HIROSHIMA UNIVERSITY

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Quadrupolar Ordered Phases in Pr-based Superconductors PrT_2Zn_{20} (T = Rh and Ir)

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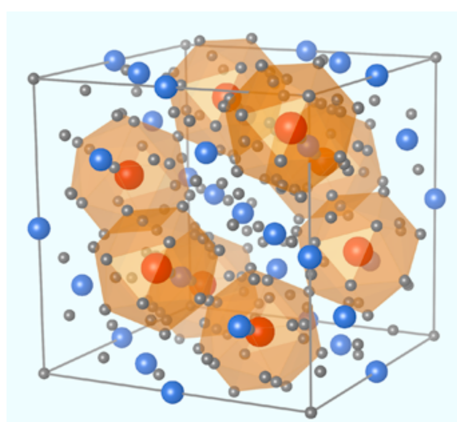
Outline

- Multipoles of non-Kramers Pr^{3+} ion with $4f^2$ configuration
- PrT_2Zn_{20} (T=Rh and Ir)
  - ❖ Crystal electric field (CEF) effect
    → Non-Kramers doublet ground state
  - ❖ Quadrupole order and superconducting transition
  - ❖ Further topic: Non-Fermi liquid behavior,
    Multi-channel Kondo effect, etc.
- Summary



Multipoles of 4*f* electrons

- Electric Monopole, e^-

Strong spin-orbit interaction → $\boldsymbol{J} = \boldsymbol{L} \pm \boldsymbol{S}$

- Magnetic Dipole ･･･ J_x, J_y, J_z
- Electric Quadrupole

  O_2^0 $(= 2J_z^2 - J_x^2 - J_y^2)$: Γ_3

  O_2^2 $(= J_x^2 - J_y^2)$

  O_{yz}, O_{zx}, O_{xy} : Γ_5

  $(O_{\alpha\beta} = J_\alpha J_\beta + J_\beta J_\alpha)$

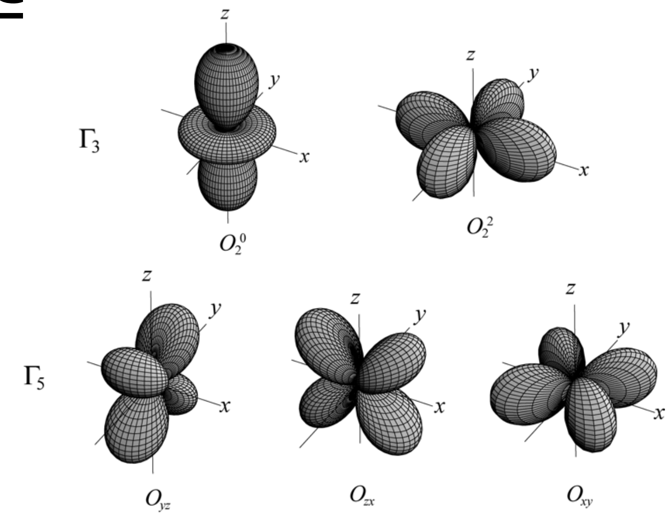
- Magnetic Octupole

  T_x^a, T_y^a, T_z^a (Γ_4)

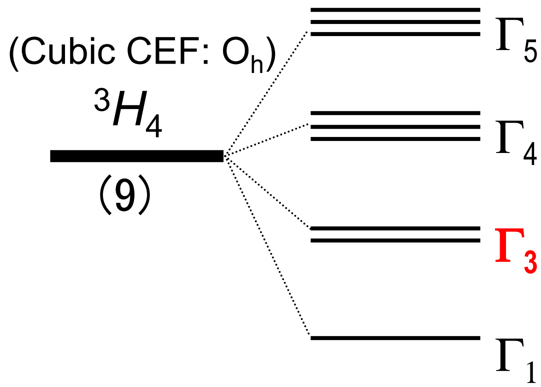
  T_x^b, T_y^b, T_z^b (Γ_5)

  T_{xyz} (Γ_2)

Quadruples of 4f electrons



Pr^{3+} : $4f^2$ configuration (J=4)



	Dipole	Quadru-pole	Octu-pole
Γ_5	○	○	×
Γ_4	○	○	×
Γ_3	×	○	○
Γ_1	×	×	×

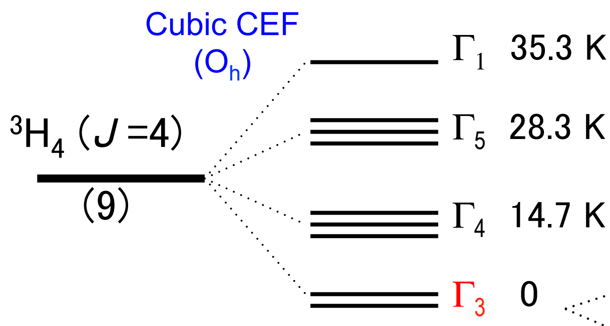
How to remove the entropy of the degenerated state?

Cubic Pr-based compounds

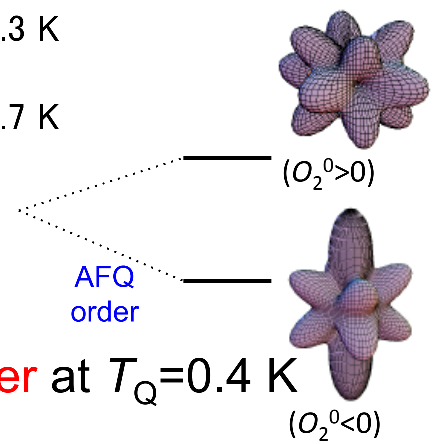
	Crystal Structure	Point group	CEF GS	Magnetic order	Multipole order	SC transition
$PrSn_3$	$AuCu_3$	O_h	Γ_1- Γ_4	AFM T_N=8.6 K	—	—
$PrPb_3$	$AuCu_3$	O_h	Γ_3	—	AFQ T_Q=0.4 K	—
PrPtBi	MgAgAs	O_h	Γ_3	—	FQ T_Q=1.35 K	—
$PrInAg_2$	BiF_3	O_h	Γ_3	—	—	—
$PrMg_3$	Fe_3Al	O_h	Γ_3	—	—	—
$Pr_3Pd_{20}Ge_6$	C_6Cr_{23}	O_h, T_d	Γ_5, Γ_3	—	AFQ T_Q=0.26 K	—
$Pr_3Pd_{20}Si_6$	C_6Cr_{23}	O_h, T_d	Γ_5, Γ_3	AFM T_N=0.14 K	AFQ T_Q=0.21 K	—
$PrOs_4Sb_{12}$	AT_4X_{12}	T_h	Γ_1- $\Gamma_4^{(1)}$	—	AFQ (B>2 T)	T_c=1.85 K
$PrRu_4P_{12}$	AT_4X_{12}	T_h	Γ_1, $\Gamma_4^{(2)}$ (T<T_{co}=63 K)	—	AFQ T_Q=0.11 K	—
$PrFe_4P_{12}$	AT_4X_{12}	T_h	Γ_1- $\Gamma_4^{(1)}$	—	Scalar-type T_M=6.5 K	—
$PrPt_4Ge_{12}$	AT_4X_{12}	T_h	Γ_1	—	—	T_c=8 K

Non-Kramers Pr^{3+} ions in crystals

Pr^{3+} ion: $4f^2$ configuration (L=5, S=1, J=4)



In the Γ_3 doublet, there is no magnetic dipole, but quadrupoles O_2^0 and O_2^0, and octupole T_{xyz}.

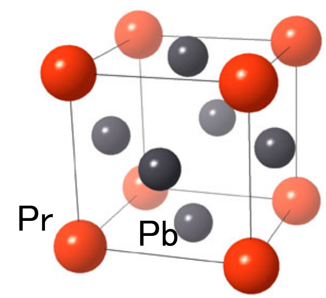


Quadrupoles of $4f$ electrons

$PrPb_3$ Simple cubic structure

Antiferro-quadrupole (AFQ) order at T_Q=0.4 K

E. Bucher *et al*., J. Low. Temp. **2** (1974) 322.



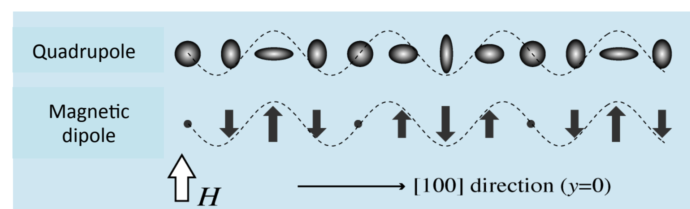
Crystal structure of $PrPb_3$

Incommensurate quadrupole structures

⇒ Indirect RKKY-type interaction.

