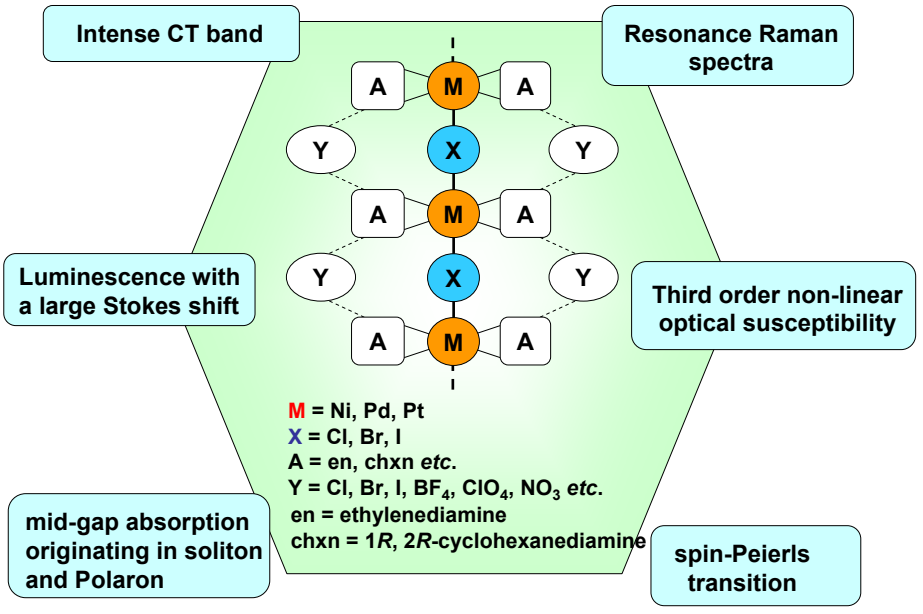
化学的圧力により誘起されるCDW - Mott-Hubbard 相転移

高石慎也[1,2]、高村光仁[1]、山下正廣[1,2]、松崎弘幸[3]、岡本博[3]、
田中久暁[4]、黒田新一[4]、西川浩之[5]、大塩寛紀[5]

[1]東北大院理、[2]CREST、[3]東大新領域、[4]名大院工、[5]筑波大数理

擬一次元ハロゲン架橋錯体 (MX chains)



MX錯体の電子状態

Pt, Pd complexes: 電荷密度波 (CDW)状態

‥ M^{2+} ‥‥X - M^{4+} - X ‥‥ M^{2+} ‥‥ X - M^{4+} - X ‥‥ M^{2+} ‥

$[PdBr(chxn)_2]Br_2$, $[PtBr(en)_2]Br_2$ *etc.*

S* > *U

(*chxn* : 1*R*, 2*R* - cyclohexanediamine)

Ni complexes: Mott-Hubbard (MH) 状態

— M^{3+} —X— M^{3+} —X— M^{3+} —X— M^{3+} —X— M^{3+} —

$[NiBr(chxn)_2]Br_2$, $[NiCl(chxn)_2]Cl_2$ *etc.*

U* > *S

U **: On-site Coulomb 反発**

S **: 電子-格子相互作用**

This Study

More than 300 compounds

- Ni compounds ⇨ MH state (*U* > *S*)
- Pd or Pt compounds ⇨ CDW state (*S* > *U*)

Without exception !

MH-CDW phase transition in Pd compound

Strategy

U: 金属イオン固有のパラメータ

S: 架橋ハロゲン、<u>一次元鎖構造</u>に依存

⇩

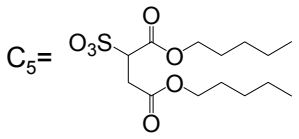
化学的圧力の利用

Chemical Pressure

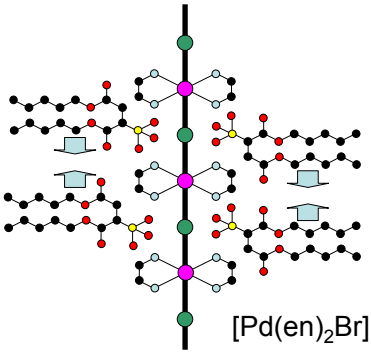
In order to apply chemical pressure ・・・

アルキル鎖間の引力的相互作用 (fastener effect)

