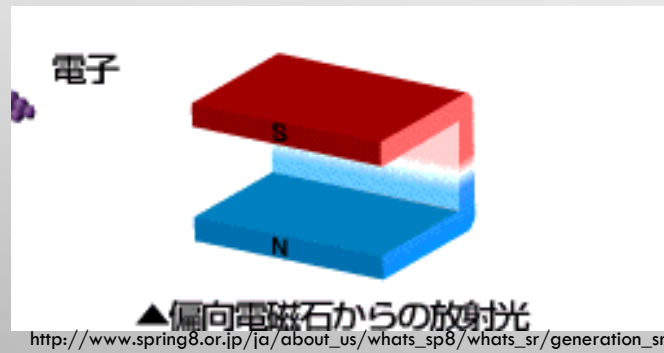
1. When a distinguished but elderly scientist states that something is possible, he is almost certainly right. When he states that something is impossible, he is very probably wrong.
2. The only way of discovering the limits of the possible is to venture a little way past them into the impossible.

可能性の限界を測る唯一の方法は、
その限界を少しだけ超越するまで挑戦することである

3. Any sufficiently advanced technology is indistinguishable from magic.
十分に発達した科学技術は、魔法と見分けがつかない

私はなぜ KEK PFスタッフ から名大に異動したのか？
総研大生 垣内徹の憂鬱

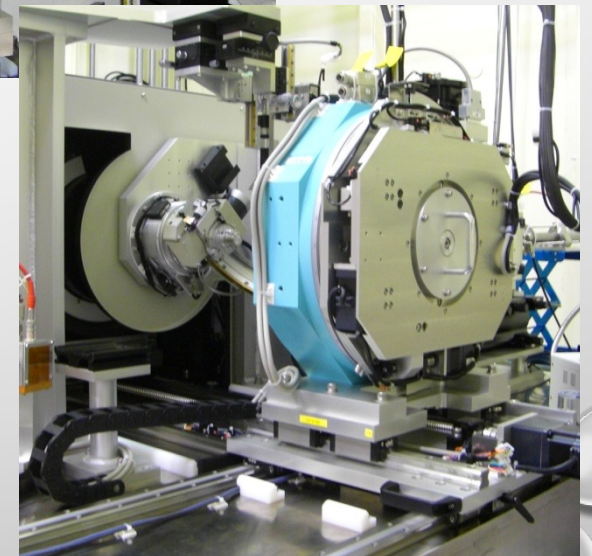
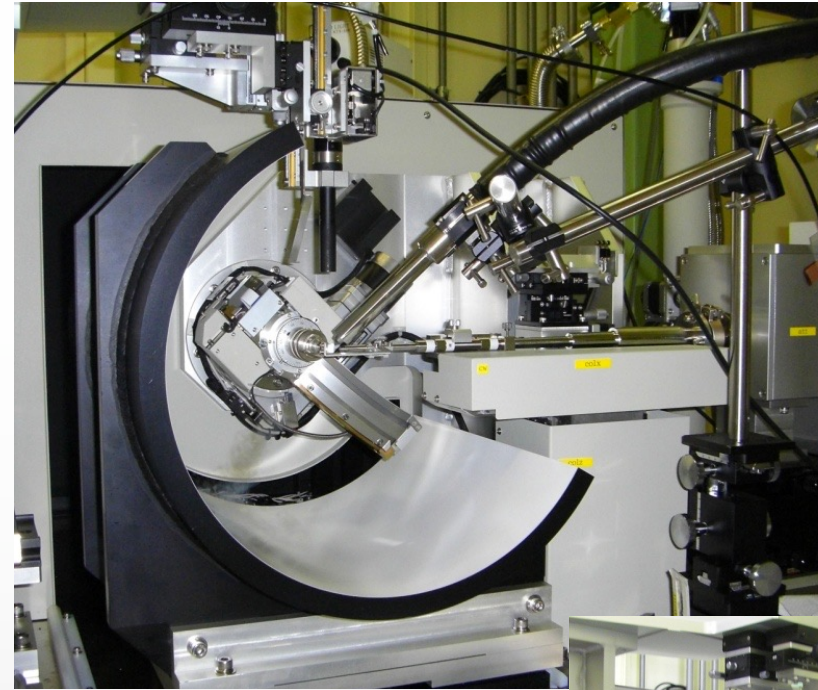
大型放射光施設を使い倒す



SPring-8 BL02B1 単結晶IPカメラ

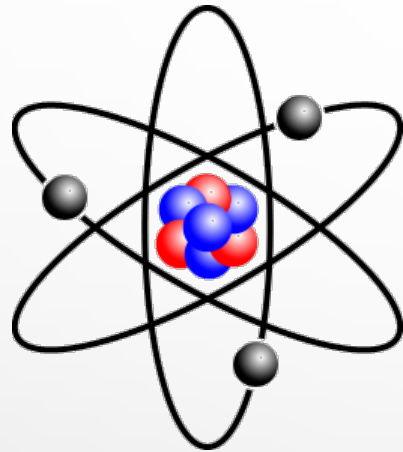
2008年3月28日納入

X線波長	1.00 ~ 0.35 Å (Si (111)の場合)
入射X線強度	$\sim 10^{10}$ cps
カメラ半径	191.3 mm
2 θ 範囲	赤道面 $-60 \sim 145^\circ$ 水平面 $\pm 42.5^\circ$
ピクセルサイズ	0.1×0.1 (mm) (2 θ 方向 $0.03^\circ/\text{pixel}$)
ゴニオメーター	3軸 $\omega: -130 \sim 220^\circ$, $\chi: -5 \sim 60^\circ$, $\phi: -180 \sim 360^\circ$ 1軸 (冷凍機用) $\omega: -177 \sim 177^\circ$
温度制御	低温ガス吹付け (> 20 K) 高温ガス吹付け (< 1000 K) 冷凍機 (> 7 K)

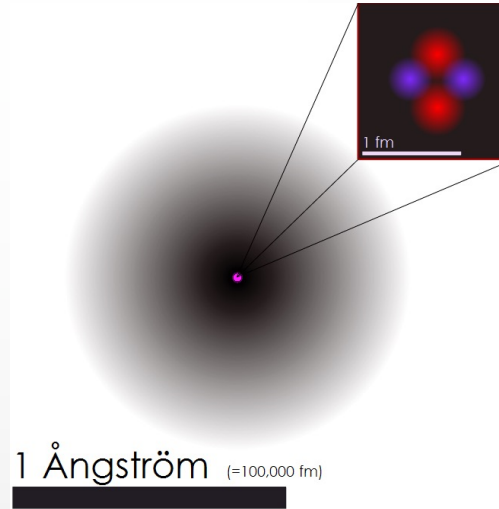


SPring-8/JASRI
杉本 邦久 (現 近畿
大)
高田 昌樹 (現 東北
大)

原子



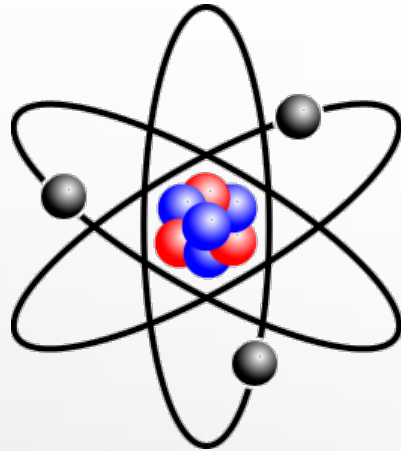
Wikipedia



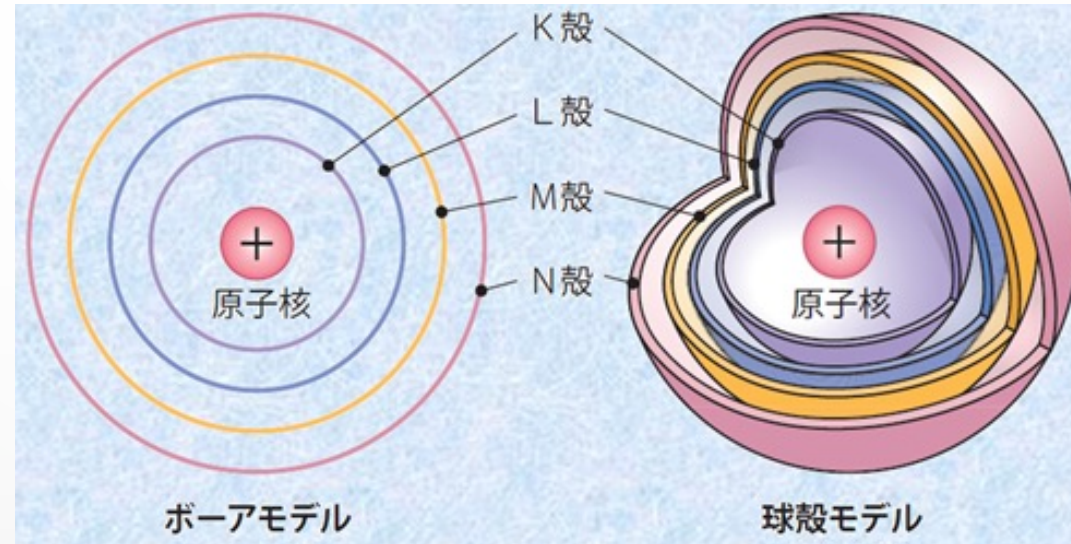
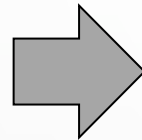
Wikipedia

原子核による中心場の電子の運動 → 古典論的には電子は原子核に落ち込む
原子の成り立ちは量子論による説明が必要

ボーアモデルから球殻モデルへ



Wikipedia



<https://sekatsu-kagaku.sub.jp/ionizationenergy-and-electronaffinity.htm>

主量子数	電子殻	軌道名	磁気量子数	収容できる電子数	最大収容電子数
n=1	K殻	1s	m=0	2	2
n=2	L殻	2s	m=0	2	8
		2p	m=0, ±1	6	
n=3	M殻	3s	m=0	2	18
		3p	m=0, ±1	6	
		3d	m=0, ±1, ±2	10	
n=4	N殻	4s	m=0	2	32
		4p	m=0, ±1	6	
		4d	m=0, ±1, ±2	10	
		4f	m=0, ±1, ±2, ±3	14	

水素様原子の電子状態

陽子：質量 M , 電荷 $+e$

電子：質量 m_e , 電荷 $-e$

$$\mu = \frac{Mm_e}{M + m_e}$$

水素原子全体の Schrödinger 方程式は μ を換算質量として

$$\left\{ -\frac{\hbar^2}{2\mu} \nabla^2 + V(\mathbf{r}) \right\} \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})$$

ラプラシアンを極座標表示にすると

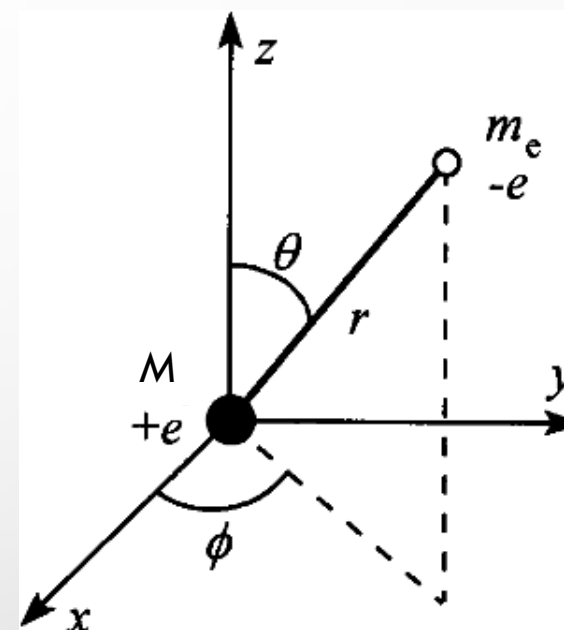
$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

ポテンシャル $V(r)$ はクーロンポテンシャルなので

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

$M \gg m_e$ であるから $\mu \approx m_e$ として (Born–Oppenheimer 近似)

$$-\frac{\hbar^2}{2m_e r^2} \left\{ \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right\} - \frac{e^2}{4\pi\epsilon_0 r} \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$



水素様原子の電子状態

この方程式を解くためには $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$ と変数分離を仮定する。

動径部分は

$$\frac{1}{R(r)} \left\{ \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m_e r^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) R(r) \right\} = \beta$$

角度部分は

$$-\frac{1}{Y(\theta, \phi)} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = \beta$$

更に、 $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ とすると、最終的には

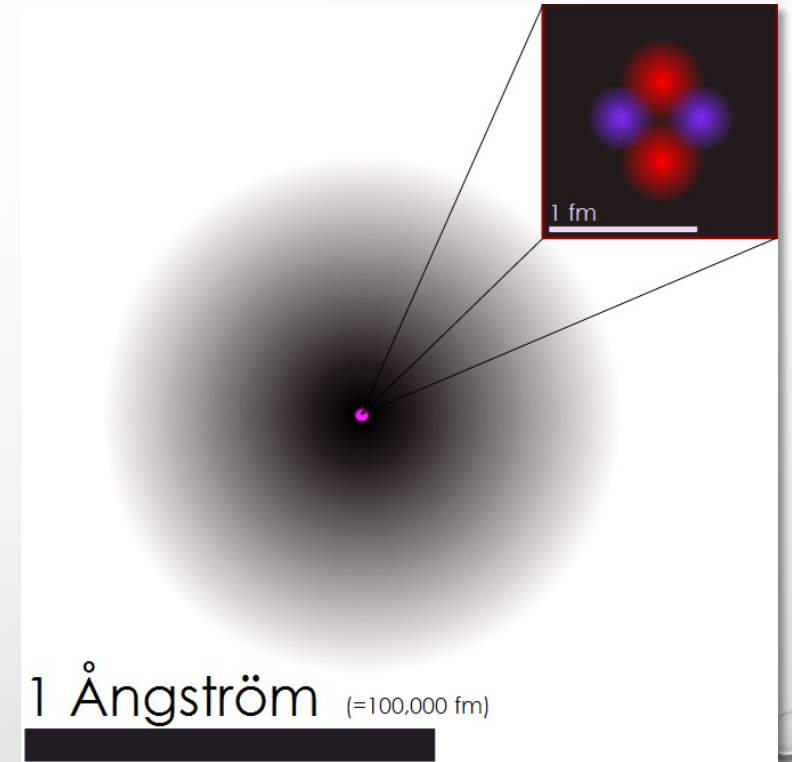
$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi)$$

$$\Theta(\theta) = (-1)^{\frac{m+|m|}{2}} \sqrt{l + \frac{1}{2}} \sqrt{\frac{(l - |m|)!}{(l + |m|)!}} P_l^m(\cos \theta)$$

$$R(r) = - \left(\frac{2}{na_0} \right)^{\frac{3}{2}} \sqrt{\frac{(n - l - 1)!}{2n \{(n + l)!\}^3}} \exp \left(-\frac{r}{na_0} \right) r^l L_{n+l}^{2l+1} \left(\frac{2r}{na_0} \right)$$

と解かれる。すなわち、3つの量子数 n, l, m で電子軌道が記述される。

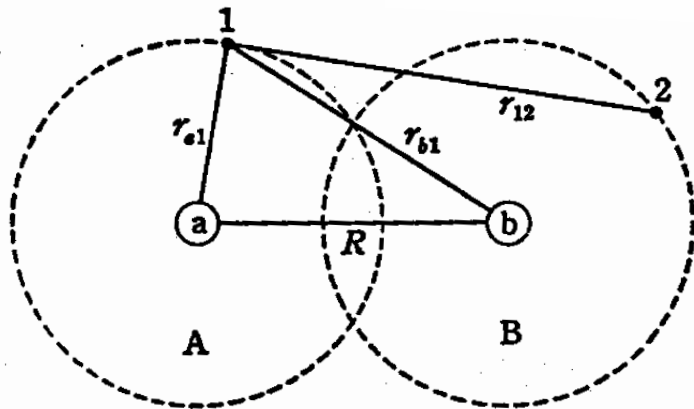
n : 主量子数, l : 方位量子数, m : 磁気量子数



Wikipedia

結合電子の分布は？ ～分子軌道入門～

水素分子の場合(強結合近似)



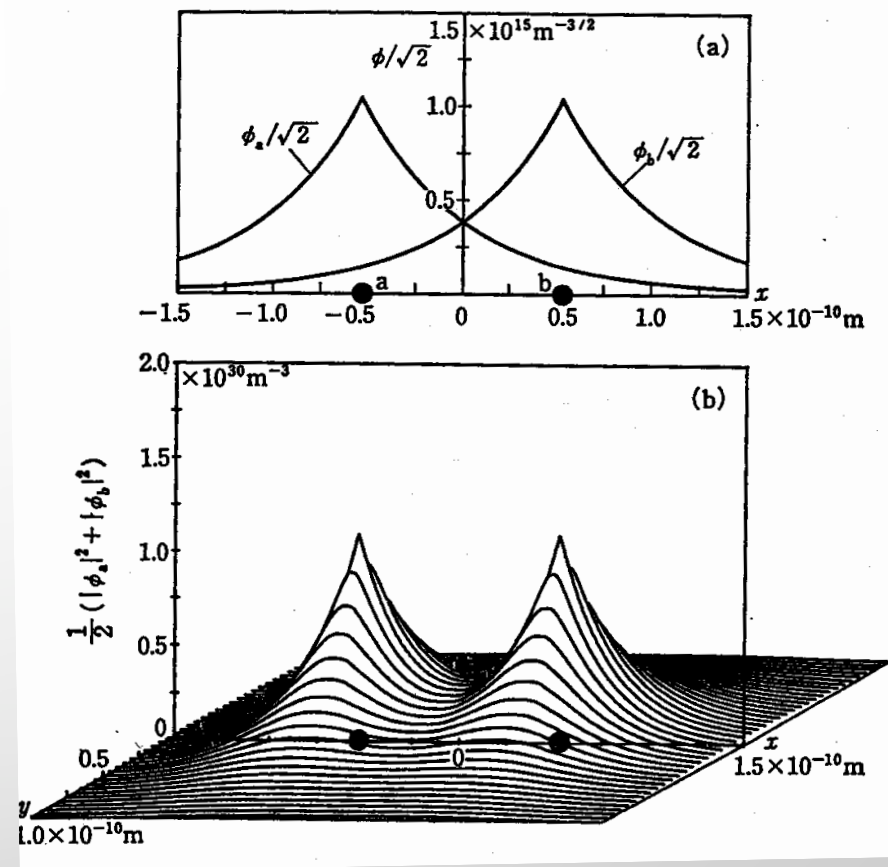
原子1の電子軌道波動関数とエネルギー; ϕ_a, ϵ_a
原子2の電子軌道波動関数とエネルギー; ϕ_b, ϵ_b
ハミルトニアンは

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + \frac{e^2}{4\pi\epsilon_0^2} \left(-\frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} + \frac{1}{R} \right)$$

分子の波動関数 Ψ は ϕ_a と ϕ_b の線形結合で書けるだろう

$$\psi = c_a \phi_a + c_b \phi_b$$

独立な2つの1s軌道の電子密度

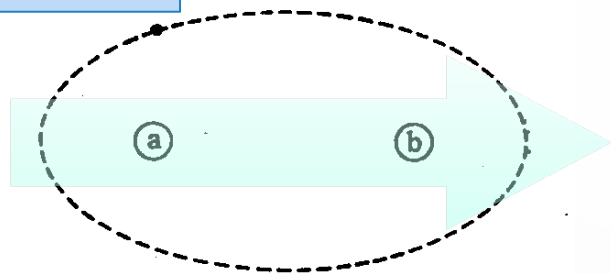


結合電子の分布は？ ～分子軌道入門～

水素分子の場合(強結合近似)

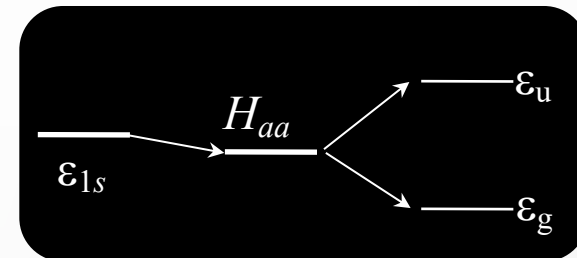
$$\psi = c_a \phi_a + c_b \phi_b$$

$$c_a^2 = c_b^2$$

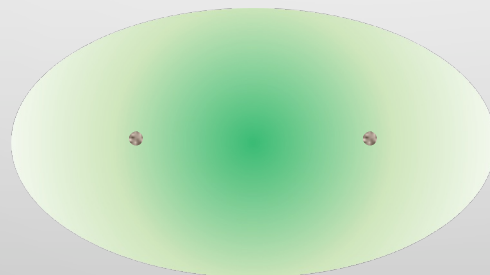
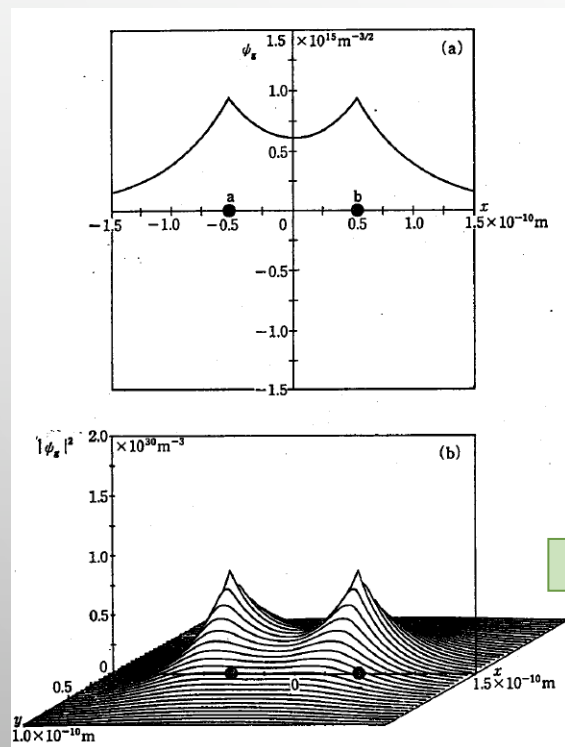


$$\psi_{g,u} = \frac{1}{\sqrt{2 \pm 2S}} (\phi_a \pm \phi_b)$$

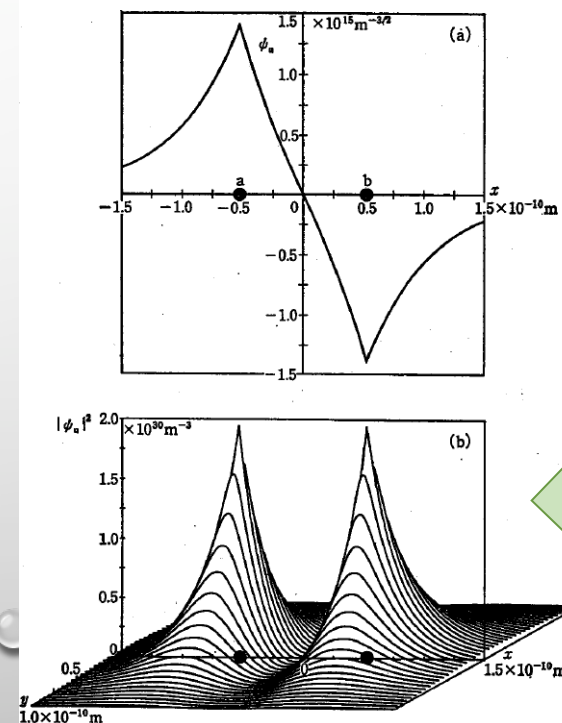
S:重なり積分



対称分子軌道関数 ψ_g と電子密度 $|\psi_g|^2$



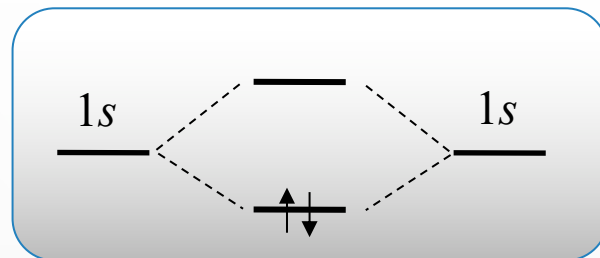
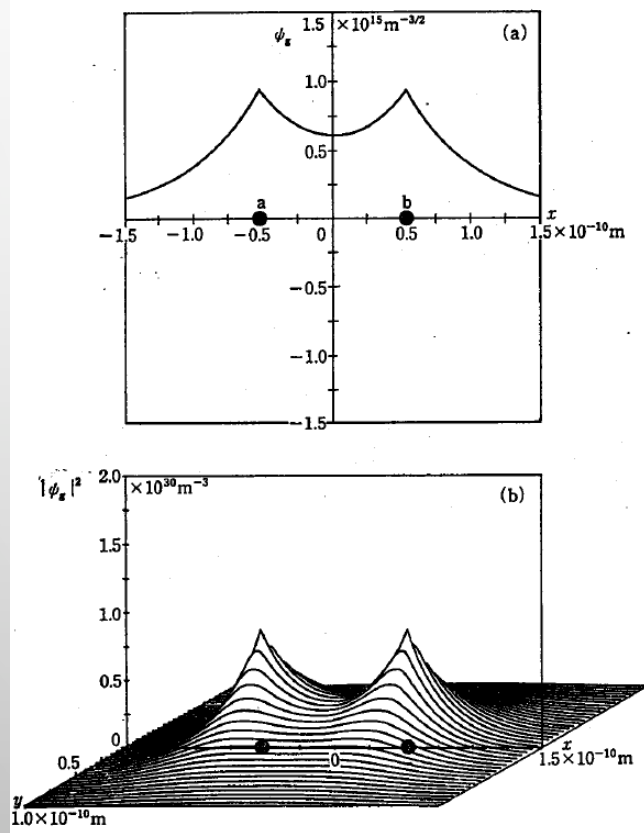
非対称分子軌道関数 ψ_u と電子密度 $|\psi_u|^2$



