Magnetically ordered sublattice in conventional superconductors

Ternary (lanthanide) compounds

$LnRh_4B_4$, $LnMo_6S_8$, $LnMo_6Se_8$

Two weakly interacting systems of electrons

Mobile, SCing subsystem - Rh_4B_4, Mo_6S_8, Mo_6Se_8 "clusters"

Localized magnetic subsystem - Ln sublattice

Weak exchange interaction between Ln μ's and conduction electron s's ($\mathcal{J} \sim 0.01 eV$)

$\Rightarrow$ SCing, $T_M \sim T_c$

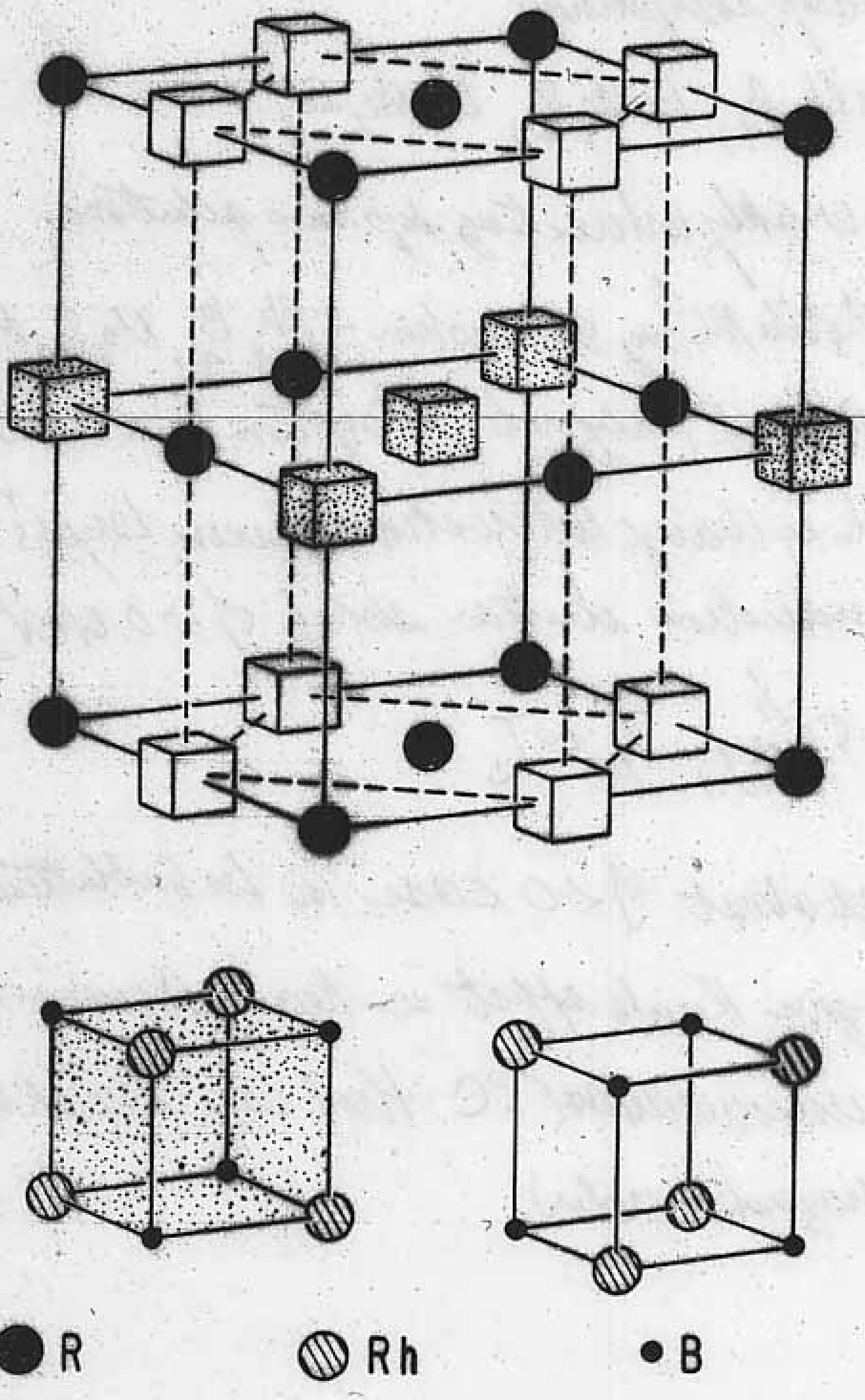
What about $\mathcal{J} < 0$ case in Ln sublattice

This gives Kondo effect $\Rightarrow$ heavy fermion behavior

$\Rightarrow$ unconventional SC that can coexist with magnetic order

Crystal structure

RRh_4B_4



Antiferromagnetic superconductors

- **Compounds**

RMo_6S_8	R = Gd, Tb, Dy, Er	(U. Geneva)
RMo_6Se_8	R = Gd, Tb, Er	(UCSD)
RRh_4B_4	R = Nd, Sm, Tm	(UCSD)

- **SC & AFM coexist in H = 0**

$\langle H_{ex} \rangle = 0$ over scale of ξ $\quad \uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow \quad \xi >> a$

$|\leftarrow a \rightarrow|$

- **AFM modifies SC'ing properties**

e.g., H_{c2} vs T

H_{c2} increases or decreases below T_N — nonuniversal

Mechanisms

Enhancement

(1) Decrease in $\langle M \rangle$ below $T_N \Rightarrow$ reduced pair breaking

Suppression

(1) μ fluctuations near $T_N \Rightarrow$ increased pair breaking

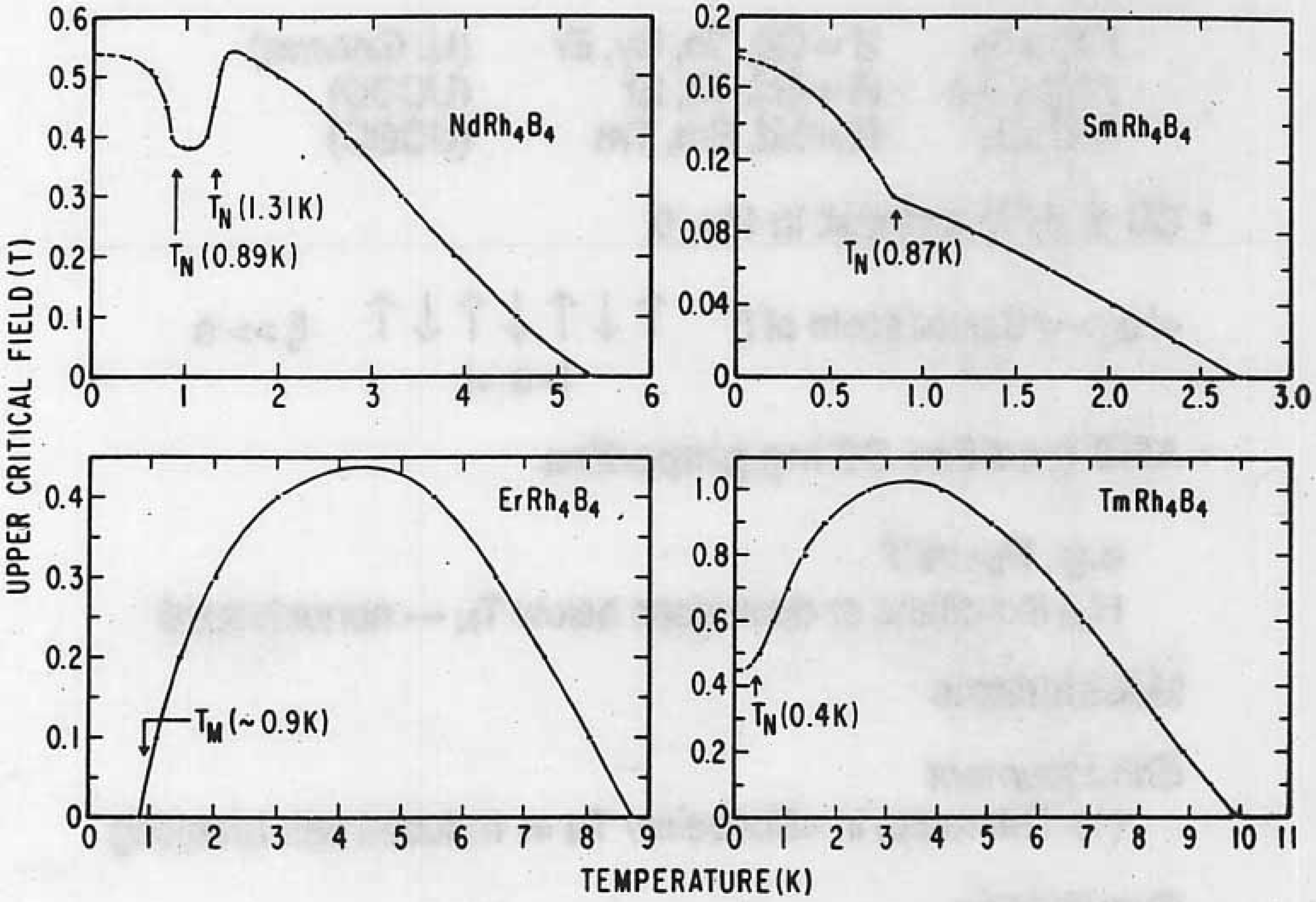
(2) AFM magnons $\Rightarrow$ repulsive electron-electron interaction

(3) Gap in E(**k**) due to change in lattice periodicity $\Rightarrow$ reduction of available phase space for virtual pair scattering

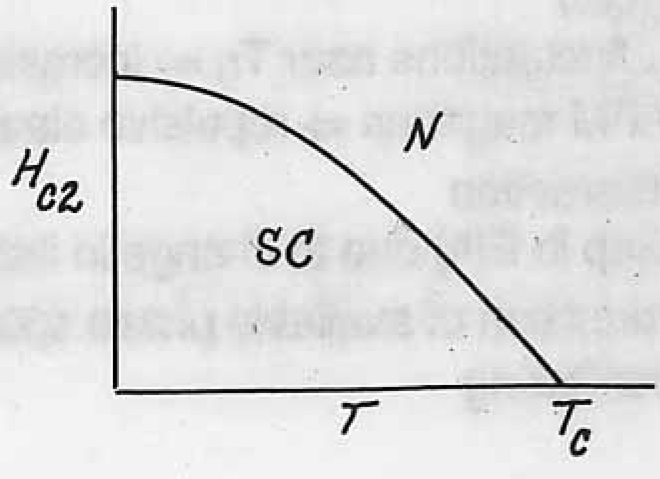
$H_{c2}(T)$ of RRh_4B_4 magnetic superconductors

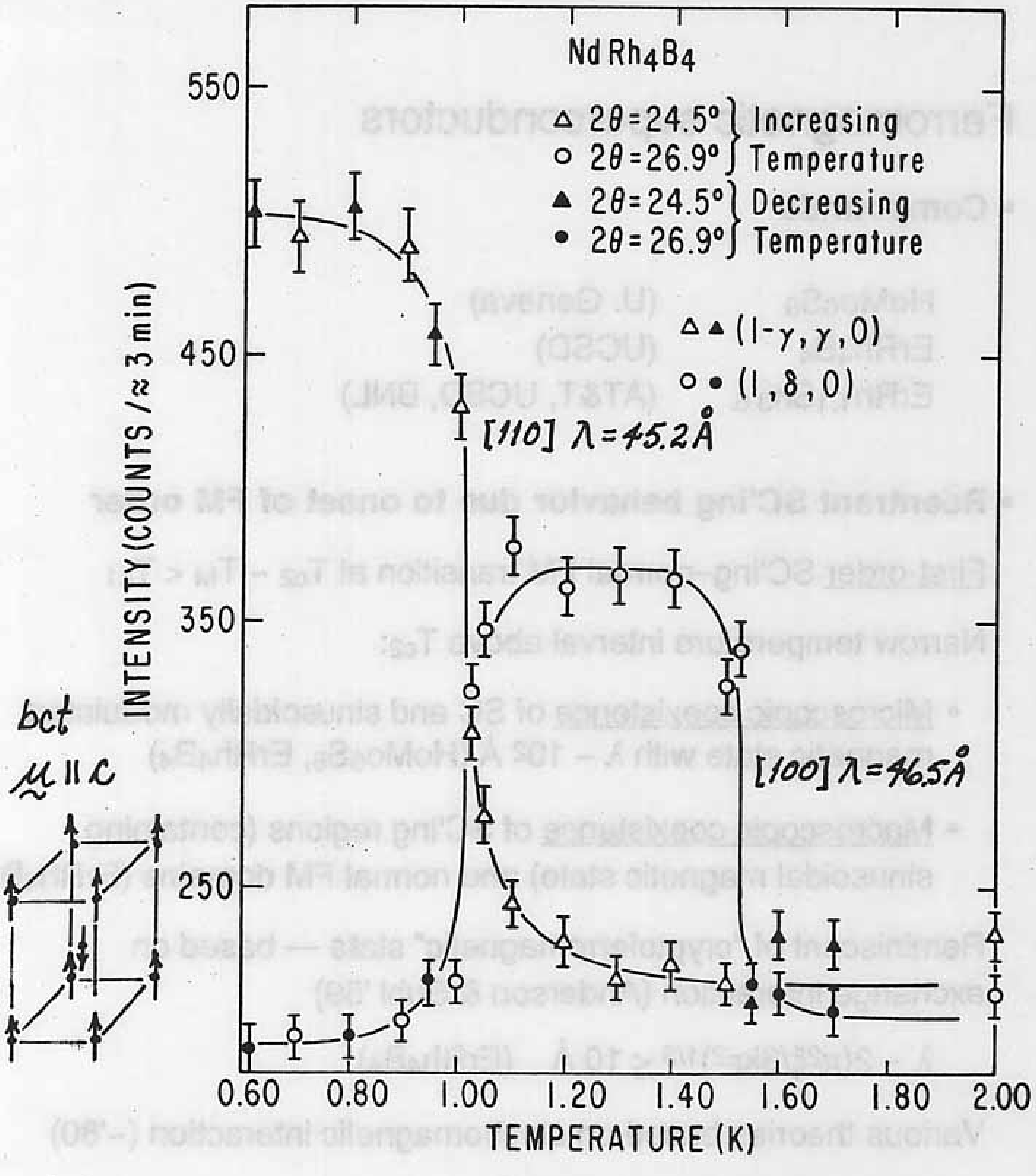
AFM-SC's: $NdRh_4B_4$, $SmRh_4B_4$, $TmRh_4B_4$

FM-SC: $ErRh_4B_4$



Conventional SC:





C.F. Majkrzak, D.E. Cox, G. Shirane, H.A. Mook,
H.C. Hamaker, H.B. MacKay, Z. Fisk & M.B. Maple '82

Ferromagnetic superconductors

- **Compounds**

$HoMo_6S_8$	(U. Geneva)
$ErRh_4B_4$	(UCSD)
$ErRh_{1.1}Sn_{3.6}$	(AT&T, UCSD, BNL)

- **Reentrant SC'ing behavior due to onset of FM order**

First-order SC'ing–normal FM transition at $T_{c2} \sim T_M < T_{c1}$

Narrow temperature interval above T_{c2}:

  - Microscopic coexistence of SC and sinusoidally modulated magnetic state with $\lambda \sim 10^2$ Å ($HoMo_6S_8$, $ErRh_4B_4$)
  - Macroscopic coexistence of SC'ing regions (containing sinusoidal magnetic state) and normal FM domains ($ErRh_4B_4$)

Reminiscent of "cryptoferromagnetic" state — based on exchange interaction (Anderson & Suhl '59)

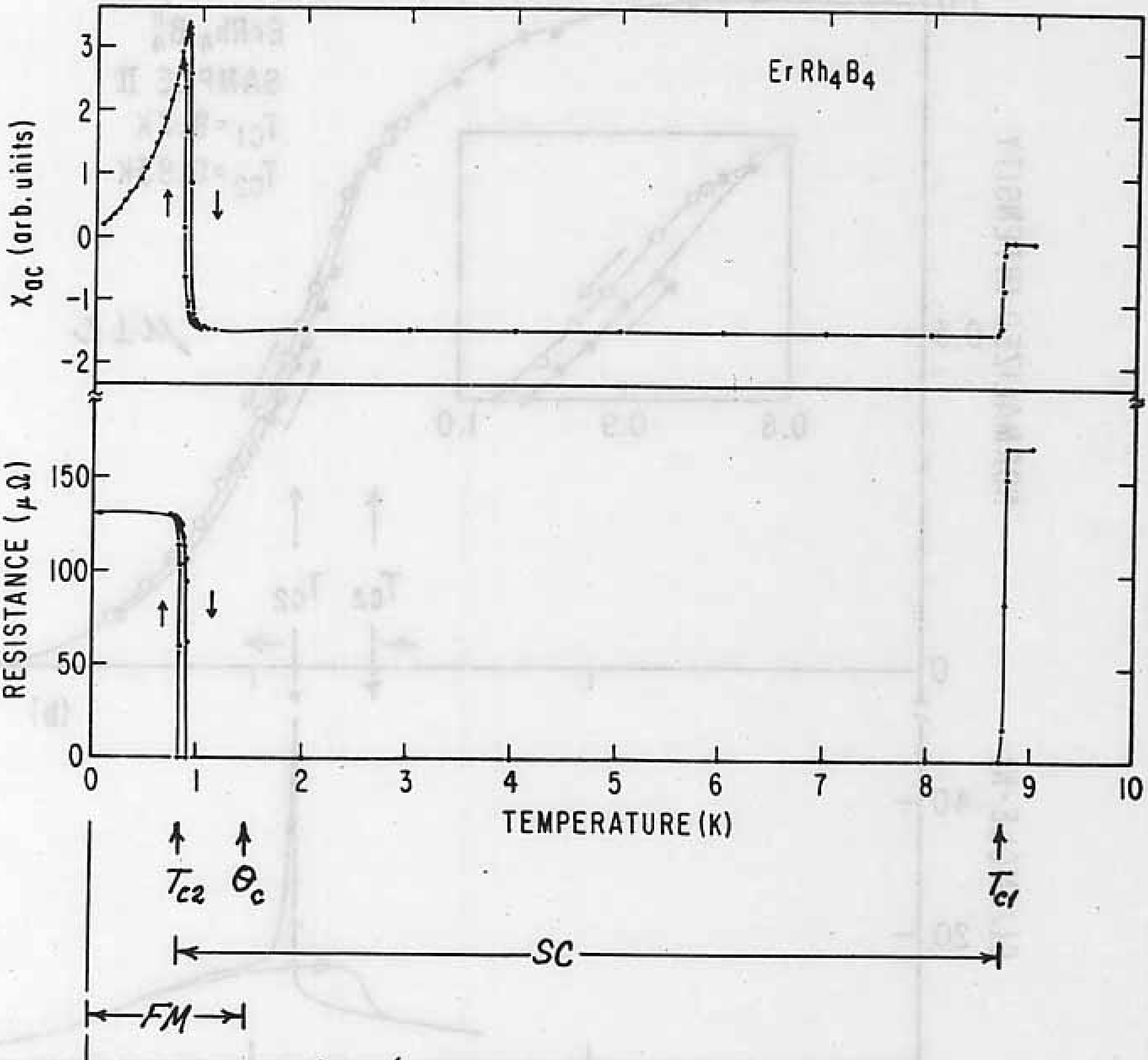
$\lambda \sim 2(\pi^2\xi/3k_F^2)^{1/3} \lesssim 10$ Å ($ErRh_4B_4$)

Various theories based on electromagnetic interaction (~'80)

$\lambda \sim (4\pi^3 D/C)^{1/4}\lambda_L^{1/2} \sim 10^2$ Å

Spontaneous vortex lattice

Reentrant SC due to FM order: $ErRh_4B_4$ ($HoMo_6S_8$)



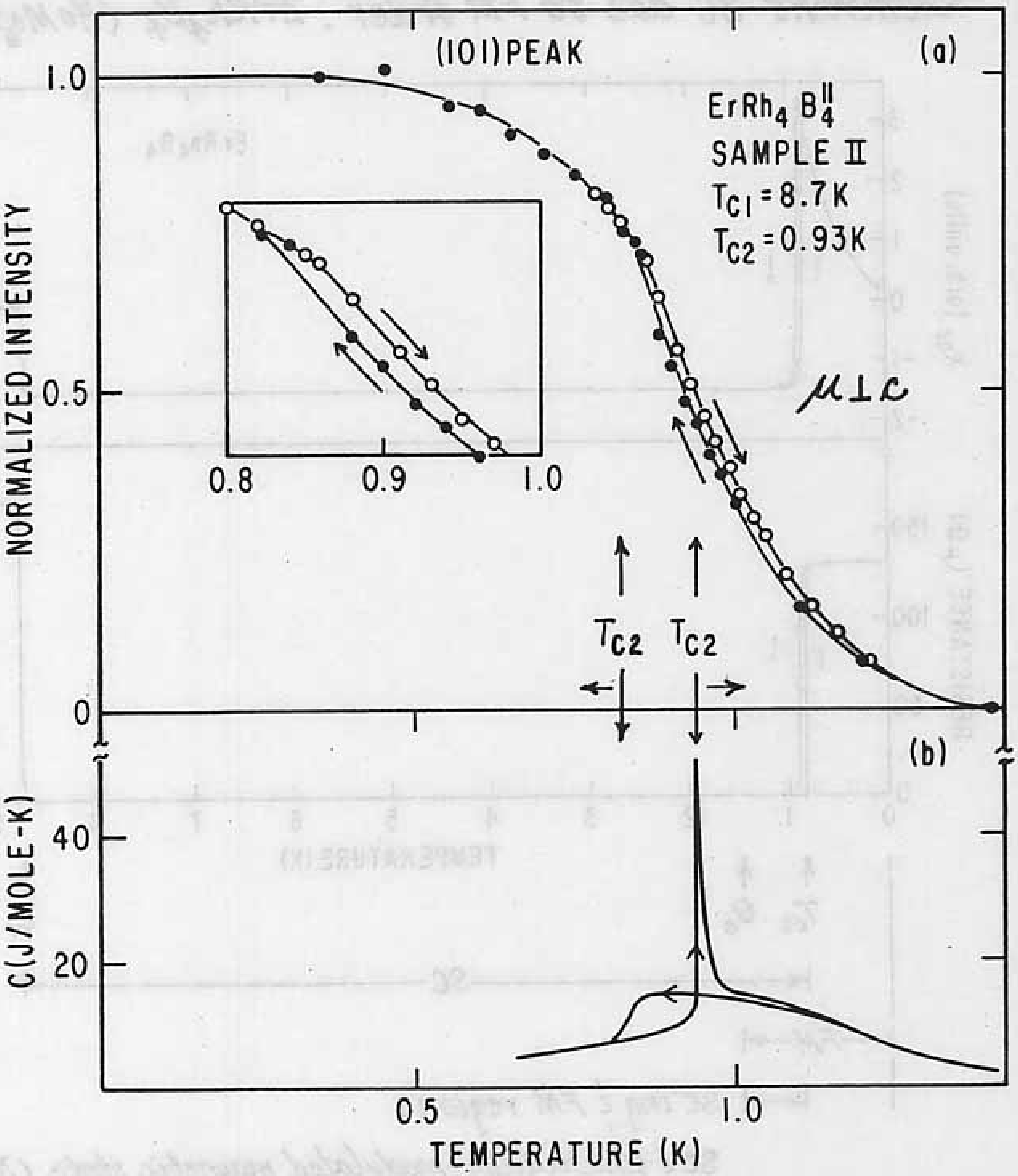
SC'ing & FM regions

SC & sinusoidally-modulated magnetic state ($\lambda \sim 100 Å$)

* Fertig, Johnston, DeLong, McCallum, Maple, Matthias '77

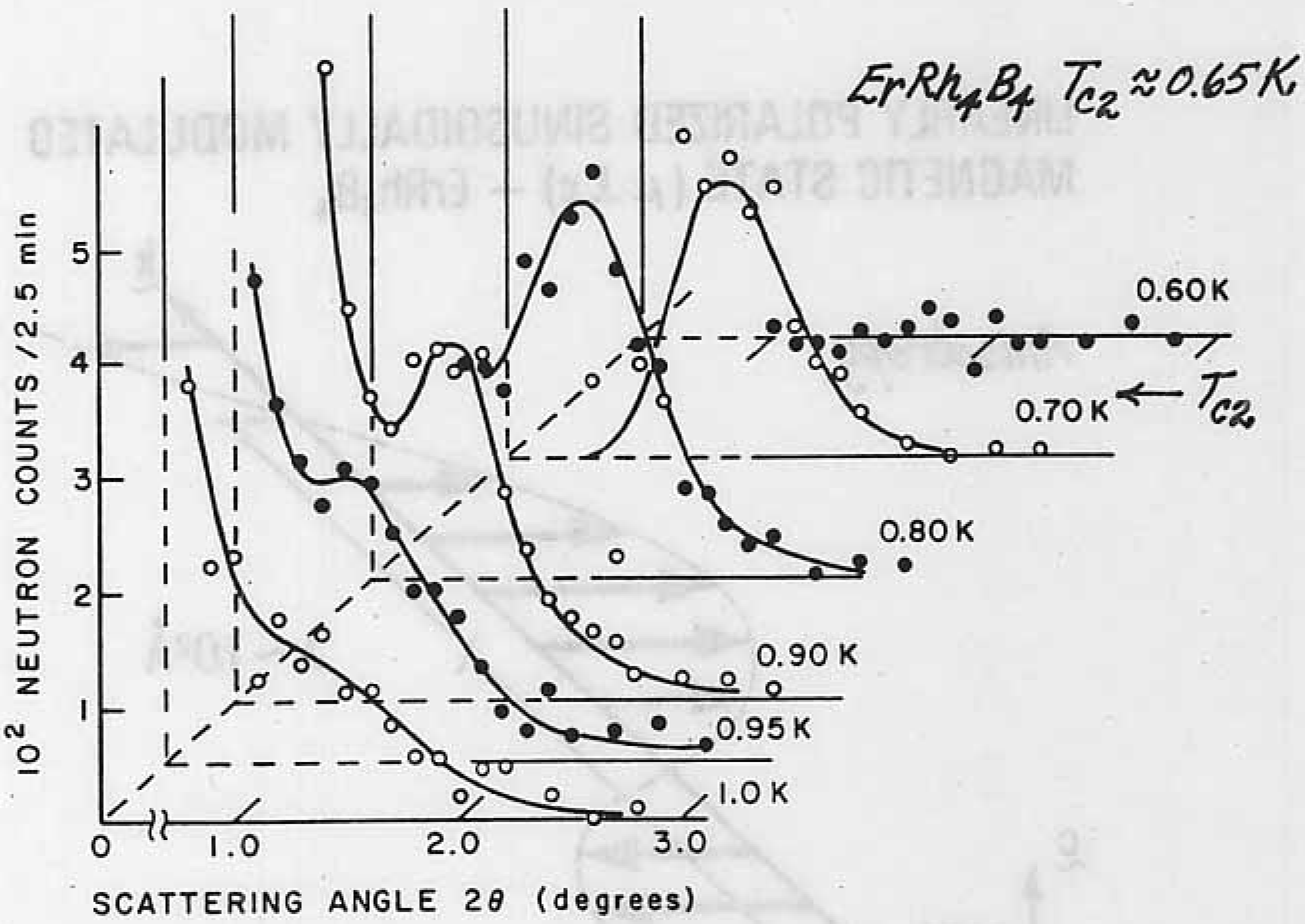
* Moncton, McWhan, Schmidt, Shirane, Thomlinson, Maple, MacKay, Woolf, Fisk, Johnston '80 (neutron scattering)

→ Macroscopic coexistence of SC & normal FM domains



D.E. Moncton, D.B. McWhan, P.H. Schmidt, G. Shirane, W. Thomlinson, M.B. Maple, H.B. MacKay, L.D. Woolf, Z. Fisk & D.C. Johnston '80

⇒ Microscopic coexistence of SC & sinusoidally-modulated magnetic state with $\lambda \sim 10^2 \text{Å}$

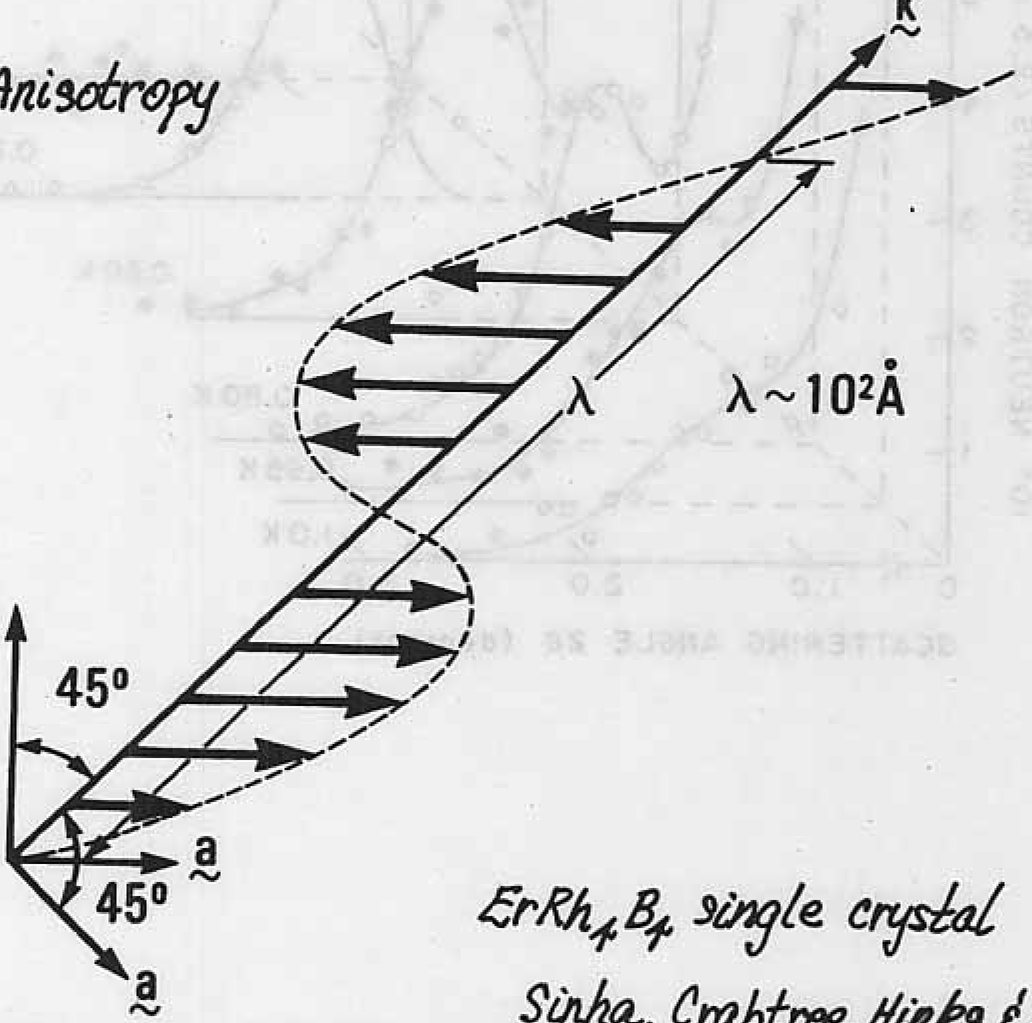


D.E. Moncton, D.B. McWhan, P.H. Schmidt, G. Shirane, W. Thomlinson, M.B. Maple, H.B. MacKay, L.D. Woolf, Z. Fisk & D.C. Johnston '80

Similar behavior – $HoMo_6S_8$ Lynn et al. '81

LINEARLY POLARIZED SINUSOIDALLY MODULATED MAGNETIC STATE ($\mu \perp c$) – $ErRh_4B_4$

Anisotropy



$ErRh_4B_4$ single crystal

Sinha, Crabtree, Hinks & Mook '81

Theories

Anderson, Suhl '59

Suhl '78

Blount, Varma '79

Bulaevski, Rusinov, Kulik '79

Matsumoto, Umezawa, Tachiki '79

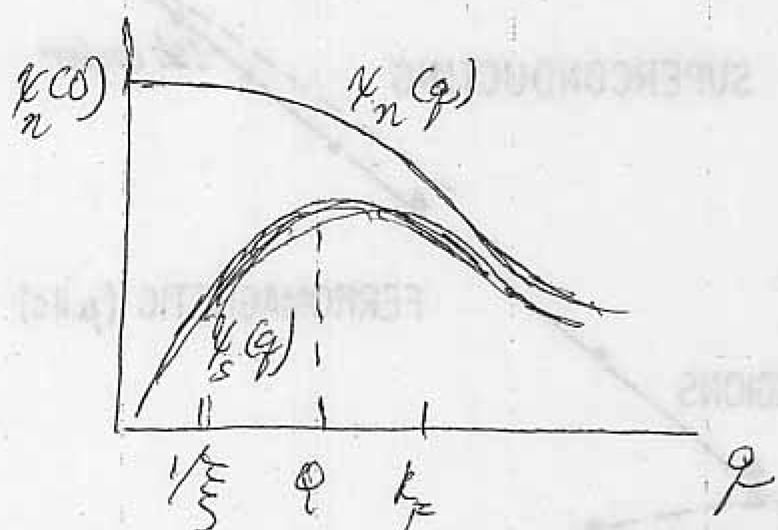
. . . .