Y (Counterions)



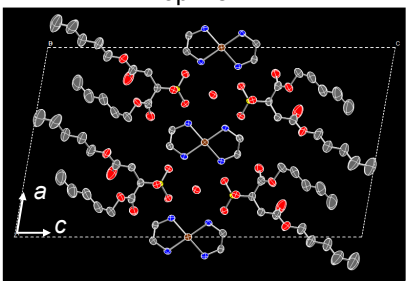
M (Metal) = Pd
X (Halogen)= Br
A (Ligand)= en



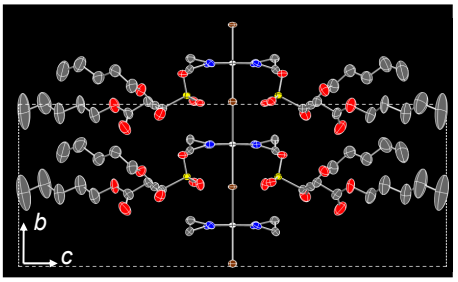
$[Pd(en)_2Br](C_5Y)_2$

Crystal Structure of $[Pd(en)_2Br](C_5Y)_2$ (250 K)

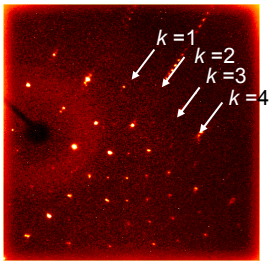
Top view

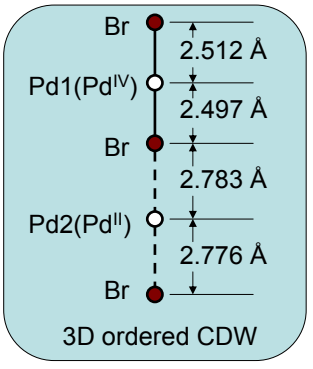


Side view

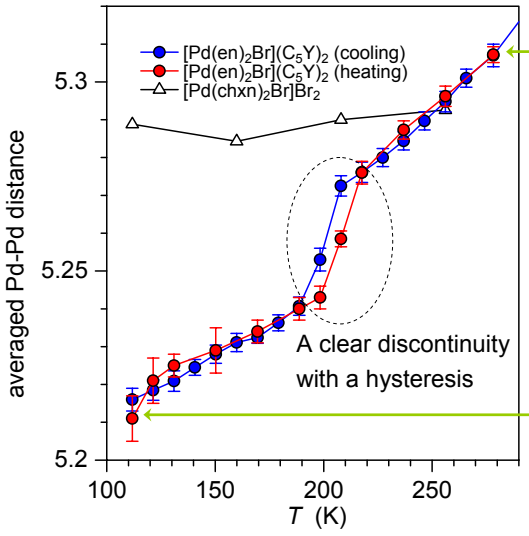


Monoclinic
C 2
a = 15.725(9) Å
b = 10.569(6) Å
c = 28.364(16) Å
β = 100.012(7)°
V = 4642(4) Å^3
Z = 4
T = 250(2) K