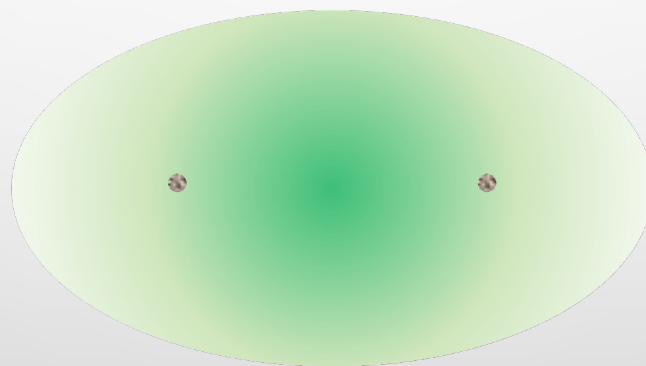
分子軌道と結合電子

水素分子の場合

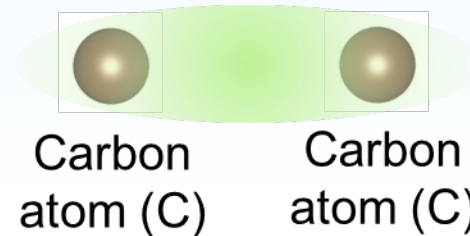
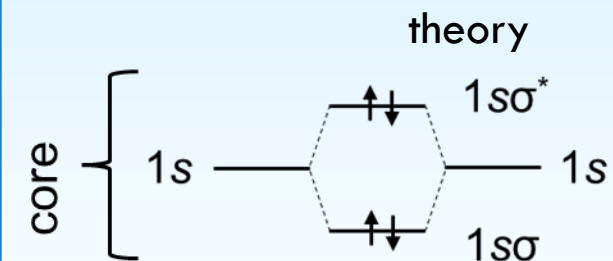
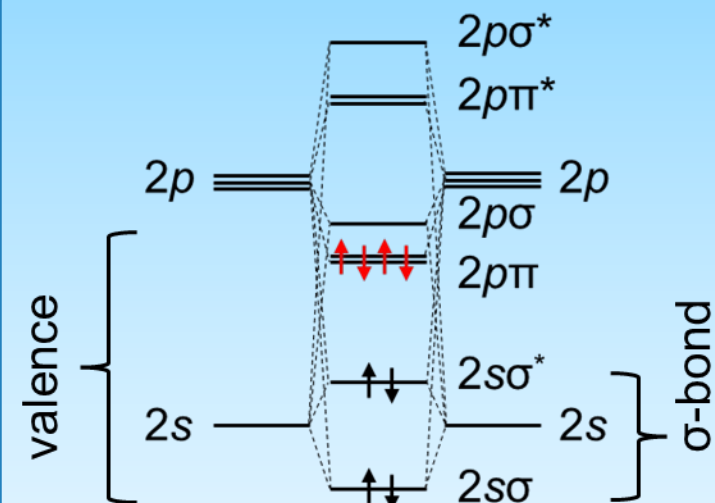
対称分子軌道関数 ψ_g と
電子密度 $|\psi_g|^2$



$$\psi_g = \frac{1}{\sqrt{2 + 2S}} (\varphi_a + \varphi_b)$$



炭素原子間の σ 結合



超精密価電子密度分布観測への挑戦

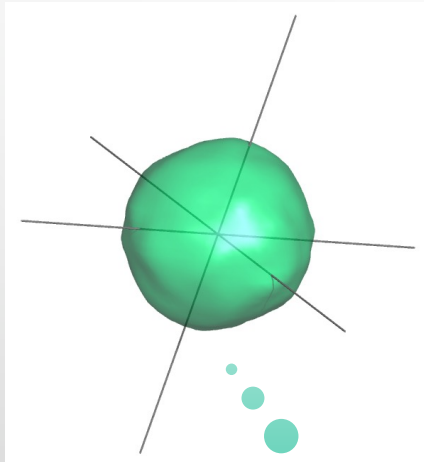


鬼頭俊介
(現 東大)

価電子密度は原子の全電子密度から内殻電子密度を差し引くことで得られるはず

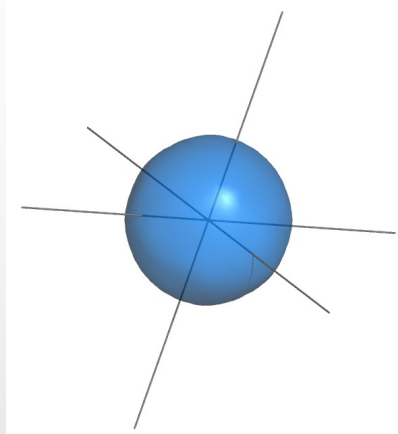
全電子

ρ_{all}



内殻電子

ρ_{core}



価電子

ρ_{valence}



但し全電子密度分布は
観測可能量ではない!

価電子密度解析はどこまで化学を語れるか

有機分子結晶における 超精密価電子密度分布観測

共同研究者

神戸大／北大
北大
愛媛大

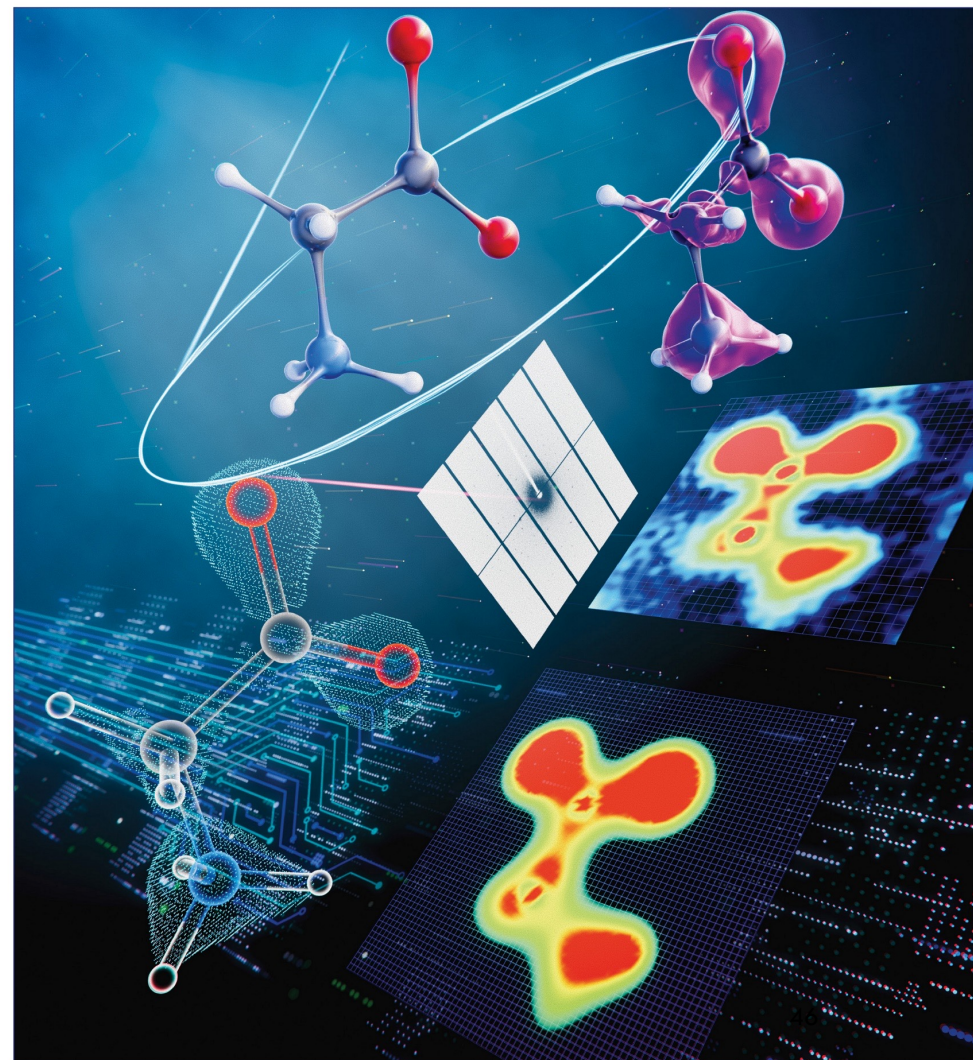
常田 貴夫
長谷部 匡敏
内藤 俊雄



原武史(名大 D3)

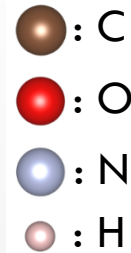
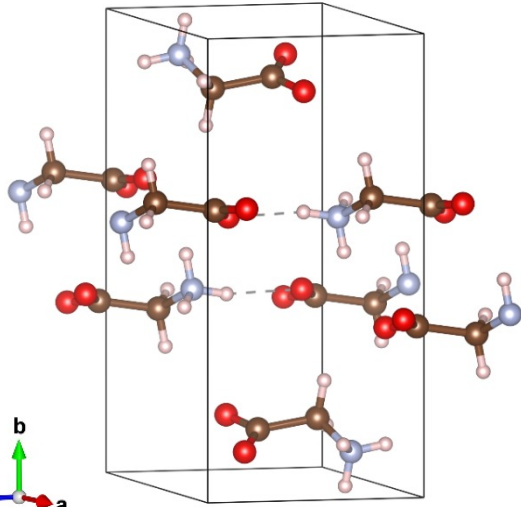
Xxxxx XX, XXXX
Volume XX
Number XX
pubs.acs.org/JACS

J | A | C | S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

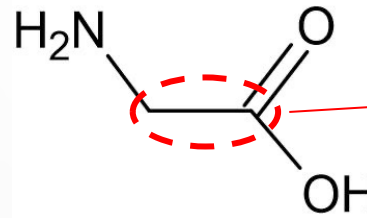


Glycine

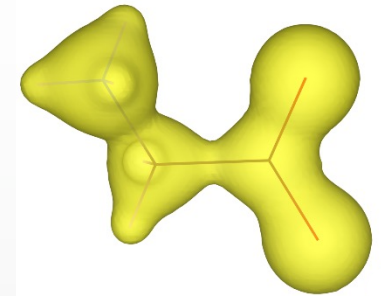
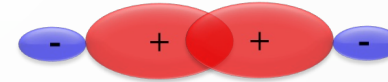
Crystal structure of "Glycine"



Glycine molecule



sp^3 hybrid orbitals
 +
 C-C single(σ) bond

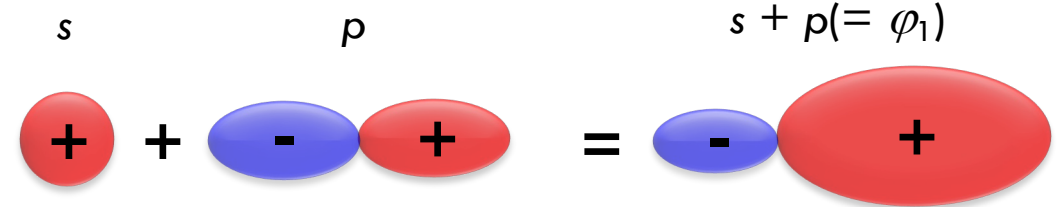


VESTA Simulation

~ σ bond formed by sp hybrid orbitals ~

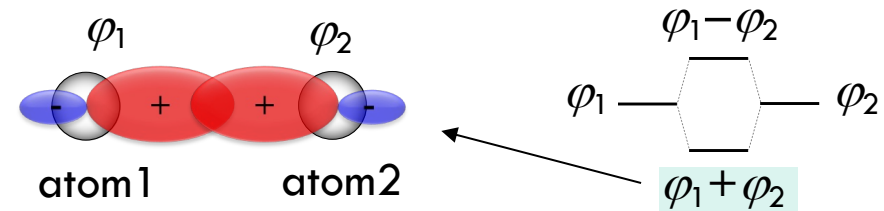
sp hybrid orbitals

(at atom1)



σ bond

(between atom1 and atom2)



Total
(Exp.)

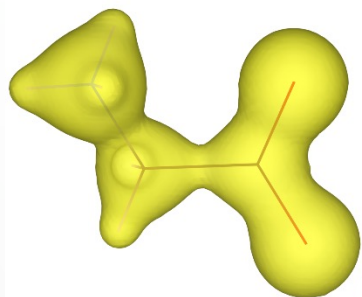
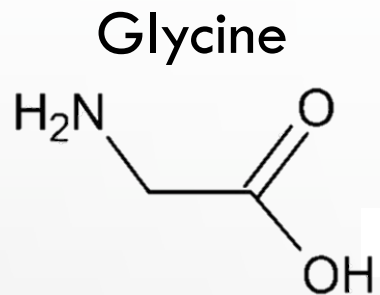
Core
(model)



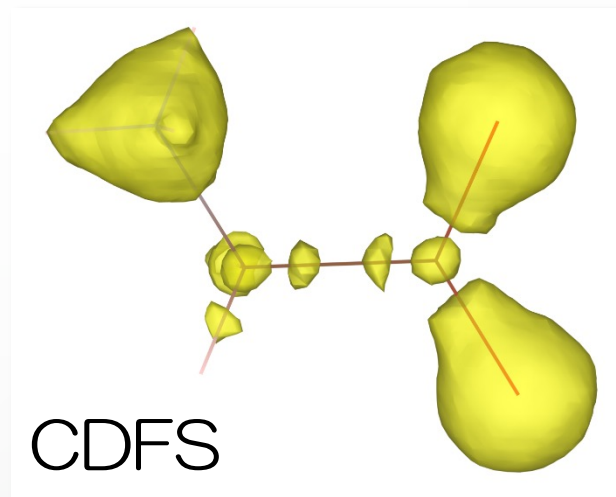
H:

C, N, O: $[\text{He}](1s^2)$

超精密価電子密度分布への挑戦



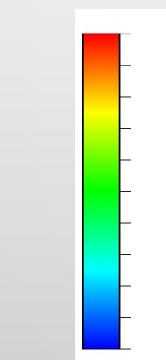
VESTA Simulation



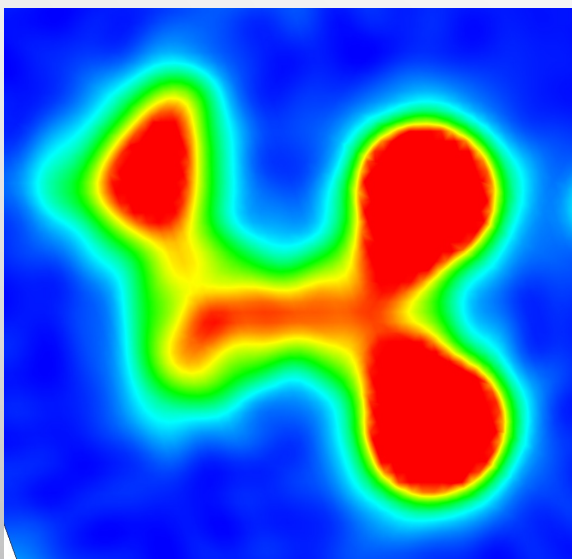
CDFS

$1.8 \text{ e}/\text{\AA}^3$

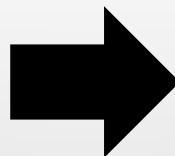
$d > 0.50 \text{\AA}$



$0.0 \text{ e}/\text{\AA}^3$

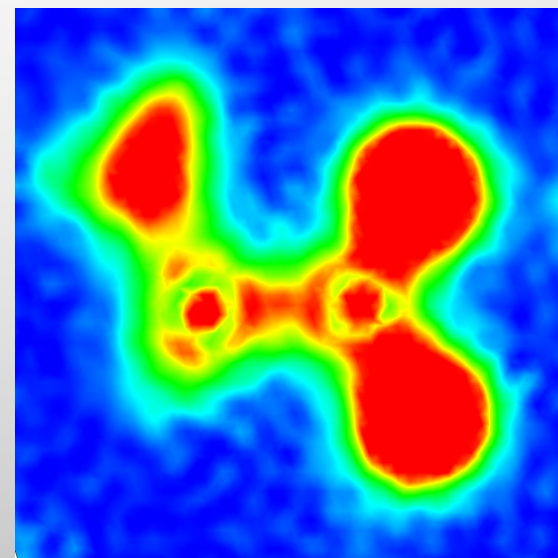


Intrinsic?



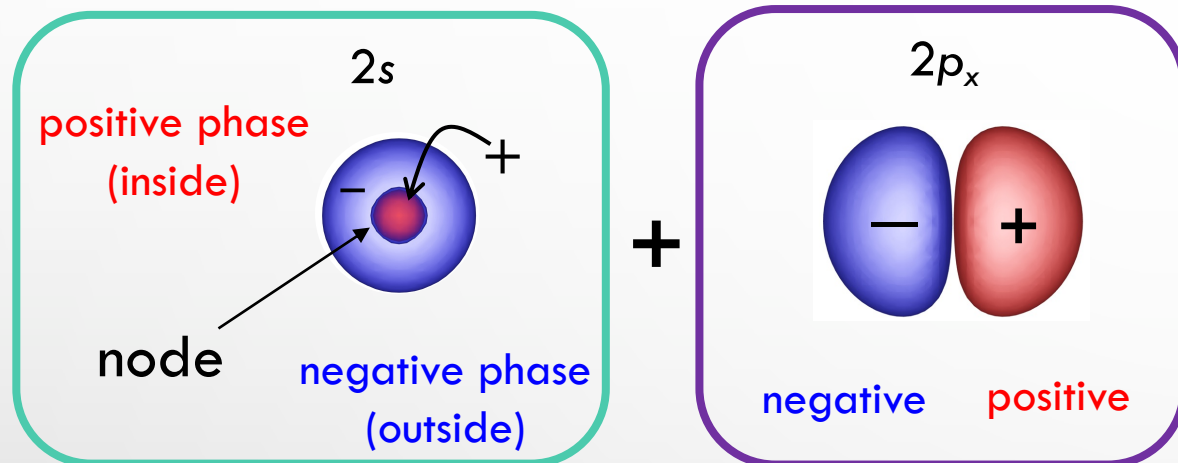
Detector: IP $\rightarrow$ CdTe-PILATUS
Optimized exp. conditions
Fine Slicing mode