Quadrupoles are partially quenched.

T. Onimaru *et al*., Phys. Rev. Lett. **94** (2005) 197201.



Incommensurate quadrupole structure in $PrPb_3$. (T. Onimaru *et al*., PRL, 2005.)

$PrInAg_2$, $PrMg_3$:

No ordering, Quadrupole Kondo effect

A. Yatskar *et al*., Phys. Rev. Lett. **77** (1996) 3637., H. Tanida *et al*., J. Phys. Soc. Jpn. **75** (2006) 073705.

Composite order in two-channel Kondo lattice

S. Hoshino *et al*., J. Phys. Soc. Jpn. **82,** 044707 **(**2013.)

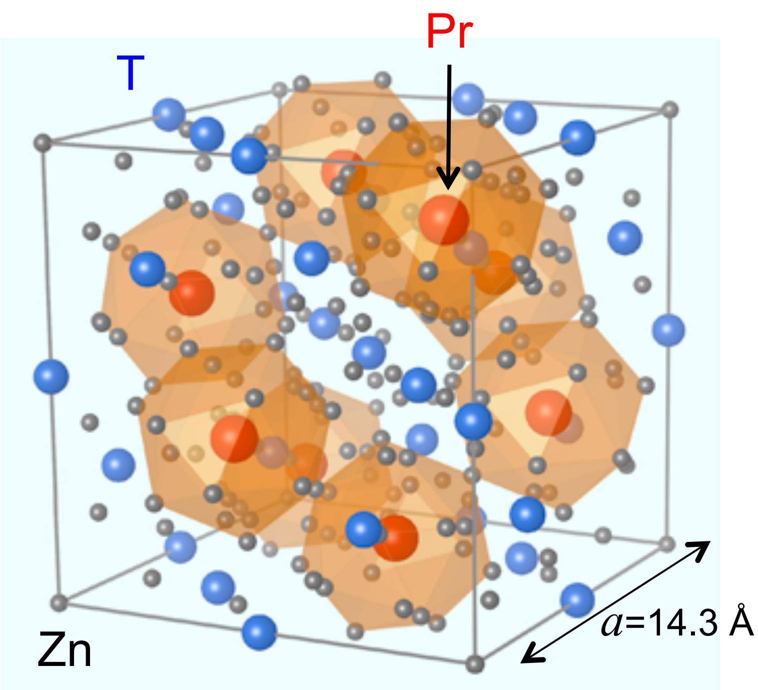
Crystal structure of PrT_2Zn_{20} (T=Ru, Rh, Ir)

T. Nasch *et al*., Z. Naturforsch. B **52** (1997) 1023.
T. Onimaru *et al*, J. Phys. Soc. Jpn. **79** (2010) 033704.

Cubic $CeCr_2Al_{20}$-type
(Space group: $Fd\bar{3}m$)

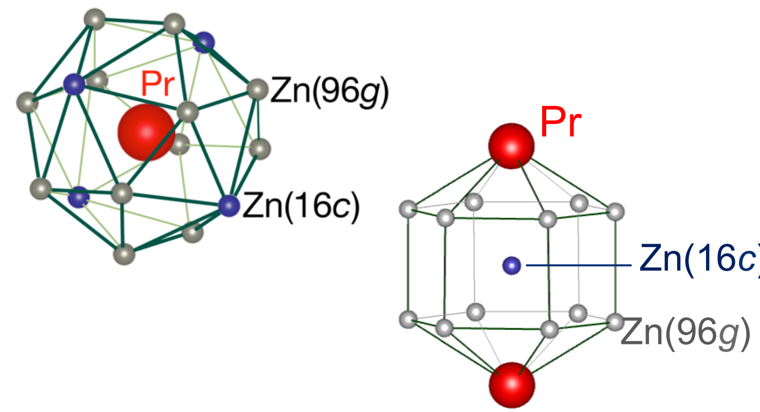
PrT_2Zn_{20}

T=Ru
Rh
Ir



The Pr ions are encapsulated into highly symmetric Zn-cages.

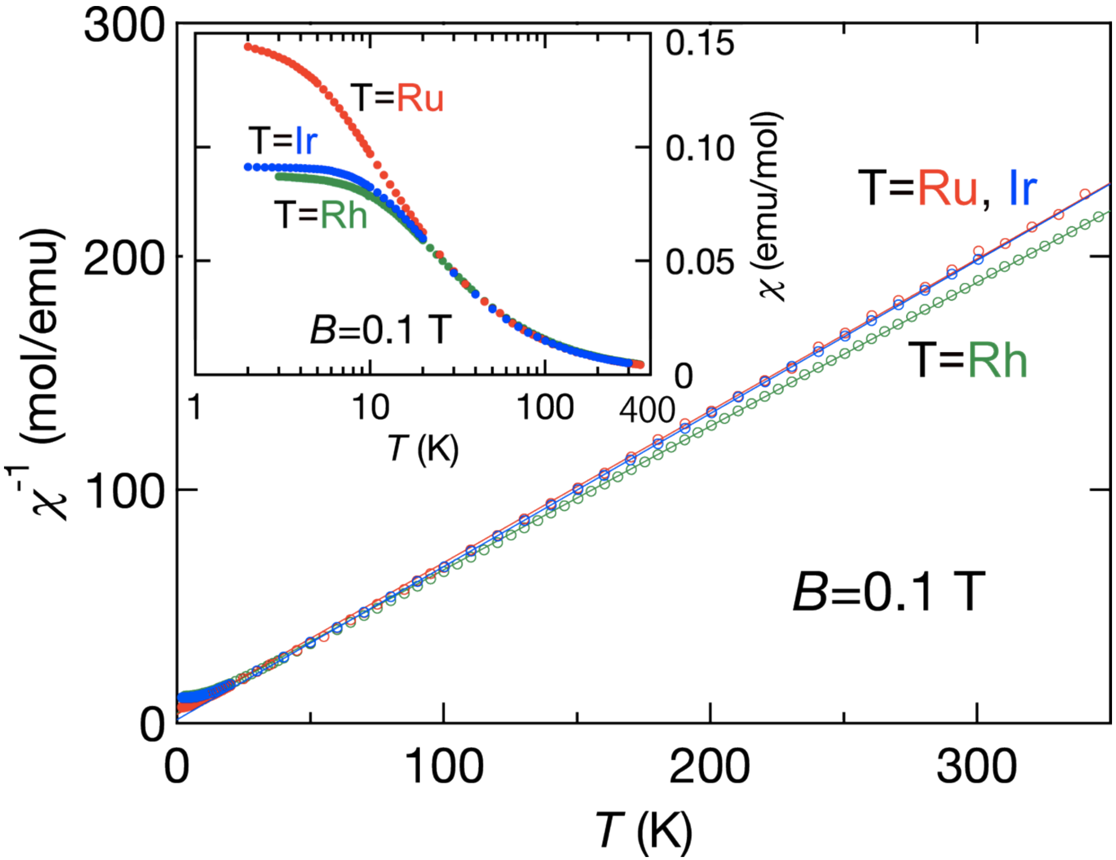
Pr site : Cubic T_d point group



Zn(16c) atoms insides Pr and Zn(96g) cage

- Non-Kramers Γ_3 doublet for Pr^{3+} ion → Quadrupole moments are active.
- Strong hybridization of the 4*f* electrons with conduction electrons
  → Heavy fermion state and Kondo effect
- Anharmonic atomic vibrations couple with 4f and conduction electrons.

Magnetic susceptibility: PrT_2Zn_{20} (T=Ru, Rh, Ir)



T. Onimaru *et al*., J. Phys.: Condens. Matter **24** (2012) 294207.

χ obeys the Curie-Weiss law above 30 K.

⇒ Effective magnetic moment μ_{eff}

3.50(2) μ_B/f.u. for T=Ru

3.54(2) μ_B/f.u. for T=Rh

3.49(2) μ_B/f.u. for T=Ir

Pr ions are trivalent.