Anderson-Suhl ('59) Cryptoferromagnetism

$$F_n(H) - F_s(H) = \frac{1}{2} N(E_F)\Delta^2 - \frac{1}{2}\left[\chi_n(q) - \chi_s(q)\right] H^2$$

∃ wavenumber $Q \ni F_n(H) - F_s(H) > 0$

$$\Rightarrow \frac{N(E_F)\Delta^2}{H^2} > \chi_n(Q) - \chi_s(Q)$$



Maximize $\chi_s(q) \Rightarrow Q = (3\pi k_F^2/\xi_0)^{1/2} \Rightarrow \lambda \approx 50\,\mathring{A}$

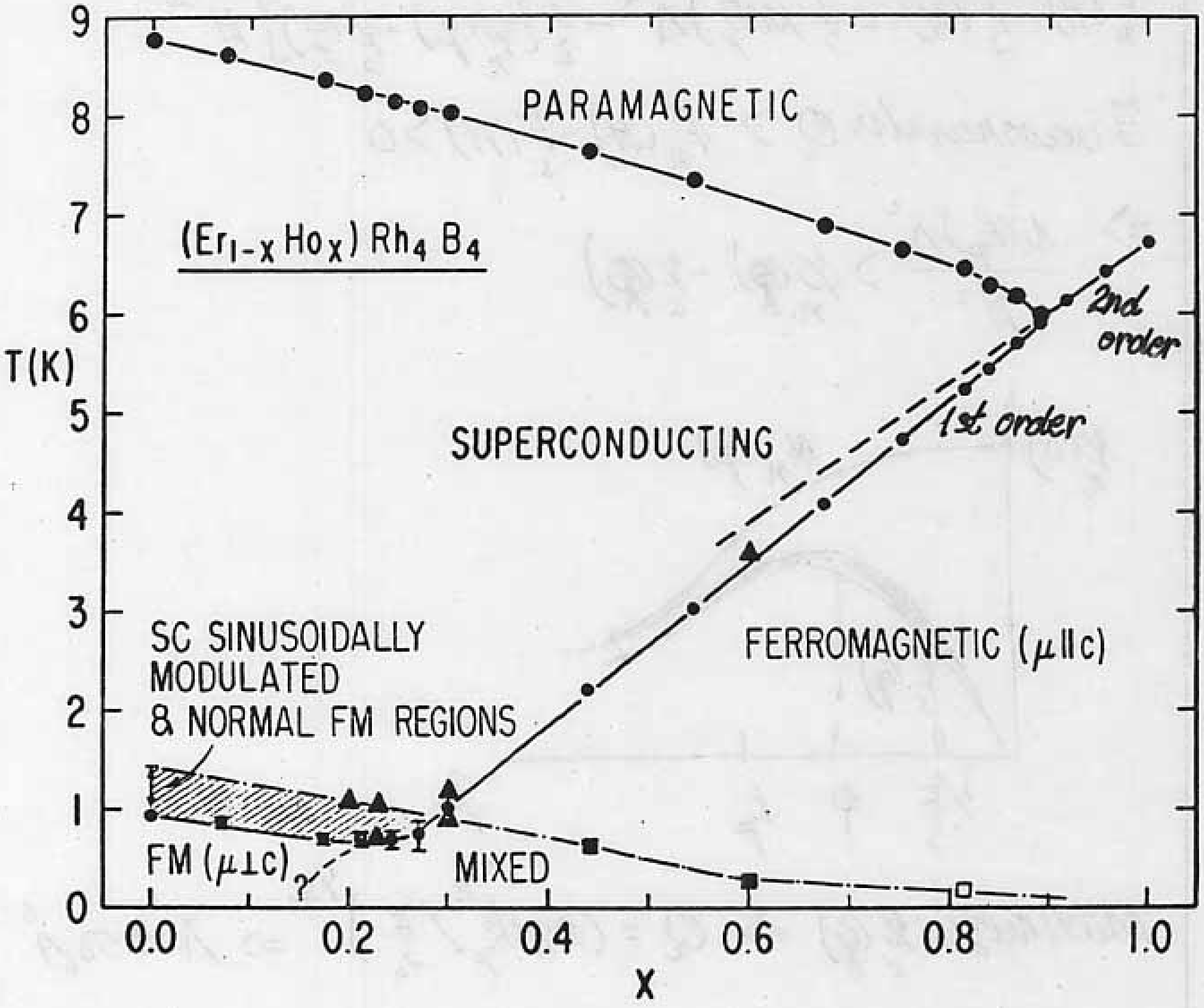
NOTE! w/o ordering at finite $q = Q$

FM: $\delta F_M \sim c N(k_B T_M)$ N - no. atoms

SC: $\delta F_S \sim (k_B T_C/E_F) N(k_B T_C)$

$\Rightarrow c \gg k_B T_C/E_F \Rightarrow$ FM ground state

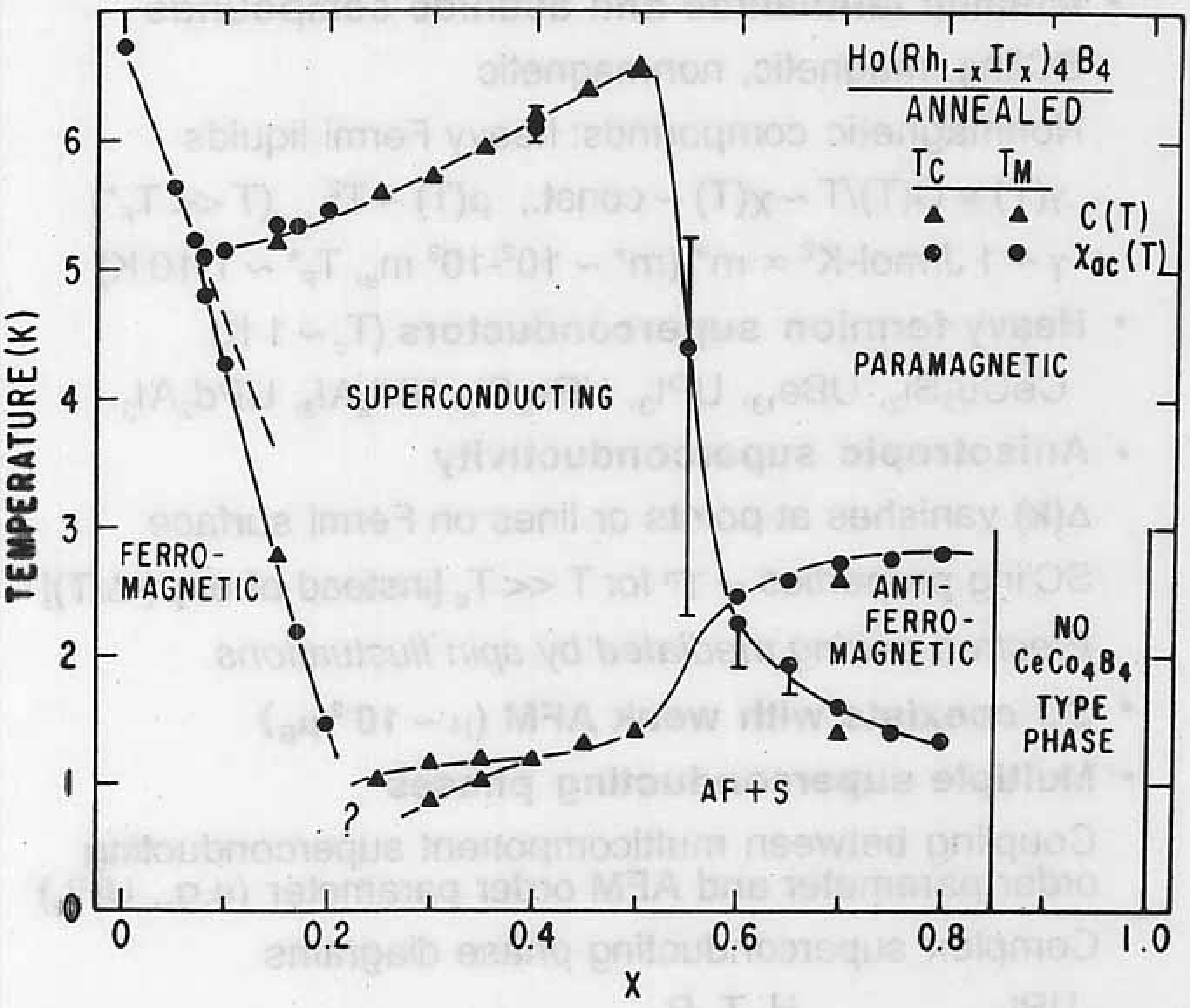
$(Er_{1-x}Ho_x)Rh_4B_4$ FM – $\mu \perp c$ vs $\mu \parallel c$



D.C. Johnston, W.A. Fertig, M.B. Maple & B.T. Matthias '78

H.A. Mook, W.C. Koehler, M.B. Maple, Z. Fisk,
D.C. Johnston & L.D. Woolf '82

$Ho(Rh_{1-x}Ir_x)_4B_4$ FM vs AFM



H.C. Ku, F. Acker & B.T. Matthias '80

K.N. Yang, S.E. Lambert, H.C. Hamaker, M.B. Maple,
H.A. Mook & H.C. Ku '82

S.E. Lambert, M.B. Maple, O.A. Pringle & H.A. Mook '85

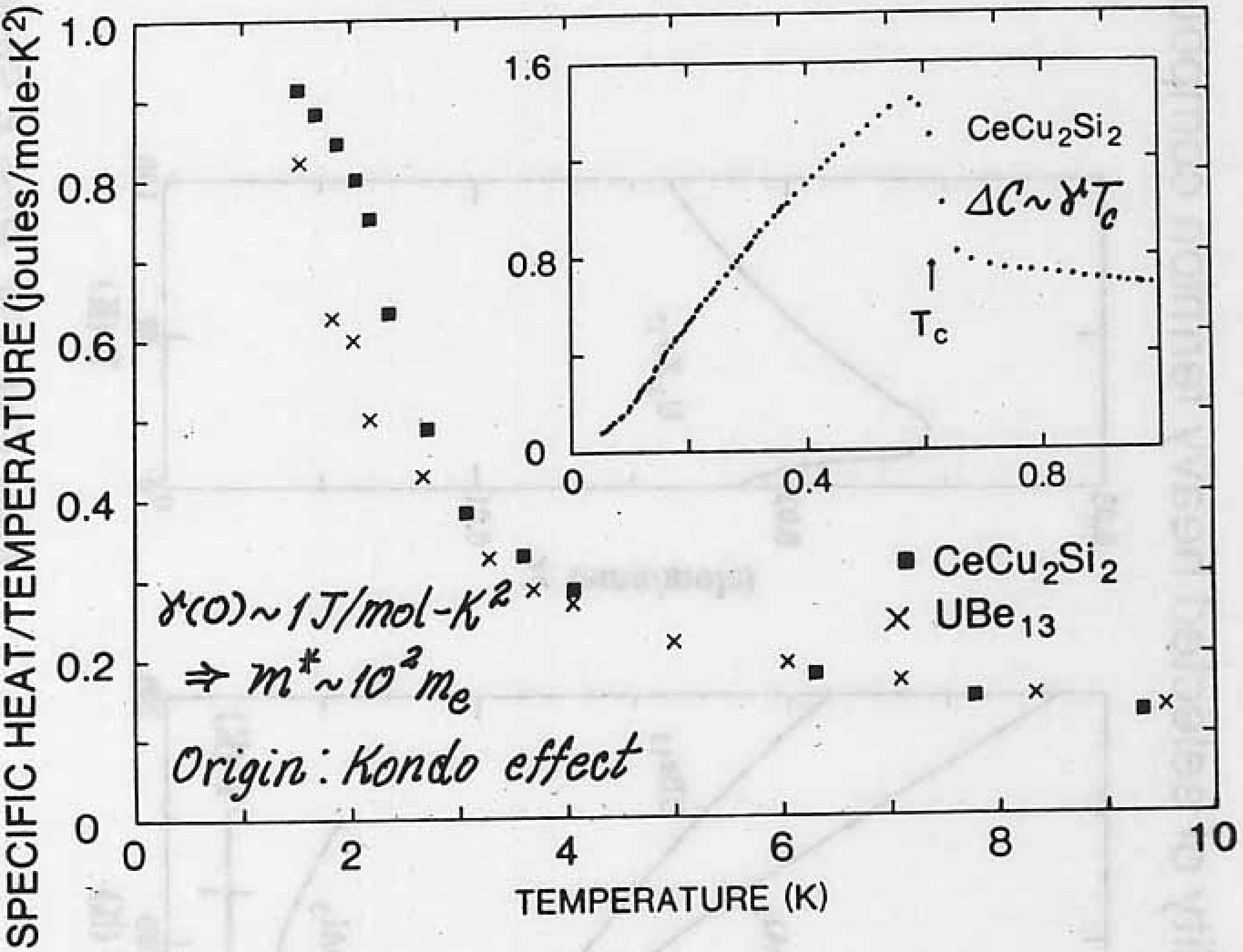
~'9c

Heavy fermion compounds

- **Metallic lanthanide and actinide compounds**
  SC'ing, magnetic, nonmagnetic
  Nonmagnetic compounds: heavy Fermi liquids
  $\gamma(T) \equiv C(T)/T \sim \chi(T) \sim \text{const.}, \ \rho(T) \sim T^2 \quad (T \ll T_F^*)$
  $\gamma \sim 1$ J/mol-K$^2 \propto m^*$ ($m^* \sim 10^2$-$10^3\ m_e$, $T_F^* \sim 1$-10 K)
- **Heavy fermion superconductors** ($T_c \sim 1$ K)
  $CeCu_2Si_2$, UBe_{13}, UPt_3, URu_2Si_2, UNi_2Al_3, UPd_2Al_3
- **Anisotropic superconductivity**
  $\Delta(\mathbf{k})$ vanishes at points or lines on Fermi surface
  SC'ing properties $\sim T^n$ for $T \ll T_c$ [instead of $\exp(-\Delta/T)$]
  Electron pairing mediated by spin fluctuations
- **SC coexists with weak AFM** ($\mu \sim 10^{-2}\ \mu_B$)
- **Multiple superconducting phases**
  Coupling between multicomponent superconducting order parameter and AFM order parameter (e.g., UPt_3)
  Complex superconducting phase diagrams

UPt_3	H, T, P
$U_{1-x}Th_xBe_{13}$	T, x, P

- **Chemical substitution**
  Suppresses SC and weak AFM
  Induces local moment AFM or FM ($\mu \sim 1\ \mu_B$)
  UPt_3 — Th for U; Pd, Au for Pt ⇒ local moment AFM
  URu_2Si_2 — Rh for Ru ⇒ local moment AFM
  Re, Tc for Ru ⇒ local moment FM



$\gamma(0) \sim 1 J/mol\text{-}K^2$

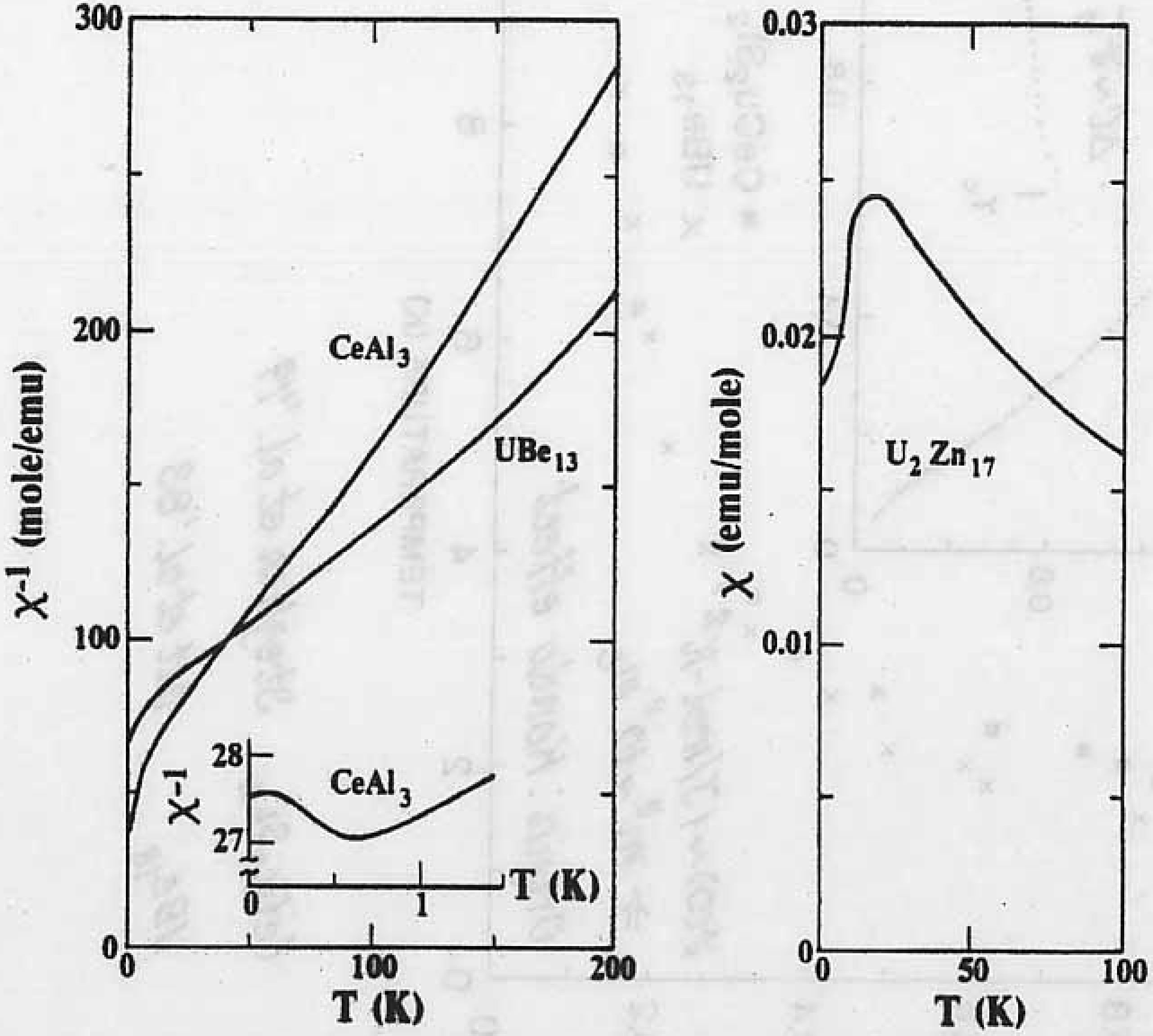
$\Rightarrow m^* \sim 10^2 m_e$

Origin: Kondo effect

$CeCu_2Si_2$ Steglich et al. '79

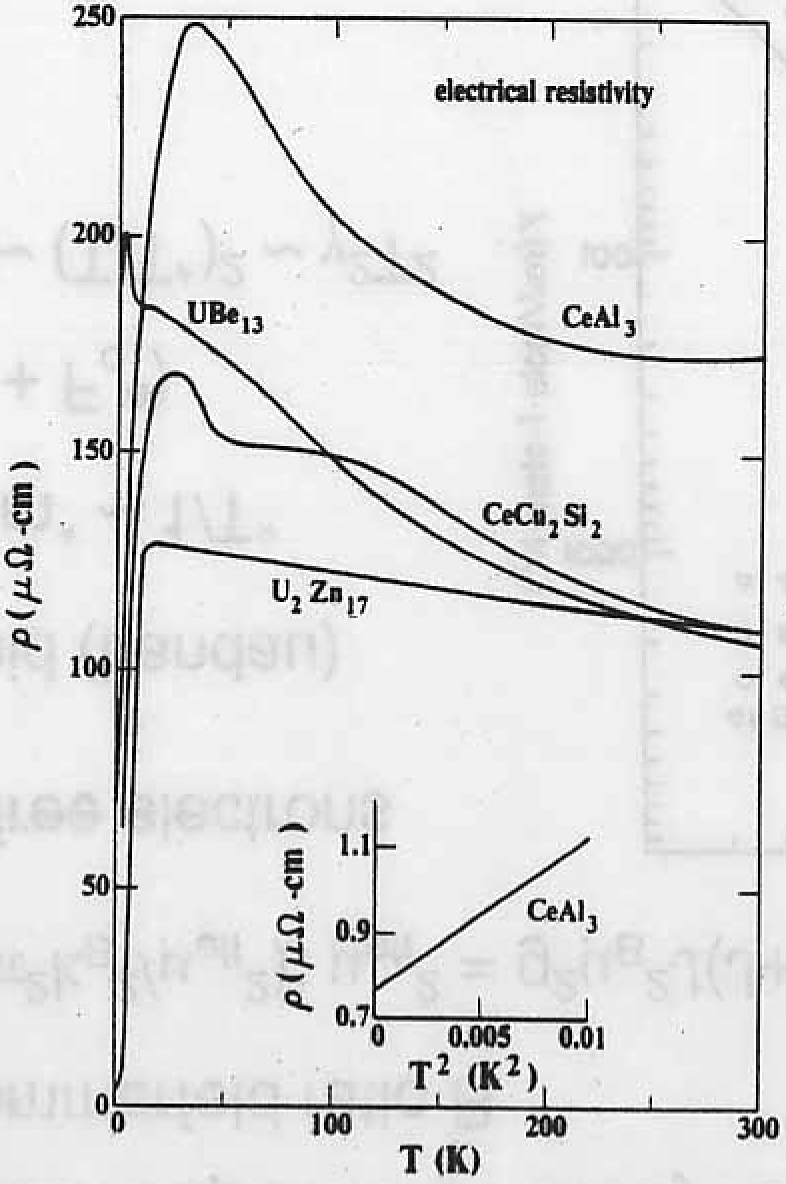
UBe_{13} Ott et al. '83

Magnetic susceptibility of selected heavy fermion compounds



After Fisk, Ott, Rice & Smith 86

Electrical resistivity of selected heavy fermion compounds



After Fisk, Ott, Rice & Smith 86

Fermi liquid aspects of heavy fermion metals

Wilson-Sommerfeld ratio R

$R = (\chi/\gamma)(\pi^2 k_B^2/\mu_{eff}^2)$; $\mu_{eff}^2 = g^2\mu_B^2 J(J+1)$

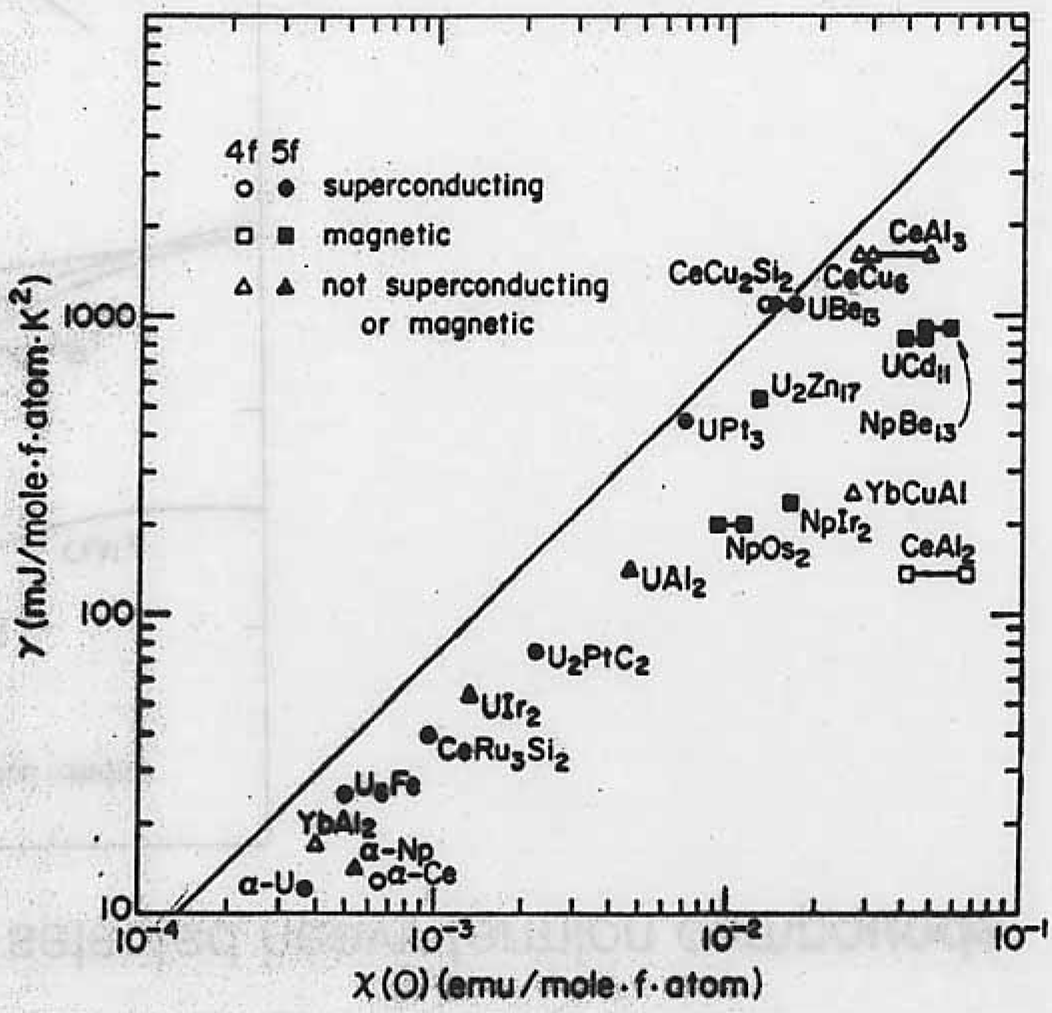
$R \approx 1$ for free electrons

Fermi liquid (Landau)