$d > 0.30 \text{\AA}$

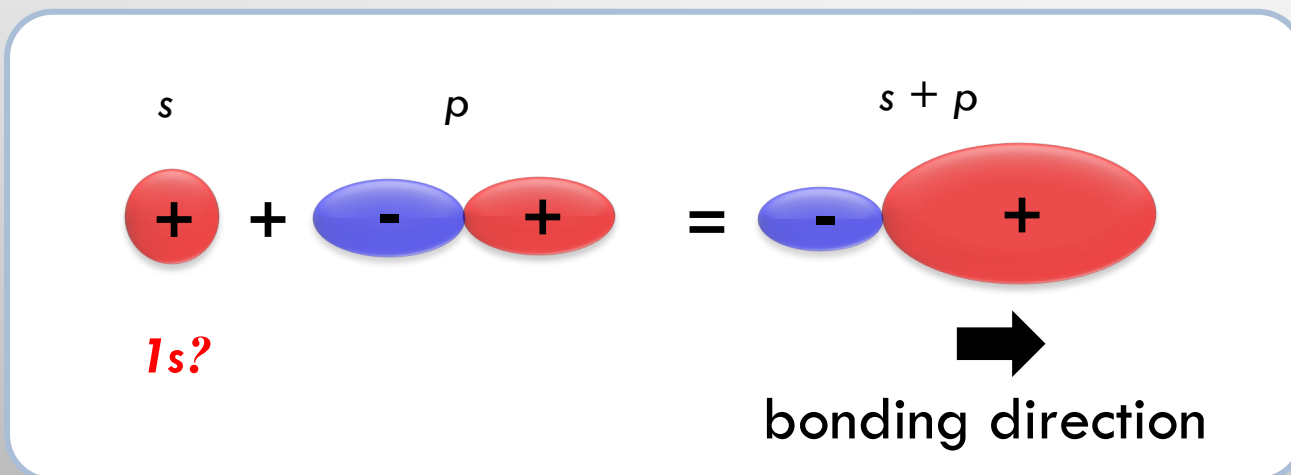
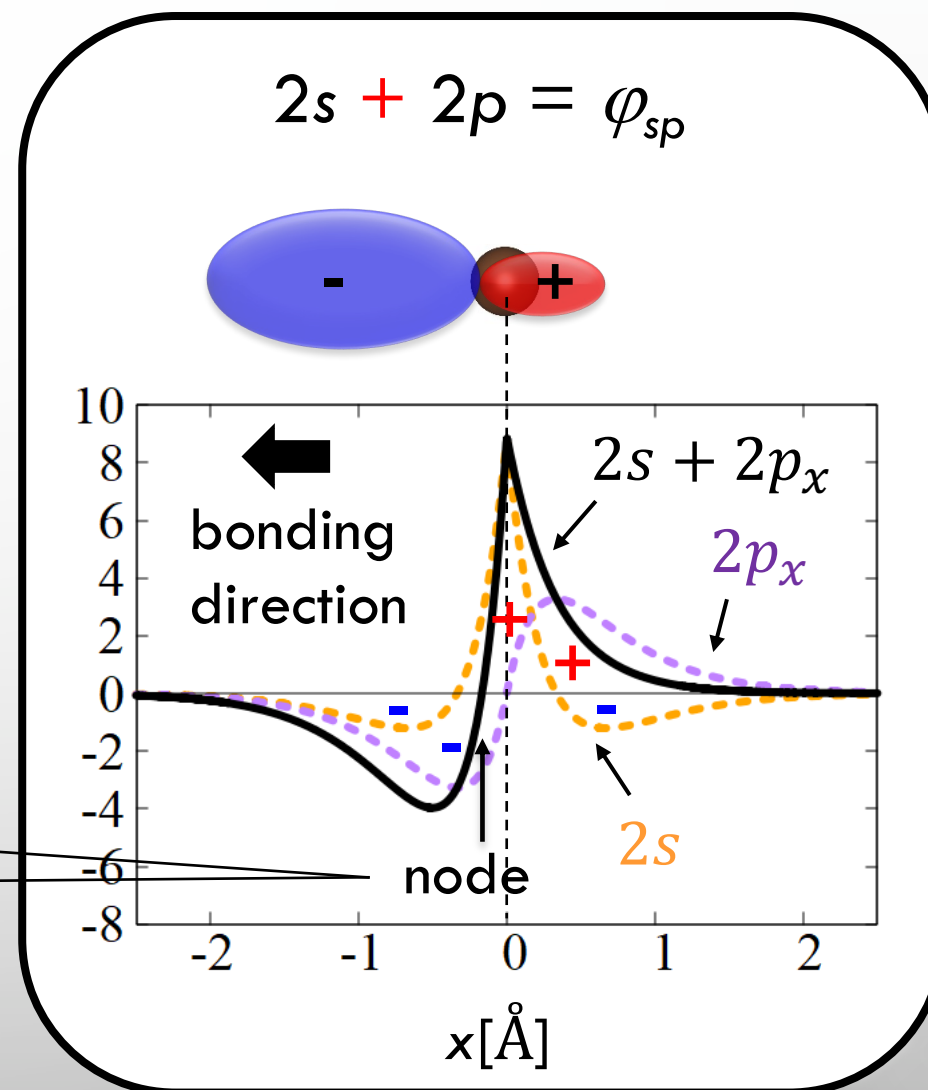


混成軌道による共有結合とは？

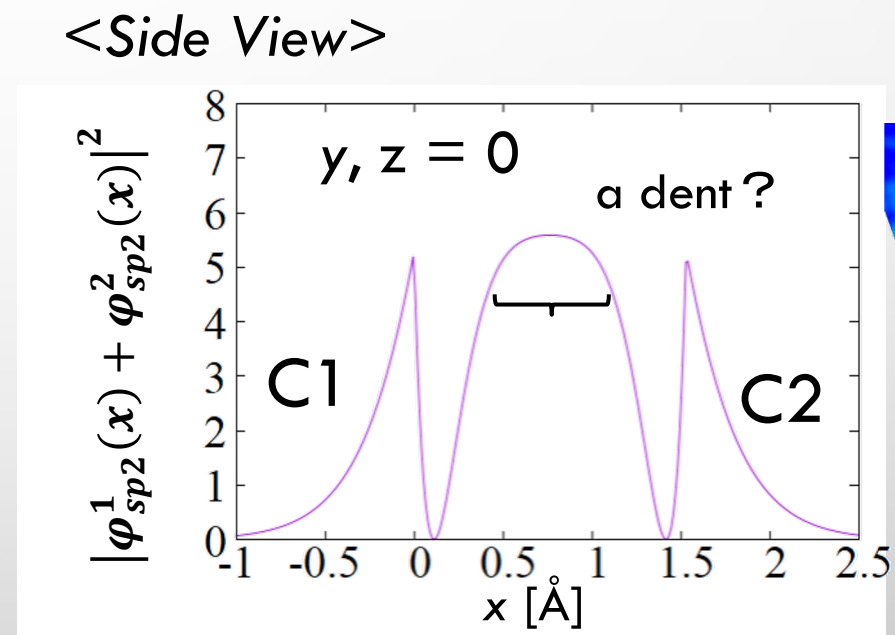
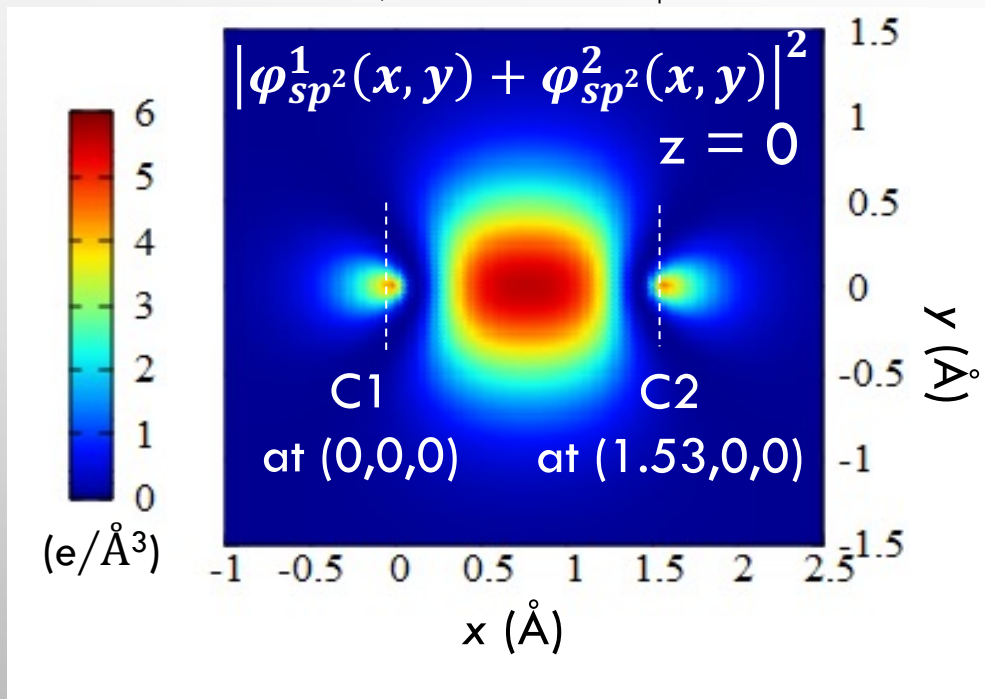
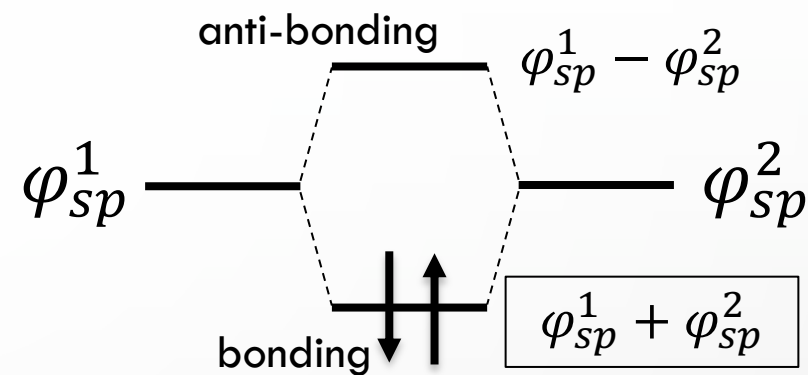
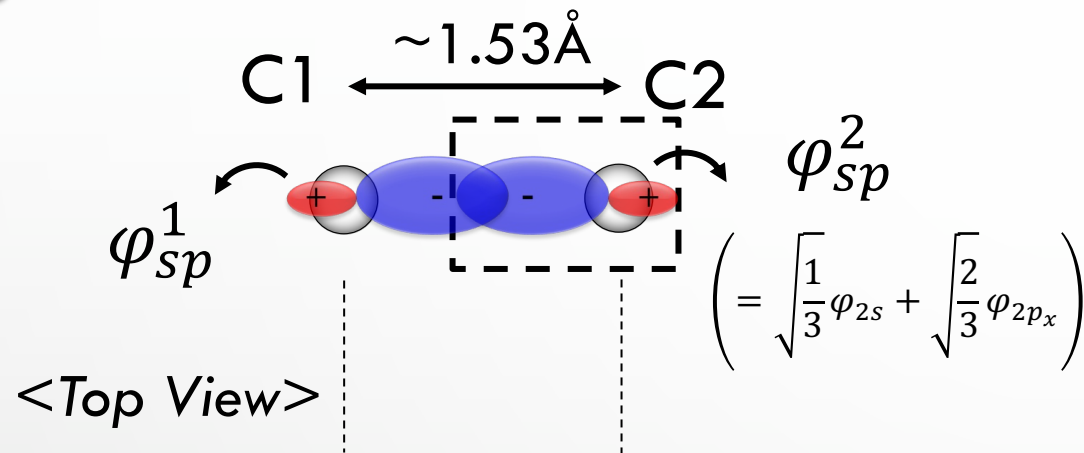
Atomic orbitals



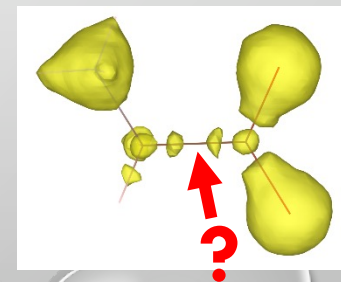
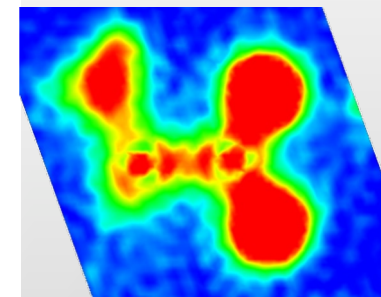
Hybrid orbital



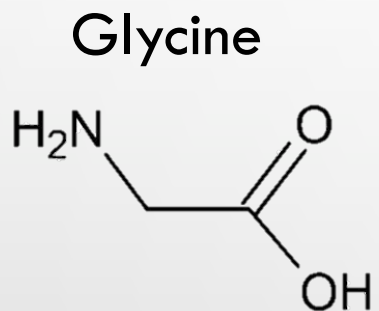
Simple picture of σ bond



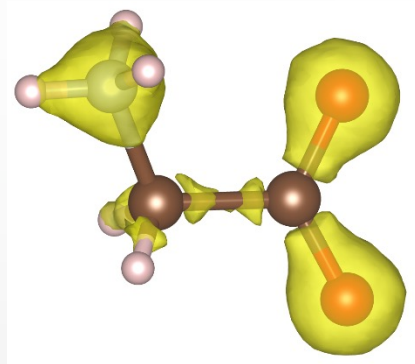
CDFS(Glycine)



Comparison with DFT calculation



< Experiment >

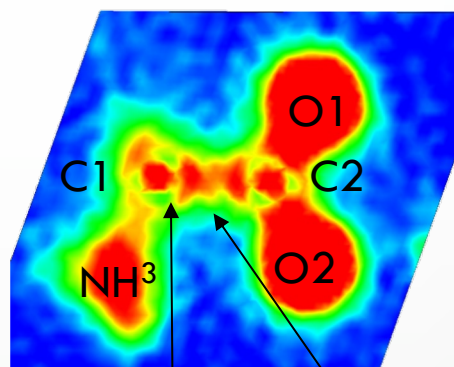


1.50 e/Å³

1.7 e/Å³

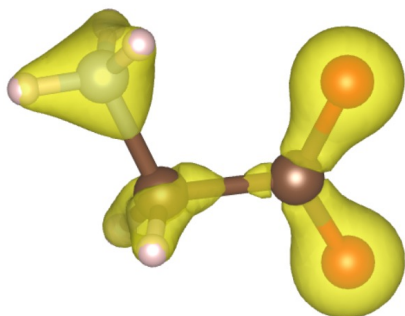


0.0 e/Å³



Directly comparable to quantum chemical calculations.

< Calculation >



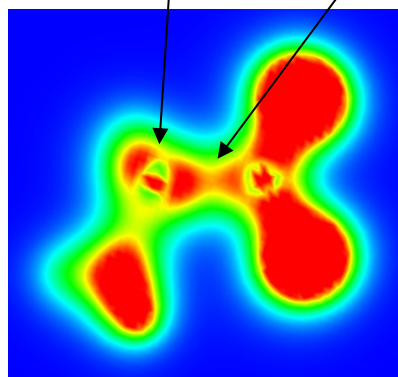
1.69 e/Å³

LC-BLYP, cc-pVTZ

2.0 e/Å³



0.0 e/Å³



node

dent

Caused by MO construction

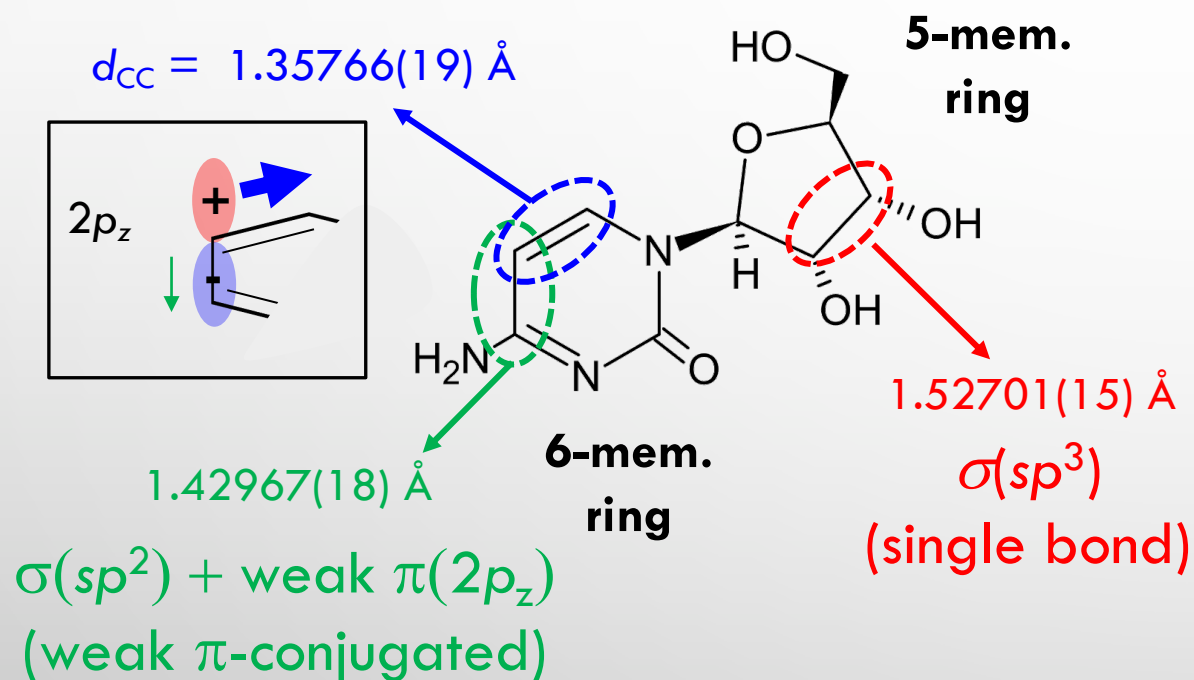
The nodes & dents also can be seen in the DFT result.

北大 長谷部、常田

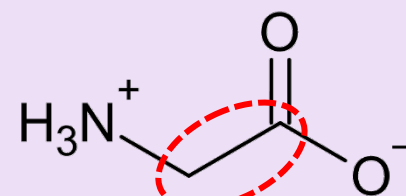
The difference of C-C bonding mode

$\sigma(sp^2) + \text{strong } \pi(2p_z)$
(weak double bond)

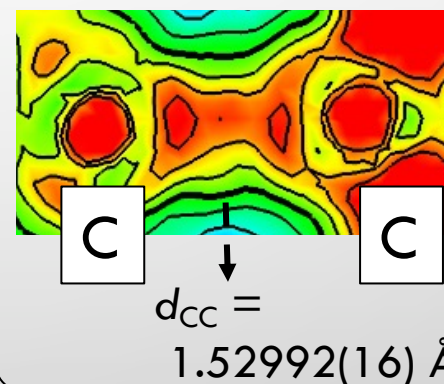
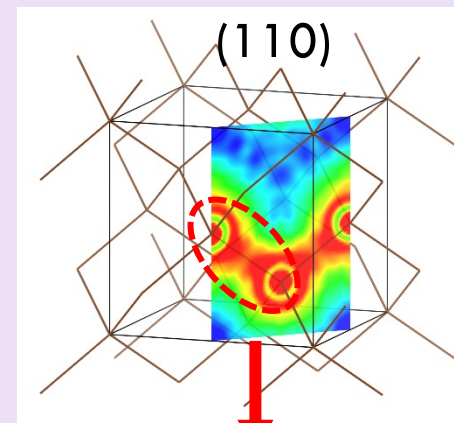
Cytidine



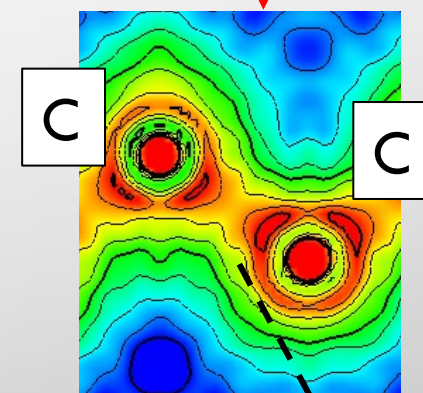
Glycine



Diamond



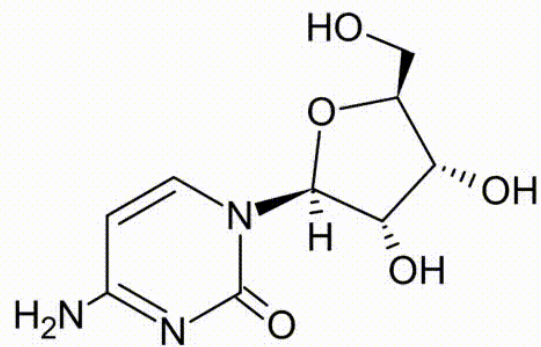
$\sigma(sp^3)$ (single bond)



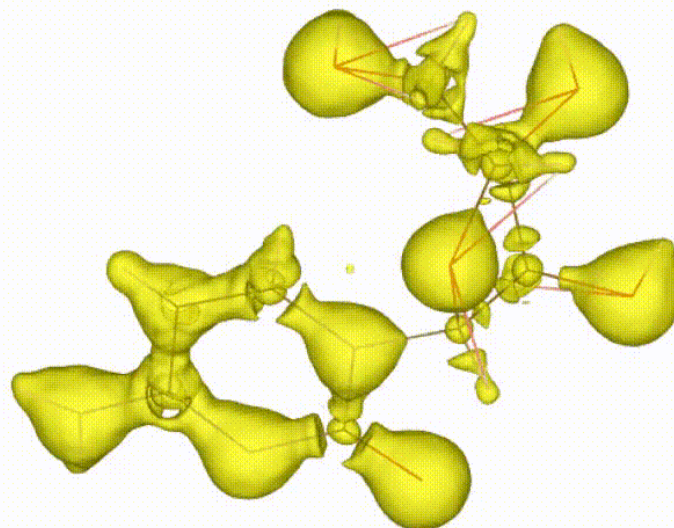
$d_{CC} = 1.54715(0) \text{ \AA}$

Cytidine 価電子密度分布

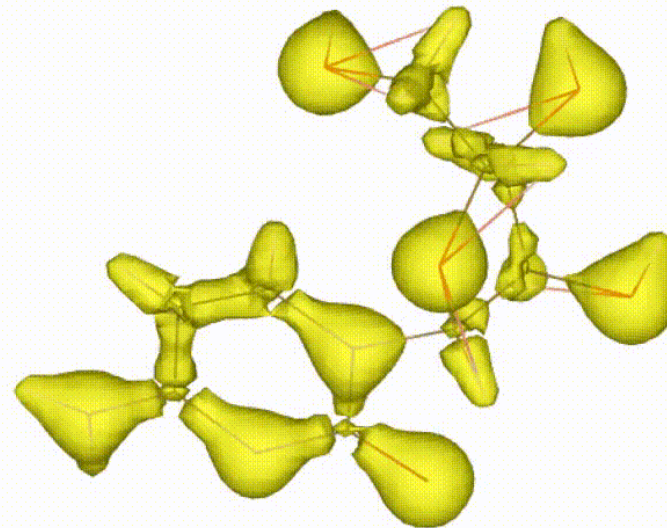
Cytidine



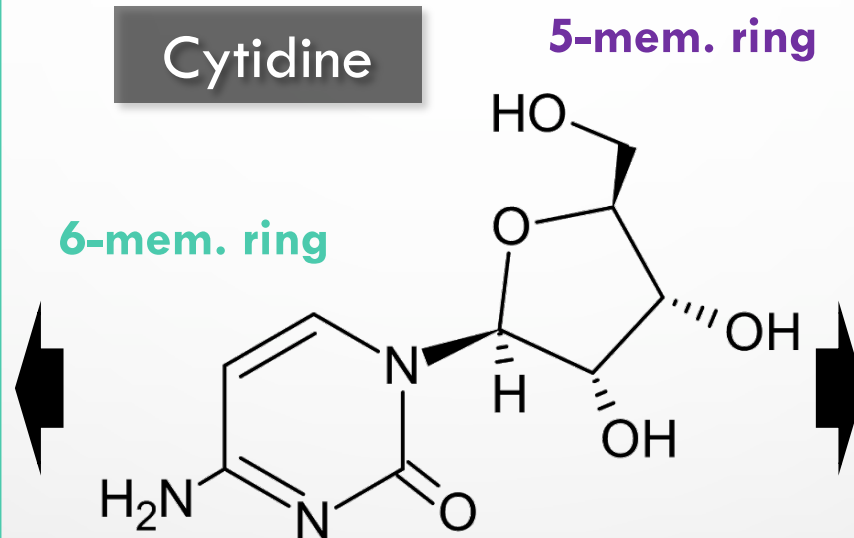
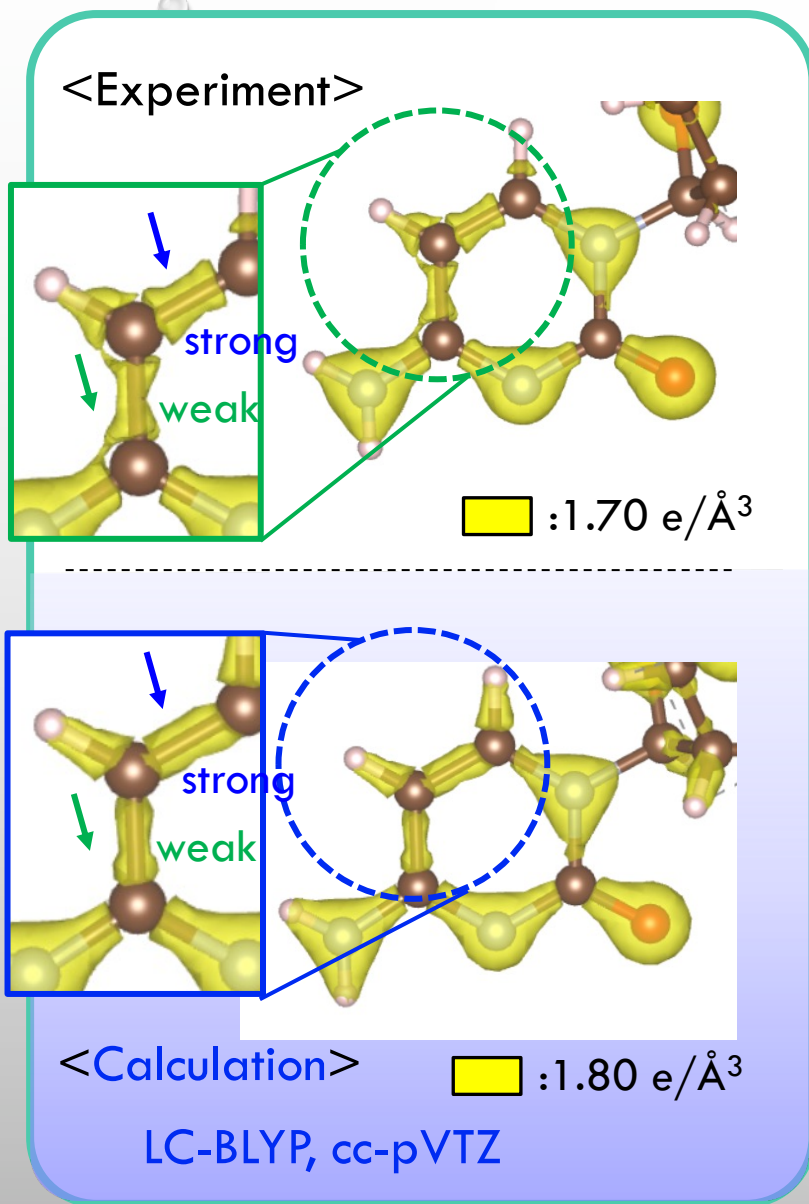
Experiment (3D)



