

# ICMR Summer School on Novel Superconductors

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Lecture 1 (Tuesday, 8/11/09):

*Interplay between superconductivity and magnetism in  
f-electron systems  
(conventional superconductivity)*

Lecture 2 (Wednesday, 8/12/09):

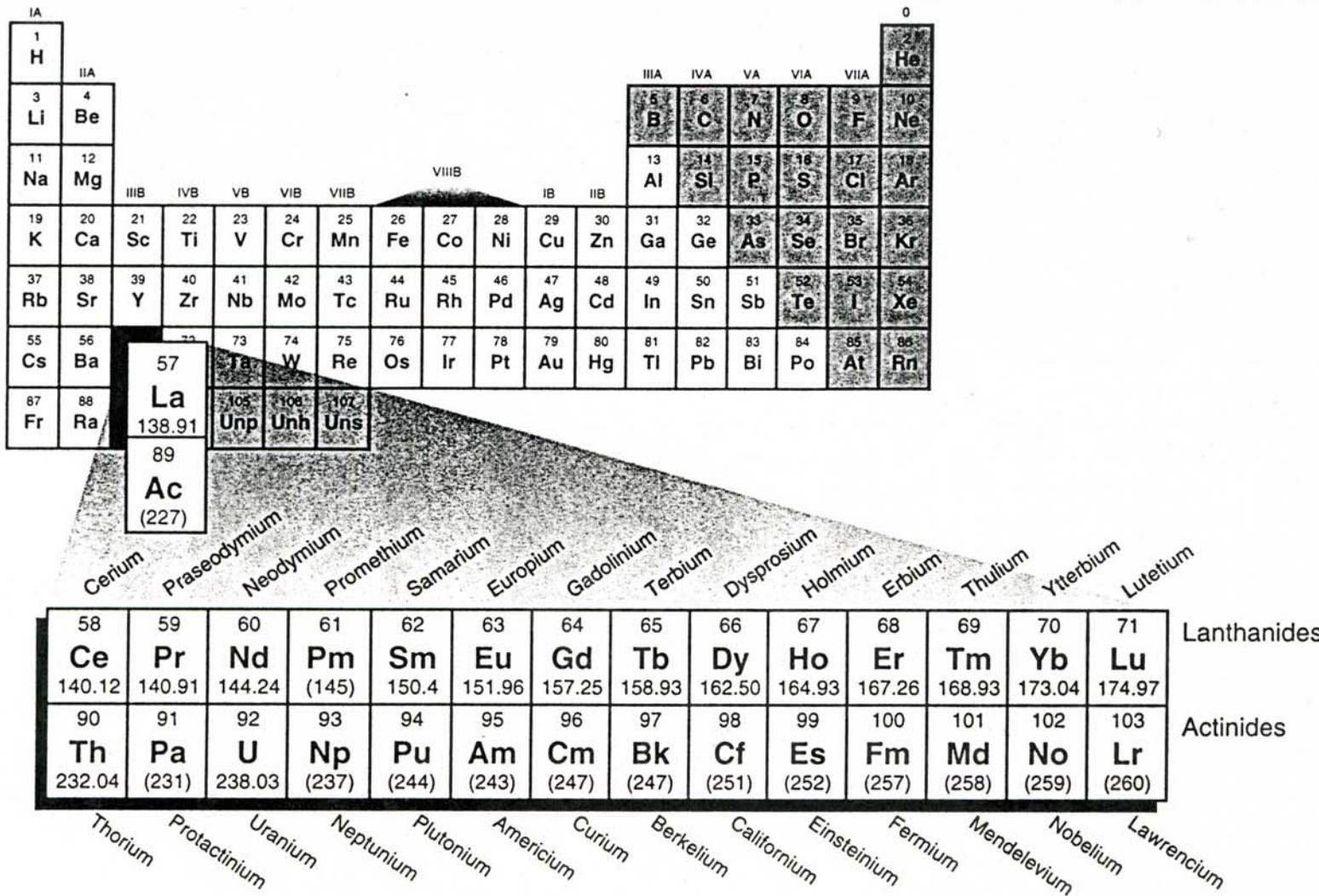
*Unconventional superconductivity, magnetic and charge order,  
and quantum criticality in heavy fermion f-electron materials  
(unconventional superconductivity)*

## *f-electron materials*

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- f-electron materials – multinary compounds and alloys containing rare earth (R) and actinide (A) ions with partially-filled f-electron shells and localized magnetic moments
- Localized magnetic moments of R and A ions interact with the momenta and spins of the conduction electrons
- Certain R ions (Ce, Pr, Sm, Eu, Tm, Yb) and A ions exhibit valence instabilities; i.e., localized f-states hybridize with conduction electron states
- Competing interactions — readily “tuned” by x, P, H (“knobs”)
- Wide variety of correlated electron phenomena
  - Rich and complex phase diagrams in the hyperspace of T, x, P, H
- Situations involving competing interactions
  - One phenomenon survives at the expense of another
  - Interactions conspire to produce a new phenomenon (e.g., sinusoidally-modulated magnetic state that coexists with SC in FM superconductors)
- Brief survey – point of view of experimentalist
- Materials driven physics!
  - Materials – reservoir of new electronic states and phenomena
  - Opened up new research directions in condensed matter physics

# f-electron materials



## Examples

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- Destruction of SC at  $T_{c2} < T_{c1}$  (reentrant SC) due to Kondo effect &
- Kondo effect (impurities and lattice) &
- Destruction of SC at  $T_{c2} < T_{c1}$  (reentrant SC) due to FM order &
- Occurrence of sinusoidally modulated magnetic state ( $\lambda \sim 100 \text{ \AA}$ ) that coexists with SC in FM superconductors &
- Coexistence of SC & AFM order &
- Coexistence of SC & itinerant FM &
- Magnetic field induced SC (MFIS) &
- Heavy fermion compounds ( $m^* \sim 10^2 m_e$ ) &
- Unconventional SC in heavy fermion compounds &
  - Electron pairing with  $L > 0$ , nodes in SCing energy gap, magnetic pairing mechanism
- Occurrence of SC near magnetic QCPs accessed by pressure &
- NFL behavior associated with QCPs &
- Heavy fermion behavior and SC in  $\text{PrOs}_4\text{Sb}_{12}$ , possibly due to electric quadruple, rather than magnetic dipole, fluctuations &

## Lecture 1:

### Interplay between superconductivity and magnetism in f-electron systems

#### Outline:

- (1) f-electron materials
- (2) Conventional superconductivity
- (3) Magnetic interactions in superconductors
- (4) Paramagnetic impurities in superconductors
- (5) Magnetic field induced superconductivity (MFIS)
- (6) Magnetic ordering via the RKKY interaction
- (7) Magnetically ordered superconductors

### Lecture 2:

Unconventional superconductivity, magnetic and charge order,  
and quantum criticality in heavy fermion f-electron materials

#### Outline:

- (1) Unconventional superconductivity
- (2) Heavy fermion compounds
- (3) Superconductivity in heavy fermion compounds
- (4) Competition between Kondo effect and RKKY interaction
- (5) Non-Fermi liquid (NFL) behavior and quantum criticality
- (6) SC near antiferromagnetic (AFM) quantum critical points (QCPs)  
under pressure
- (7) Coexistence of SC and itinerant ferromagnetism
- (8) Heavy fermion behavior and unconventional SC in  $\text{PrOs}_4\text{Sb}_{12}$ ;  
evidence for electron pairing via electric quadrupole interactions

*Local moment paramagnetism and magnetic order*

## *Local moment paramagnetism: magnetization*

$$\mathbf{M} = -g_J \mu_B \mathbf{J}$$

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (\text{determined from Hund's rules})$$

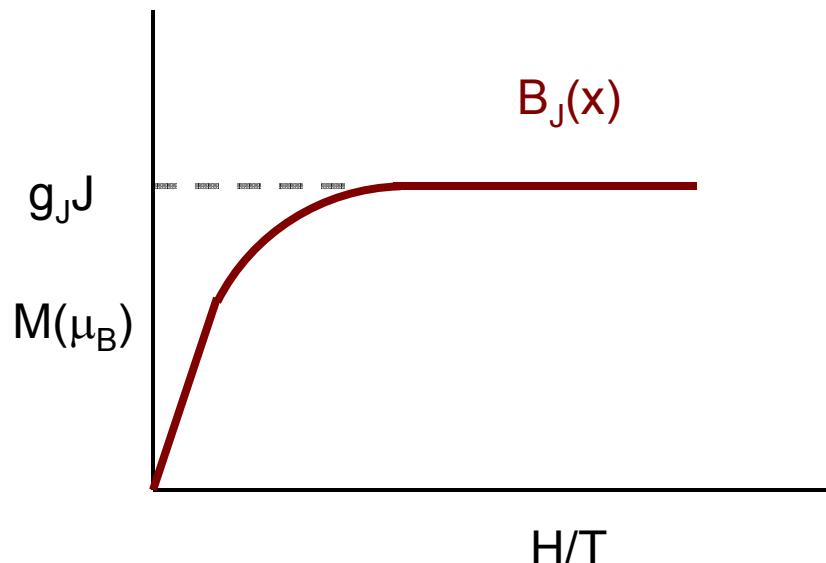
$$g_J = 1 + [J(J+1) + S(S+1) - L(L+1)]/2J(J+1) \quad \text{Landé g-factor}$$

$$\mu_B = e\hbar/2mc = 0.927 \times 10^{-20} \text{ erg/gauss}$$

$$E = m_J g_J \mu_B H; m_J = J, J-1, \dots, -J \quad (2J+1 \text{ equally spaced levels})$$

$$M = N g_J J \mu_B B_J(x); \quad x = g_J J \mu_B H / k_B T$$

$$B_J(x) = [(2J+1)/2J] \operatorname{ctnh}[(2J+1)x/2J] - (1/2J) \operatorname{ctnh}(x/2J) \quad \text{Brillouin function}$$



## *Local moment paramagnetism: magnetization*

$x \ll 1$

$$M \approx [Ng_J^2J(J+1)\mu_B^2/3k_B T]H = (N\mu_{\text{eff}}^2/3k_B T)H = \chi(T)H$$

$$\chi(T) = M/H = N\mu_{\text{eff}}^2/3k_B T = C/T$$

Curie law

$$C = N\mu_{\text{eff}}^2/3k_B$$

Curie constant

$$\mu_{\text{eff}} = g_J[J(J+1)]^{1/2}\mu_B$$

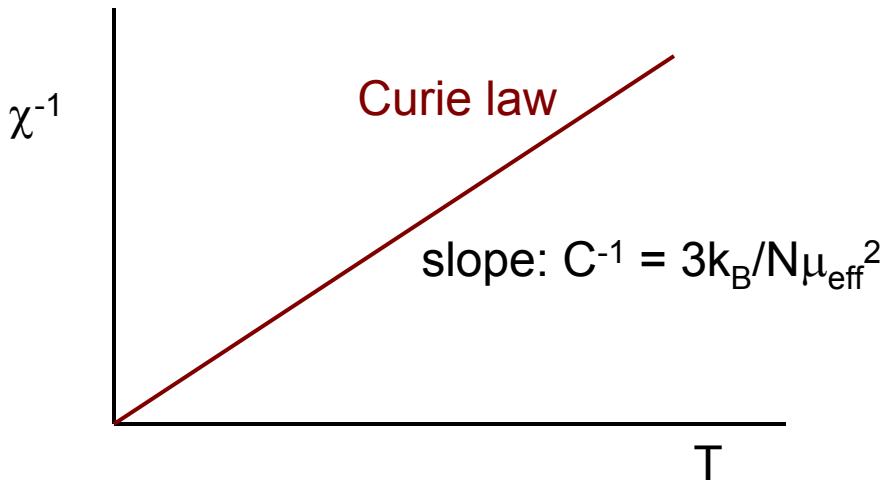
Effective moment

$x \gg 1$

$$M \approx g_J J \mu_B$$

Saturation moment

$x \ll 1$



## *Local moment paramagnetism: Hund's rules*

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S, L, J for lanthanide ion determined from Hund's rules

Hund's rules:

Lanthanide ion with configuration  $4f^n$

4f electron:  $l = 3$ ,  $s = 1/2$

$S = \text{maximum value } \sum(s_z)_i$

$L = \text{maximum value } \sum(l_z)_i$  (subject to Pauli principle)

$J = |L-S|$  4f shell less than half filled ( $n < 7$ )

$J = L+S$  4f shell more than half filled ( $n \geq 7$ )

e.g.,  $\text{Ce}^{3+}$  ( $4f^1$ )  $S = 1/2$ ,  $L = 3$ ,  $J = |L-S| = 5/2$

$\text{Pr}^{3+}$  ( $4f^2$ )  $S = 1$ ,  $L = 5$ ,  $J = |L-S| = 4$

$\text{Gd}^{3+}$  ( $4f^7$ )  $S = 7/2$ ,  $L = 0$ ,  $J = L+S = 7/2$  (so-called "S-state" ion)

$\text{Yb}^{3+}$  ( $4f^{13}$ )  $S = 1/2$ ,  $L = 3$ ,  $J = L+S = 7/2$  (one f-“hole”)

$2J+1$  degeneracy of Hund's rule ground state multiplet can be lifted by crystalline electric field (CEF)  $\Rightarrow$  CEF ground and excited states

## Local moment magnetic ordering

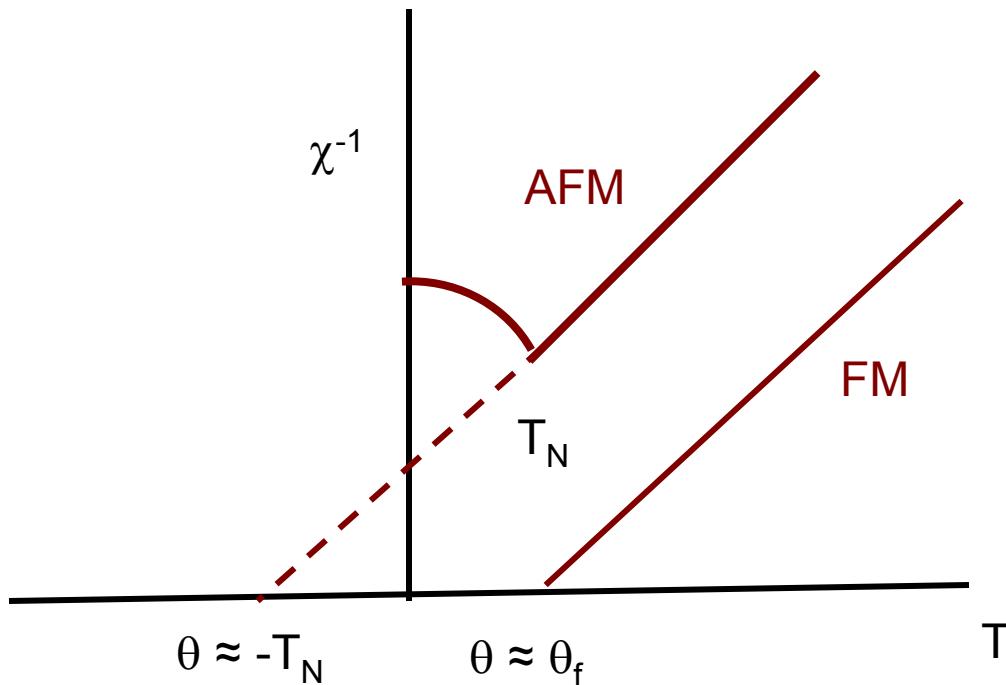
$$\chi(T) = N\mu_{\text{eff}}^2/3k_B(T-\theta)$$

Curie-Weiss law

$\theta$  – Curie-Weiss temperature

Ferromagnetic order:  $\theta \approx \theta_f$  (Curie temperature)

Antiferromagnetic order:  $\theta \approx -T_N$  (Néel temperature)



*Conventional superconductivity*

## Conventional superconductivity

Attractive interaction (electron-phonon)

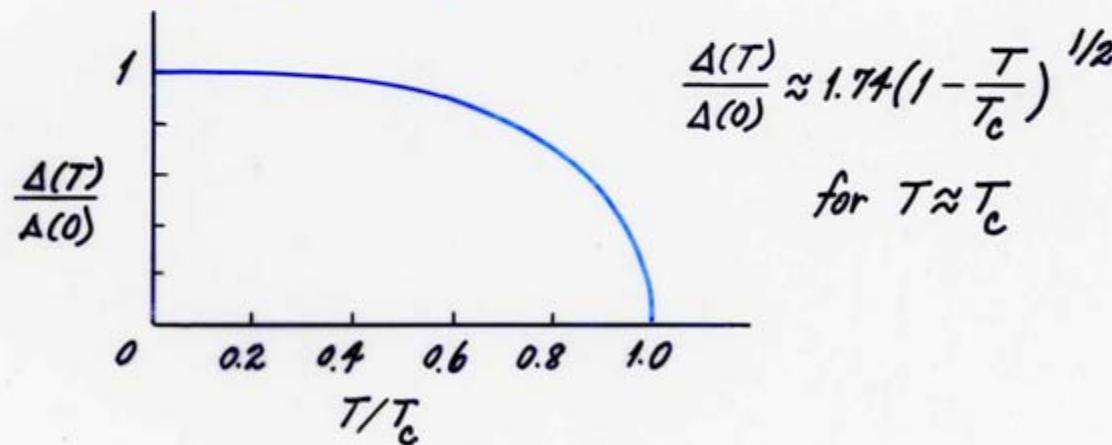
$(\tilde{k} \uparrow, -\tilde{k} \downarrow)$  "Cooper pairs"

$$T_c \sim \Theta_0 \exp[-1/N(0)V]$$

$$F_n(0) - F_s(0) = \frac{1}{2} N(0) \Delta^2(0) \quad \Delta(0) = 1.764 k_B T_c$$

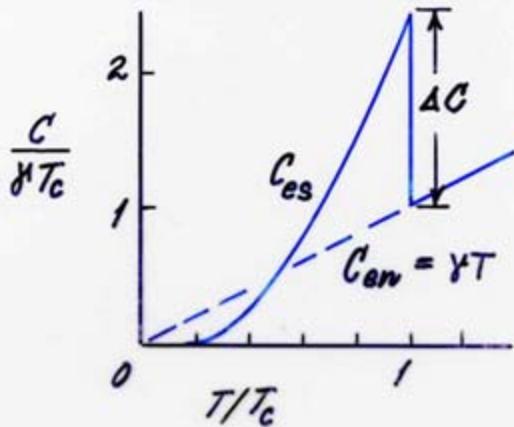
$$\xi_0 = 0.18 \frac{\hbar v_F}{k_B T_c} \quad \text{coherence length}$$

Energy gap (order parameter)



