Hierarchical structure in electronic multipole orders and fluctuations

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Our COE team for multipoles

- Sample preparation and thermodynamic measurements
  - H. Onodera, A. Tobo
- Neutron and X-ray scatterings
  - K.Iwasa, K.Ohoyama, L. Hao
- Theory
  - Y.Kuramoto, H.Kusunose, A.Kiss,
  - K. Kubo (JAERI), G.Sakurai (D3), H. Kono (D2), J.Otsuki (M2)

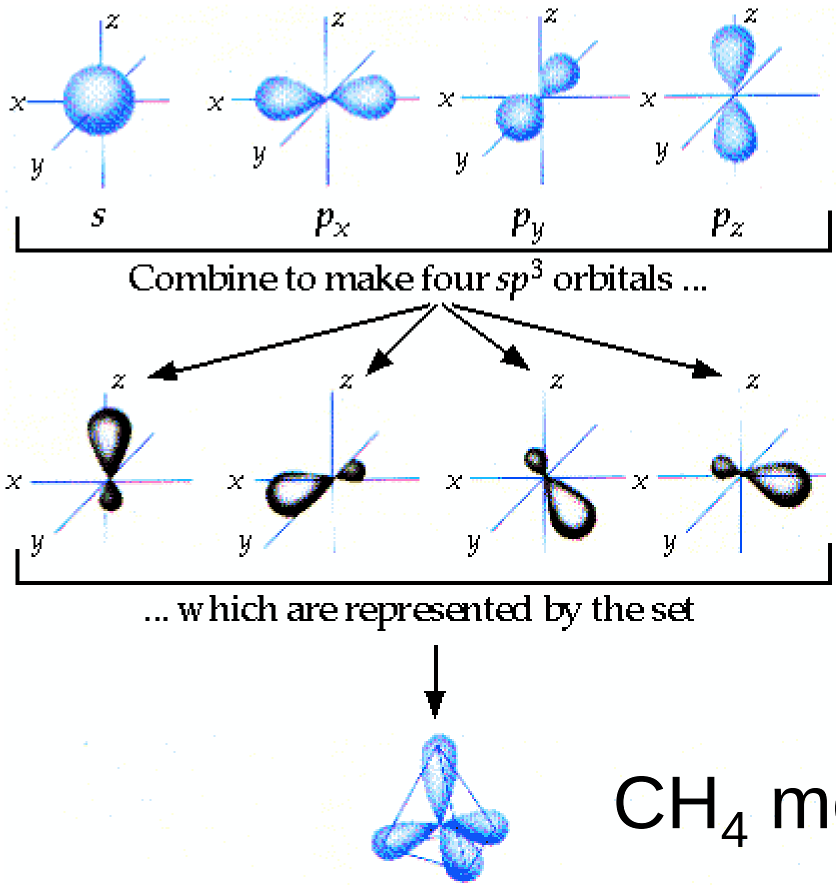
Collective and dual behaviors of electrons

- Single electron
  - Known very well ?
- Interacting electrons
  - Unexpected consequences
  - Superconductivity, ferromagnetism, …

Dual natures

- Itinerant state : k , σ (spin), ν (band)
- Localized state + spin-orbit interaction
  - Orbital degeneracy => multipole moments

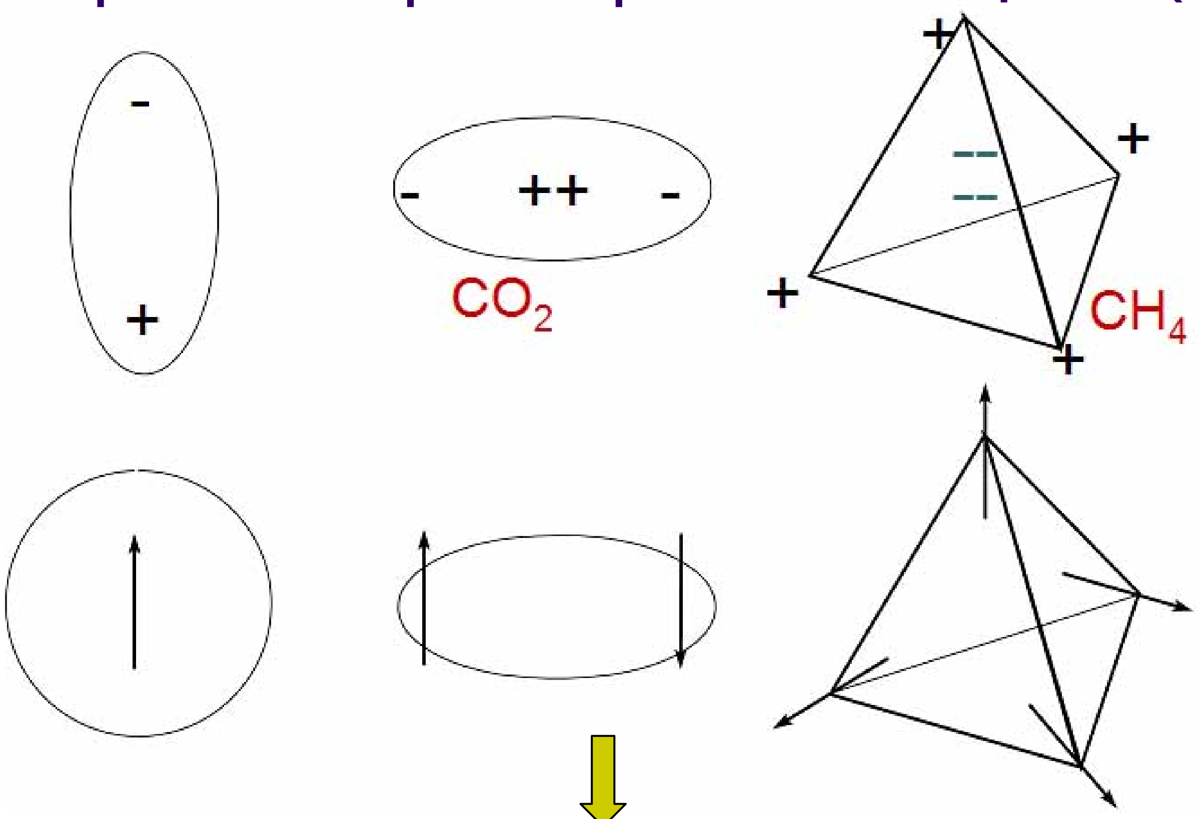
Electron orbitals (in chemistry)



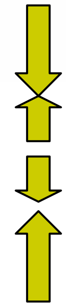
CH_4 molecule

Multipole moments

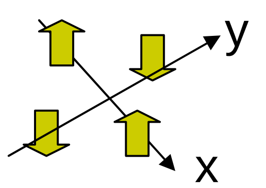
	dipole	quadrupole	octupole (xyz)
electric			
magnetic			



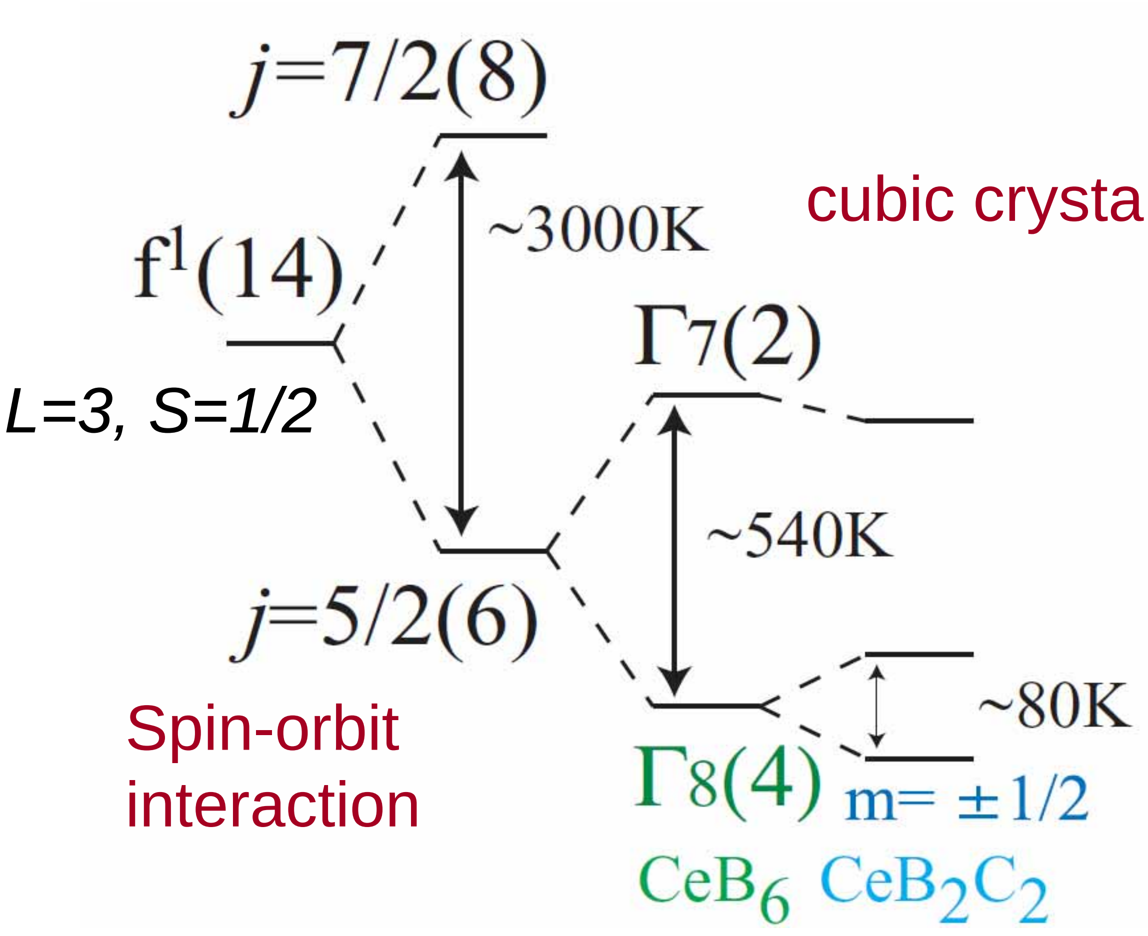
Other octupoles: $z(5z^2-r^2)$



$z(x^2-y^2)$



Splitting of f¹ enegy levels with strong spin-orbit interaction

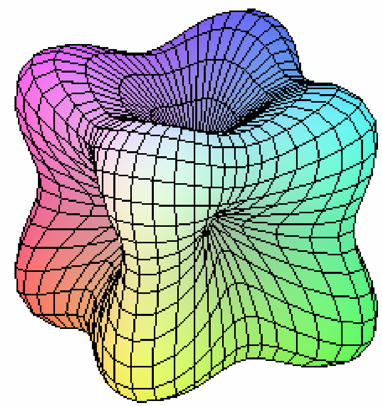


Examples of 4f¹ electron orbitals in cubic crystalline electric field (CEF) potential

$$L = 3,\ S = 1/2,\ J = 5/2$$

Γ_7

Kramers doublet



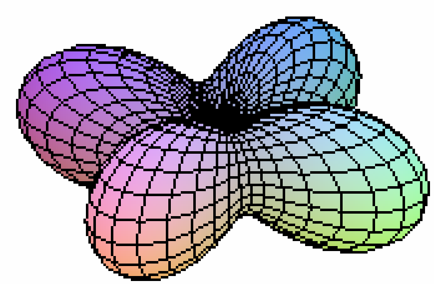
$$|\uparrow\rangle = \sqrt{\frac{1}{6}}\left|+\frac{5}{2}\right\rangle - \sqrt{\frac{5}{6}}\left|-\frac{3}{2}\right\rangle$$

$$|\downarrow\rangle = \sqrt{\frac{1}{6}}\left|-\frac{5}{2}\right\rangle - \sqrt{\frac{5}{6}}\left|+\frac{3}{2}\right\rangle$$