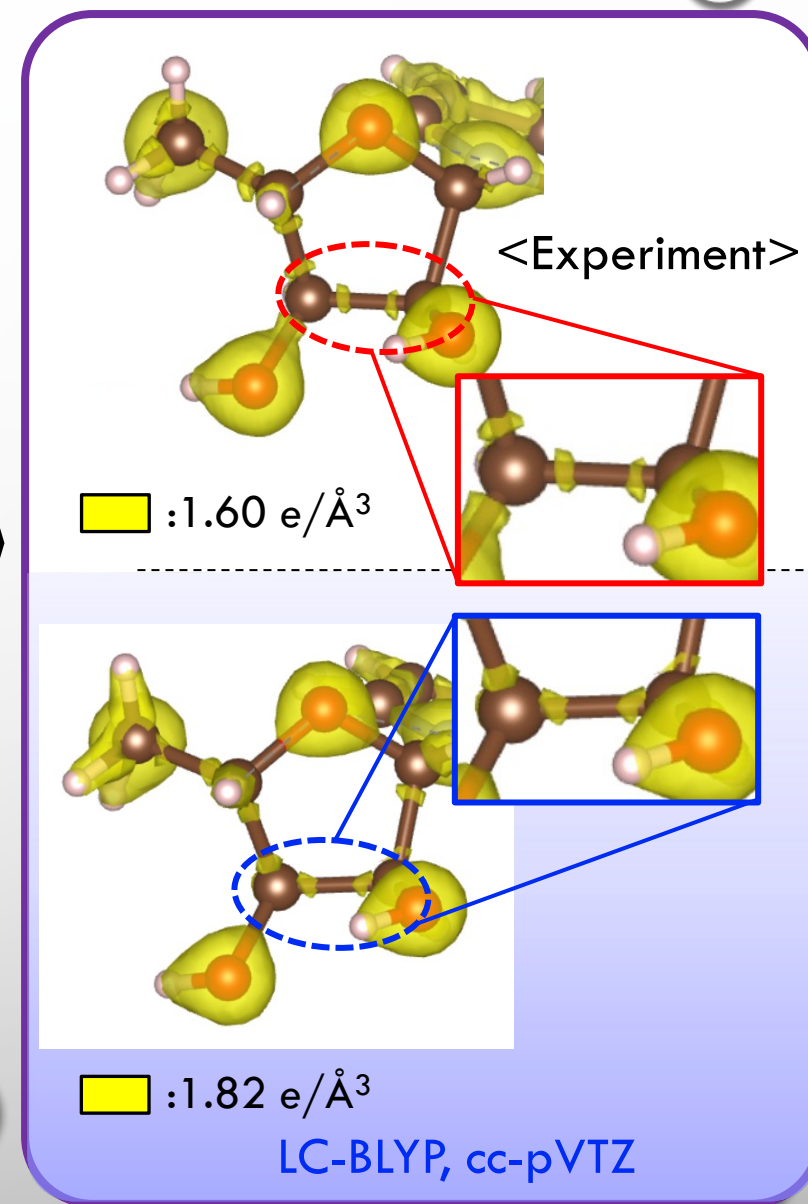
Theory (3D)



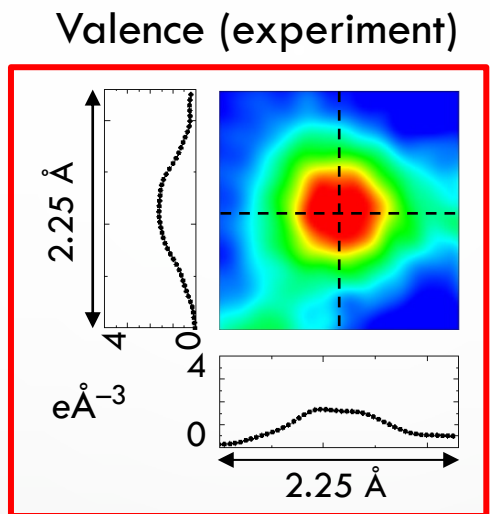
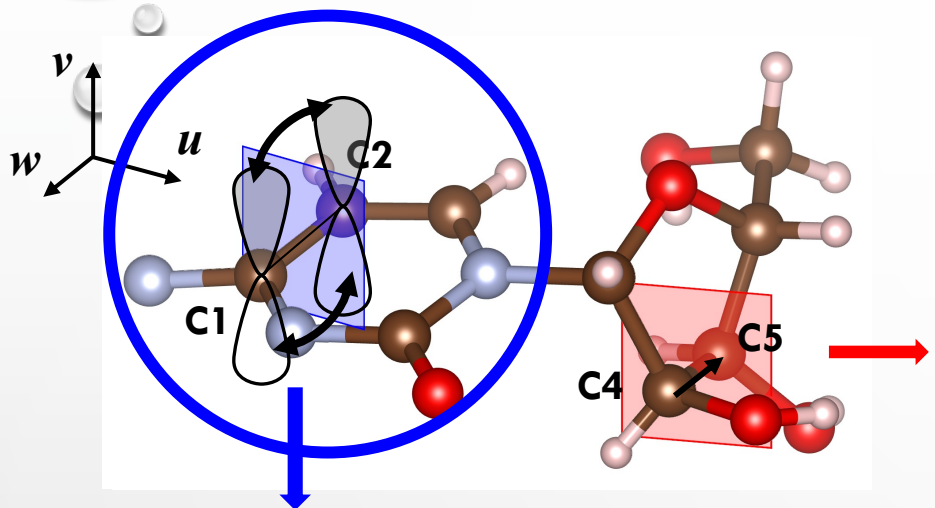
Comparison with DFT calculation



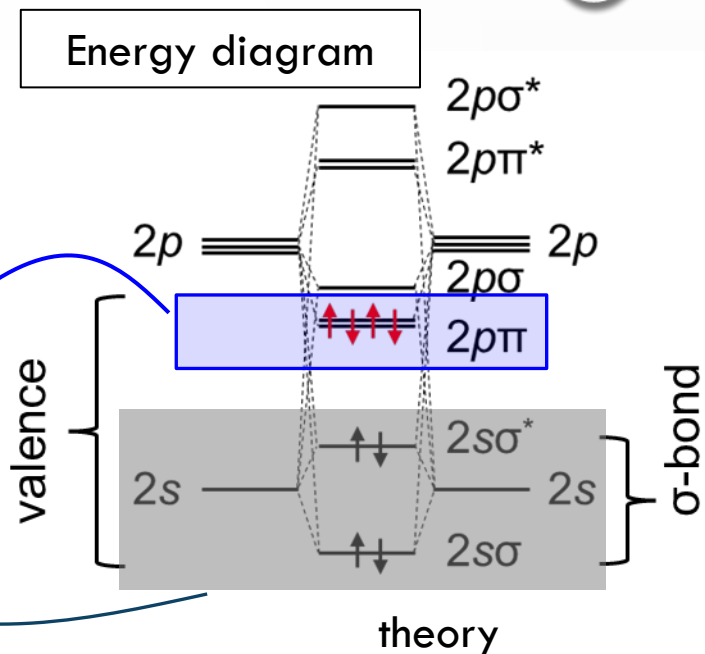
The calculated DFT result corresponds well to the experimental CDFS one.



Can we see π -orbitals?



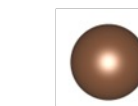
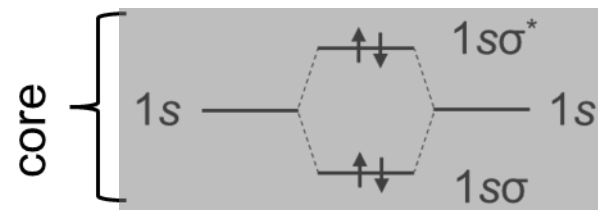
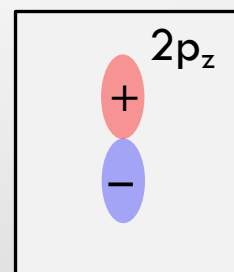
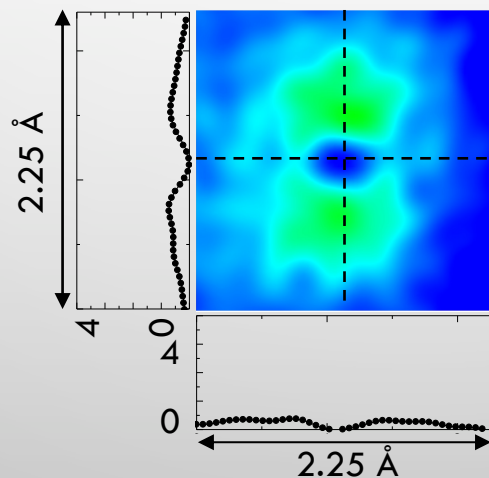
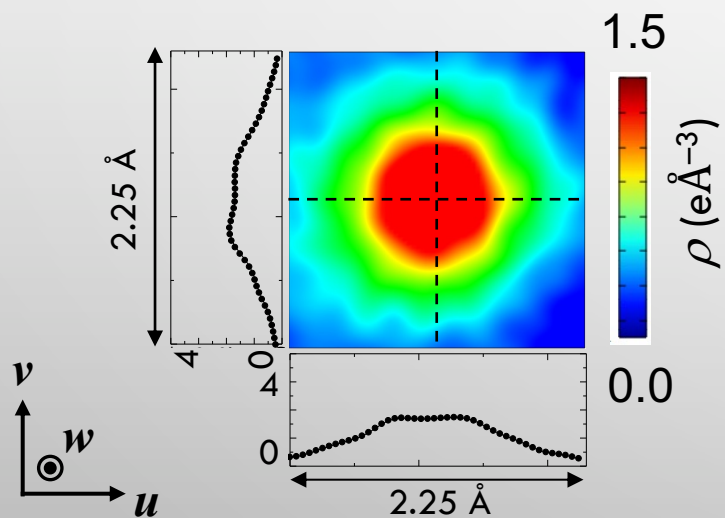
isotropic
→ 2σ bond



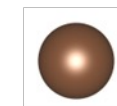
valence (experiment)

valence(experiment) - σ -bond(theory)

➤ π only ?

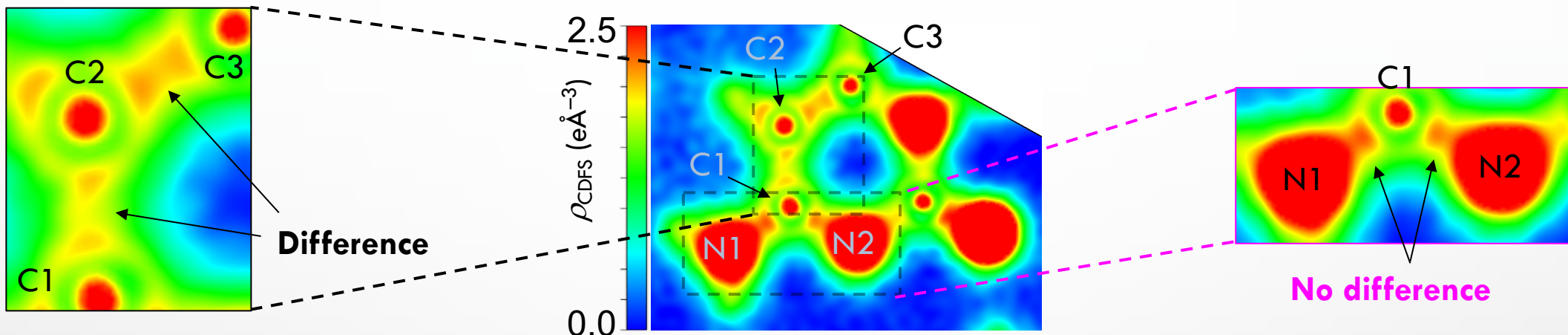


Carbon atom (C)

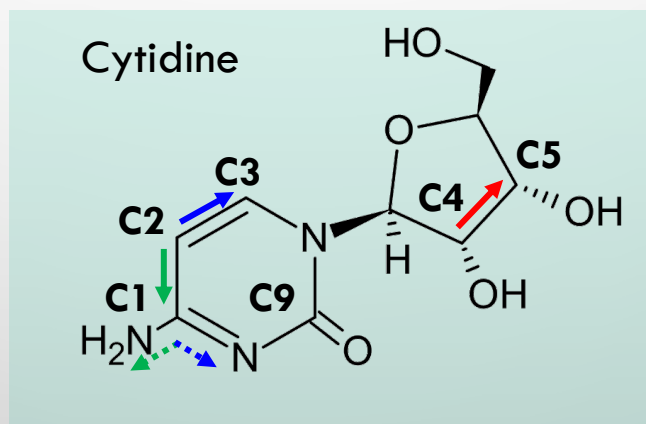
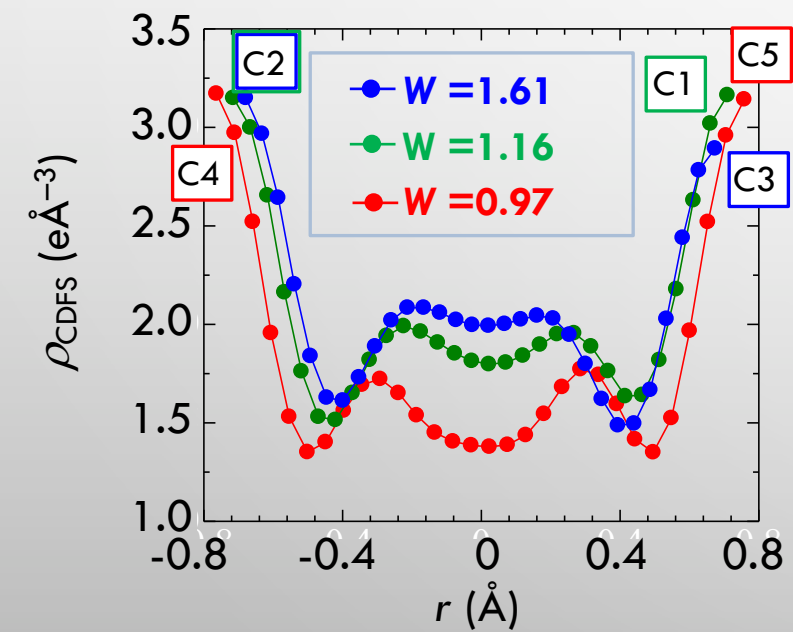


Carbon atom (C)

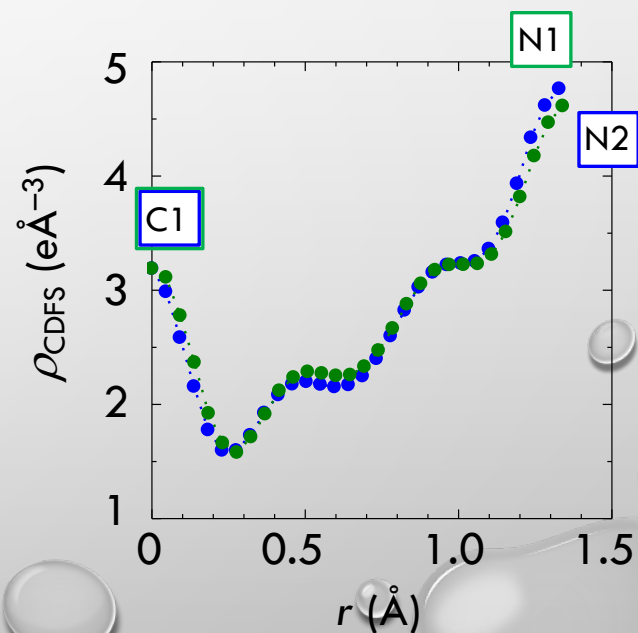
Mysterious behavior of VED for bond orders



Curve (1D) plots on the C–C bonds

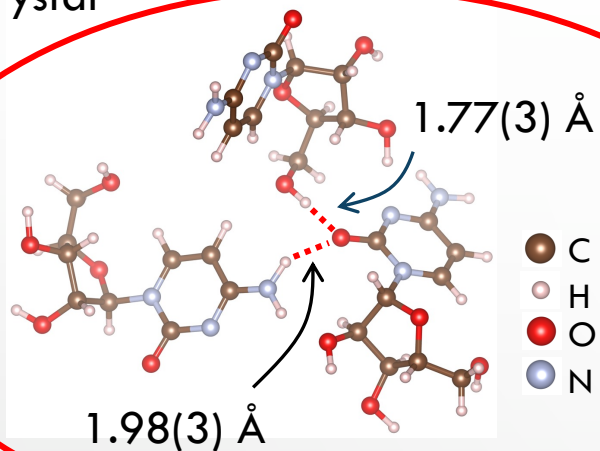


Curve (1D) plots on the C–N bonds



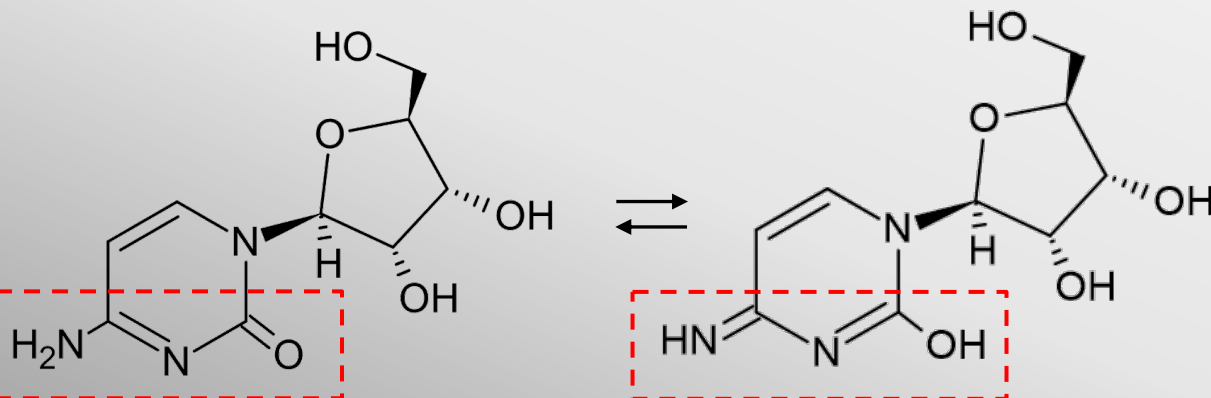
Chemical resonance in hetero ring

In a crystal

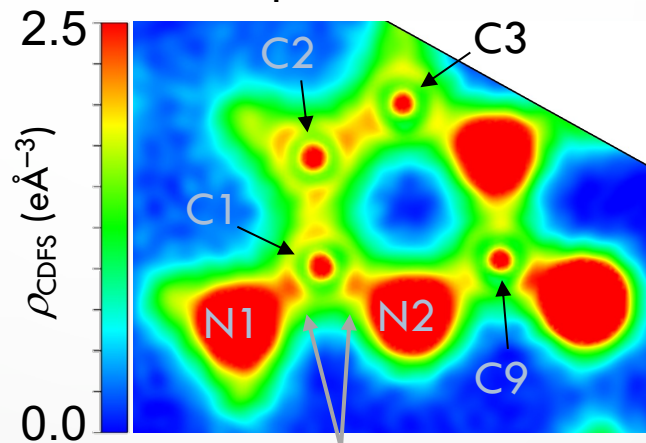


Proton exchange between O and H

【Chemical resonance by proton exchange】

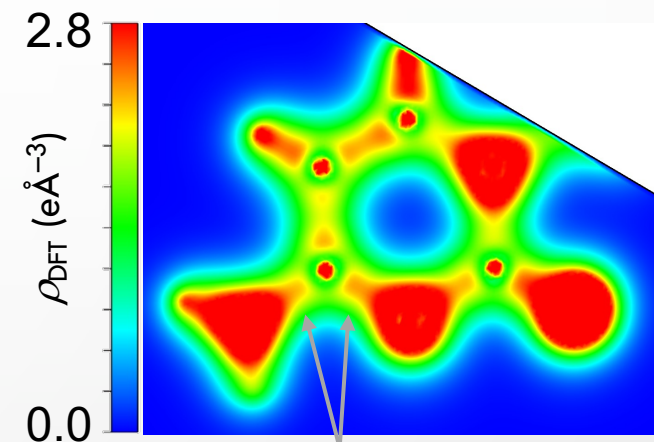


Experiment



No difference

DFT calculation



No difference

Based on experimental
structure parameters

Precise crystal structure obtained **experimentally**

Highly reliable theoretical calculation

アーサー・C・クラークの三法則

1. When a distinguished but elderly scientist states that something is possible, he is almost certainly right. When he states that something is impossible, he is very probably wrong.

