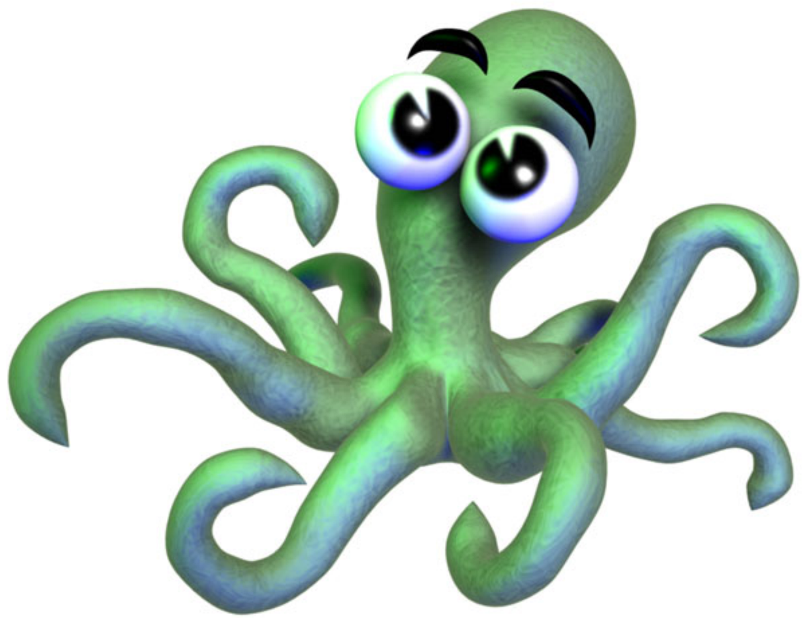
Electronic Higher Multipoles in Solids



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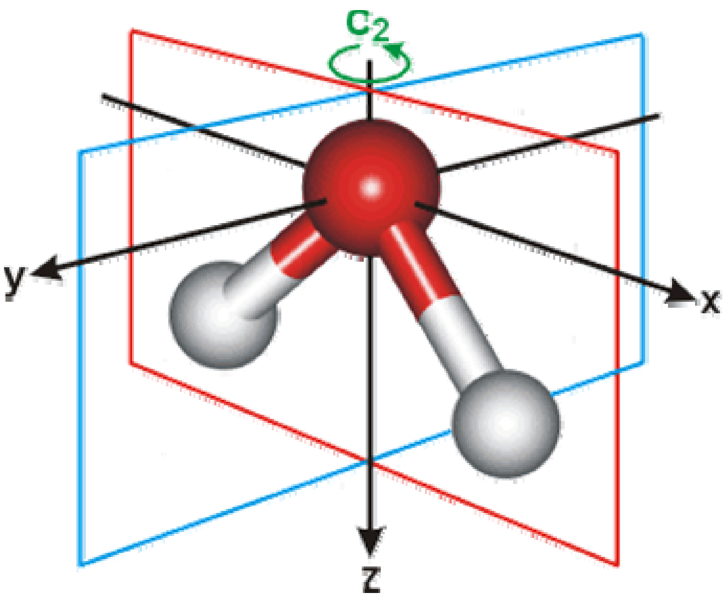
Outline

- Elementary examples of multiple moments
- Role of multipole moments in solids
- Case studies
  - octupole order in $Ce_{1-x}La_xB_6$ (Kramers $4f^1$)
  - scalar order in Pr skutterudites (non-Kramers $4f^2$)
- Mysterious order in $SmRu_4P_{12}$ (Kramers $4f^5$ =>octupole?)
- Summary

Electric dipole (O_2) and electric octupole (CH_4)



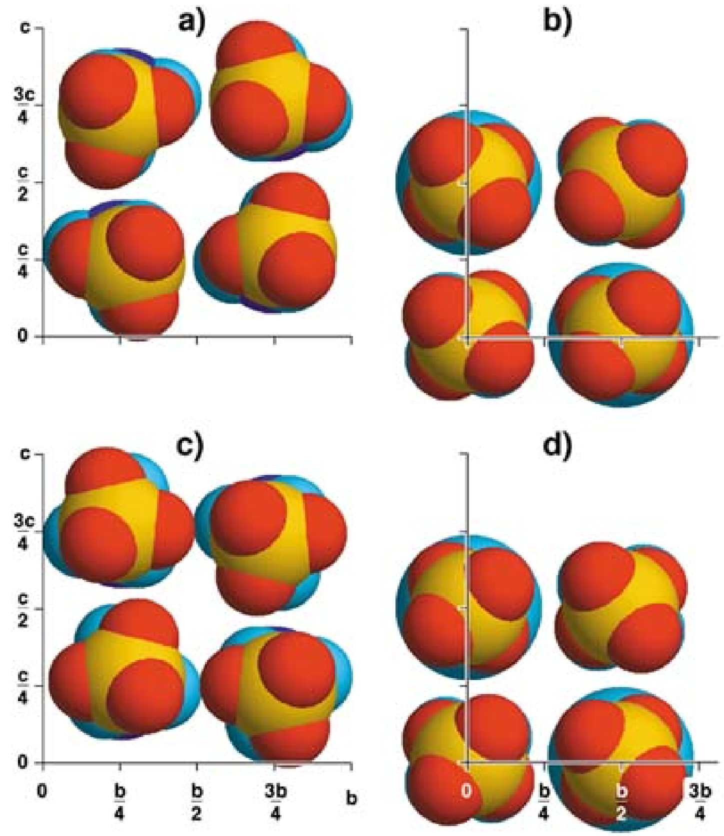
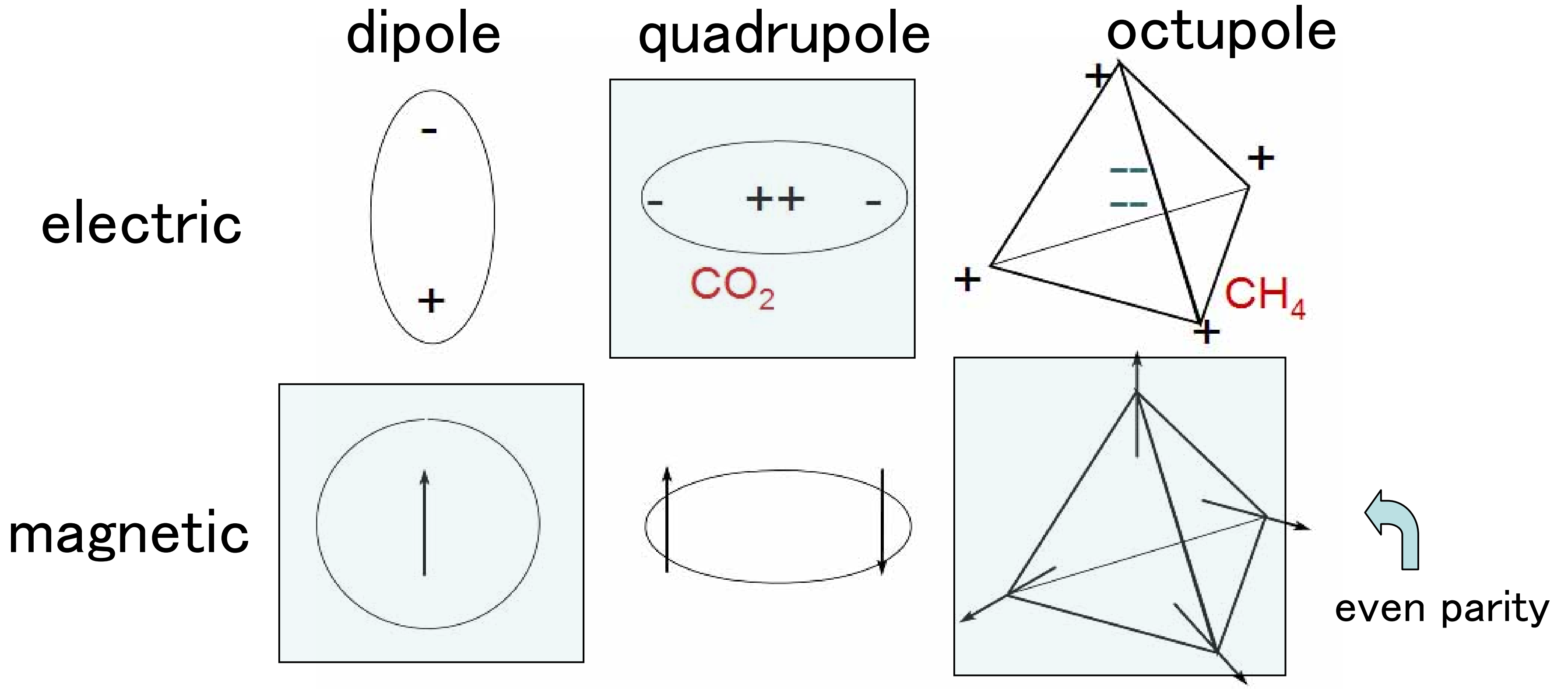


Figure 1: Arrangement of the methane molecules in the b–c–plane of the Cmca space group of phase III. a) and c) show cuts through the planes at x = 0, 1/2 with m molecules, b) and d) represent planes x = 1/4, 1/2 with 2–site molecules. The underlying blue colour represents orientations in phase II (measurements at hrpd, isis).

Multipole moments



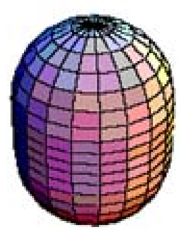
Electronic state with ang.mom. J => multipoles up to rank $2J$

Large spin-orbit coupling in f-electron systems => $J \gg 1$ possible

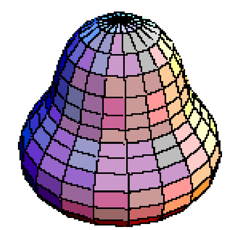
Multipole oscillations: $\cos^n\theta$

monopole （n=0）

dipole （n=1）



quadrupole （n=2）



octupole （n=3）

popular in nuclear physics => http://walet.phy.umist.ac.uk/P615/

Hidden orders in solids

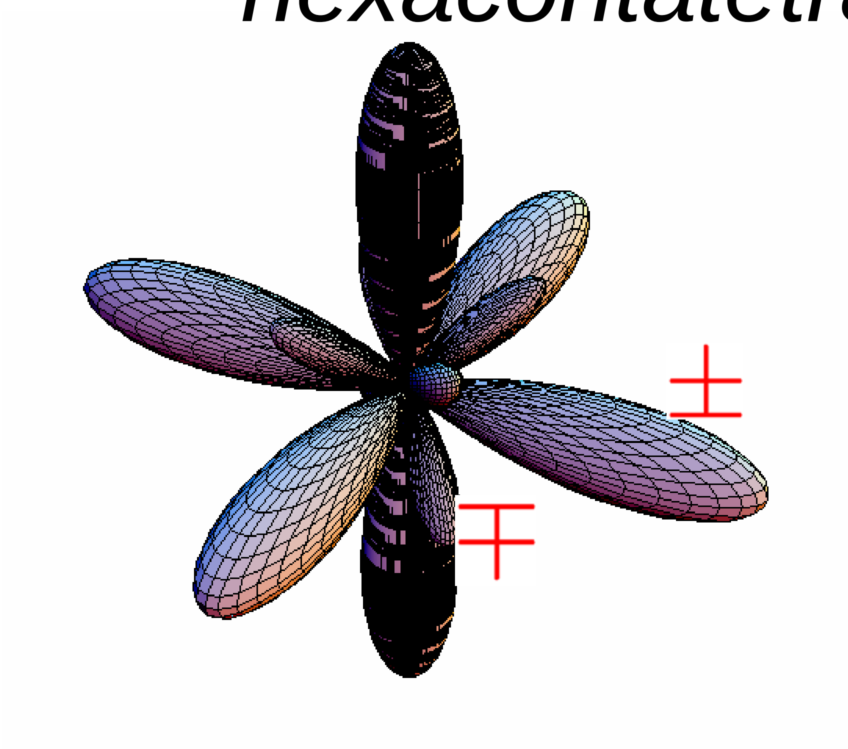
- dependent on the stage of development

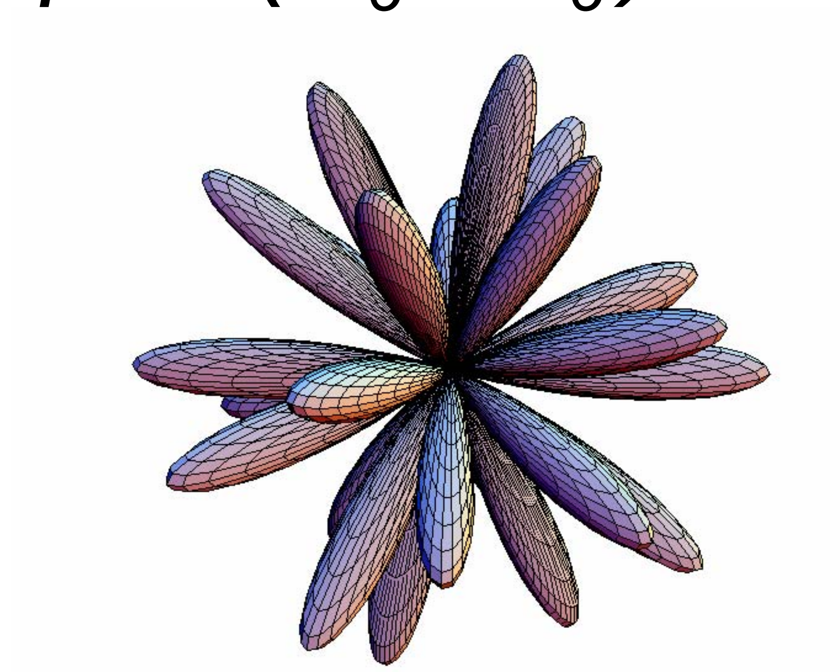
- antiferromagnetism (Neel, 1936)
- antiferroelectricity
- multipoles $2^n = 2,4,8,16,32,64,\ldots$
  - n=2 (quadrupole)
  - n=3 (octupole) octopus
  - n=4（hexadecapole)
  - n=5 (triakontadipole)
  - n=6 (hexacontatetrapole)