# Conventional superconductivity

Specific heat



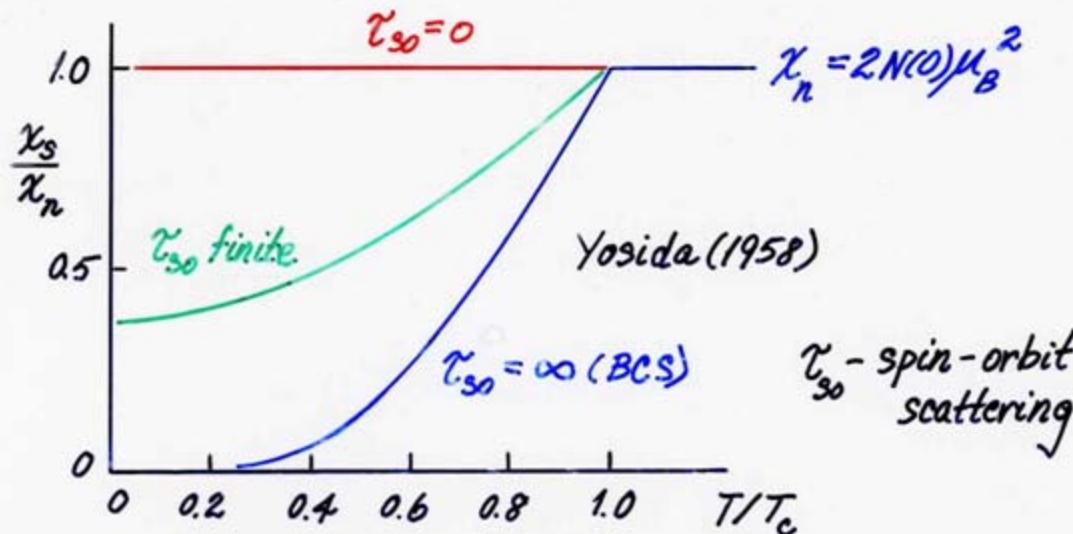
$$\Delta C / \delta T_c = 1.43$$

$$C_{es}/\delta T_c \approx a \exp(-bT_c/T)$$

$$a = 8.5, b = 1.44 \quad (2.5 < T_c/T < 6)$$

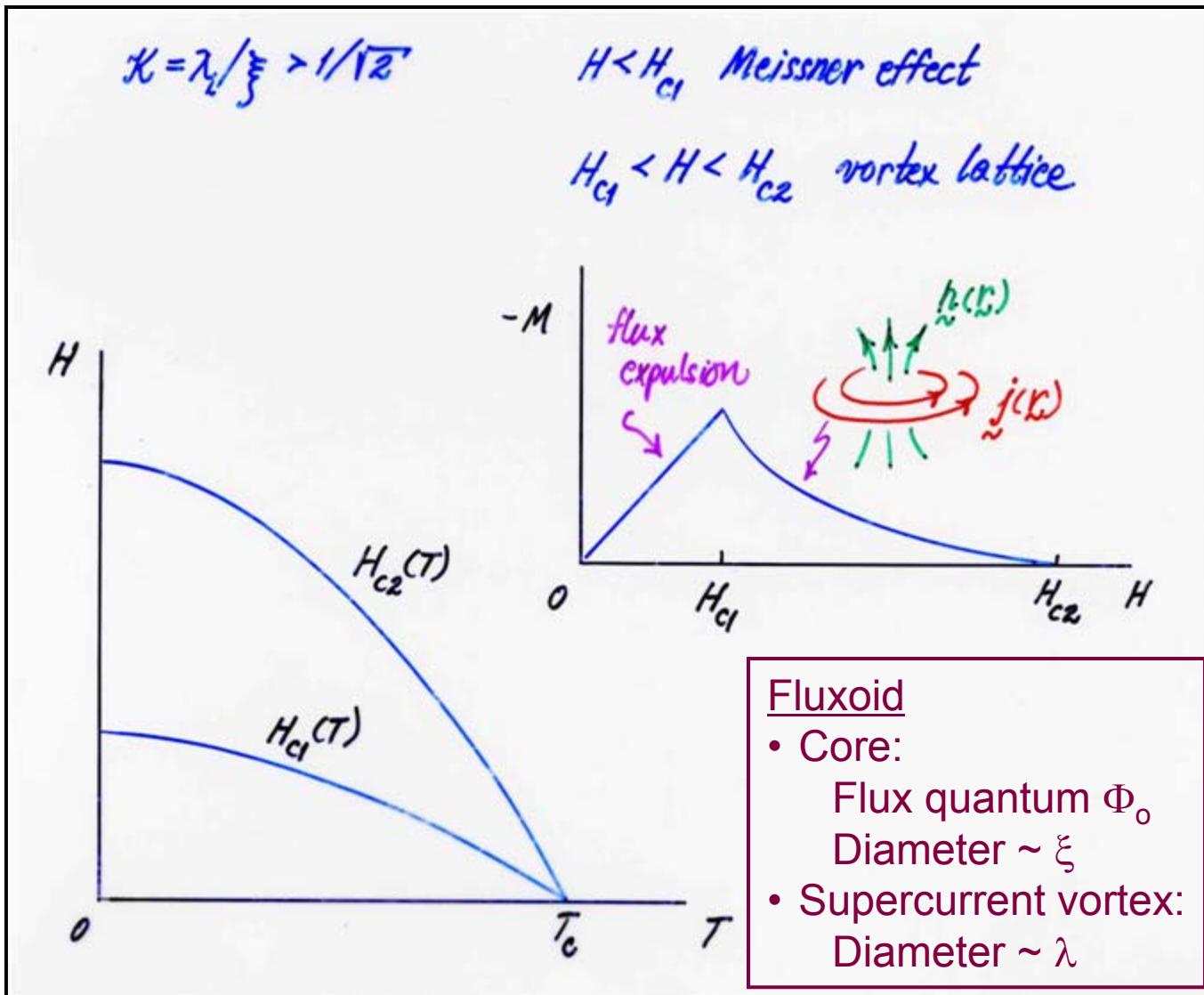
$$a = 26, b = 1.62 \quad (7 < T_c/T < 11)$$

spin susceptibility



# Conventional superconductivity

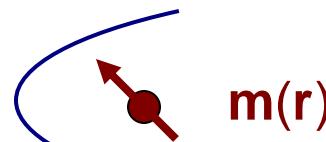
## Type II superconductivity (compounds, alloys)



# Superconducting-magnetic interactions

Superconductor containing R ions (magnetic moment  $\mu$ )

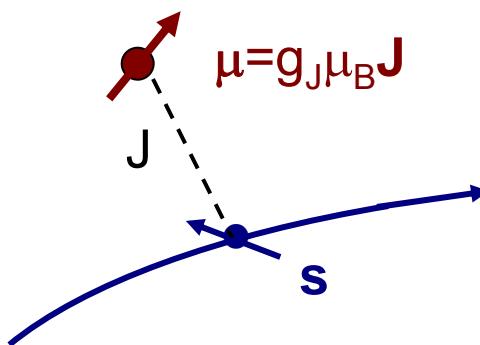
Electromagnetic



$$(e/mc)(\mathbf{p} \cdot \mathbf{A})$$

$$\mathbf{j}(\mathbf{r})$$

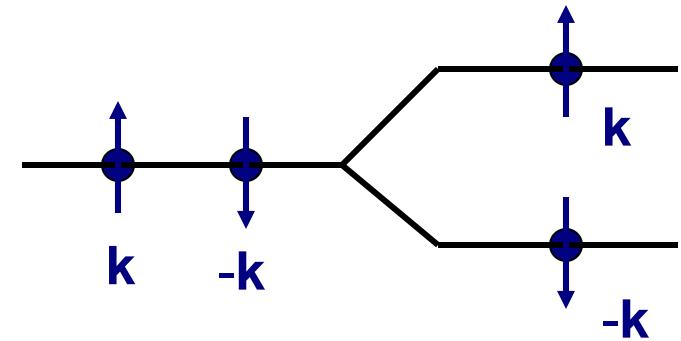
Exchange



$$H_{ex} = -2J(g_J - 1)\mathbf{J} \cdot \mathbf{s}$$

“Pair breaking” interactions

Conventional SC:  $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$



# *Paramagnetic impurities in superconductors*

- **Origin**

*Theory – Ginzburg (57)*

*Experiments – Matthias, Suhl, Corenzwit (58)*

- **Background (57-76)**

*Experiments*

- Binary and pseudobinary R impurity systems; e.g.,  $\text{La}_{1-x}\text{R}_x$ ,  $\text{Y}_{1-x}\text{R}_x\text{Os}_2$
- Rapid depression of  $T_c$  with  $x$  ( $x_{\text{cr}} \sim 1$  at% for  $\text{La}_{1-x}\text{Gd}_x$ )
- Results – provocative, inconclusive wrt coexistence of two phenomena (chemical clustering, short-range or “glassy” magnetic order)

*Theory*

- Striking predictions, inapplicable to systems then under investigation

*Spin-off*

- Understanding of effects of paramagnetic impurities on superconductivity – CEF, Kondo effect, LSF, etc.

- **Revival (~76)**

*Experiments – Binary, ternary and quaternary R and U compounds*

⇒ new, unusual physical effects and phenomena

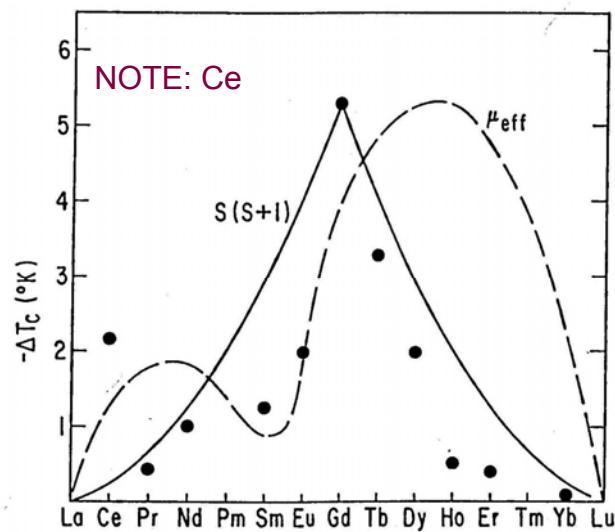
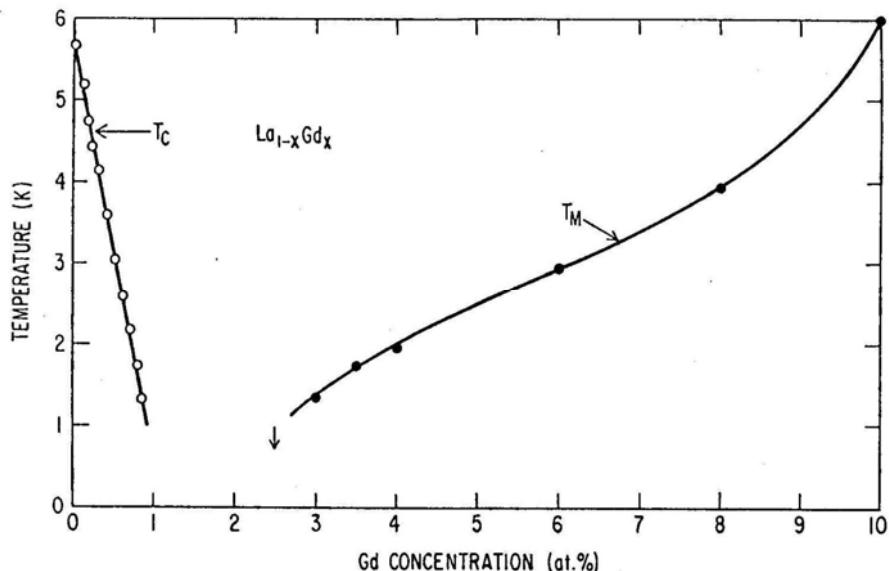
*Theory – Intense activity*

# Paramagnetic impurities in superconductors

Matthias, Suhl, Corenzwit (58) —

- $T_c(x)$  for  $\text{La}_{1-x}\text{R}_x$   
 $R = \text{Gd}$ :  $T_c(x) \rightarrow 0 \text{ K}$  for  $x \approx 1 \text{ at.\%}$

- Depression of  $T_c$  for  $x=1 \text{ at.\%}$ ,  
 $-\Delta T_c = T_{co} - T_c$ , correlates with  
S of R solute

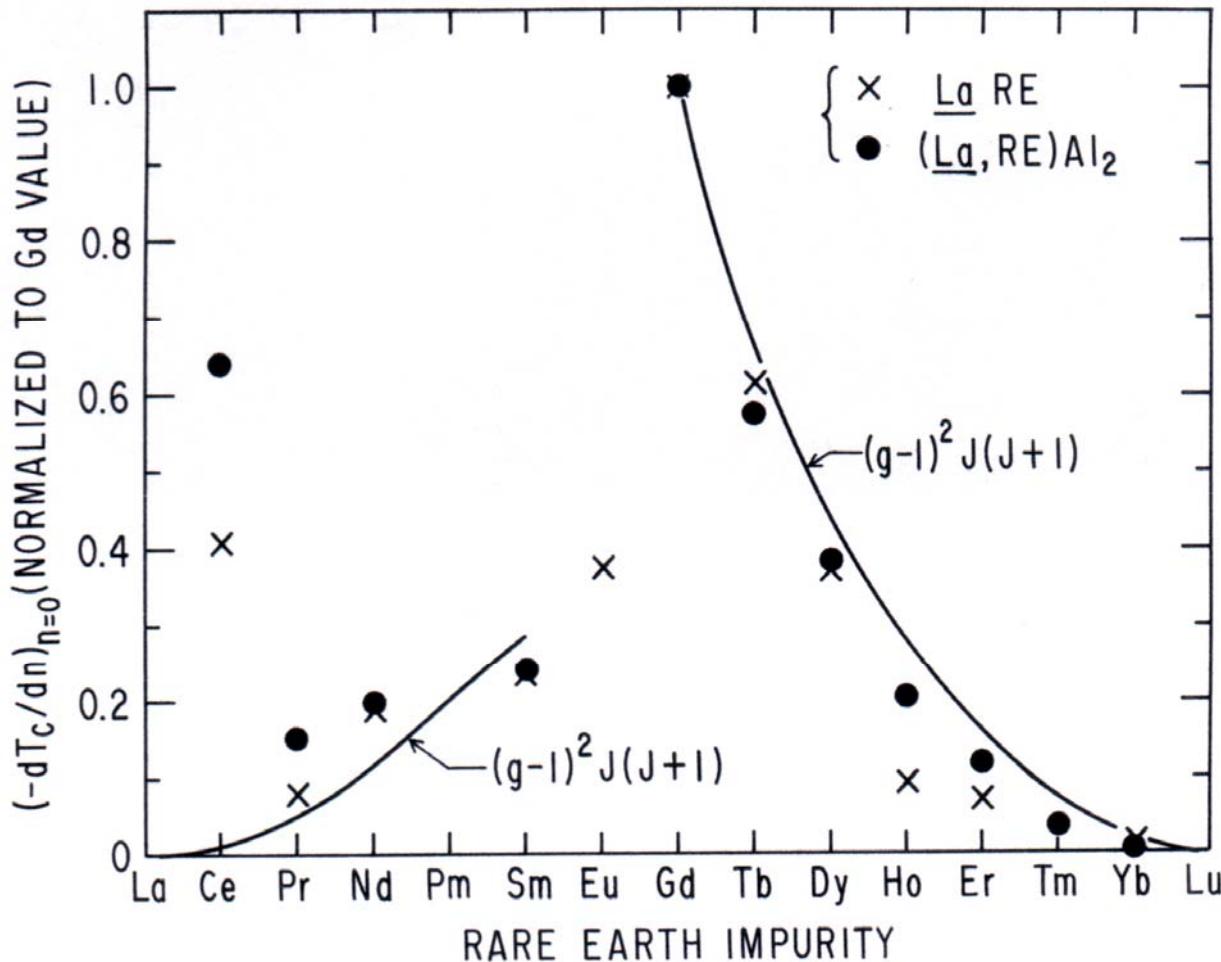


Herring (58); Suhl & Matthias (59) —

Exchange interaction:  $H_{int} = -2(g_J-1)\mathbf{J}\cdot\mathbf{J}\cdot\mathbf{s}$

$\Delta T_c \propto J^2(g_J-1)^2 J(J+1)$ ; deGennes factor  $\equiv (g_J-1)^2 J(J+1)$

# Paramagnetic impurities in superconductors



LaRE ( $T_{co} = 6$  K)

*Matthias, Suhl,  
Corenzwit (58)*

(LaRE)Al<sub>2</sub> ( $T_{co} = 3.3$  K)

*Maple (70)*

$J \sim 0.1$  eV

Anomalous depression of  $T_c$  for Ce  $\Rightarrow$  hybridization of Ce localized 4f and itinerant electron states  $\Rightarrow J \sim -\langle V_{kf}^2 \rangle / E_f < 0 \Rightarrow$  Kondo effect

LaCe: *Sugawara, Eguchi (66); (LaCe)Al<sub>2</sub>: Maple, Fisk (68)*

# Paramagnetic impurities in superconductors

Pair breaking  $\Rightarrow$  rapid suppression of SC

- Two cases:
- $J > 0$  (ferromagnetic)
  - $J < 0$  (antiferromagnetic)

•  $J > 0$  (ferromagnetic)

$$\frac{T_c}{T_{c_0}} = \ln(\alpha/\alpha_{cr}) \quad \text{Abrikosov, Gor'kov (AG-1960)}$$

$\alpha$  - pair breaking parameter

$$\alpha = \tau_{ex}^{-1} = \pi^{-1} n N(0) J^2 (g_J - 1)^2 J(J+1)$$

$$\alpha_{cr} = k_B T_{c_0} / 4\pi \gamma \quad (\ln \gamma = 0.57721 - \text{Euler's const.})$$

Explicitly -

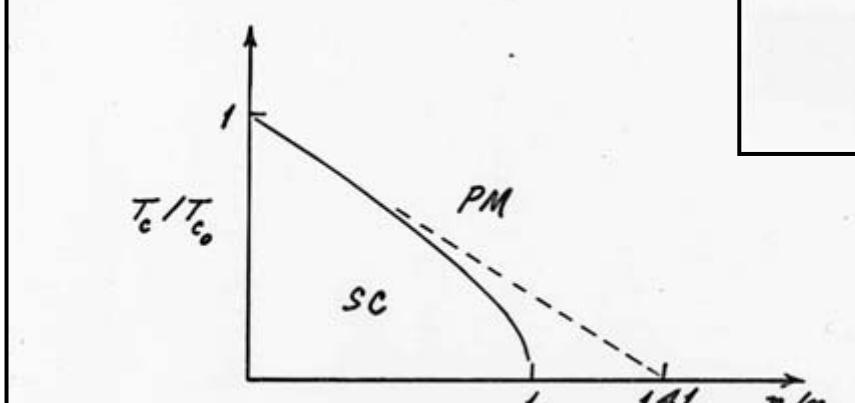
$$\ln\left(\frac{T_c}{T_{c_0}}\right) = \psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2} + 0.17 \frac{\alpha/T_{c_0}}{\alpha_{cr}/T_c}\right)$$

$\psi$  - digamma function

Limit  $\alpha \rightarrow 0$  -

$$\frac{T_c}{T_{c_0}} = 1 - 0.691(\alpha/\alpha_{cr}) = 1 - 0.691(n/n_{cr})$$

# Paramagnetic impurities in superconductors



Linear region  $n/n_{cpr} \ll 1$

$$\frac{dT_c}{dn} \Big|_{n=0} = -(\pi^2/2) k_B^{-1} N(0) J^2 \underbrace{(g_J - 1)^2}_{\text{de Gennes factor}} J(J+1)$$

(maximum at  $G_d$ )

Other predictions -

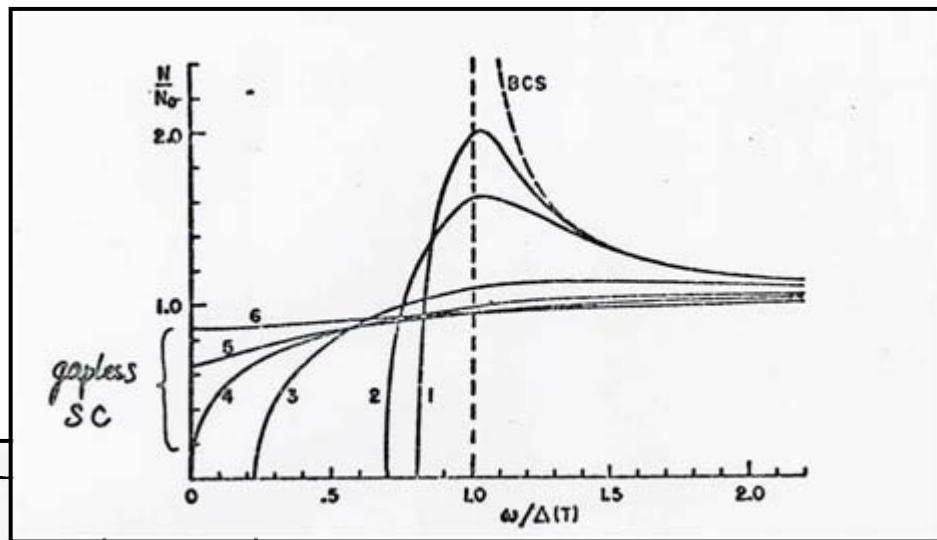
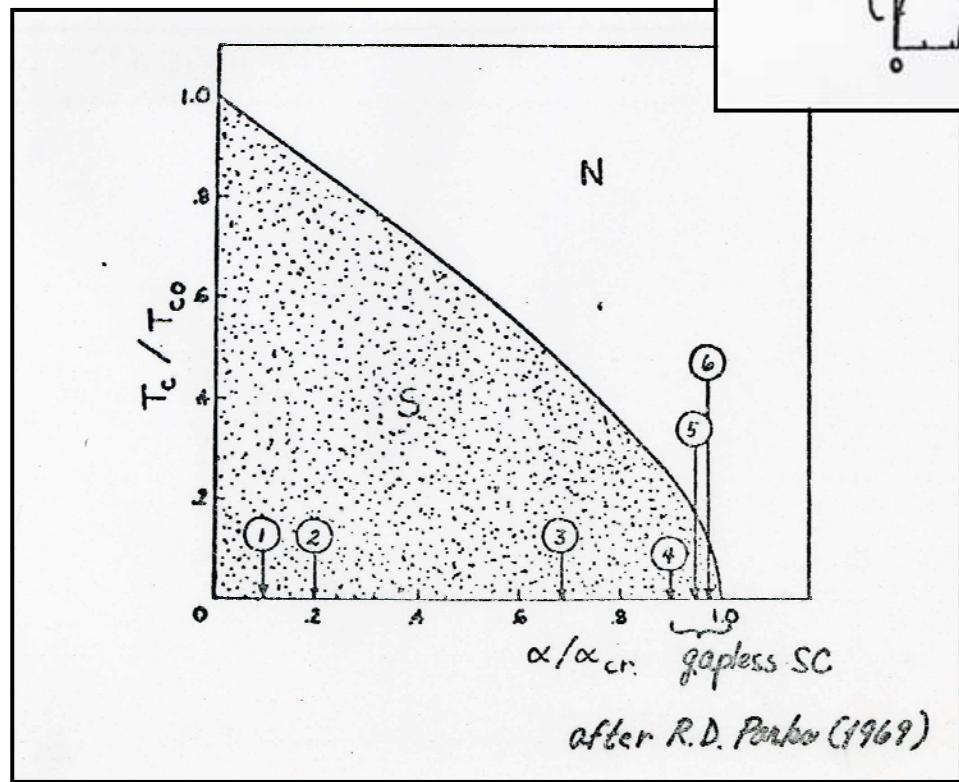
$$\Delta C/AC_0 = Vn (T_c/T_{c_0})$$

deviates from BCS law of corresponding states ( $\Delta C/AC_0 = T_c/T_{c_0}$ )