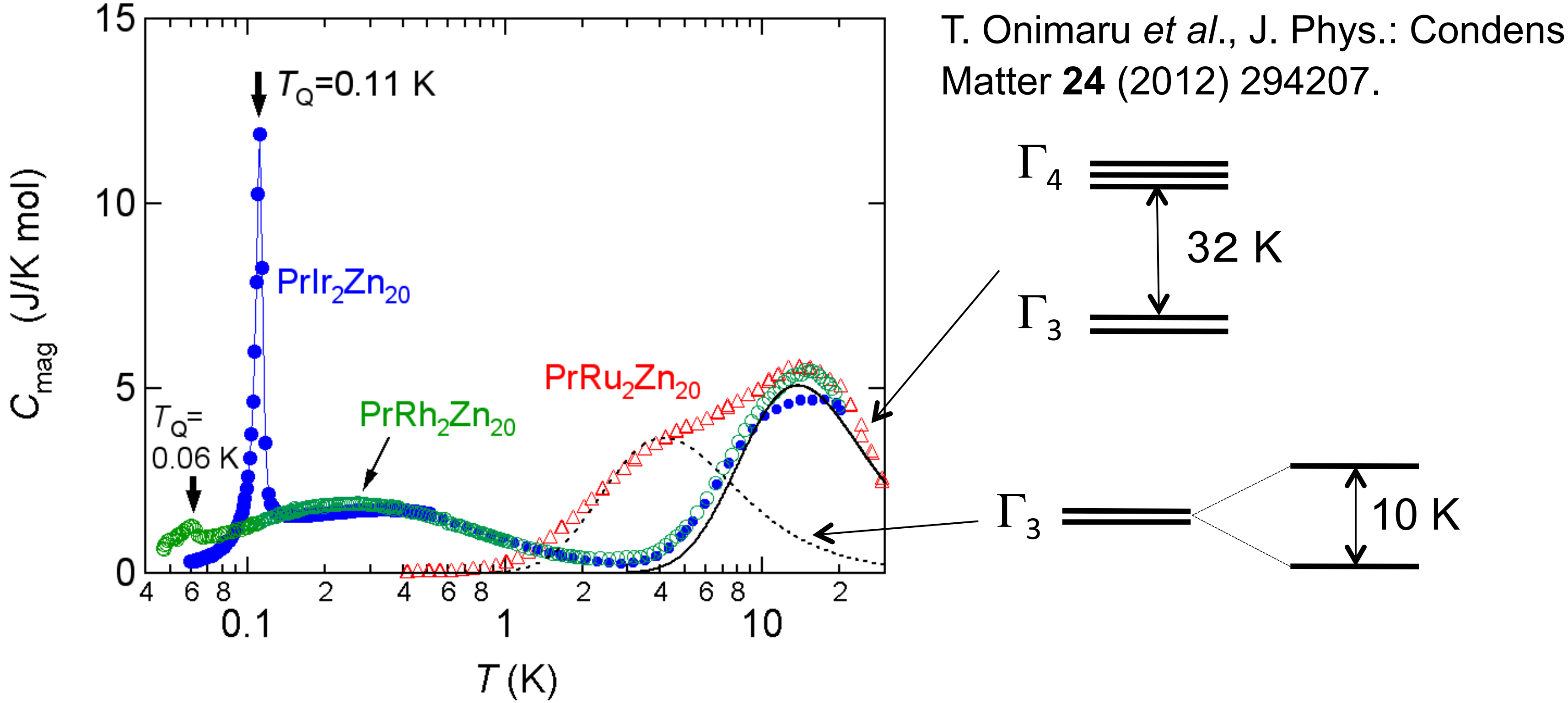
⇒ The CEF effect is weak.

・ The small negative θ_P's indicate weak magnetic interaction between the Pr-ions.

・ Van-Vleck paramagnetic behavior.

⇒ The CEF ground states is non-magnetic Γ_1 or Γ_3.

Magnetic specific heat



・Schottky-type peaks appear at 12 K. ➔ CEF ground state: Γ_3 doublets

$PrRu_2Zn_{20}$: Structural transition at T_S=138 K

・Shoulder-like anomaly ➔ Splitting of Γ_3 doublet by the lattice modulation.

T. Onimaru *et al,* Phys. Rev. Lett. **106** (2011) 177001.

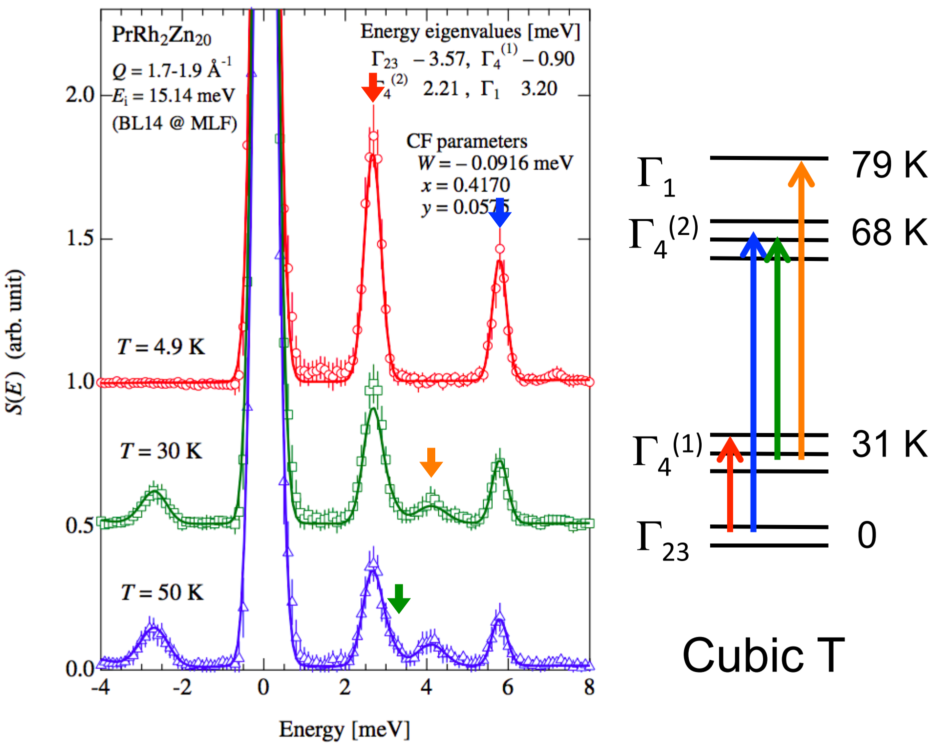
I. Ishii, *et al.*, J. Phys. Soc. Jpn. **80**, 093601 (2011).

T. Onimaru *et al,* Phys. Rev. B **86** (2012) 184426.

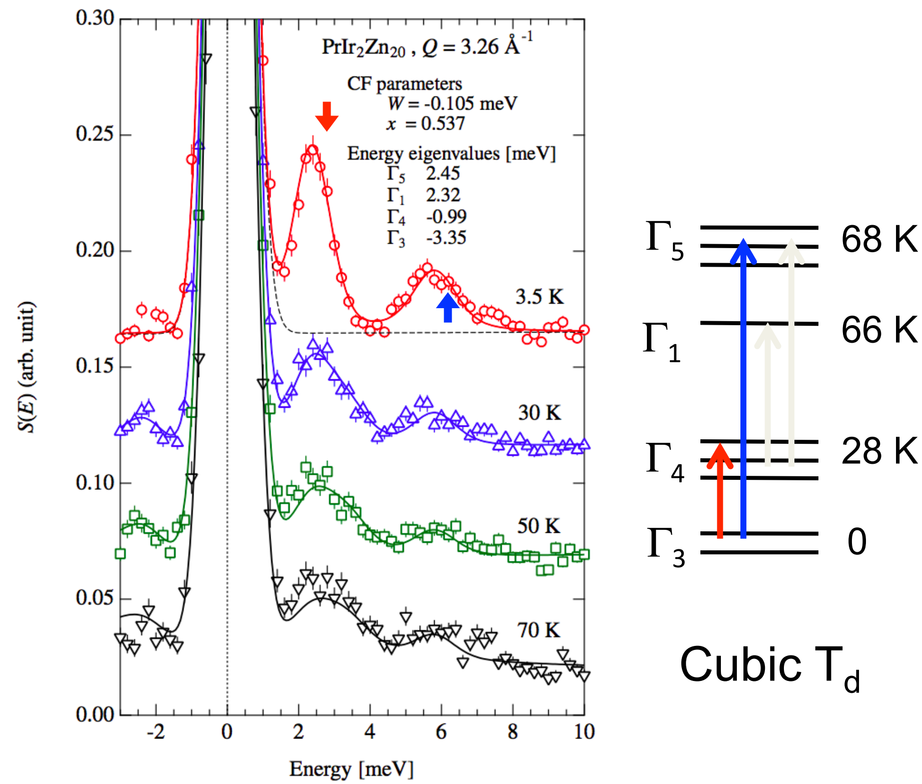
Inelastic neutron scattering

K. Iwasa *et al.*, J. Phys. Soc. Jpn. **82** (2013) 043707.

$PrRh_2Zn_{20}$



$PrIr_2Zn_{20}$



cf. Structural transition at 170~470 K.