Special multipoles
=> scalar in point group

hexadecapole (O_4)

hexacontatetrapole (O_6^c, O_6^t)





$O_4 \propto x^4+y^4+z^4-3r^4/5$

$O_6^t \propto (x^2-y^2)(y^2-z^2)(z^2-x^2)$

Role of higher multipoles of localized electrons

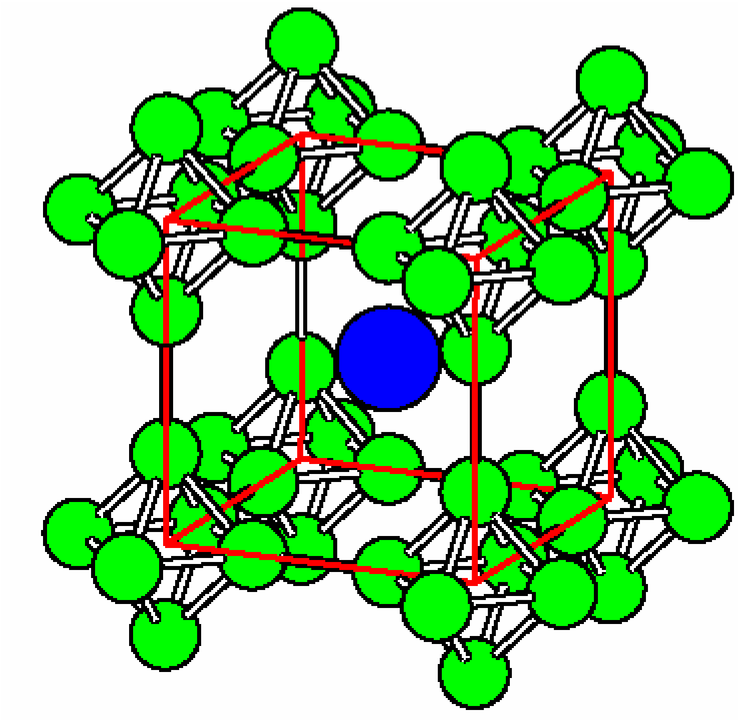
- Leading to unusual magnetism, elastic anomaly…
- Strong spin-orbit interaction + discrete symmetry
  - Mixing of multipoles with different ranks (x => J_x)
    e.g., Γ_{5g}: *xy, yz, zx* with
    $xy(7z^2-1), yz(7x^2-1), zx(7y^2-1)$
  - Coupling to crystalline lattice

diffraction from superlattice?

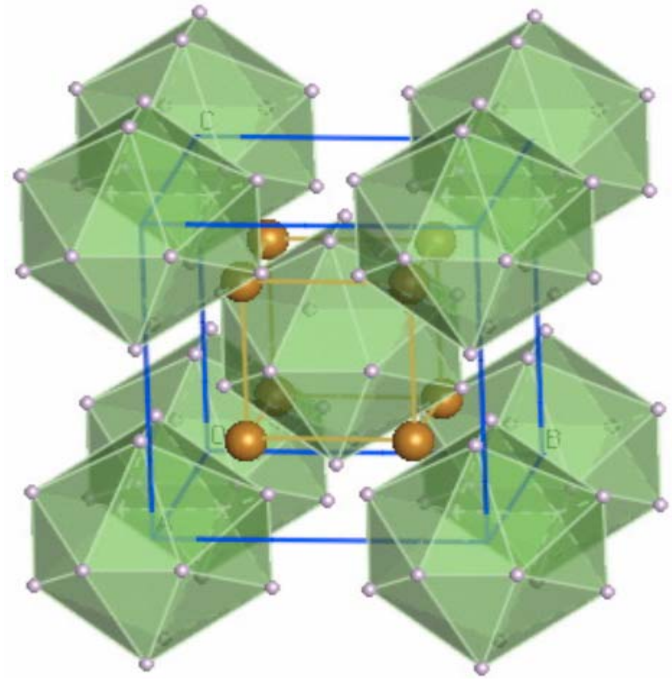
=> resonant X-ray scattering (2005),

neutron scattering (2007) in $Ce_{0.7}La_{0.3}B_6$

Clathrate structures



RB_6 (R=La, Ce, Pr,…)



R skutterudite: RT_4X_{12}

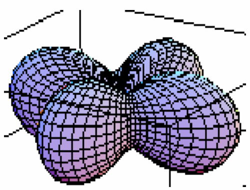
Ce $4f^1$ under cubic crystal field

$J=5/2 \Rightarrow \Gamma_7$ (2 fold)+ Γ_8 (4 fold)

Γ_8 wave functions with $J = L - S = 5/2$

"+" orbital

↑↓



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

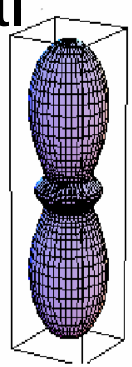
$$|+,\downarrow\rangle = \sqrt{\frac{5}{6}}|-\frac{5}{2}\rangle + \sqrt{\frac{1}{6}}|+\frac{3}{2}\rangle$$

$$|-,\uparrow\rangle = |+\frac{1}{2}\rangle$$

"-" orbital

$$|-,\downarrow\rangle = |-\frac{1}{2}\rangle = \sigma_x|-,\uparrow\rangle = \tau_x|+,\downarrow\rangle$$

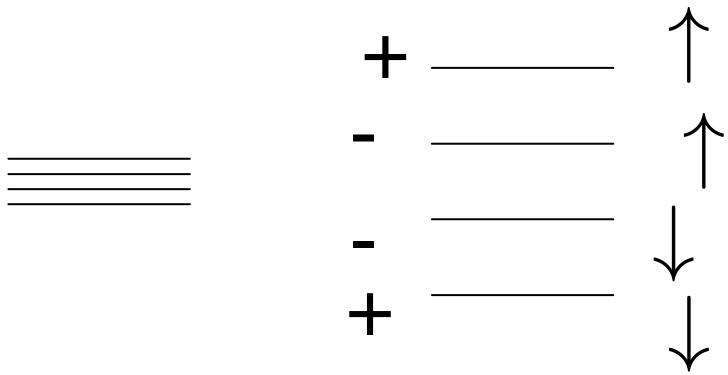
↑↓



$$\sigma_\alpha, \tau_\alpha : \text{pseudo spins}$$

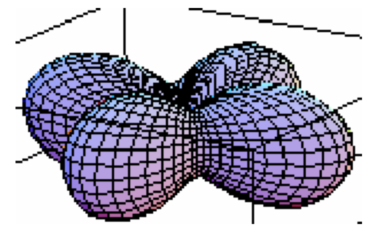
Splitting of Γ_8 level

- Magnetic field (H_z)

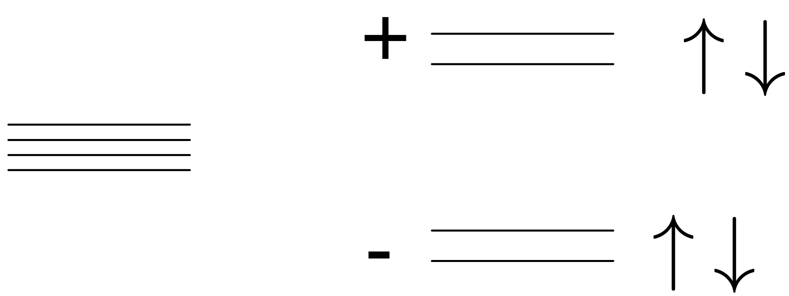


"+" orbital

↑↓

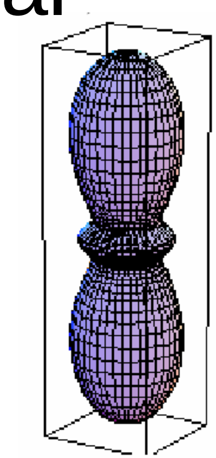


- Quadrupole field (O_2^0)



"-" orbital

↑↓



Examples of multipole operators

Quadrupole operators (time reversal: even)

$$O_{xy} = \sqrt{3} J_x J_y = \tau^y \sigma^z$$

$$O_2^0 = \frac{1}{2}(2J_z^2 - J_x^2 - J_y^2) = 4\tau^z$$

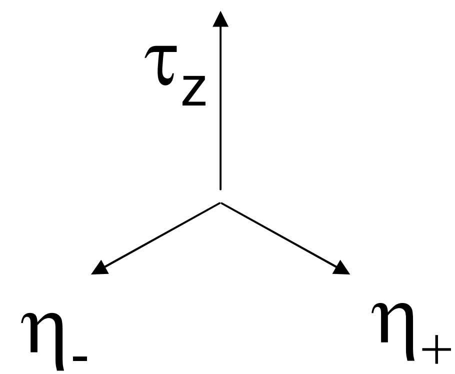
Octupole operators (time reversal: odd)

$$T^{2u} = \sqrt{15} J_x J_y J_z = \tau^y$$

$$T_z^{5u} = \frac{\sqrt{15}}{2} J_z (J_x^2 - J_y^2) = \tau^x \sigma^z$$

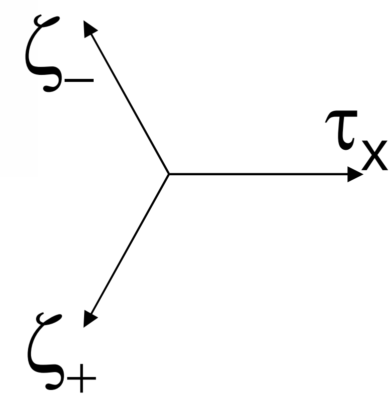
Table I. The multipole operators in the Γ_8 subspace.

A	Γ	symmetry	X^A
1	$2u$	$\sqrt{15}xyz$	τ^y
2	$3g$	$(3z^2-r^2)/2$	τ^z
3		$\sqrt{3}(x^2-y^2)/2$	τ^x
4	$4u1$	x	σ^x
5		y	σ^y
6		z	σ^z
7	$4u2$	$x(5x^2-3r^2)/2$	$\eta^+\sigma^x$
8		$y(5y^2-3r^2)/2$	$\eta^-\sigma^y$
9		$z(5z^2-3r^2)/2$	$\tau^z\sigma^z$
10	$5u$	$\sqrt{15}x(y^2-z^2)/2$	$\zeta^+\sigma^x$
11		$\sqrt{15}y(z^2-x^2)/2$	$\zeta^-\sigma^y$
12		$\sqrt{15}z(x^2-y^2)/2$	$\tau^x\sigma^z$
13	$5g$	$\sqrt{3}yz$	$\tau^y\sigma^x$
14		$\sqrt{3}zx$	$\tau^y\sigma^y$
15		$\sqrt{3}xy$	$\tau^y\sigma^z$

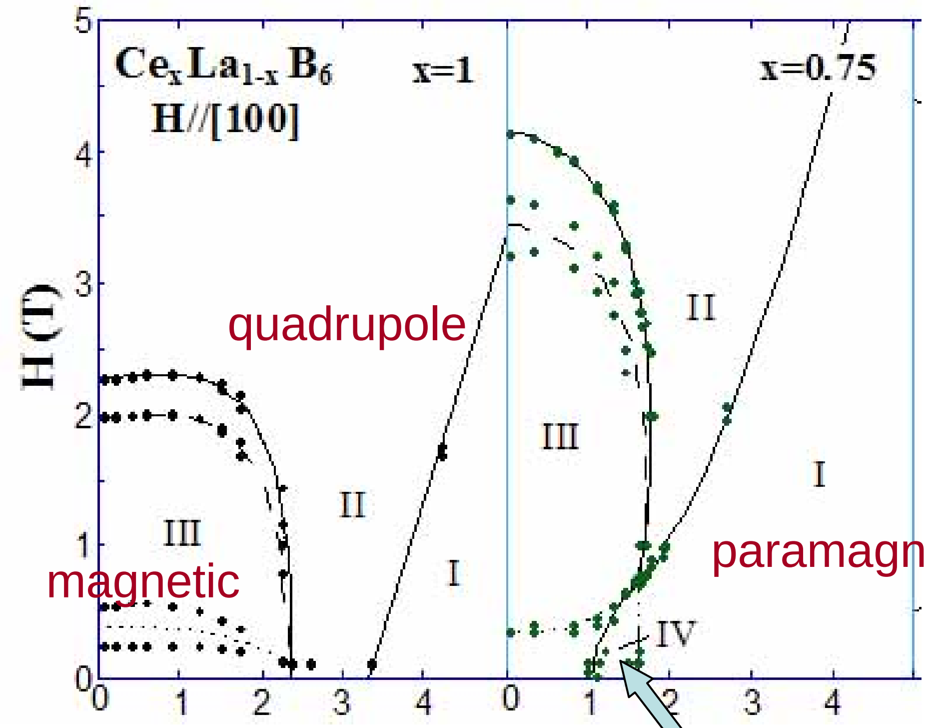


$$\eta^{\pm} = \frac{1}{2}(\pm\sqrt{3}\tau^x - \tau^z),$$

$$\zeta^{\pm} = -\frac{1}{2}(\tau^x \pm \sqrt{3}\tau^z).$$



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



Tayama *et al.* JPSJ (1997)