高名で年配の科学者が可能であると言った場合、その主張はほぼ間違いない。

また不可能であると言った場合には、その主張はまず間違っている

2. The only way of discovering the limits of the possible is to venture a little way past them into the impossible.

可能性の限界を測る唯一の方法は、その限界を少しだけ超越するまで挑戦することである

3. Any sufficiently advanced technology is indistinguishable from magic.
十分に発達した科学技術は、魔法と見分けがつかない



萬條 太駿
(現 SP8/JASRI)

小山 千翔
(名大 M2)

価電子密度解析でどこまで軌道の物理を語れるか？

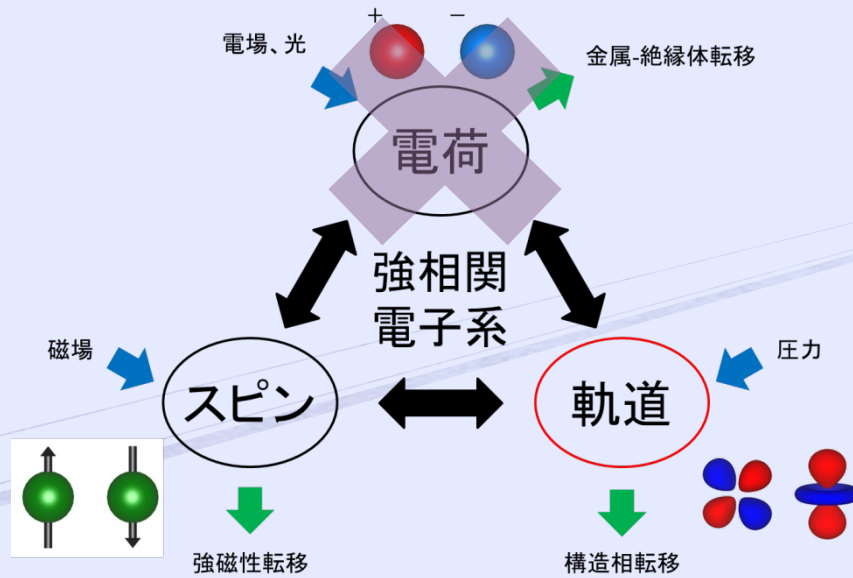
主な共同研究者
東大新領域／理研
早大理工

有馬孝尚
勝藤拓郎

軌道自由度は直接観測可能か？

縮退軌道の電子状態の実空間観測への挑戦！

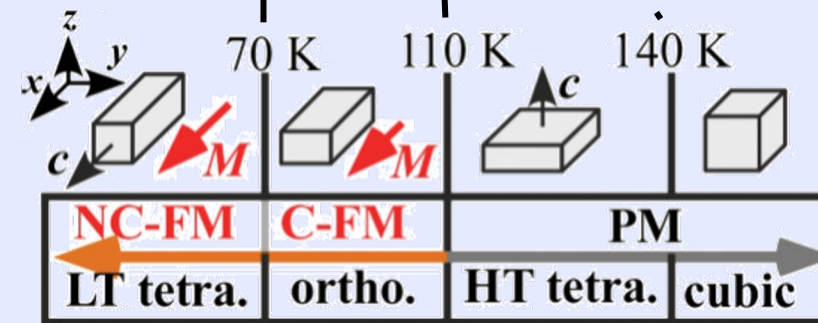
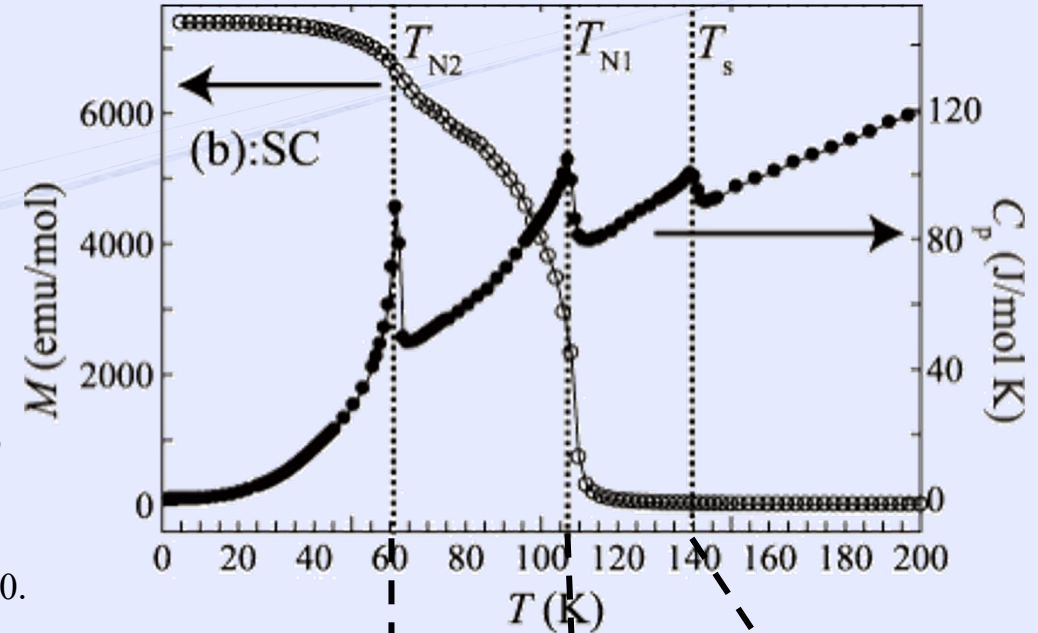
Spinel Oxide : FeV_2O_4



- D. B. Rogers *et al.*; J. Phys. Chem. Solids. **24** (1963) 347-360.
- M. Tanaka *et al.*; J. Phys. Soc. Jpn. **21** (1966) 262-267.
- S. Sarker *et al.*; Phys. Rev. B **84** (2011) 235112.
- J.-S. Kang *et al.*; Phys. Rev. B **85** (2012) 165136.
- S. Nakamura *et al.*; J. Phys. Soc. Jpn. **85** (2016) 014702.

構造相転移の駆動力は軌道自由度

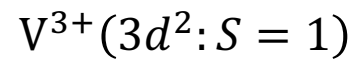
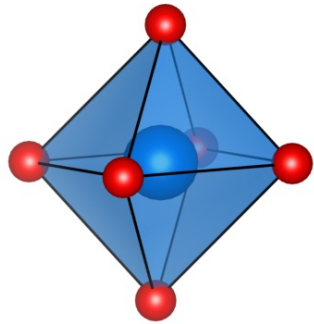
S. Kawaguchi, *et al.*; J. Phys.: Condens. Matter **25** (2013) 416005



Y. Nii *et al.*; Phys. Rev. B **86** (2012) 125142.

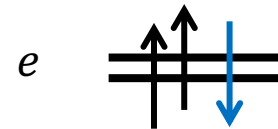
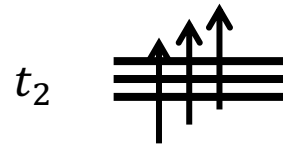
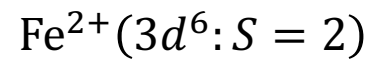
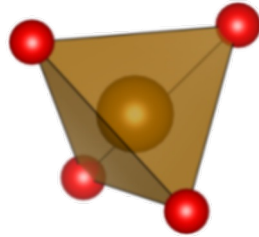
Spinel Oxide : FeV_2O_4

VO_6
Octahedron

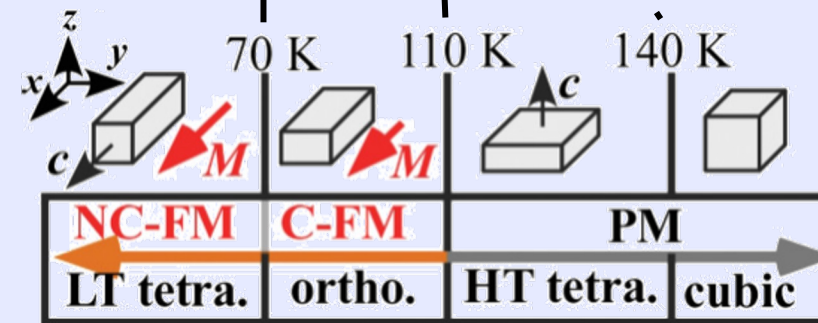
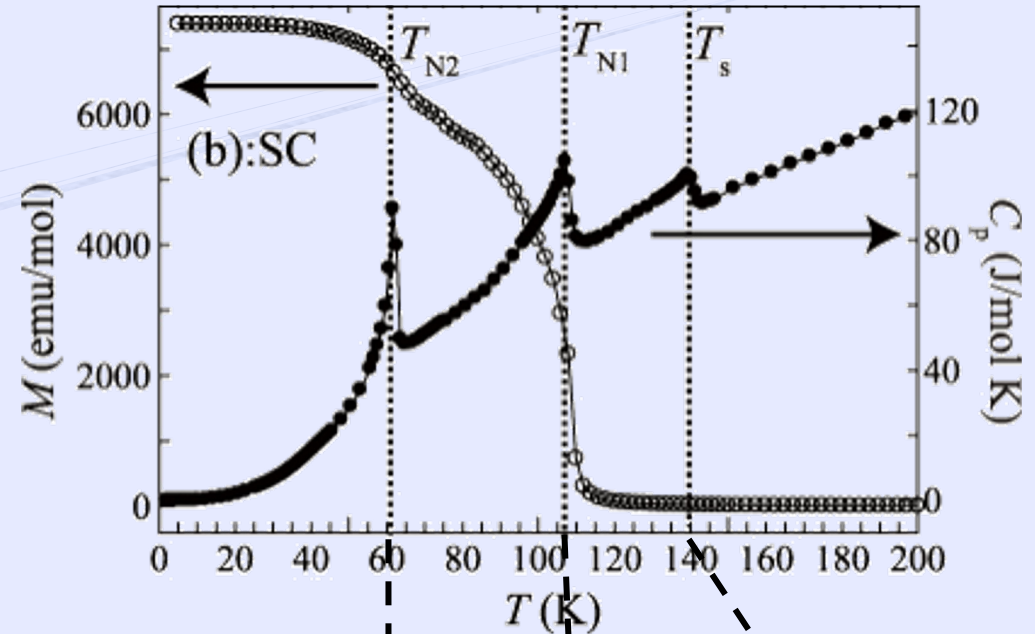


2 sites have degree of orbital

FeO_4
tetrahedron



S. Kawaguchi, *et al.*; J. Phys.: Condens. Matter **25** (2013) 416005

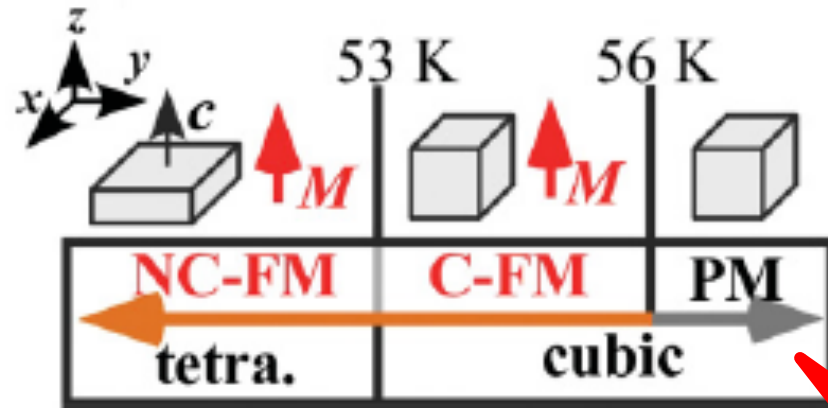


Y. Nii *et al.*; Phys. Rev. B **86** (2012) 125142.

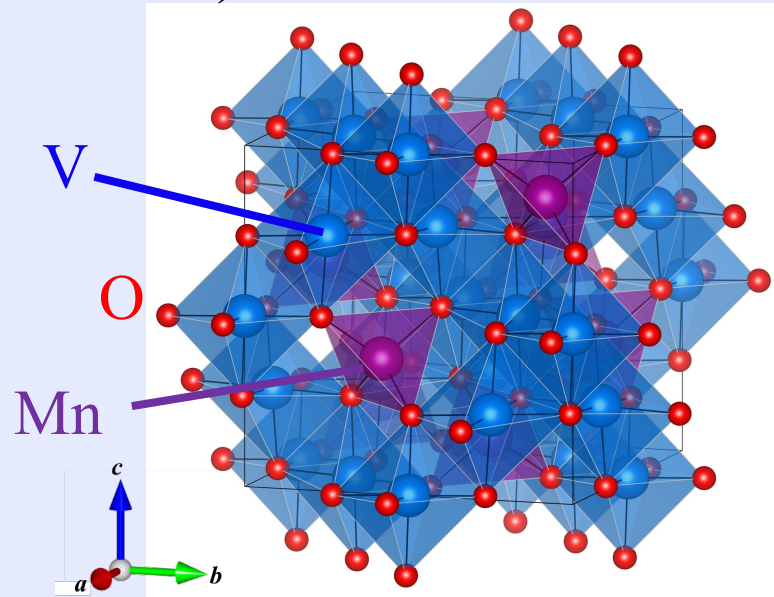
多段階構造相転移による双晶形成

Spinel-type vanadium oxide MnV_2O_4

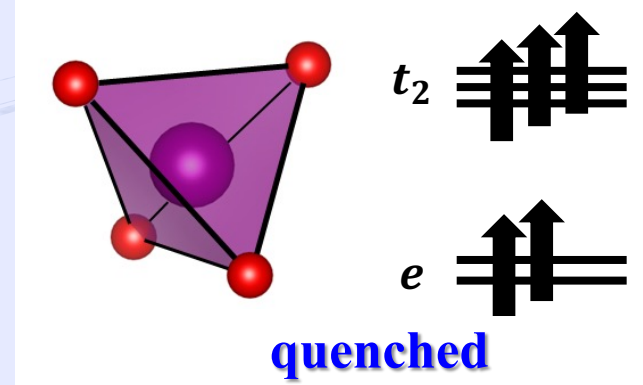
Y. Nii *et al.* *Phys. Rev. B* **86**.125142 (2012)



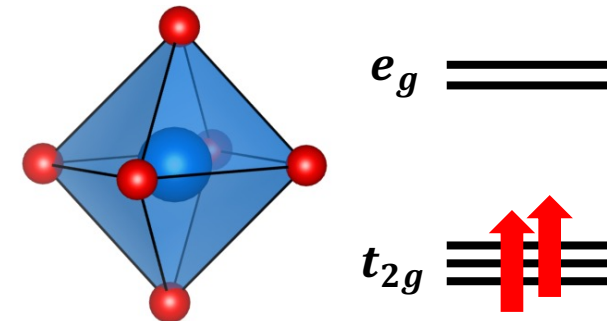
(Mott insulator)



MnO_4 tetrahedron $\text{Mn}^{2+}(3d^5: S = 5/2)$



VO_6 octahedron $\text{V}^{3+}(3d^2: S = 1)$

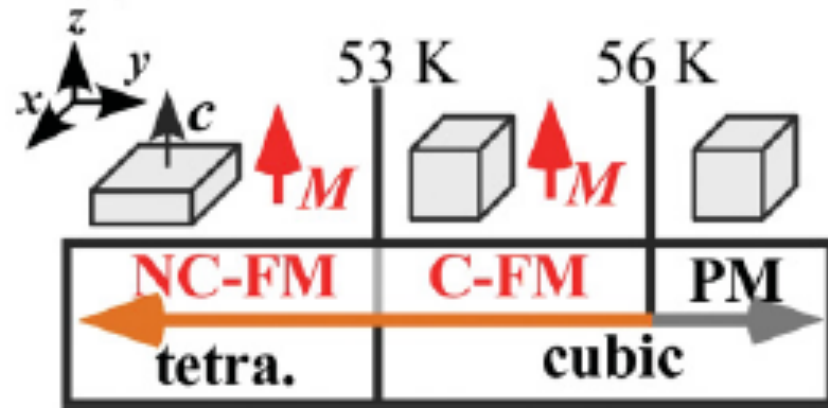


Driving force of phase transition

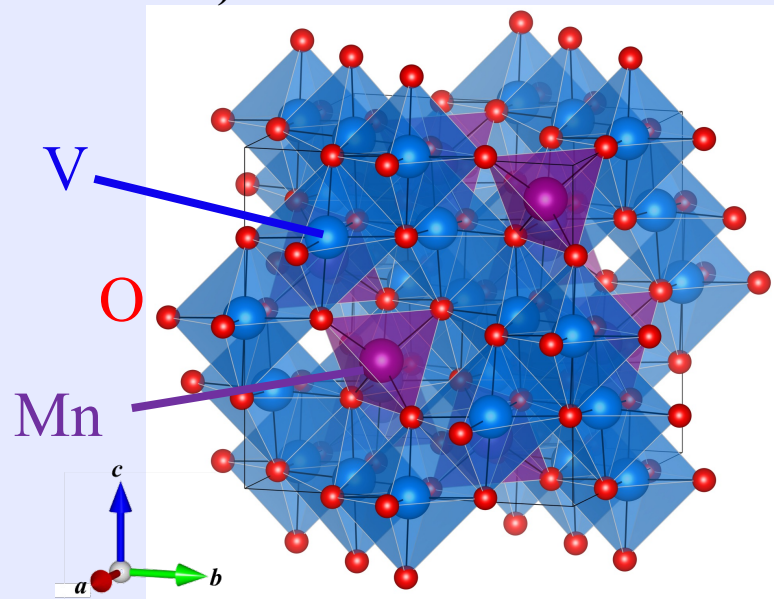
Orbital degrees of freedom

Spinel-type vanadium oxide MnV_2O_4

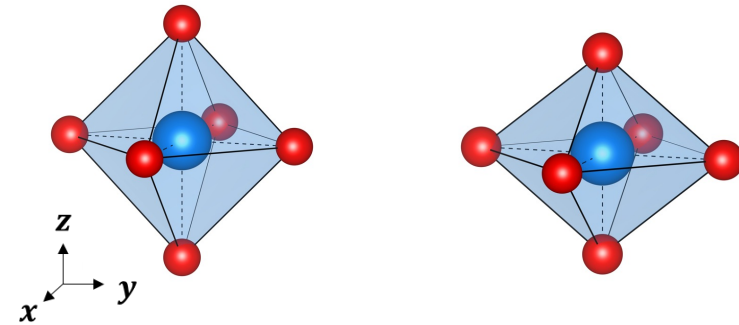
Y. Nii *et al.* *Phys. Rev. B* **86**.125142 (2012)



(Mott insulator)



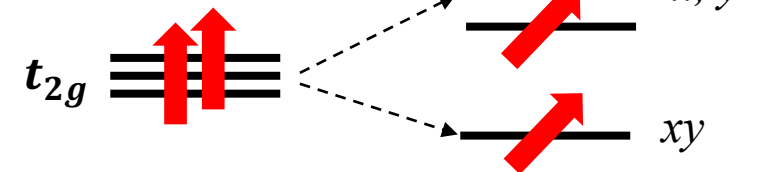
Compressed along c -axis direction



Cubic phase

Tetragonal phase

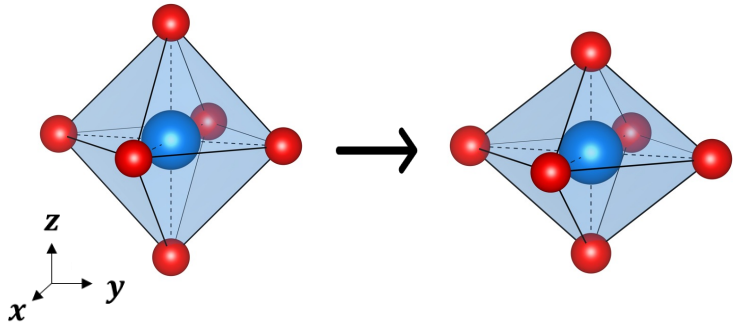
e_g =



Ground state of spinel-type oxide AV_2O_4

✓ VO_6 octahedron

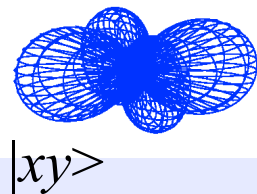
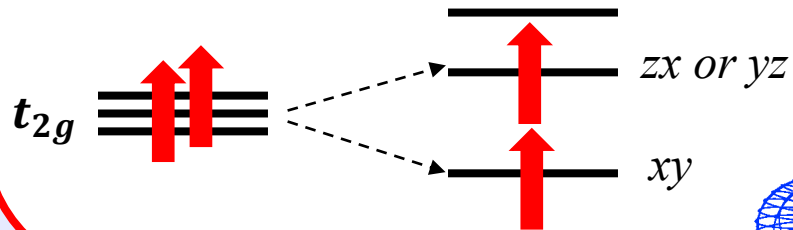
Compressed along c -axis direction



Cubic phase

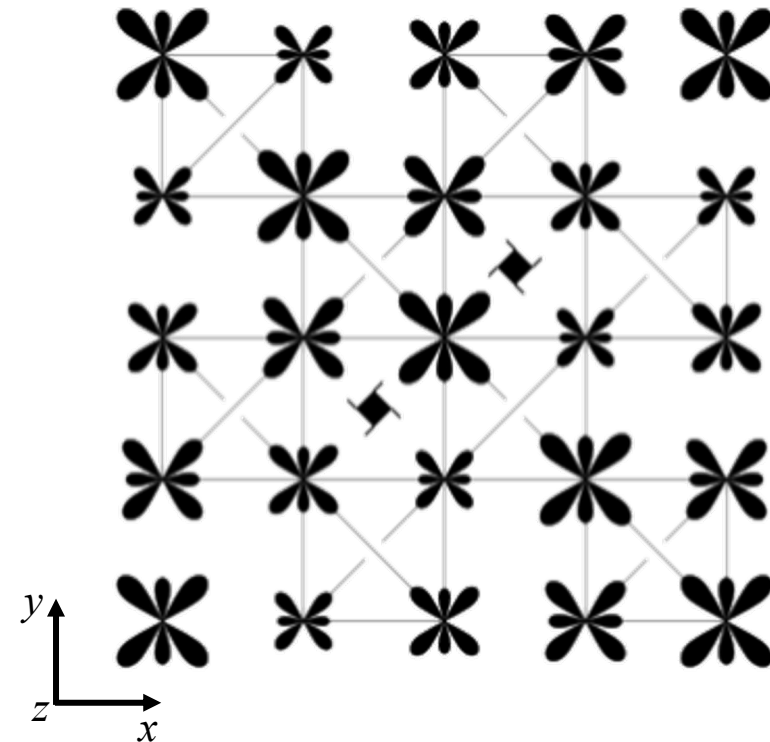
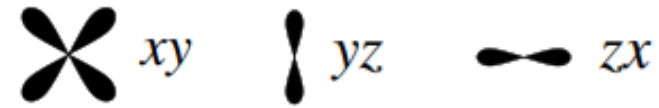
Tetragonal phase

e_g



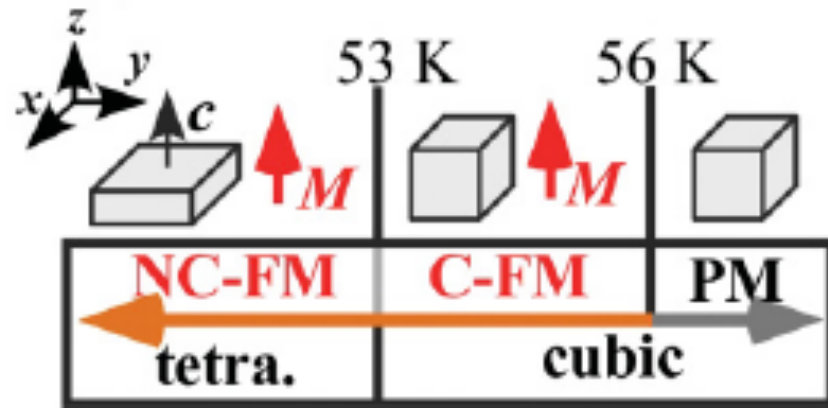
Magnetic transition and orbital degrees of freedom in vanadium spinels