- Spectra are well reproduced by the CEF level schemes with the nonmagnetic doublet ground state.

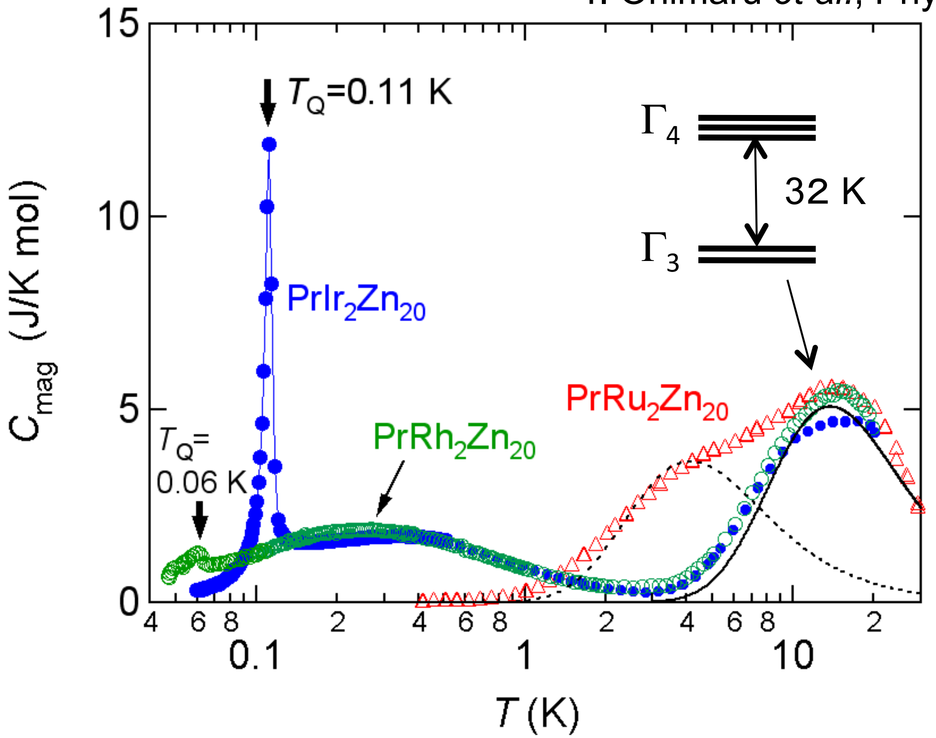
PrT_2X_{20} (T: Transition metal, X: Al, Zn)

	Lattice parameter (Å)	Structural transition	CEF ground state	Quadrupole order	SC transition
$PrRu_2Zn_{20}$	14.3467(4)	T_S=138 K	Singlet ($T < T_S$)	—	— (>0.04 K)
$PrRh_2Zn_{20}$	14.2702(3)	T_S=170 ~470 K	Γ_{23} doublet (T) ($T < T_S$)	AFQ T_Q=0.06 K	T_c=0.06 K
$PrOs_2Zn_{20}$	14.365(5)	T_S=87 K	?	— (>0.4 K)	— (>0.4 K)
$PrIr_2Zn_{20}$	14.2729(2)	—	Γ_3 doublet	AFQ T_Q=0.11 K	T_c=0.05 K
$PrTi_2Al_{20}$	14.723(7)	—	Γ_3 doublet	FQ T_Q=2 K	T_c=0.2 K (a. p.) T_c=1 K (~8 GPa)
PrV_2Al_{20}	14.591(2)	—	Γ_3 doublet	AFQ T_Q=0.6 K	—
$PrNb_2Al_{20}$	14.7730(3)	—	Γ_3 doublet	—	—

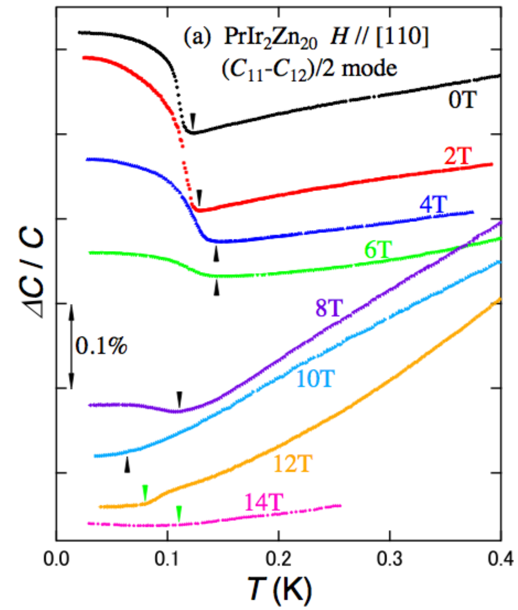
T. Onimaru *et al.*, JPSJ **79** (2010) 033704.
T. Onimaru *et al.*, PRL **106** (2011) 177001.
T. Onimaru *et al.*, PRB **86** (2012) 184426.
K. Wakiya *et al.*, JKPS **62** (2013) 2143.
A. Sakai and S. Nakatsuji, JPSJ **80** (2011) 063701.
R. Higashinaka *et al.*, JPSJ **80** (2011) SA048.
A. Sakai *et al.*, JPSJ **81** (2012) 083702.
K. Matsubayashi *et al.*, PRL **109** (2012) 187004.