Γ_8

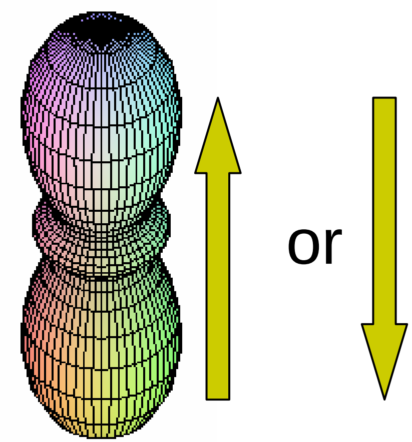
Kramers doublet

- orbital doublet



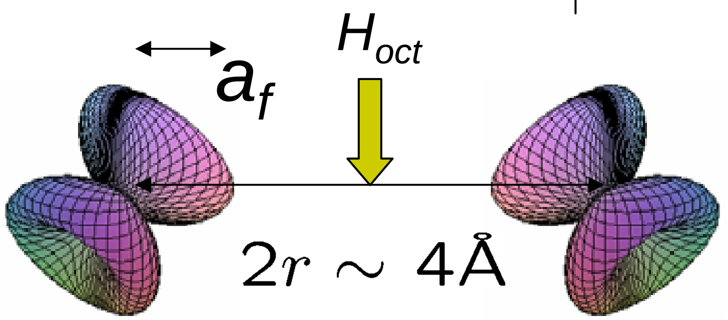
$$|+\uparrow\rangle = \sqrt{\frac{5}{6}}\left|+\frac{5}{2}\right\rangle + \sqrt{\frac{1}{6}}\left|-\frac{3}{2}\right\rangle$$

$$|+\downarrow\rangle = \sqrt{\frac{5}{6}}\left|-\frac{5}{2}\right\rangle + \sqrt{\frac{1}{6}}\left|+\frac{3}{2}\right\rangle$$



$$|-,\sigma\rangle = |\pm 1/2\rangle$$

Hierarchical structure of internal magnetic field



- Dipole moment

  H_{dip} » μ_B/r^3 » $0.1T$
- Octupole moment

  H_{oct} » $\mu_B(a_f/r)^2/r^3$ » $10^{-1} H_{dip}$
- No hierarchy in intersite interactions
  - cf. Heisenberg theory of exchange interaction

    J_{exch} » Ce^2/r À $\mu_B{}^2/r^3$ » α^2e^2/r » $10^{-4}e^2/r$
  - RKKY interaction => octupole order may be realized without dipole order!

Role of higher multipoles

- Controlling the phase transition as hidden order parameters.
- Supporting unusual physical properties from behind.
- Strong spin-orbit interaction =>
  - Detectable by neutrons and X-rays?
  - Excitation spectrum of multipoles?
  - Interaction with conduction electrons?

Modes of Research

- Neutron scattering (+polarization)
  - Tohoku University facilities at JAERI Tokai
- X-ray scattering by synchrotron radiation
  - Spring-8 and Tsukuba
- Theory
  - Faithful account of electronic structure
  - Simplified models with essential physics

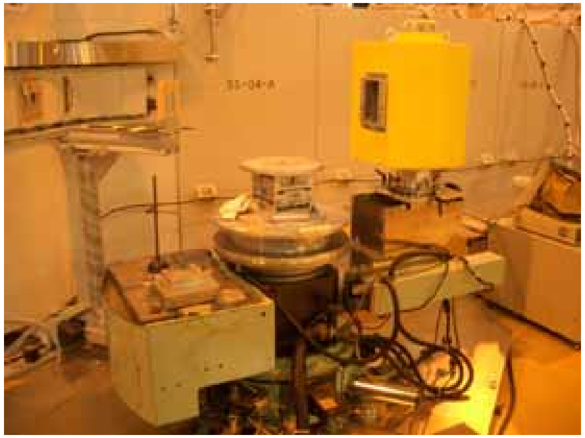
東北大学が所有または管理している装置 (JAERI at Tokai)

粉末回折装置HERMES (金研)
結晶構造、磁気構造解析
(希土類、3d酸化物、強相関系)

三軸分光器TOPAN (理学研究科)
原子や磁気モーメントの運動・ゆらぎの観測
(高温超伝導、誘電体、強相関系)

日本原子力研究所
(茨城県東海村)

単結晶四軸回折装置FONDER
(物性研所有:多元研グループが管理)
有機物など複雑な構造での構造解析



単結晶回折装置KSD (金研)
(三軸分光器に改造中)

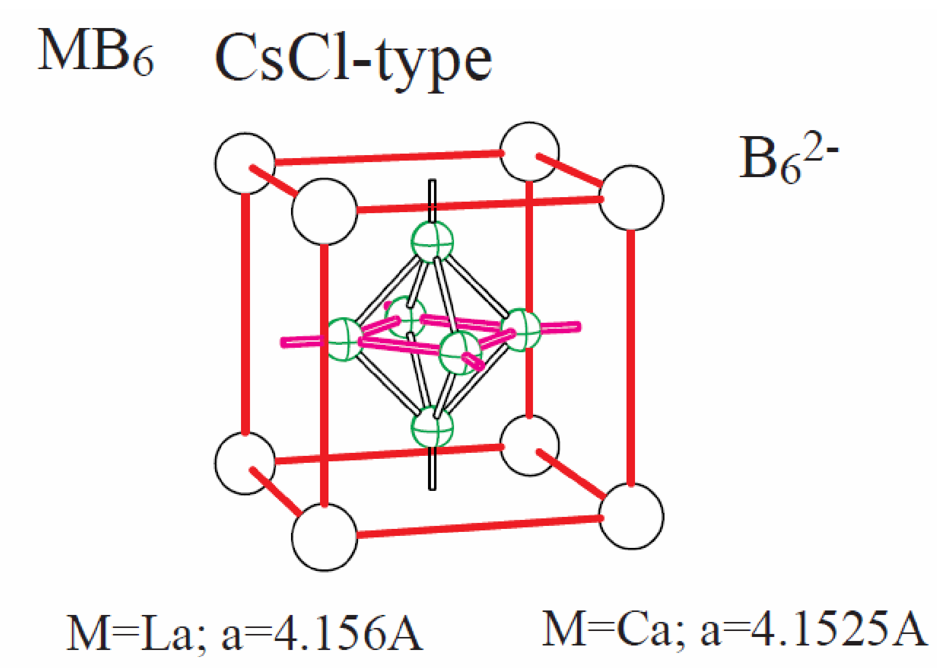
Target systems

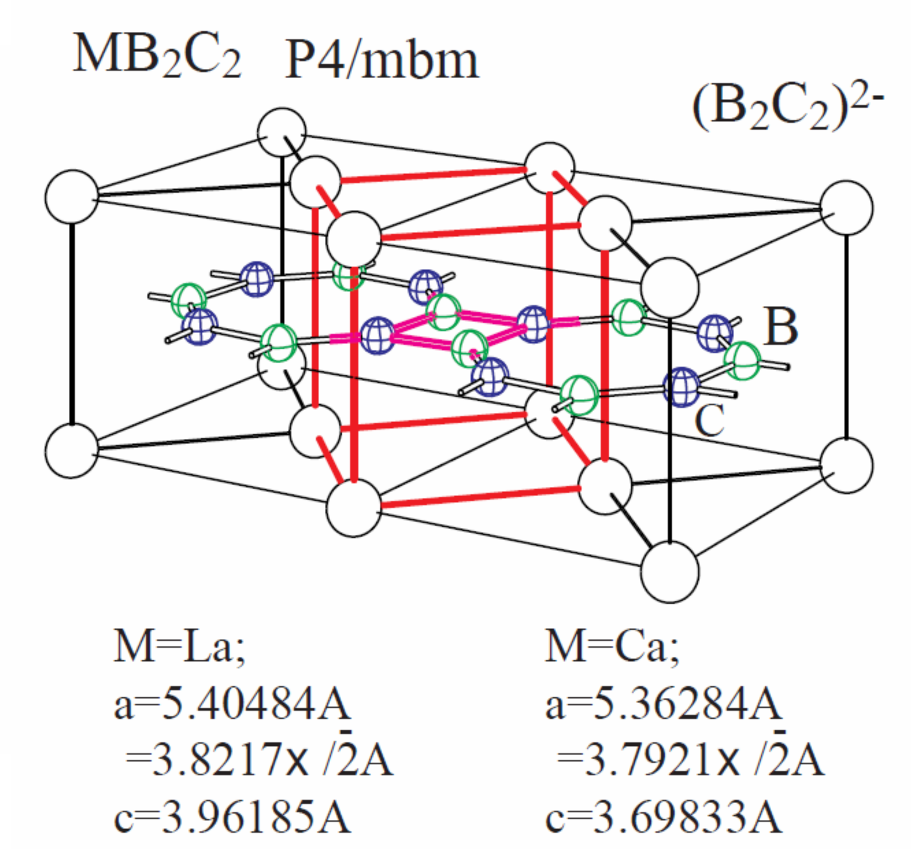
- Rare-earth hexaborides:
  - CeB_6, $Ce_xLa_{1-x}B_6$
- Rare-earth diborocarbides:
  - RB_2C_2 (R= Ce, Dy, Gd, Ho, Tb, Er…)
- Pr skutterudites:
  - $PrFe_4P_{12}$, $PrRu_4P_{12}$, $PrOs_4Sb_{12}$…

Common structural features:

Clathrate-like lattices => cage+guest ions

Hexaborides vs diborocarbides

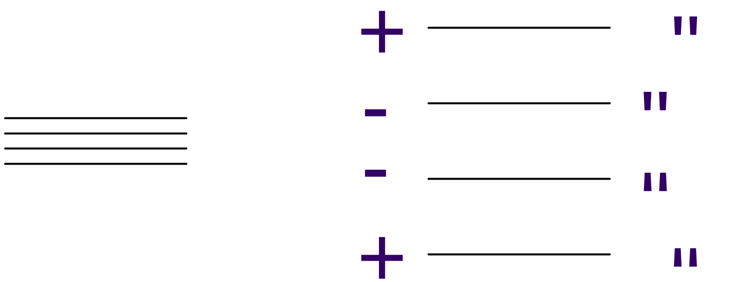


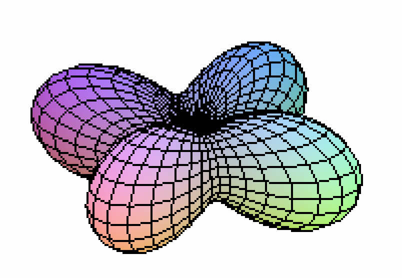


Splitting of the Γ_8 level

- Magnetic field (H_z)

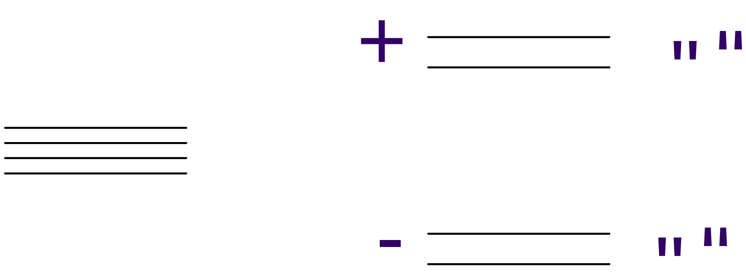
”+” orbital

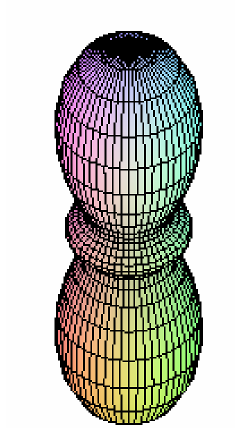




- Strain field (ε_{zz})

”-” orbital





Broken T-reversal

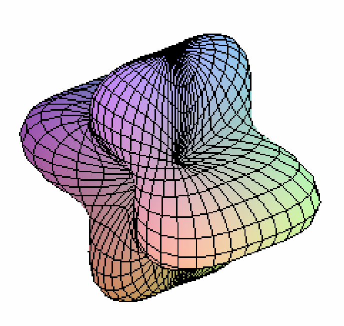
+ unbroken orbital degeneracy

T_{xyz} octupolar basis

$\langle T_{xyz} \rangle$

Γ_8

$|+\downarrow\rangle \pm i|-\downarrow\rangle$

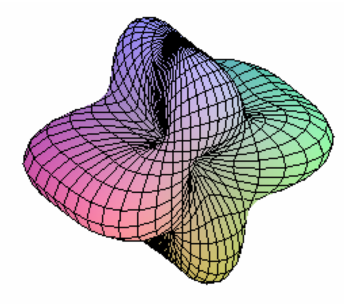


$3\sqrt{3}/2$

+

*

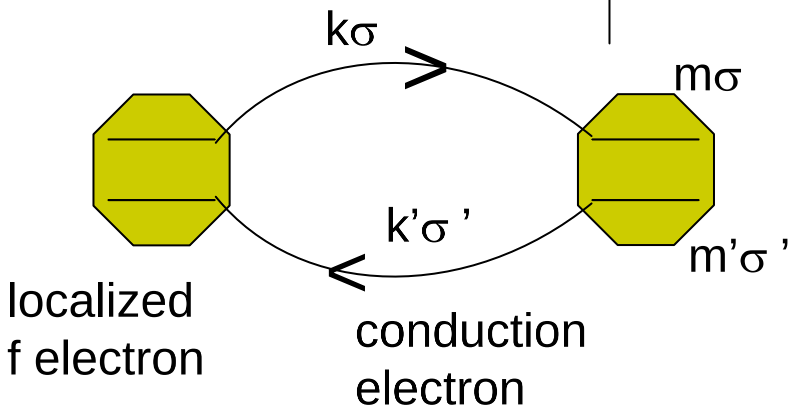
$|+\uparrow\rangle \pm i|-\uparrow\rangle$

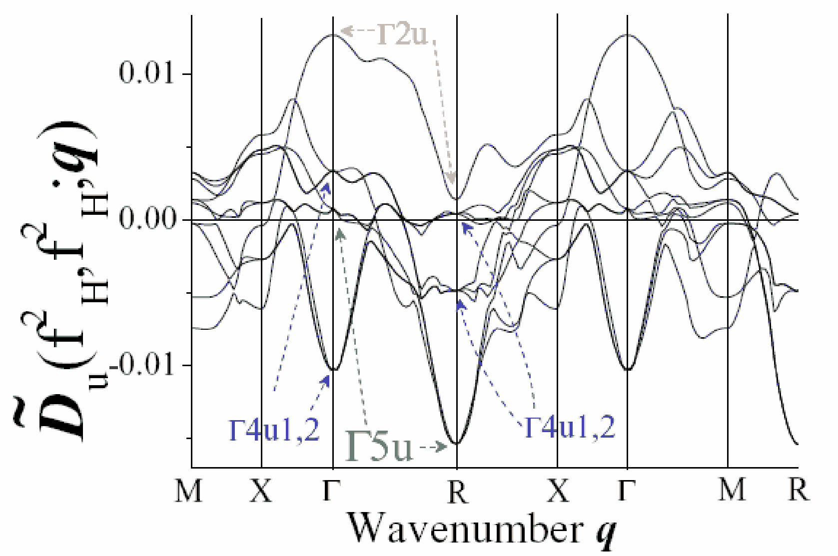


$-3\sqrt{3}/2$

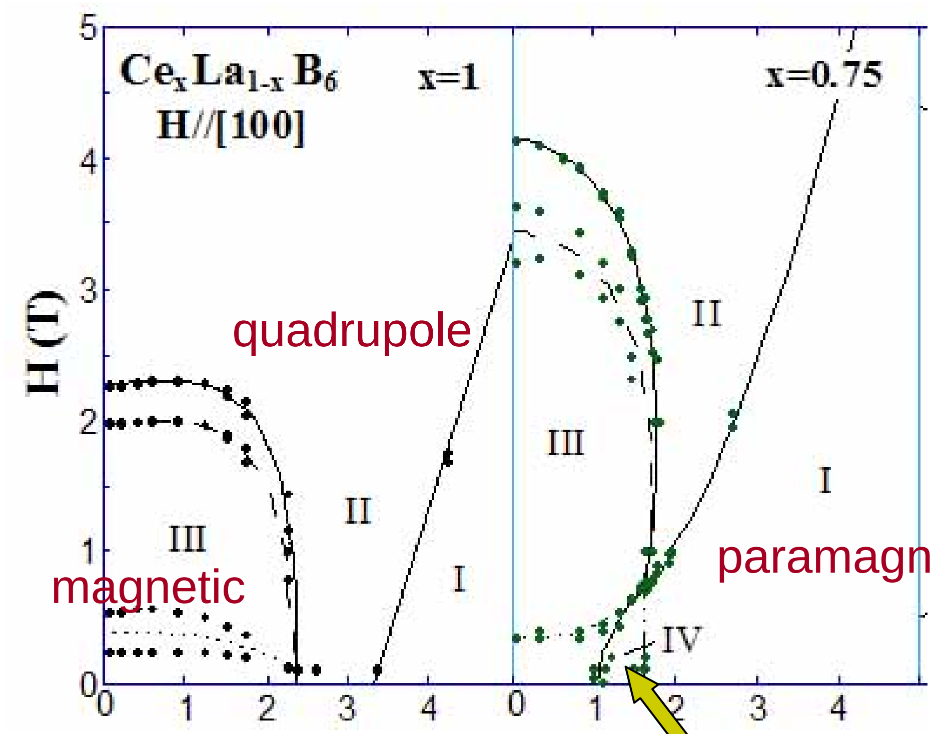
Microscopic origin of multipolar interactions

- RKKY interaction
  - (mσ) => (J,J_z) => (Γγ)
    spin-orbit crystal field
- Octupolar interaction Γ_{5u} is the same order as the dipolar interaction Γ_{4u}
  - G. Sakurai (Ph.D thesis)





Strange ordered phase (phase **IV**) in $Ce_xLa_{1-x}B_6$



T (K)

Order parameter?

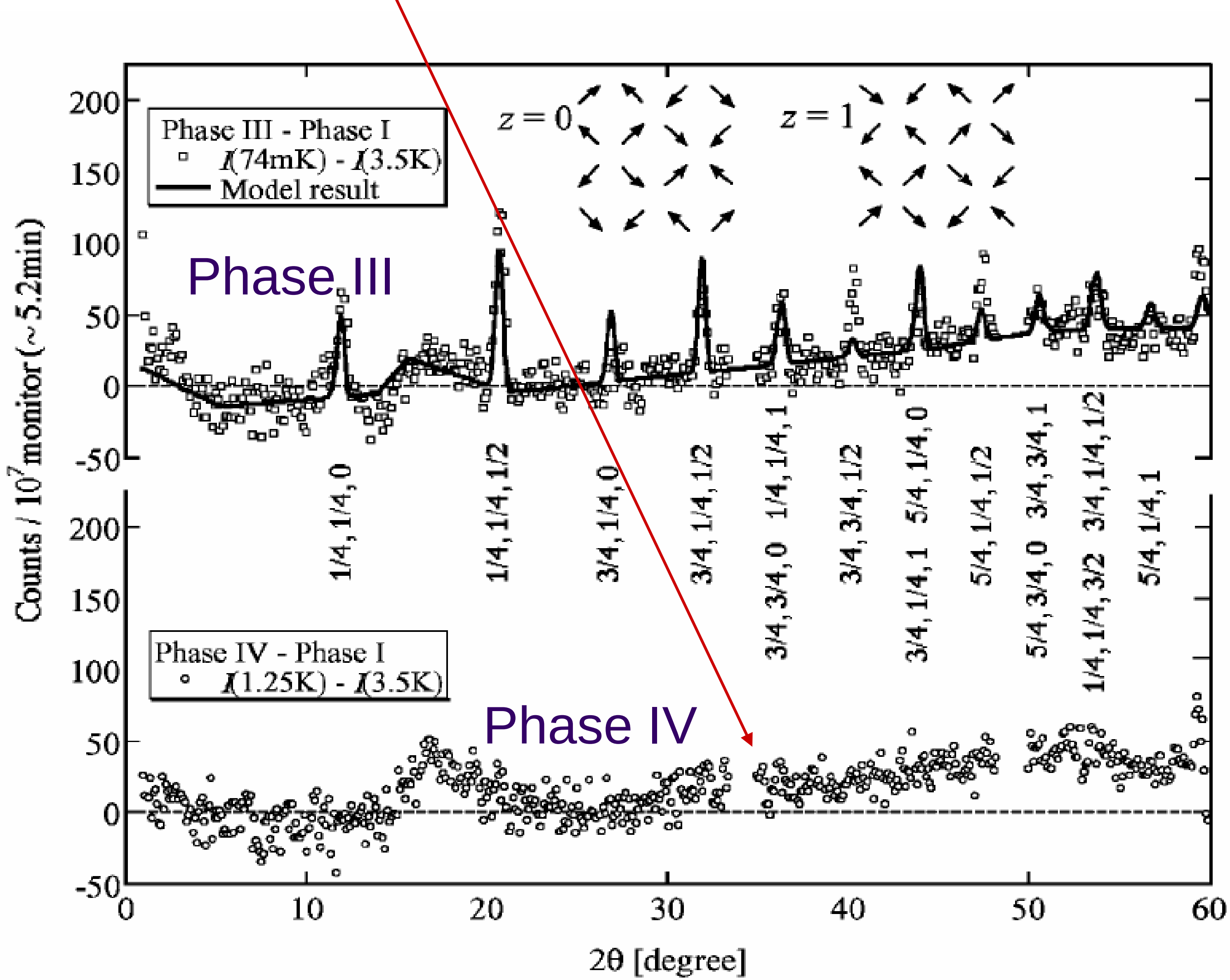
Tayama *et al.* JPSJ (1997)