$\gamma = C/T \sim m^* \sim 1/T^*$

$\chi \sim m^*/(1 + F_o^a)$

$\Delta\rho = AT^2 \sim (T/T^*)^2 \sim \gamma^2 T^2$



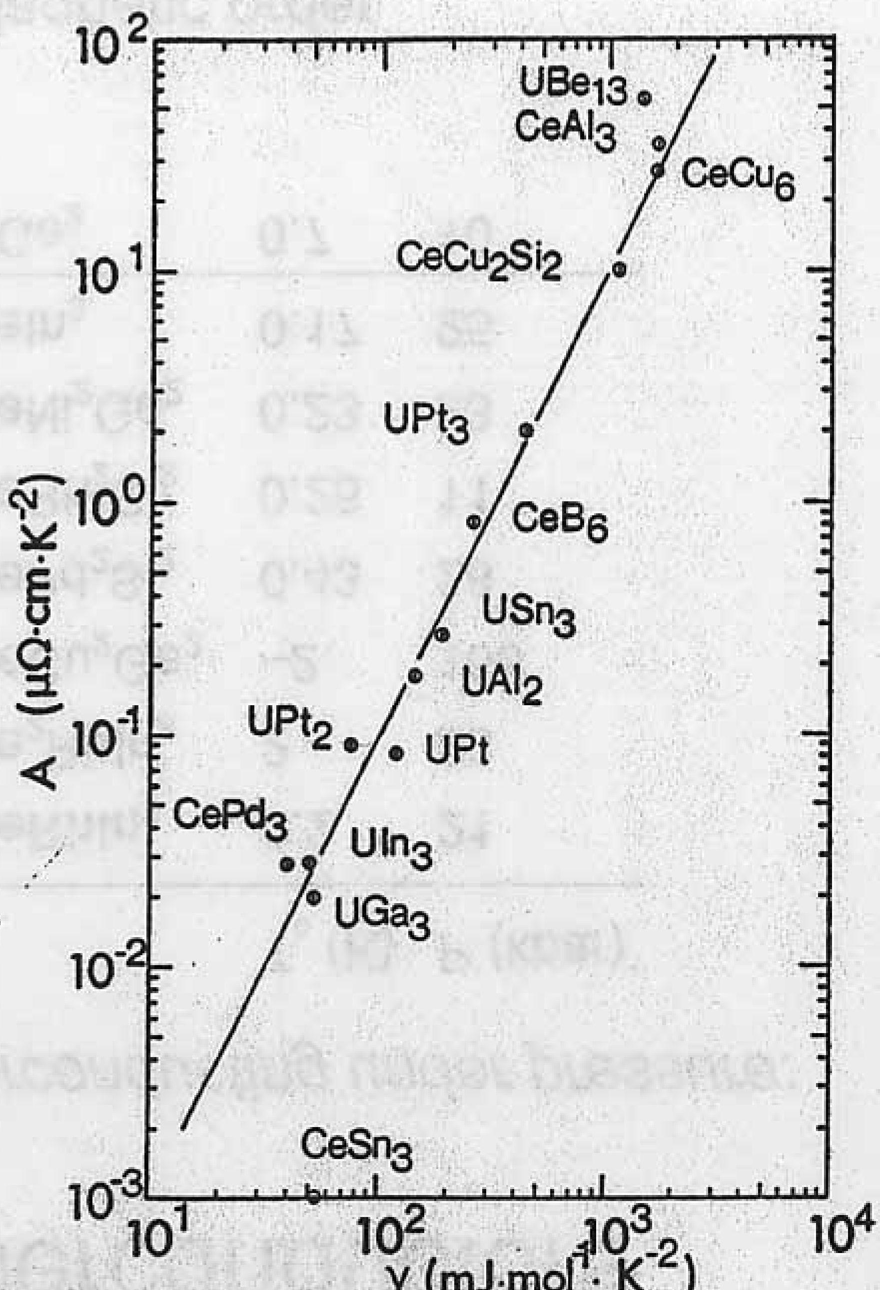
Electron-electron scattering

Heavy quasiparticles

$\rho_{\text{el-el}}(T) \sim (T/T_F)^2 \sim AT^2 \sim \gamma^2 T^2$

$\Rightarrow A \sim \gamma^2,\ \ln A \propto 2\ln\gamma$

Kadowaki-Woods plot '86



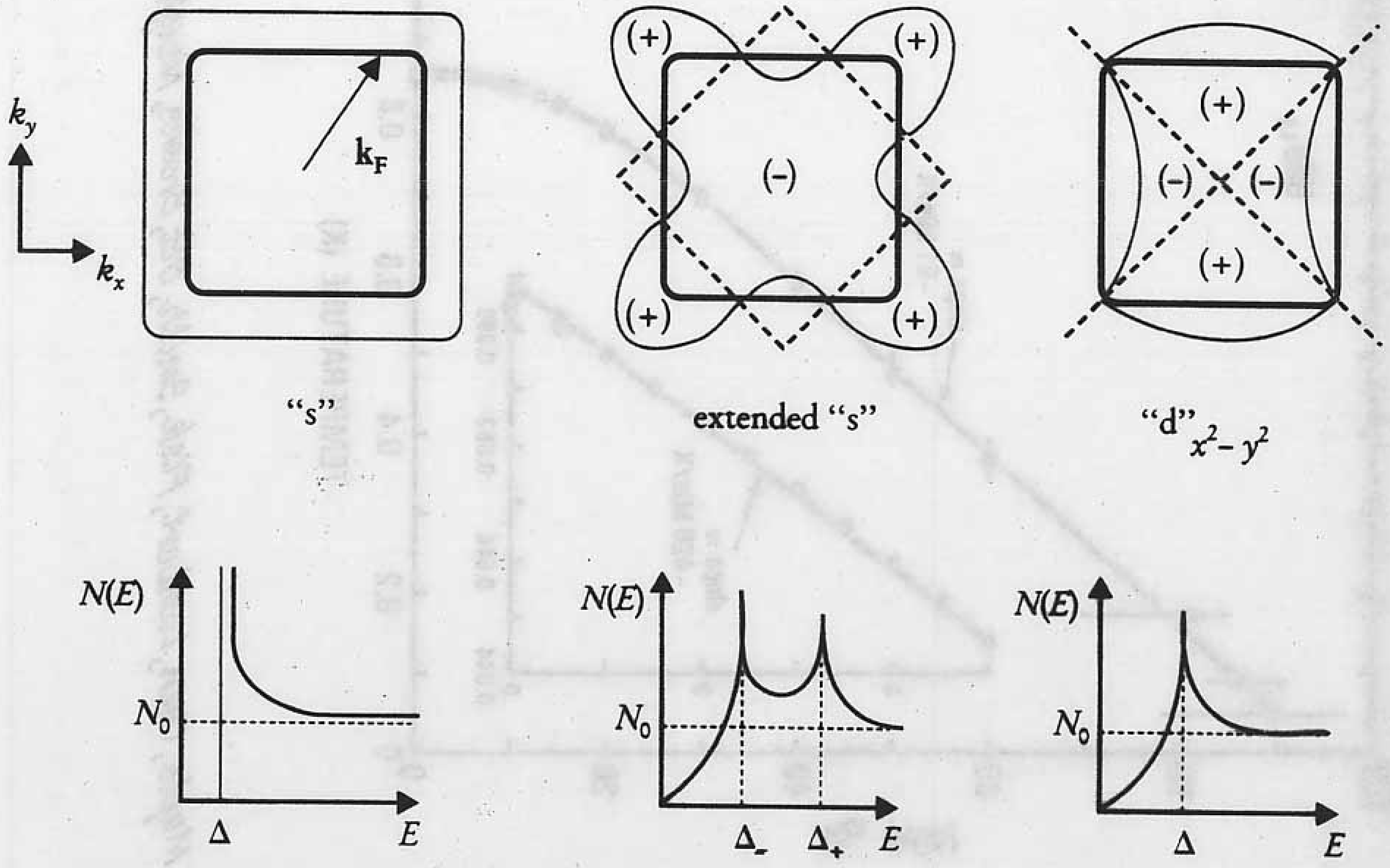
Heavy fermion superconductors

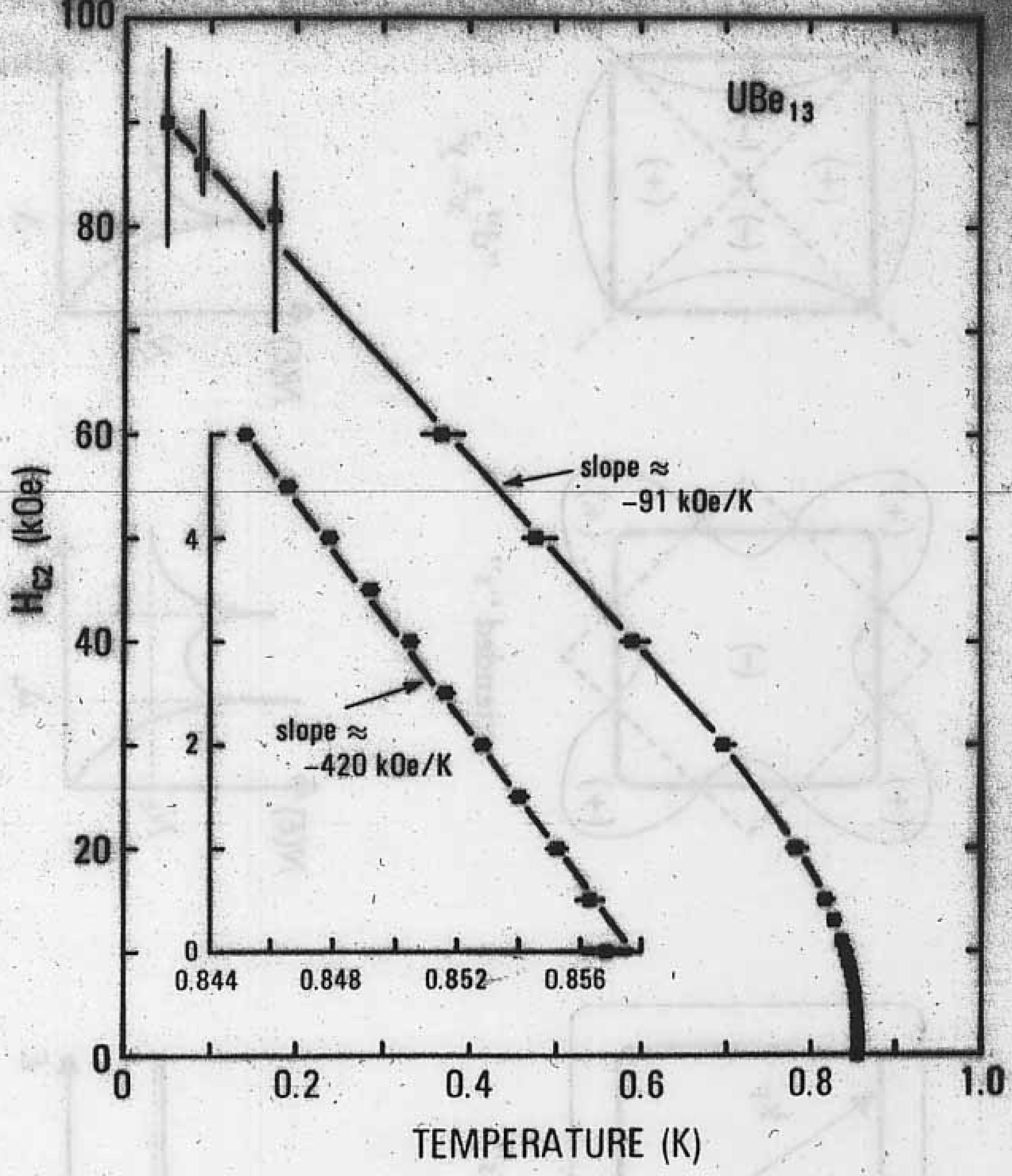
		T_c (K)
	$CeCoIn_5$	**2.3**
*	$CeCu_2Si_2$	0.49
	$CeIrIn_5$	**0.4**
	U_6Fe	3.7
*	UPd_2Al_3	2.0
*	URu_2Si_2	1.5
*	UNi_2Al_3	1.0
	UBe_{13}	0.85
*	UPt_3	0.55
*	URhGe	0.4
	$PrOs_4Sb_{12}$	1.8
	$PuCoGa_5$	18

Superconducting under pressure:

		T_c (K)	P (kbar)
*	**$CeRhIn_5$**	**2.2**	**21**
*	Ce_2RhIn_8	2	23
*	$CeCu_2Ge_2$	~2	165
*	$CePd_2Si_2$	0.43	28
*	$CeRh_2Si_2$	0.26	11
	$CeNi_2Ge_2$	0.23	23
*	$CeIn_3$	0.17	25
*	UGe_2	0.7	10

* Magnetic order


k_y
k_x
$\mathbf{k}_F$
"s"
(+)
(-)
extended "s"
"d" $_{x^2-y^2}$
$N(E)$
N_0
Δ
E
Δ_-
Δ_+



Maple, Chen, Lambert, Fisk, Smith, Ott, Brooks, Naughton '85

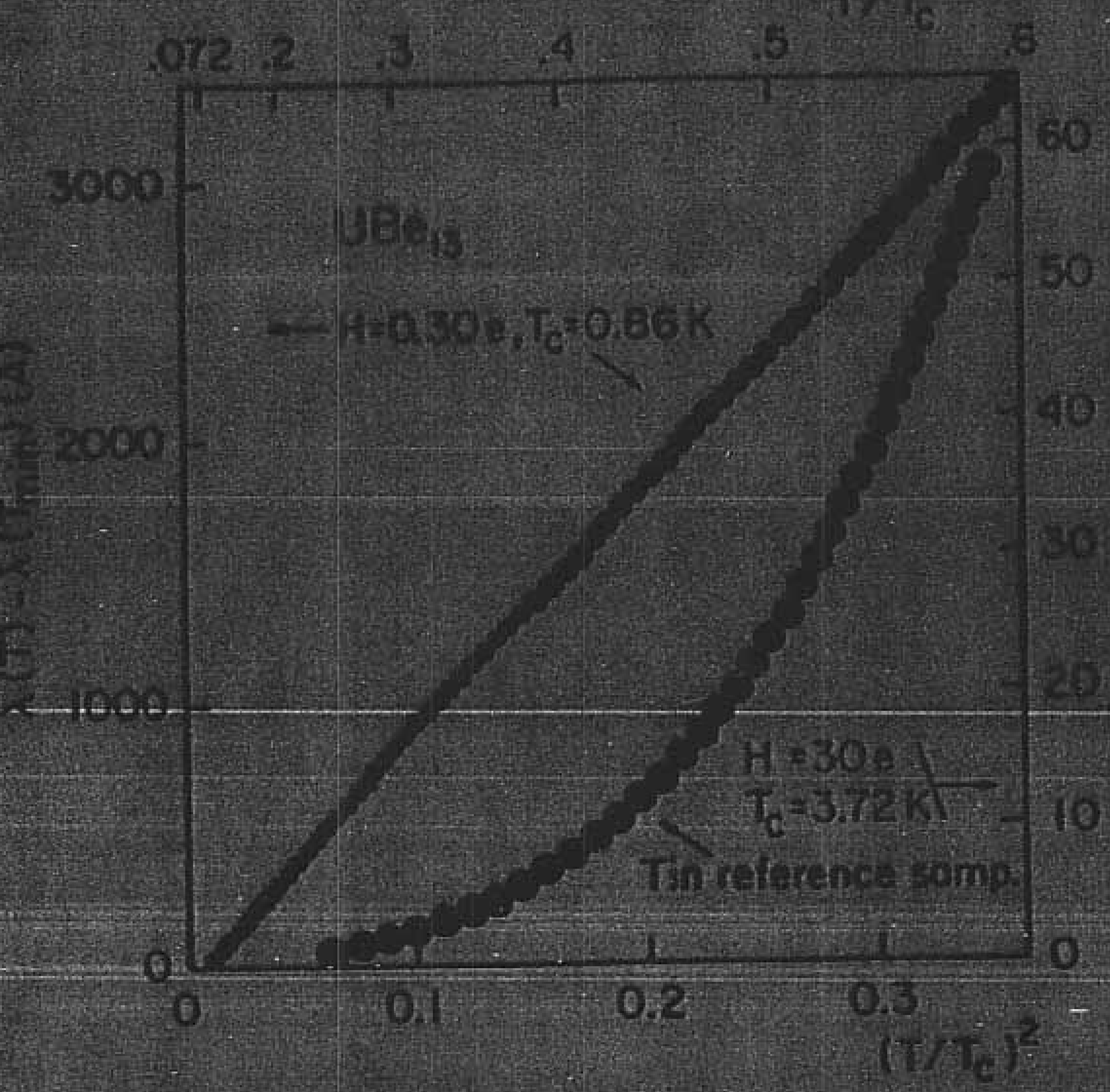
Anisotropic SC: $\Delta(\mathbf{k})$ vanishes at points or lines on FS

SC'ing properties ~ T^n

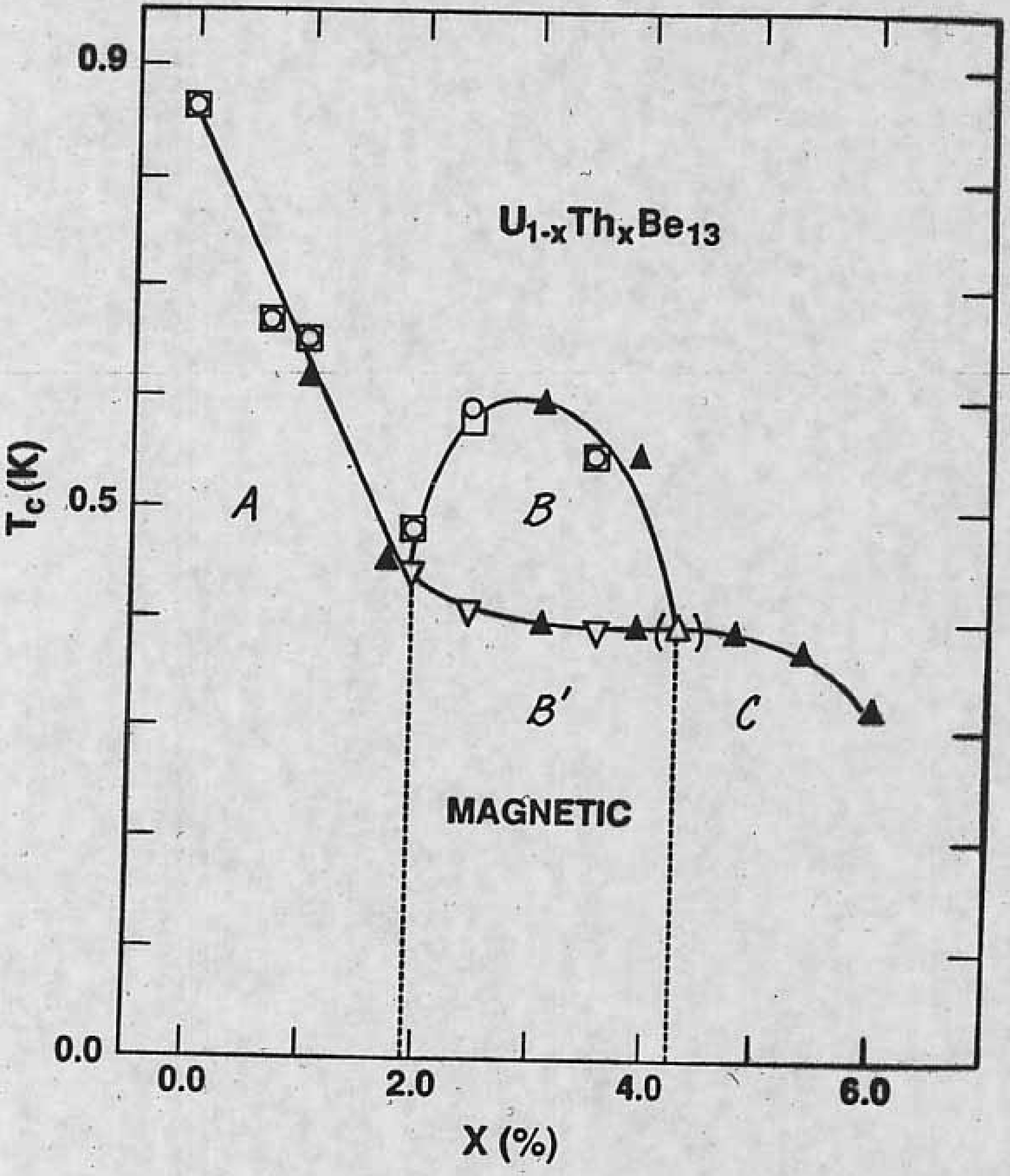
Isotropic SC (BCS): $\Delta(\mathbf{k})$ ~ constant

SC'ing properties ~ $\exp(-\Delta/T)$

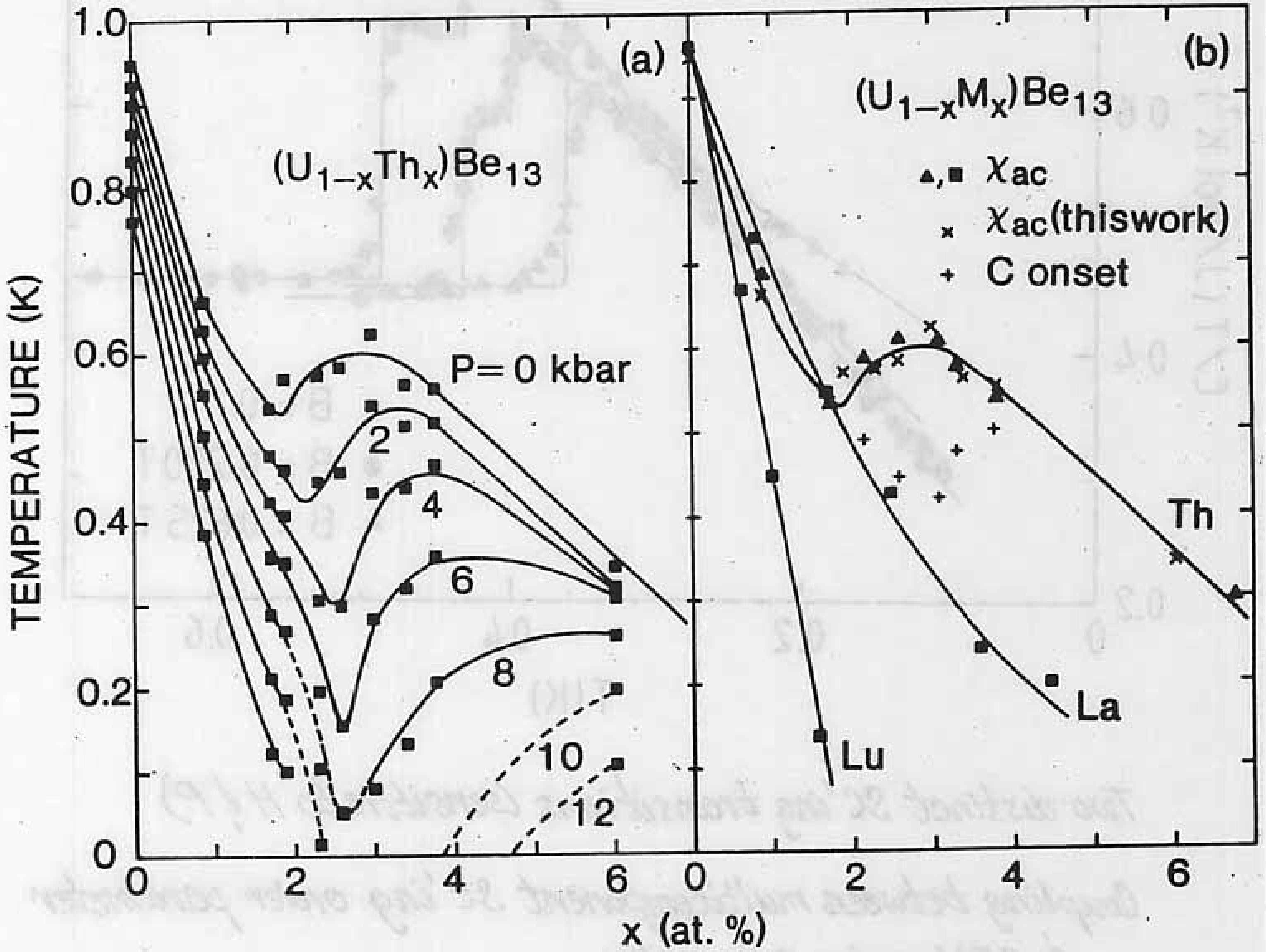
UBe_{13}: $\lambda \sim T^2$ (odd parity SC)



Gross, Chandrasekhar, Einzel, Andres, Hirshfeld, Ott, Beuers, Fisk, Smith '86

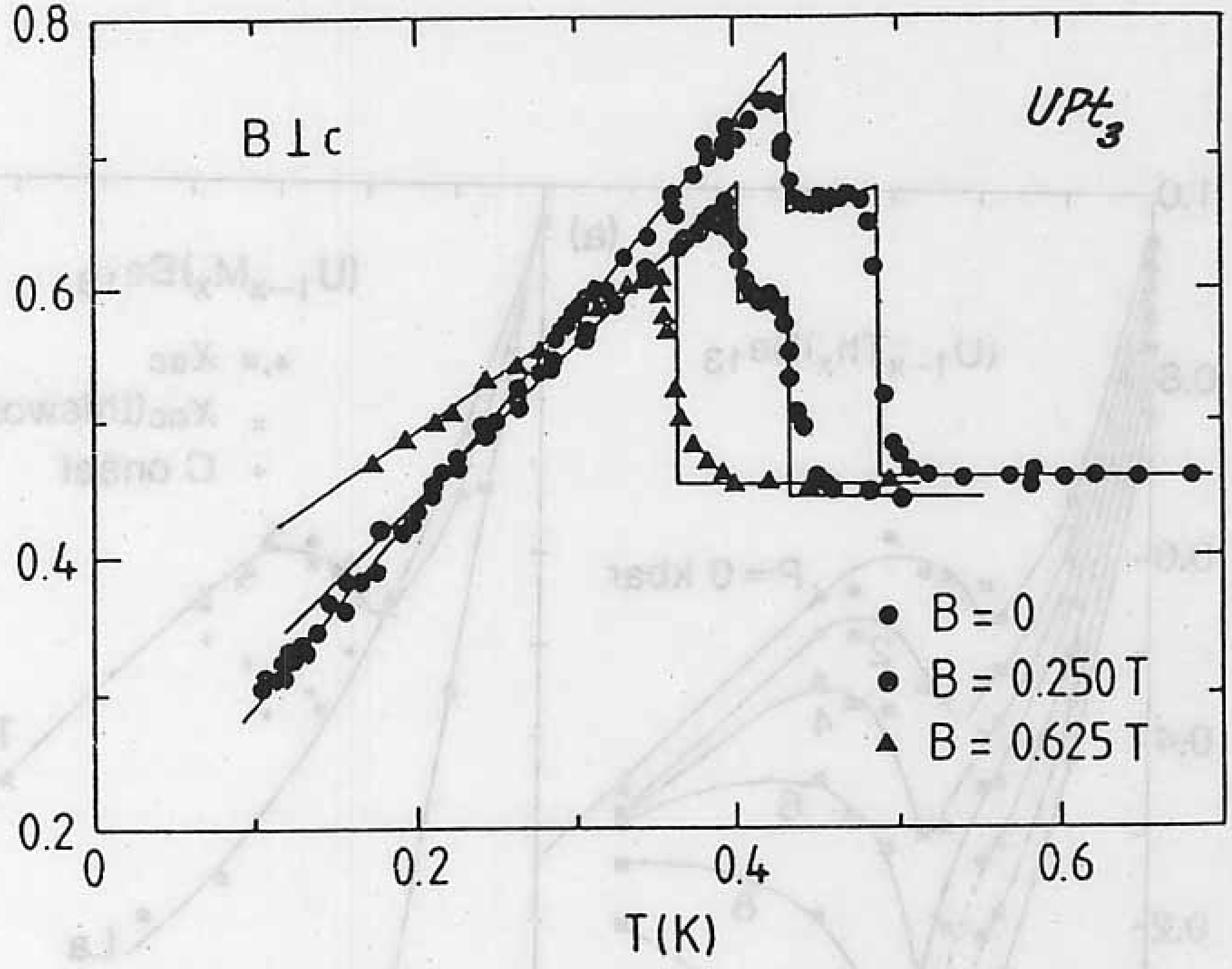


R.H.Heffner et al. '90



S.E. Lambert, Y. Dalichaouch, M.B. Maple, J.L. Smith & Z. Fisk (1986)

Hasselbach, Taillefer, Flouquet '89

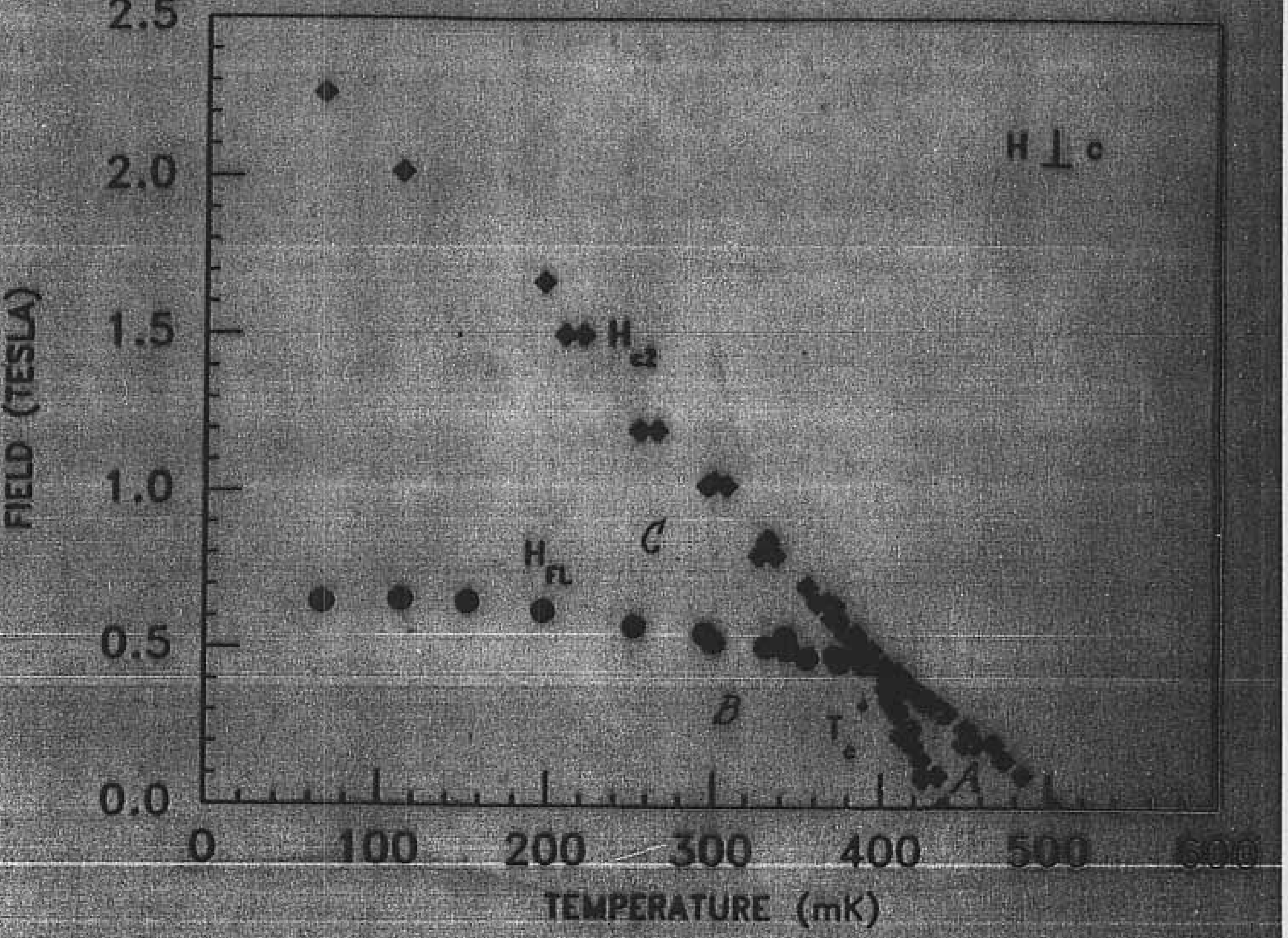


Two distinct SC'ing transitions (sensitive to H & P)