Magnetic specific heat

T. Onimaru *et al.*, Phys. Rev. Lett. **106** (2011) 177001.
T. Onimaru *et al.*, Phys. Rev. B **86** (2012) 184426.



Elastic modulus $(C_{11}-C_{12})/2$

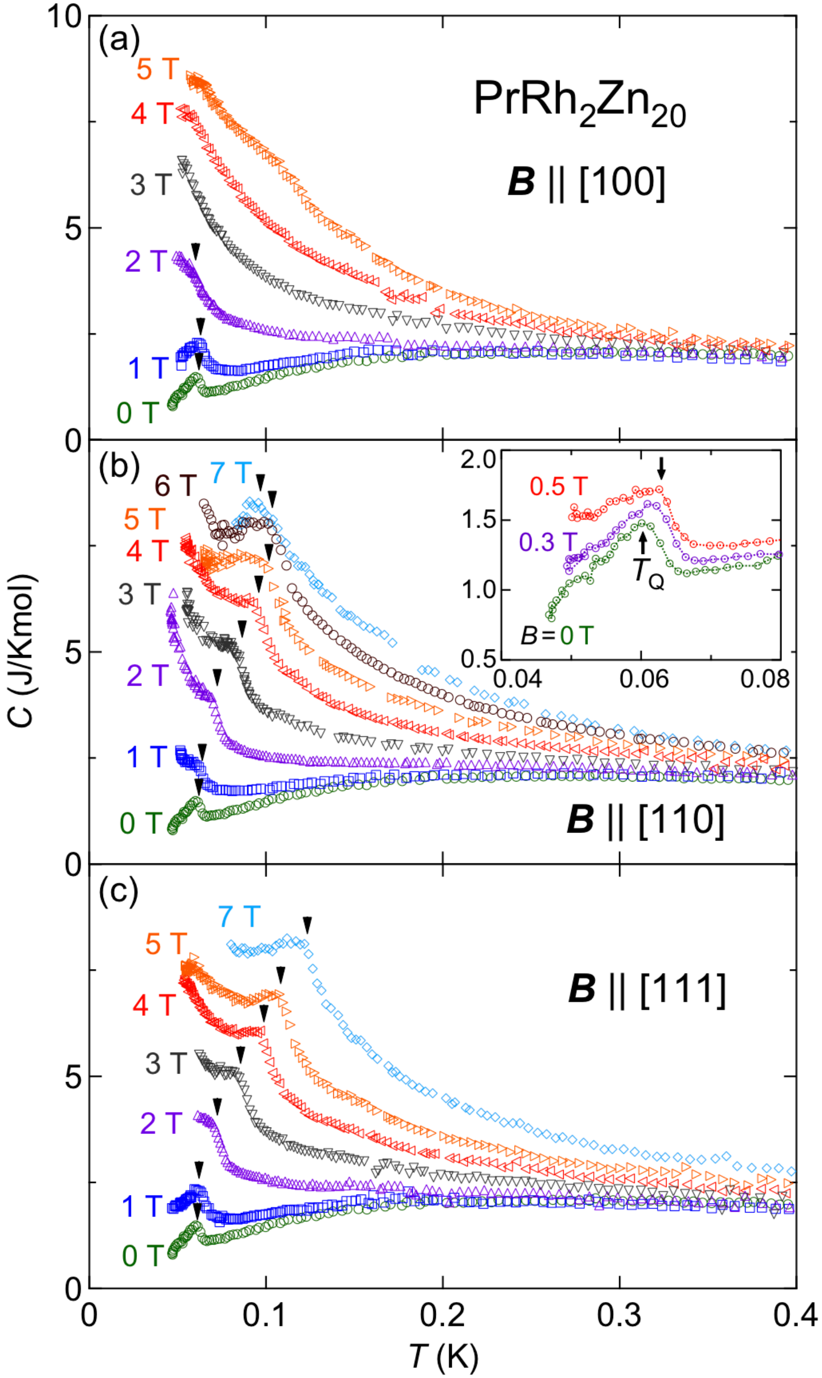


I. Ishii *et al.*, J. Phys. Soc. Jpn. **80** (2011) 093601.

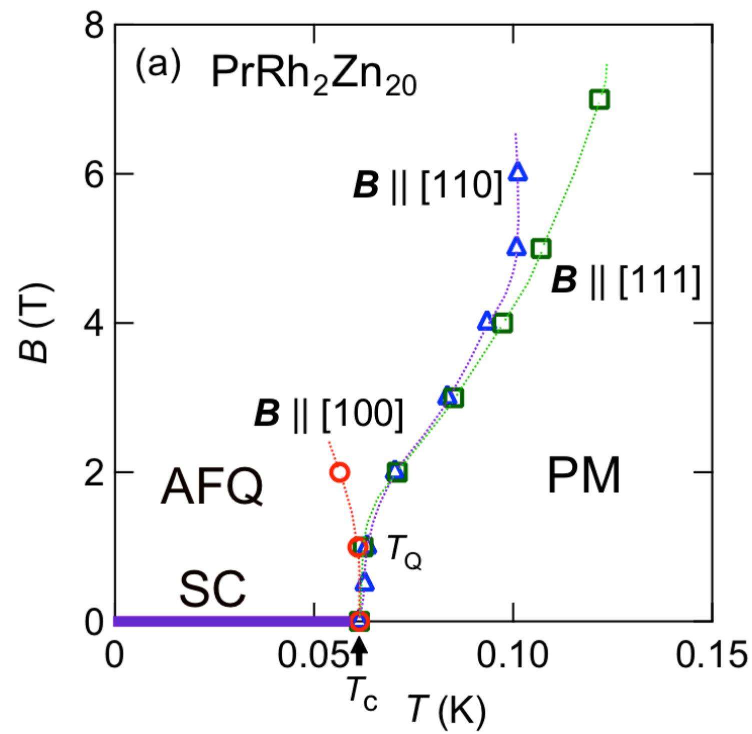
- Sharp peaks appear at low temperatures.

$PrRh_2Zn_{20}$ Antiferroquadrupole (AFQ) ordering at T_Q=0.06 K.
I. Ishii *et al.*, Phys. Rev. B **87** (2013) 205106.

$PrIr_2Zn_{20}$ AFQ ordering at T_Q=0.11 K.
I. Ishii *et al.*, J. Phys. Soc. Jpn. **80** (2011) 093601.



$PrRh_2Zn_{20}$



i. Anisotropic behavior of T_Q.

T_Q: [100] < [110] < [111]

ii. T_Q increases with increasing B for [110] and [111].

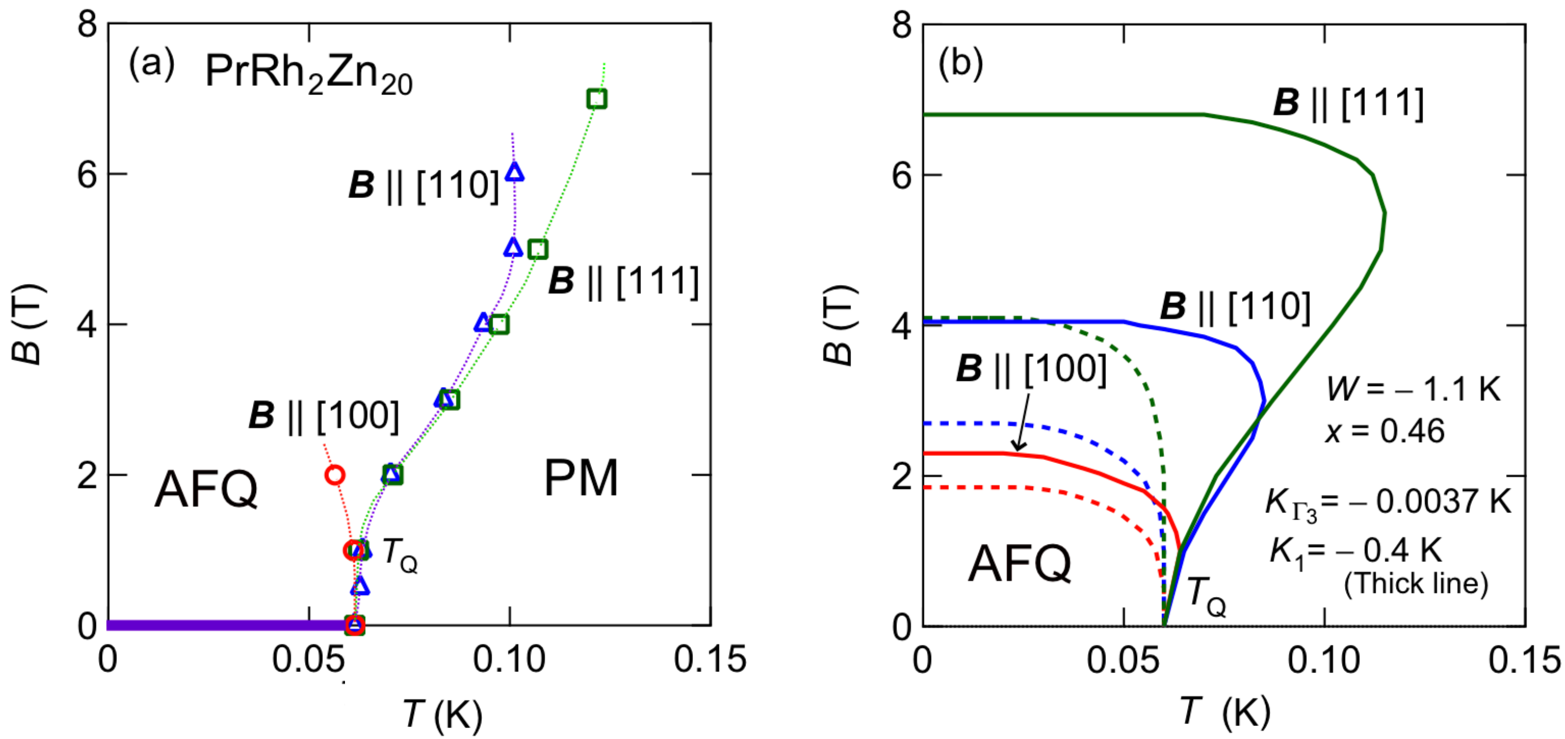
AFQ ordering occurs at T_Q=0.06 K.