- No magnetic order by neutrons
- μSR detects small internal fields
- Gigantic elastic anomaly and slight lattice distortion

Possible octupole order

Iwasa et al :Physica B 329-333 (2003) 582

No magnetic Bragg peaks in phase IV



Takagiwa et al

Journal of the Physical Society of Japan
Vol. 71, No. 1, January, 2002, pp. 31–34

μSR

T_{IV}» 1.4 K

H_{int} » 0.1T

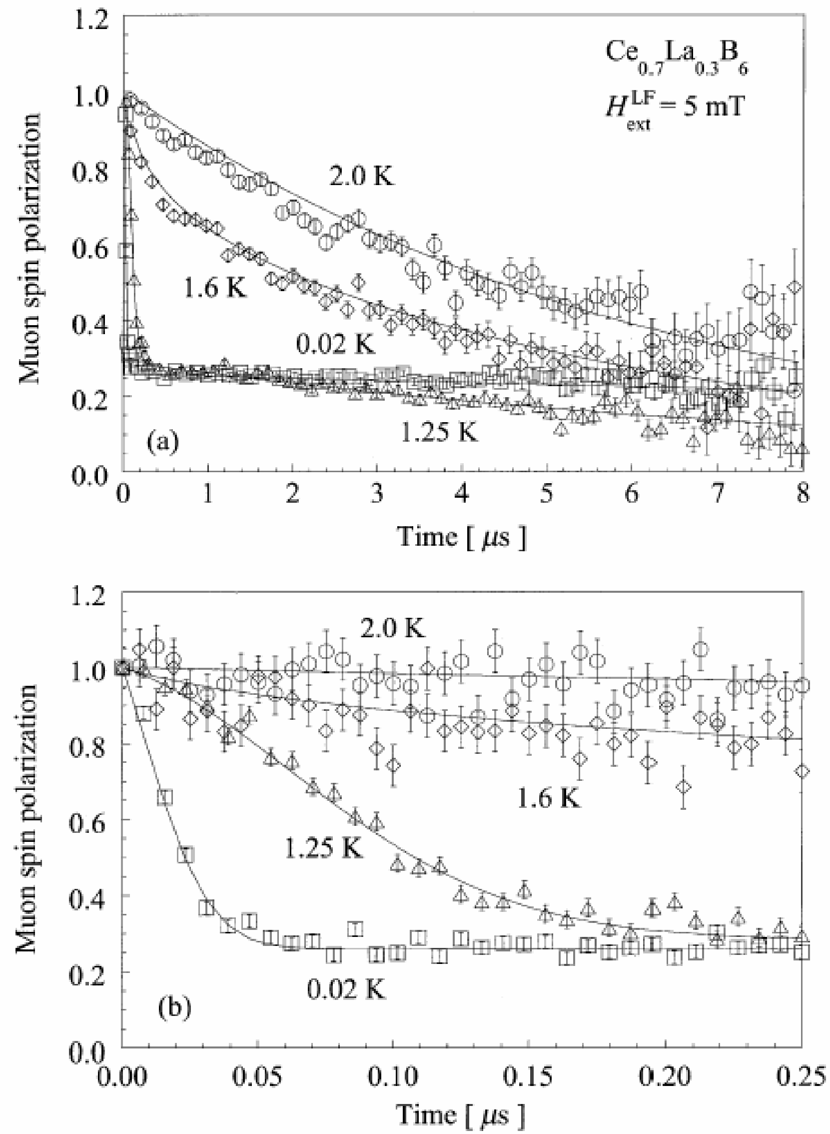
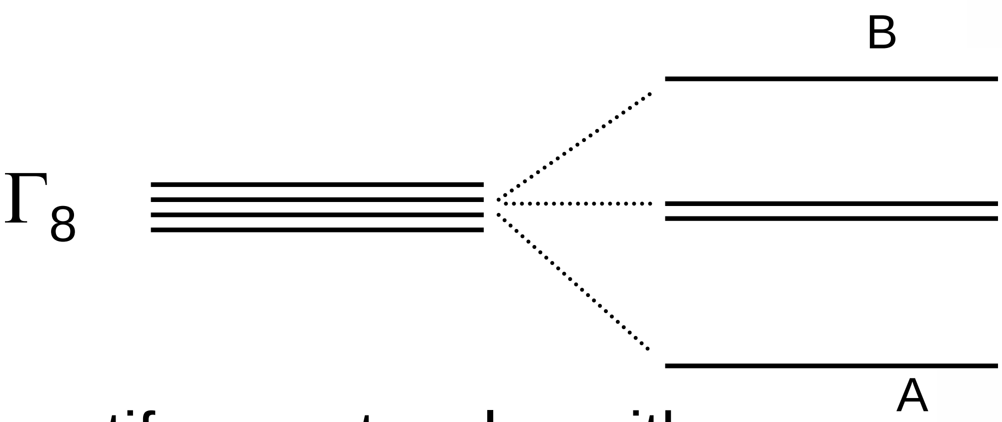
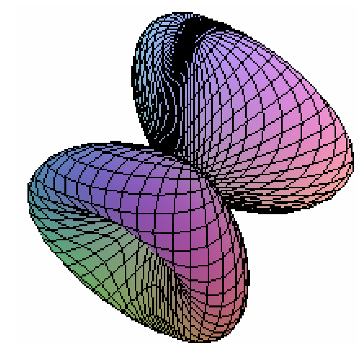


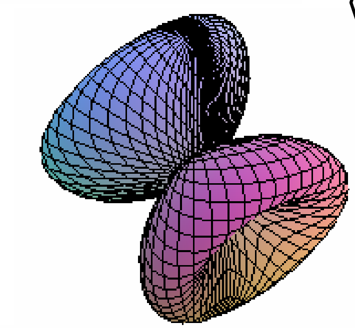
Fig. 1. (a) LF-μSR time spectra (muon spin polarization) in $Ce_{0.7}La_{0.3}B_6$ at temperatures of 2.0 K, 1.6 K (in phase I), 1.25 K and 0.02 K (in phase IV) and (b) an expanded view of (a). Solid curves are the results fitted by the function described in the text.

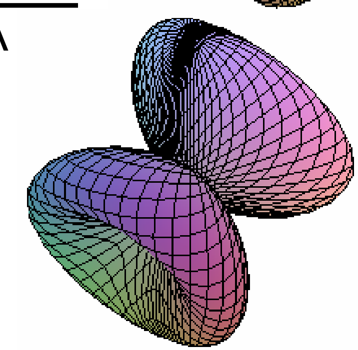
Broken T-reversal and broken orbital degeneracy

$T_x^\beta + T_y^\beta + T_z^\beta$ octupolar basis









$3\sqrt{2}$

$\langle T_x^\beta + T_y^\beta + T_z^\beta \rangle$

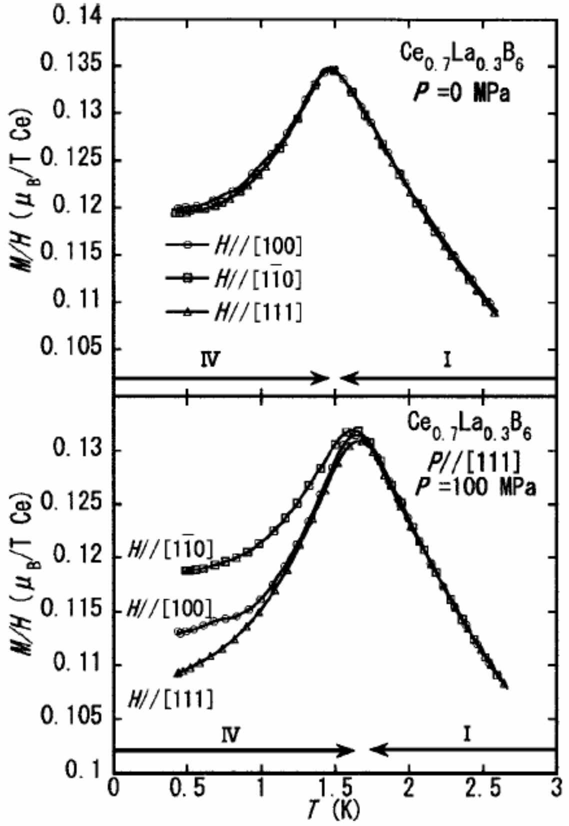
0

$-3\sqrt{2}$

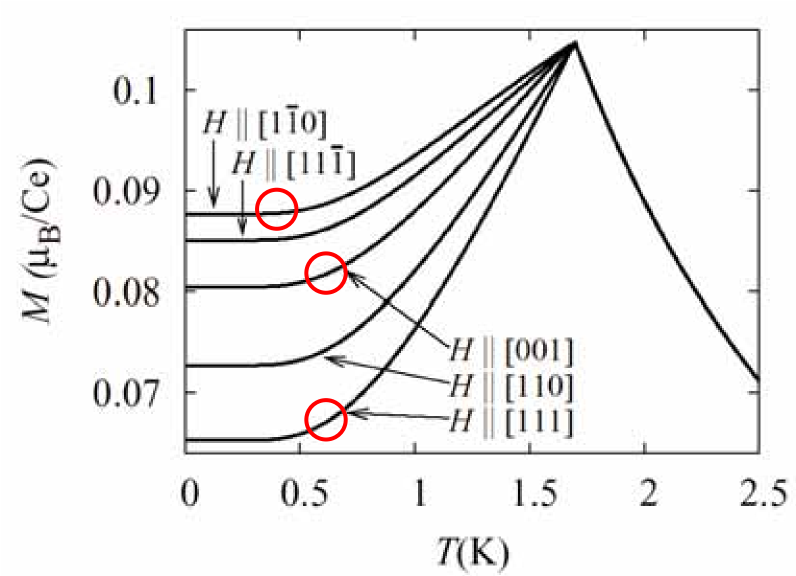
antiferro-octupoles with A,B sublattices)
ferro-quarupoles)
lattice distortion +
(1/2,1/2,1/2) Bragg peak

Magnetic anisotropy in $Ce_{0.7}La_{0.3}B_6$ under uniaxial stress

Magnetization (Exp.)