Coupling between multicomponent SC'ing order parameter & AFM order parameter

AFM: $T_N \approx 5K$, $\mu \approx 0.02\mu_B/U$ (basal plane)
Aeppli et al. '88

Adenwalla, Ketterson, Yip, Lin, Levy, Sarma '92
Ultrasonic velocity measurements



B-phase:

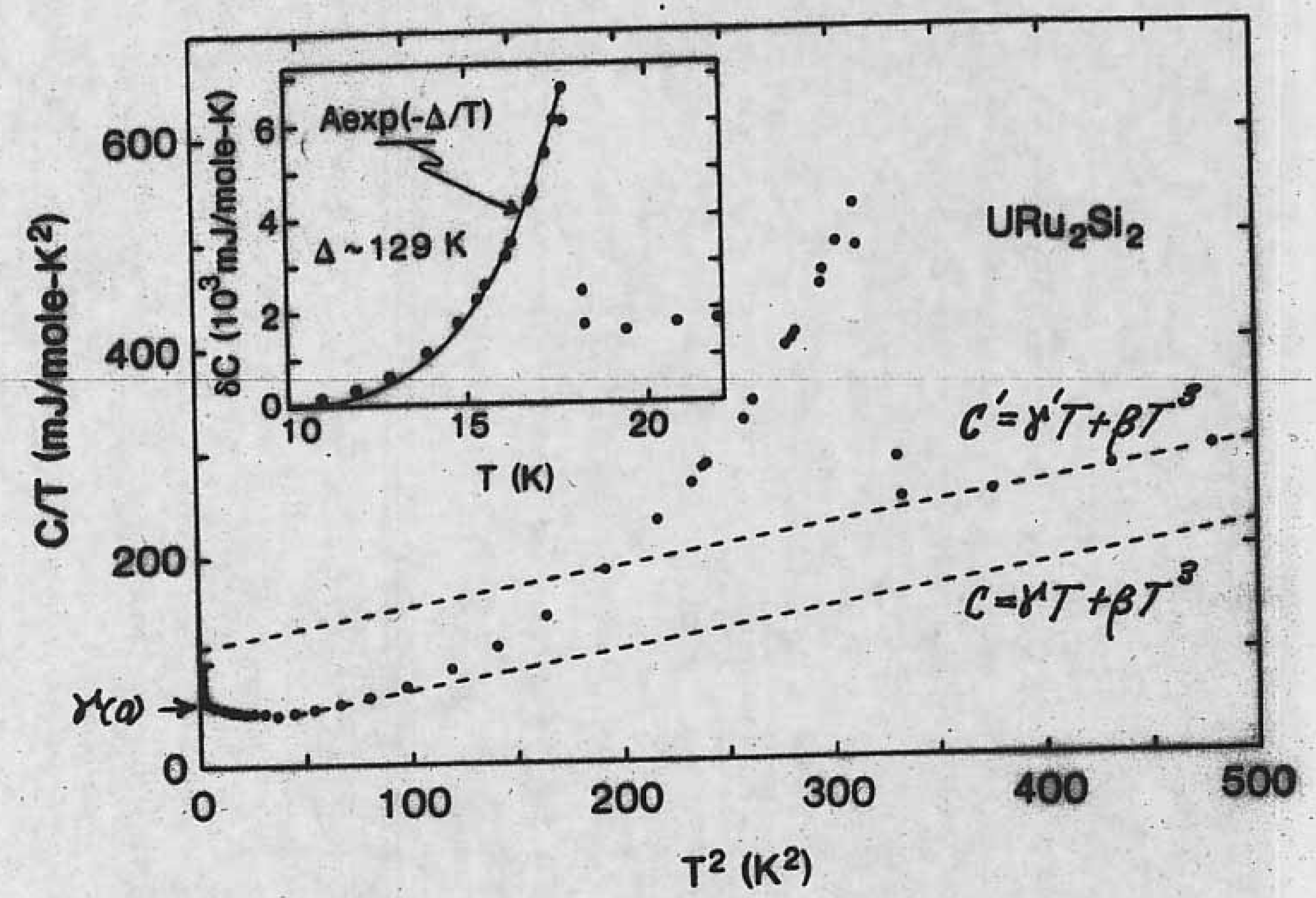
(1) Point contact spectroscopy ⇒ gap-like feature
Goll *et al.* '93

(2) Zero field μSR – increase in internal magnetic field
Luke *et al.* '93

Odd-parity, spin-triplet SC'ing state — Sauls '94

URu_2Si_2: heavy electron AFM–SC

Schlabitz et al. '86 polycrystalline material
Palstra et al. '85 single crystals



BCS-type mean field transition at $T_N = 17.5$ K

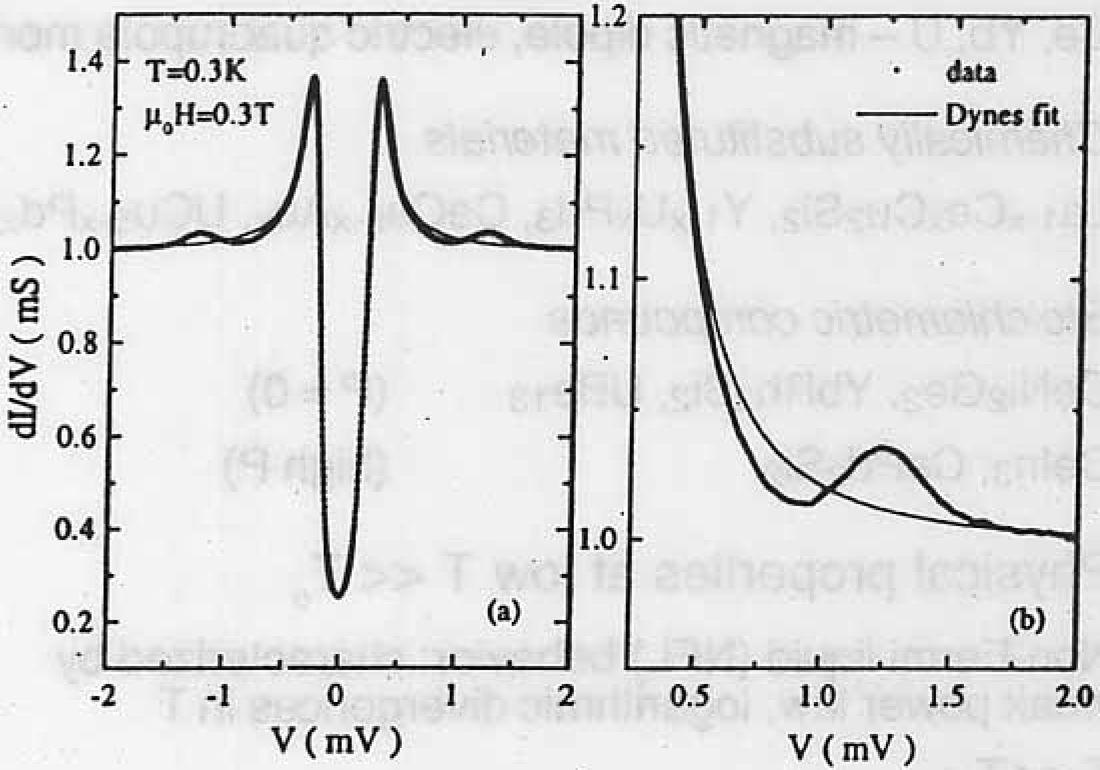
$\delta C \approx A\exp(-\Delta/T)$; $\Delta \sim 10^2$ K ~ 10 meV

AFM ($\mu \approx 0.02\ \mu_B$/U) coexists with SC

$\gamma(0)/\gamma' \approx 0.6 \Rightarrow \sim 40$ % Fermi surface removed by SDW

Maple, Dalichaouch, Kohara, Rossel, Torikachvili, McElfresh, Thompson '86

Electron tunneling $UPd_2Al_3 - Pb$



UPd_2Al_3 Geibel et al. '91

Moderately heavy electron

AFM-SC

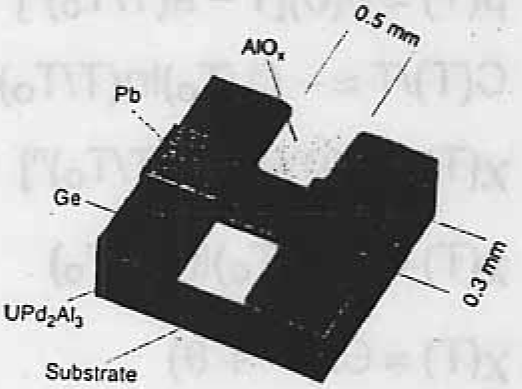
$\gamma = 140\,mJ/mol\,K^2$

$T_N = 14.6\,K$ ($\mu = 0.85\mu_B$)

$T_c \approx 2K$

d-wave pairing, line nodes

Gapped dispersive spin excitations with $\Delta E \sim 1.5\,meV$ at magnetic Bragg point $Q = (0, 0, 1/2)$ Sato et al. '97



Jourdan, Huth, Adrian '98

Non-Fermi liquid behavior in f-electron materials

- Materials – Ce, Yb & U intermetallic compounds

  Ce, Yb, U – magnetic dipole, electric quadrupole moments

  Chemically substituted materials

  $La_{1-x}Ce_xCu_2Si_2$, $Y_{1-x}U_xPd_3$, $CeCu_{6-x}Au_x$, $UCu_{5-x}Pd_x$, . . .

  Stoichiometric compounds

  $CeNi_2Ge_2$, $YbRh_2Si_2$, UBe_{13} $(P = 0)$
  $CeIn_3$, $CePd_2Si_2$ (high P)

- Physical properties at low $T \ll T_o$

  Non-Fermi liquid (NFL) behavior: characterized by weak power law, logarithmic divergences in T

  $T \ll T_o$:

  - $\rho(T) \approx \rho(0)[1 - a(T/T_o)^n]$ $(1 \leq n \leq 1.5;\ a > 0 \text{ or } < 0,\ |a| \sim 1)$
  - $C(T)/T \approx -(1/T_o)\ln(T/T_o)$ $S(0) \sim (k_B/2)\ln(2)$
  - $\chi(T) \approx \chi(0)[1 - c(T/T_o)^n]$ $(n \sim 0.5;\ c \sim 1)$

    $\chi(T) \approx -(1/T_o)\ln(T/T_o)$

    $\chi(T) \approx C/(T^\alpha + \theta)$
  - $\chi''(\omega,T)$: ω/T scaling

  T-dependence below T_o:
  * Appreciable ⇒ lower energy scale than Fermi liquid (FL)
  * Scales with T_o

- Magnetic or charge degrees of freedom
- Two scenarios

  Single ion

    Unconventional Kondo effect (multichannel?)

  Inter-ionic interactions

    Fluctuations of OP in vicinity of x_c or P_c where magnetic or quadrupolar phase transition vanishes

- Atomic disorder (distribution of T_K's; Griffiths' phase)
- Stoichiometric f-electron compounds under pressure

  SC observed in narrow range of P in vicinity of P_c where $T_M \rightarrow 0$ K in single crystal specimens with $l \gg \xi_o$

AFM:	$CePd_2Si_2$, $CeIn_3$	Cambridge
	$CeCu_2Ge_2$	Geneva
	$CeNi_2Ge_2$	Dresden, Cambridge
FM:	UGe_2	Cambridge, Grenoble
	$ZrZn_2$	Karlsruhe, Cambridge

Models of NFL behavior in f-electron materials

Single ion

- **Multichannel Kondo effect** — *Nozieres & Blandin '80; ...*

  Two-channel, spin-1/2 Kondo effect: two channels of **conduction electrons "overscreen"** spin-1/2 impurity ion

  ⇒ **Residual spin at T = 0 K** ⇒ Local NFL (single ion QCP)

  Quadrupolar Kondo effect (U^{4+}, Γ_3 g.s.) — *Cox '87*

- **Kondo disorder** — *Bernal et al. '95; Miranda et al. '96*

  Local disorder ⇒ Distribution of coupling **constants** $\mathbf{N(E_F)}\mathcal{J}$

  ⇒ Distribution of values of $T_K \sim T_F \exp(-1/N(E_F)|\mathcal{J}|)$

  Impurities with $T_K < T$ remain magnetic ⇒ **NFL behavior**

Inter–ionic interactions

- **Fluctuations of OP near 2nd order phase transition at T = 0 K** — *Hertz '76, Moriya '85; Millis '93; Continentino '93;…*

  QCP – groundstate changes from ordered to **disordered as control parameter** (x, P) changed

  Quantum fluctuations in OP near QCP ⇒ **NFL behavior**

- **Griffith's phase** — *Castro Neto, Castilla, Jones '97*

  Competition between Kondo effect & RKKY **interaction + disorder** ⇒ Inhomogeneous system: **paramagnetic FL phase (Kondo effect) & magnetic clusters** (RKKY) ⇒ **NFL behavior**

Other

- **Electronic polarons plus disorder** — *Liu '97*
- **Proximity to disorder–induced metal–insulator transition** — *Süllow et al. '00*

The $M_{1-x}U_xPd_3$ (M = Sc, Y) systems

$Y_{1-x}U_xPd_3$

- **NFL behavior for $0 < x < \sim 0{,}2$**

  $\rho(T,H)$, $C(T)$, $M(T,H)$ for $0 \le x \le 0.55$

  Quadrupolar Kondo model

  Seaman, Maple, Lee, Ghamaty, Torikachvili, Kang, Liu, Allen, Cox '91

- **NFL behavior for $x = 0.2$**

  $\rho(T,H)$, $C(T,H)$, $M(T,H)$ for $x = 0.2$

  Second order magnetic phase transition at T = 0 K

  Andraka, Tsvelik '91

- **NFL behavior scales with T_K and x ($0 \le x \le 0.2$)**

  Single ion effect

  $\Delta\rho(T) = \Delta\rho(0)[1 - a(T/T_K)]$ QKE: no

  QKE: $\Delta\rho(T) = \Delta\rho(0)[1 - a(T/T_K)^{1/2}]$

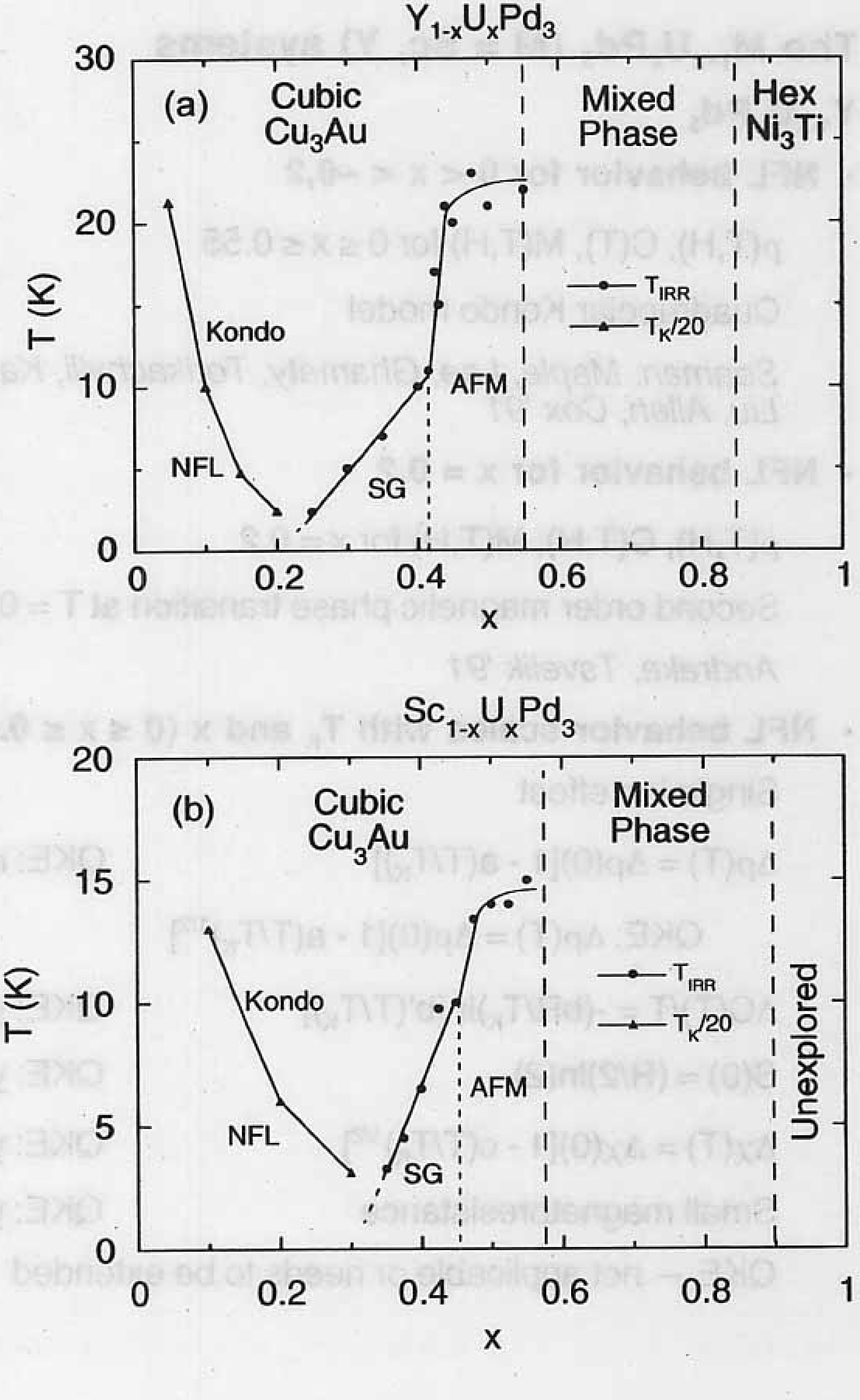
  $\Delta C(T)/T = -(bR/T_K)\ln[b'(T/T_K)]$ QKE: yes

  $S(0) \approx (R/2)\ln(2)$ QKE: yes

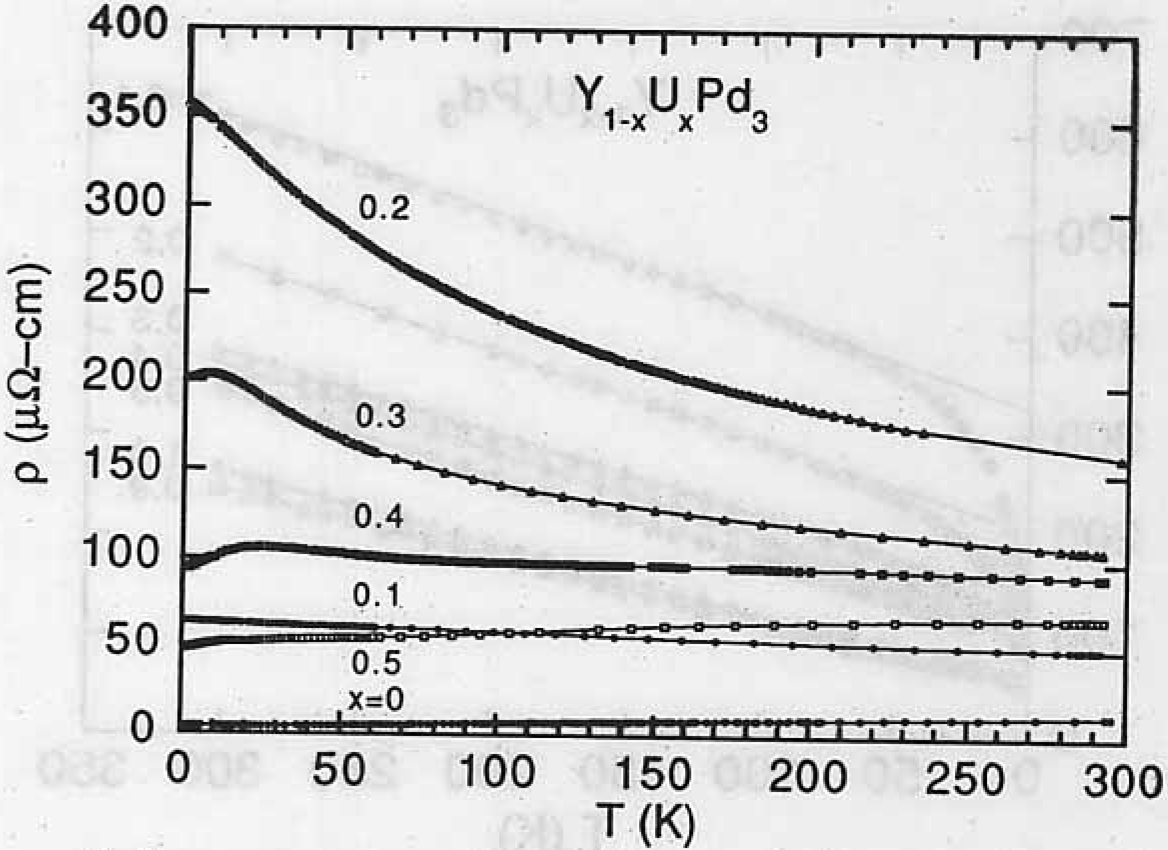
  $\Delta\chi(T) = \Delta\chi(0)[1 - c(T/T_K)^{1/2}]$ QKE: yes

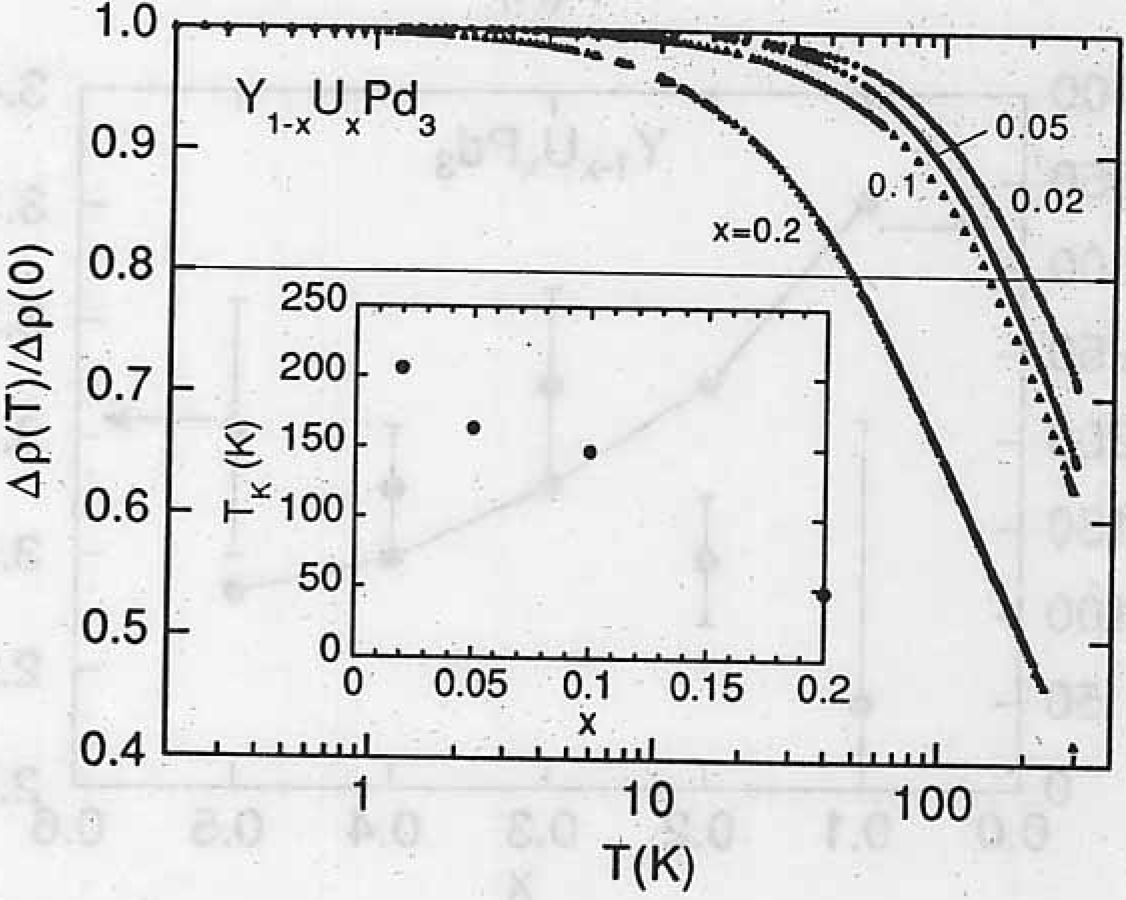
  Small magnetoresistance QKE: yes

  QKE — not applicable or needs to be extended


$Y_{1-x}U_xPd_3$
(a)
Cubic Cu_3Au
Mixed Phase
Hex Ni_3Ti
Kondo
NFL
SG
AFM
T_{IRR}
$T_K/20$
T (K)
x
30
20
10
0
0
0.2
0.4
0.6
0.8
1
$Sc_{1-x}U_xPd_3$
(b)
Cubic Cu_3Au
Mixed Phase
Unexplored
Kondo
NFL
SG
AFM
T_{IRR}
$T_K/20$
T (K)
x
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1

High-T electrical resistivity

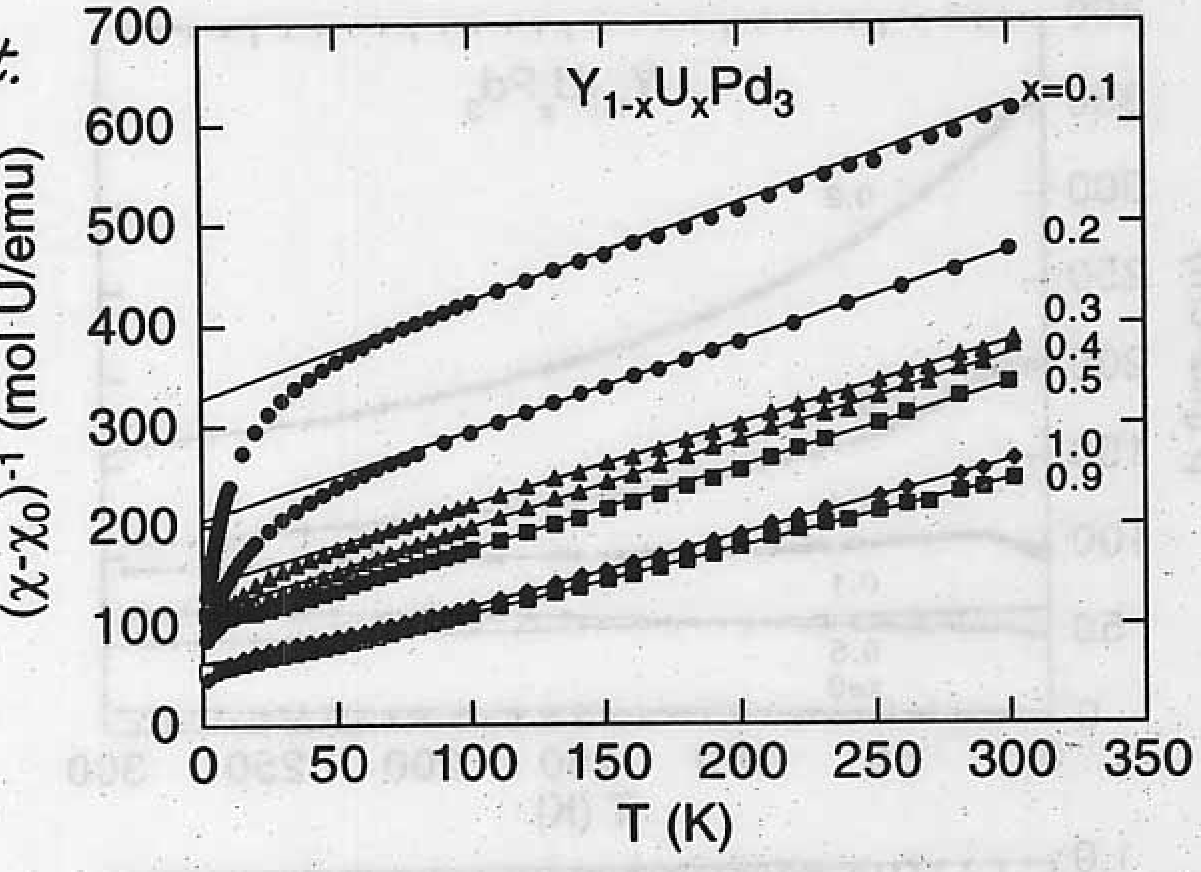


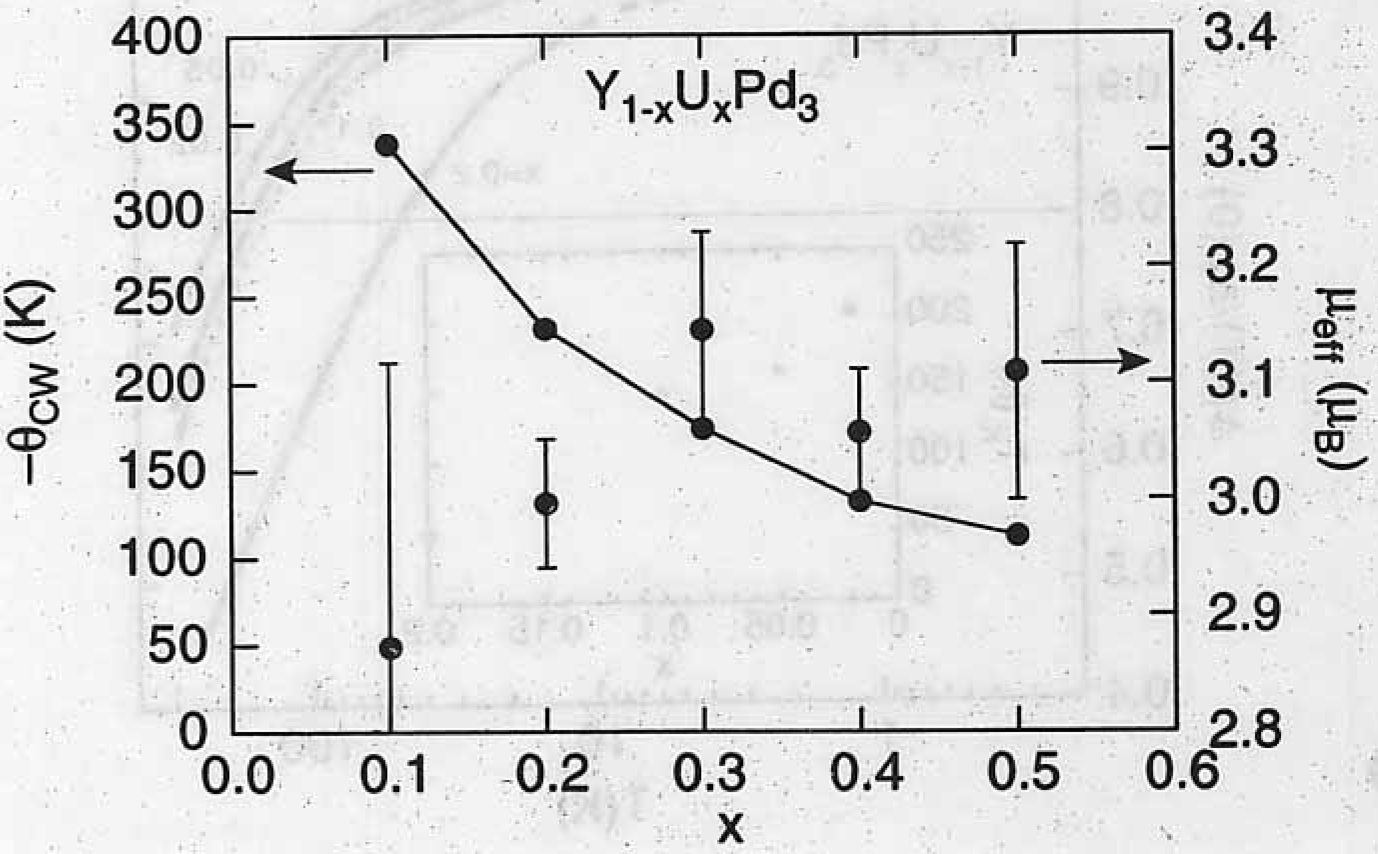


High-T $\chi - \chi_0 = \frac{C}{T-\theta_{cw}}$; $C = N\mu_{eff}^2 / 3k_B$, $-\theta_{cw} \approx 3\text{-}4\ T_K$

mag.