AFQ ordered state: $PrRh_2Zn_{20}$

T. Onimaru *et al.*, Phys. Rev. B **86** (2012) 184426.

Two-sublattice mean-field model

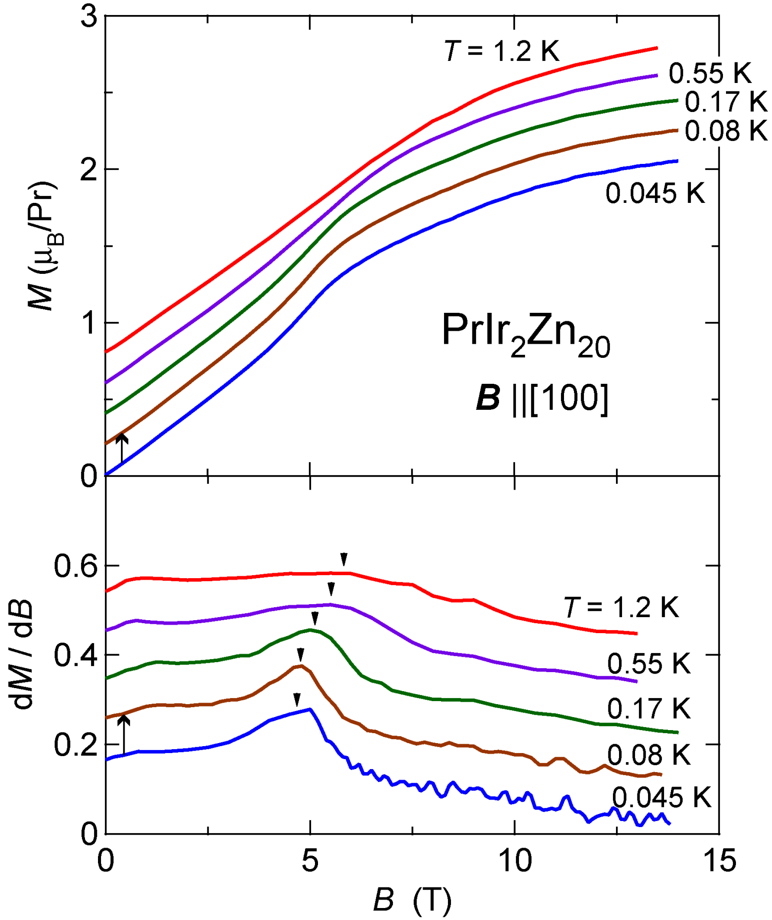
$$H^I_{A(B)} = H_{CEF} - g_J \mu_B J H - \left(K_1 \langle J \rangle_{B(A)} + K_2 \langle J \rangle_{A(B)}\right) J - K_{\Gamma 3}\left(\langle O_2^0 \rangle_{B(A)} O_2^0 + \langle O_2^2 \rangle_{B(A)} O_2^2\right)$$



・Two sub-lattice mean-field calculation well reproduces the anisotropic *B*-*T* phase diagrams.

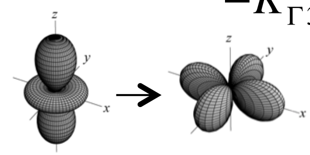
・Antiferromagnetic interaction between the field-induced magnetic moments of the Pr^{3+} ions stabilizes the AFQ ordered state.

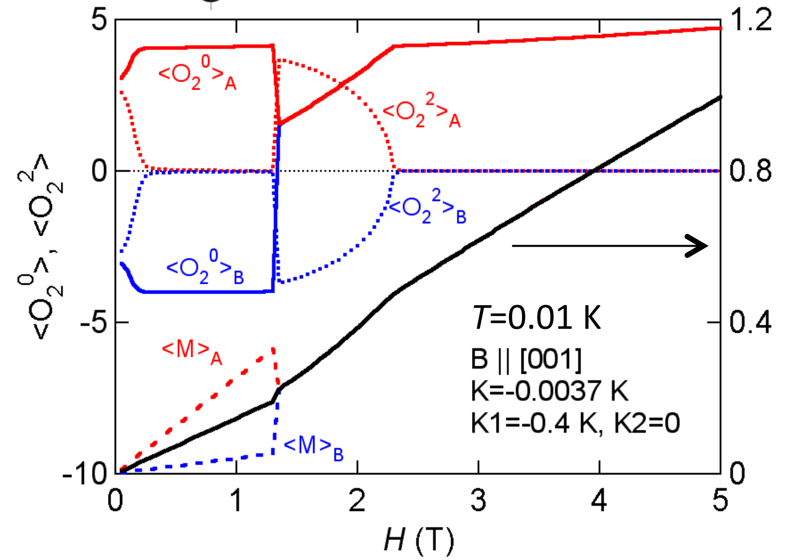
Metamagnetic behavior in $\boldsymbol{B}$ || [100]



Two-sublattice mean-field model

$$H^{I}_{A(B)} = H_{CEF} - g_J \mu_B J H - \left(K_1 \langle J \rangle_{B(A)} + K_2 \langle J \rangle_{A(B)} \right) J$$
$$- K_{\Gamma 3} \left(\langle O_2^0 \rangle_{B(A)} O_2^0 + \langle O_2^2 \rangle_{B(A)} O_2^2 \right)$$





・Metamagnetic behavior was observed at around B=5 T.

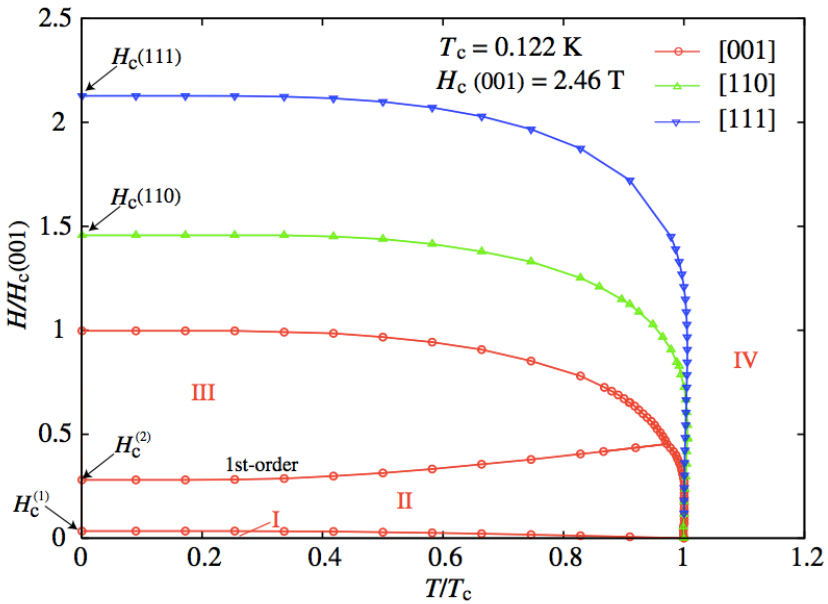
・In mean-field model calculation, order parameter is changed in B, where metamagnetic behavior is found, resulting from level-crossing.

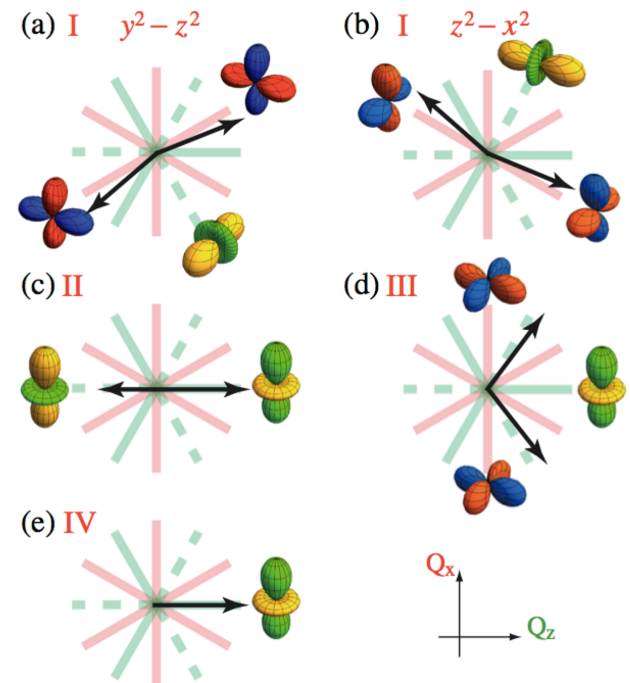
➔ Switching of the OP possibly changes the conduction band?