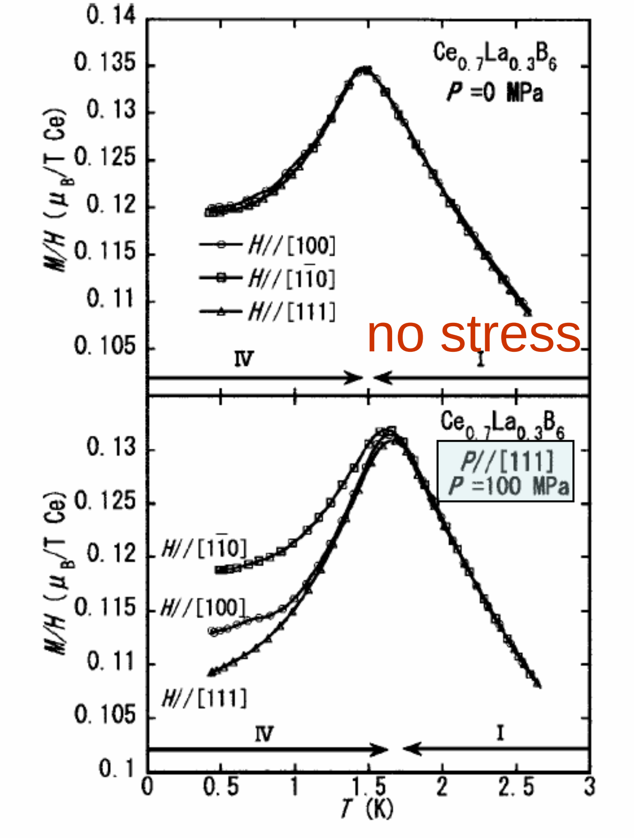
- No magnetic order by neutrons
- NMR and μSR detect internal fields
- Gigantic elastic anomaly and slight lattice distortion

octupole order?

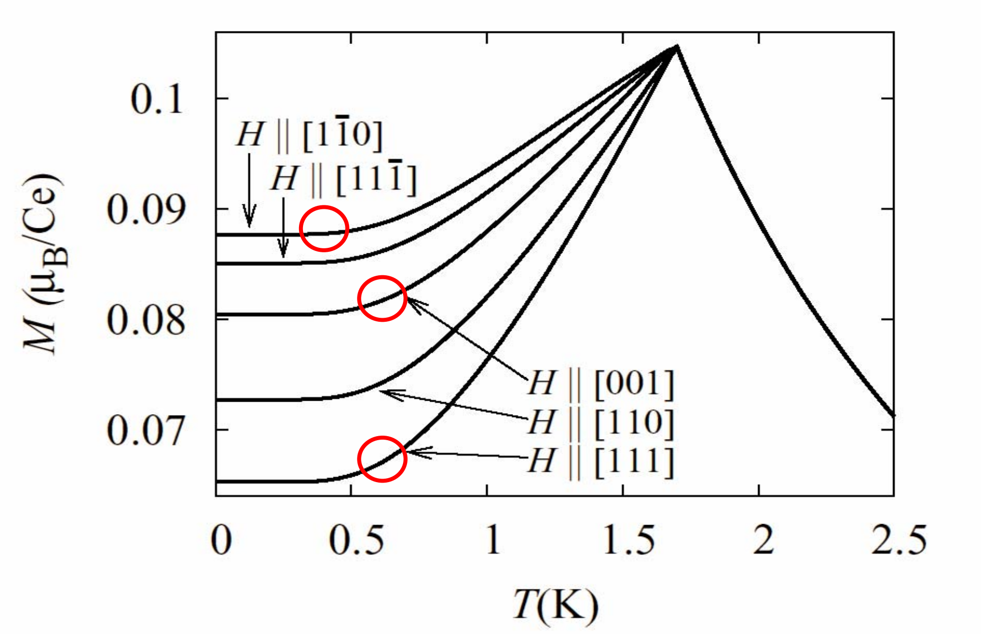
(Kuramoto, Kusunose, Kubo: '00-)

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

Magnetization (Exp.)



Theoretical (mean-field) prediction



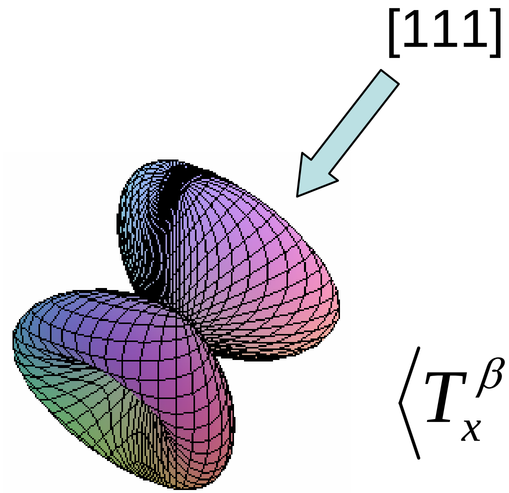
Single octupole domain under uniaxial stress along [111]

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

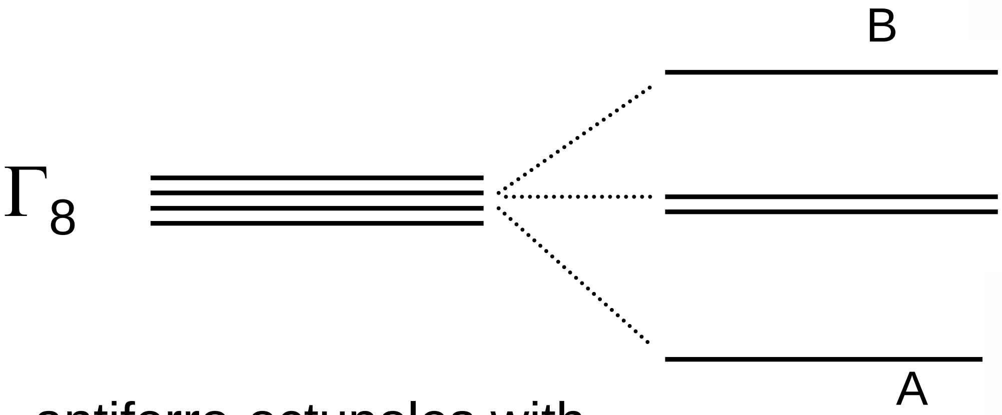
Experiment: T. Morie *et al*.: J. Phys. Soc. Jpn. **73** (2004) 2381.

Broken T-reversal and broken orbital degeneracy in $Ce_{0.7}La_{0.3}B_6$

$T_x^{\beta} + T_y^{\beta} + T_z^{\beta}$ octupolar field



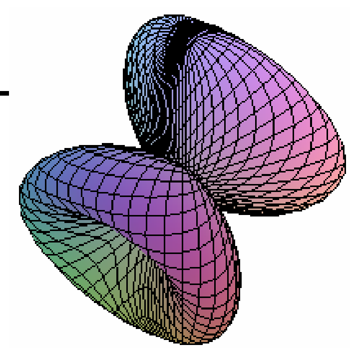
$\langle T_x^{\beta} + T_y^{\beta} + T_z^{\beta} \rangle$



$3\sqrt{2}$

0

$-3\sqrt{2}$



antiferro-octupoles with
A,B sublattices =>
ferro-quadrupoles =>
(0,0,0) lattice distortion (Goto) +
(1/2,1/2,1/2) Bragg peak (Mannix)

Resonant X-ray scattering (RXS)

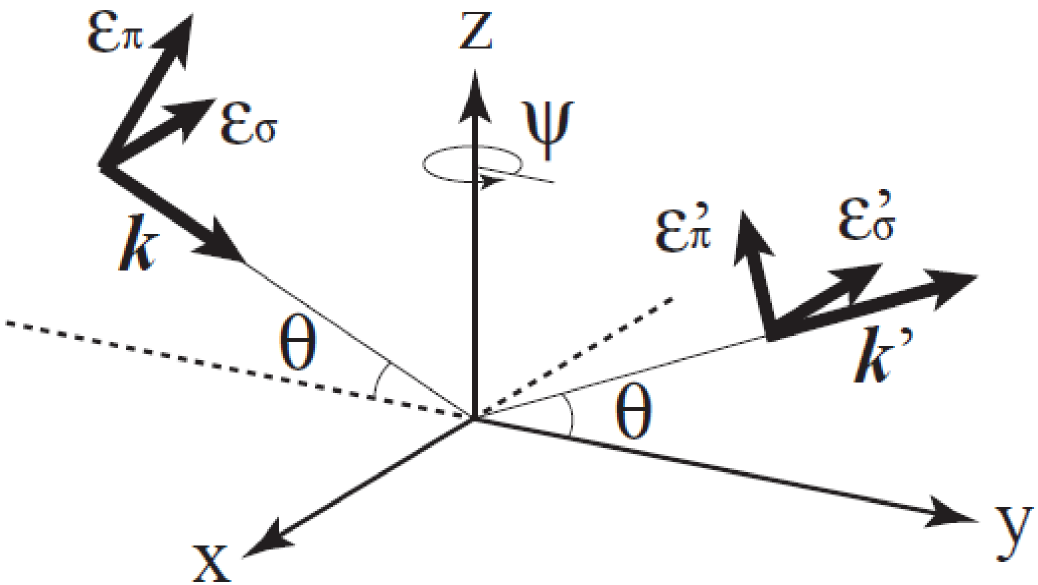


Fig. 1. The coordinate system corresponding to the RXS experiment. The azimuthal angle ψ dependence is obtained by rotating the $\boldsymbol{r} = (x, y, z)$ coordinate system around the z axis relative to the photon $\boldsymbol{k}$ vector, i.e., $\boldsymbol{k}$ is in the yz plane at $\psi = 0$. The σ and π polarization vectors are also shown ($\boldsymbol{\epsilon}_\sigma \times \boldsymbol{\epsilon}_\pi = \boldsymbol{k}/|\boldsymbol{k}|$).

Scattering amplitude in RXS

$$F_{\mathrm{reso}} = -\frac{\Delta^2}{\hbar^2 c^2} \sum_m \frac{W_{fi}^{(m)}}{\hbar\omega - \Delta + i\Gamma/2},$$

$$W_{fi}^{(m)} = \langle f|\boldsymbol{\epsilon}' \cdot \boldsymbol{P}|m\rangle\langle m|\boldsymbol{\epsilon} \cdot \boldsymbol{P}|i\rangle$$ E1: dipole

$$+\langle f|\mathrm{Tr}(\hat{X}' \cdot \hat{Q})|m\rangle\langle m|\mathrm{Tr}(\hat{X} \cdot \hat{Q}|i\rangle,$$ E2: quadrupole