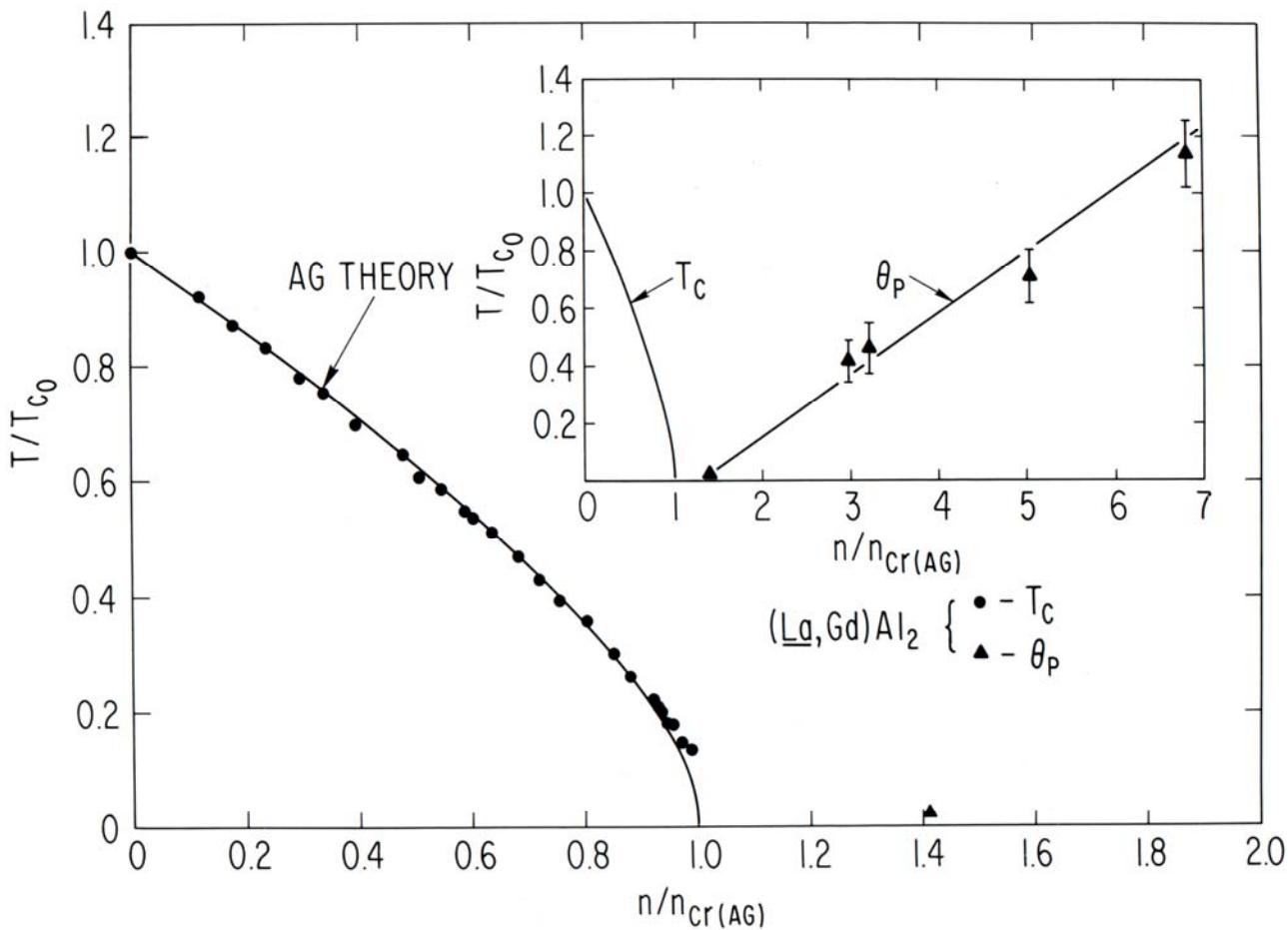
Gapless SC  $\Delta \leftrightarrow \Omega$

$\Omega \rightarrow 0$  faster than  $\Delta \rightarrow 0$  with  $\alpha$

# Gapless superconductivity



# $La_{1-x}Gd_xAl_2$ ; $T_c$ vs $x$ phase boundary



$T_{co} = 3.3$  K  
 $n_{cr} = 0.59$  at.% Gd

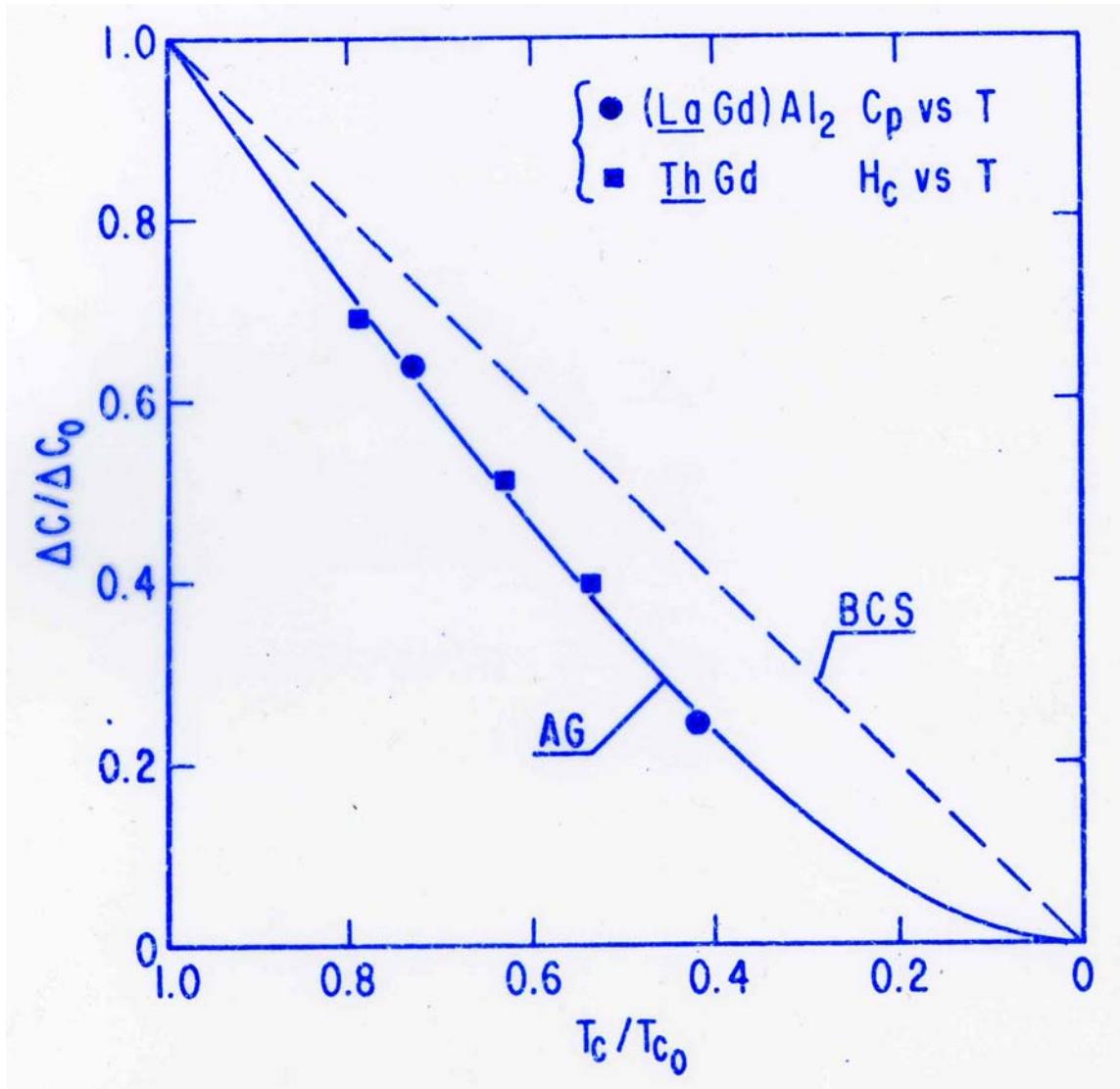
“Gapless” superconductivity

*M. B. Maple (68)*

*Woolf, Reif (65)* - tunneling  $Pb_{1-x}Gd_x$

*Finnemore et al. (65)* - specific heat  $La_{1-x}Gd_x$

$La_{1-x}Gd_xAl_2$ ; specific heat jump vs  $T_c$



W. R. Decker, D. K. Finnemore (68)  
C. A. Luengo, M. B. Maple (73)

## SCing metal containing paramagnetic impurities (spin S)

- AFM exchange interaction

$$H_{ex} = -2JS \cdot s \text{ with } J < 0$$

- Formation of many body singlet state below  $T_K$

$$T_K \sim T_F \exp(-1/N(E_F)|J|) \quad T_K \rightarrow \text{effective } T_F$$

- Normal State

- $T > T_K$ : Local moment behavior

$$\chi(T) \sim N\mu_{eff}^2/3k_B(T-\theta) \text{ where } \theta \sim -3T_K$$

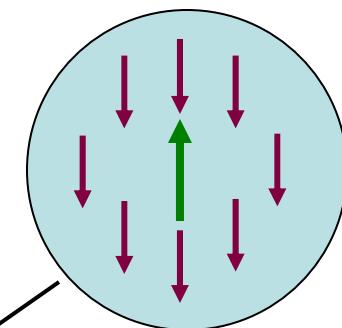
$$\rho(T) \sim -\ln T \text{ ("resistivity minimum")}$$

- $T \ll T_K$ : Many body singlet

Nonmagnetic heavy Fermi liquid (FL)

$$\chi(T) \propto \gamma(T) = C(T)/T \sim \text{const.}$$

$$\rho(T) \approx \rho(0)[1-(T/T_K)^2]$$



## *Kondo effect in superconductors*

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- Superconducting state

Competition between:

- (1) Singlet spin paired ( $k\uparrow, -k\downarrow$ ) SCing state ( $E_{SC} \sim k_B T_c$ );
- (2) Kondo many body singlet state ( $E_K \sim k_B T_K$ )

- $T_K \ll T_{co}$ : Reentrant  $T_c(x)$  curve!
- $T_K \gg T_{co}$ : Exponential-like depression of  $T_c$  with  $x$
- $T_K \approx T_{co}$ : Maximum in initial rate of depression of  $T_c$

Theory: *Müller-Hartmann, Zittartz (70-71);*

*Zuckermann (68); Ludwig, Zuckermann (71)*

## Paramagnetic impurities in superconductors

$$T_c/T_c^* = \ln(\alpha/\alpha_{cr})$$

$$\alpha/\alpha_{cr} = nB \left\{ \frac{\pi^2 S(S+1)}{\ln^2(T/T_K) + \pi^2 S(S+1)} \right\}$$

Müller-Hartmann & Zittartz (MHZ - 1971)

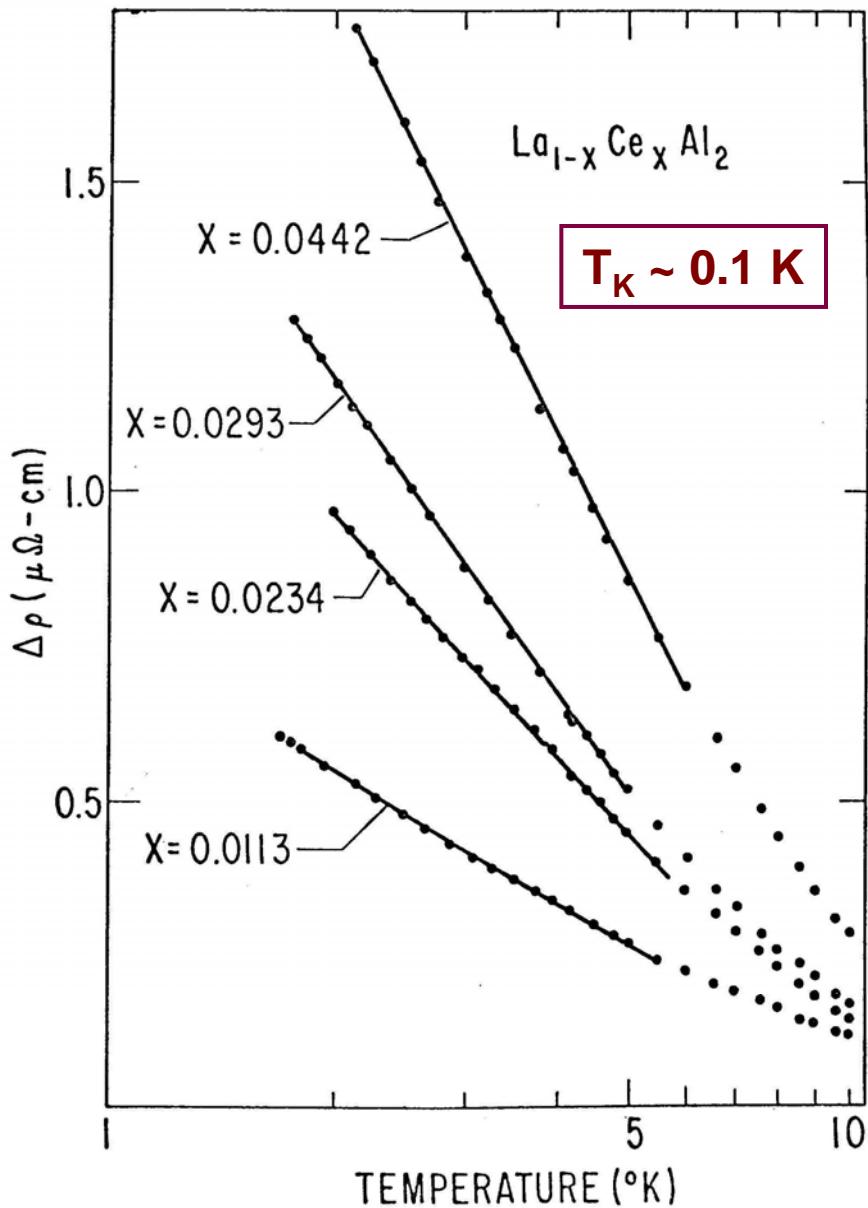
Other predictions -

$\Delta C/C_0$  vs  $T_c/T_c^*$  deviates from both BCS

law of corresponding states & AG theory

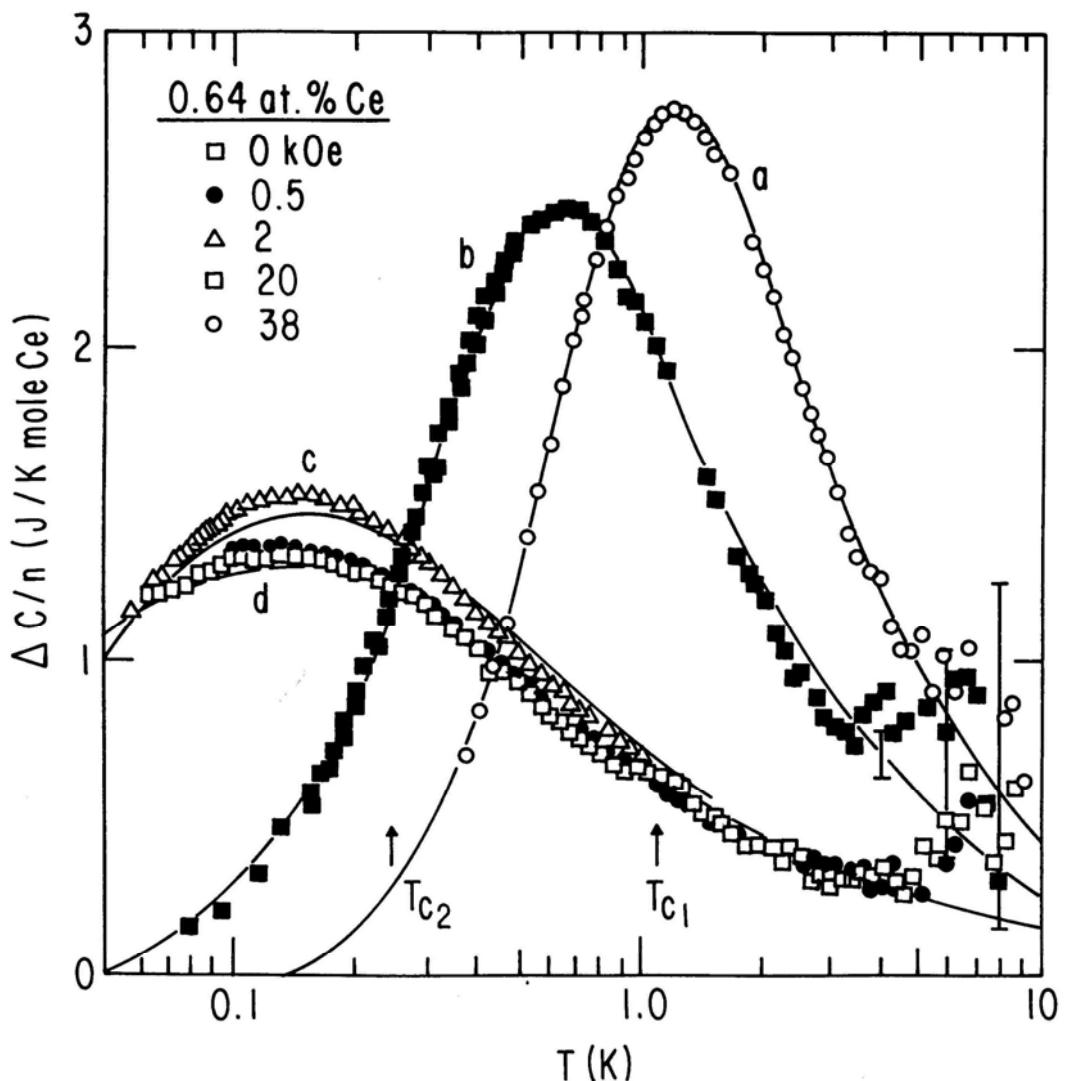
Bound state in energy gap

## Kondo effect in $\text{La}_{1-x}\text{Ce}_x\text{Al}_2$ : electrical resistivity



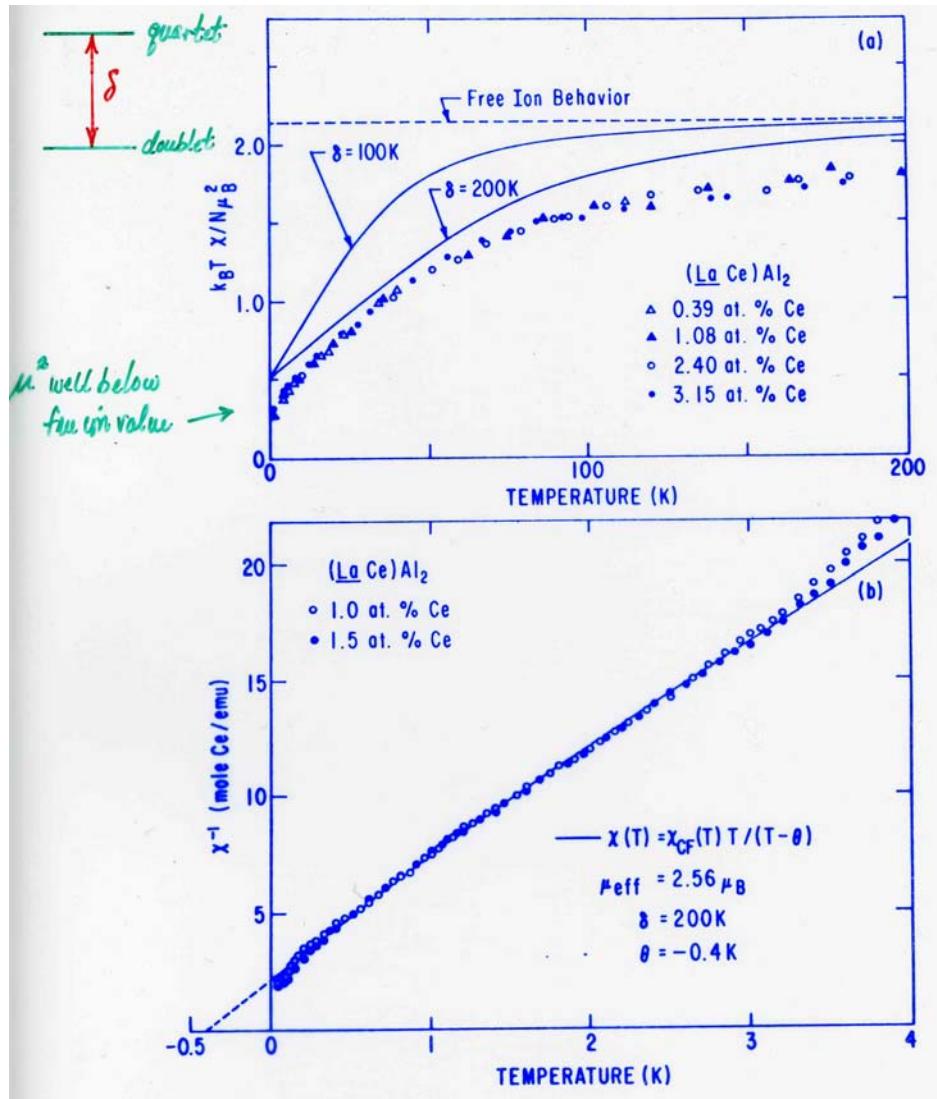
Magnetic scattering  
“Kondo” contribution  
to electrical resistivity:  
 $\Delta\rho(T) = \rho(x, T) - \rho(0, T)$