Temperature Dependence of Pd-Pd distance



5.31 Å at 293 K

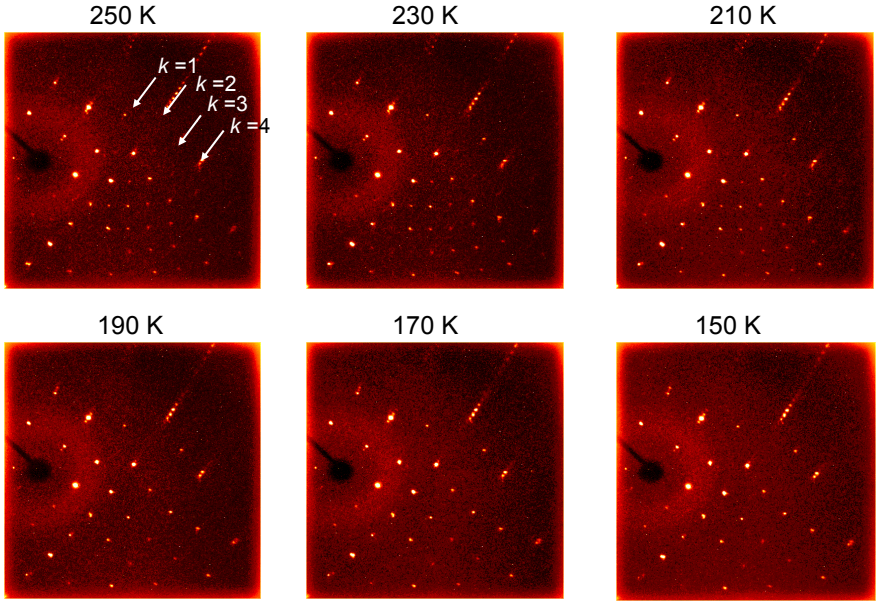
ca. 0.1 Å(2%)

Suppression of thermal motion of alkyl chain

5.21 Å at 110 K

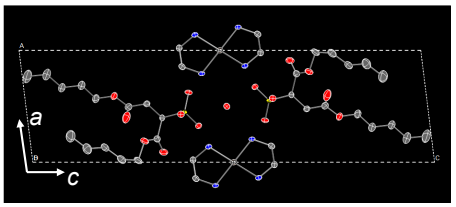
一次相転移の存在

Temperature dependence of the Superlattice Reflections



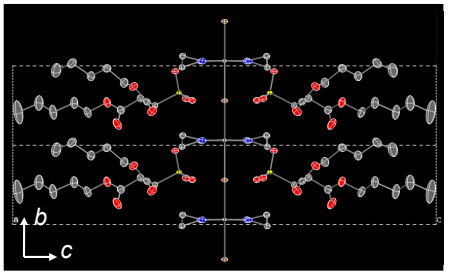
Crystal Structure of $[Pd(en)_2Br](C_5Y)_2$ (150 K)

Top view

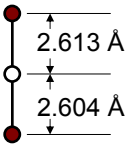


Monoclinic
P 2
a = 7.8326(18) Å
b = 5.2167(12) Å
c = 28. 043(6) Å
β = 97.071(5)°
V = 1137.1(4) Å^3
Z = 1
T = 150(2) K

Side view



Two-fold periodicity disappeared
⇨ ***All Pd are equivalent***



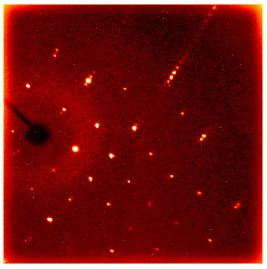
Intermediate between Pd^{IV}-Br and Pd^{II}-Br distances

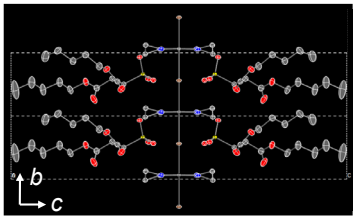
Pd^{III}-Pd^{III} MH state?

Phase Trtansition in $[Pd(en)_2Br](C_5Y)_2$

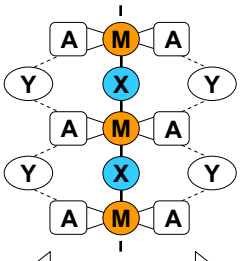
U > *S*

Pd^{3+}-Pd^{3+} MH state





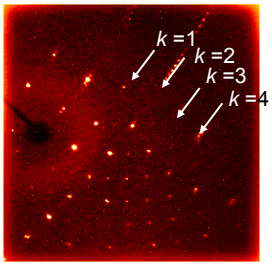
MX-chains
(Peierls Hubbard system)