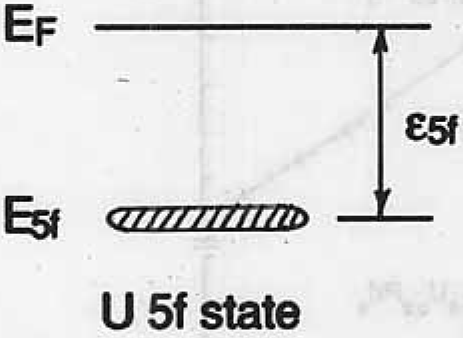
suscept.





$Y_{1-x}U_xPd_3$ — Fermi Level Tuning (FLT) of T_K

- PES/BIS measurements (UM/UCSD — *Kang et al. '89*)
  $\Rightarrow \varepsilon_{5f} = (E_F - E_{5f})$ <u>increases</u> with x (by ~1 eV as $x = 0 \rightarrow 1$)

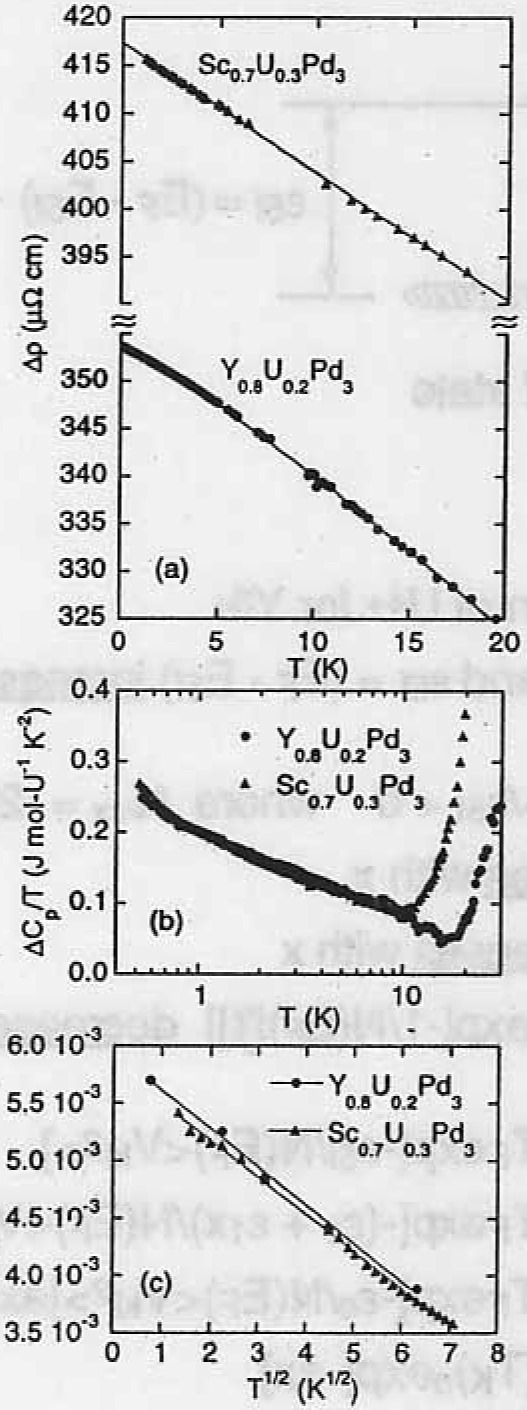


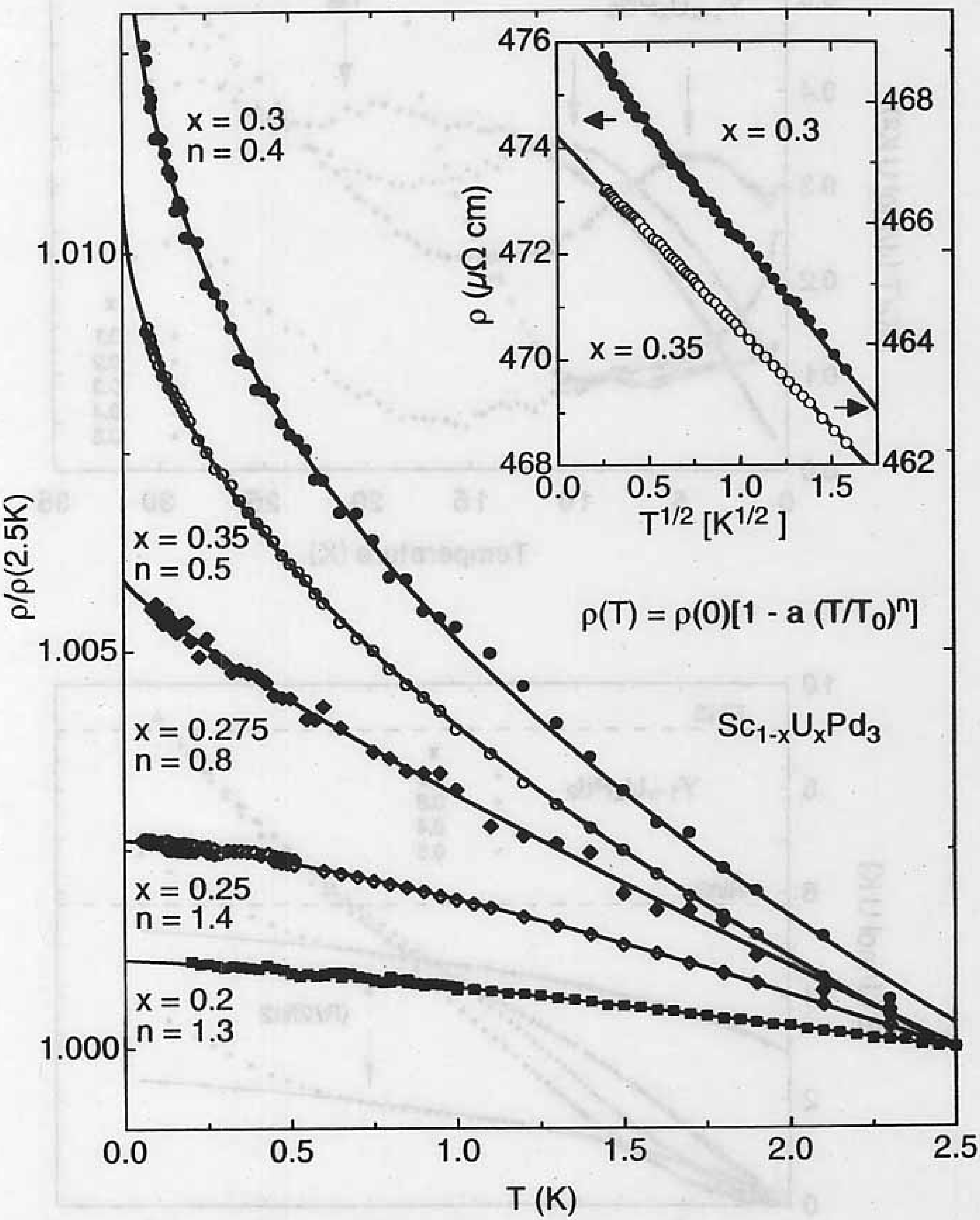
$$\varepsilon_{5f} = (E_F - E_{5f}) \sim \varepsilon_o + \varepsilon_1 x \quad (\varepsilon_1 \approx 1 \text{ eV})$$

- Substitution of U^{4+} for Y^{3+}
  $\Rightarrow n_e$, E_F, and $\varepsilon_{5f} = (E_F - E_{5f})$ <u>increase</u> with x

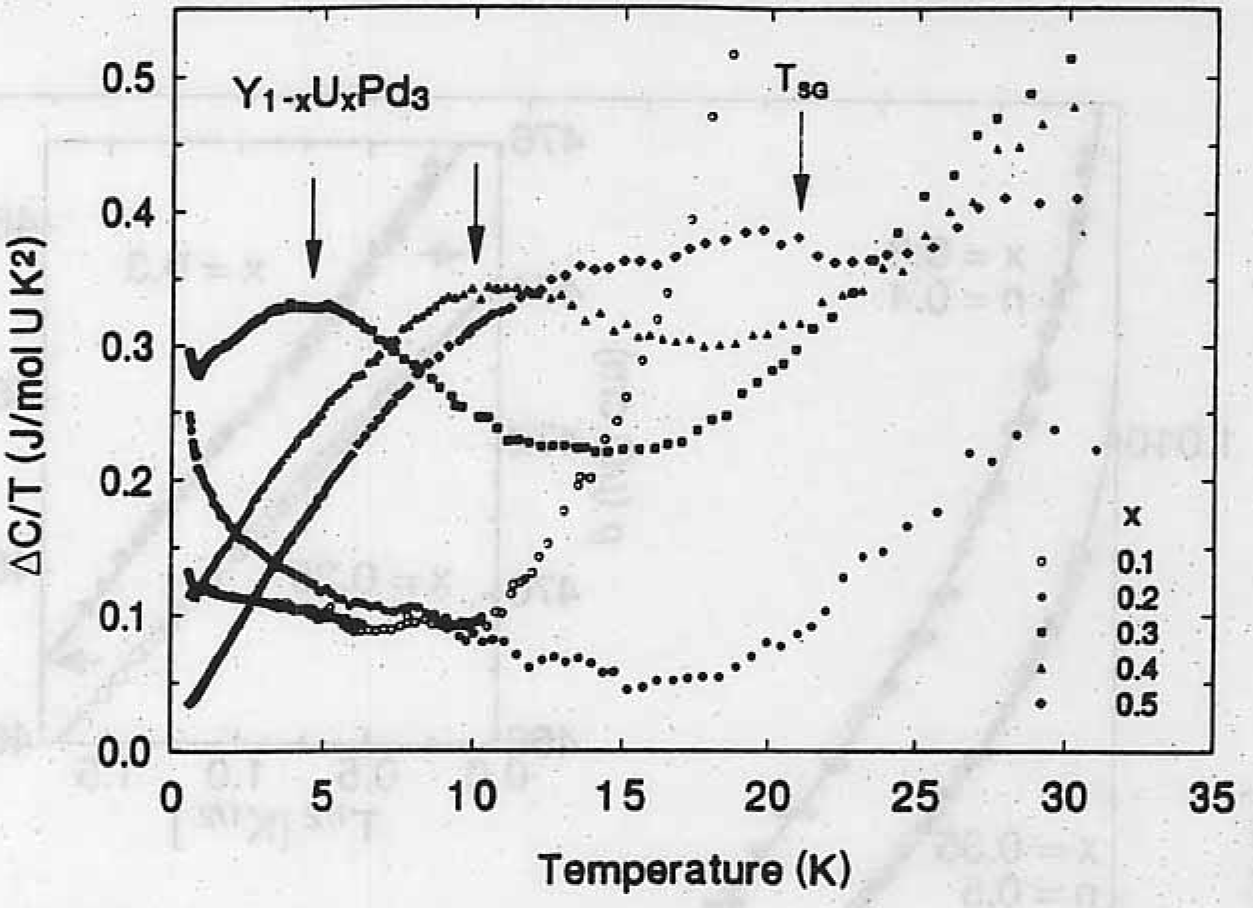
- $\mathcal{J} \sim -\langle V_{kf}^2 \rangle / \varepsilon_{5f} < 0$ where $\mathcal{H}_{ex} = -2\mathcal{J}\mathbf{S}\cdot\sigma(0)$
  ε_{5f} <u>increases</u> with x
  $\Rightarrow |\mathcal{J}|$ <u>decreases</u> with x
  $\Rightarrow T_K \sim T_F \exp[-1/N(E_F)|\mathcal{J}|]$ <u>decreases</u> with x

  i.e., $T_K \sim T_F \exp[-\varepsilon_{5f}/N(E_F)\langle V_{kf}^2 \rangle]$
  $\sim T_F \exp[-(\varepsilon_o + \varepsilon_1 x)/N(E_F)\langle V_{kf}^2 \rangle]$
  $\sim T_F \exp[-\varepsilon_o/N(E_F)\langle V_{kf}^2 \rangle]\exp[-\varepsilon_1 x/N(E_F)\langle V_{kf}^2 \rangle]$
  $\sim (T_K)_o \exp[-\alpha x]$

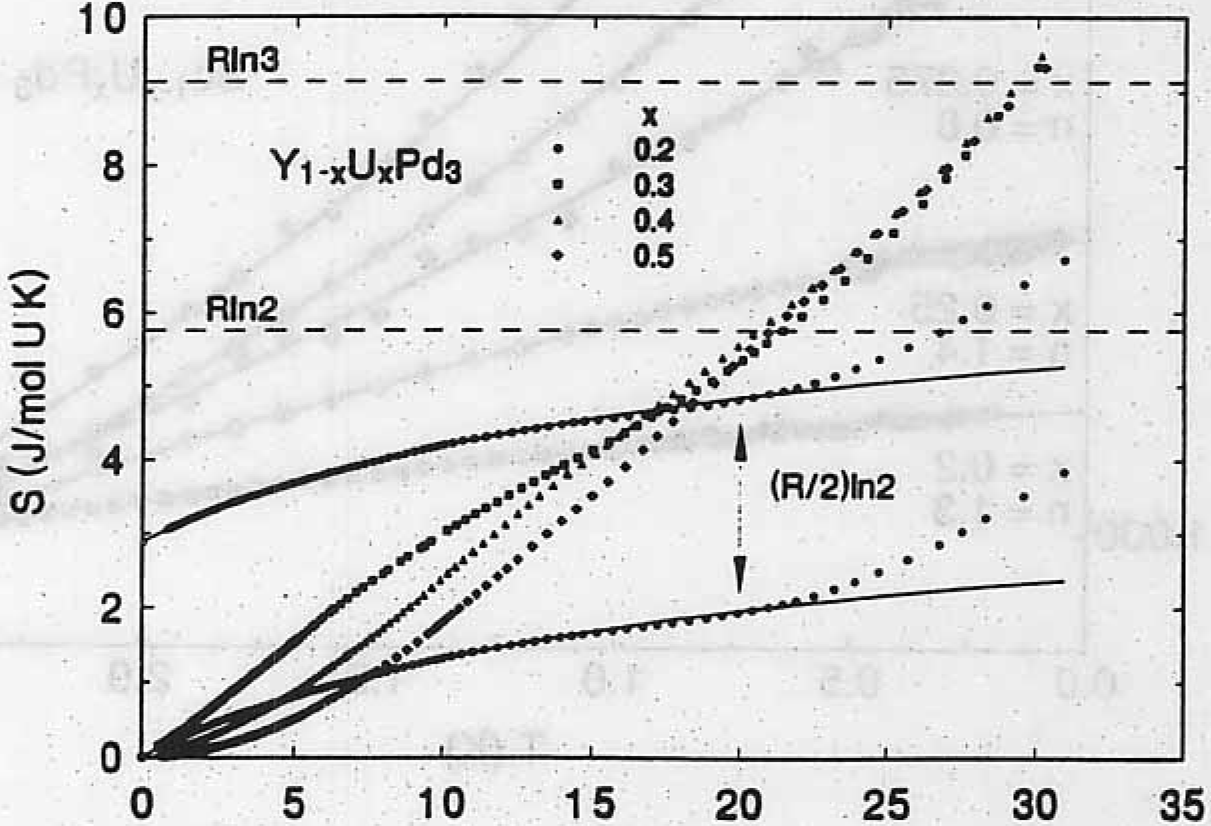
420
415
410
405
400
395
350
345
340
335
330
325
Δρ (μΩ cm)
Sc0.7U0.3Pd3
Y0.8U0.2Pd3
(a)
0
5
10
15
20
T (K)
0.4
0.3
0.2
0.1
0.0
ΔCp/T (J mol-U-1 K-2)
Y0.8U0.2Pd3
Sc0.7U0.3Pd3
(b)
1
10
T (K)
6.0 10-3
5.5 10-3
5.0 10-3
4.5 10-3
4.0 10-3
3.5 10-3
χint (cm3 mol-U-1)
Y0.8U0.2Pd3
Sc0.7U0.3Pd3
(c)
0
1
2
3
4
5
6
7
8
T1/2 (K1/2)



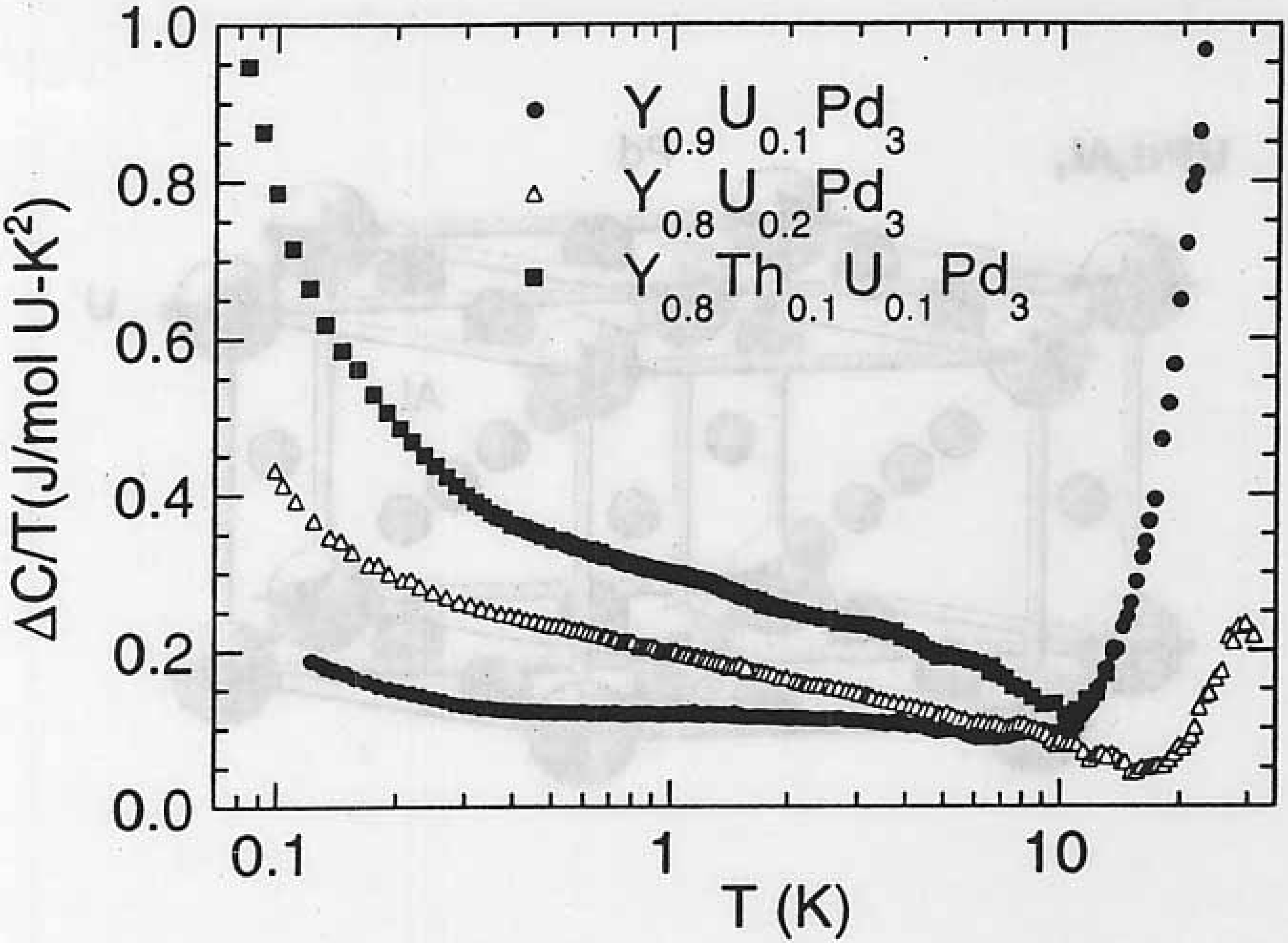
ρ/ρ(2.5K)
1.010
1.005
1.000
0.0
0.5
1.0
1.5
2.0
2.5
T (K)
x = 0.3
n = 0.4
x = 0.35
n = 0.5
x = 0.275
n = 0.8
x = 0.25
n = 1.4
x = 0.2
n = 1.3
ρ(T) = ρ(0)[1 - a (T/T0)n]
Sc1-xUxPd3
476
474
472
470
468
468
466
464
462
ρ (μΩ cm)
x = 0.3
x = 0.35
0.0
0.5
1.0
1.5
T1/2 [K1/2]



$Y_{1-x}U_xPd_3$
T_{SG}
$\Delta C/T$ (J/mol U K^2)
0.0
0.1
0.2
0.3
0.4
0.5
0
5
10
15
20
25
30
35
Temperature (K)
x
0.1
0.2
0.3
0.4
0.5



Rln3
Rln2
$Y_{1-x}U_xPd_3$
x
0.2
0.3
0.4
0.5
(R/2)ln2
S (J/mol U K)
0
2
4
6
8
10
0
5
10
15
20
25
30
35
Temperature (K)



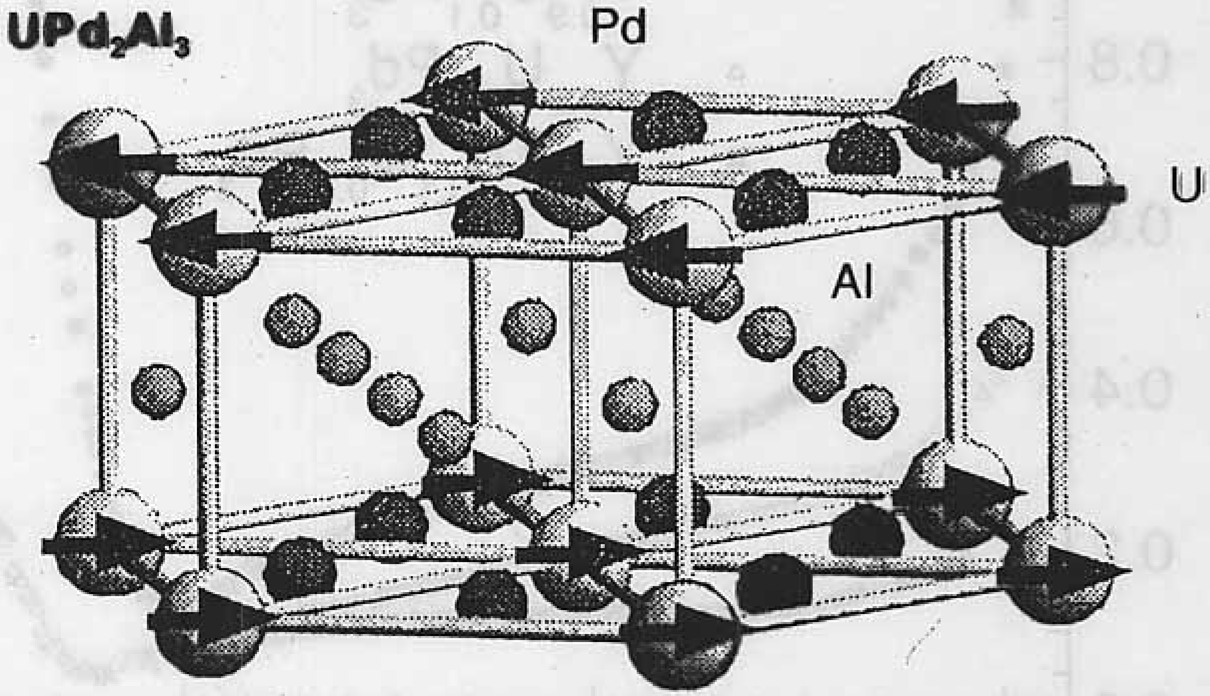
C(T) data between ~0.5 K and ~10–20 K described by

$$\Delta C(T)/T = (-bR/T_K)\ln[b'(T/T_K)] + \gamma$$

Same form as two-channel spin-1/2 Kondo effect where b = 0.251, b' = 2.44 and residual entropy S(0) = (R/2)ln(2)
Tsvelik '85; Sacramento & Schlottmann '89

Upturn in ΔC(T)/T below ~0.6 K ⇒ removal of residual entropy

Compound	T_K(K)	γ(mJ/mol U–K^2)
$Y_{0.9}U_{0.1}Pd_3$	220	11.5
$Y_{0.8}U_{0.2}Pd_3$	42	12.2
$Y_{0.8}Th_{0.1}U_{0.1}Pd_3$	30	12.8



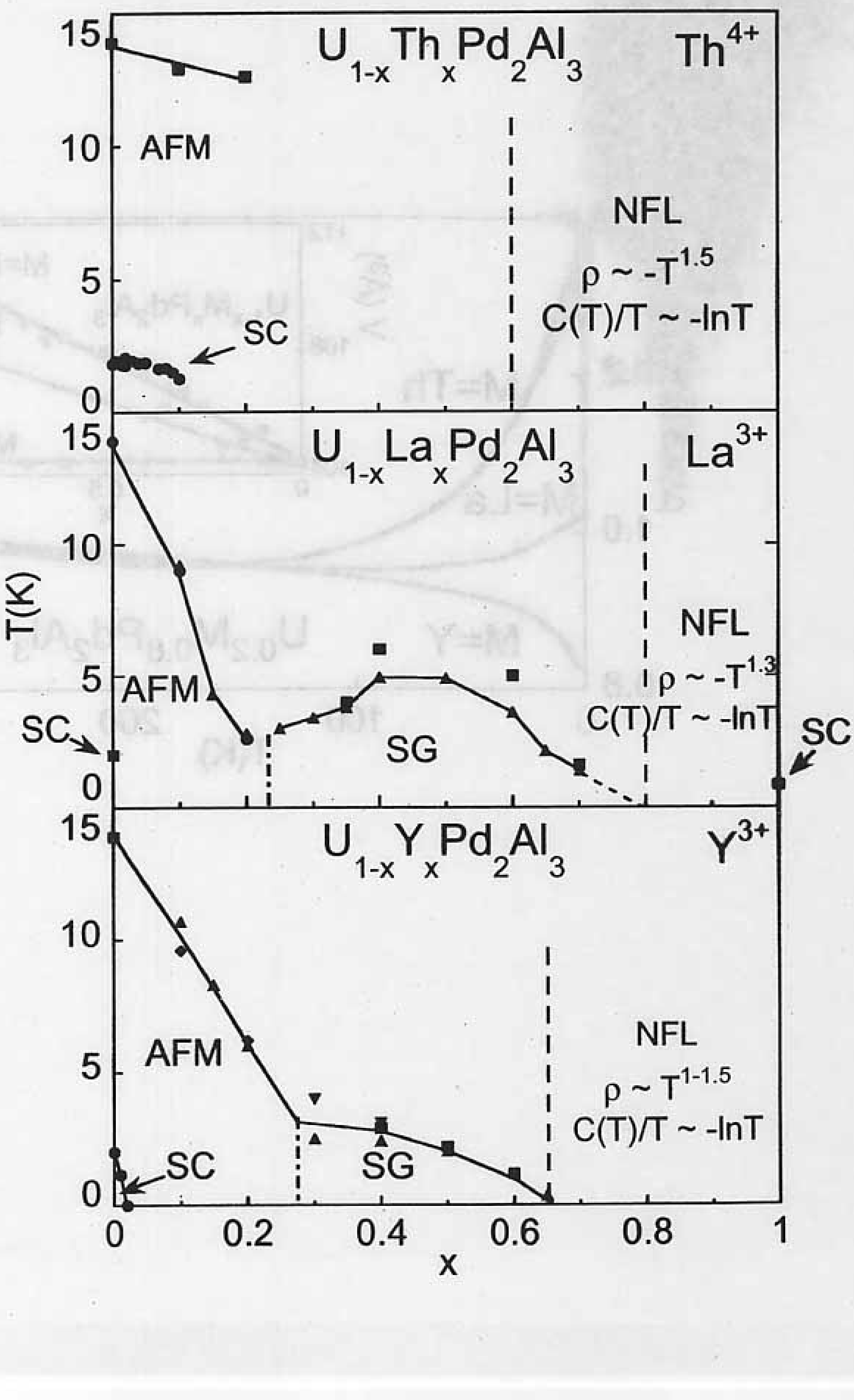
The $U_{1-x}M_xPd_2Al_3$ (M = Th, Y, La) systems