# Kondo effect in $\text{La}_{1-x}\text{Ce}_x\text{Al}_2$ : specific heat



S. D. Bader, N. E. Phillips, M. B. Maple, C. A. Luengo (75)

# Kondo effect in $\text{La}_{1-x}\text{Ce}_x\text{Al}_2$ : magnetic susceptibility

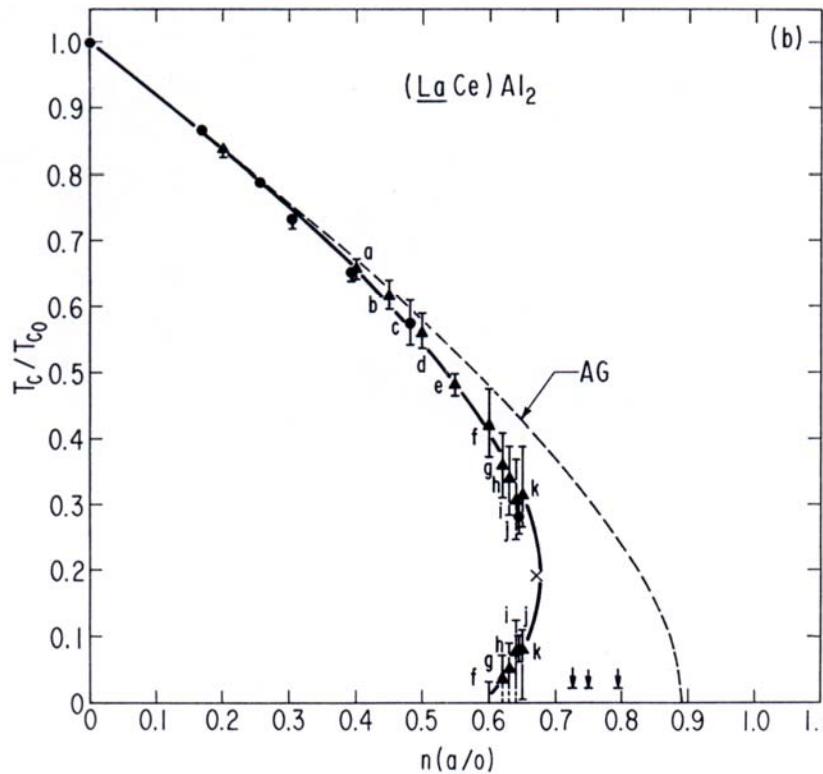
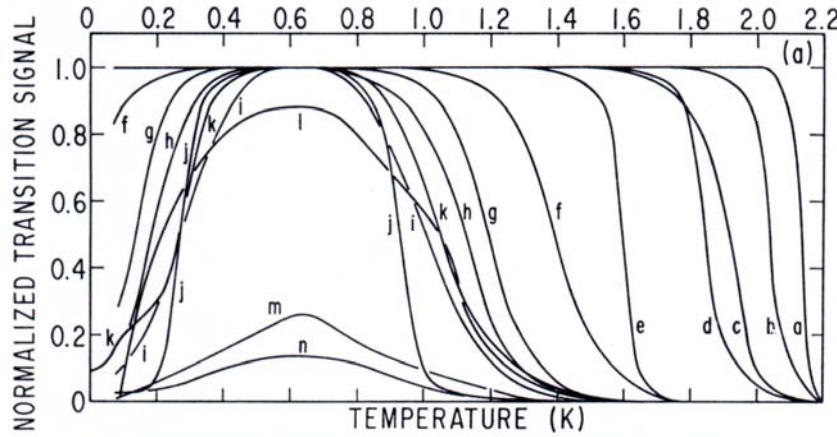


- Ce has ground state doublet and excited state quartet with splitting  $\delta \sim 100 \text{ K}$  in CEF
- $\theta_p \approx -0.5 \text{ K} \Rightarrow T_K \approx 0.1 \text{ K}$

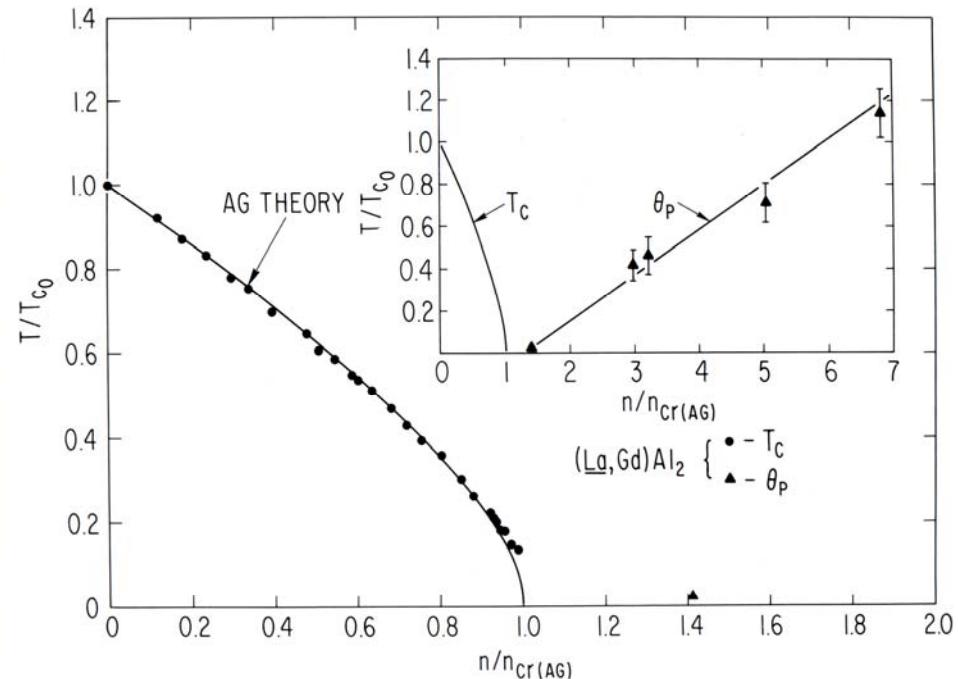
(a) M. B. Maple (69)

(b) W. Felsch, K. Winzer, G. v. Minnigerode (75)

# Kondo effect in $\text{La}_{1-x}\text{Ce}_x\text{Al}_2$ : reentrant $T_c$ vs $x$ curve

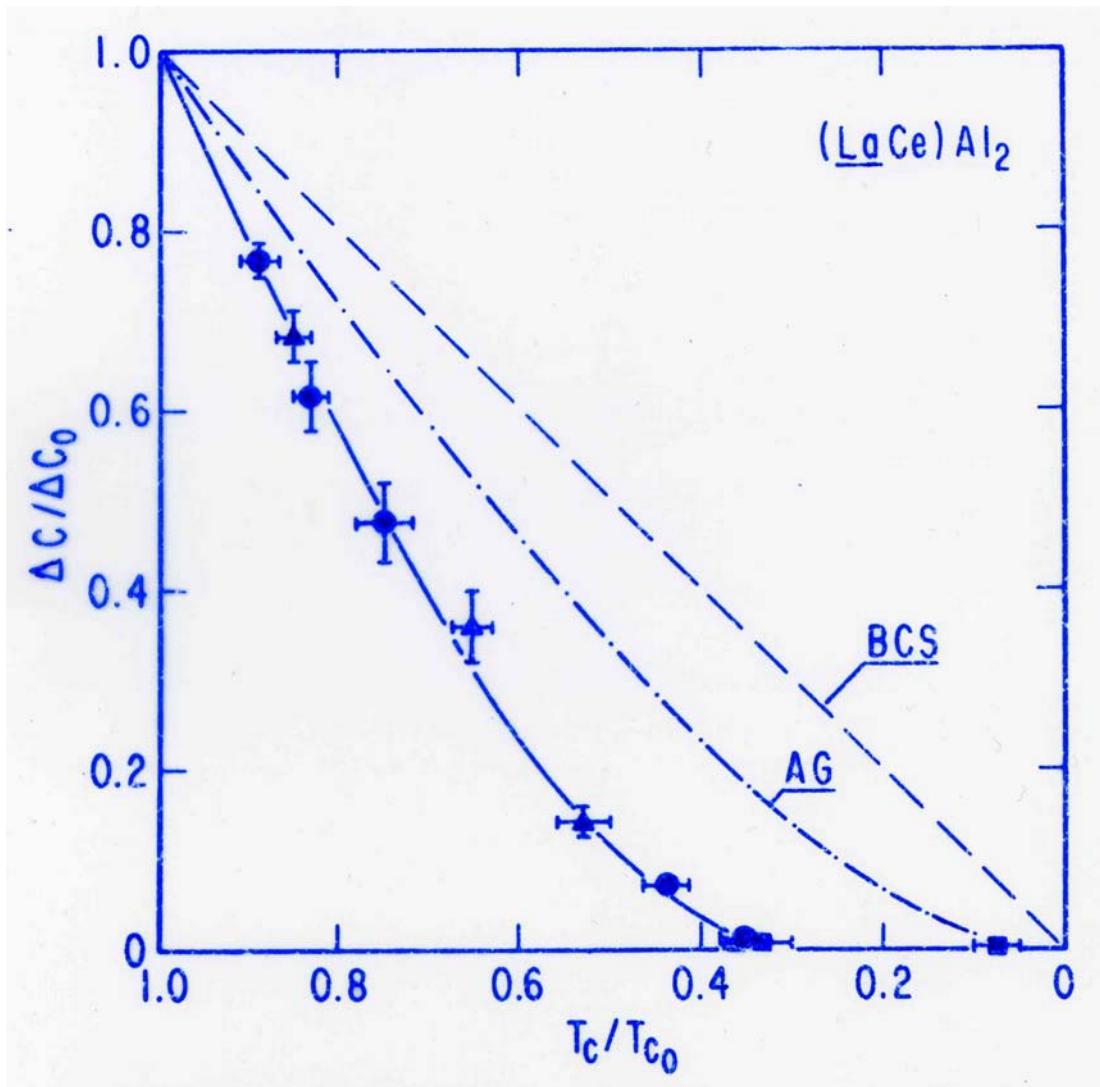


- Kondo effect:  $T_K \ll T_{co}$   
“reentrant SC”
- Riblet, Winzer (71) (U. Köln)
- Maple, Fertig, Mota, DeLong, Wohlleben, Fitzgerald (72) (UCSD)



Maple (68)

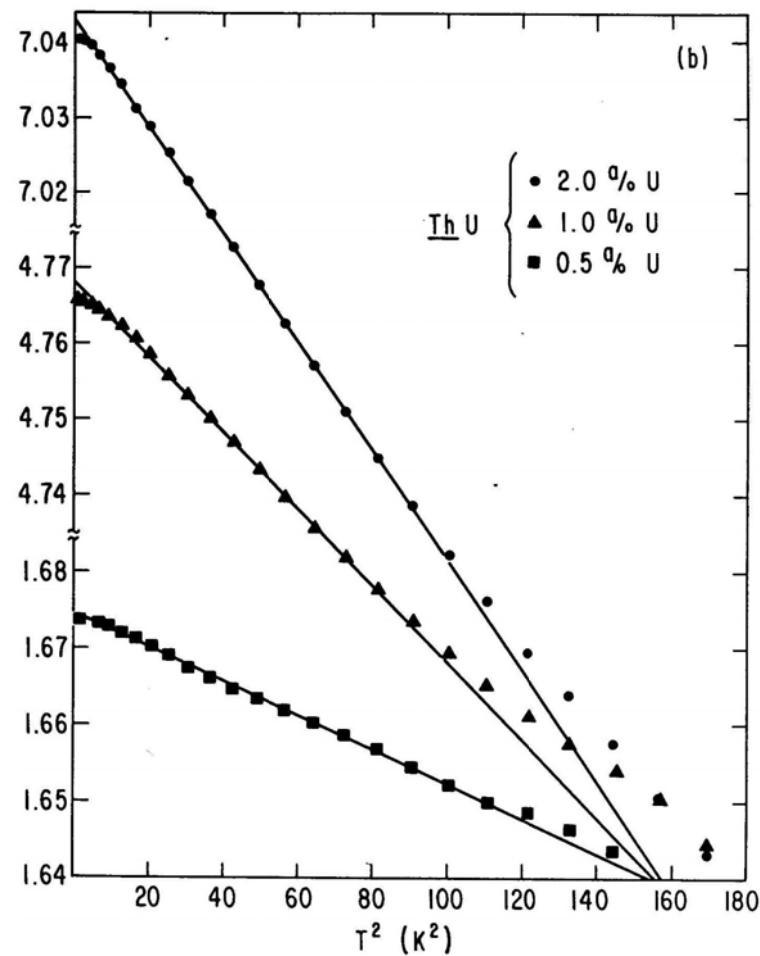
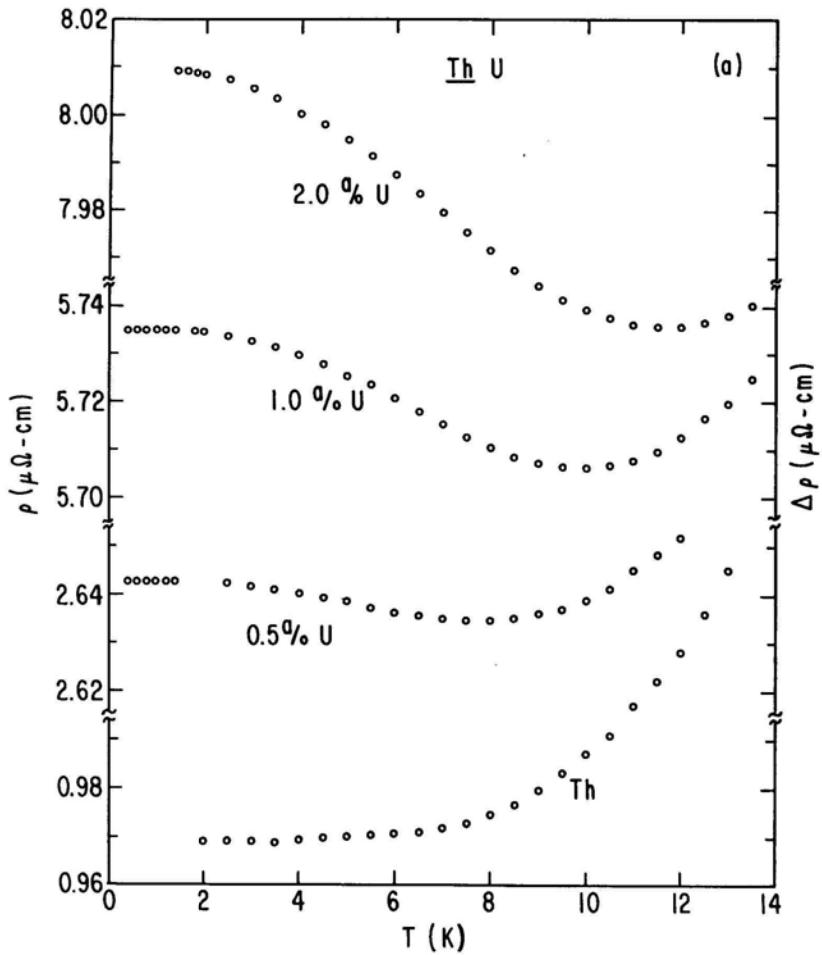
# Kondo effect in $\text{La}_{1-x}\text{Ce}_x\text{Al}_2$ : specific heat jump vs $T_c$



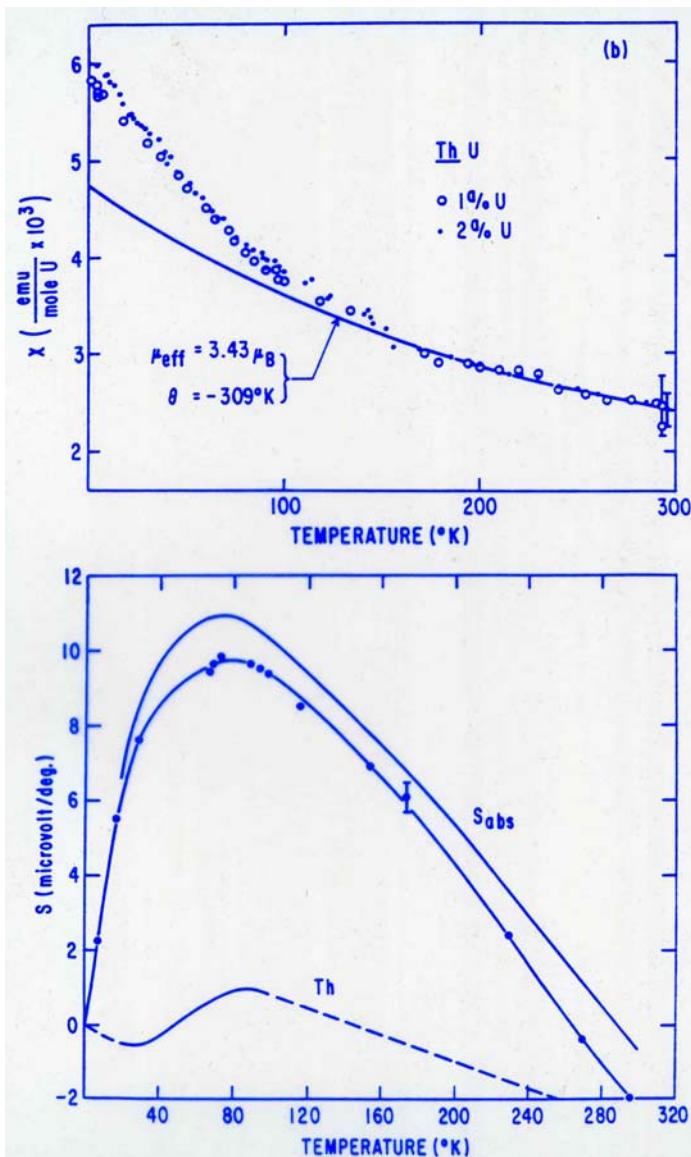
- C. A. Luengo, M. B. Maple, W. A. Fertig (72)
- H. Armbrüster, F. Steglich (73)
- S. D. Bader, N. E. Phillips, M. B. Maple, C. A. Luengo (73)

# Kondo effect in $\text{Th}_{1-x}\text{U}_x$ : electrical resistivity

- $\text{Th}_{1-x}\text{U}_x$ : conventional Kondo effect (Fermi liquid - low T)
  - $\Delta\gamma \approx 270 \text{ mJ/mol U-K}^2$
  - $\Delta\rho(T) = \rho_0[1-(T/T_K)^2]$ ;  $T_K \approx 100 \text{ K}$



# Kondo effect in $\text{Th}_{1-x}\text{U}_x$ : magnetic susceptibility and thermopower



$\text{Th}_{1-x}\text{U}_x$ :

- $\chi(T) = C/(T-\theta)$

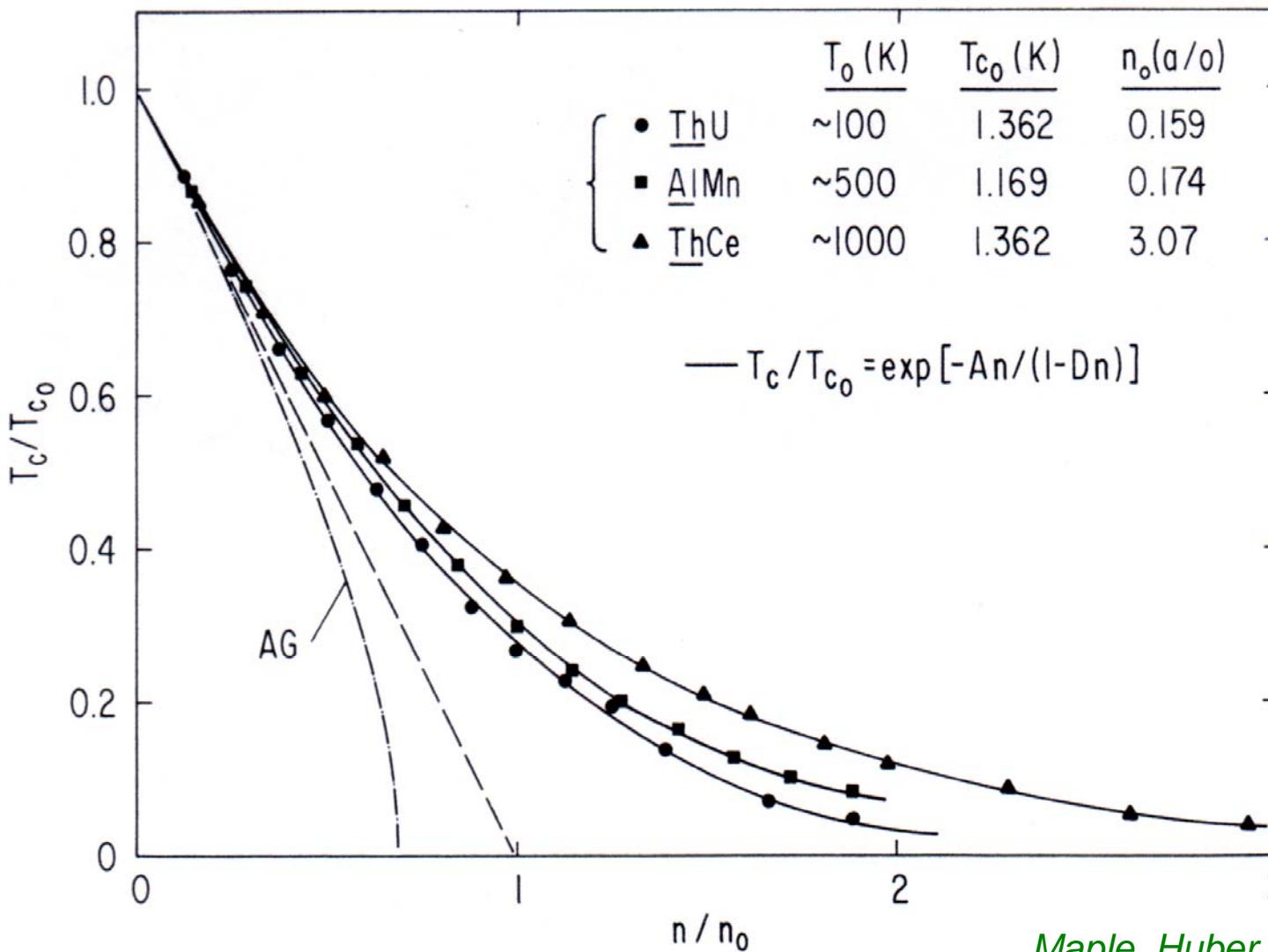
- $\theta \approx -3 T_K$

- $C = N\mu_{\text{eff}}^2/3k_B$

- Peak in thermoelectric power  
 $\Rightarrow T_K \approx 100 \text{ K}$

# Kondo effect in $\text{Th}_{1-x}\text{U}_x$ : exponential $T_c$ vs $x$ curve

Comparison of  $T_c$  vs  $x$  curves of  $\text{Th}_{1-x}\text{U}_x$ ,  $\text{Al}_{1-x}\text{Mn}_x$ ,  $\text{Th}_{1-x}\text{Ce}_x$