H. Tsunetsugu and Y. Motome, *Phys Rev B* **68**.060405(2003).

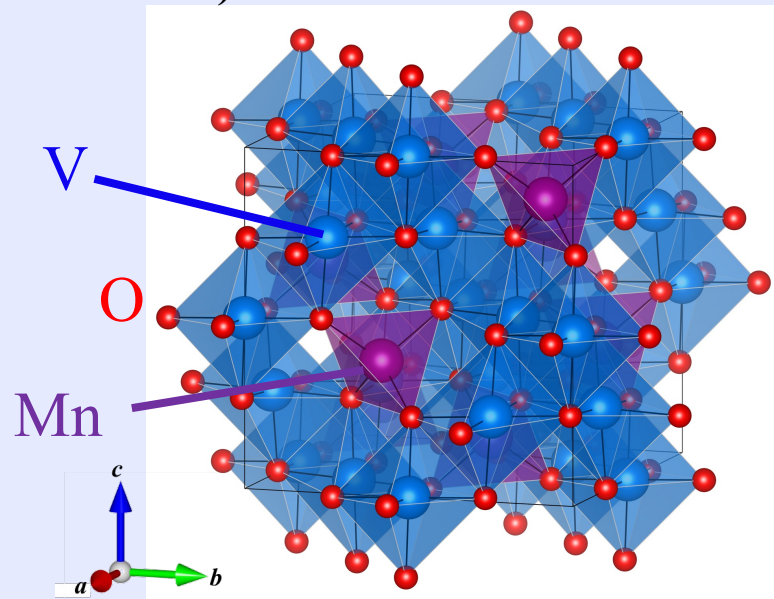


Spinel-type vanadium oxide MnV_2O_4

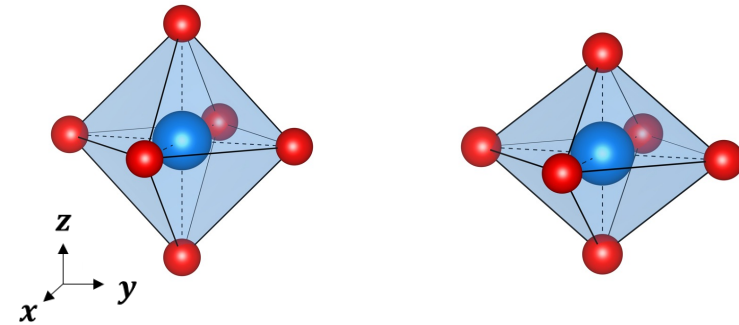
Y. Nii *et al.* *Phys. Rev. B* **86**.125142 (2012)



(Mott insulator)



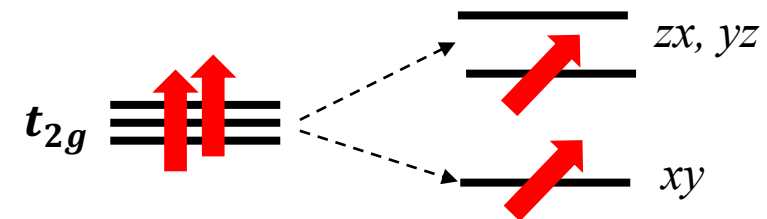
Compressed along c -axis direction



Cubic phase

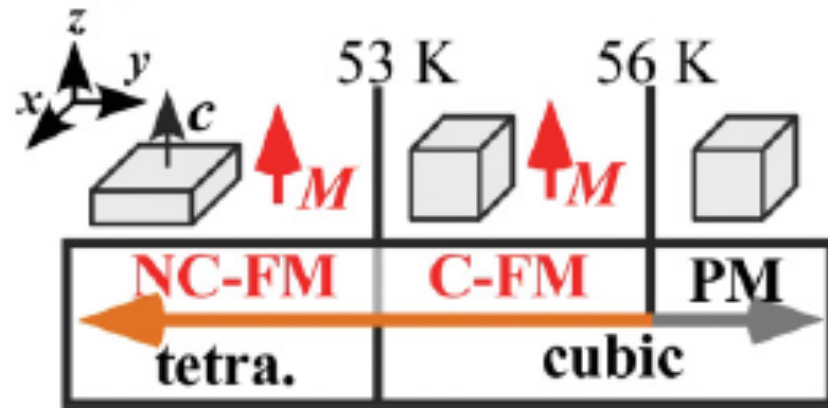
Tetragonal phase

e_g =

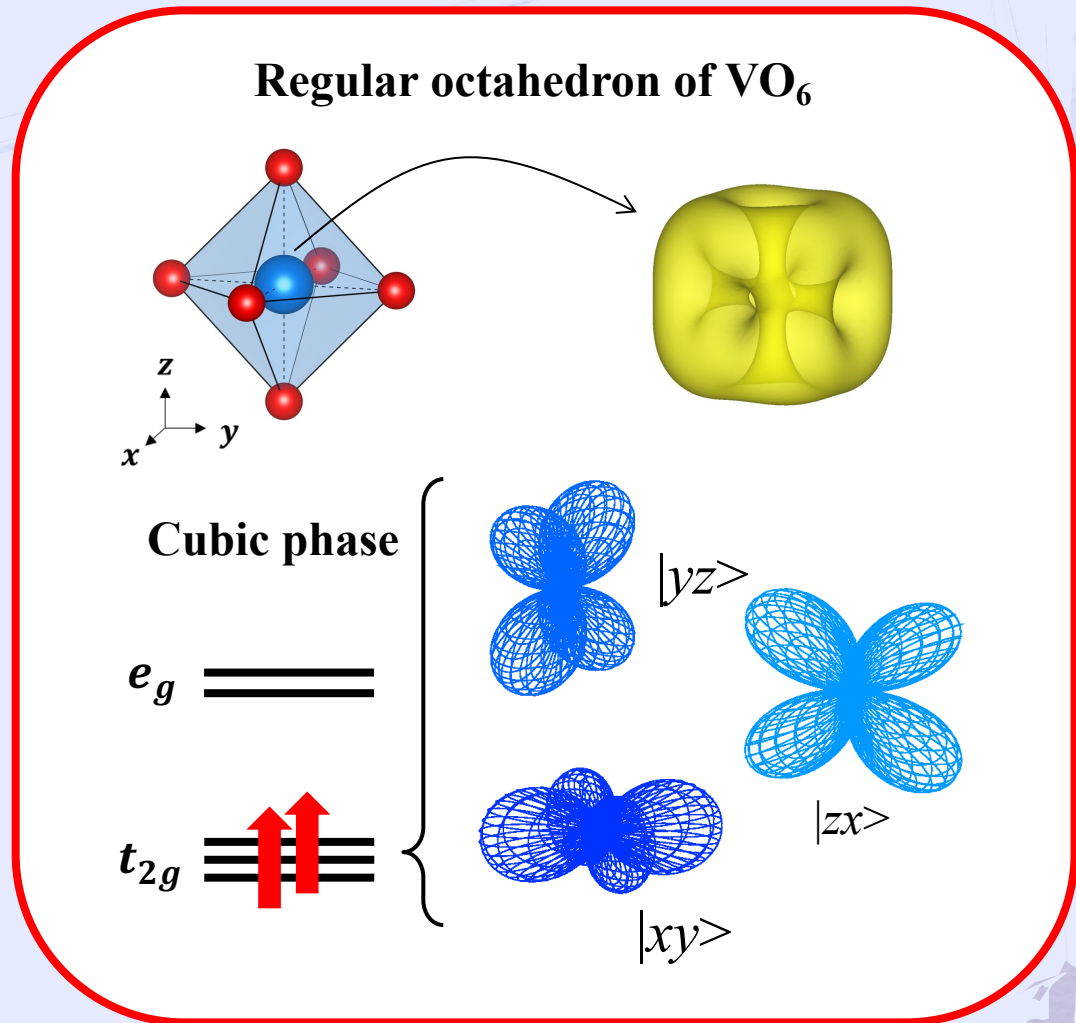
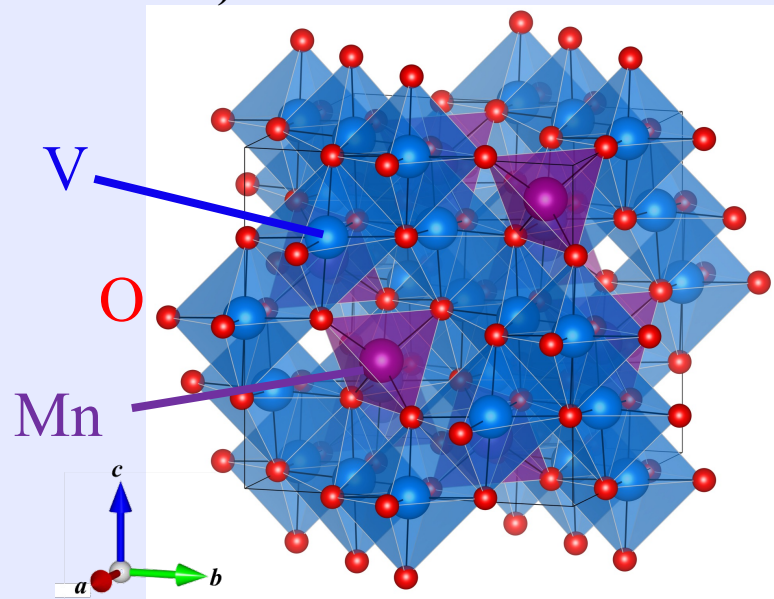


Spinel-type vanadium oxide MnV_2O_4

Y. Nii *et al.* *Phys. Rev. B* **86**.125142 (2012)

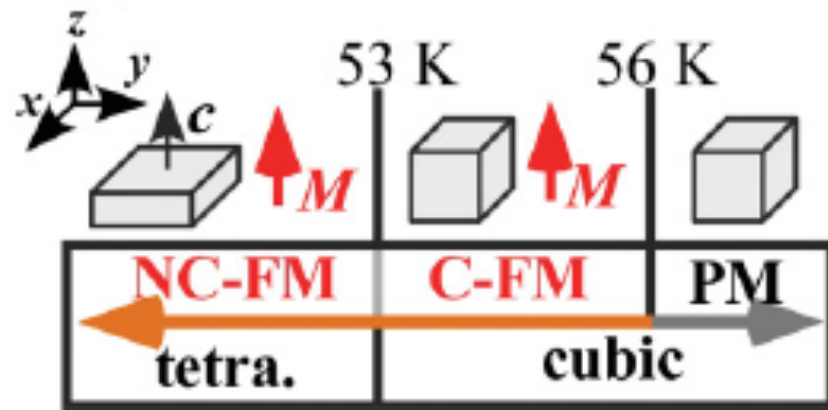


(Mott insulator)

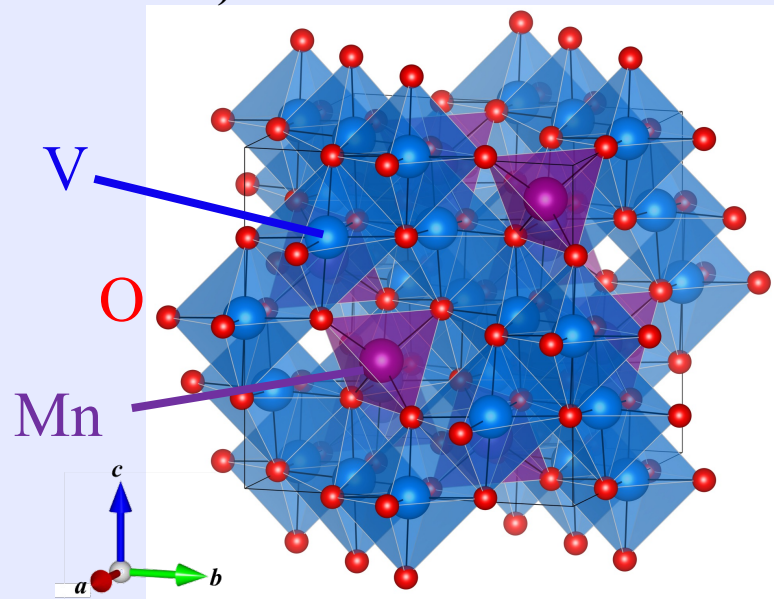


Spinel-type vanadium oxide MnV_2O_4

Y. Nii *et al.* *Phys. Rev. B* **86**.125142 (2012)



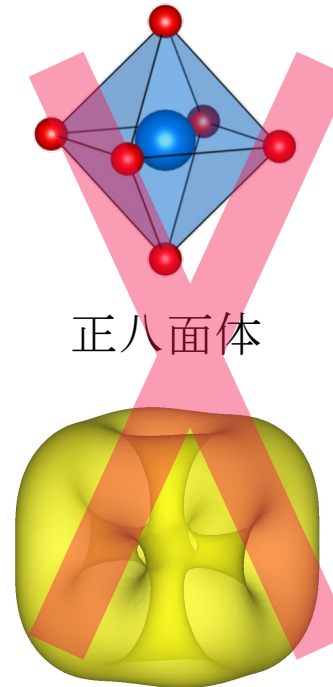
(Mott insulator)



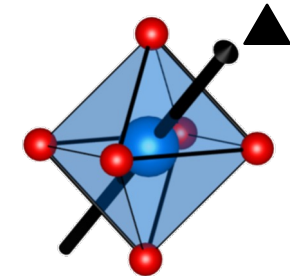
FeV_2O_4 立方晶相 $Fd\bar{3}m$

$\text{V}^{3+} : 3 d^2$ の価電子密度

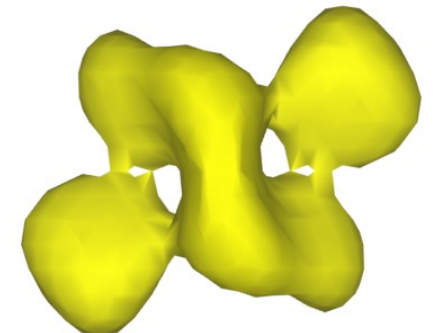
観測価電子密度



正八面体

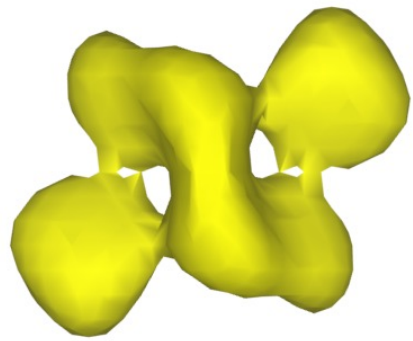
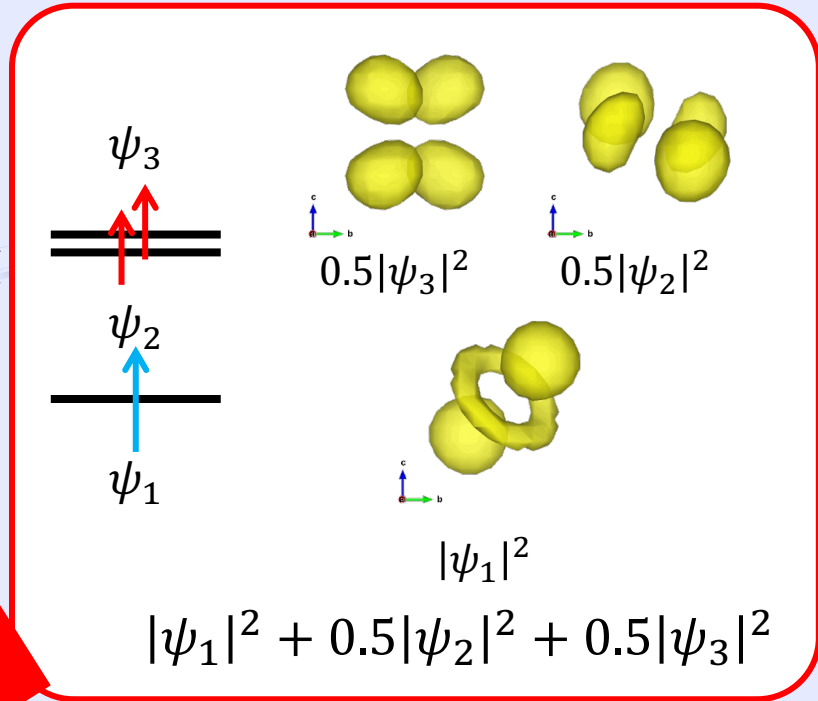
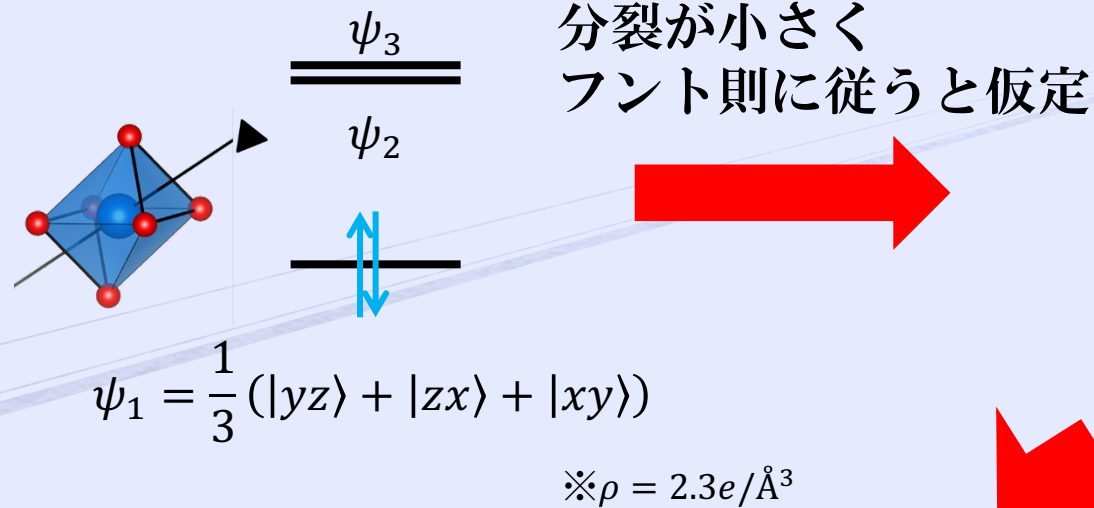


D_{3d} 歪み $\sim 0.3\text{\AA}$

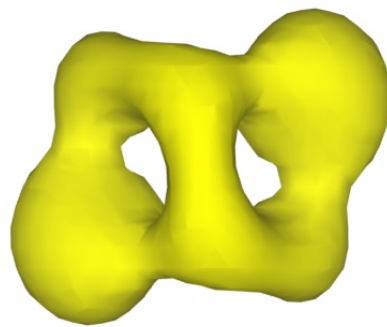


T. Manjo *et al.*, *Materials Advances*, 3, 3192-3198 (2022).

Valence electron density of V^{3+} in cubic phase



観測価電子密度



計算価電子密度

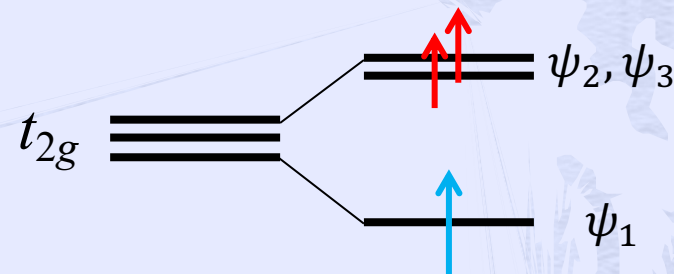
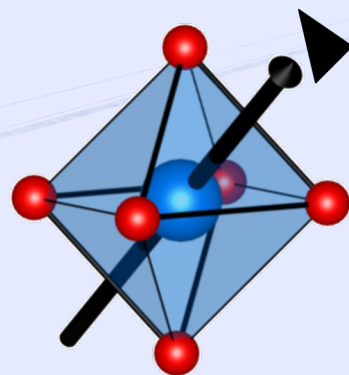
縮退軌道の電子は各軌道に
等確率で占有！

T. Manjo, S. Kitou, N. Katayama, S. Nakamura,
T. Katsufuji, Y. Nii, T. Arima, J. Nasu, T. Hasegawa,
K. Sugimoto, D. Ishikawa, A. Q. R. Baron, and H. Sawa,
Materials Advances (2022), 3, 3192-3198 (2022).

“縮退軌道”ということ

$$\psi_1 = \frac{1}{\sqrt{3}}(|yz\rangle + |zx\rangle + |xy\rangle) \leftarrow 3\text{回回転軸が主軸}$$

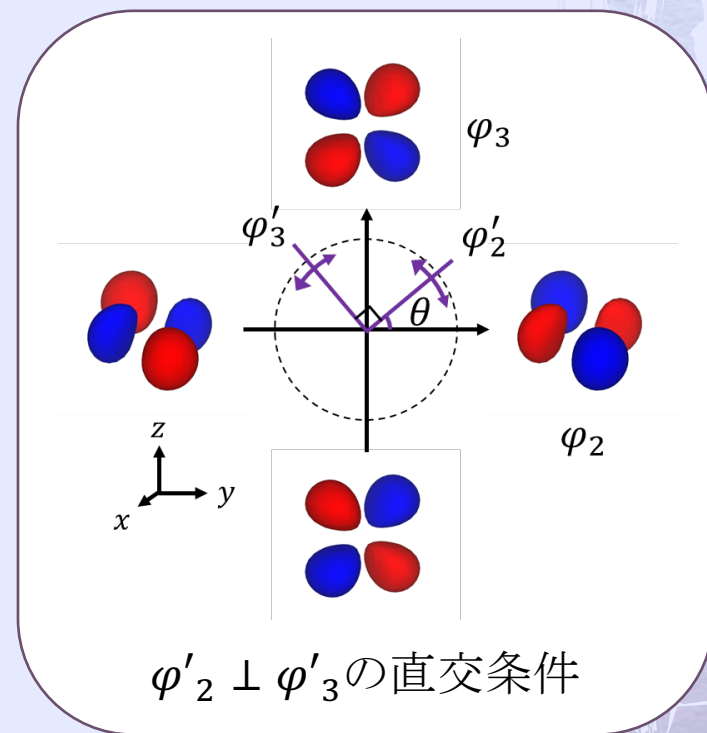
$$\psi_1 \text{ との規格・直交条件} \quad \begin{cases} \psi_2 = \frac{1}{\sqrt{6}}(|yz\rangle + |zx\rangle - 2|xy\rangle) \\ \psi_3 = \frac{1}{\sqrt{2}}(|yz\rangle - |zx\rangle) \end{cases}$$



$$\begin{aligned} &\psi_2, \psi_3 \text{ の選び方はuniqueではない} \\ &\psi_2 \perp \psi_3 \text{ の直交条件あり} \end{aligned} \quad \begin{cases} \varphi'_2 = \psi_2 \cos \theta + \psi_3 \sin \theta \\ \varphi'_3 = -\psi_2 \sin \theta + \psi_3 \cos \theta \end{cases}$$

位相項 $\theta \rightarrow \theta(\mathbf{r}, t)$ 回折実験は結晶全体の平均

$$\rho_v(\mathbf{r}) = \frac{1}{N} \sum_j^{crystal} (|\psi_{1,j}|^2 + |\psi_2 \cos \theta_j(t) + \psi_3 \sin \theta_j(t)|^2)$$

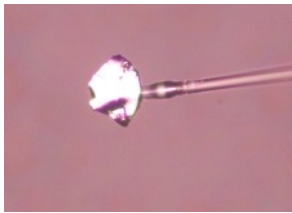
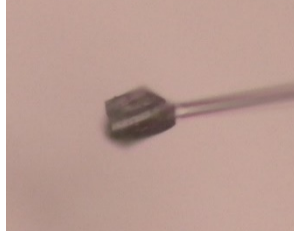
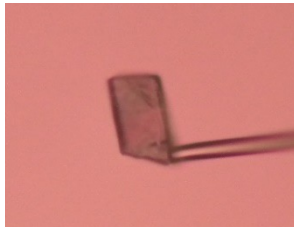


時間・空間平均の積分表現:
$$\frac{1}{2\pi} \int_0^{2\pi} (|\psi_1|^2 + |\psi_2 \cos \theta + \psi_3 \sin \theta|^2) d\theta = |\psi_1|^2 + \frac{1}{2} |\psi_2|^2 + \frac{1}{2} |\psi_3|^2$$

価電子密度解析のための条件

- ◆ 高品質な単結晶試料、適切なサイズへの結晶加工
- ◆ 安定した高品質・高エネルギーのX線
等間隔モード、トップアップ運転
十分な統計精度、理想的には $d > 0.25\text{\AA}$ の分解能
- ◆ 広い逆格子空間の測定 (completeness $\sim 100\%$)

X-ray energy: $\sim 40\text{ keV}$
Detector: PILATUS3 X CdTe
Temperature: $\sim 30\text{K}$

	FeV_2O_4	Glycine	Cytidine
Crystal shape			
Size[μm^3]	$40 \times 30 \times 10$	$90 \times 60 \times 30$	$100 \times 60 \times 60$

Core Differential Fourier Synthesis method

Single crystal XRD

$$\rho_v(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{K}} \left[\left(|F_{\text{obs.}}(\mathbf{K})|P - \left| \sum_j f_j^{\text{core}} T_j e^{-i\mathbf{K} \cdot \mathbf{r}_j} \right| P_{\text{core}} \right) e^{i\mathbf{K} \cdot \mathbf{r}} \right] + \frac{N_v}{V}$$

P : phase term

f : atomic form factor

T : atomic displacement prm.