Theoretical prediction

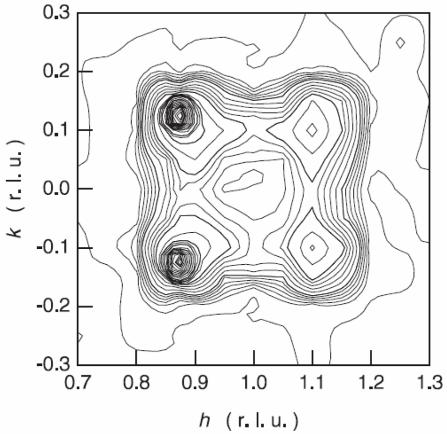


Single octupole domain under uniaxial stress along [111]

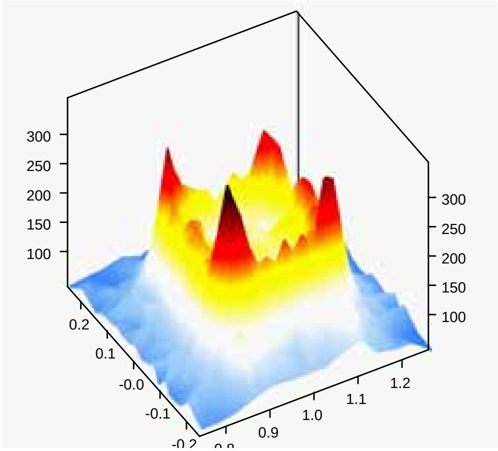
Theory：K. Kubo and Y. Kuramoto: J. Phys. Soc. Jpn. **73** (2004) 216.

Experiment：T. Morie *et al*.: J. Phys. Soc. Jpn. **73** (2004) 2381.

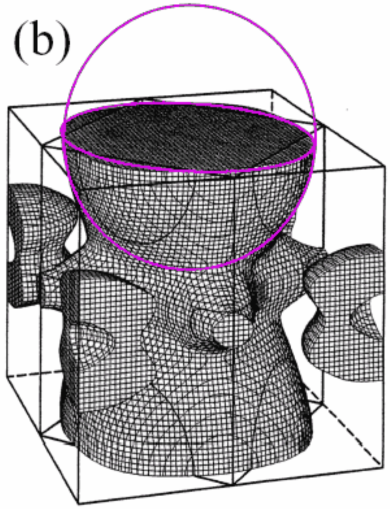
Anomalous magnetic correlation in RB_2C_2 (R=Ho,Tb,Er) by Fermi surface effects?



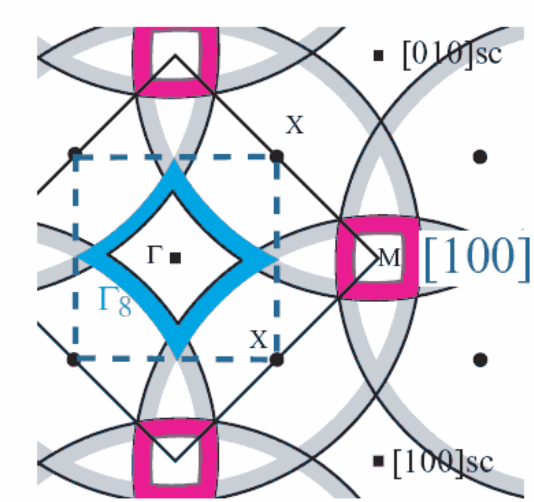
Neutron scattering: Ohoyama et al.
Theory in progress: Sakurai et al.