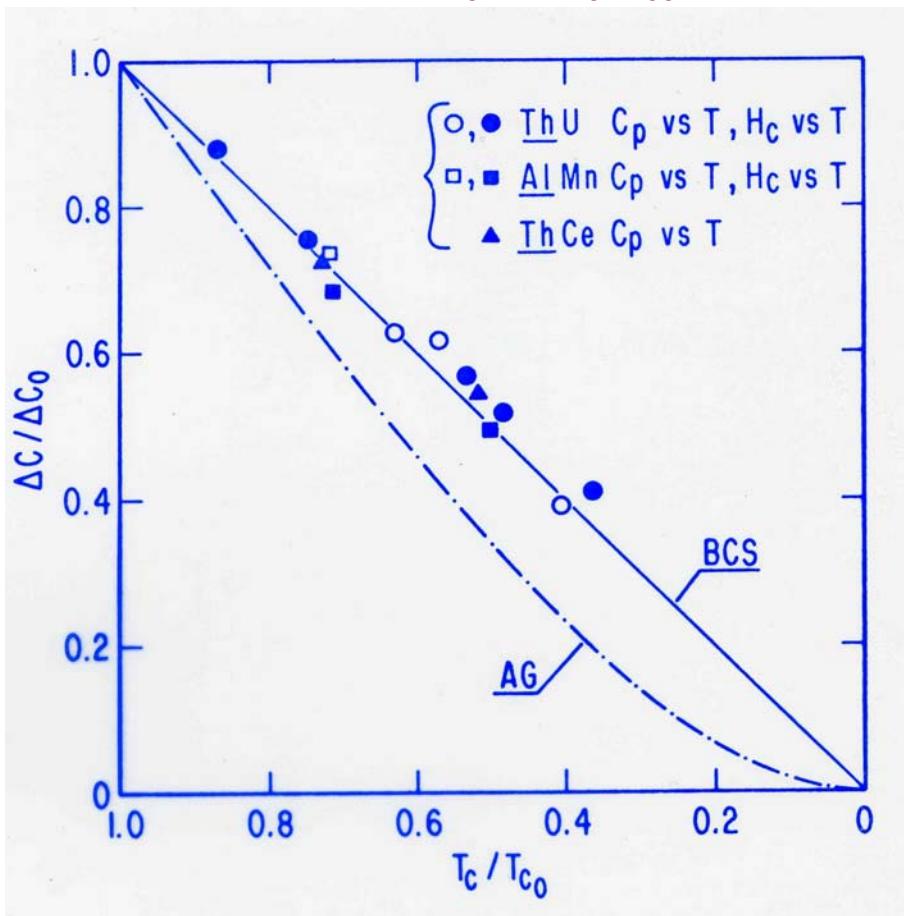


Kondo effect:  
 $T_K \gg T_{co}$

Maple, Huber, Coles, Lawson (70);  
Huber, Maple (70)

# Kondo effect in $\text{Th}_{1-x}\text{U}_x$ : specific heat jump vs $T_c$

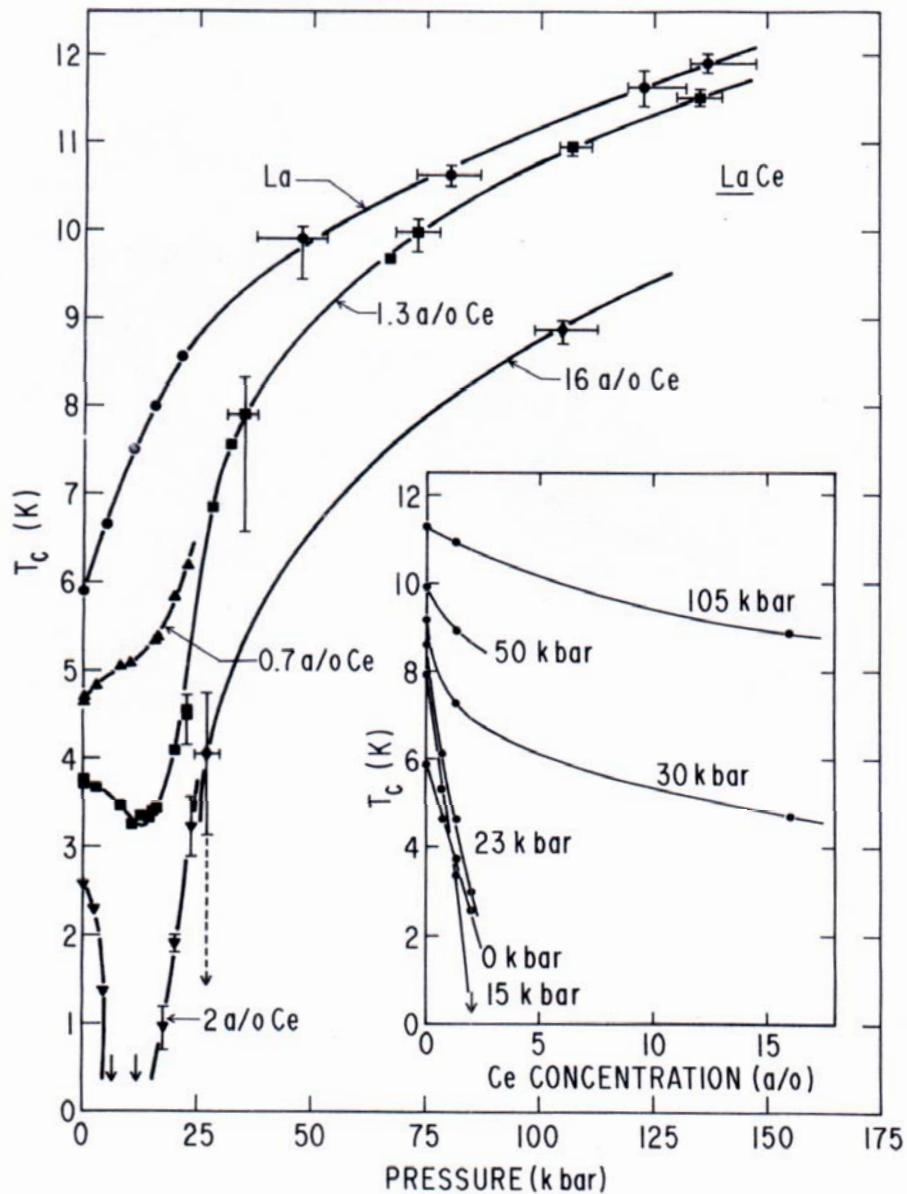
Comparison of  $\Delta C/\Delta C_0$  vs  $T_c/T_{\text{co}}$  curves of  $\text{Th}_{1-x}\text{U}_x$ ,  $\text{Al}_{1-x}\text{Mn}_x$ ,  $\text{Th}_{1-x}\text{Ce}_x$



$T_c \ll T_K$ : Conforms to  
BCS law of corresponding  
states  $\Delta C/\Delta C_0 = T_c/T_{\text{co}}$

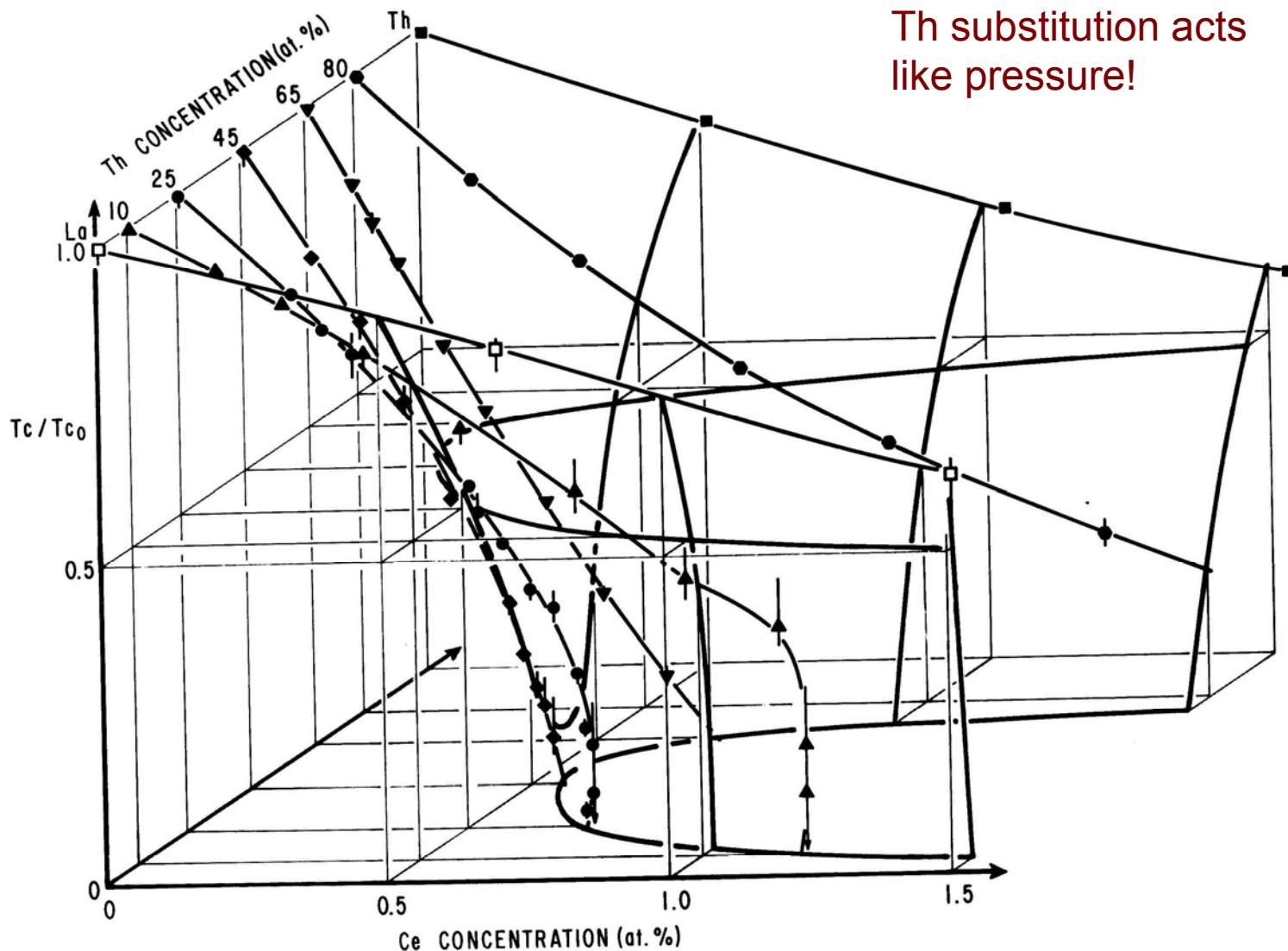
- ( $\circ$ ) C. A. Luengo, J. M. Cotignola, J. Sereni, A. R. Sweedler, M. B. Maple, J. G. Huber (72)
- ( $\bullet$ ) H. L. Watson, D. T. Peterson, D. K. Finnemore (73)
- ( $\square$ ) D. L. Martin (61)
- ( $\blacksquare$ ) F. W. Smith (72)
- ( $\blacktriangle$ ) C. W. Dempsey (70)

# Pressure-induced demagnetization of Ce impurities in La



- $|J|$  &  $T_K$  increase with P  
⇒  $T_K/T_{co}$  increases with P from << 1 to >> 1 through  $T_K/T_{co} \approx 1$  at  $\sim 15$  kbar  
⇒ maximum in  $\Delta T_c$  at  $\sim 15$  kbar
- Analogue of Ce  $\gamma-\alpha$  transition
- *Maple, Wittig, Kim (69)*

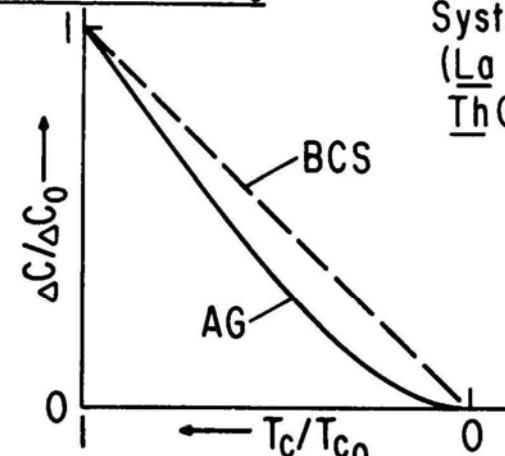
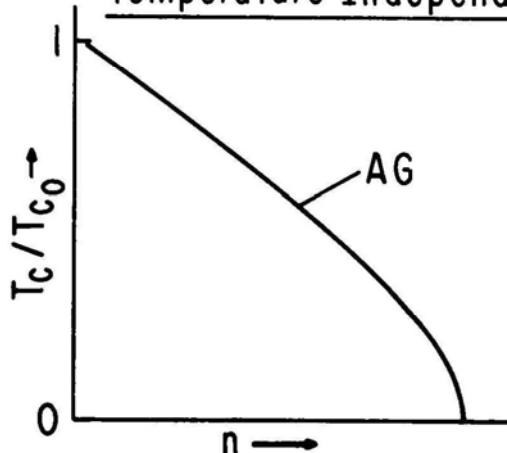
# *Demagnetization of Ce impurities in $(La_{1-y}Th_y)_{1-x}Ce_x$*



# Paramagnetic impurities in superconductors: summary

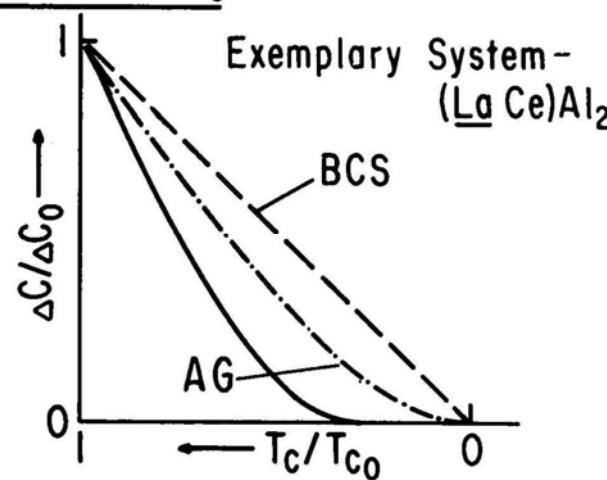
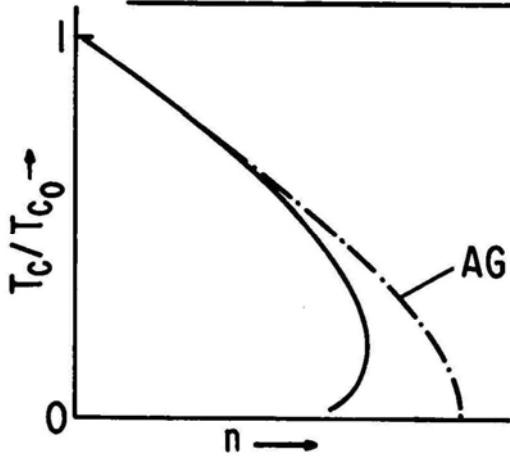
## I. Long-Lived Local Moments

### A. Weak Itinerant-Local Electron Mixing - $J > 0$ ; Temperature Independent Pair Breaking



Exemplary  
Systems -  
 $(\underline{L}a \underline{G}d)Al_2$   
 $\underline{T}h \underline{G}d$

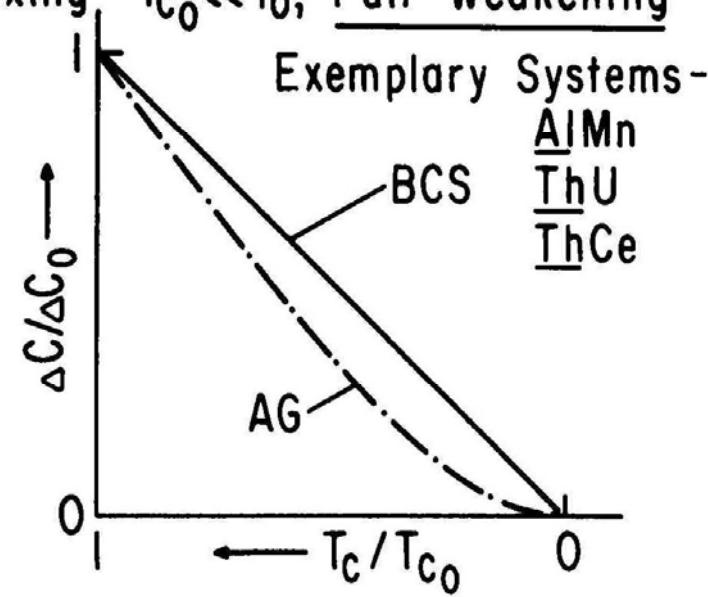
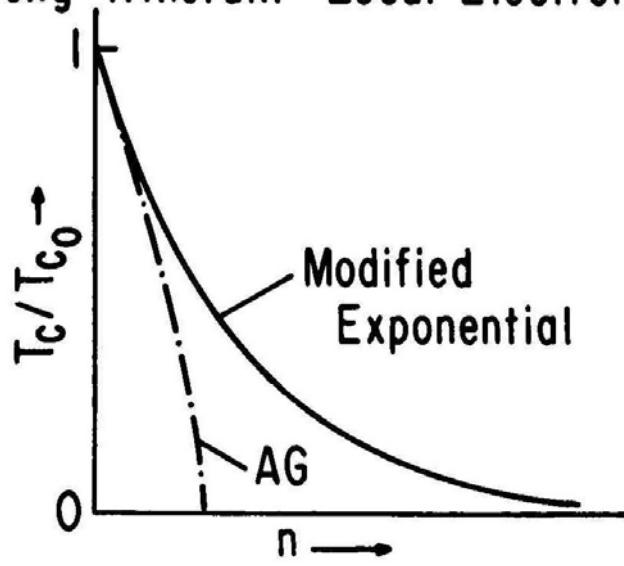
### B. Moderate Itinerant-Local Electron Mixing - $J < 0$ and $T_{c0} \gg T_K$ ; Temperature Dependent Pair Breaking



Exemplary System -  
 $(\underline{L}a \underline{C}e)Al_2$

## II. Short-Lived Local Moments

Strong Itinerant-Local Electron Mixing -  $T_{C0} \ll T_0$ ; Pair Weakening



*Magnetic field induced superconductivity (MFIS)*

# Origin of the upper critical field $H_{c2}$

(1) ORBITAL CRITICAL FIELD  $H_{c2}^*$

$$H_{c2}^* = \frac{\Phi_0}{2\pi} \frac{e}{\hbar c}^2 \quad \Phi_0 = hc/e$$

$$(1) \frac{e}{mc} (\vec{p} \cdot \vec{A}) = \frac{e\hbar}{mc} (\vec{k} \cdot \vec{A}) \longrightarrow H_{c2}^*$$

$$(2) -\vec{\mu} \cdot \vec{H} = -g\mu_B (\vec{s} \cdot \vec{H}) \longrightarrow H_p$$