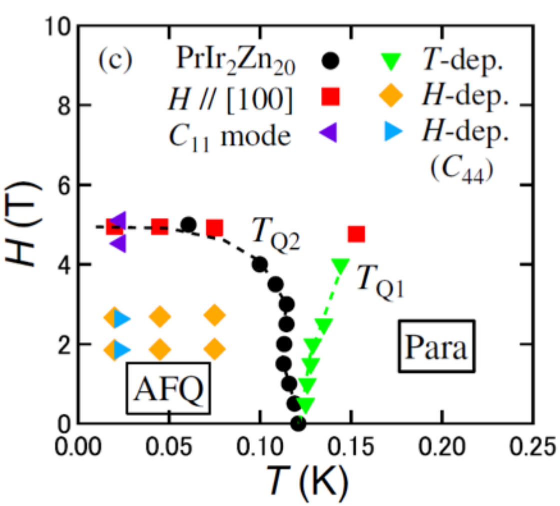
Order parameter of the AFQ phase

Mean-field calculation

K. Hattori and H. Tsunetsugu, JPSJ **83**, 034709 (2013).







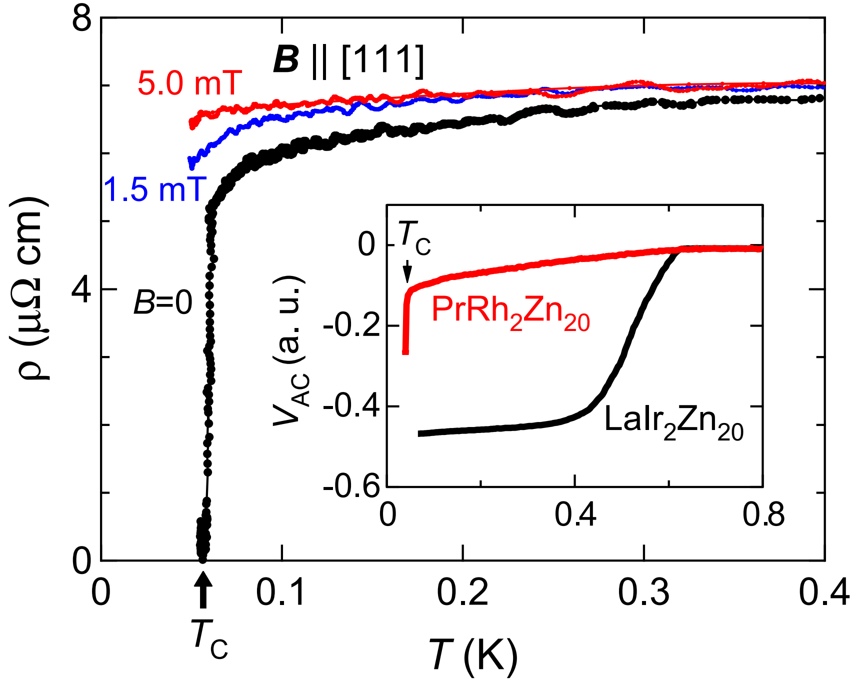
I. Ishii *et al.*, JPSJ. **80** (2011) 093601.

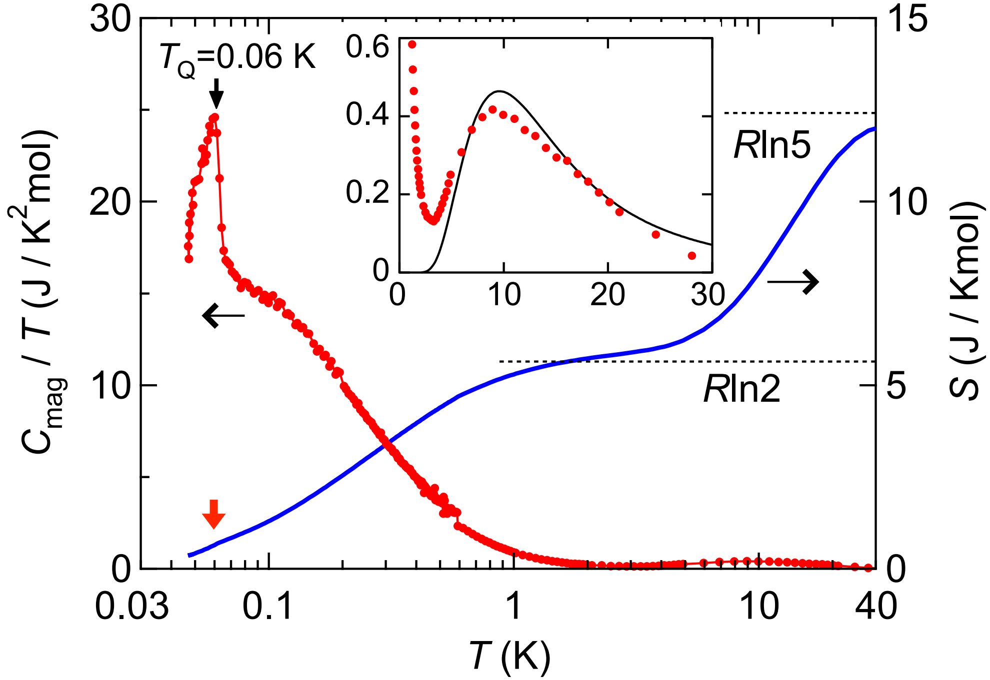
- Phase I: O_2^2 AFQ + small O_2^0 FQ
- Phase II: Collinear O_2^0 AFQ
- Phase III: Canted AFQ
- Phase IV: Paramagnetic state

- Gapless spin-wave excitation at the boarder of the O_2^2 AFQ phases.
- Unusual singularities of χ_Q at $T=T_Q$ for H=0 and the critical field for [111].

Simultaneous Superconducting and AFQ transitions in $PrRh_2Zn_{20}$

T. Onimaru *et al.*, Phys. Rev. B **86** (2012) 184426.



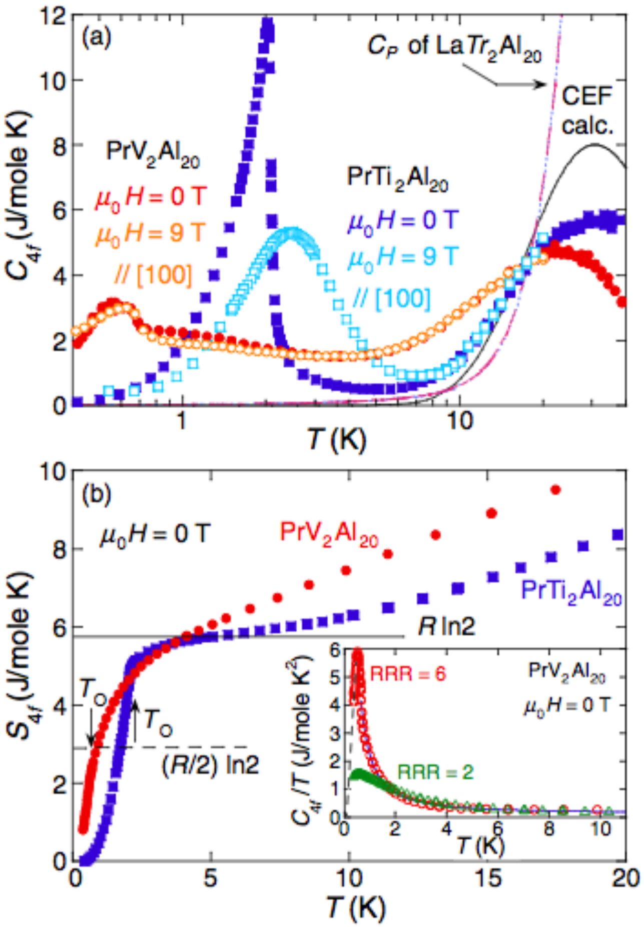


- Superconducting transition occurs at T_c=0.06 K.
- The magnetic entropy at T_Q is only 0.1*R*ln2 which is much smaller than *R*ln2 expected for an order of the nonmagnetic doublet ground state.