HoB_2C_2

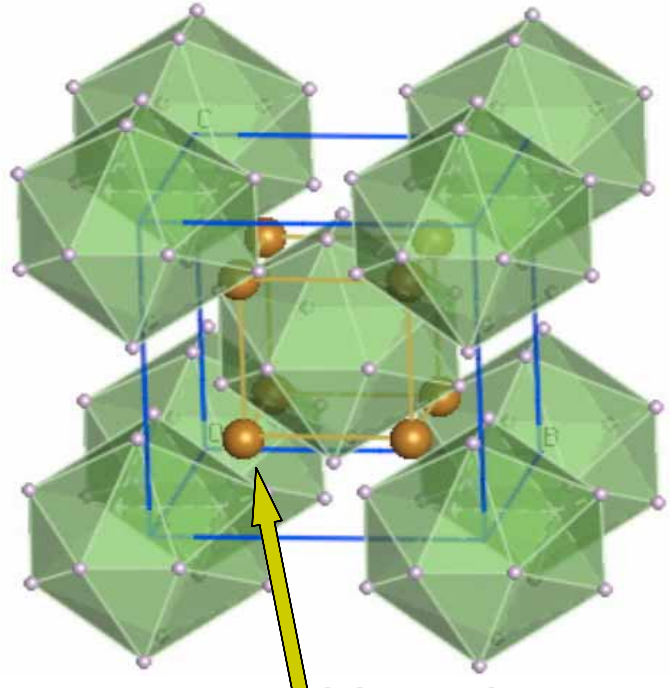


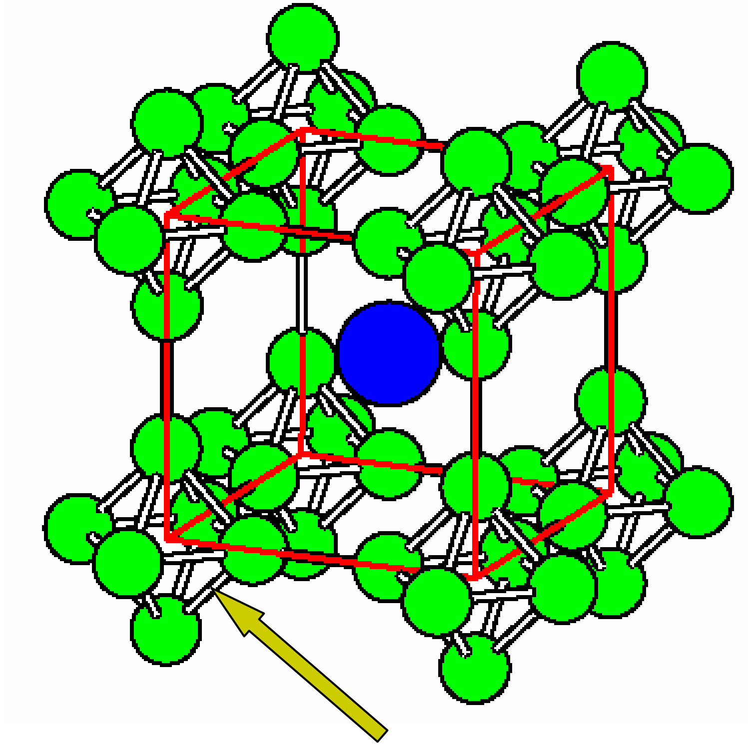
Fermi surface



Kohn anomaly

Clathrate-like structures





Pr skutterudite: PrT_4X_{12}

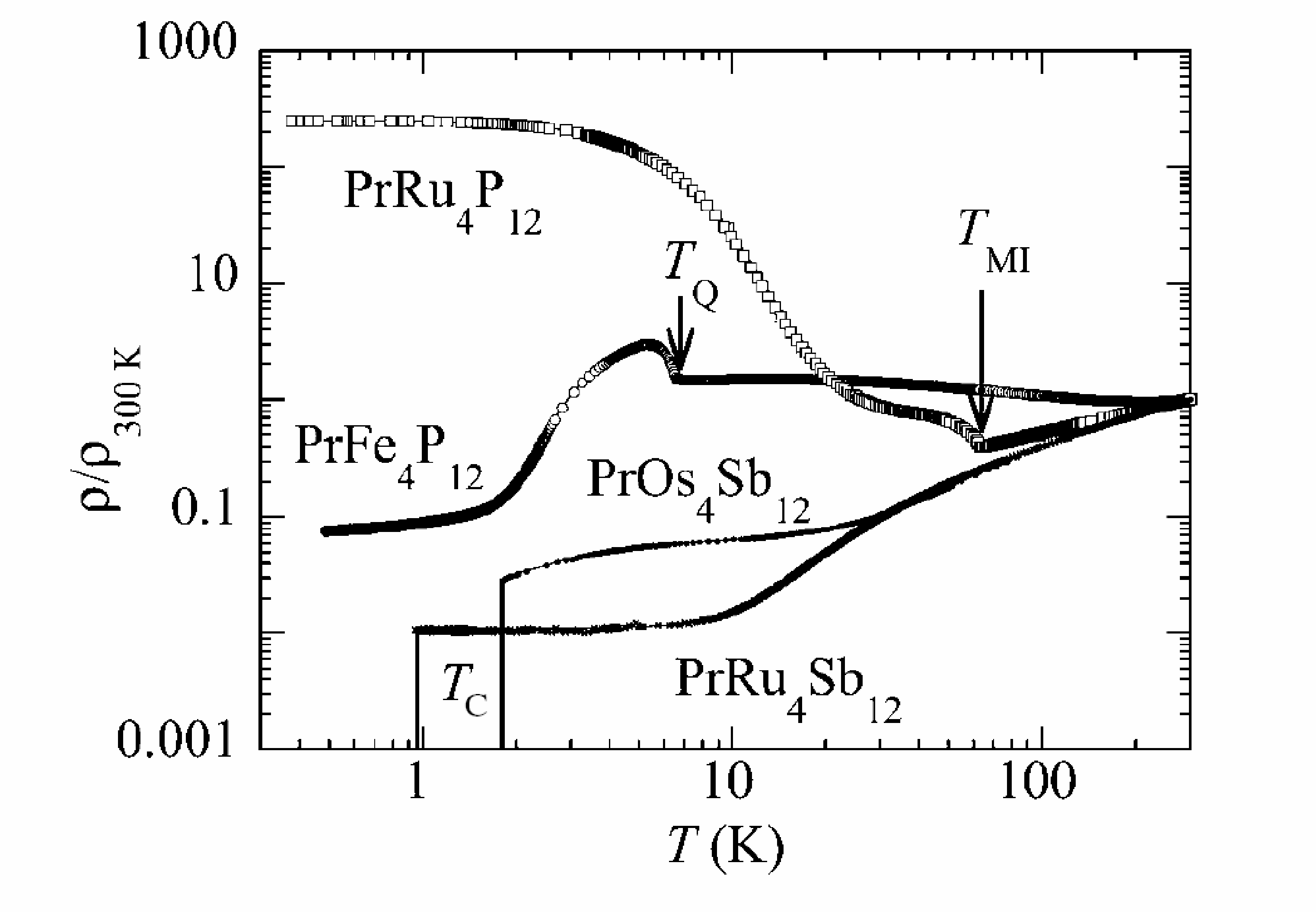
ground state: nondegenerate

PrB_6

ground state: triplet

Resistivity ρ *(T)* in Pr skutterudites

H. Sato et al.: J. Phys.: Condens. Matter 15 (2003) S2063–S2070

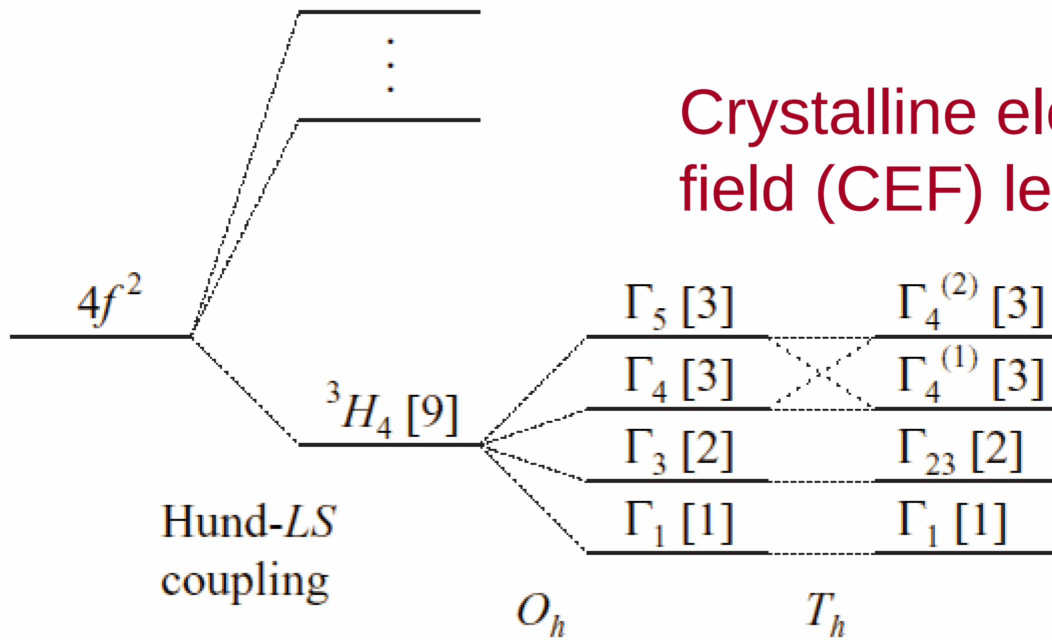


Pr skutterudites: quantum zoo

- Phase diagram with multiple orders
  - $PrFe_4P_{12}$ => Antiferro-quadrupole (AFQ) order
  - $PrOs_4Sb_{12}$ => AFQ and superconductivity
- Metal insulator transition and temperature-dependent f-electron levels
  - $PrRu_4P_{12}$
- Kondo effect in resistivity and magnetic response
  - $PrFe_4P_{12}$

controlling parameter ?) p-f hybridization !

J=4 CEF levels in point-group symmetries O_h and T_h

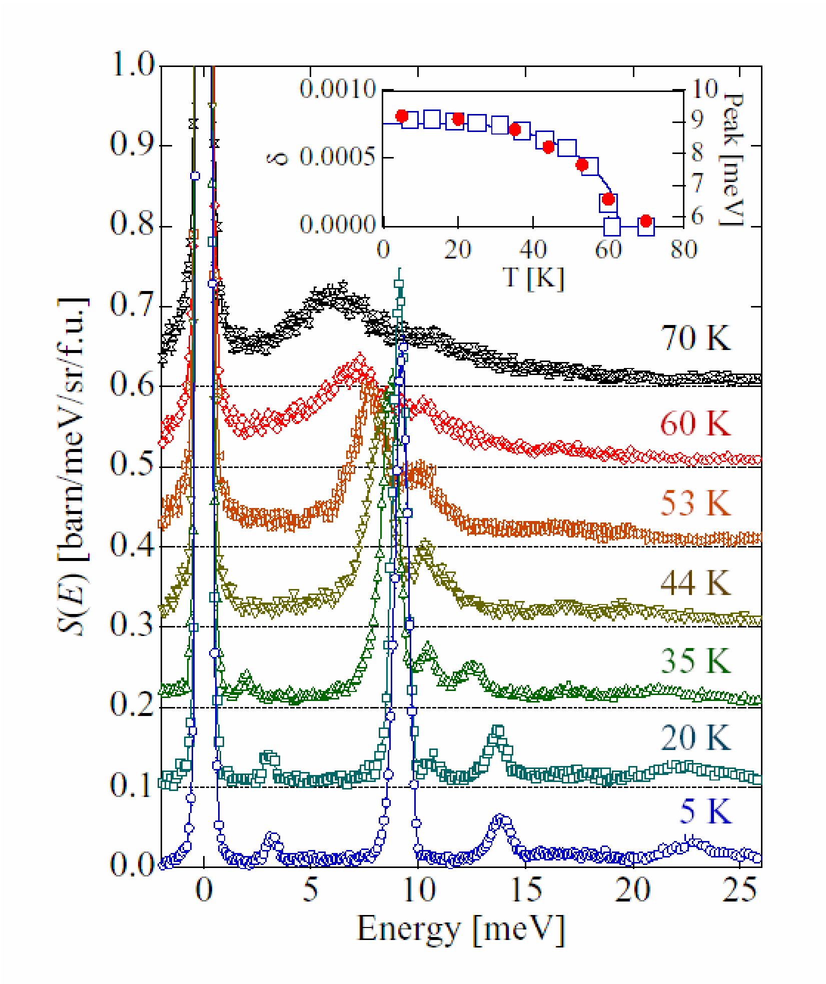


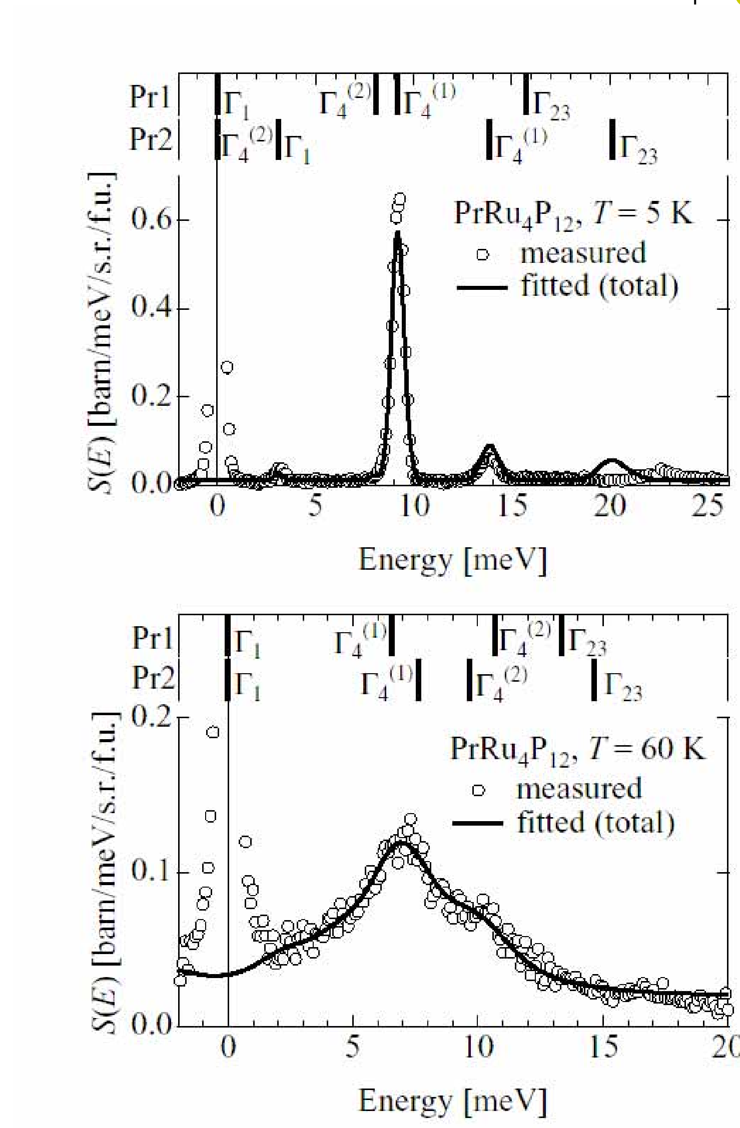
Crystalline electric field (CEF) levels

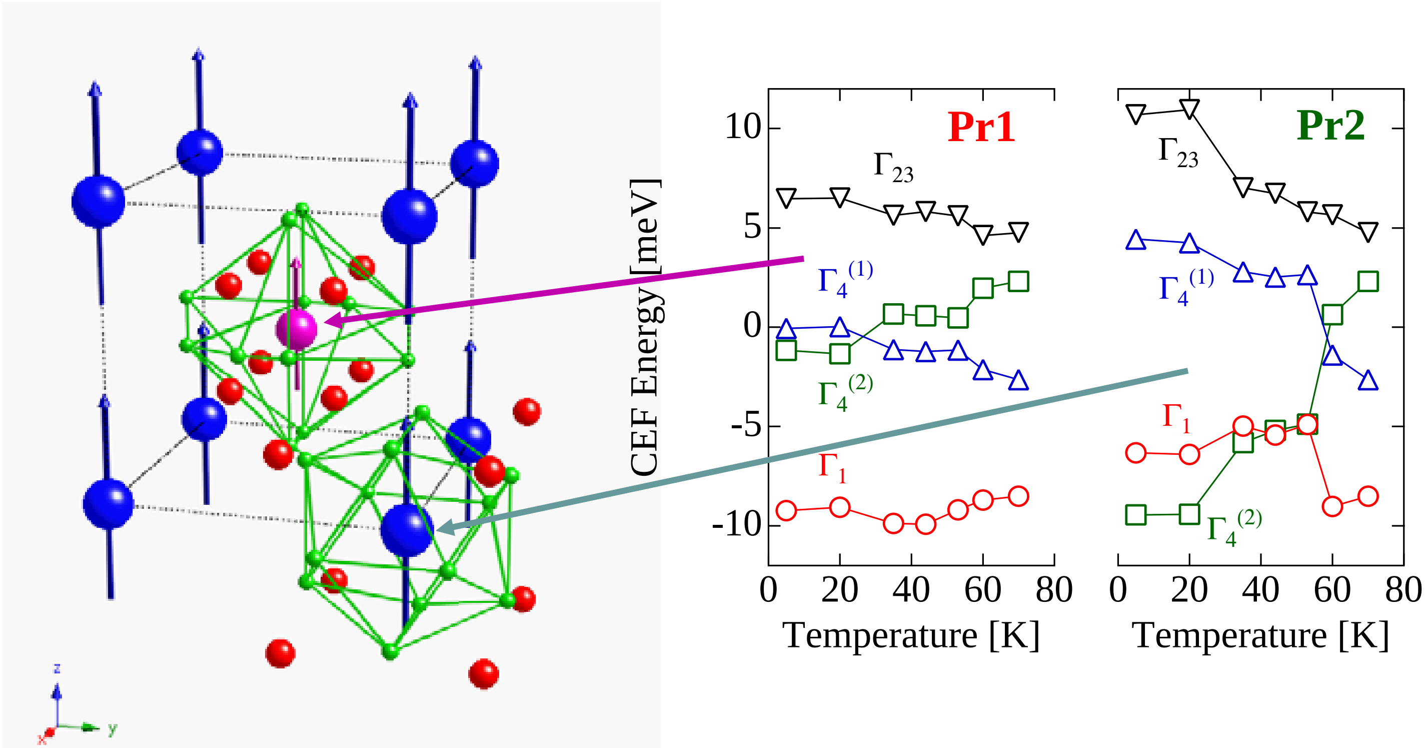
L=5, S=1, J=4

Neutron scattering of $PrRu_4P_{12}$

(Iwasa et al.: 2004)