(2) PARAMAGNETIC LIMITING FIELD  $H_p$

normal state

$$F_n(H) = F_n(0) - \frac{1}{2} \chi_n H^2$$

superconducting state

$$F_s(H) = F_s(0) - \frac{1}{2} \chi_s H^2$$

first order transition from superconducting  
to normal state when

$$F_n(H_p) - F_s(H_p) = 0$$

$$= [F_n(0) - F_s(0)] - \frac{1}{2} (\chi_n - \chi_s) H_p^2$$

$$= \frac{1}{2} N(0) \Delta^2 - \frac{1}{2} (\chi_n - \chi_s) H_p^2$$

## Origin of the upper critical field $H_{c2}$

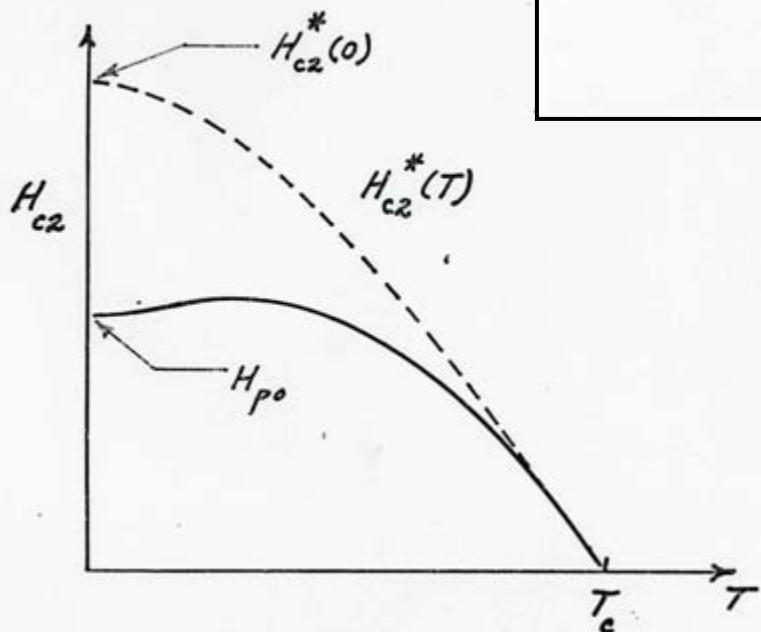
$$\Rightarrow H_p = \left[ \frac{N(0)}{\chi_n - \chi_s} \right]^{1/2} \Delta$$

BCS superconductor at  $T=0$   $\begin{cases} \chi_s = 0 \\ \chi_n = \frac{1}{2} N(0) g^2 \mu_B^2 \end{cases}$

$$H_{po} = \frac{\sqrt{2} \Delta(0)}{g \mu_B} = 18.4 T_c \text{ (kOe)}$$

Clogston-Chandrasekhar limit (1962)

$H_{c2}$  vs  $T$



- To increase  $H_{c2}$  above  $H_p$
- Increase spin-orbit scattering  
⇒ increase  $\chi_s$
  - Compensate applied field with exchange field ⇒ MFIS

# Magnetic field induced superconductivity

## SCHEME FOR RAISING PARAMAGNETICALLY LIMITED $H_{c2}$

Consider  $(Eu_{1-x}M_x)Mo_6S_8$  where  $M = Sn, Pb, La, Ho, Yb$

$H_{c2}$  determined by two interactions which "break" superconducting electron pairs ( $\vec{k}\uparrow, \vec{k}\downarrow$ ):

(1)  $\vec{p} \cdot \vec{A} = \hbar(\vec{k} \cdot \vec{A}) \rightarrow$  orbital critical field  $H_{c2}^*$

(2)  $-\mu \cdot \vec{H} = -2\mu_B(\vec{s} \cdot \vec{H}) \rightarrow$  paramagnetic limiting field  $H_p$

Assume  $H_{c2} \sim H_p < H_{c2}^*$

$Eu^{2+} \Rightarrow J = S = 7/2 \Rightarrow \mu = 7\mu_B$

$\mathcal{H}_{ex} = -2J \sum_s \vec{s}_s \cdot \vec{s}_s = -\mu \cdot \vec{H}_{ex}^I$  where  $\mu = 2\mu_B \sum_s \vec{s}_s$ ,  $\vec{H}_{ex}^I = (J/\mu_B) \sum_s \vec{s}_s$

$\vec{H}_T = \vec{H} + \vec{H}_{ex}$  where  $\vec{H}_{ex} = n \vec{H}_{ex}^I$

$J < 0 \Rightarrow H_T = H - |\vec{H}_{ex}| < H$

$H_{ex} \approx \langle S_z \rangle = SB_{7/2}(7\mu_B H/k_B T)$  (Brillouin function)

## *Magnetic field induced superconductivity*

SC for  $|H_T| = |H - H_{ex}| \leq H_p$  or  $|H_{ex}| - H_p \leq H \leq H_{ex} + H_p$

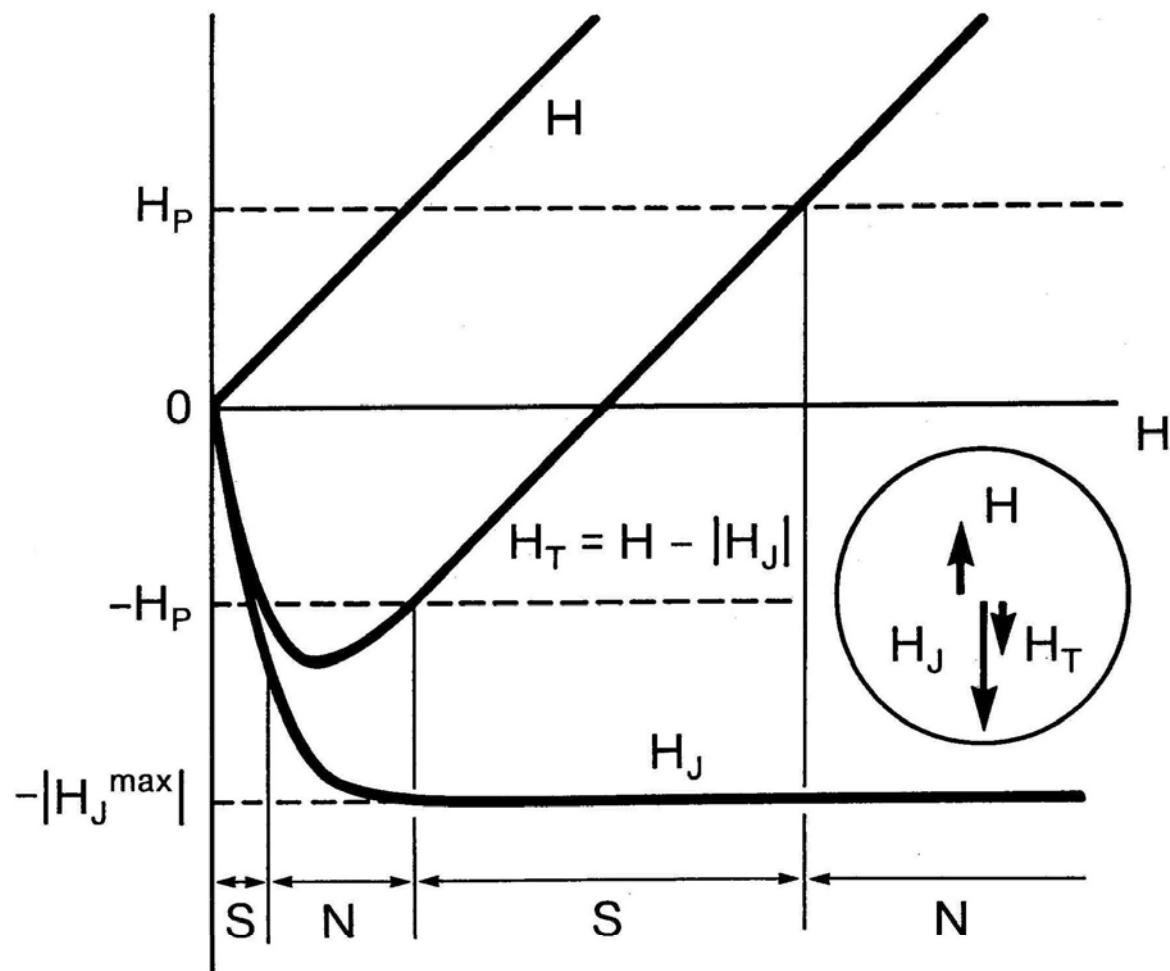
- ⇒ (1) Enhancement of  $H_{c2}$ ;
- (2) Magnetic field induced SC!

FM with  $\beta < 0$  in  $H \rightarrow$  SC! (Jaccarino & Peter, '62)

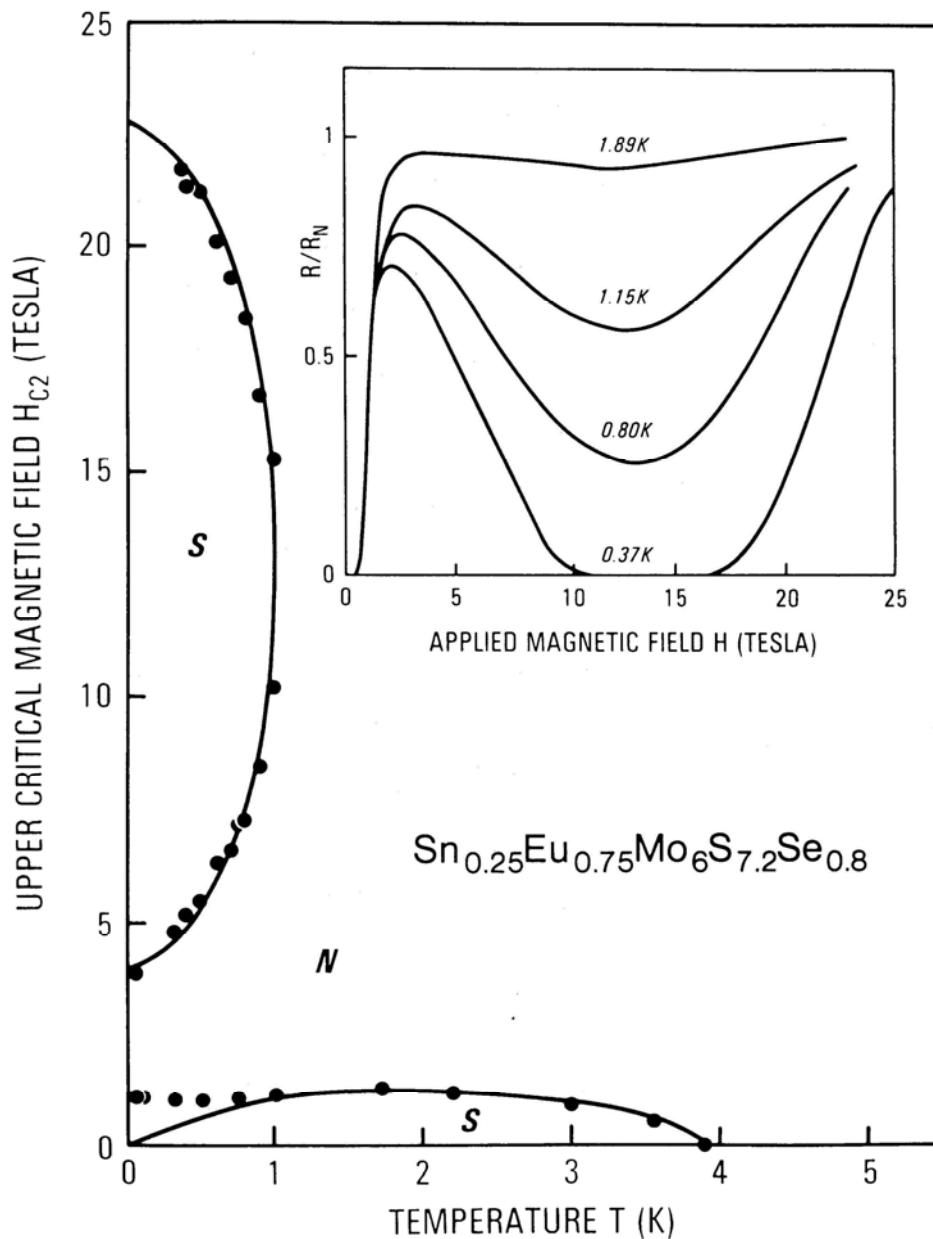
Not yet been observed!

## Magnetic field induced superconductivity

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# Magnetic field induced superconductivity



φ. Fisher et al. (83)

## Magnetic ordering via RKKY interaction

$$\begin{aligned}
 \mathcal{H}_{int} &= -2g(g_J-1) \vec{J} \cdot \vec{s} \delta(\vec{r}) \\
 &= -[2(g_J-1)g/\mu_B] \vec{J} \delta(\vec{r}) \cdot (g\mu_B \vec{s}) \\
 &= \vec{H}_{eff}(\vec{r}) \cdot \vec{s}
 \end{aligned}$$

$$\vec{H}_{eff}(\vec{r}) = [2(g_J-1)g/\mu_B] \vec{J} \delta(\vec{r})$$

$$\vec{H}_{eff}(\vec{q}) = [2(g_J-1)g/\mu_B] \vec{J}$$

$$s(\vec{r}) = \vec{s}(\vec{r})/g\mu_B = \frac{1}{g\mu_B V} \sum_{\vec{q}} \chi(\vec{q}) H_{eff}(\vec{q}) e^{i\vec{q} \cdot \vec{r}}$$

$$= [2(g_J-1)g^2 \mu_B^2 V] \sum_{\vec{q}} \chi(\vec{q}) e^{i\vec{q} \cdot \vec{r}} \vec{J}$$

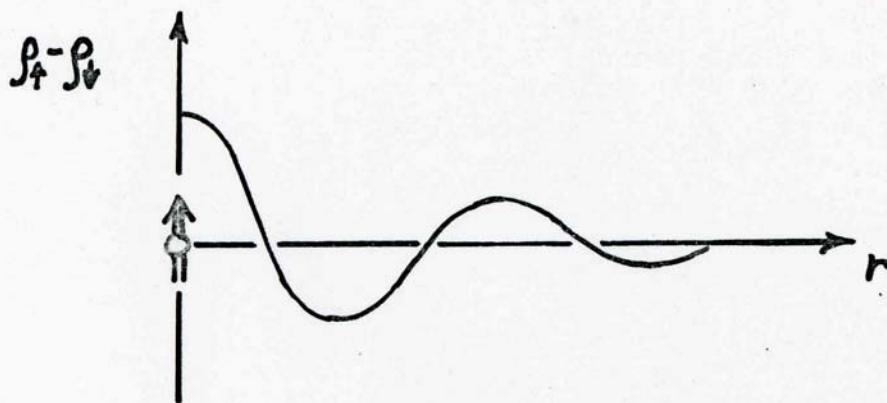
$$\chi(\vec{q}) = \chi_p F\left(\frac{\vec{q}}{2k_F}\right)$$

$$= \chi_p \left[ \frac{1}{2} + \frac{k_F}{2q} \left( 1 - \frac{q^2}{4k_F^2} \right) \log \left| \frac{2k_F+q}{2k_F-q} \right| \right]$$

$$\text{where } \chi_p = 2N(0)\mu_B^2$$

$$s(\vec{r}) \sim \left\{ \frac{\sin(2k_F r) - 2k_F r \cos(2k_F r)}{(2k_F r)^2} \right\} \sim \frac{\cos(2k_F r)}{(2k_F r)^3}; k_F r \gg 1$$

## Magnetic ordering via RKKY interaction



Leads to ferromagnetic, antiferromagnetic, or complicated magnetic structures -

$$H_{RKKY} = - \frac{4(g_J-1)^2 g^2}{g^2 \mu_B^2 V} \sum_q \chi(q) e^{i \vec{q} \cdot \vec{r}} \frac{\hat{J}_i \cdot \hat{J}_j}{\tilde{z}_i \tilde{z}_j}$$

ELECTRON BAND STRUCTURE  
SUPERCONDUCTIVITY

*Magnetically ordered superconductors*

## *Magnetically ordered superconductors*

- Superconducting ternary R Compounds (ordered R sublattice)
    - $\text{RMo}_6\text{S}_8$  *Fischer, Treyvaud, Chevrel, Sergent (75)*
    - $\text{RMo}_6\text{Se}_8$  *Shelton, McCallum, Adrian (76)*
    - $\text{RRh}_4\text{B}_4$  *Matthias, Corenzwit, Vandenberg, Barz (77)*

- Antiferromagnetic superconductors

## Coexistence of SC & AFM

- $\text{RMo}_6\text{Se}_8$       R= Gd,Tb,Er      *UCSD (77)*
  - $\text{RMo}_6\text{S}_8$       R= Gd,Tb,Dy,Er      *U. Geneva (77)*
  - $\text{RRh}_4\text{B}_4$       R= Nd,Sm,Tm      *UCSD (79)*
  - $\text{RNi}_2\text{B}_2\text{C}$                                       *Nagarajan et al. (94); Cava et al. (94)*
  - $\text{RNi}_2\text{B}_2\text{C}$       (single crystals)      *Canfield et al. (94)*

- Ferromagnetic superconductors

Destruction of SC by onset of FM at  $T_{c2} \sim \theta_C < T_{c1}$

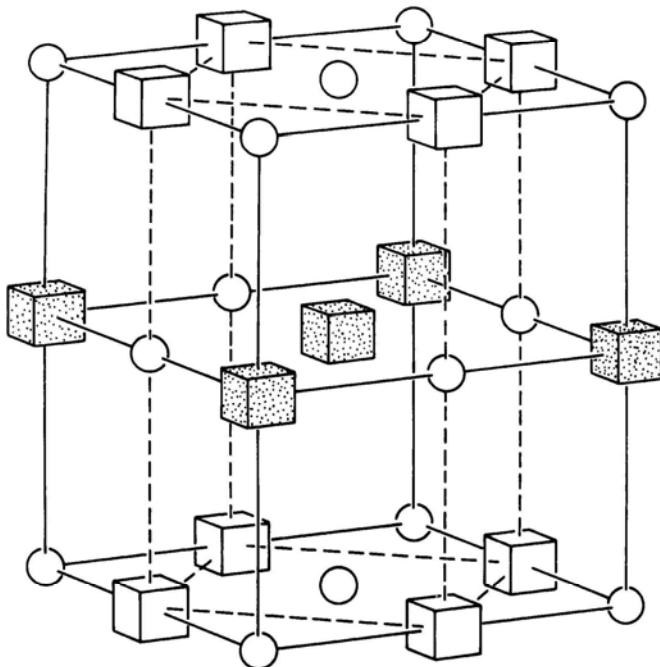
SC-FM interactions – sinusoidally-modulated magnetic state ( $\lambda \sim 100$  Å)

that coexists with SC near  $T_{c2}$

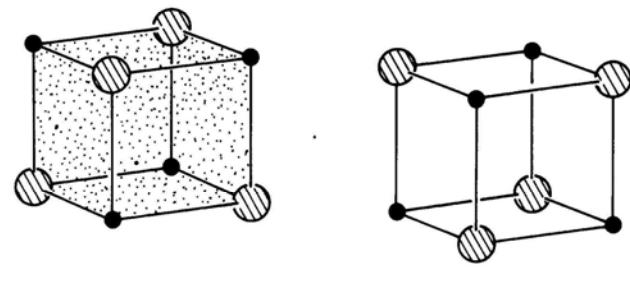
- $\text{ErRh}_4\text{B}_4$  *UCSD (77)*
  - $\text{HoMo}_6\text{S}_8$  *U. Geneva (77)*
  - $\text{ErRh}_{1.1}\text{Sn}_{3.6}$  *AT&T, UCSD, BNL (80)*

# $RRh_4B_4$ crystal structure

Magnetic Superconductor  
 $RRh_4B_4$



Two weakly interacting subsystems:  
RhB “molecular units” or clusters  $\rightarrow$  SC  
R magnetic moments  $\rightarrow$  magnetic order  
Comparable values of  $T_c$  and  $T_M$