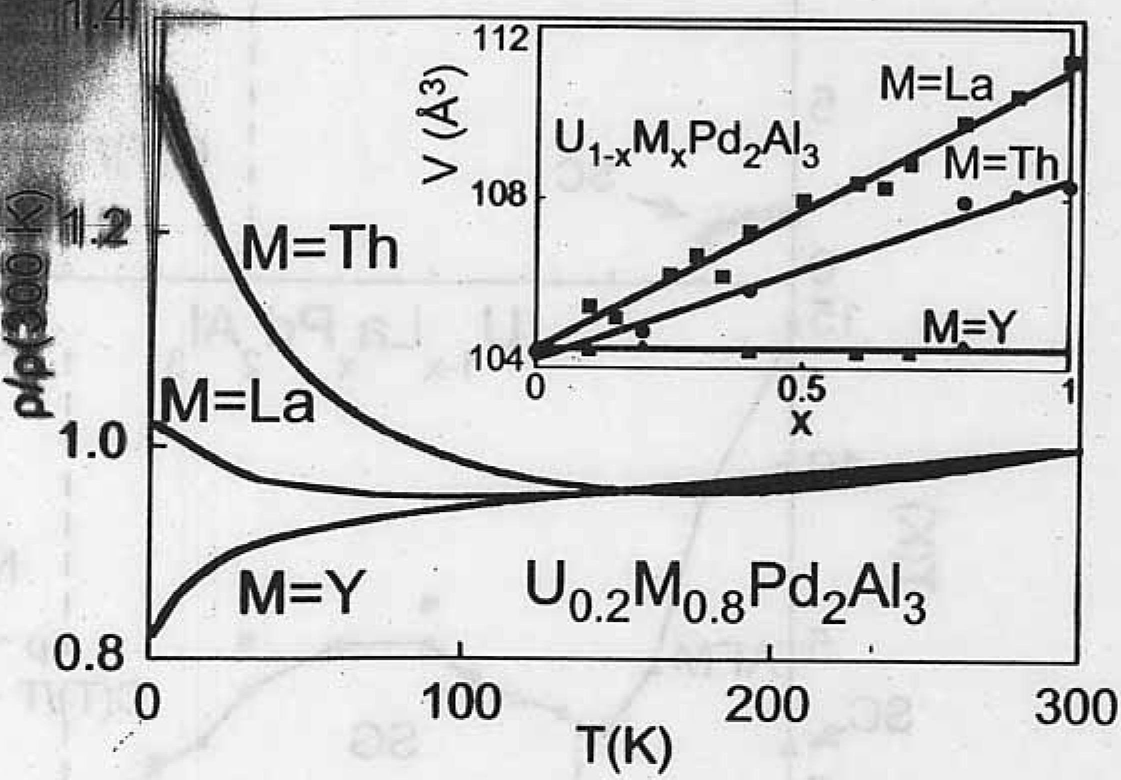
- **Parent compound**

  UPd_2Al_3 *C. Geibel et al. '91*
  Moderately heavy electron AFM-SC
  $\gamma = 140$ mJ/mol-K^2, $T_N = 14.6$ K, $T_c \approx 2$ K
  Hexagonal $PrNi_2Al_3$ structure

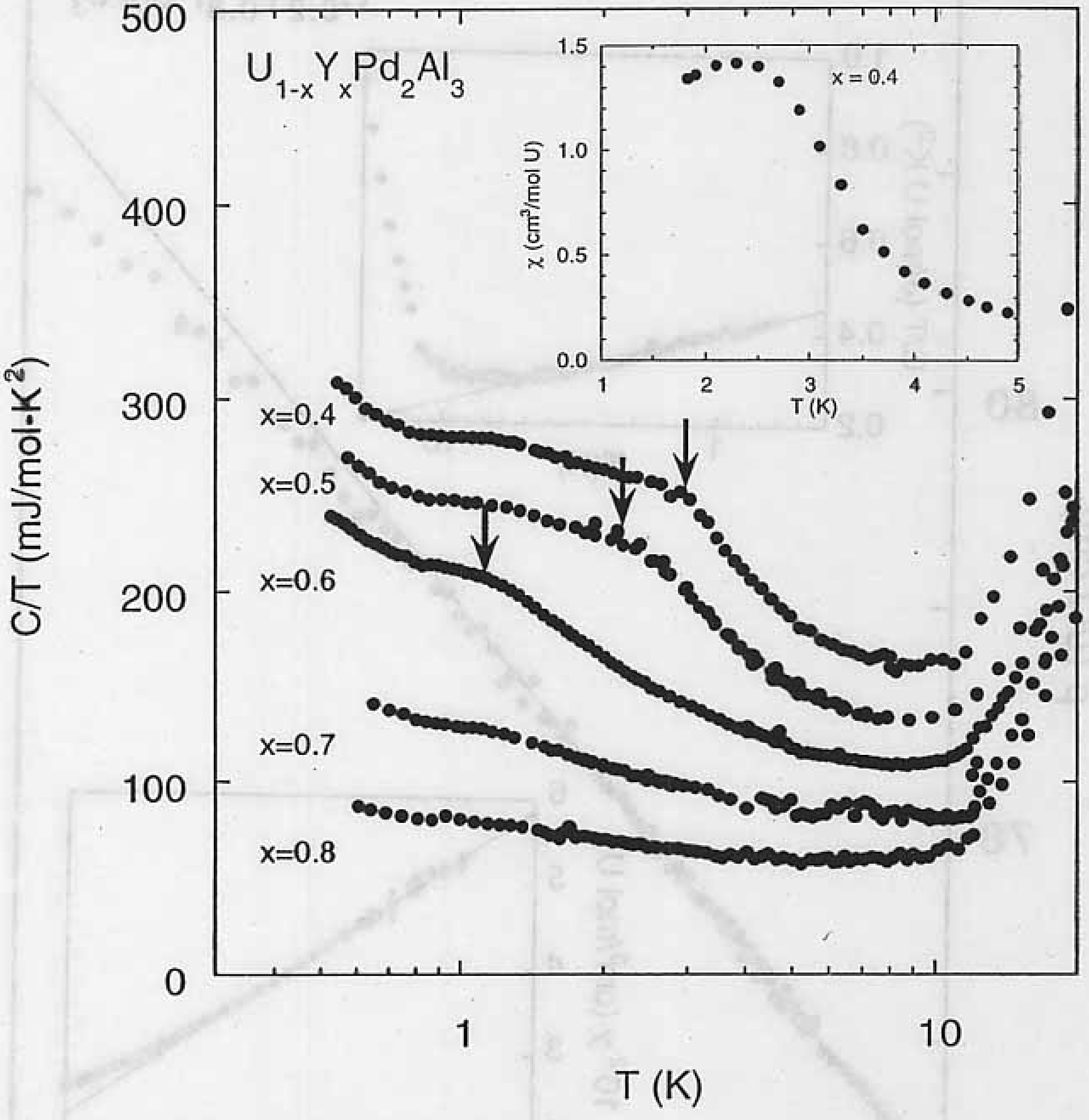
- **Neutron & X-ray scattering**

AFM stacking along c-axis of	*Krimmel et al. '92*
FM sheets in basal plane	*Kita et al. '94*
($\mu \approx 0.85\ \mu_B$)	*Paolasini et al. '94*

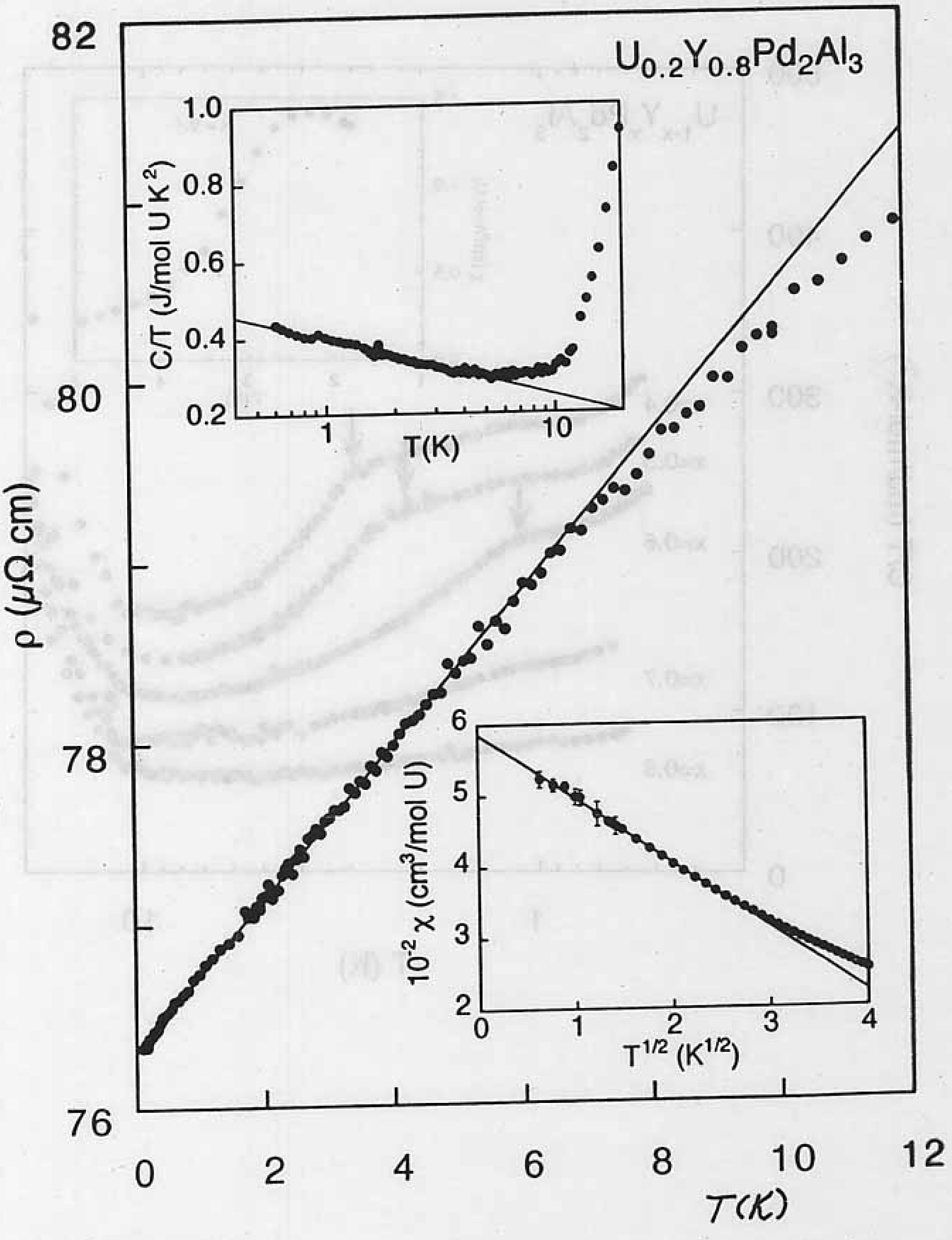

U$_{1-x}$Th$_x$Pd$_2$Al$_3$
Th^{4+}
AFM
SC
NFL
ρ ~ -T$^{1.5}$
C(T)/T ~ -lnT
U$_{1-x}$La$_x$Pd$_2$Al$_3$
La^{3+}
AFM
SC
SG
NFL
ρ ~ -T$^{1.3}$
C(T)/T ~ -lnT
SC
U$_{1-x}$Y$_x$Pd$_2$Al$_3$
Y^{3+}
AFM
SC
SG
NFL
ρ ~ T$^{1-1.5}$
C(T)/T ~ -lnT
T(K)
15
10
5
0
0
0.2
0.4
0.6
0.8
1
x



ρ/ρ(300 K)
1.4
1.2
1.0
0.8
M=Th
M=La
M=Y
$U_{0.2}M_{0.8}Pd_2Al_3$
0
100
200
300
T(K)
V (Å^3)
112
108
104
0
0.5
1
x
$U_{1-x}M_xPd_2Al_3$
M=La
M=Th
M=Y

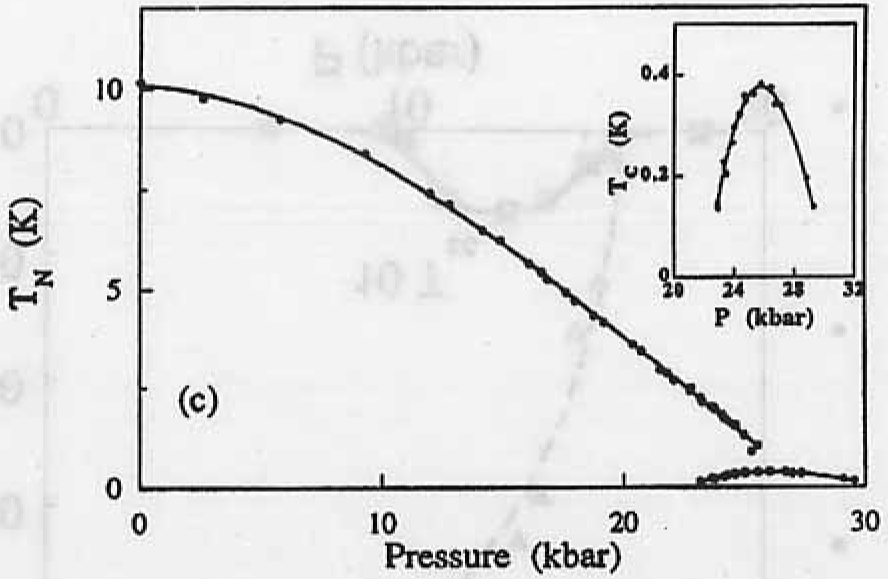


$U_{1-x}Y_xPd_2Al_3$
C/T (mJ/mol-K^2)
T (K)
500
400
300
200
100
0
1
10
x=0.4
x=0.5
x=0.6
x=0.7
x=0.8
x = 0.4
χ (cm^3/mol U)
T (K)
0.0
0.5
1.0
1.5
1
2
3
4
5

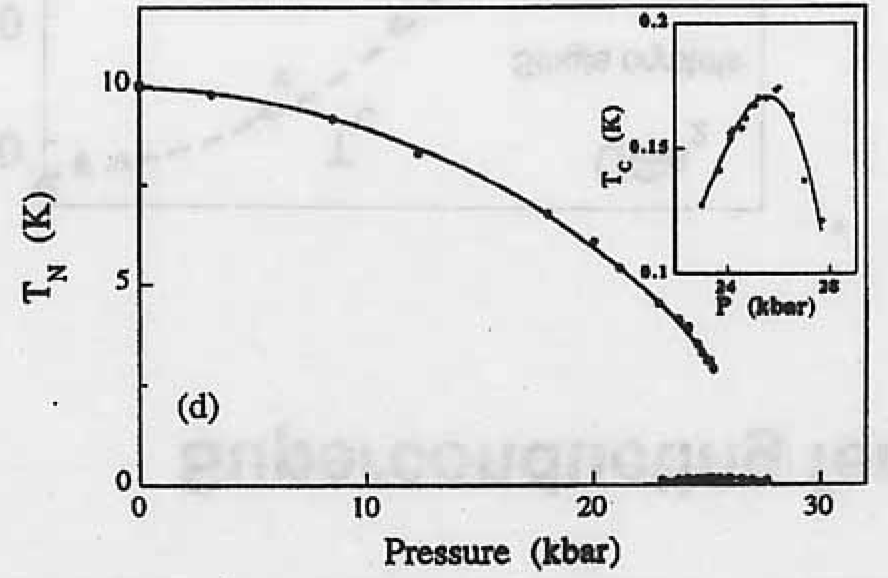


E. J. Freeman et al. '98 - UCSD

Superconductivity near AFM QCP accessed by application of pressure (high purity single crystal specimens)



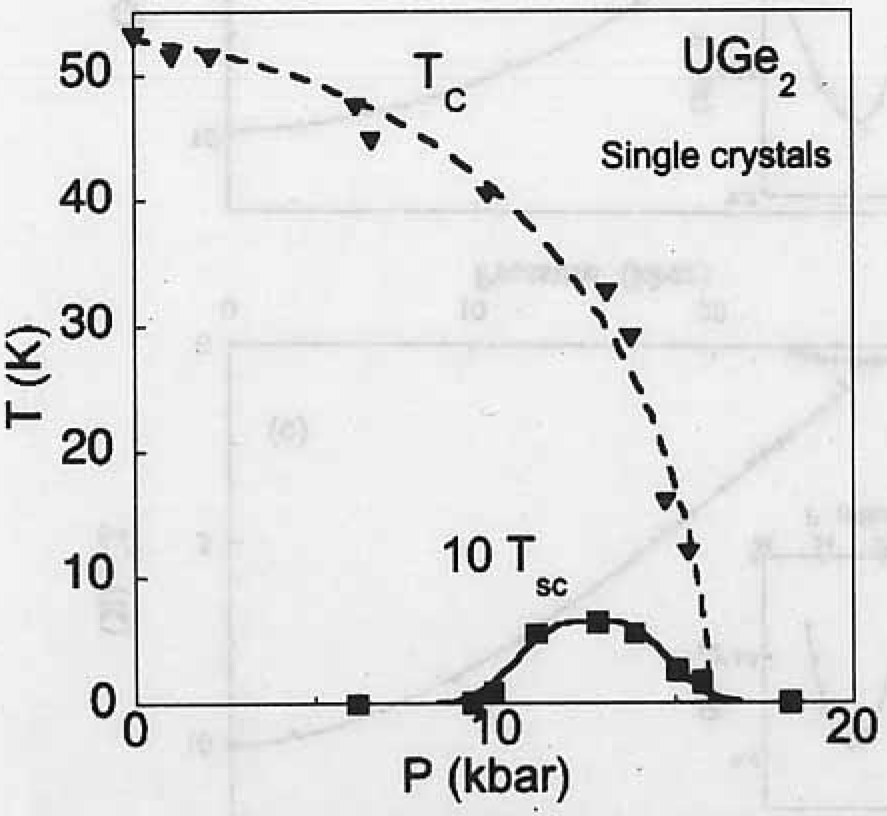
$CePd_2Si_2$
$P \approx 28$ kbar
$\rho \approx \rho_o + AT^{1.2}$
$T_c \leq T \leq 40$ K



$CeIn_3$
$P \approx 28$ kbar
$\rho \approx \rho_o + AT^{1.5}$
$T_c \leq T \leq 4$ K

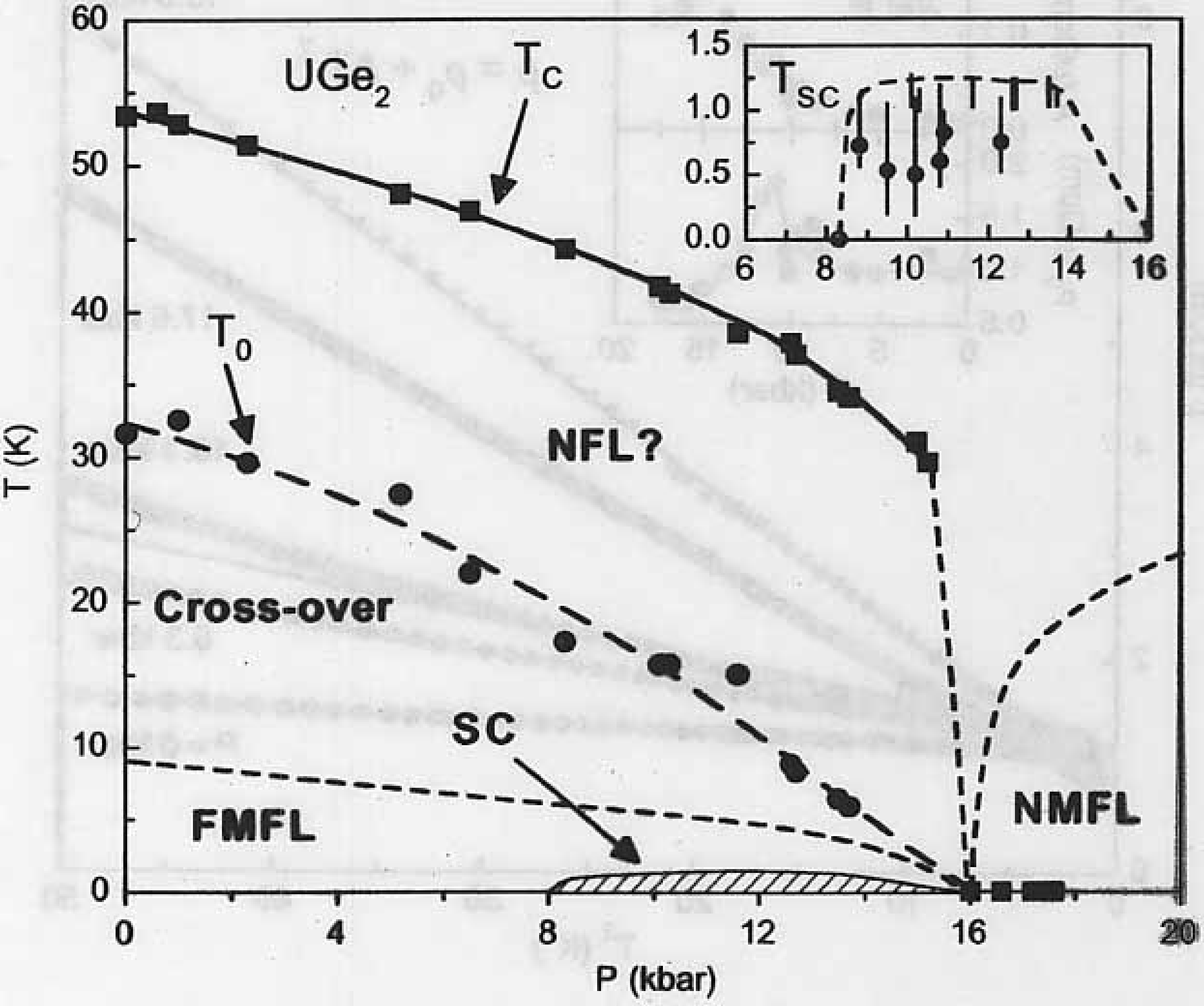
S. R. Julian, G. G. Lonzarich et al. '98

Superconducting ferromagnet UGe_2



- First pressure-induced superconducting ferromagnet (Saxena et al. ‘00)
- Itinerant electron FM with $T_C = 53$ K ($P = 0$)
- $\gamma \approx 35$ mJ/mol K^2
  $m^* \approx 20\, m_e$ (Onuki et al. ‘93)
- Curie temperature suppressed at $P_C \approx 16$ kbar (Oomi et al. ‘98)

Polycrystalline UGe_2

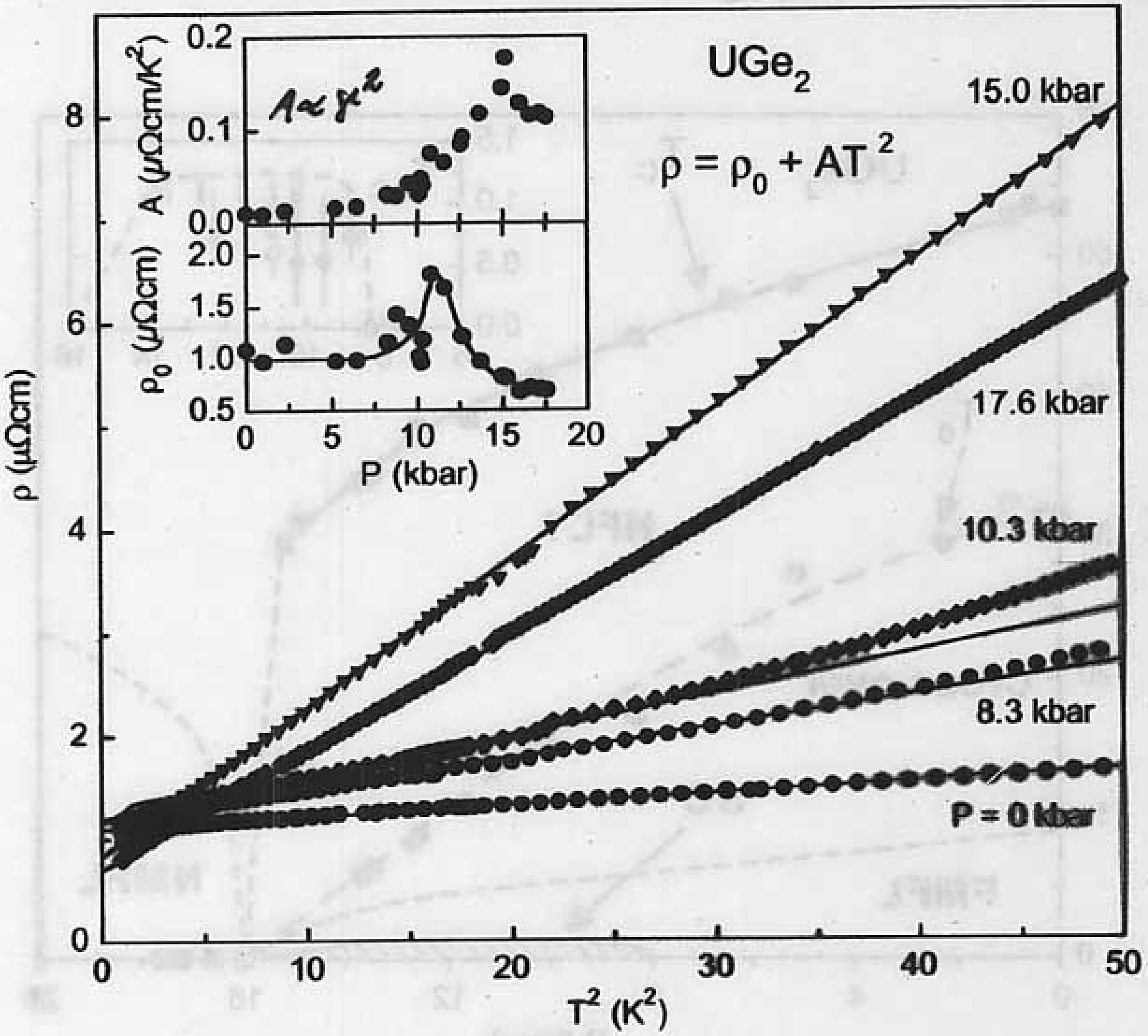


1. C(P,T): *Vollmer, Pfleiderer, v. Löhneysen, Bauer, Maple '01*

   $\Delta C/\gamma T_c \sim 0.2$ at 15 kbar $\Rightarrow$ bulk SC (~ 20 vol% at 15 kbar)
   SC'ing volume increases with P
   γ increases with P; γ(15 kbar)/γ(0) ~ 3
   (similar results for single crystal; *Tateiwa et al. '01*)

2. $l \sim \xi_o \sim 10^2$ Å for polycrystalline UGe_2 with $\rho_o \sim 4\ \mu\Omega$cm

   p-wave SC? $l \sim \xi_o \Rightarrow T_c \to 0$ K - Sr_2RuO_4 *MacKenzie et al. '98*
   Inhomogeneous SC, FM filamentary structure?
   $ErRh_4B_4$ – narrow range of T between T_{c2} & θ_c



Kadowaki-Woods relation ('86)

$$\rho = \rho_0 + AT^2$$

$$A = (1\times10^{-5}\,\mu\Omega cm)(mol\text{-}K/mJ)^2\gamma^2 \propto \gamma^2$$

THEORY- Coexistence of SC & FM

S-wave.

K.B. Blagoev, J.R. Engelbrecht, K.S. Bedell '98,'99 T-P phase diag

H. Suhl '01

A.A. Abrikosov '01

* N.I. Karchov, K.B. Blagoev, K.S. Bedell, P.B. Littlewood '01

p-wave.

K. Levin, O. Valls '78

D. Fay, J. Appel '80

K. Machida, T. Ohmi '01

A.R. Schick, W.E. Pickett '01

T.R. Kirkpatrick, D. Belitz, T. Vojta, R. Narayanan '01

⋮

Why is $PrOs_4Sb_{12}$ interesting?
And, what does it have to do with quantum criticality?