Detectable up to hexadecapoles by E2 scattering

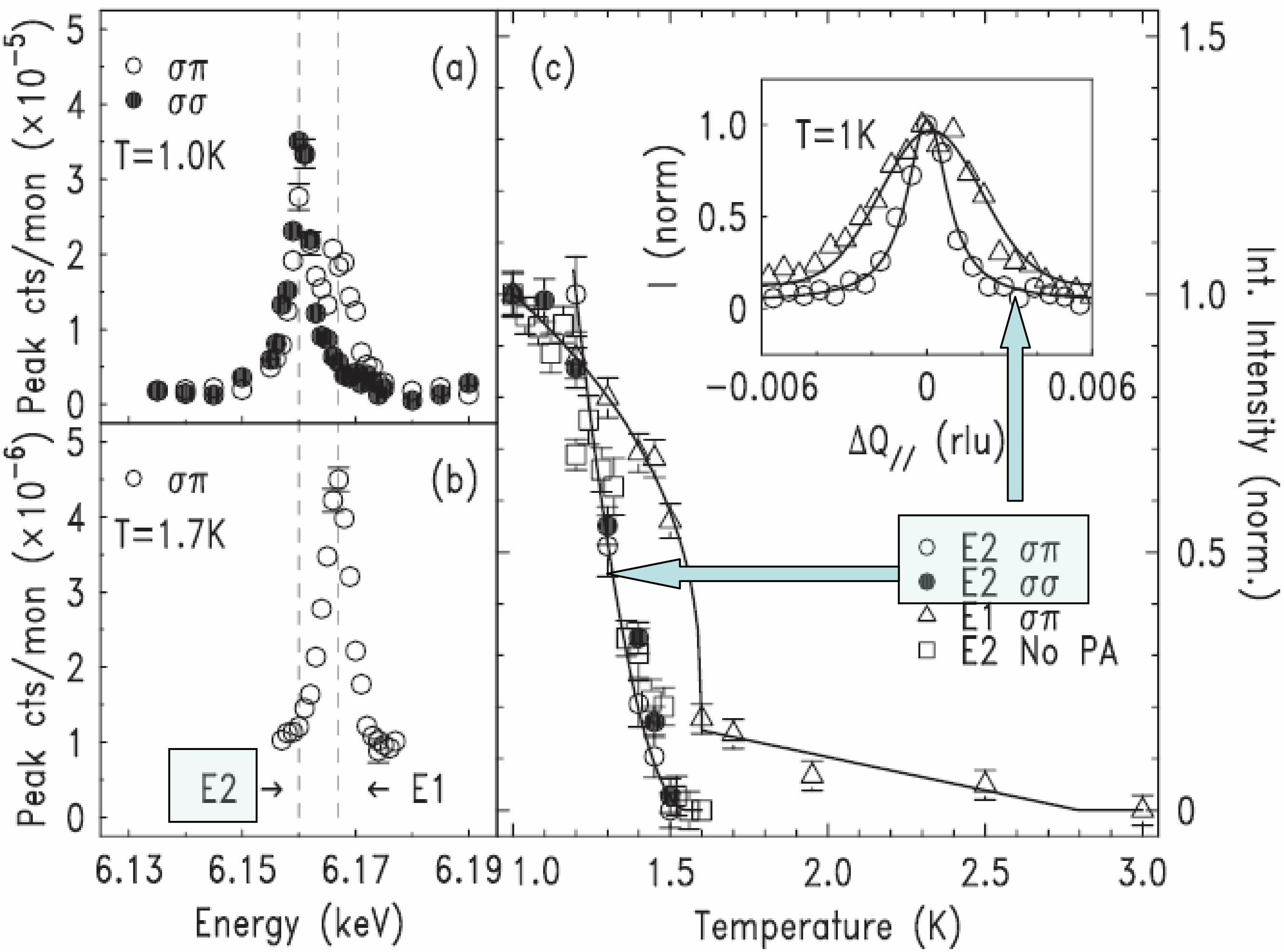
Approximation: energy levels for intermediate states *m* are all represented by Δ.

⇒ Irreducible tensor technique is applicable

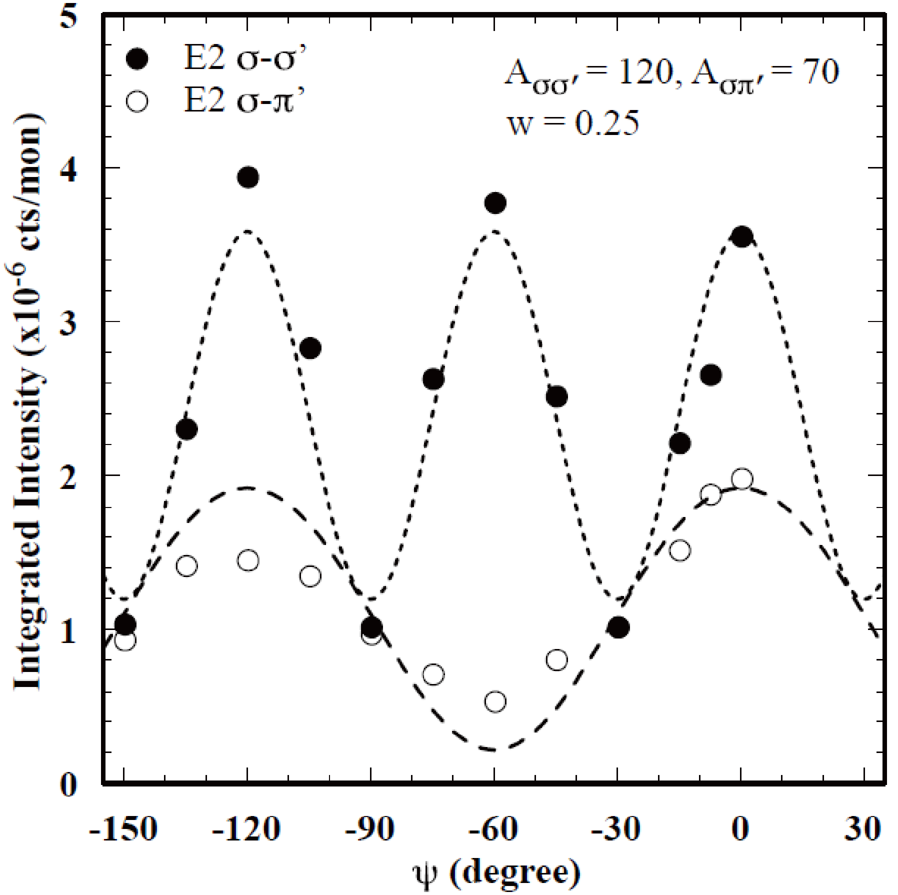
(S.W. Lovesey et al: Physics Reports 411 (2005) 233.)

Resonant X-ray scatt. on $Ce_{0.7}La_{0.3}B_6$ (D. Mannix et al. PRL'05)

All data were taken at $(\frac{3}{2}\,\frac{3}{2}\,\frac{3}{2})$ and azimuth $\Phi = 0°$.



Azimuthal scan around [111] of $Ce_{0.7}La_{0.3}B_6$



Experiment: D. Mannix et al.: Phys. Rev. Lett **95** (2005) 117206
Theory: H. Kusunose and Y.K: JPSJ, **74**, (2005) 3139

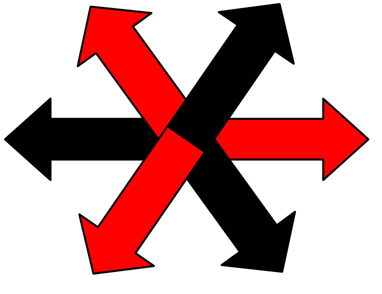
Contribution of four domains

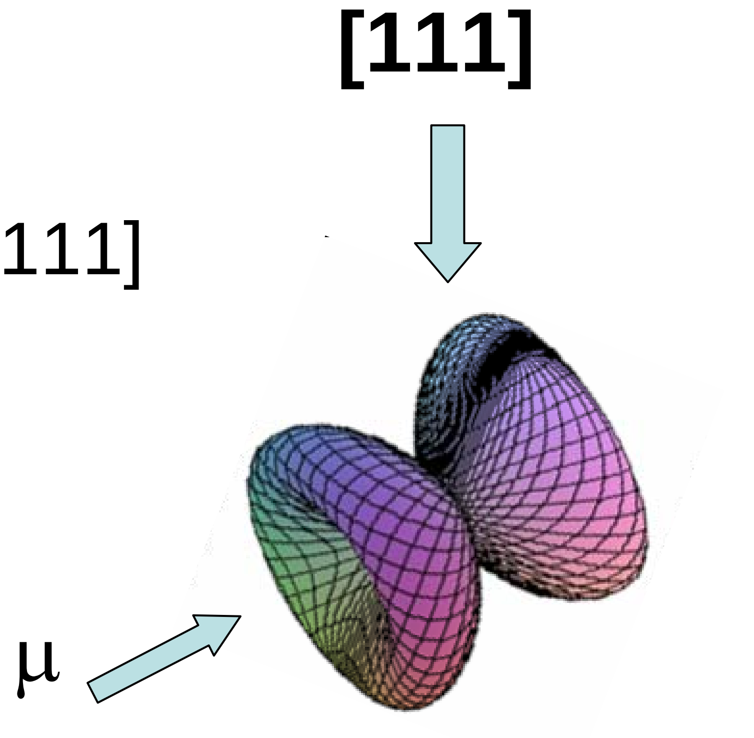
$$I_\alpha = A_\alpha \left[w |f_{5u}^{[111]}(\alpha)|^2 + \frac{1-w}{3} \sum_\mu |f_{5u}^{\mu}(\alpha)|^2 \right]$$

$\alpha = \sigma\sigma'$ or $\sigma\pi'$

μ=[-1,1,1], [1, -1,1], [1, 1,-1]

=> threefold pattern around [111] is possible.





Neutron scattering on $Ce_{0.7}La_{0.3}B_6$

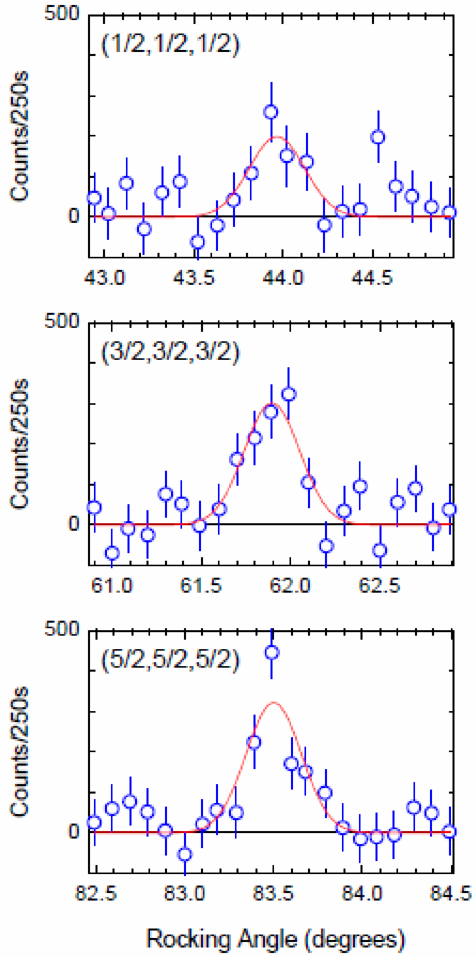


Fig. 2. (Color online) Difference diffraction patterns between 0.25 K and 2 K under a zero magnetic field at $\boldsymbol{\kappa} = (\frac{h}{2}, \frac{h}{2}, \frac{l}{2})$ along the [1,1,1] direction in $Ce_{0.7}La_{0.3}B_6$. The lines are Gaussian fits.

Kuwahara et al.: JPSJ 76 (2007) 093702

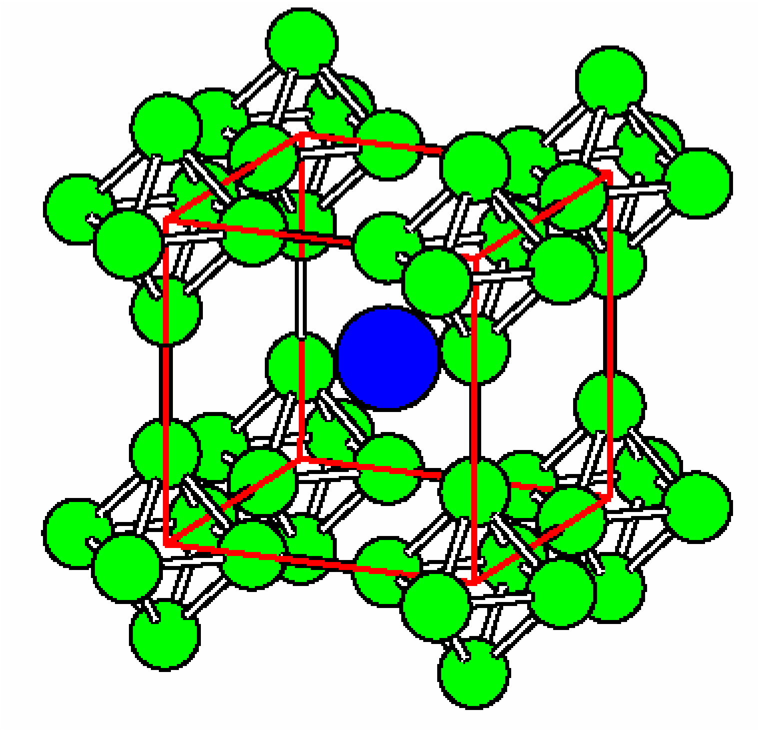
$$\int_{\text{cell}} d\mathbf{r}\mathbf{M}(\mathbf{r}) = 0$$

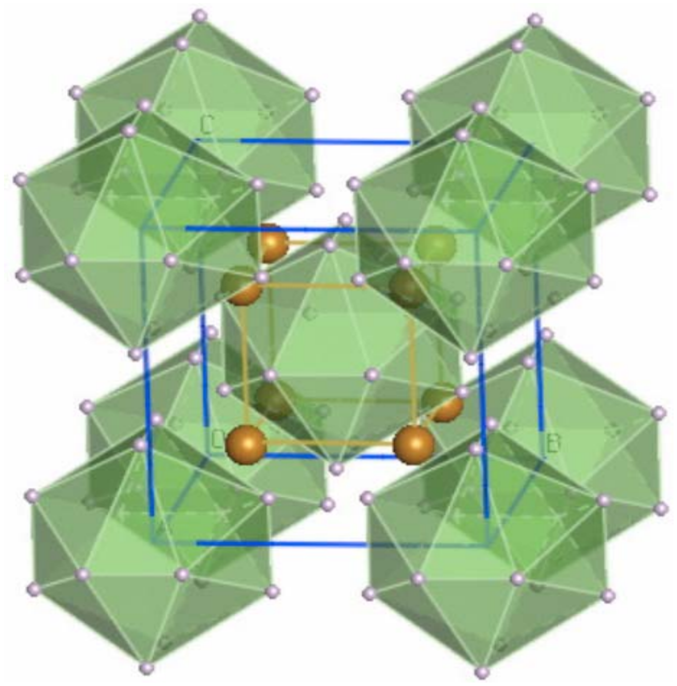
for each Ce site.