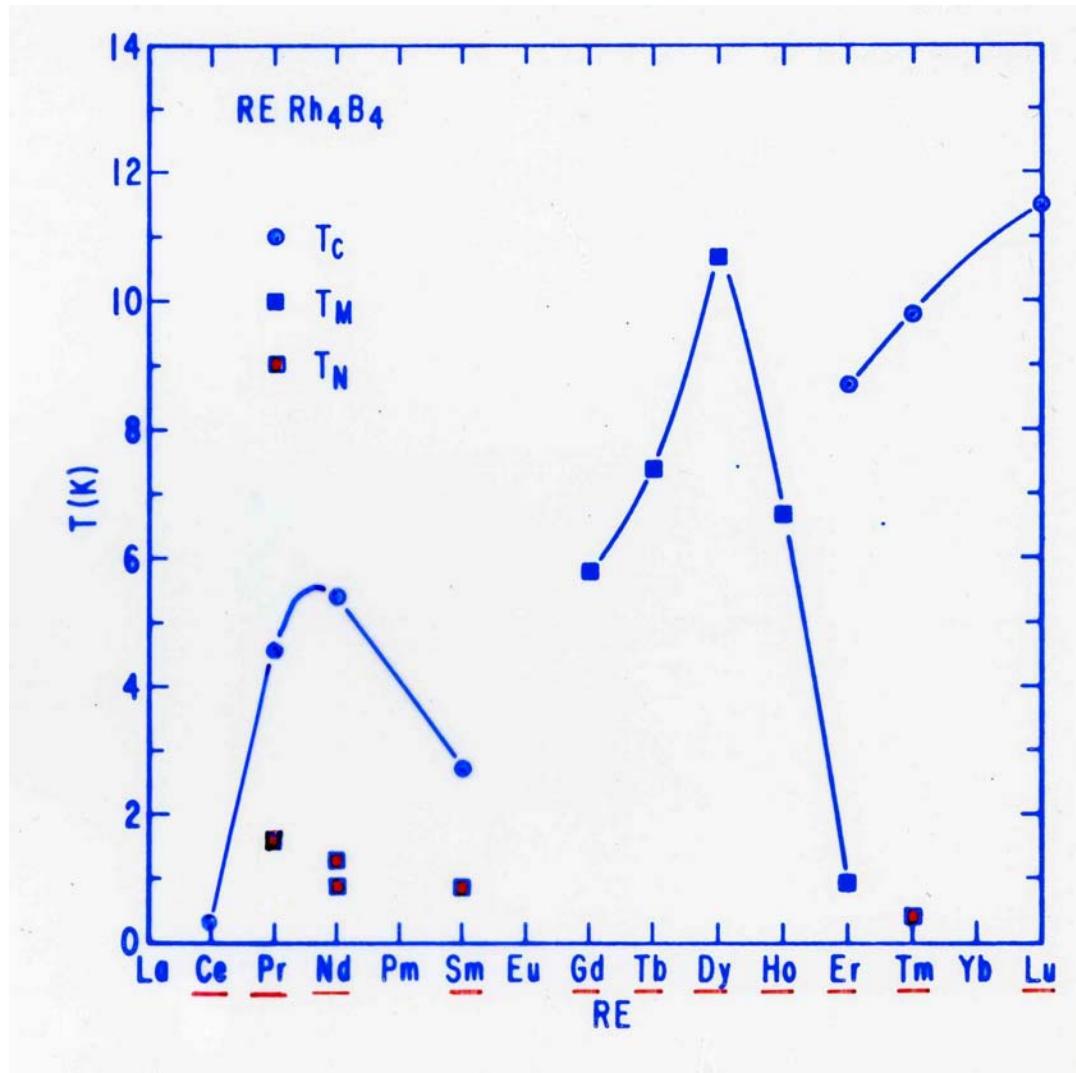


○ R

◎ Rh

● B

# Superconducting and magnetic ordering temperatures of $RRh_4B_4$ compounds

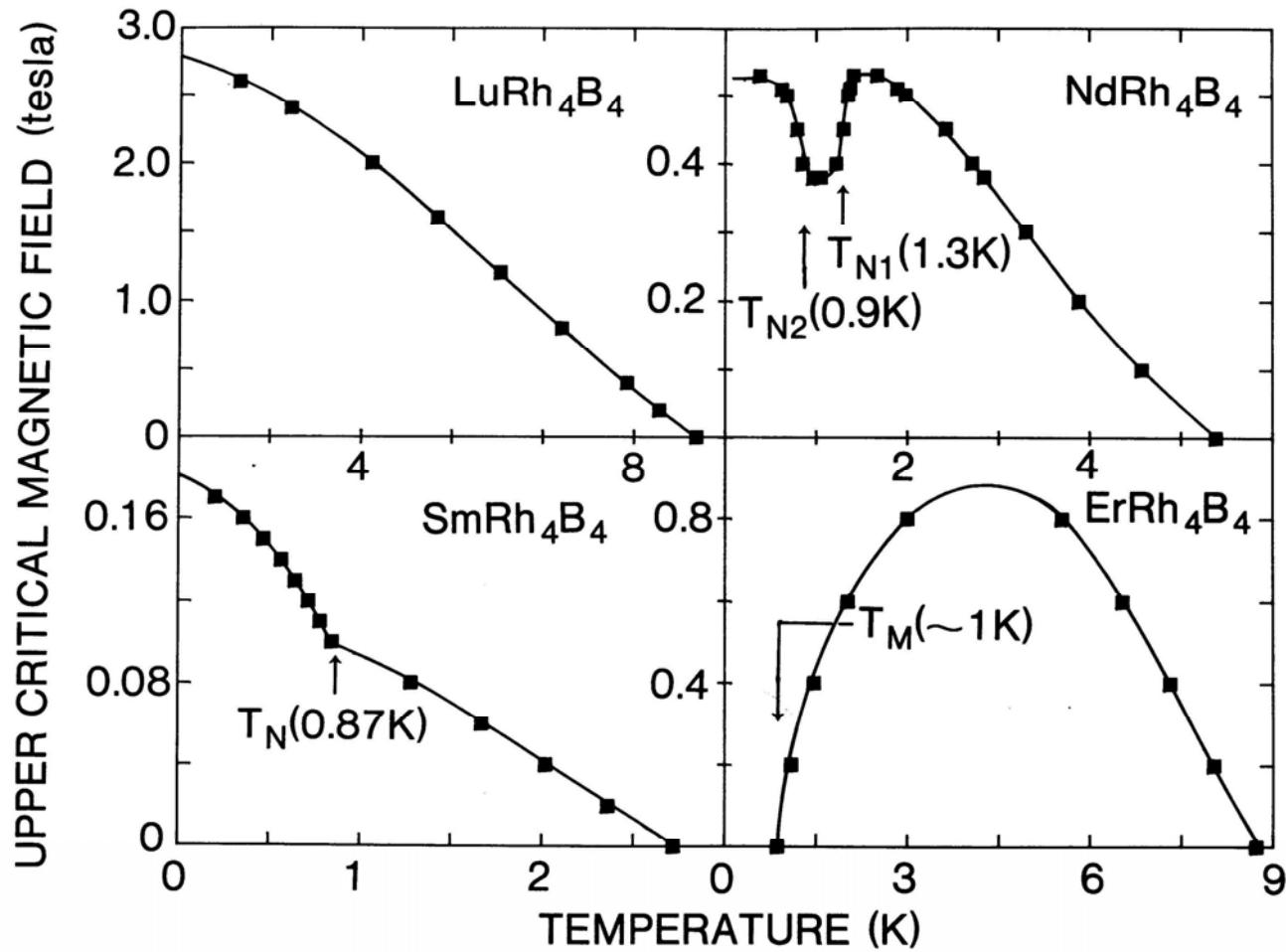


After M. B. Maple, H. C. Hamaker, L. D. Woolf (82)

B. T. Matthias, E. Corenzwit, J. M. Vandenberg, H. Barz (77)

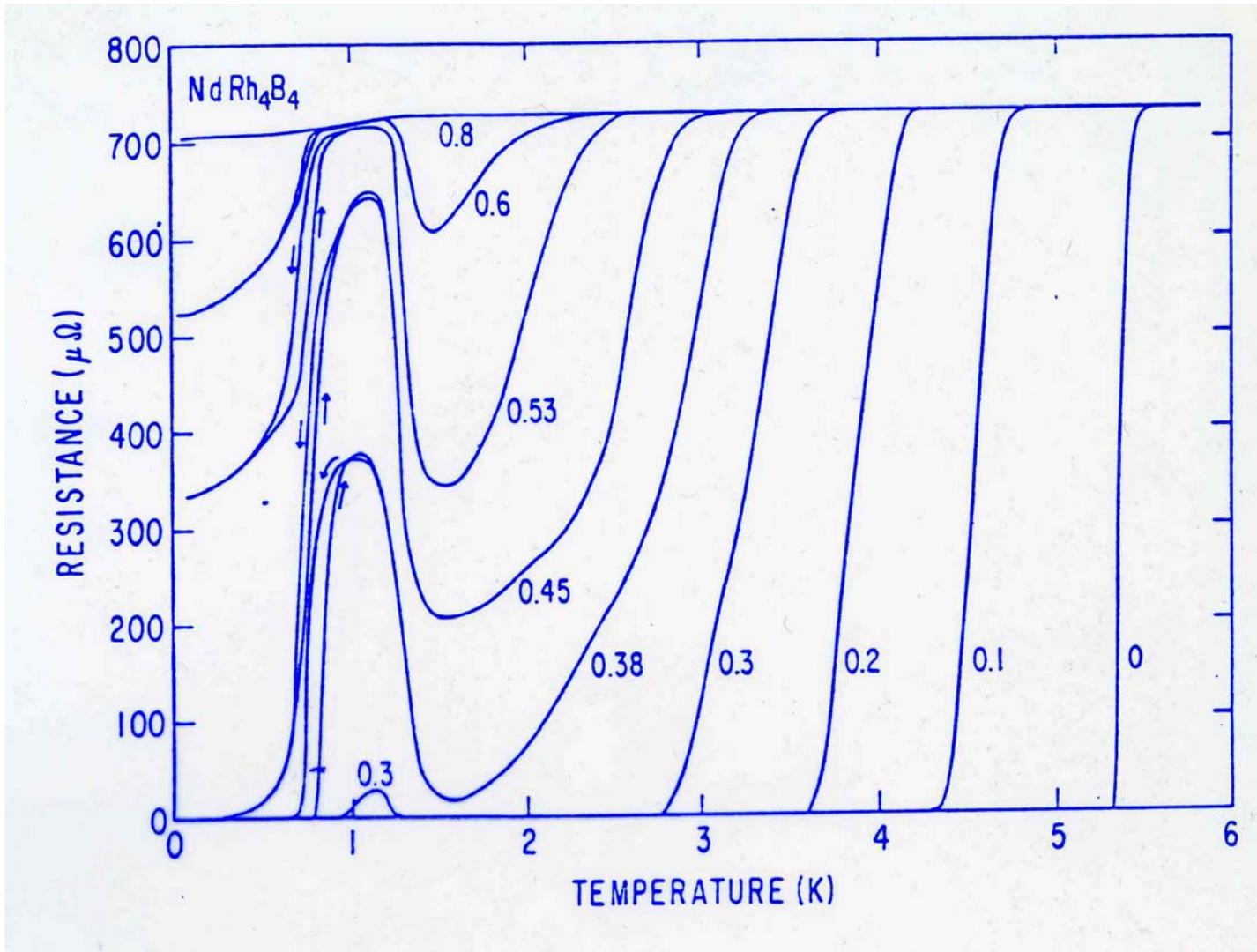
\* Ce, Pr – T. Ooyama, K. Kumagai, J. Nakajima, M. Shimotomai (87)

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



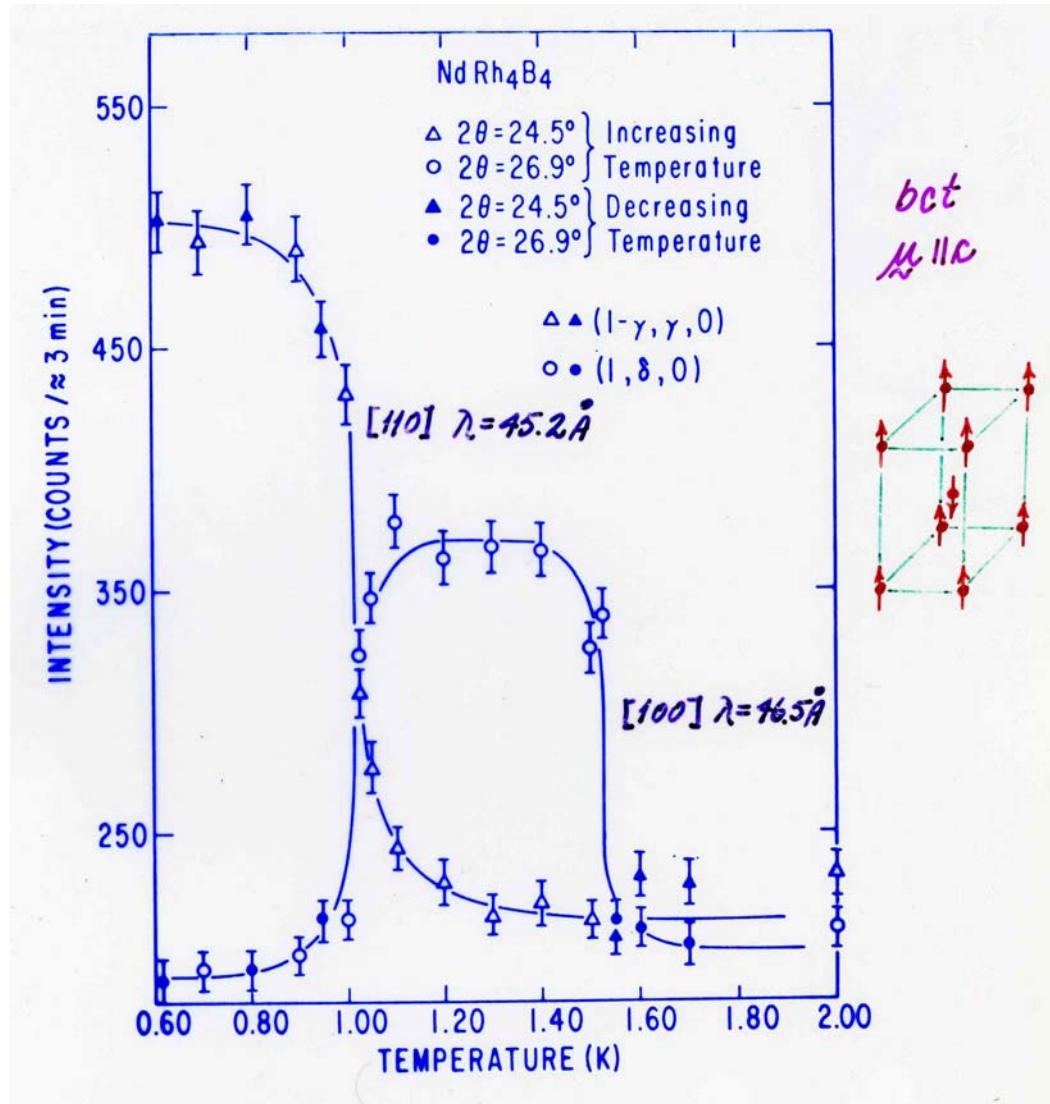
- Nonmagnetic SC:  $LuRh_4B_4$
- AFM-SCs:  $NdRh_4B_4$ ,  $SmRh_4B_4$
- FM-SC:  $ErRh_4B_4$

# Magnetic superconductor $NdRh_4B_4$ : resistive transition curves



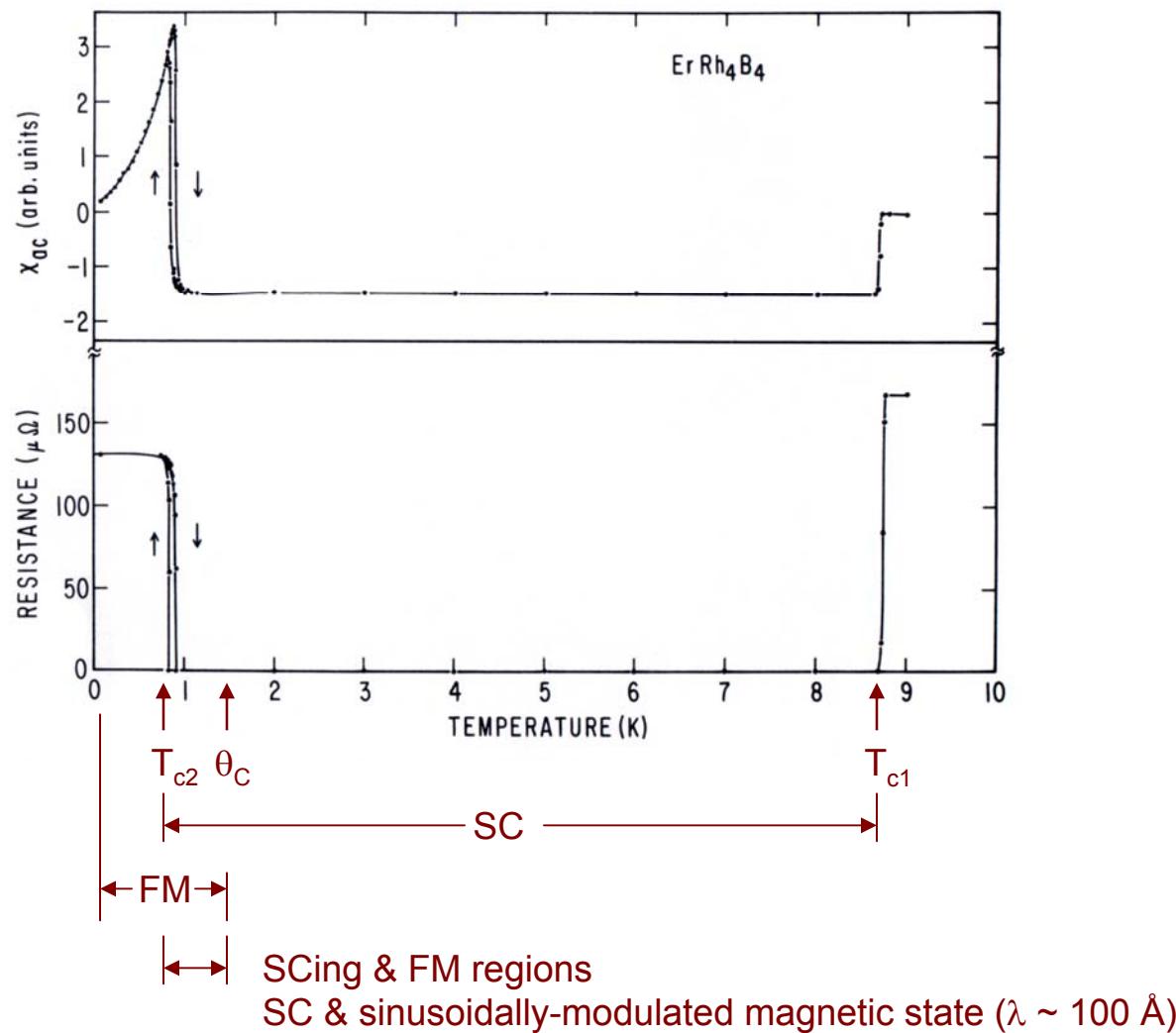
H. C. Hamaker, L. D. Woolf, H. B. MacKay, Z. Fisk, M. B. Maple (79)

# Magnetic superconductor $\text{NdRh}_4\text{B}_4$ : neutron scattering



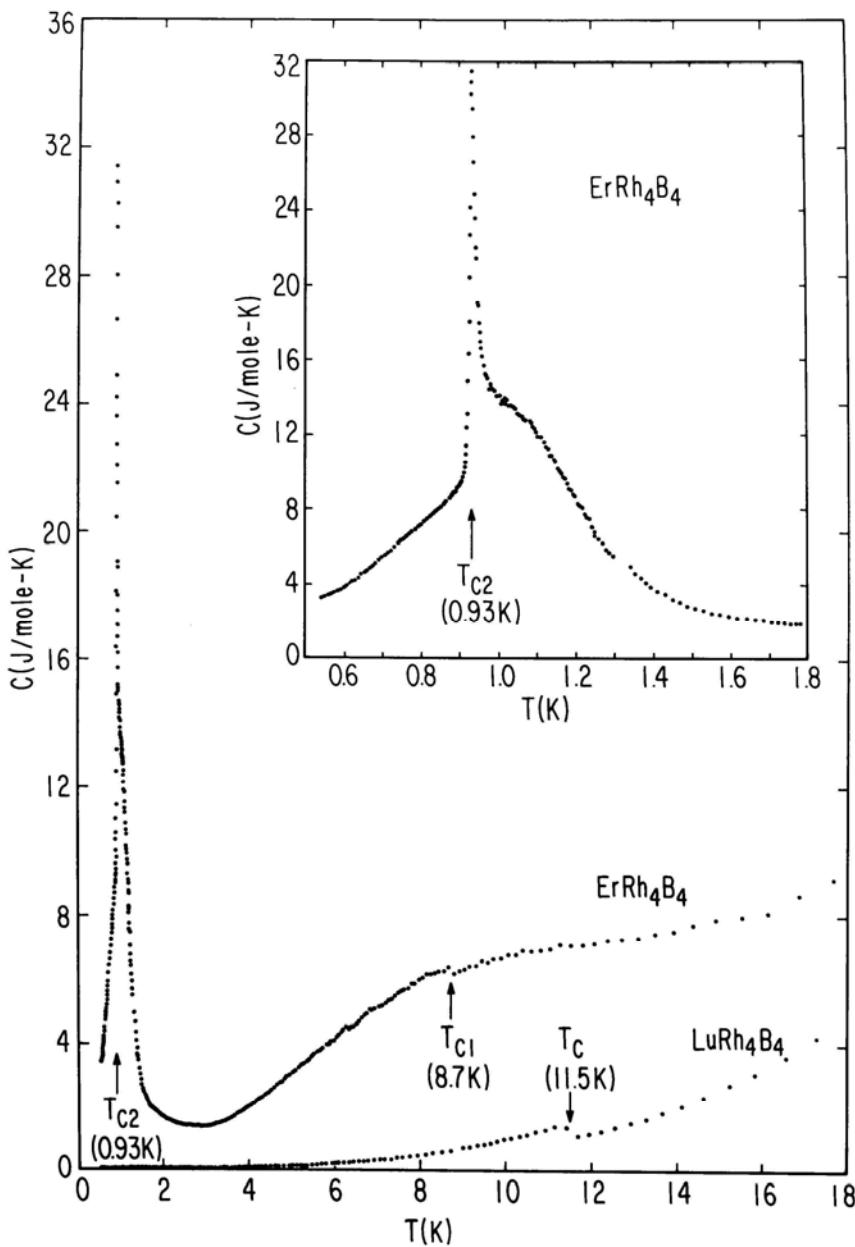
C. F. Majkrzak, D. E. Cox, G. Shirane, H. A. Mook,  
H. C. Hamaker, H. B. MacKay, Z. Fisk, M. B. Maple (82)