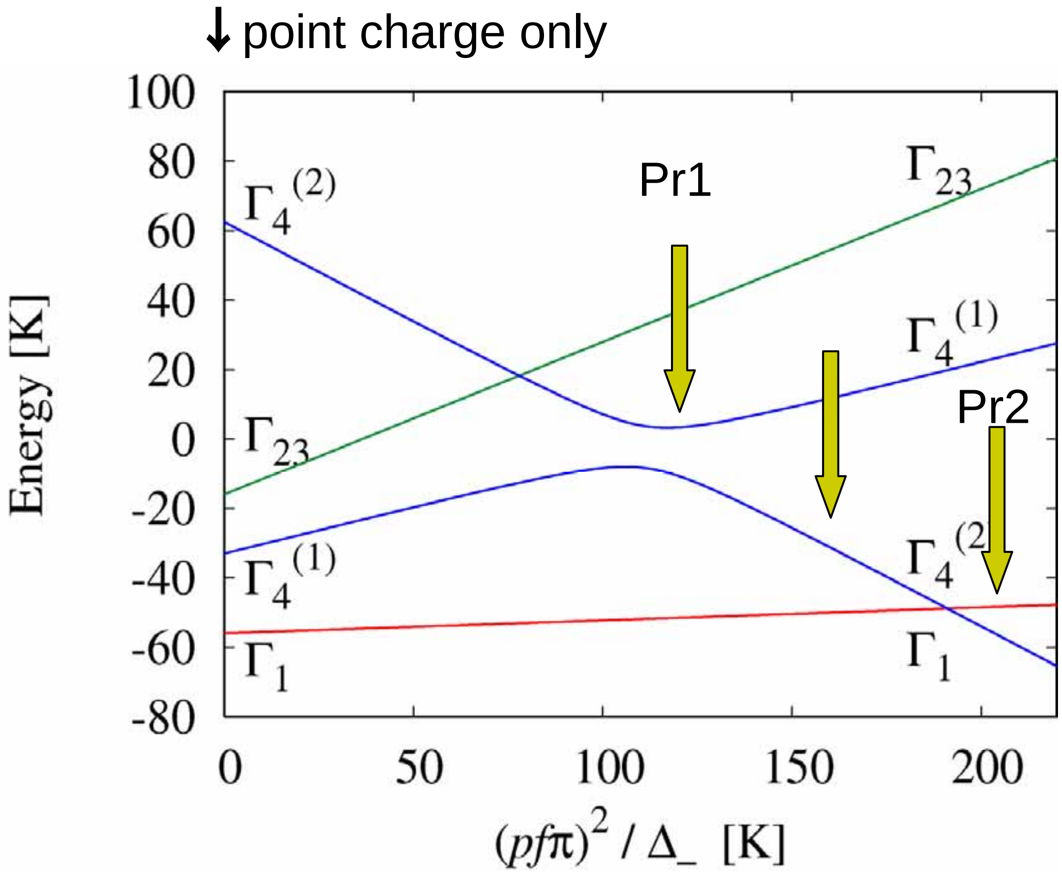
●The CEF states change below the M-I transition of $PrRu_4P_{12}$, and superlattice crystal-structure is observed.

●Two inequivalent CEF schemes for the Pr-ion states below $T_{\text{M-I}}$.

- ●Pr_1 and Ru ions move closer : Γ_1 - $\Gamma_4^{(2)}$ - $\Gamma_4^{(1)}$ - Γ_{23}
- ●Pr_2 and Ru move farther: $\Gamma_4^{(2)}$ - Γ_1 - $\Gamma_4^{(1)}$ - Γ_{23}

●These phenomena are explained by
the strong hybridization (p-f mixing) effect.

CEF levels: point charge + hybridization



$$1/\Delta_- = 1/\Delta_3 - 1/\Delta_1$$

- Hybridization ($pf\pi$) only is relevant to the a_u band.
- Point-charge parameters: Z_t=2, Z_p=-11/12

$PrOs_4Sb_{12}$?

$$(pf\pi)^2/\Delta_- = 190\text{K}$$
$$\rightarrow \Delta_1 \simeq 5\text{eV}, \; \Delta_3 \simeq 3\text{eV},$$
$$(pf\pi) \simeq 0.35\text{eV}$$

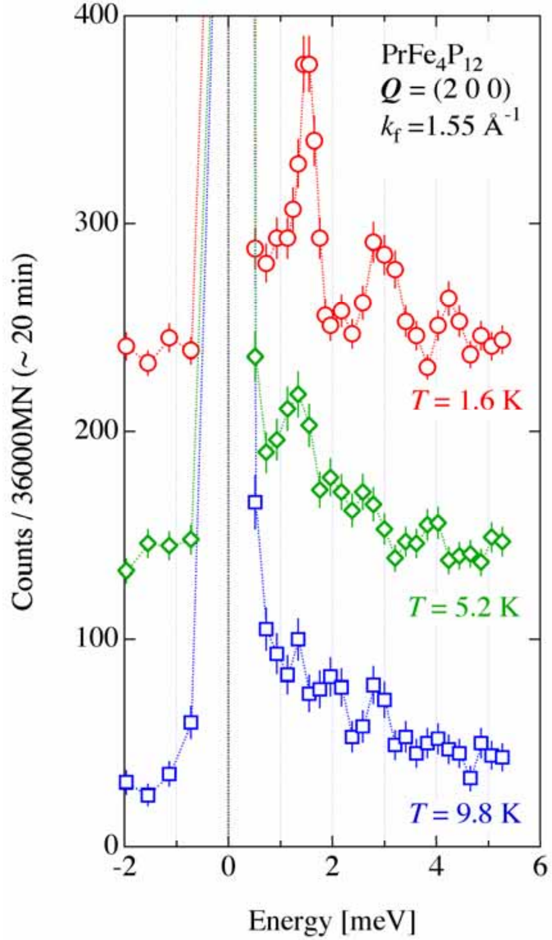
f^1 and f^3 intermediate states compete to make CEF levels

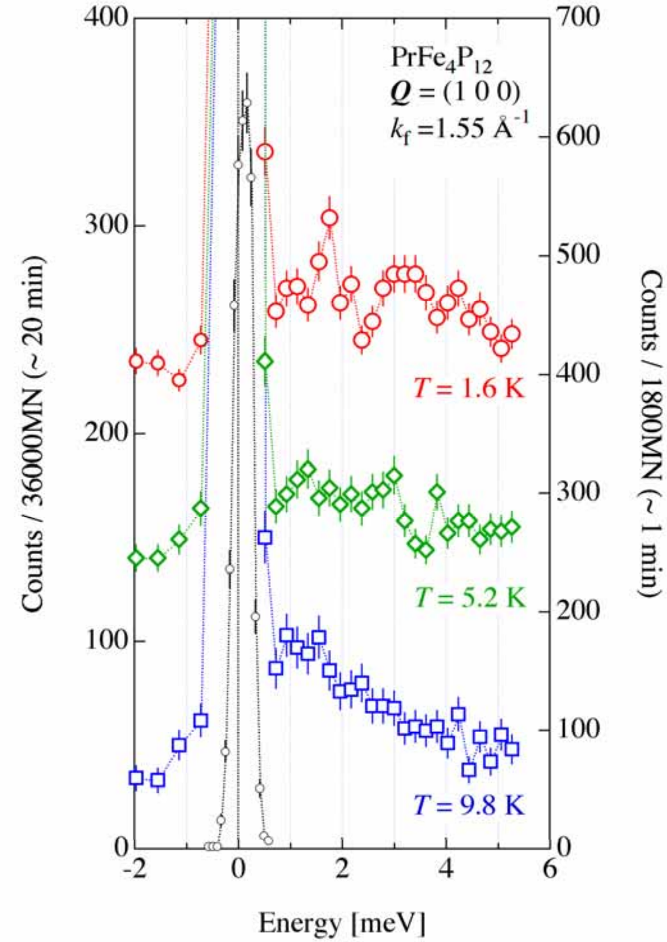
$PrFe_4P_{12}$

Iwasa et al (2003)

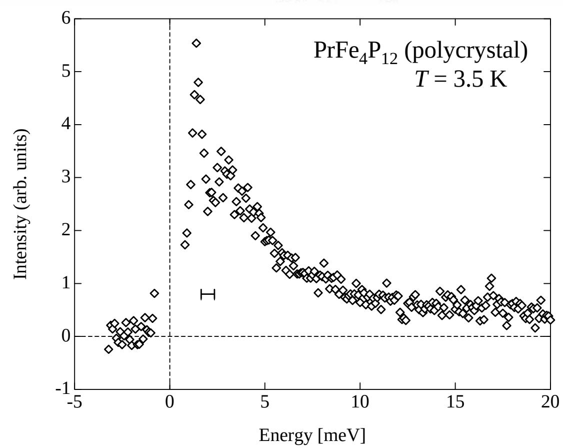
Peak position:
T-independent
=>
CEF excitation!
Why so broad?