However, octupole gives

$$\int_{\text{cell}} d\mathbf{r}\mathbf{M}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} \neq 0$$

Clathrate structures



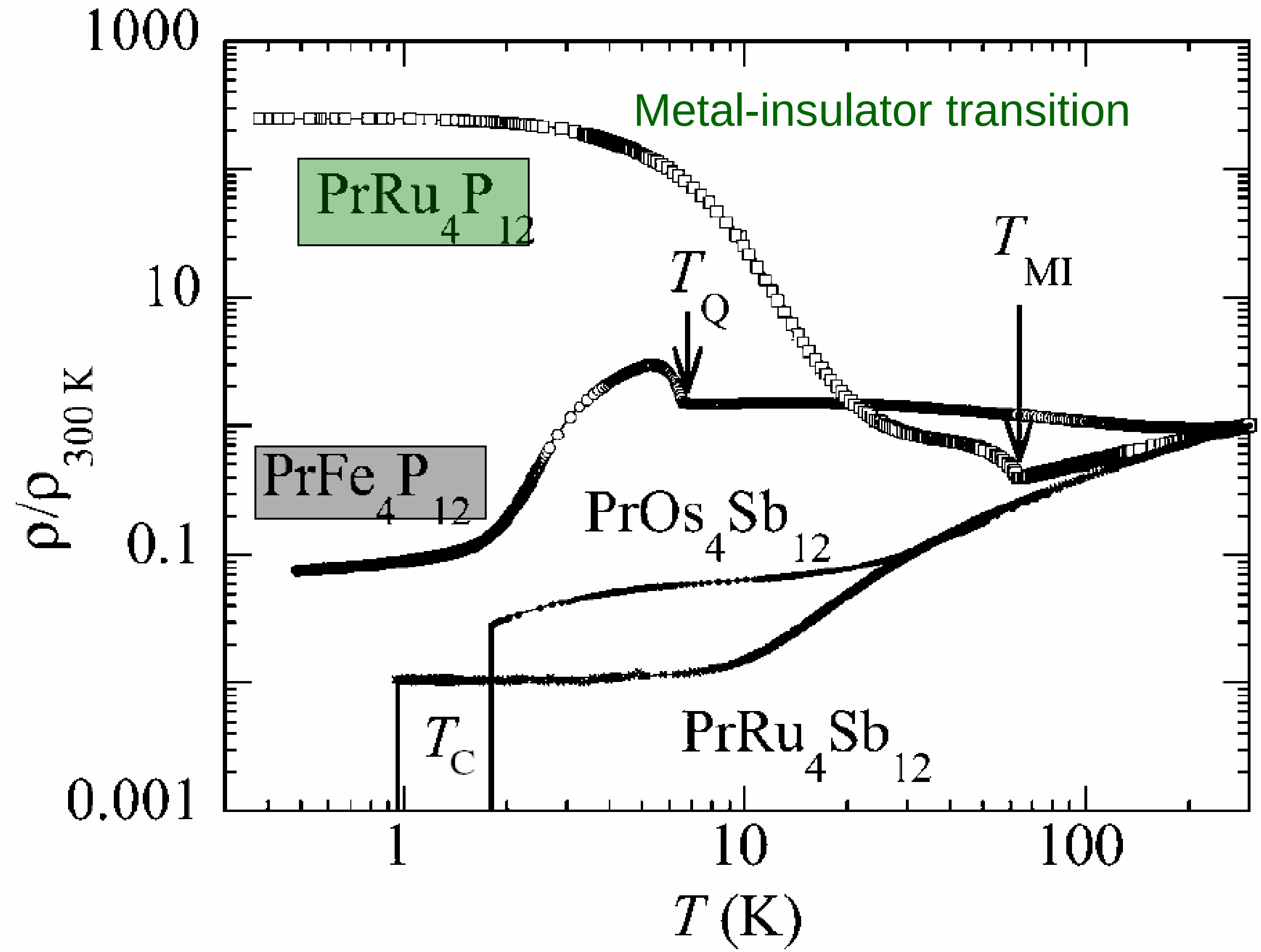


RB_6 (R=La, Ce, Pr,…)

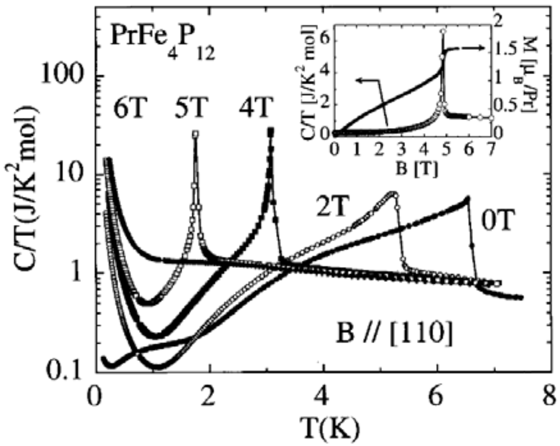
R skutterudite: RT_4X_{12}

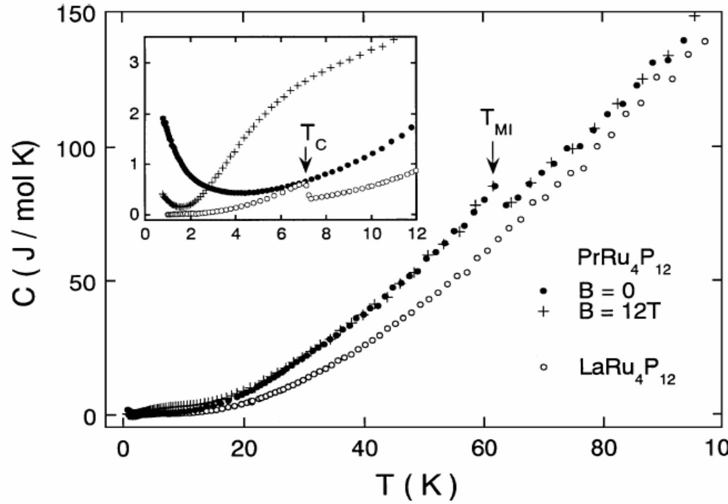
Resistivity $\rho(T)$ in Pr skutterudites

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

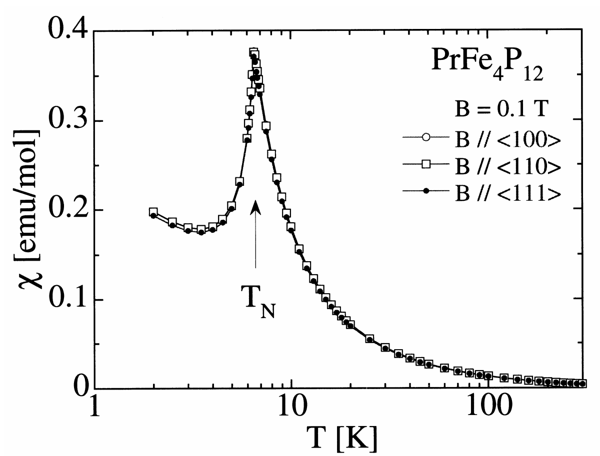


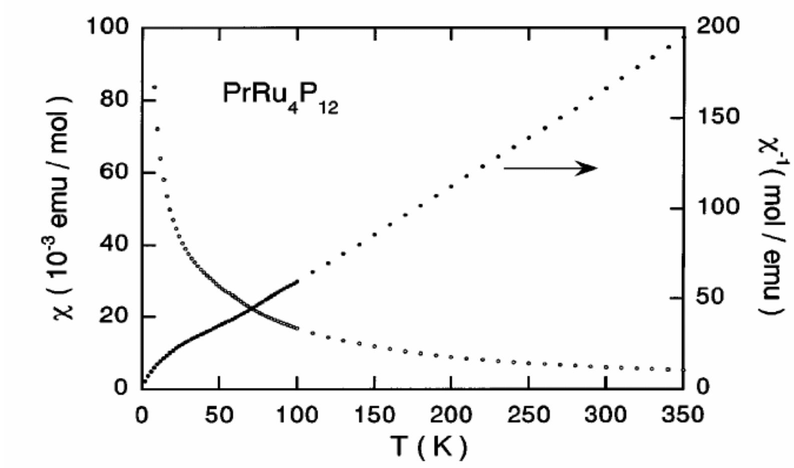
$PrFe_4P_{12}$ *vs* $PrRu_4P_{12}$





Isotropic χ below T_N

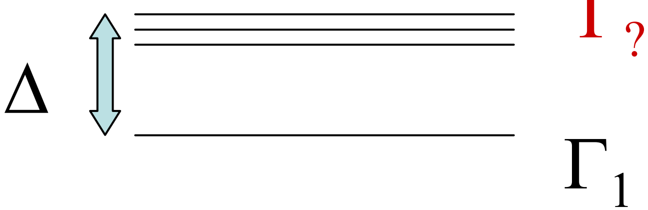




Aoki et al., Matsuda et al.,

Sekine et al.

Non-Kramers CEF levels ($4f^2$)



Γ_4 : dipole, Γ_5 : quadrupole

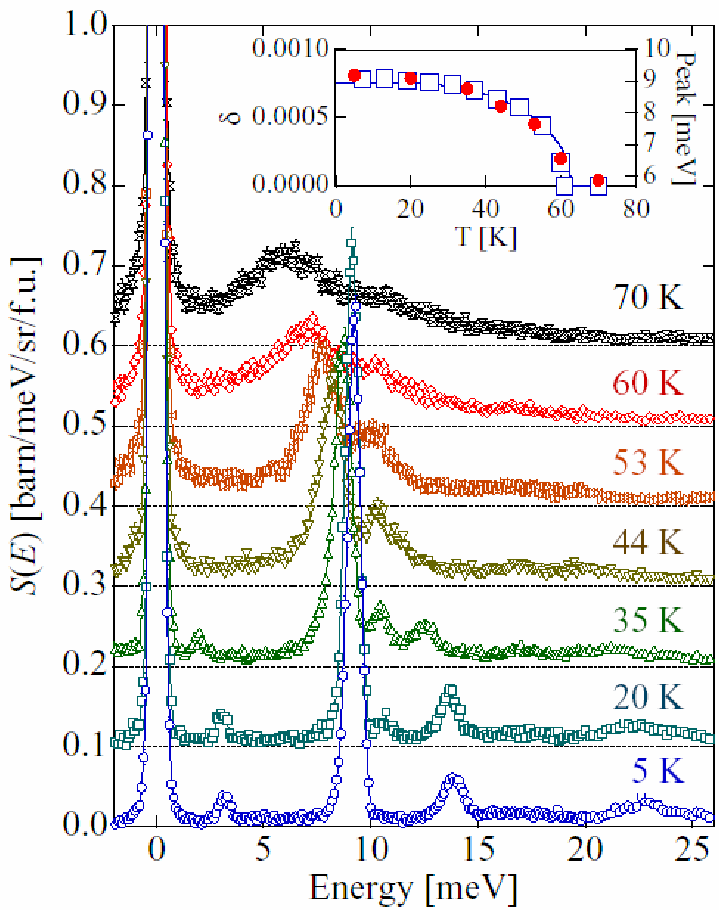
Γ_4 and Γ_5 mix in the T_h point group

$PrOs_4Sb_{12}$	$PrFe_4P_{12}$	$PrRu_4P_{12}$
$\Delta \sim 8K$	$\Delta \sim 0$	$\Delta(T > T_{MI}) \sim 80K$ $\Delta(Pr1) > 0$ $\Delta(Pr2) < 0$
$\Gamma_4^{(2)} \sim \Gamma_5$	$\Gamma_4^{(1)} \sim \Gamma_4$	$\Gamma_4^{(1)} + \Gamma_4^{(2)}$
$\Gamma_1 - \Gamma_5$: quadrupole	$\Gamma_1 - \Gamma_4$: dipole	
	$\Gamma_4 - \Gamma_4 \supset$ quadrupole, octupole	