- Nonmagnetic heavy Fermi liquid ($\gamma \approx 500$ mJ/mol-K^2; $m^* \approx 50\ m_e$)
- Unconventional superconductivity (different than that of Ce, U-based compounds)
- $PrOs_4Sb_{12}$: first Pr-based heavy fermion superconductor (all others: Ce, U-based)
- Formation of heavy Fermi liquid (and, possibly, superconductivity) may involve electric quadrupole fluctuations, rather than magnetic dipole fluctuations
- Pr^{3+} energy level scheme in cubic CEF:

  In cubic CEF, Pr^{3+} J = 4 Hund's rule multiplet
  $\Rightarrow \Gamma_1$ singlet, Γ_3 nonmagnetic doublet (quadrupole moment), Γ_4 & Γ_5 triplets
  Analysis of $\chi(T)$:
    Ground state: Γ_1 singlet or Γ_3 doublet
    1st excited state: Γ_5 triplet ($\Delta \approx 10$ K)
    2nd & 3rd excited states: Γ_4, Γ_1 or Γ_3 ($\Delta > \sim 10^2$ K)
- Our experiments $\Rightarrow \Gamma_3$ ground state (other experiments $\Rightarrow \Gamma_1$ ground state)

  Hybridization between Pr^{3+} localized 4f states & conduction electron states $\Rightarrow$ stage set for quadrupolar Kondo effect (2-channel, spin-1/2 Kondo effect with NFL behavior) $\Rightarrow$ quadrupolar Kondo lattice $\Rightarrow$ heavy Fermi liquid? $\Rightarrow$SC?
- High field ordered phase (HFOP) – quadrupolar order?
- Near quadrupolar quantum critical point (QCP)?
- Analogous to occurrence of SC in heavy fermion compounds in vicinity of AFM QCP, accessed by pressure; e.g., $CeIn_3$, $CePd_2Si_2$

Crystal structure of the filled skutterudites MT_4X_{12}

Filled skutterudites: derived from binary skutterudites TX_3

(T = Co, Rh, Ir; X = P, As, Sb)

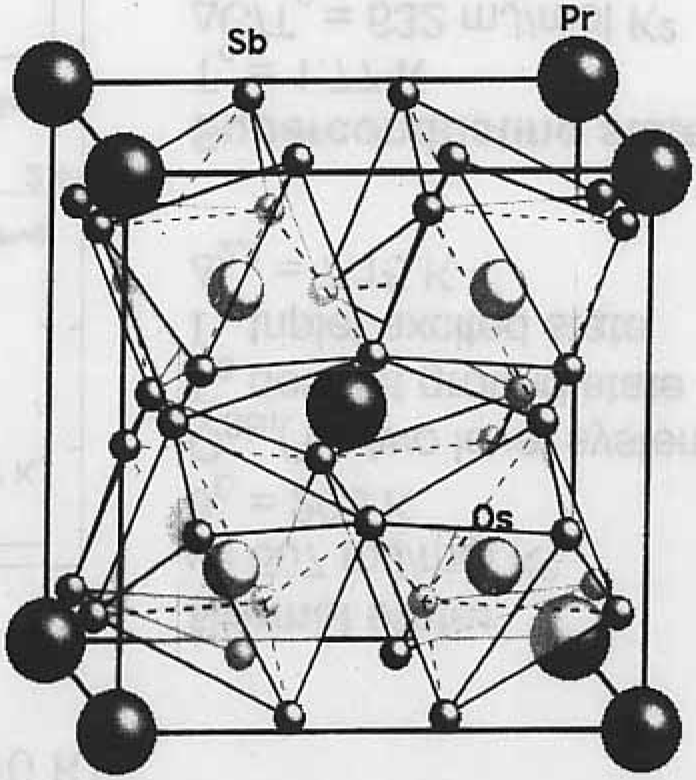
Prototype $CoAs_3$: discovered in Skutterud, Norway

M cations — bcc sublattice
(fill atomic cages in structure)
T cations — sc sublattice
X anions — distorted corner
sharing octahedra centered
by T cation

bcc structure (*Im-3*)

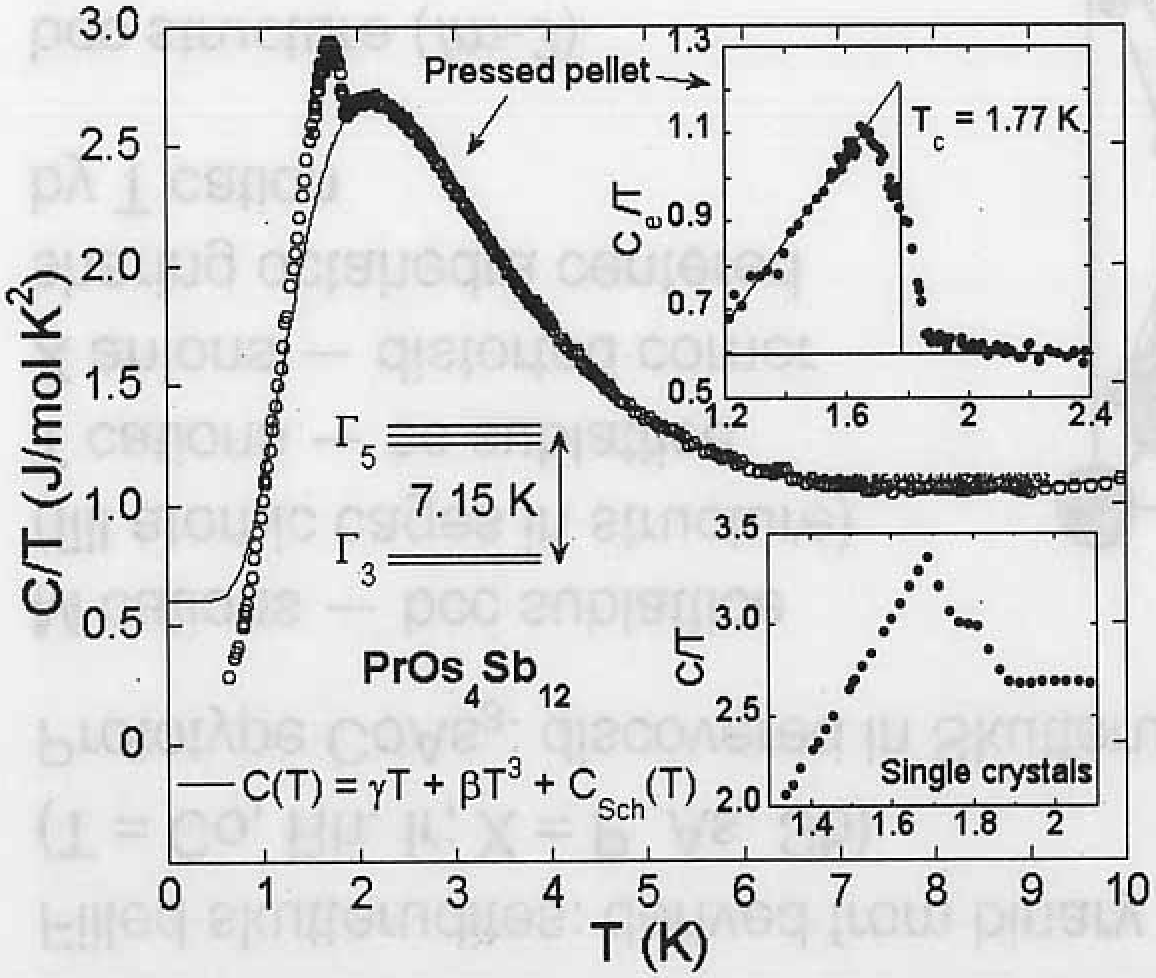
a = 9.3068 Å

W. Jeitschko &
D. J. Braun '77



Evidence for heavy fermion superconductivity in $PrOs_4Sb_{12}$

C(T) of $PrOs_4Sb_{12}$ pressed pellet (0.6 K — 10 K)



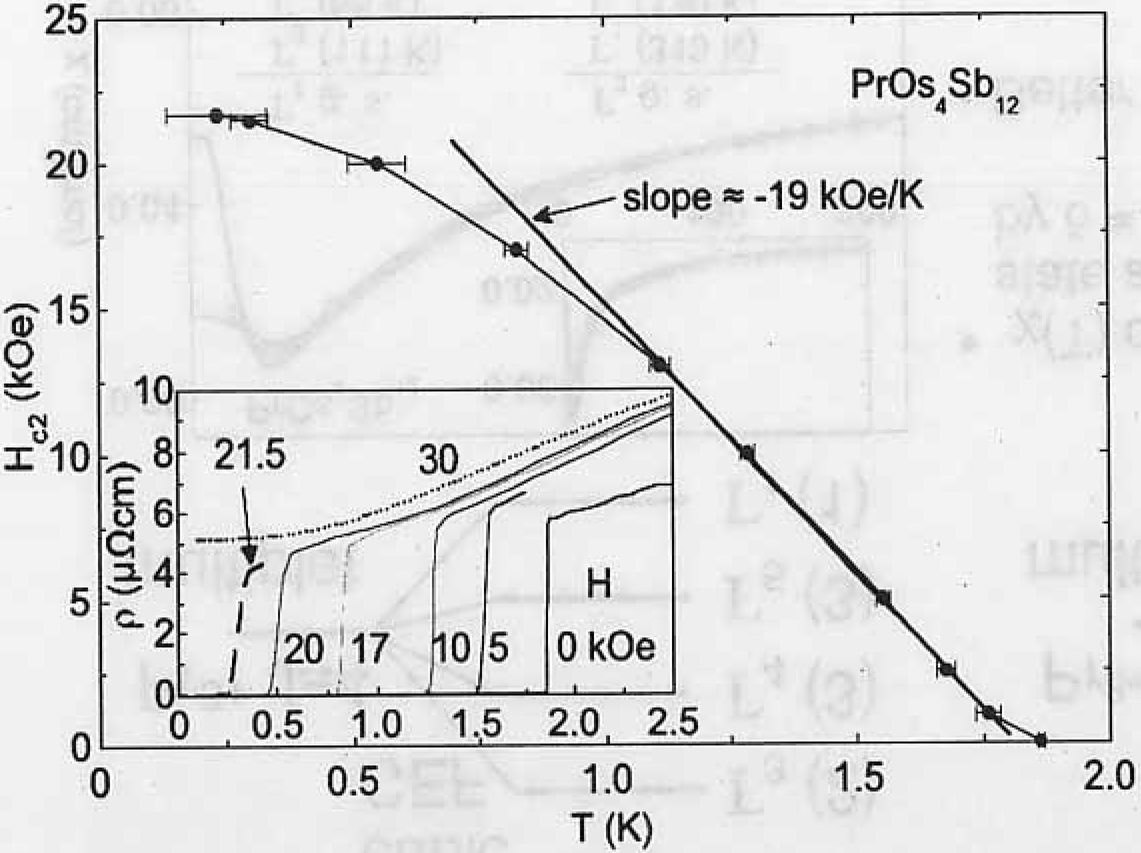
Normal state:
$\gamma = 607$ mJ/mol K^2
$\theta_D = 203$ K
$C_{Sch}(T)$: two level system
Γ_3 doublet ground state
Γ_5 triplet excited state
$\Delta_{2,3} = 7.15$ K

Superconducting state:
$T_c = 1.77$ K
$\Delta C/T_c = 632$ mJ/mol K^2
BCS: $\Delta C/\gamma T_c = 1.43$
$\gamma \approx 440$ mJ/mol K^2

Two distinct SC'ing phases?
$T_{c1} \approx 1.85$ K
$T_{c2} \approx 1.70$ K

Evidence for heavy fermion superconductivity in $PrOs_4Sb_{12}$

Upper critical field $H_{c2}(T)$



Large initial slope :

$(-dH_{c2}/dT)_{T_c} = 19\,\mathrm{kOe/K}$

$$H^*_{c2}(0) = 0.693(-dH_{c2}/dT)_{T_c}\,T_c$$

$$H^*_{c2}(0) = \frac{\Phi_0}{2\pi\xi_0{}^2} \Rightarrow \xi_0 \approx 116\,\text{Å}$$

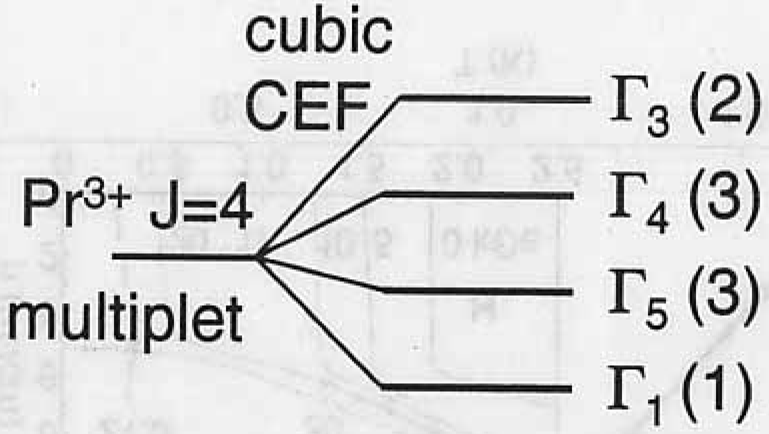
$$\xi_0 = 0.18\,\frac{\hbar v_F}{k_B T_c}$$

$$m^* = \hbar k_F / v_F \approx 50\,m_e$$

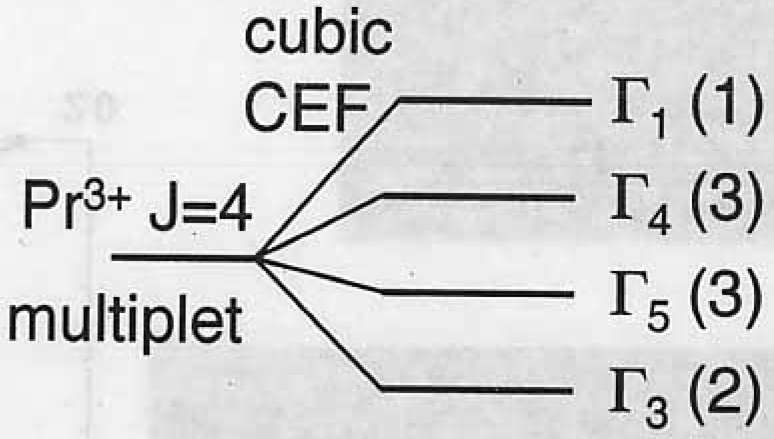
$$\gamma \approx 350\,\mathrm{mJ/mol\,K^2}$$

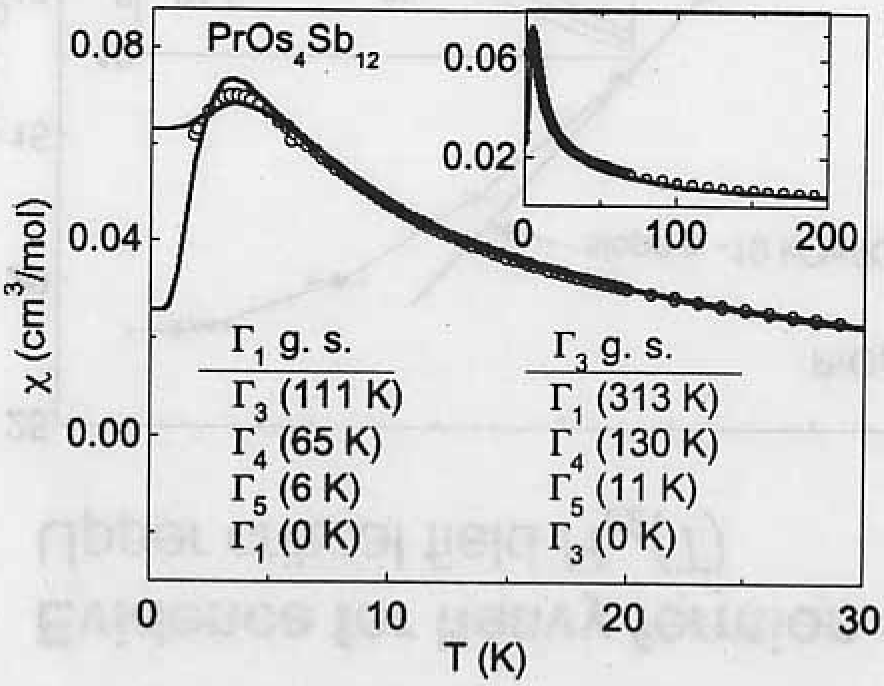
Analysis of $\chi(T)$ — Pr^{3+} ion in cubic CEF (LLW theory)

❶ Γ_1 ground state



❷ Γ_3 ground state



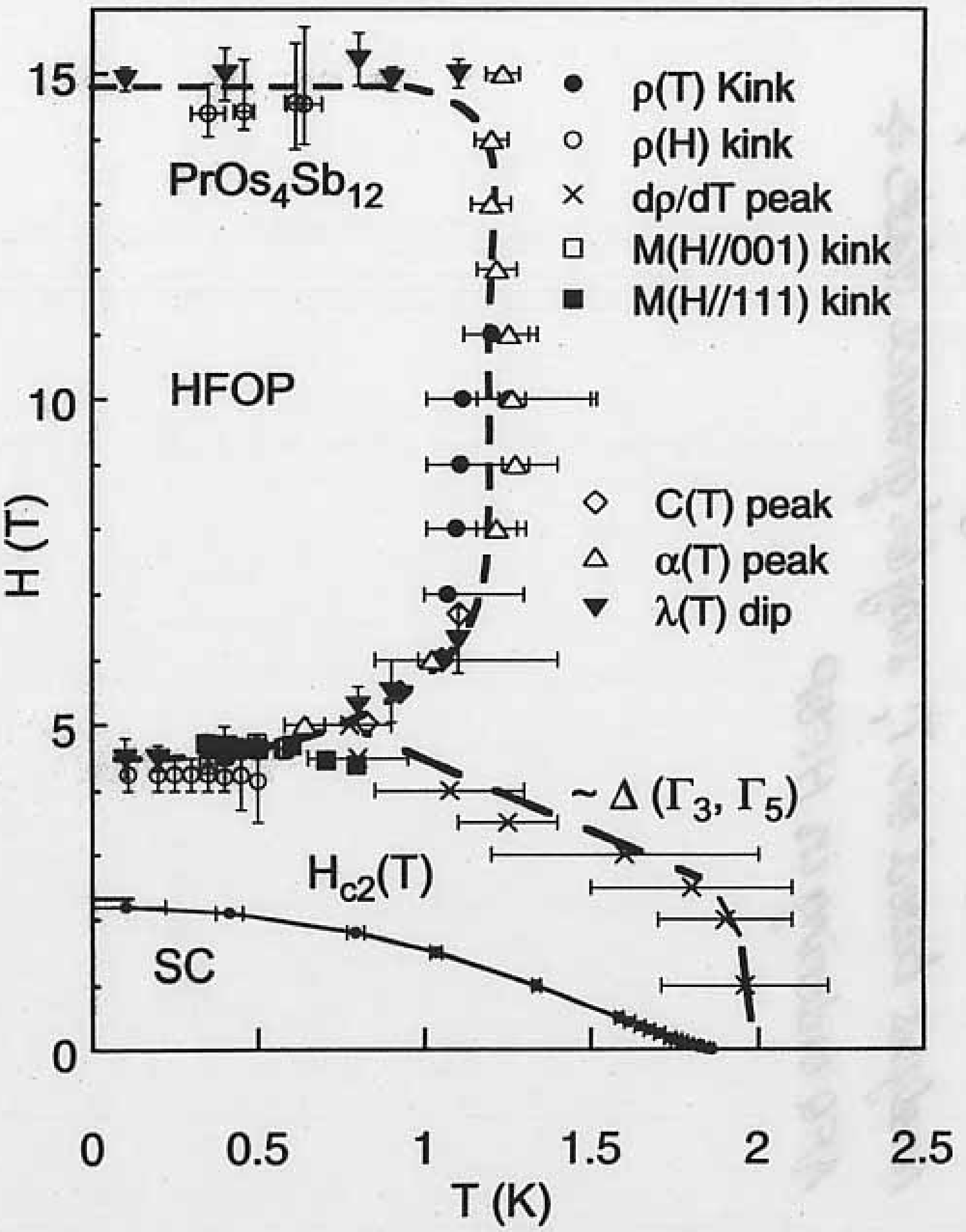


- $\chi(T)$ consistent with Γ_1 or Γ_3 ground state and Γ_5 excited state separated by $\delta \approx 10$ K

- Better fit with Γ_3 ground state

- C(T) consistent with Γ_3 ground state and low-lying Γ_5 excited state

H-T phase diagram of $PrOs_4Sb_{12}$



Neutron scattering studies of single crystal of $PrOs_4Sb_{12}$ in magnetic field along [001]

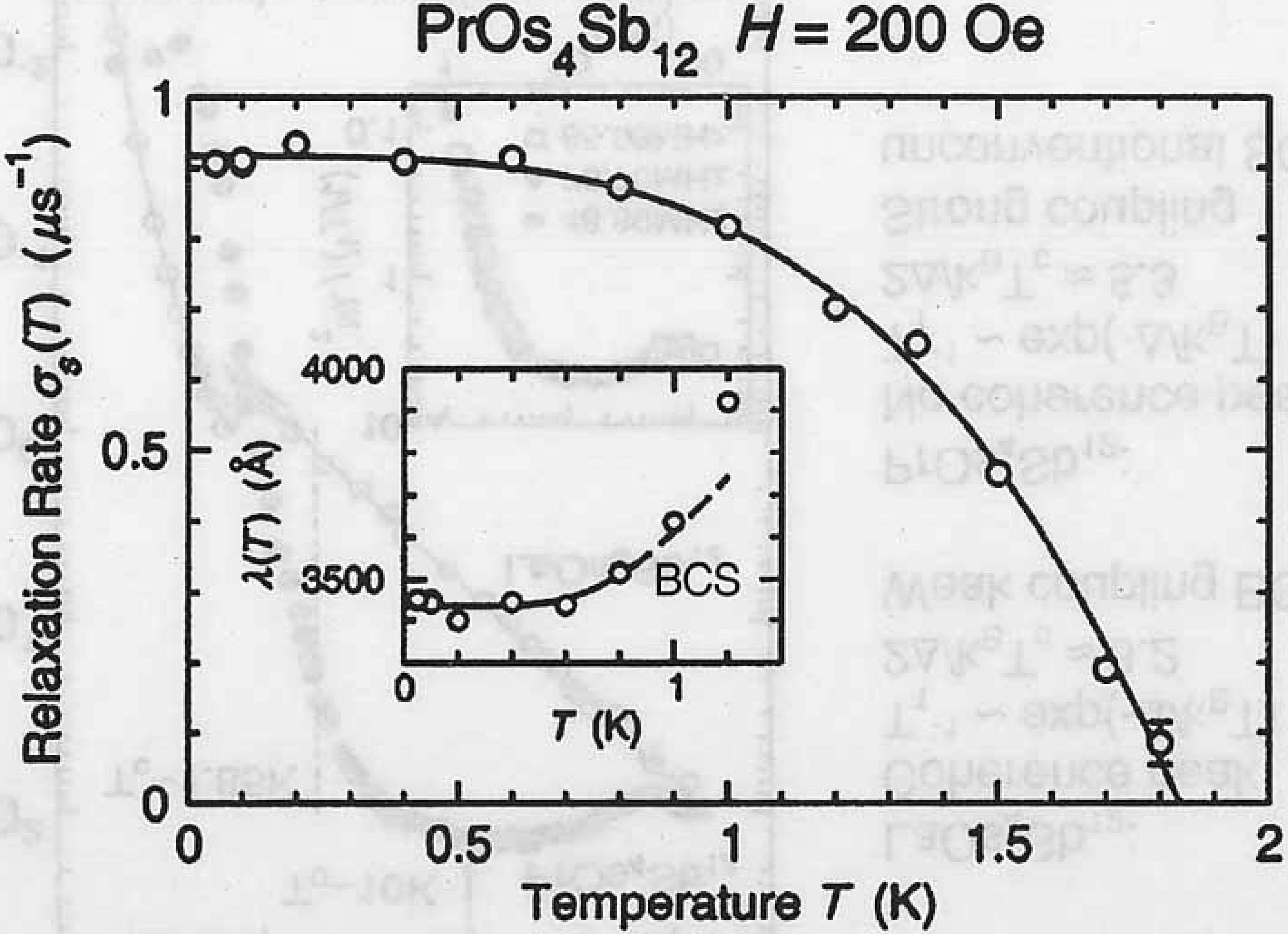
M. Kohgi et al. '03

Small AFM $\mu \parallel [010]$ in high field ordered phase (HFOP)

Analysis based on Γ_1 singlet ground state ⇒

AFQ ordering in HFOP

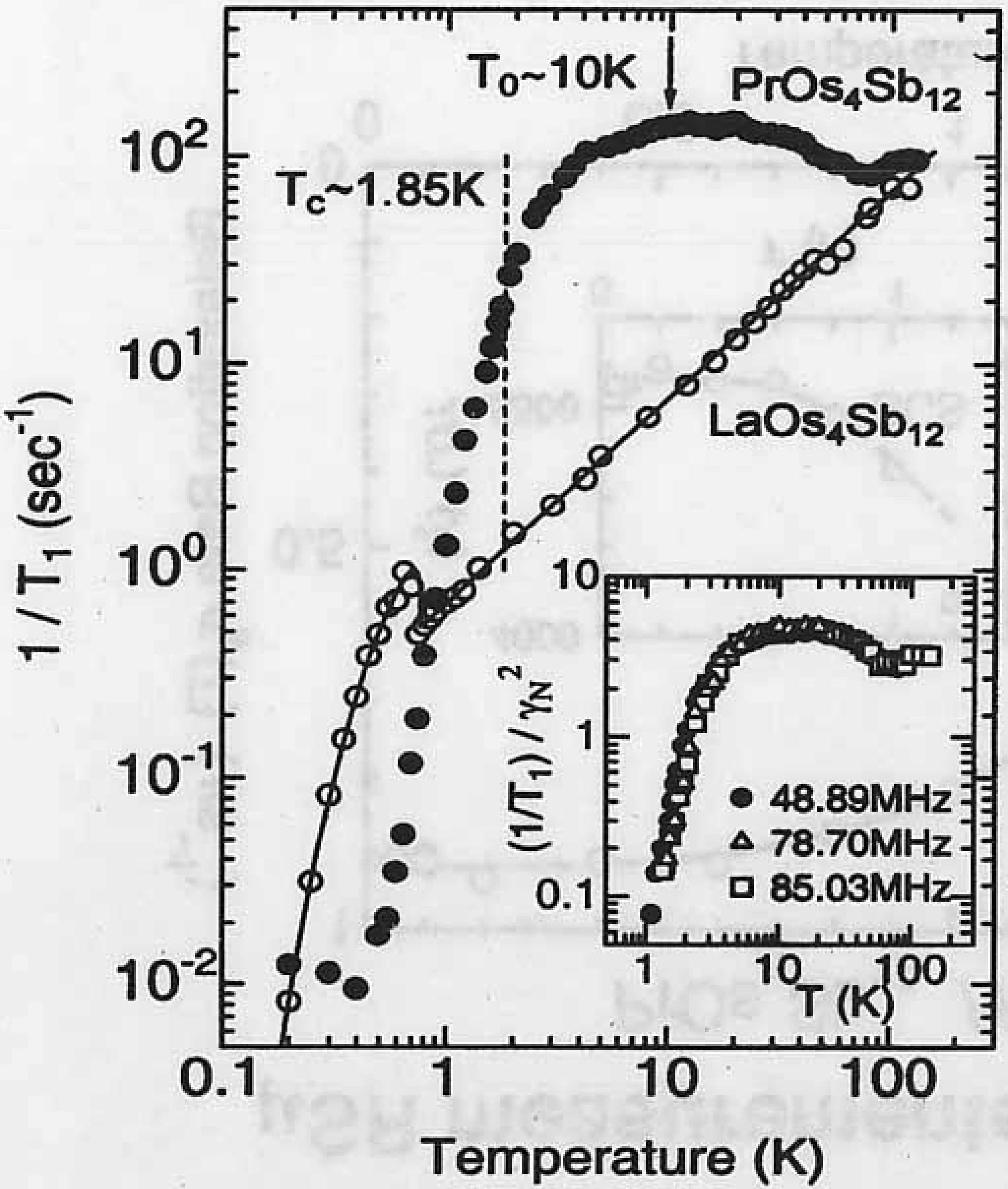
μSR measurements on $PrOs_4Sb_{12}$



$\lambda(T) = \lambda(0)[1+(\pi\Delta/2T)]^{1/2}\exp(-\Delta/T)$ *D. E. MacLaughlin et al. '02*

$\Delta/T_c = 2.1$ (BCS: $\Delta/T_c = 1.76$) $\Rightarrow$ <u>isotropic</u> $\Delta(\mathbf{k})$

Evidence for unconventional strong-coupling superconductivity in $PrOs_4Sb_{12}$ by means of Sb NQR measurements



$LaOs_4Sb_{12}$:

Coherence peak

$T_1^{-1} \sim \exp(-\Delta/k_BT)$

$2\Delta/k_BT_c \approx 3.2$

Weak coupling BCS SC

$PrOs_4Sb_{12}$:

No coherence peak

$T_1^{-1} \sim \exp(-\Delta/k_BT)$ $(T < 1.3\ T_c)$

$2\Delta/k_BT_c \approx 5.3$

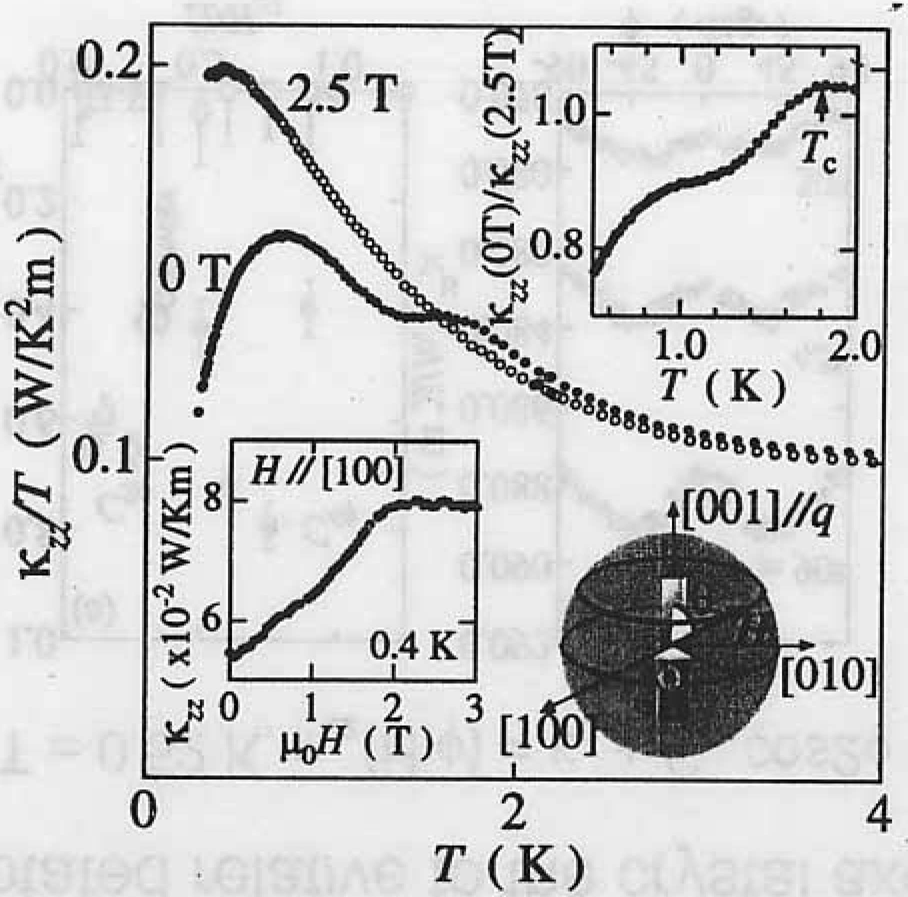
Strong coupling

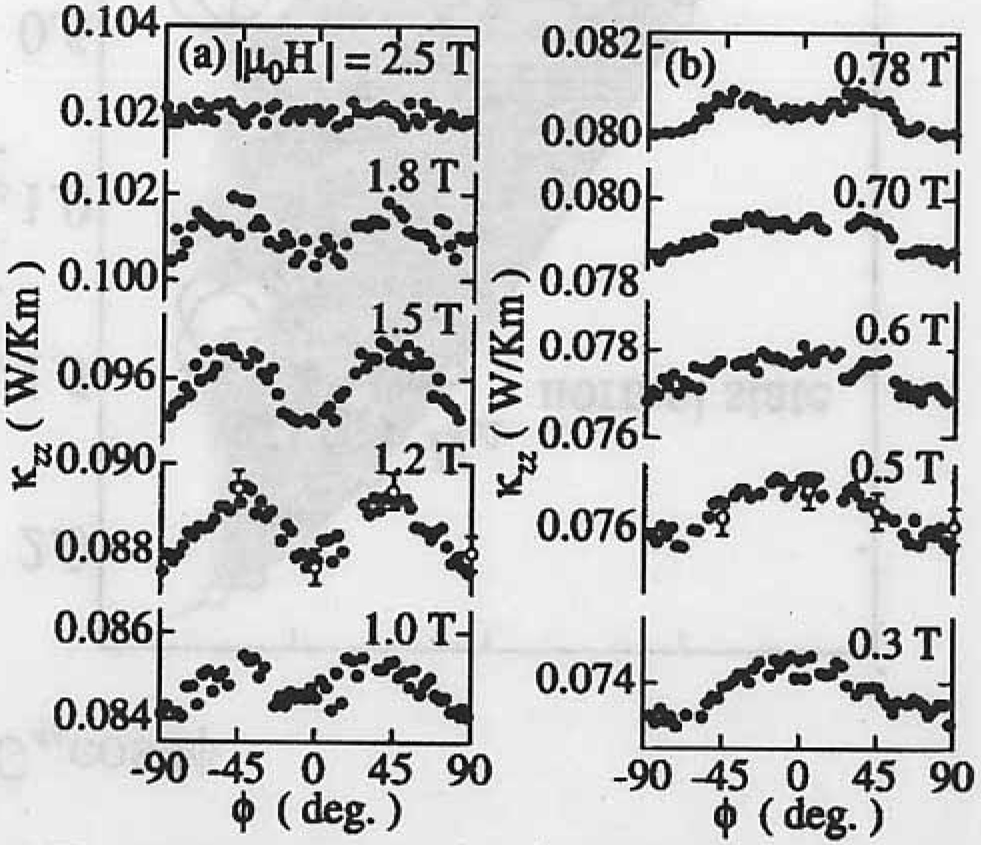
unconventional SC

H. Kotegawa et al. 02

Thermal transport studies of superconducting gap structure

Thermal transport measurements in magnetic fields rotated relative to the crystal axes





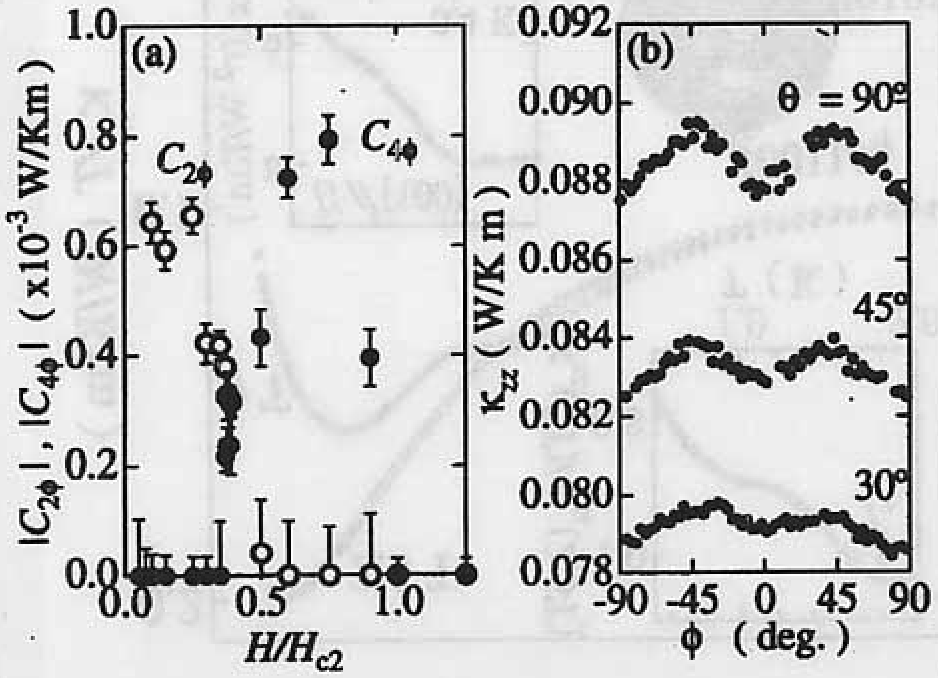
T= 0.52 K, θ = 90°, κ_{zz} minimum → node

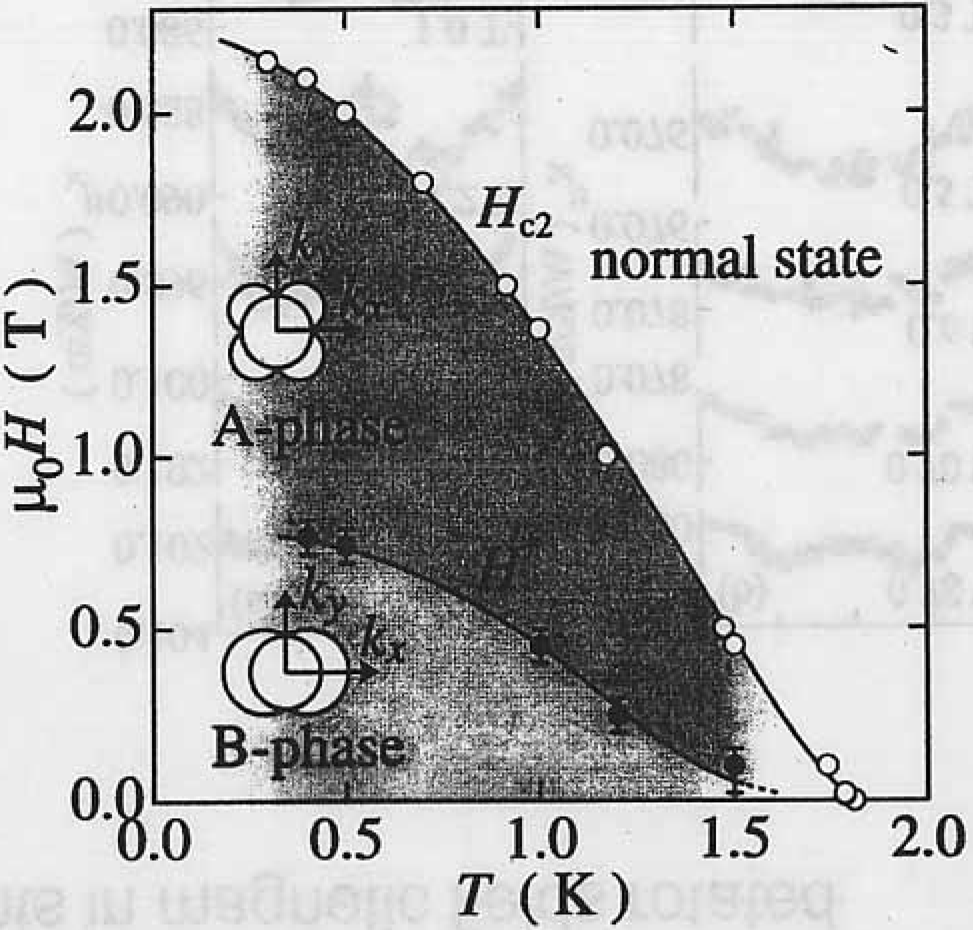
K. Izawa et al. 02

Thermal transport studies of superconducting gap structure

Thermal transport measurements made in magnetic fields rotated relative to the crystal axes

T = 0.52 K, $\kappa_{zz}(H,\phi) = \kappa_o + C_{2\phi}\cos 2\phi + C_{4\phi}\cos 4\phi$





Two Scing phases in H-T plane

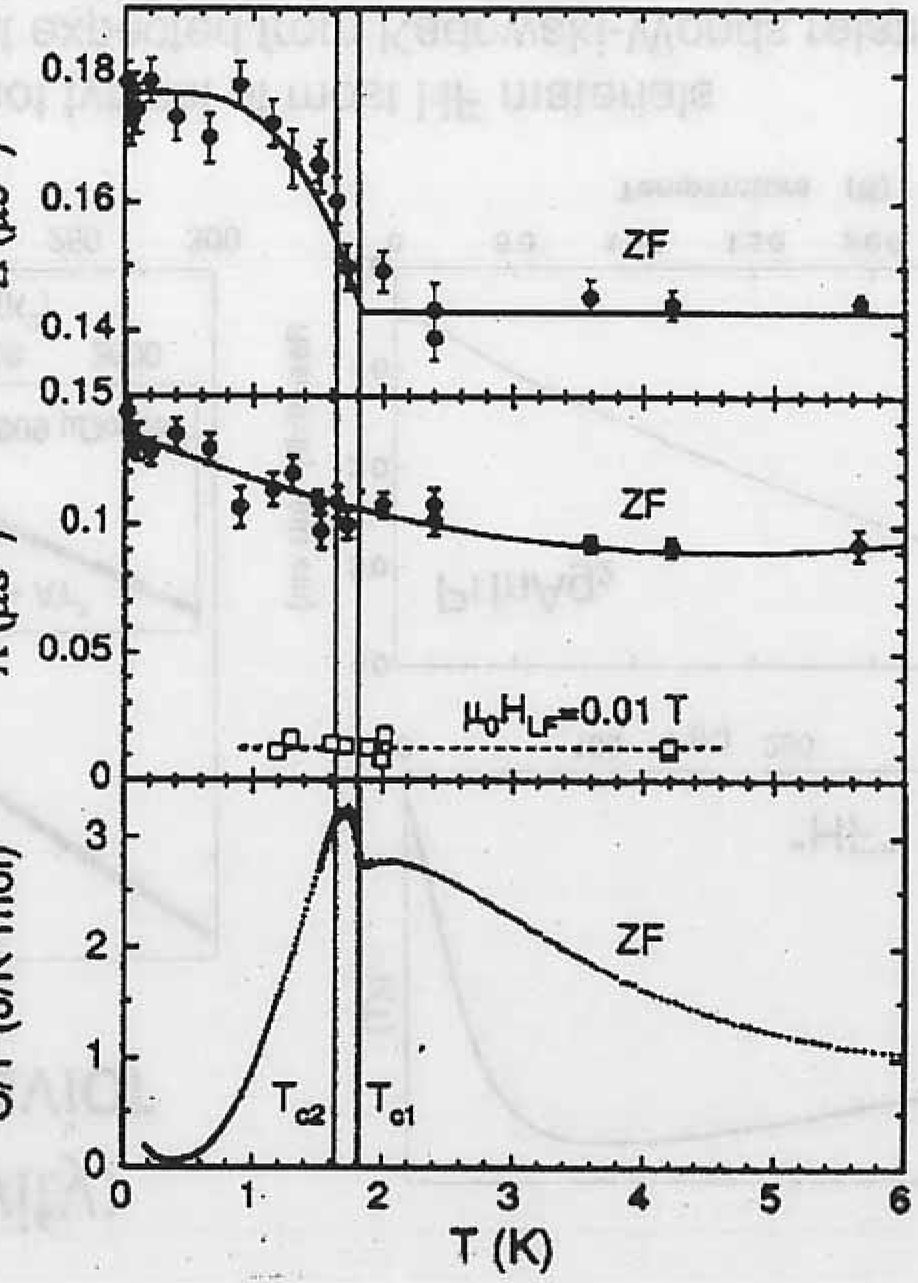
A-6 point nodes, B - 2 point nodes

K. Izawa et al. 02

ime-reversal symmetry breaking detected by SR measurements

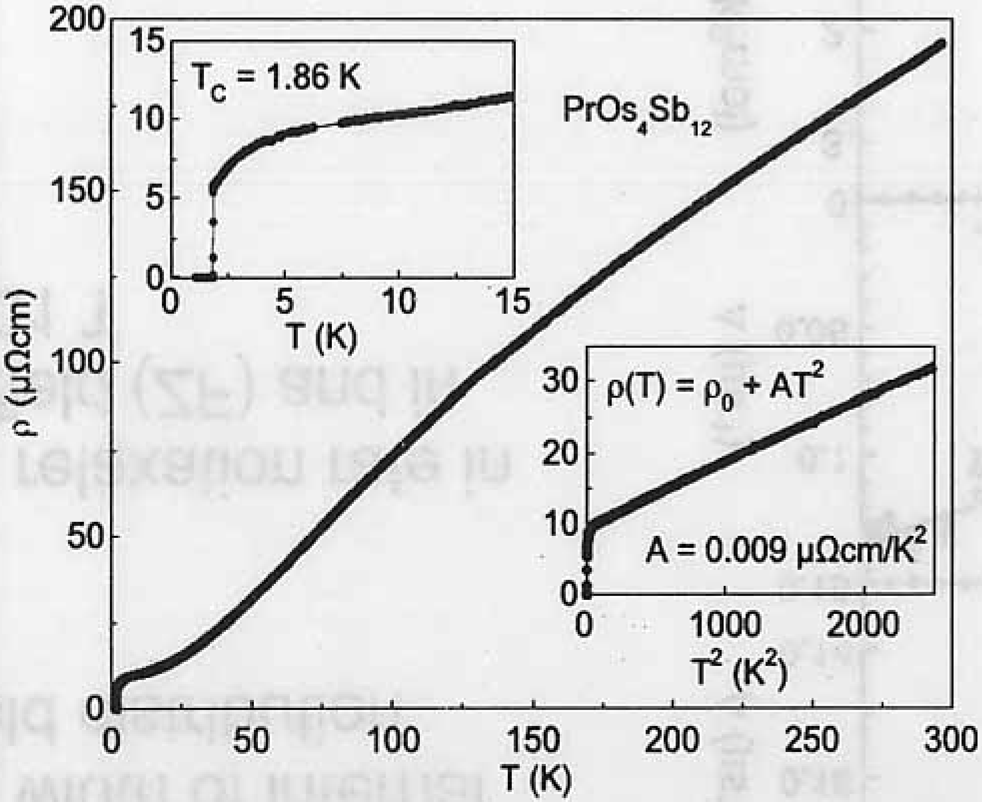
: width of internal
ield distribution

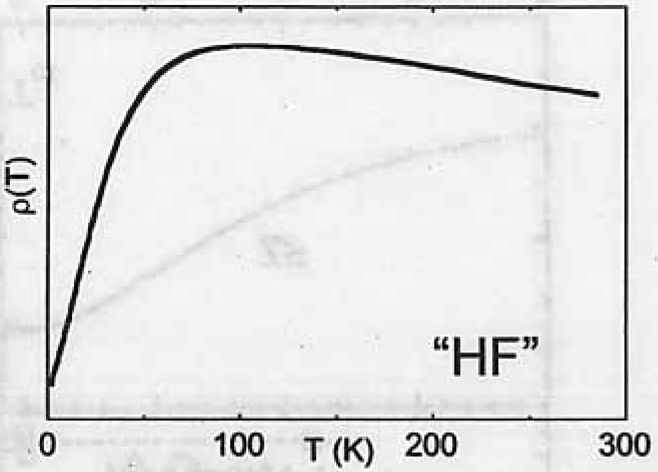
: relaxation rate in
field (ZF) and in
.01 T

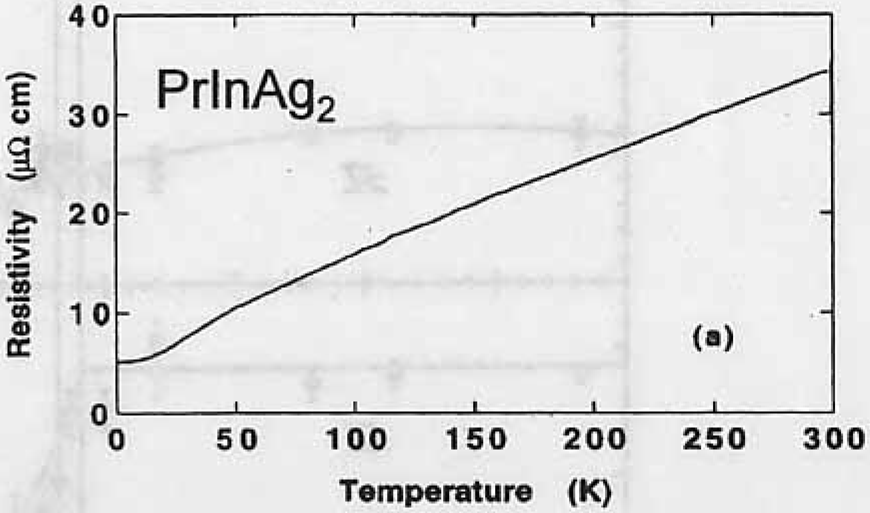


Aoki et al. 03

Electrical resistivity: atypical HF behavior

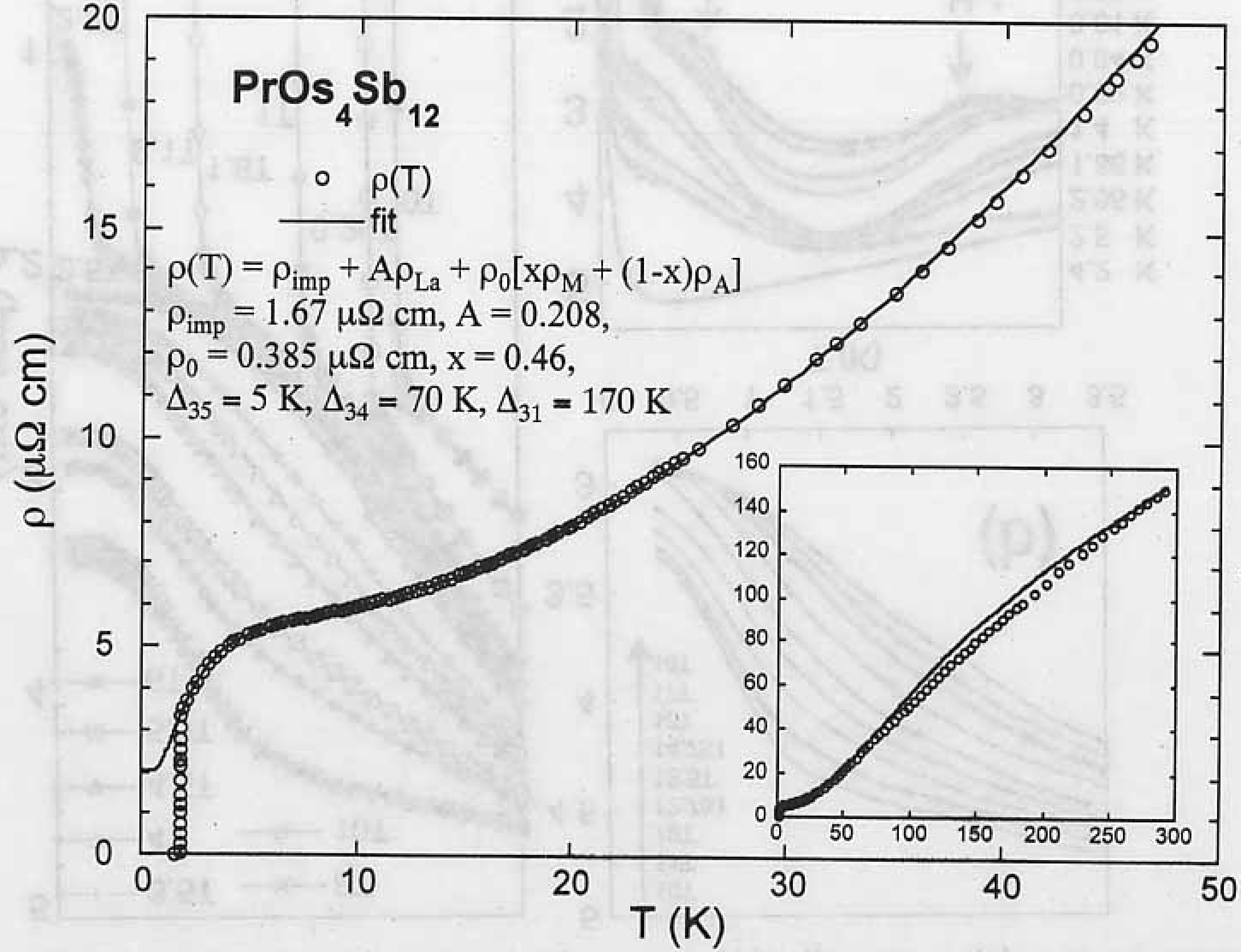




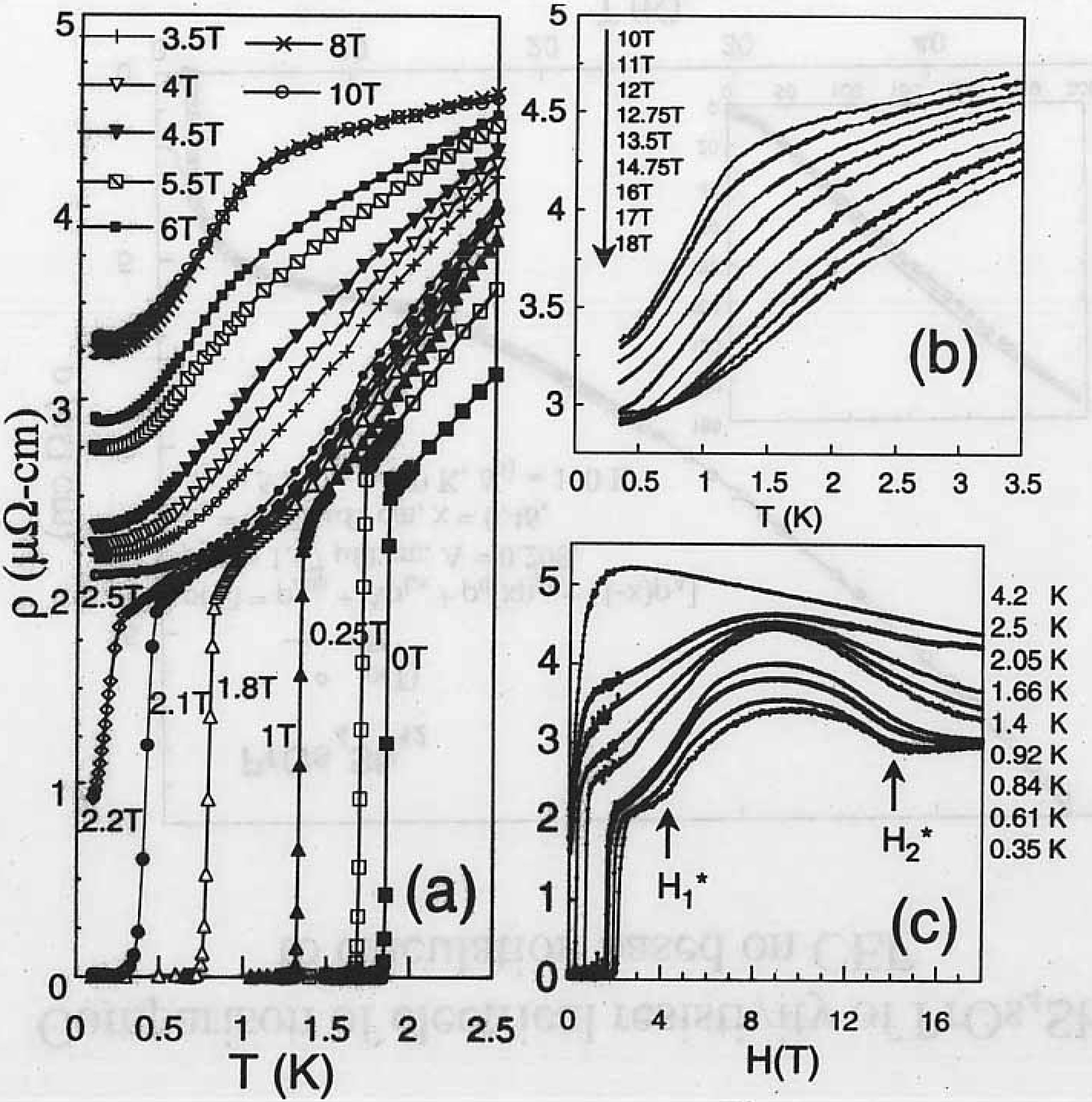


- Exhibits metallic behavior not typical of most HF materials
- T^2 coefficient A << than that expected from Kadowaki-Woods relation
  $A = 1 \times 10^{-5}$ (μΩcm-mol^2-K^2/mJ^2) $\gamma^2 \approx 1.2$ μΩcm/K^2 for $\gamma = 350$ mJ/mol K^2
- Behavior similar to that of PrInAg$_2$ ($\gamma \approx 7$ J/mol K^2) Γ_3 ground state

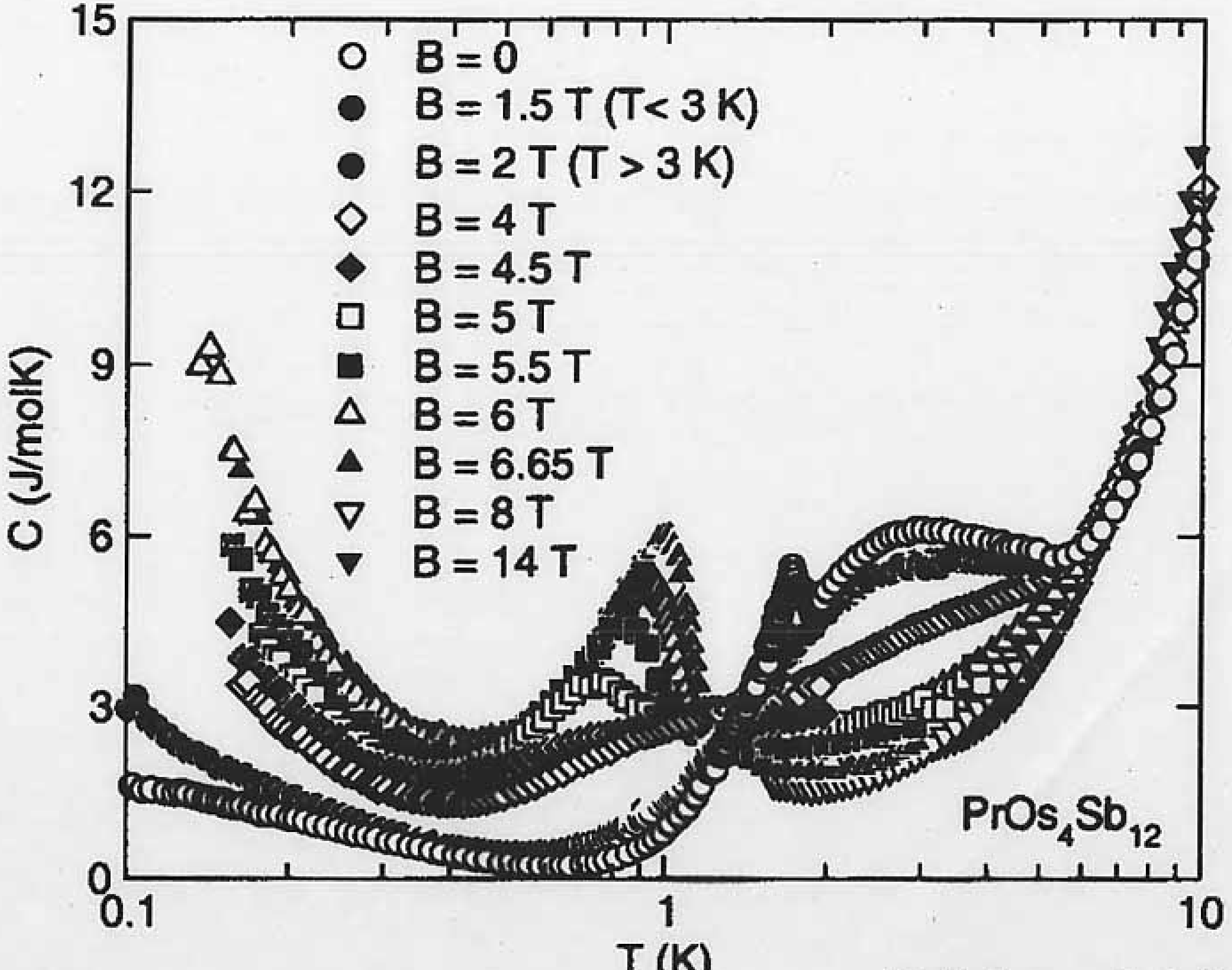
Comparison of electrical resistivity of $PrOs_4Sb_{12}$ to calculation based on CEF



High field ordered phase: $(\rho \text{ vs } T)_H$, $(\rho \text{ vs } H)_T$ for $PrOs_4Sb_{12}$



Specific heat C(T,H) of $PrOs_4Sb_{12}$



R. Vollmer et al. '02
Similar work: Aoki et al. '02