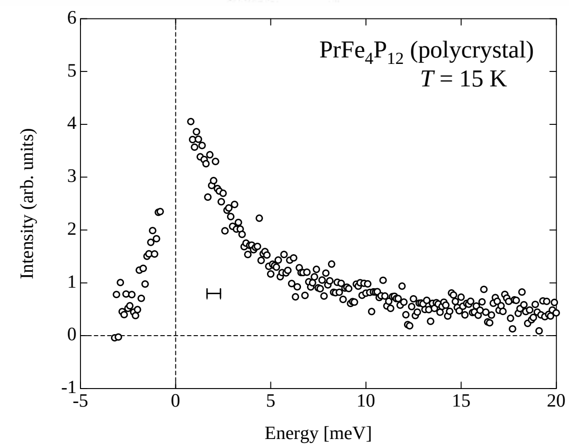
single crystal





polycrystal



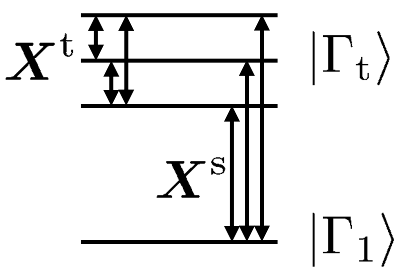


Effective exchange interaction in the singlet-triplet system

$$
\begin{aligned}
H_{\text{s-t}} &= \epsilon_{\text{t}} P_{\text{t}} + \epsilon_{\text{s}} P_{\text{s}} + \left(I_{\text{t}} \boldsymbol{X}^{\text{t}} + I_{\text{s}} \boldsymbol{X}^{\text{s}} \right) \cdot \boldsymbol{s}_c \\
&= \Delta_{\text{CEF}} \boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + (J_1 \boldsymbol{S}_1 + J_2 \boldsymbol{S}_2) \cdot \boldsymbol{s}_c
\end{aligned}
$$

$(\Delta_{\text{CEF}} = \epsilon_{\text{t}} - \epsilon_{\text{s}})$

Kondo effect occurs if J_i > 0 (antiferromagnetic exchange)



$\boldsymbol{X}^{\text{t}} = \boldsymbol{S}_1 + \boldsymbol{S}_2$

$\boldsymbol{X}^{\text{s}} = \boldsymbol{S}_1 - \boldsymbol{S}_2$

$\boldsymbol{S}_1$, $\boldsymbol{S}_2$: pseudo-spin

$$
\begin{aligned}
|\Gamma_1\rangle &= (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2} \\
|\Gamma_{\text{t}}, +\rangle &= |\uparrow\uparrow\rangle \\
|\Gamma_{\text{t}}, 0\rangle &= (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2} \\
|\Gamma_{\text{t}}, -\rangle &= |\downarrow\downarrow\rangle
\end{aligned}
$$

Effective exchange with conduction electrons

Triplet wave functions in the point group T_h (m=0,±)

$$|\Gamma_\mathrm{t}, m\rangle = \sqrt{w}|\Gamma_4, m\rangle + \sqrt{1-w}|\Gamma_5, m\rangle$$

Effective interaction

$$H_\mathrm{eff} = PH_\mathrm{hyb}(E-H_0)^{-1}QH_\mathrm{hyb}P$$

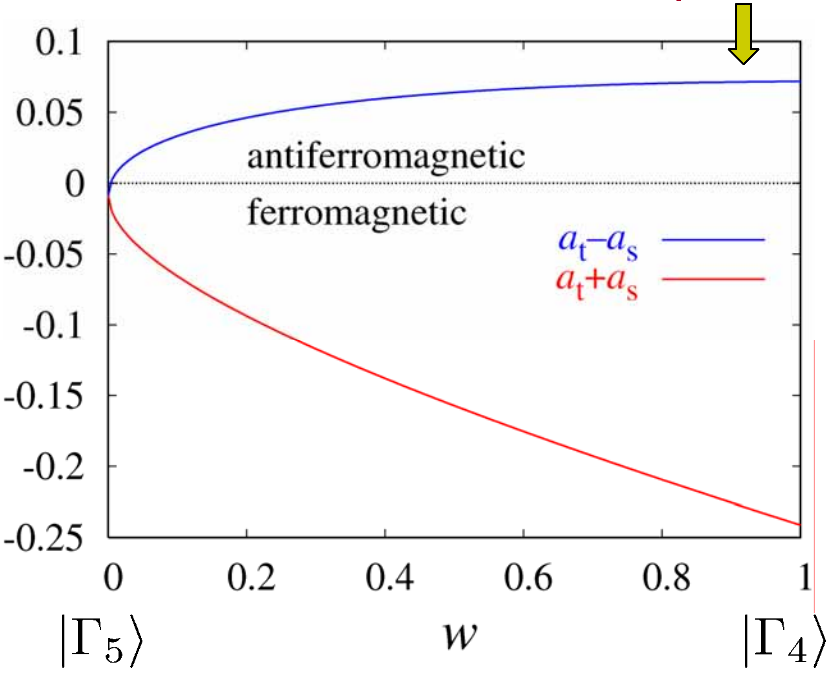
$$H_\mathrm{hyb} = V_{2u}\sum_\sigma f_\sigma^\dagger c_\sigma + \mathrm{h.c.}$$

$$J_1 = (a_\mathrm{t} + a_\mathrm{s})V_{2u}^2/\Delta$$

$$J_2 = (a_\mathrm{t} - a_\mathrm{s})V_{2u}^2/\Delta$$

$$(1/\Delta = 1/\Delta_1 + 1/\Delta_3)$$

Kondo effect can take place!

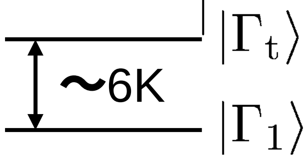


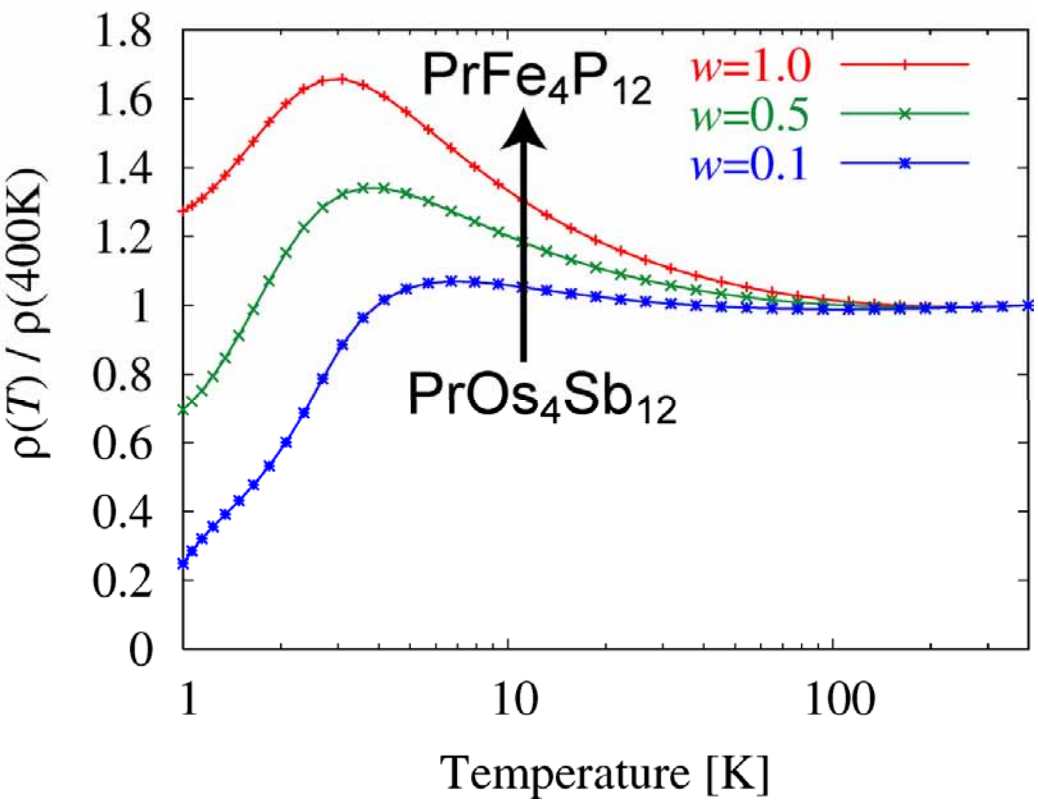
Small coupling constants in the case of Γ_1-Γ_5
Large antiferro-coupling in the case of Γ_1-Γ_4

Resistivity in the CEF pseudo-quartet model by the Non-Crossing App. (NCA) …Otsuki

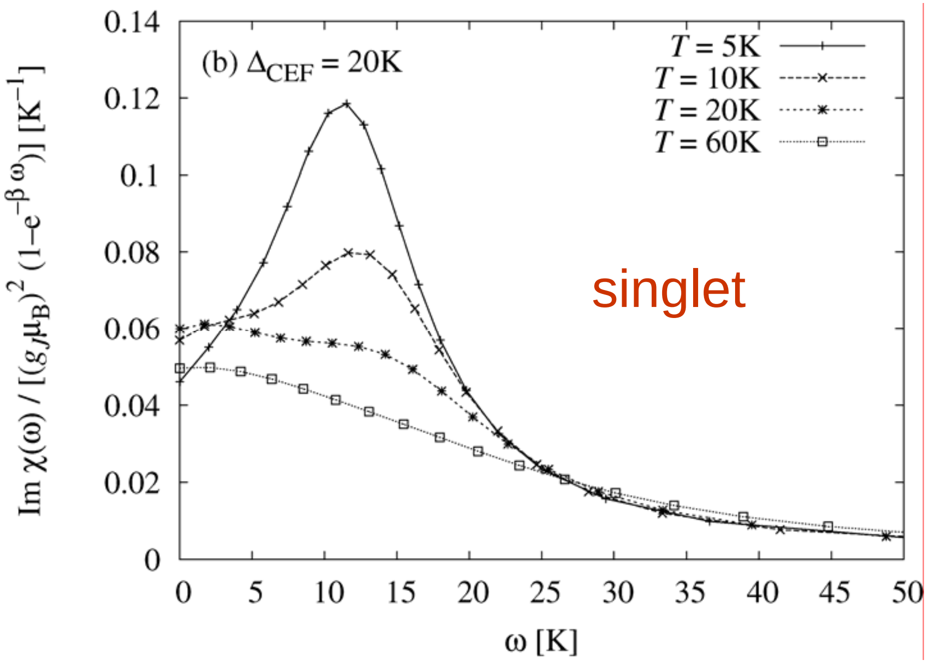
$$H_{\mathrm{int}} = \left(I_{\mathrm{t}} \boldsymbol{X}^{\mathrm{t}} + I_{\mathrm{s}} \boldsymbol{X}^{\mathrm{s}}\right) \cdot \boldsymbol{s}_c$$

$$|\Gamma_{\mathrm{t}}, m\rangle = \sqrt{w}|\Gamma_4, m\rangle + \sqrt{1-w}|\Gamma_5, m\rangle$$





Neutron scattering spectrum in the singlet-triplet model by the NCA (Otsuki)



$$J_1\rho_c = 0.2,\ \ J_2\rho_c = 0,\ \ \Delta_{\rm CEF} = 20{\rm K}$$

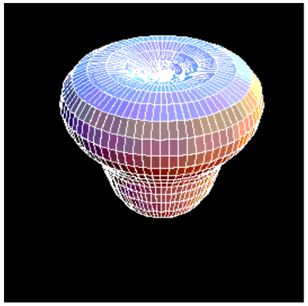
$T \gtrsim \Delta_{\rm CEF}$:

Only quasi-elastic peak

$T \lesssim \Delta_{\rm CEF}$:

Inelastic peak develops as temperature decreases.

Summary and outlook



- Octupoles can order without dipole order in $Ce_{1-x}La_xB_6$
  - theoretical prediction & exp. confirmation provided
- Peculiar magnetic correlation in RB_2C_2 probed by neutron scattering
  - to be explained in terms of the Kohn anomaly
- Anomalous local excitation and distortion in Pr skutterudites by p-f hybridization
  - to be further developed by experiment+theory cooperation