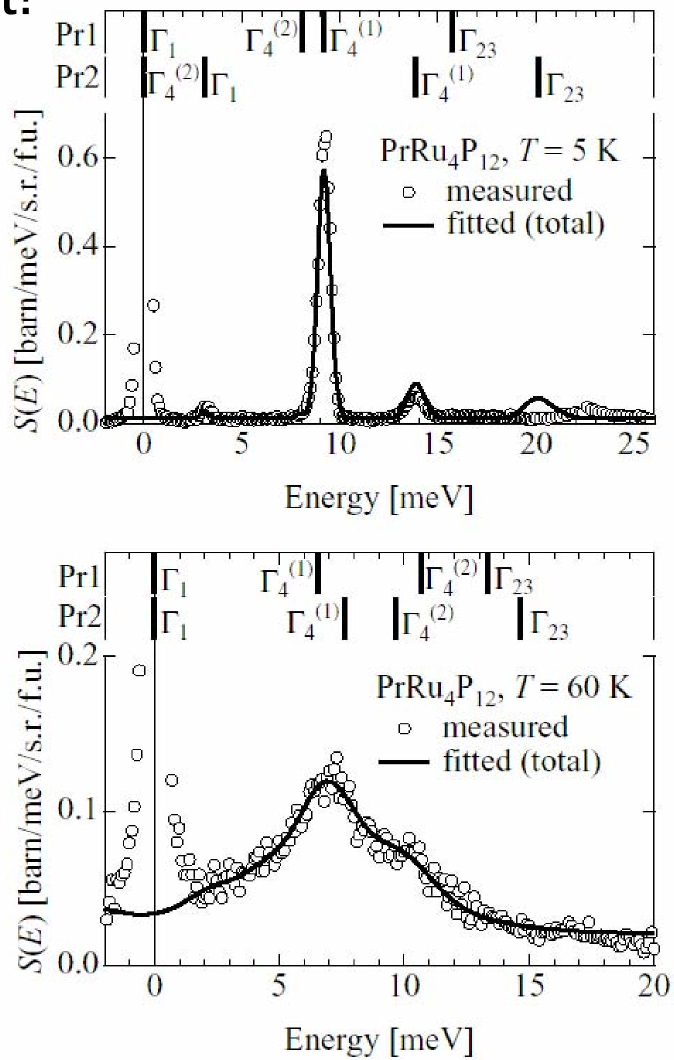
Neutron scattering of $PrRu_4P_{12}$

(Iwasa et al.: 2004)

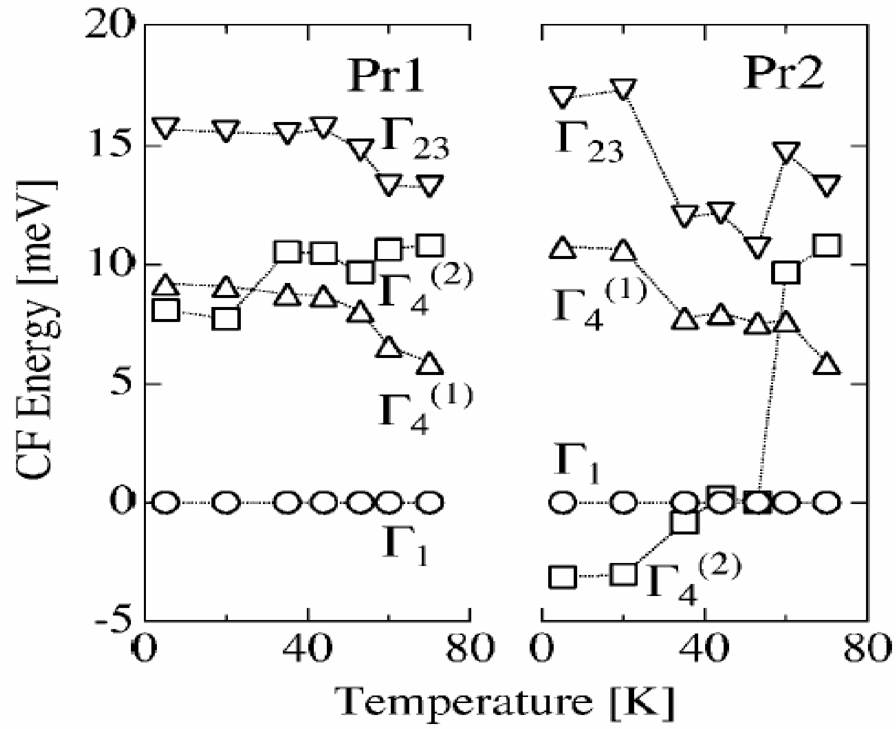
CEF: well-defined, but T-dependent!



Cubic symmetry is preserved.



T-dependent CEF splittings in $PrRu_4P_{12}$ for $T < T_{M\text{-}I}$=63K (Iwasa et al: '05)



=>Hexadecapole: $O_4=O_4^0+5O_4^4$ as the order parameter

Y.Kuramoto et al.: PTP suppl.('05)

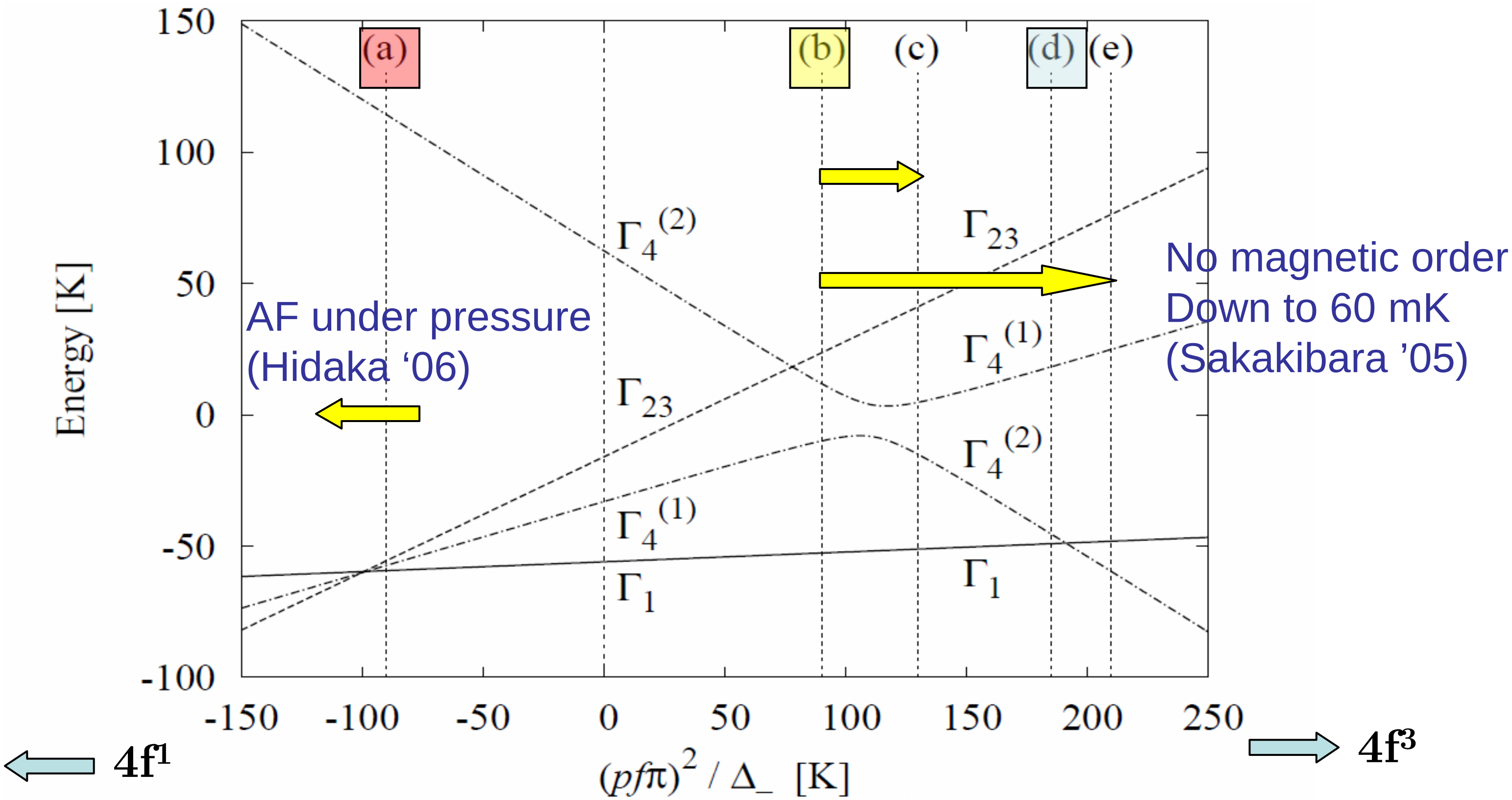
T.Takimoto: JPSJ (2006)

=>Hexacontatetrapole (O_6) can be mixed.

$$H_{\rm CEF} = W\left(xO_4 + |1-x|O_6^c + yO_6^t\right) = c_4^0 O_4 + c_{6c}^0 O_6^c + c_{6t}^0 O_6^t$$

scalar operators in T_h symmetry

Pr^{3+} ($4f^2$) CEF levels against effective hybridization strength



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

Fig. 1. CEF level structures derived from hybridization and point charge potential as a function of $(pf\pi)^2/\Delta_-$. The level sequence qualitatively corresponds to: (a) $PrFe_4P_{12}$; (b) $PrRu_4P_{12}$ in the high-temperature phase; (c) Pr1 site in $PrRu_4P_{12}$ in the low-temperature phase; (d) $PrOs_4Sb_{12}$; (e) Pr2 site in $PrRu_4P_{12}$ in the low-temperature phase. See text for details.

Y. Kuramoto et al.: Prog. Theor. Phys. Suppl. **160** (2005) 134.

Landau-type phenomenology

A. Kiss and Y.Kuramoto: JPSJ 75 (2006) 103704.

$$G = \frac{1}{2}a_s(T - T_0)\psi_Q^2 + \frac{1}{4}b\psi_Q^4 + \frac{1}{2}a_m(T - T_F)m^2 + \frac{1}{2}\lambda\psi_Q^2 m^2$$

where

ψ_Q: scalar order parameter (staggered)

m: magnetization

T_F: hypothetical Curie temperature $(= 3.5\text{K} < T_0 = 6.5\text{K})$

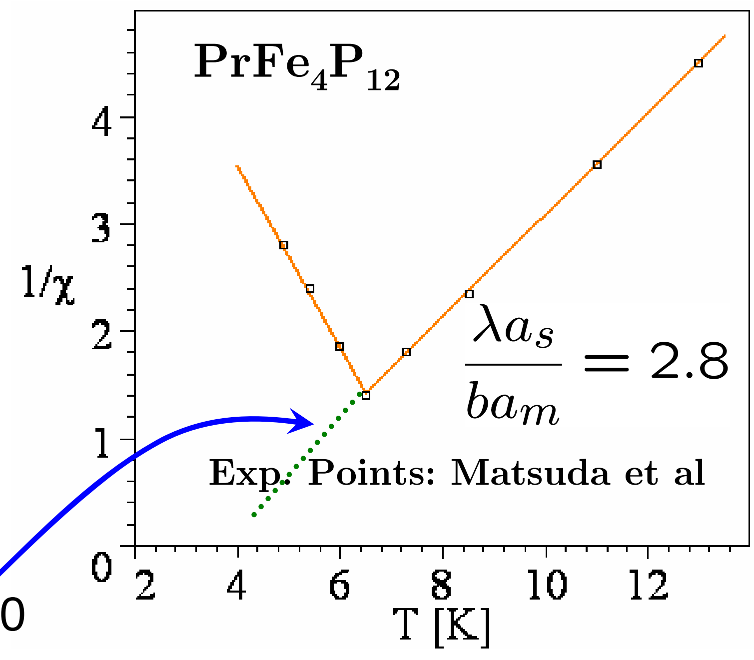
$$\chi^{-1} = \frac{\partial^2 G}{\partial m^2}$$

$T > T_0$,

$$\chi_+^{-1} = a_m(T - T_F)$$

$T < T_0$,

$$\chi_-^{-1} = \underline{(a_m - \lambda a_s/b)T} - a_m T_F + \lambda a_s T_0/b$$