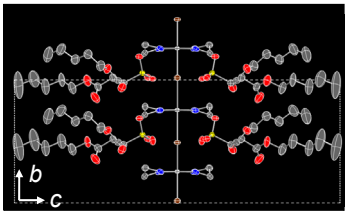


Phase Transition

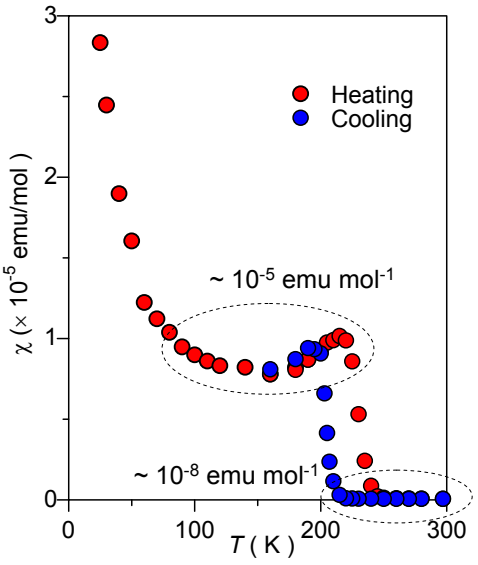
S > *U*

Pd^{2+}-Pd^{4+} CDW state





Spin Susceptibility in $[Pd(en)_2Br](C_5Y)_2$



CDW state

$\cdots Pd^{II} \cdots X—Pd^{IV}—X \cdots Pd^{II} \cdots$

d_{z^2} ↑↓ ↑↓

Diamagnetic behavior

MH state

$\cdots Pd^{III} \cdots X—Pd^{III}—X \cdots Pd^{III} \cdots$

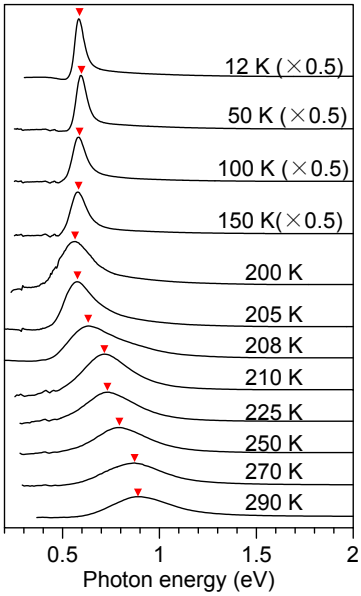
d_{z^2} ↑ ↓ ↑

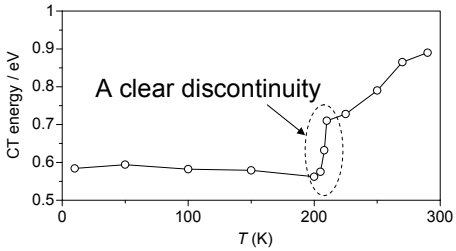
Paramagnetic behavior with strong antiferromagnetic interaction

HT phase: CDW state (Pd^{II}-Pd^{IV})

LT phase: MH state (Pd^{III}-Pd^{III})

Optical Conductivity Spectra in $[Pd(en)_2Br](C_5Y)_2$





・高温 (HT) 相

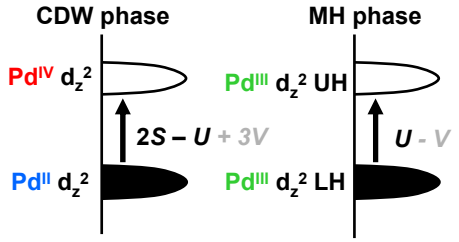
大きな温度依存性 (0.2 eV)