N_v : numbers of valence e

V : cell volume

$$\text{Valence ED(experimental)} = \text{Total ED(experimental)} - \text{Core ED(model)}$$

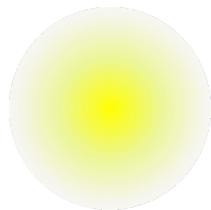
S. Kitou *et al.*, *Phys. Rev. Research* **2**. 033503 (2020).

Valence ED (e.g. $2p_x$)



=

Total ED



-

Core ED

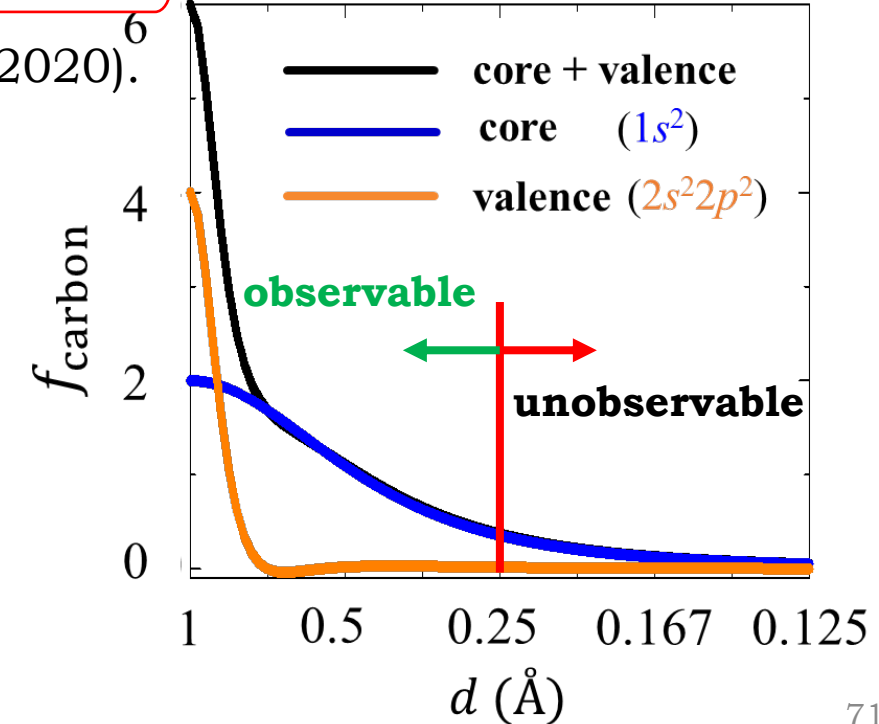


$2s^2 2p^2?$

C: $1s^2 2s^2 2p^2$

[He]($1s^2$)

~ Atomic form factor of C ~



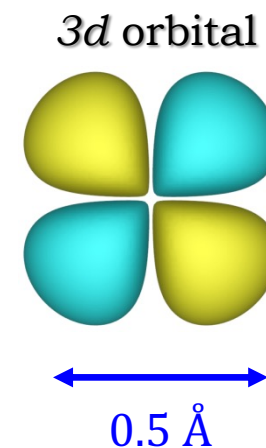
電子軌道を見るためには？

結晶構造因子と電子密度の
フーリエ変換の関係

unit cell 内電子密度

$$I_o(\mathbf{K}) \propto |F_o(\mathbf{K})|^2 \longleftrightarrow \rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{K}}^{\infty} F_o(\mathbf{K}) e^{i(\mathbf{K} \cdot \mathbf{r})}$$

$$K = |\mathbf{K}| = 2k \sin \theta = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d}$$

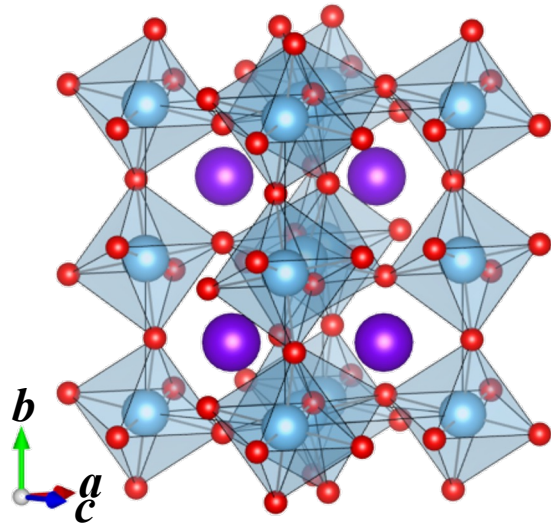


CDFS解析はフーリエ逆変換の打ち切りの影響を最小限に
抑えることはできるが、電子軌道を再現可能なQ分解能が必要！
加えて、high-Qの反射強度を観測可能なことが必要！

価電子密度解析に必要な実験条件

① $>10^6$ のダイナミックレンジ

組成: YTiO_3 : 全電子数: $39+22+8\times 3=85$



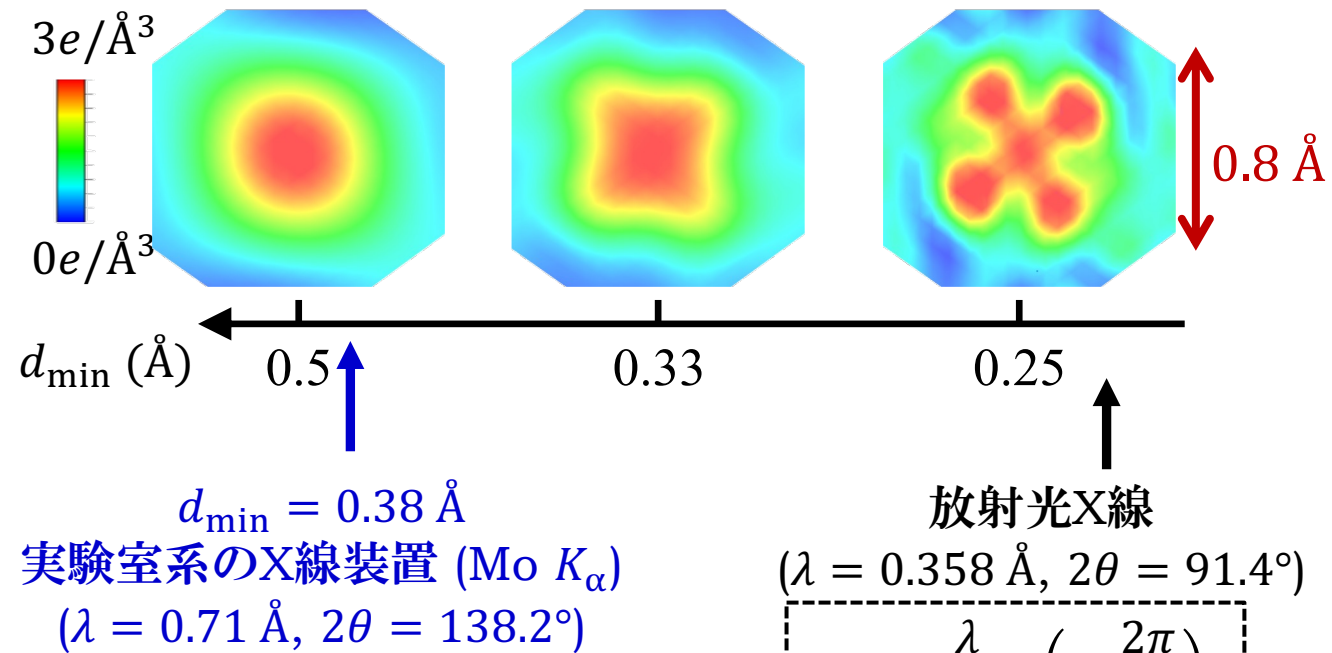
$$I(\mathbf{K}) \propto (\text{全電子数})^2$$

: $3d$ 電子1つを観測するためには

$$\frac{1^2}{85^2} = \frac{1}{7225} \sim 10^{-4}$$

少なくとも 10^6 以上の強度のダイナミックレンジが必要

② 短波長X線による高分解能データ



$$d = \frac{\lambda}{2 \sin \theta} \left(= \frac{2\pi}{|\mathbf{K}|} \right)$$

Phys. Rev. Research **2** (2020) 033503

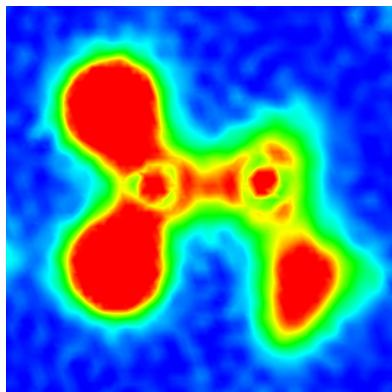
分解能と測定温度の影響

① 測定範囲による分解能の差

[Glycine]

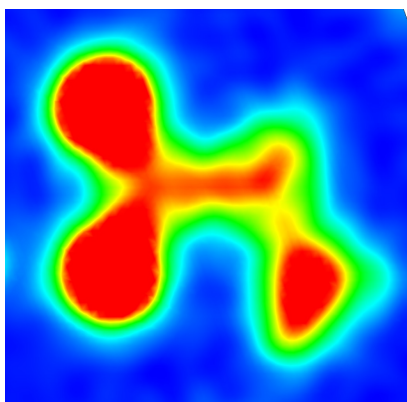
High
Resolution

$d > 0.30\text{\AA}$



Low
Resolution

$d > 0.50\text{\AA}$

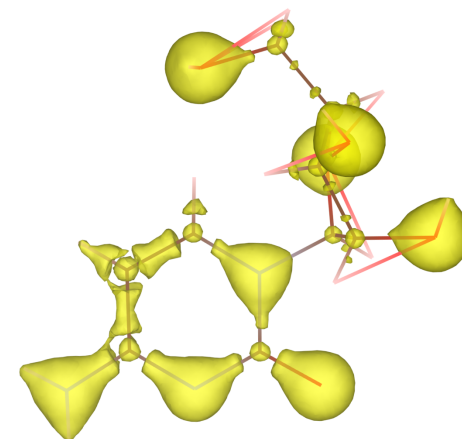


② 測定温度に対する差

[Cytidine]

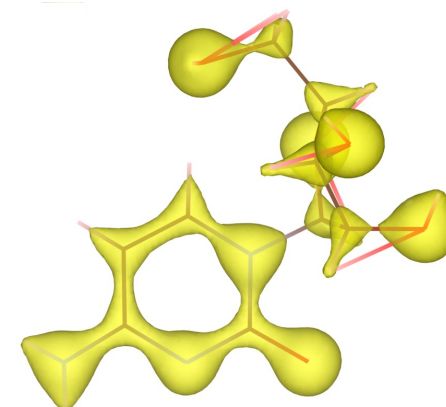
Low
Temperature

30K



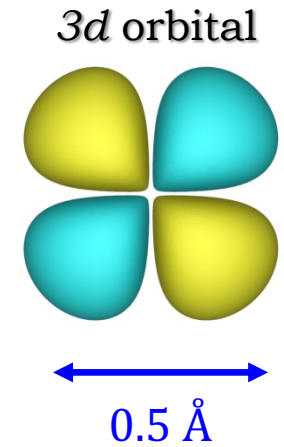
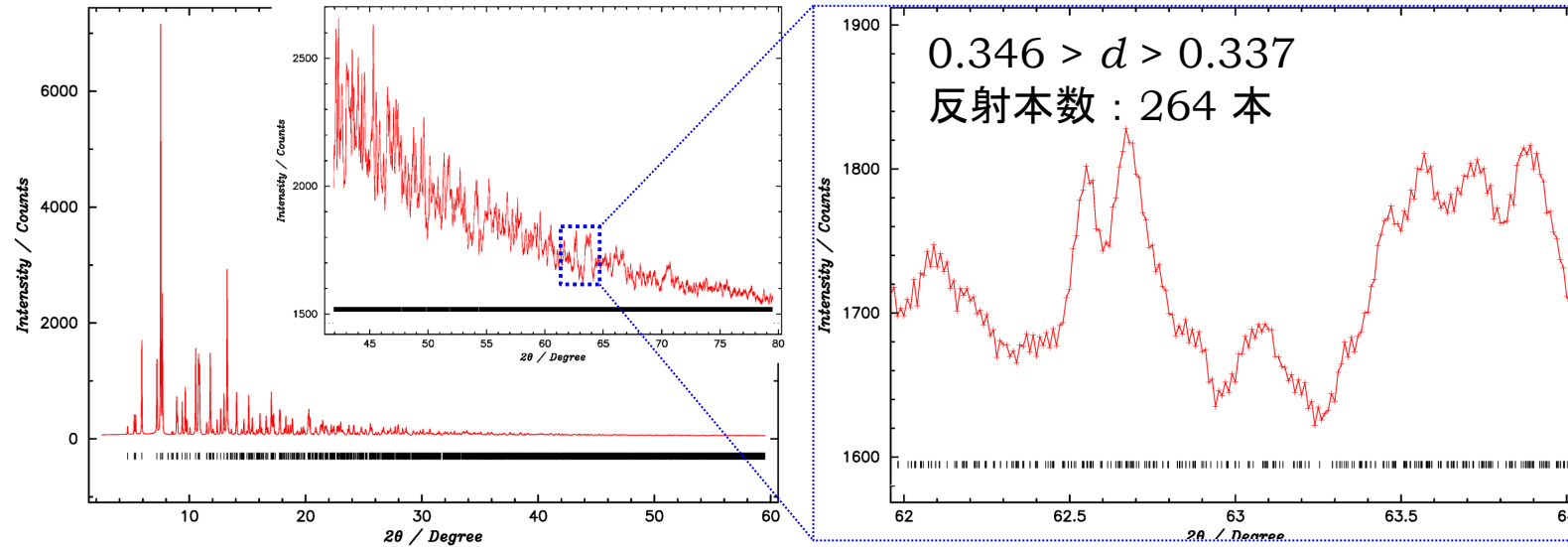
High
Temperature

100K

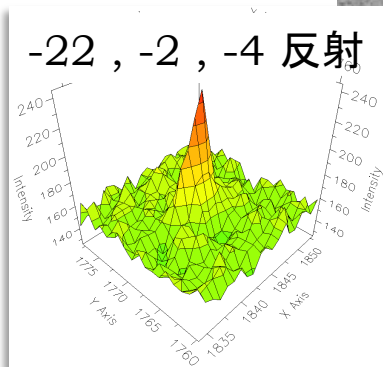


 : $1.7 e/\text{\AA}^3$

価電子密度解析は粉末回折でも可能か？ ; YTiO_3

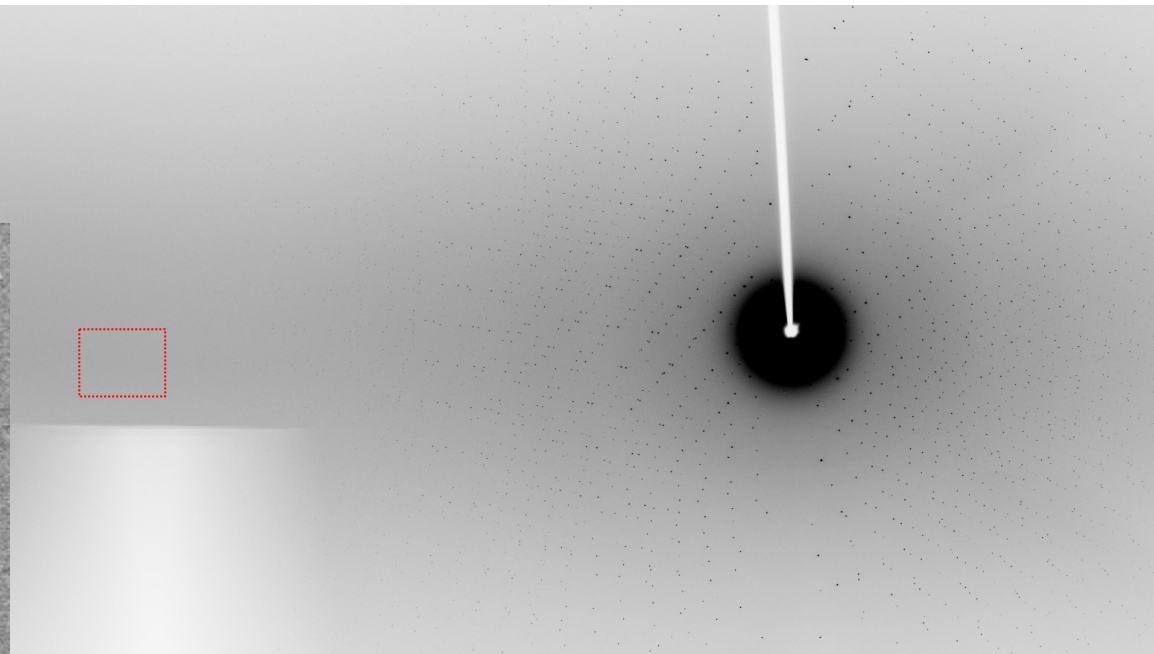


試料サイズ: $20 \times 20 \times 10 \text{ }\mu\text{m}^3$
測定波長: 35 keV
測定温度: 100 K



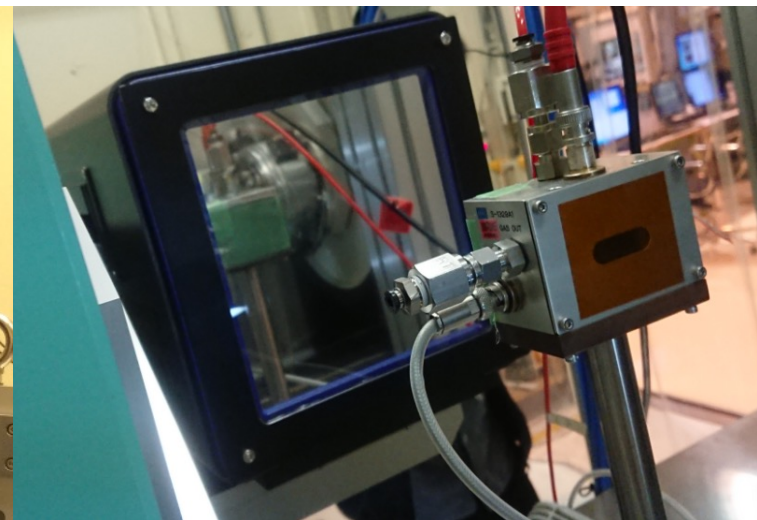
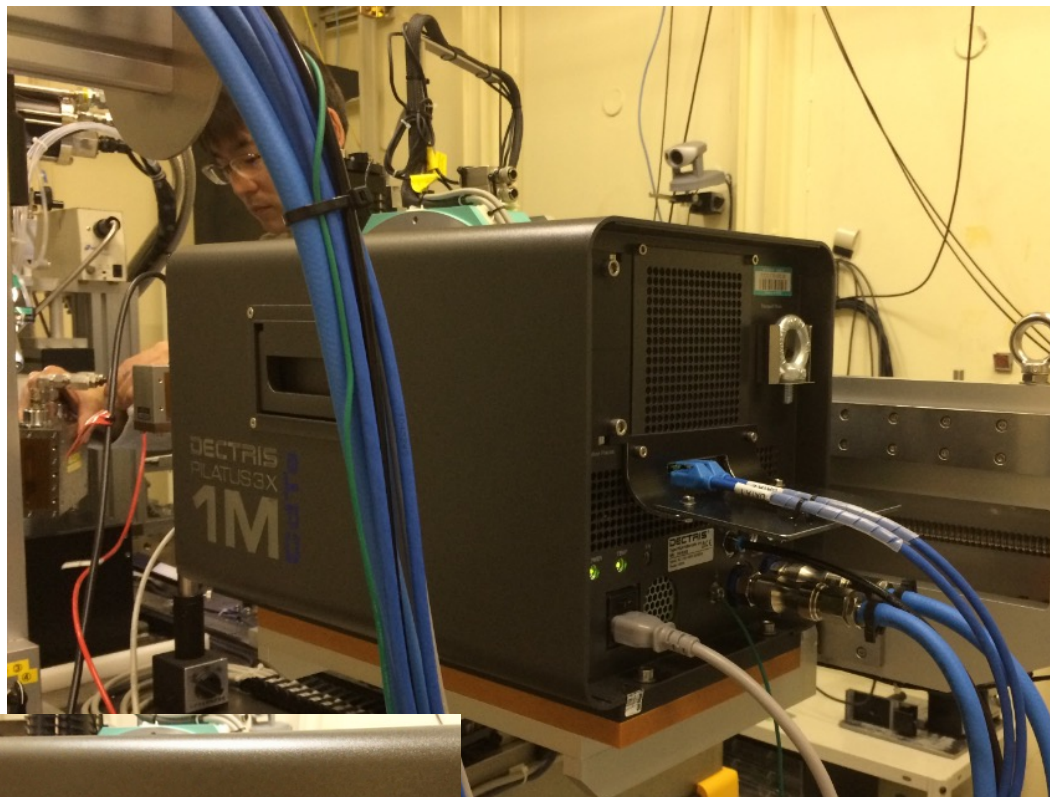
241 Count