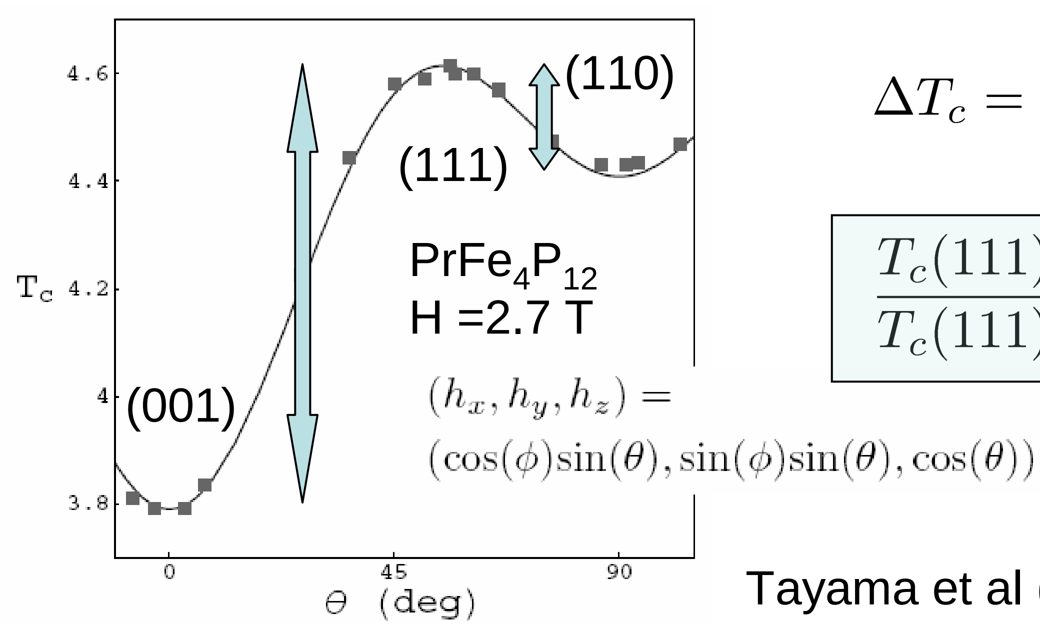
$\lambda \sim 0$

Anisotropy induced by a scalar order

Helmholtz free energy up to the lowest anisotropic term

$$\begin{aligned} F(\psi_Q, H) &= G(\psi_Q, m) - mH \\ &= \frac{1}{2}a_s(T - T_0)\psi_Q^2 + \frac{1}{4}b\psi_Q^4 - \frac{1}{2}\left(\frac{1}{\chi_+} + \lambda\psi_Q^2\right)^{-1} H^2 \\ &+ \gamma\psi_Q^2(H_x^4 + H_y^4 + H_z^4 - \frac{3}{5}H^4) + O(H^4) \end{aligned}$$

Field angle dependence of the transition temperature



$$\Delta T_c = -\frac{2\gamma}{a_s}\left(H_x^4 + H_y^4 + H_z^4 - \frac{3}{5}H^4\right)$$

$$\frac{T_c(111) - T_c(001)}{T_c(111) - T_c(110)} = 4, \quad (\gamma > 0)$$

Tayama et al ('06)

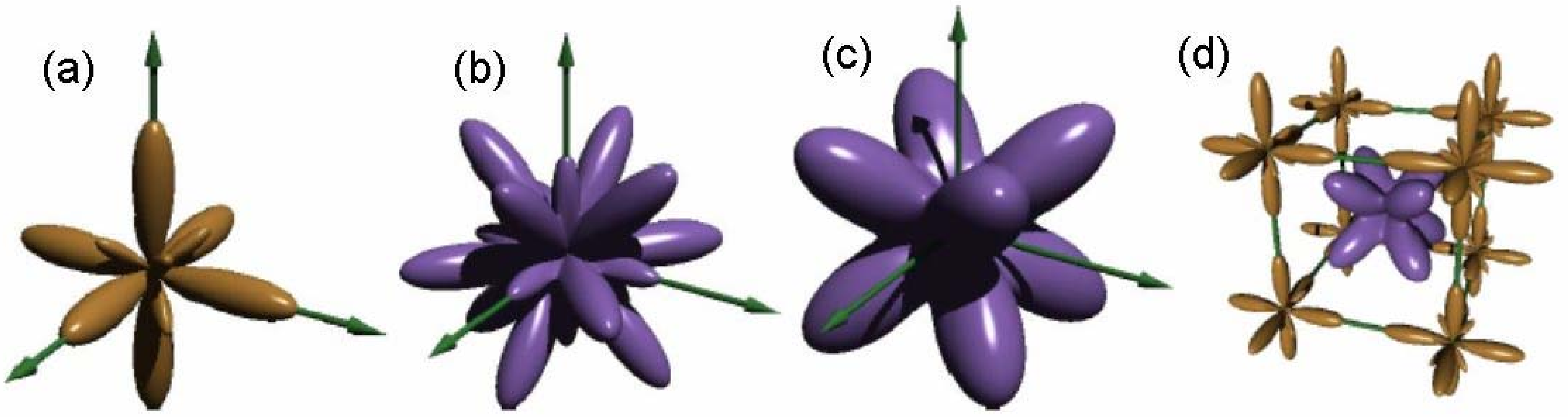
Universal ratio for scalar orders!

Other evidences in favor of the scalar order in $PrFe_4P_{12}$

- NMR spectra in the ordered phase show local cubic symmetry.
- Lattice distortion observed by neutron and X-ray does not show lower symmetry.
- Induced staggered moment is parallel or antiparallel to the magnetic field.

Scalar form factors

$$\int d\mathbf{r}\rho_{4f}(\mathbf{r}) = 2 \quad \text{for all sites}$$

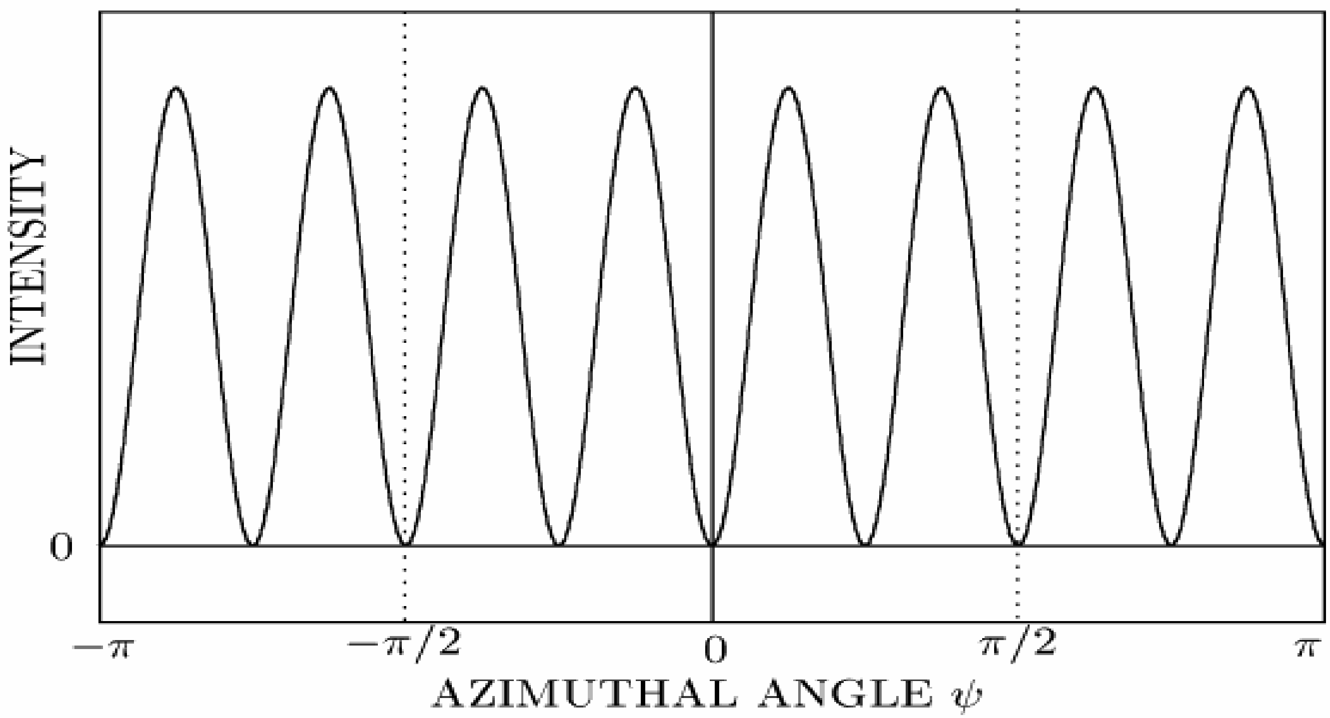


(a) Γ_1 singlet
(b) Γ_3 doublet
(c) Γ_5 triplet
(d) Staggered scalar order

Degeneracies in (b) and (c) should be lifted at $T = 0$ either by Kondo or distortion!

$\sigma-\pi'$ E2 superlattice scattering from hexadecapole $O_4^0+5O_4^4$

Around [001] axis: Intensity $\propto 2\sin^2 4\psi = 1-\cos 8\psi$



Outline

- Elementary examples of multiple moments
- Role of multipole moments in solids
- Case studies
  - octupole order in $Ce_{1-x}La_xB_6$ (Kramers $4f^1$)
  - scalar order in Pr skutterudites (non-Kramers $4f^2$)
- Mysterious order in $SmRu_4P_{12}$ (Kramers $4f^5$ =>octupole?)
- Summary

Enigmatic phase transitions in $SmRu_4P_{12}$

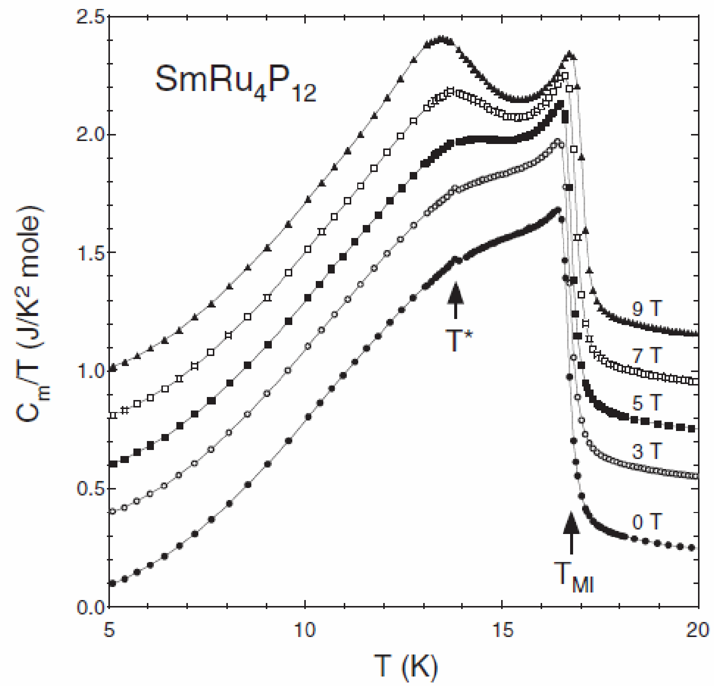
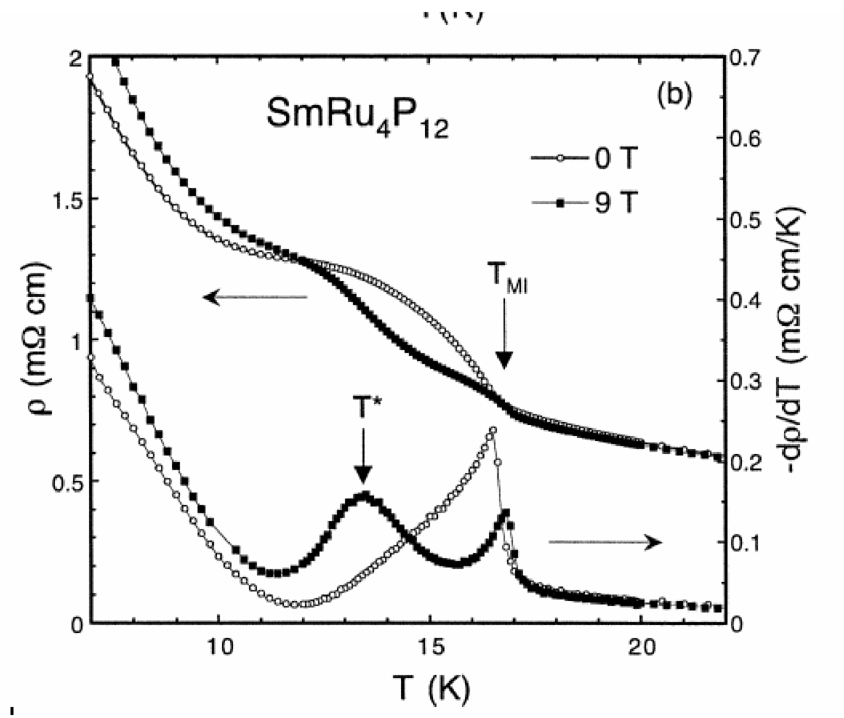


Fig. 5. Temperature dependence of C_m/T of $SmRu_4P_{12}$ between $5 \leq T \leq 20$ K in various magnetic fields, plotted as C_m/T vs T. For clarity, the data are shifted along the vertical direction by 0.1 J/K^2 mole per 1 T.