・低温 (LT) 相

ほとんど温度依存性なし

Determination of Physical Parameters

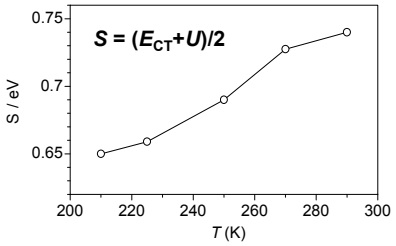
Origin of the Charge Transfer

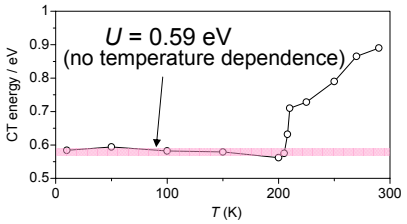


When t and V are neglected

K. Nasu, *J. Phys. Soc. Jpn.* **52**, 3865-3873 (1983).

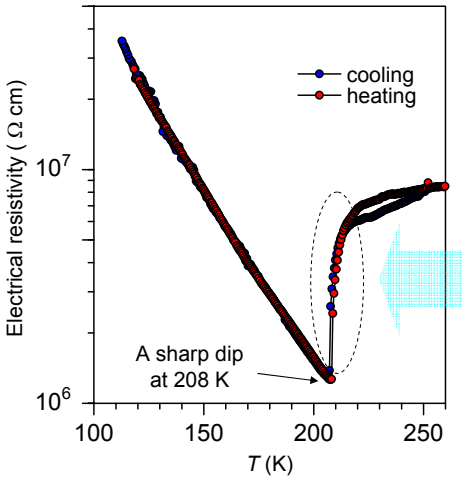
Temperature dependence of S



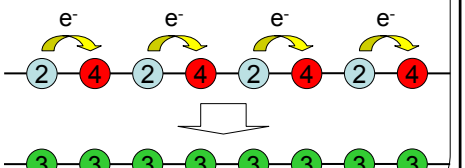


S is reduced with lowering temperature

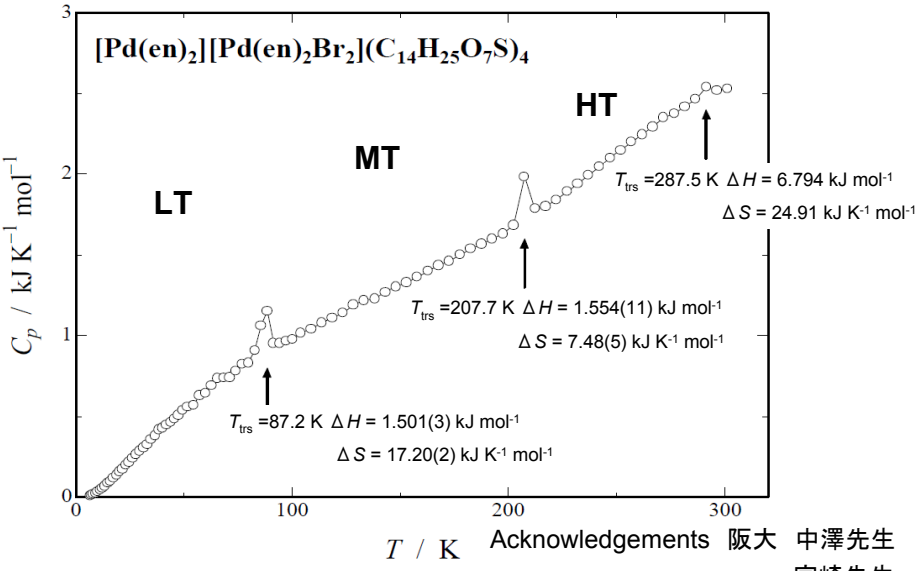
Temperature Dependence of Electrical Resistivity



Critical charge fluctuation due to the phase transition accompanied by charge transfer



Heat Capacity



Acknowledgements 阪大 中澤先生
宮崎先生

Summary

- MH state was realized in halogen-bridged Pd compound $[Pd(en)_2Br](C_5Y)$ for the first time
- CDW-MH phase transition was observed for the first time
- Physical parameters in Peierls-Hubbard model was experimentally determined
- Anomalous electrical conduction due to the charge fluctuation was observed