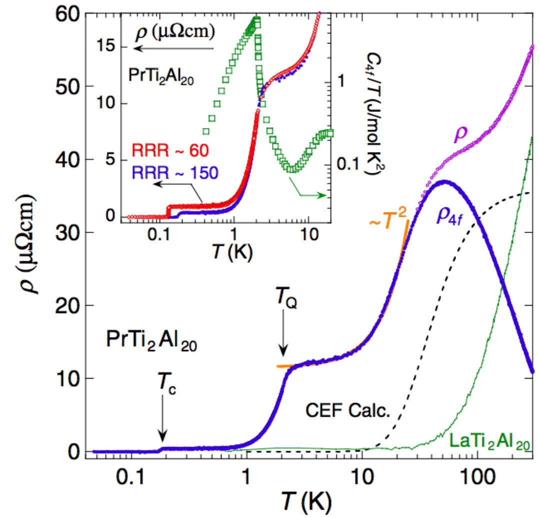
⇒ The quadrupole fluctuations remain active below T_Q ?

Ferroquadrupole order and heavy-fermion superconductivity in the isostructural $PrTi_2Al_{20}$

- FQ transition at T_Q=2 K.
- Magnetic entorpy at T_Q is 0.9Rln2.

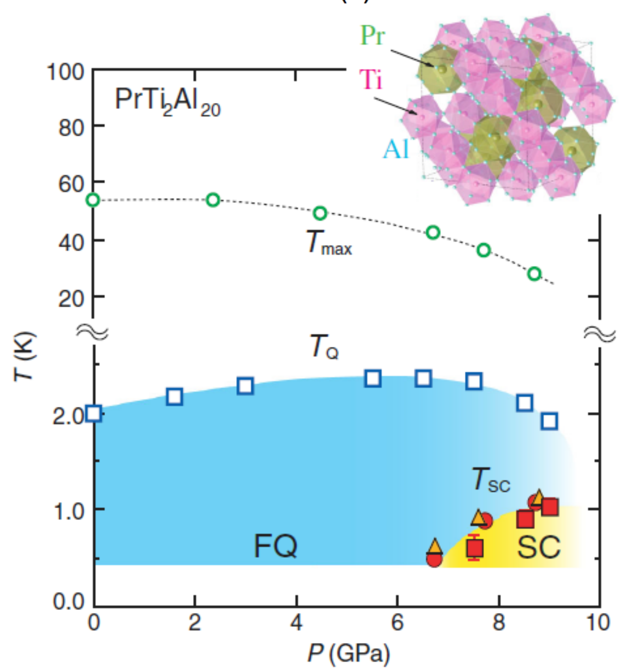


A. Sakai and S. Nakatsuji, J. Phys. Soc. Jpn. **80** (2011) 063701.



- Superconducting transition at T_c=0.2 K.
- m*=16m$_0$

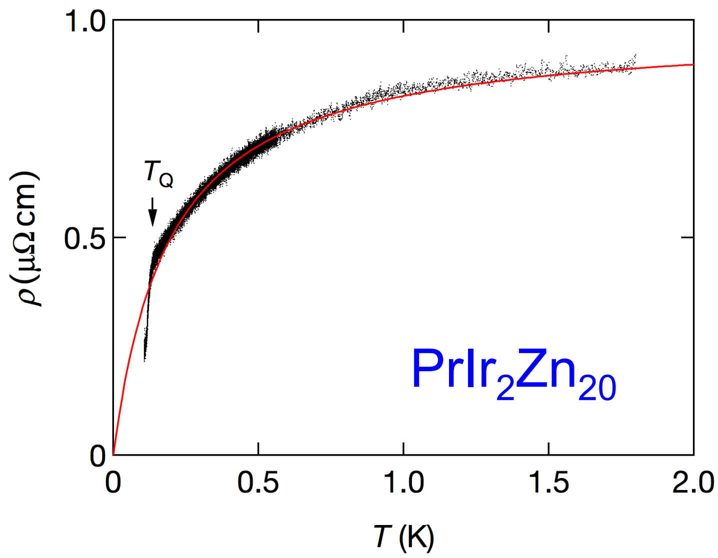
A. Sakai *et al.*, J. Phys. Soc. Jpn. **81** (2012) 083702.

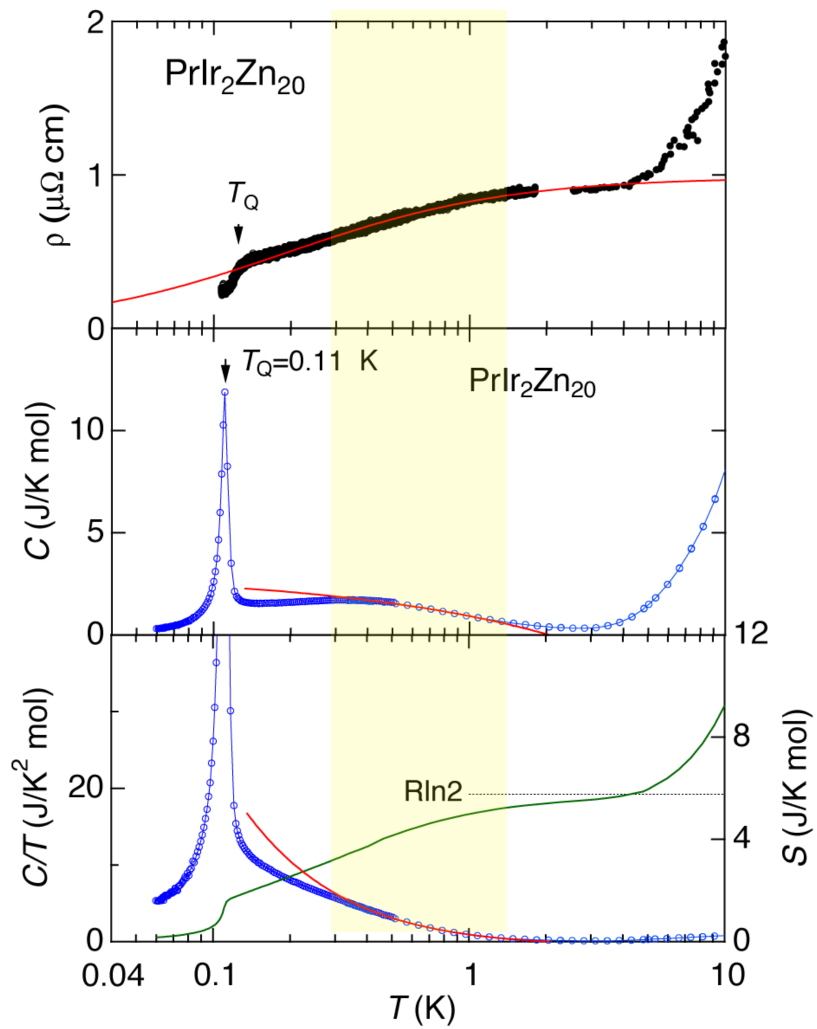


- T_c is increased up to T_c=1 K at 8 GPa
- Heavy-fermion superconductor

K. Matsubabashi *et al.*, Phys. Rev. Lett. **109** (2012) 187004.

Anomalous temperature dependence of $\rho(T)$ and $C(T)$





S/T ~ 0.031 μV/K^2 (T. Ikeura and K. Izawa)

➔ Weak hybridization between the 4*f* and conduction electrons ?

❖ Entropy of the Γ_3 doublet is released by dynamic Jahn-Teller distortion in $PrMg_3$.

K. Araki *et al.*, J. Phys. Soc. Jpn. **81** (2012) 023710.

Summary PrT_2Zn_{20} (T = Ru, Rh, and Ir)

- For T=Rh and Ir, the CEF ground state are the non-magnetic Γ_3 doublet with quadrupolar degrees of freedom.
- Antiferro-quadrupolar (AFQ) ordering at T_Q was confirmed.
  - ➢ To determine the AFQ structure and order parameters, microscopic measurements are in progress.
- Non-Fermi liquid behavior was observed above T_Q.
  - ➢ Hybridization effect must play an important role in forming the ground state.

PrT_2X_{20} (X=Al and Zn) family is appropriate for revealing characteristics of the quadrupoles such as quadrupole order, multi-channel Kondo effect, exotic superconductivity.