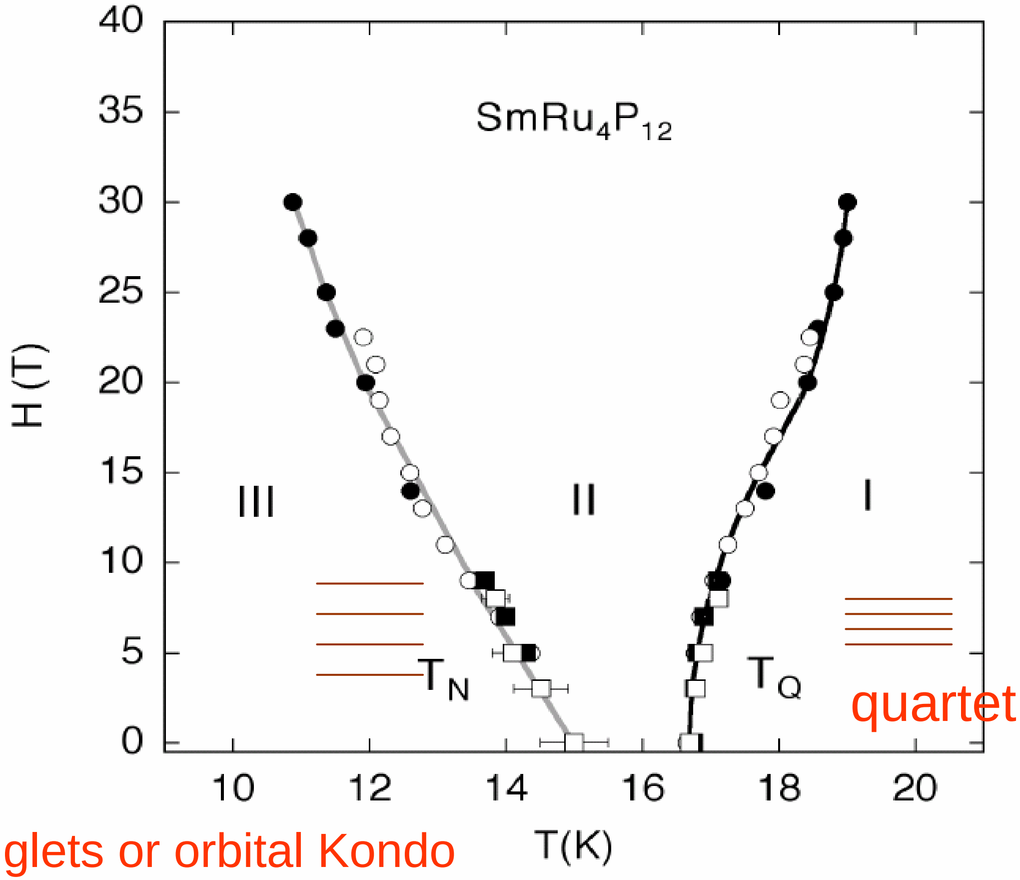
Matsuhira et al (2005)



Sekine et al (2001)

Order parameters in $SmRu_4P_{12}$?

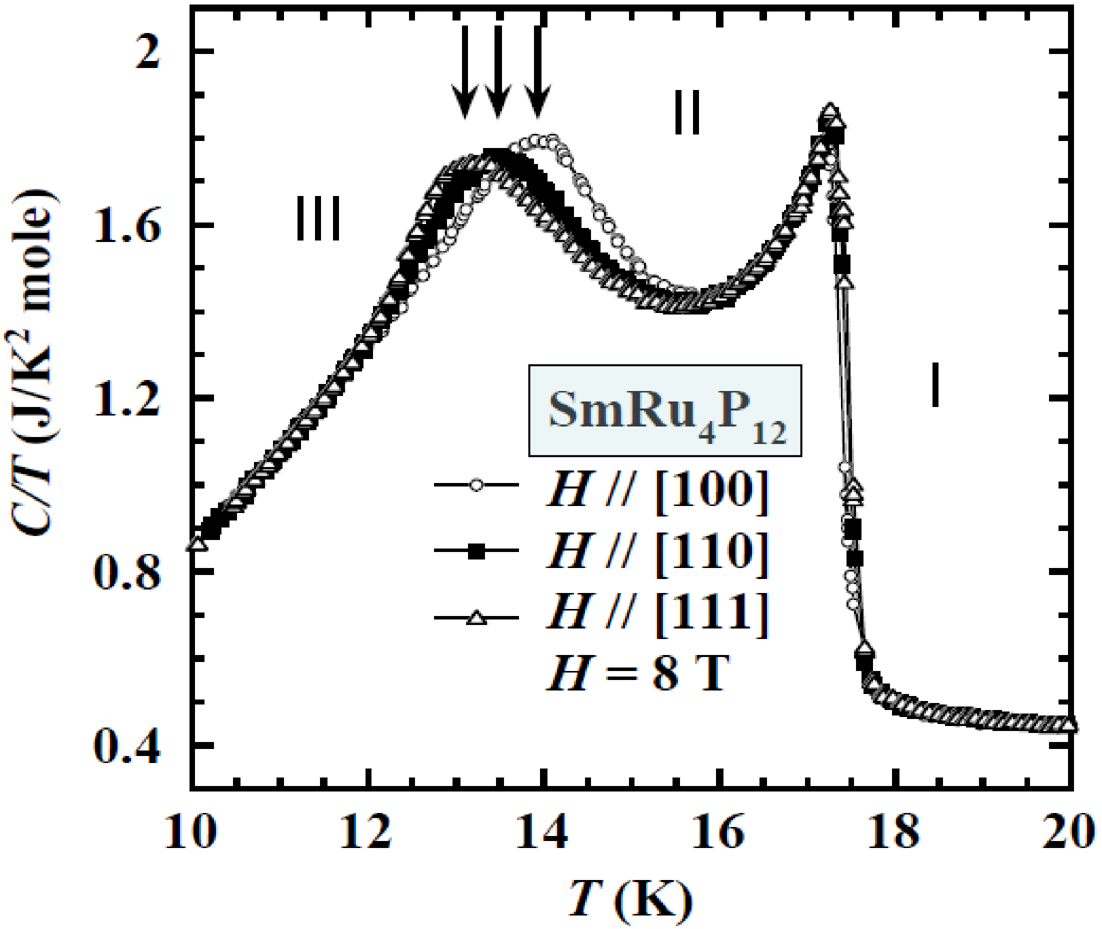
C. Sekine et al. (2003)



Four singlets or orbital Kondo

Orbital degeneracy remains in phase II =>
elastic anomaly at II-III boundary (Nakashima et al)

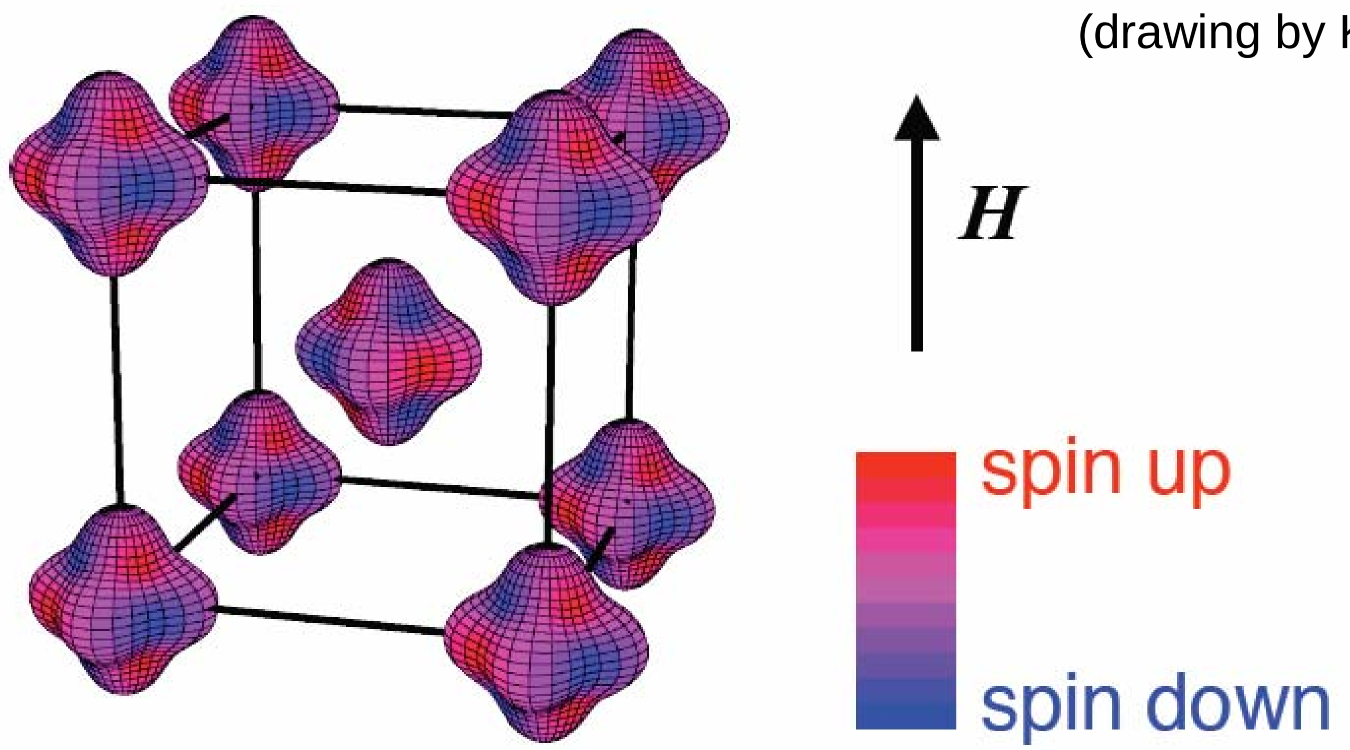
$SmRu_4P_{12}$: magnetic isotropy at I-II transition



D. Kikuchi et al.: (2006)

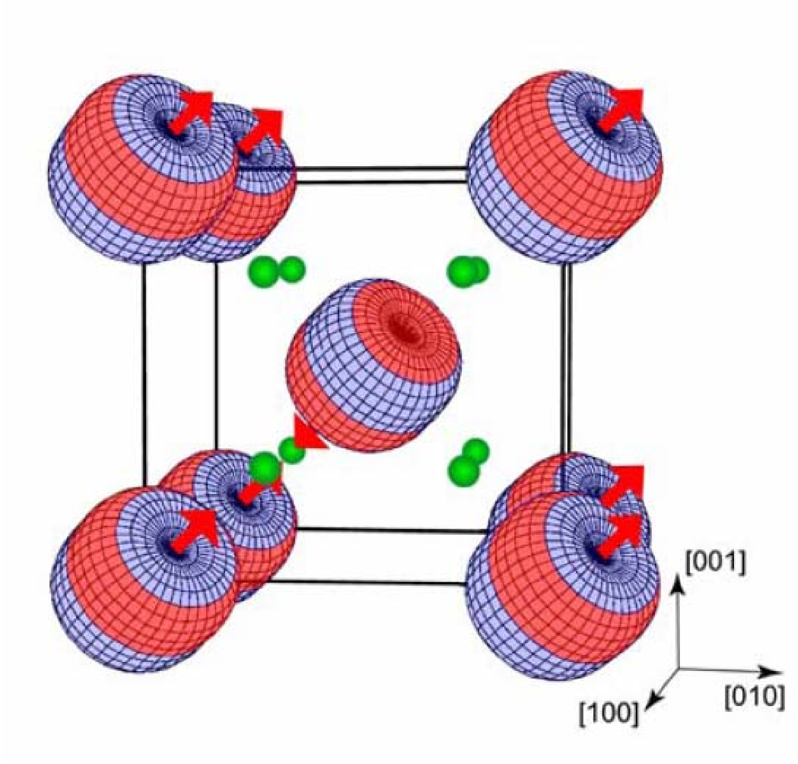
The simplest octupole order (T_{xyz})

Pseudo-scalar –inconsistent with NQR



Γ_{2u} octupole order (= $\boldsymbol{T_{xyz}}$)

Possible charge & spin density patterns in $SmRu_4P_{12}$



cf $Ce_{0.7}La_{0.3}B_6$

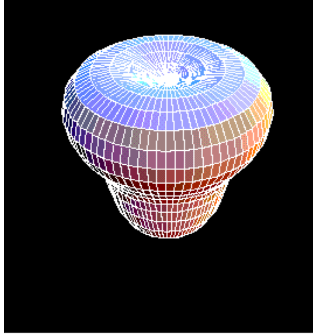
Y. Aoki et al: J. Phys. Soc. Jpn. 76 (2007) 113703

Nature of the second transition under magnetic field?

Order parameter(s) in $SmRu_4P_{12}$?

- Metal-insulator transition as in $PrRu_4P_{12}$
- Time reversal broken (NMR, muSR)
- Trigonal electric field at Sm (NQR)
  - cf (111) lattice distortion in $Ce_{0.7}La_{0.3}B_6$
- Emergence of a second transition under H
- No superlattice found so far

Summary



- Magnetic octupole order in $Ce_xLa_{1-x}B_6$
  - Induced quadrupoles => lattice distortion
  - Superlattice observation by resonant X-ray scattering and neutron scattering
- Scalar multipole orders in skutterudites
  - Phase transition keeping the local symmetry
- Unsolved problems
  - Ground state of $PrFe_4P_{12}$?
  - $SmRu_4P_{12}$, NpO_2, URu_2Si_2,…