$d = 0.25 \text{ \AA}$



PILATUS3 X CdTe 検出器

2018年春 導入



(1042, 980) pixel



カメラ長 L : 130~397.13 mm

2θ : -30° ~ 0°

測定可能な d 値:

$d > 0.32 \text{ \AA}$ ($E = 35 \text{ keV}$, $L = 130 \text{ mm}$, $2\theta = -30^{\circ}$)

PILATUS導入で生じた驚愕の変化

(例) 分子性結晶 (TMTTF)₂PF₆ の場合

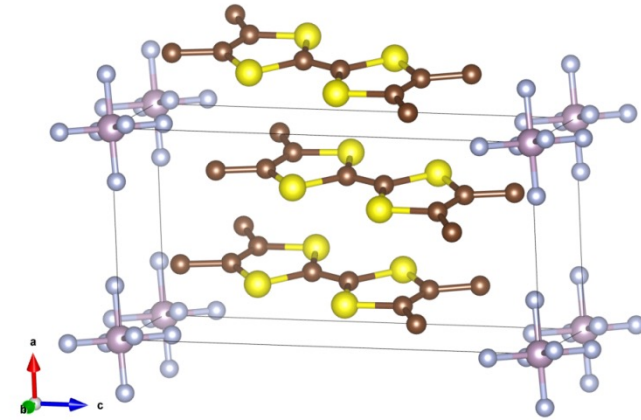
空間群: $P\bar{1}$

格子定数: $a = 6.97 \text{ \AA}$, $b = 7.53 \text{ \AA}$, $c = 13.13 \text{ \AA}$,
 $\alpha = 83.48^\circ$, $\beta = 86.93^\circ$, $\gamma = 71.00^\circ$

実空間分解能: $d > 0.4 \text{ \AA}$

測定した逆格子空間領域の割合: $\sim 100\%$

等価反射の測定回数: ~ 14 回



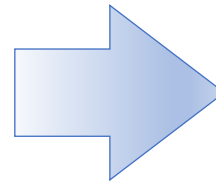
(1フレーム当たり)

露光時間: 10 min ($\Delta\omega = 10^\circ$)

IP読み取り時間: 6 min

フレーム数: 9枚 $\times$ 10セット = 90 枚

合計: 約 90 hour



(1フレーム当たり)

露光時間: 9 sec ($\Delta\omega = 3^\circ$)

IP読み取り時間: 0.95 msec

フレーム数: 60枚 $\times$ 20セット = 1200 枚

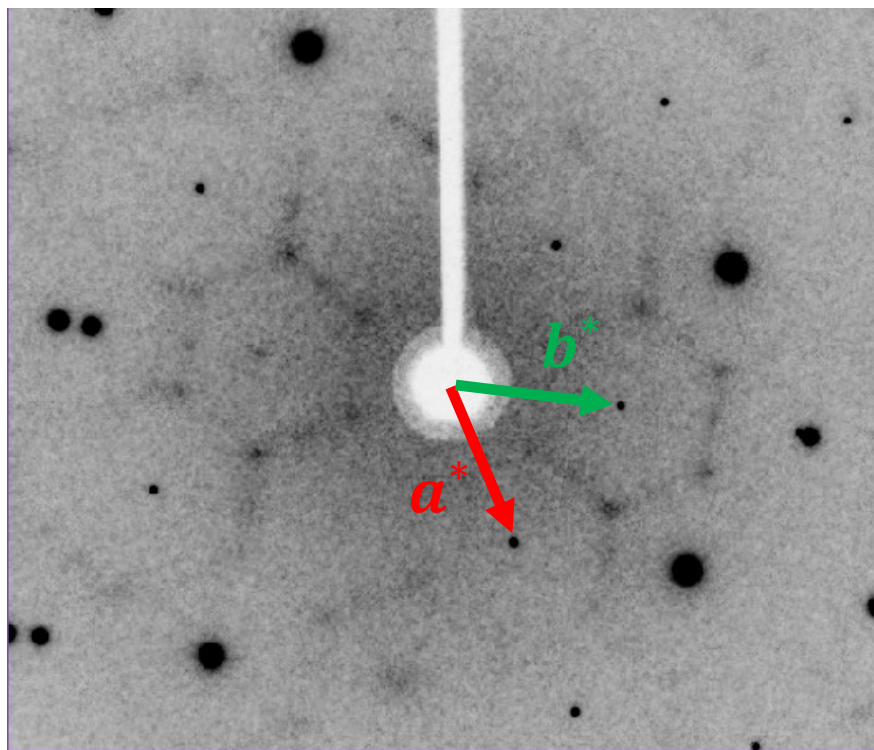
合計: 約 3 hour

“1/30” の時間でIPと同程度の測定が可能！
→ 30倍の成果があがる！？

PILATUS導入で生じた驚愕の変化 その2

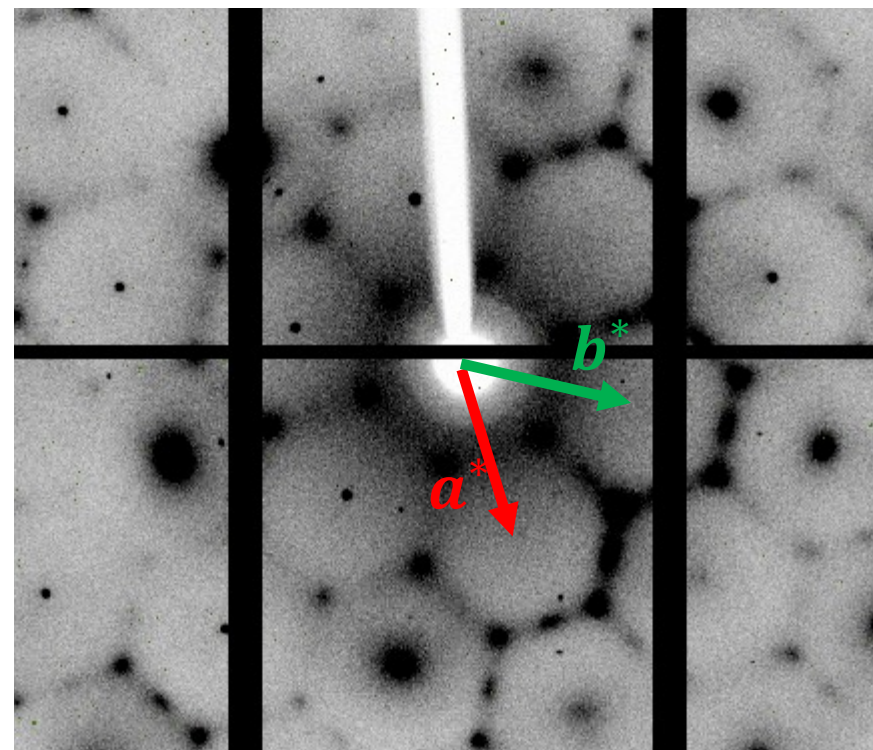
同一試料での比較

CCD



Cu_xTiSe_2 のCuイオン液体状態？

PILATUS



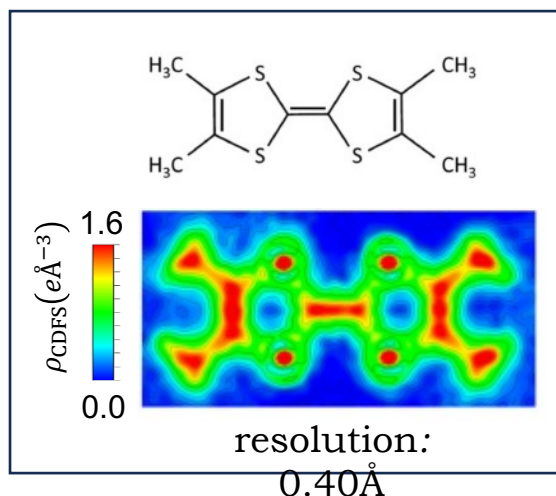
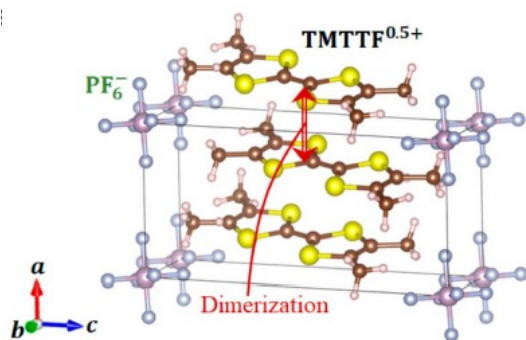
streak状の散漫散乱が
より明確に観測可能！

Physical Review B **101**, 094108 (2020)

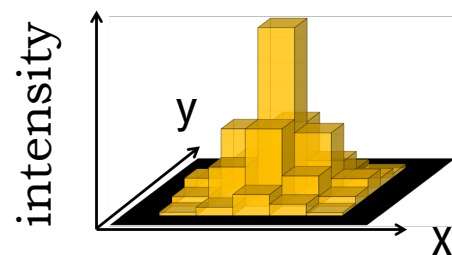
Seeking higher resolution and precision

✓ Direct observation of charge ordered state in $(\text{TMTTF})_2\text{PF}_6$

S. Kitou *et al.*, *PRL*. **119**, 065701 (2017).



Imaging Plate detector

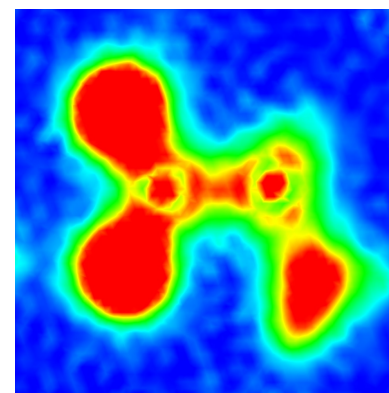


Box summation

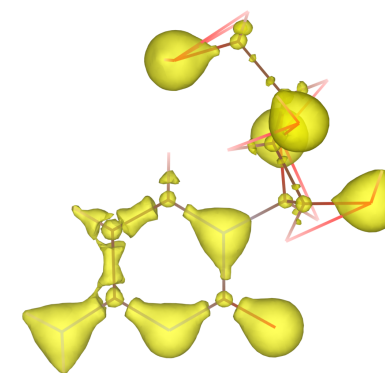
✓ Unveiling the Nature of Chemical Bonds in Real-Space

T. Hara *et al.*, *JACS*.
10.1021/jacs.4c05673.

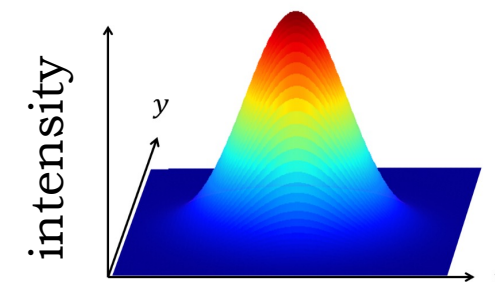
Glycin



Cytidine



Photon counting detector



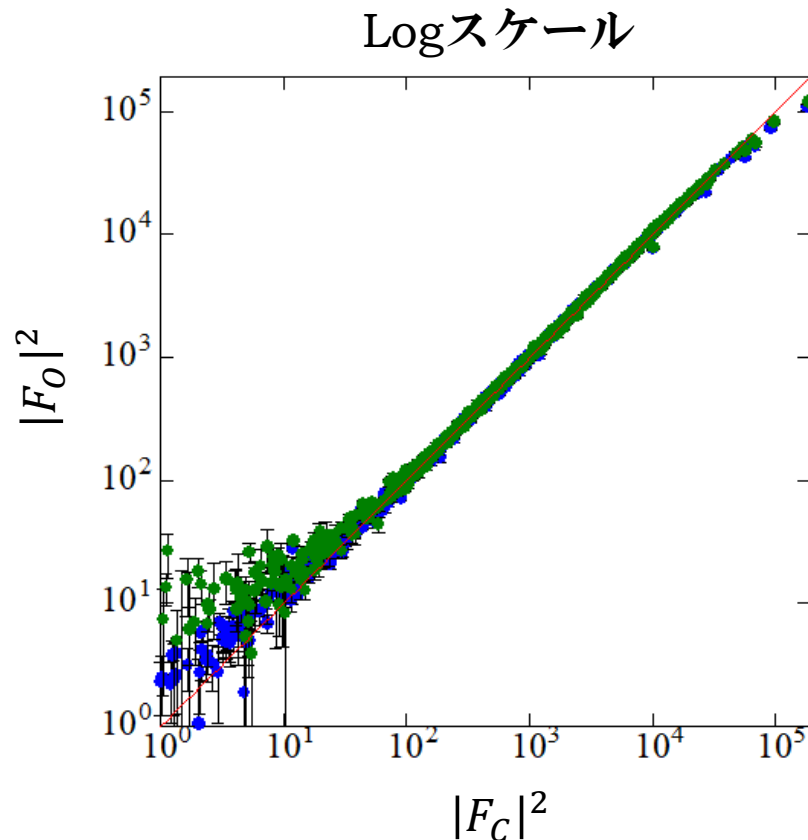
Profile fitting

Profile fitting (by CrysAlisPro) v.s. Box summation (Rapid)

● $\Delta\omega = 1^\circ$ / CrysAlisPro ● $\Delta\omega = 1^\circ$ / RAPID

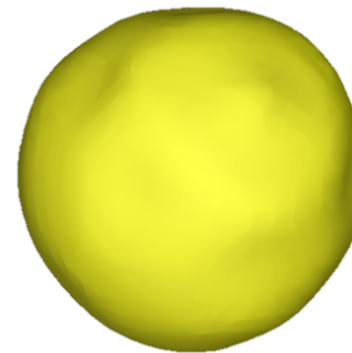
Sample : MnV_2O_4 (0432b-003)

酸素の価電子密度図



$\Delta\omega = 1^\circ$ / CrysAlisPro
 $R = 1.13 \%$

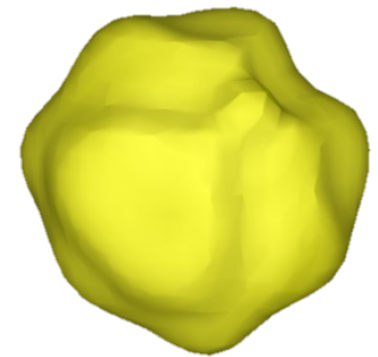
profile fitting



■ $3.0 e/\text{\AA}^3$

$\Delta\omega = 1^\circ$ / RAPID
 $R = 1.61 \%$

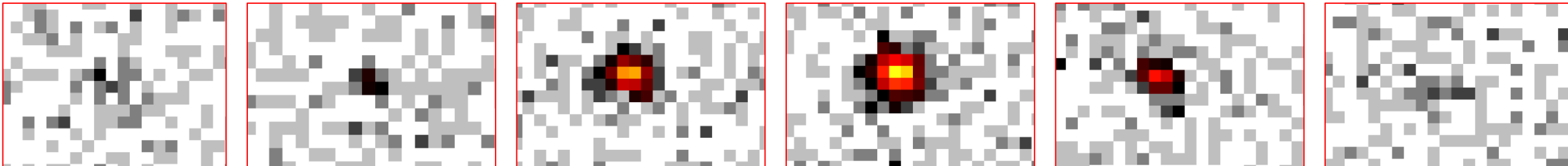
Box summation



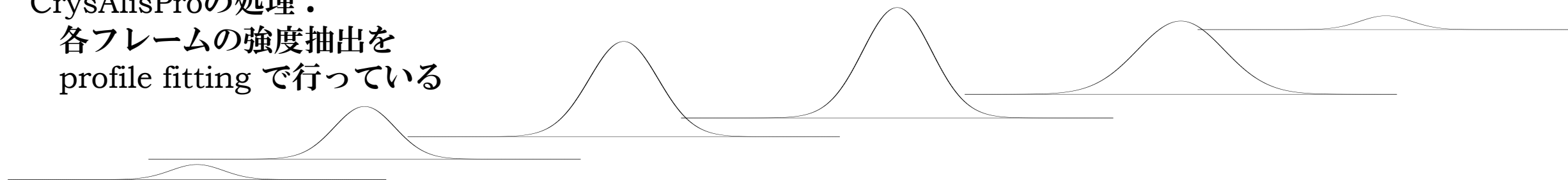
■ $4.5 e/\text{\AA}^3$

CrysAlisProの方が低強度のばらつきが小さい & 酸素の形状が等方的

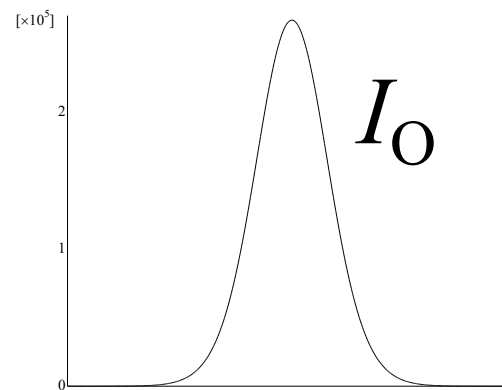
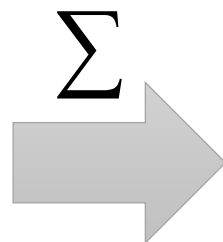
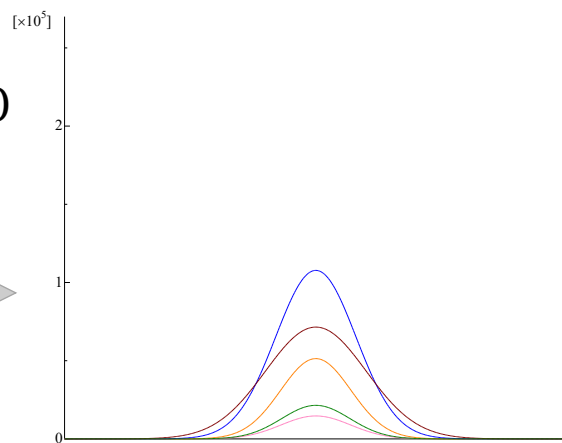
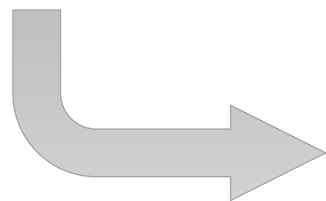
Fine slicing and Profile fitting



CrysAlisProの処理：
各フレームの強度抽出を
profile fitting で行っている



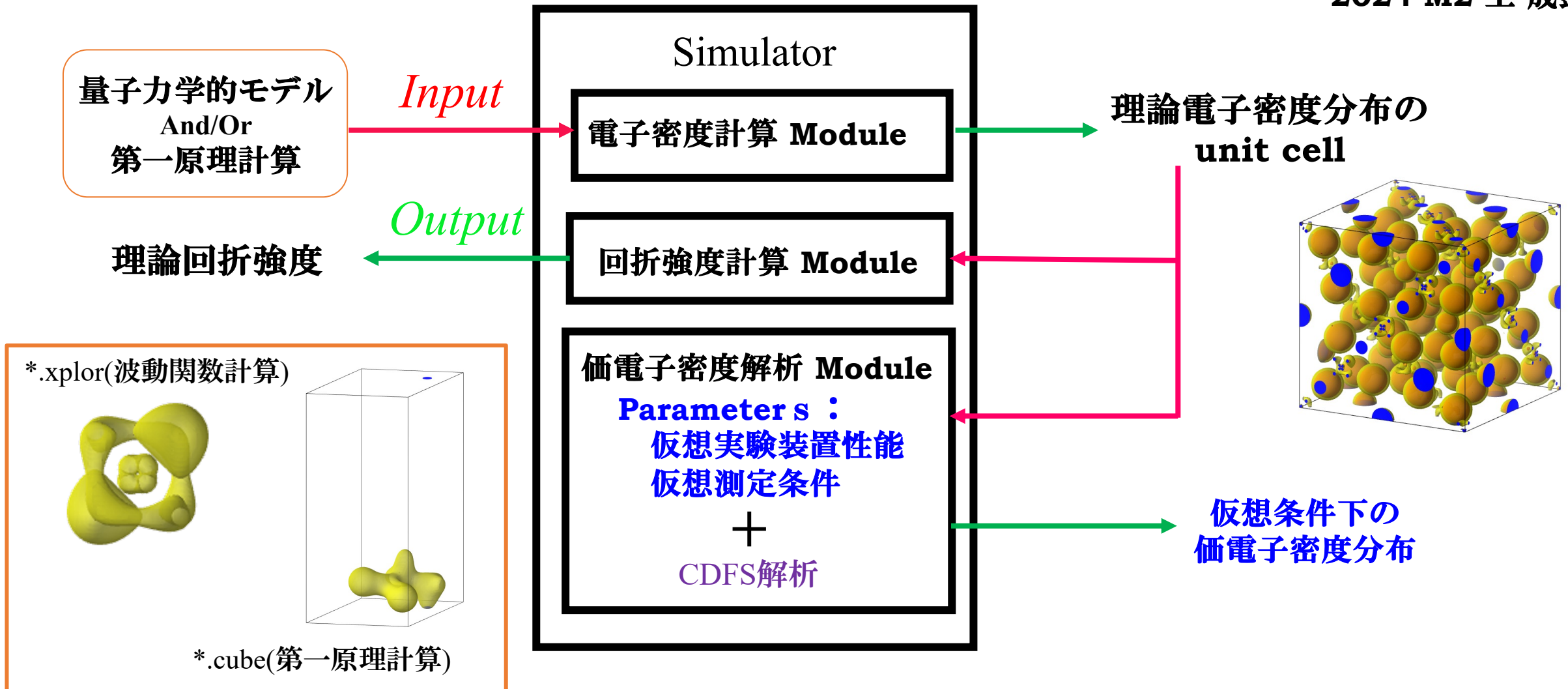
BGが1 cps程度なら
各フレームのBGはほぼ0



強度抽出時にBGの寄与～ゼロ
特に高角の弱い強度の統計精度が上がる

シミュレーターの必要性

2024 M2 王 成凱



現状の問題点と将来像

- ✓ 放射光X線の安定度について(モード毎の検証?)
- ✓ 回折系の精度について
- ✓ 極低温測定と温度制御の安定度
現状はヘリウムガス吹付装置が必須
- ✓ 検出器の選択について PILATUSからその先へ
- ✓ ビームラインをベンディングからIDへ移行?
- ✓ SPring-8の将来計画と精密解析のニーズ

協力：中村唯我氏 /JASRI

放射光精密解析は将来にわたって必要か？

- 価電子密度解析は出発点に立ったところ

- 外場応答による電子状態の変化の観測の必要性
- 超高压下の単結晶回折と価電子密度解析の必要性
- ドメインを含んだ精密解析の必要性

→ 多くの分野での検証が必要性を決める！

皆様の研究が重要！ 奮って手法活用にご参加ください

感謝

- ☆ 青学時代の恩師、研究室の皆さま
- ☆ 物性研時代の加藤研、木下研、武居研の皆さま
- ☆ 千葉大時代の研究室の学生、共闘して頂いた皆さま
- ☆ KEK PF/物構研のスタッフ、院生・PD、歴代秘書の皆さま
- ☆ 名大のスタッフ、学生・院生・PD、歴代秘書の皆さま
- ☆ **そして、信じられないくらい多くの共同研究者の皆様**

皆様の益々のご多幸・ご活躍をお祈り申し上げます



Theoretical result

構造物性研究は理論と実験の架け橋

Experimental results

*Thank you for your kind
attention*