## Reentrant SC due to FM order: $ErRh_4B_4$



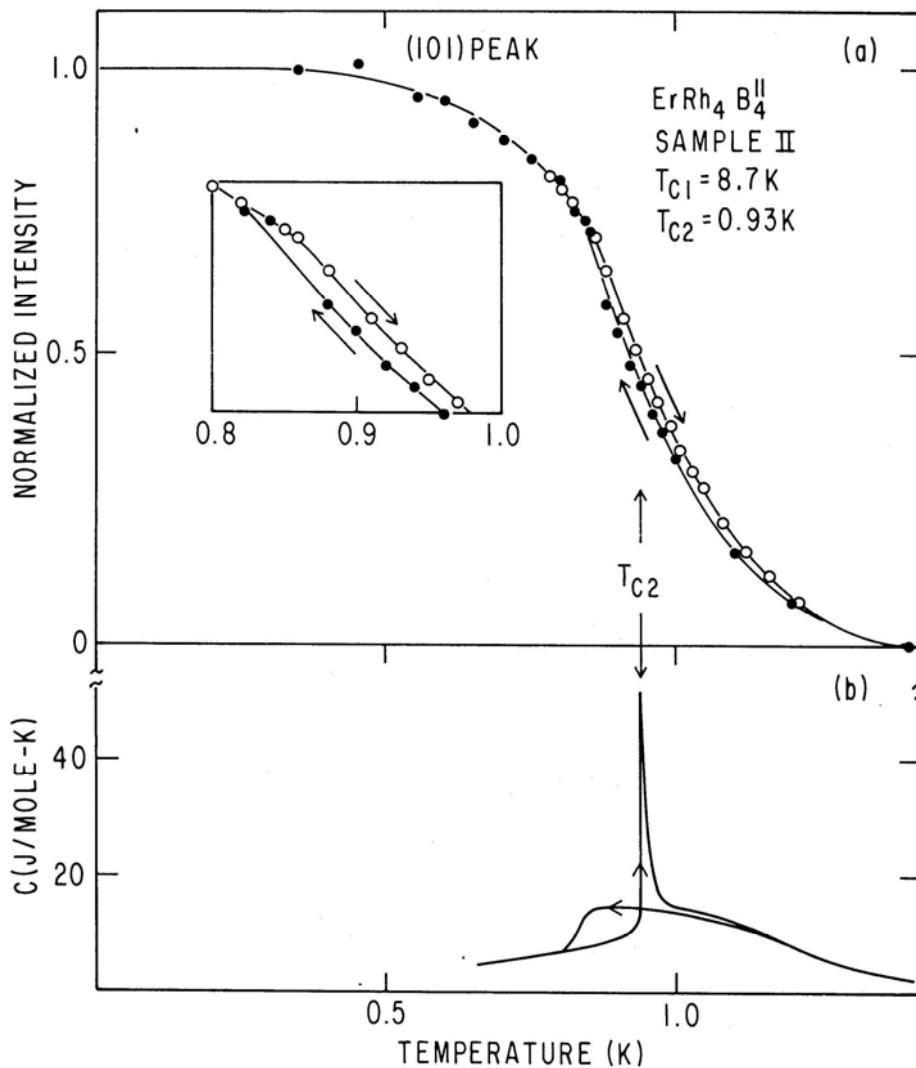
- Fertig, Johnston, DeLong, McCallum, Maple, Matthias (77)
- Moncton, McWhan, Schmidt, Shirane, Thomlinson, Maple, MacKay, Woolf, Fisk, Johnston (80) (neutron scattering)

# Reentrant FM SC $\text{ErRh}_4\text{B}_4$ : specific heat



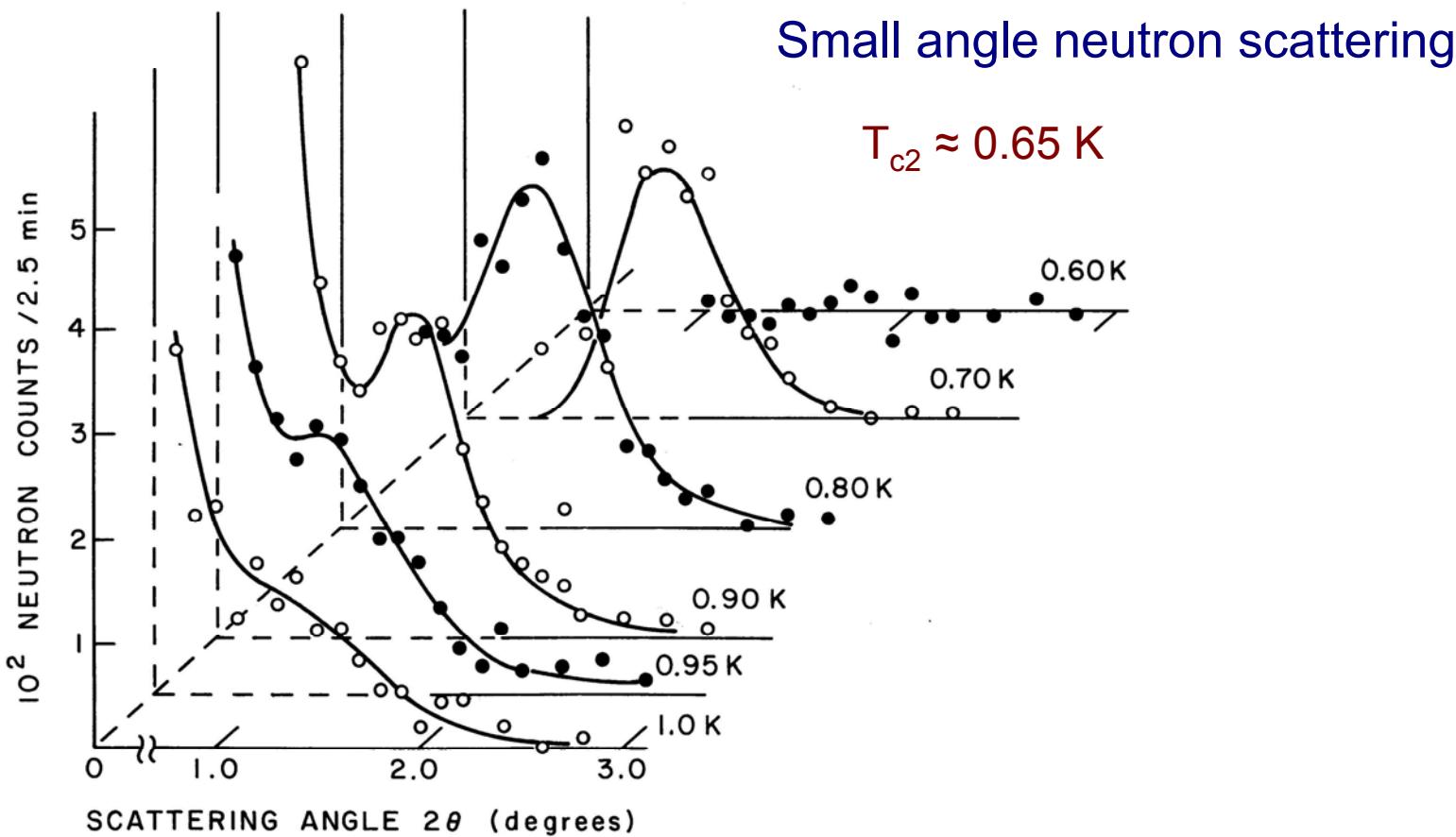
*L. D. Woolf, D. C. Johnston,  
H. B. MacKay, R. W. McCallum,  
M. B. Maple (79)*

# Macroscopic coexistence of SC & normal FM domains



Moncton, McWhan, Schmidt, Shirane, Thomlinson,  
Maple, MacKay, Woolf, Fisk, Johnston (80)

Microscopic coexistence of SC & sinusoidally-modulated magnetic state with  $\lambda \sim 100 \text{ \AA}$



Moncton, McWhan, Schmidt, Shirane, Thomlinson,  
Maple, MacKay, Woolf, Fisk, Johnston (80)

Similar behavior –  $\text{HoMo}_6\text{S}_8$   
Lynn et al. (81)

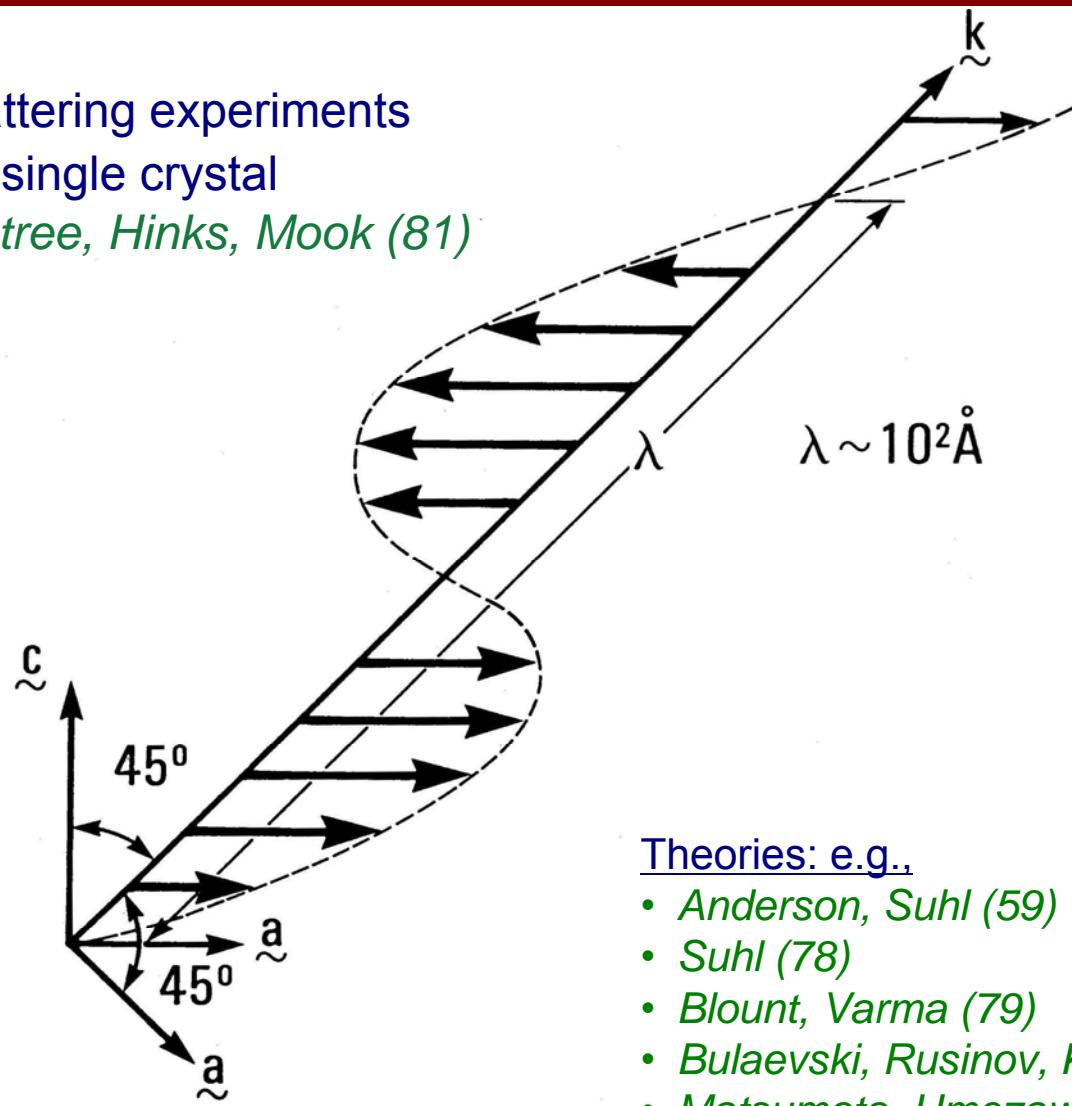
# LINEARLY POLARIZED SINUSOIDALLY MODULATED MAGNETIC STATE ( $\mu \perp c$ ) – $\text{ErRh}_4\text{B}_4$

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Neutron scattering experiments

on  $\text{ErRh}_4\text{B}_4$  single crystal

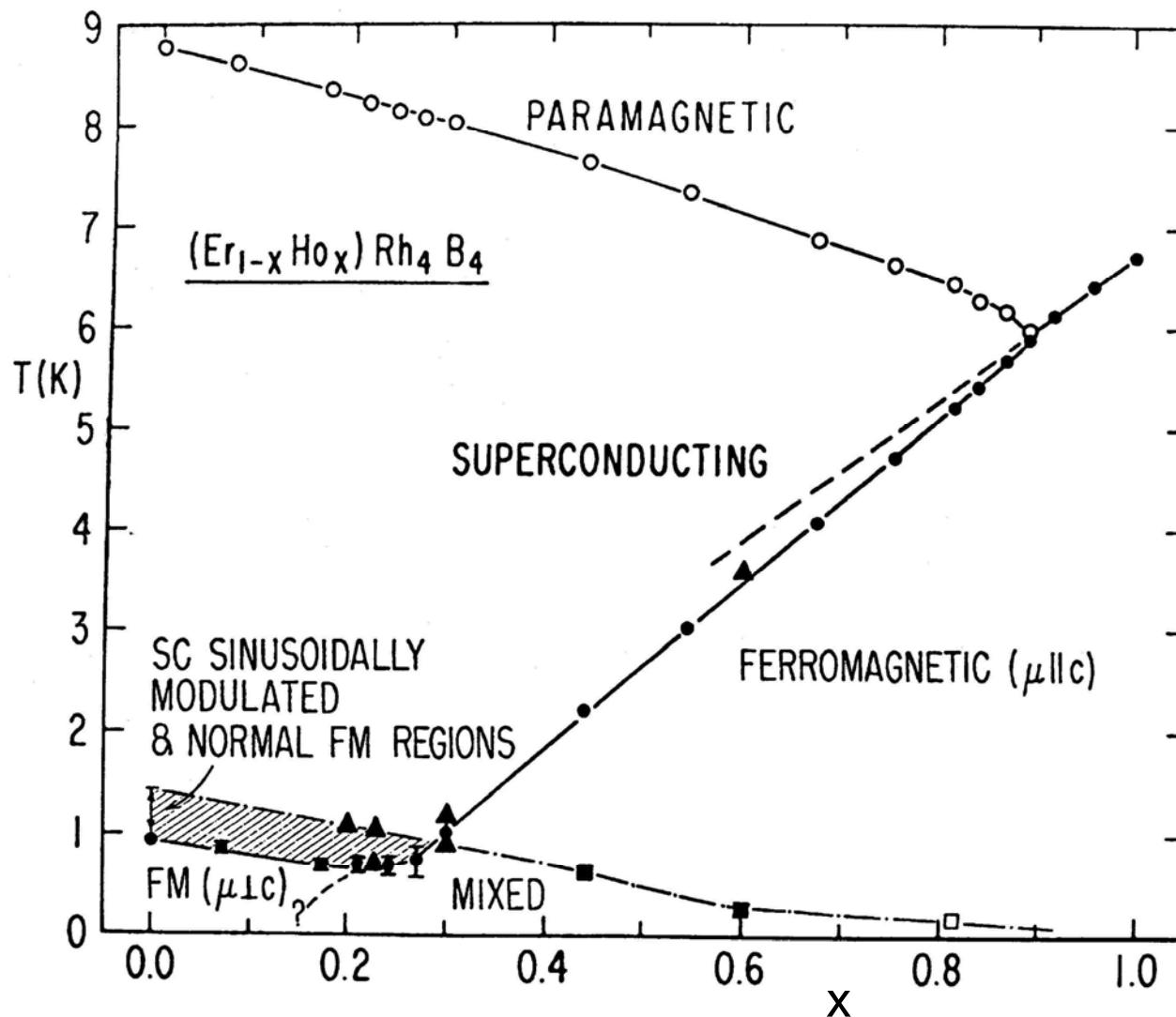
*Sinha, Crabtree, Hinks, Mook (81)*



Theories: e.g.,

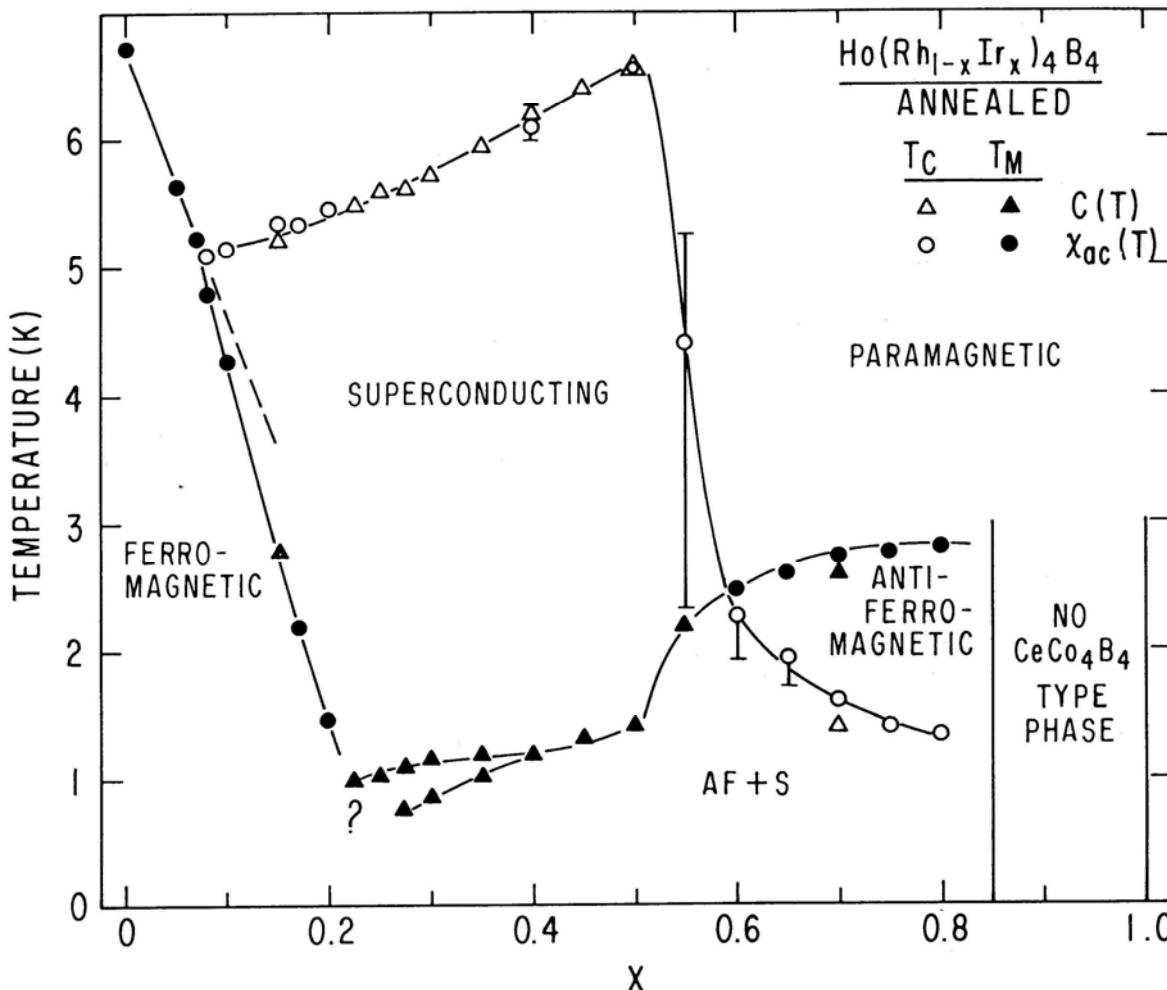
- *Anderson, Suhl (59)*
- *Suhl (78)*
- *Blount, Varma (79)*
- *Bulaevski, Rusinov, Kulik (79)*
- *Matsumoto, Umezawa, Tachiki (79)*

*(Er<sub>1-x</sub>Ho<sub>x</sub>)Rh<sub>4</sub>B<sub>4</sub>: FM –  $\mu \perp c$  vs  $\mu // c$*



*Johnston, Fertig, Maple, Matthias (78);  
Mook, Koehler, Maple, Fisk, Johnston, 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)

## Oscillatory magnetic state in FM SCs

ErRh<sub>4</sub>B<sub>4</sub>, HoMo<sub>6</sub>S<sub>8</sub>:  $\lambda \sim 10^2 \text{ \AA}$  (neutron scattering)

Explanation based on electromagnetic interaction

e.g.; Blount & Varma (1979)

Ferrell, Battacharjee & Bagchi (1979)

Matsuda, Umezawa & Tachiki (1979)

Suhl (1980)

$$\tilde{h}_m(x) = \gamma(-i\nabla) \tilde{m}(x) + \tilde{h}(x)$$

$\tilde{h}_m(x)$  - molecular field acting on RE ion

$\tilde{m}(x)$  - RE magnetic moment

$\tilde{h}(x)$  - magnetic field generated by persistent current

$$\tilde{h}_m(q) = \gamma(q) \tilde{m}(q) + \tilde{h}(q) = \gamma(q) \tilde{m}(q) - 4\pi F(q) \tilde{m}(q)$$

$$= [\gamma(q) - 4\pi F(q)] \tilde{m}(q) = \tilde{\gamma}(q) \tilde{m}(q)$$

# Oscillatory magnetic state in FM SCs

Normal:

$$\tilde{\chi}(q) = (T_n - Dq^2)/C$$

$T_n$  - Curie temperature

$D$  - magnetic stiffness coefficient

$C = N\mu_{\text{eff}}^2 / 3k_B$  - Curie constant

$\tilde{\chi}(q)$  maximum at  $q=0 \Rightarrow \lambda = \infty$

$\Rightarrow$  FM for  $T \leq T_n$  (2nd order)

Superconducting:

$$\tilde{\chi}(q) = \tilde{\chi}(q) - 4\pi F(q) ; F(q) = \frac{\exp(-\xi q^2/2)}{\lambda^2 q^2 + \exp(-\xi q^2/2)}$$

$\xi$  - coherence length

$\lambda$  - London penetration depth

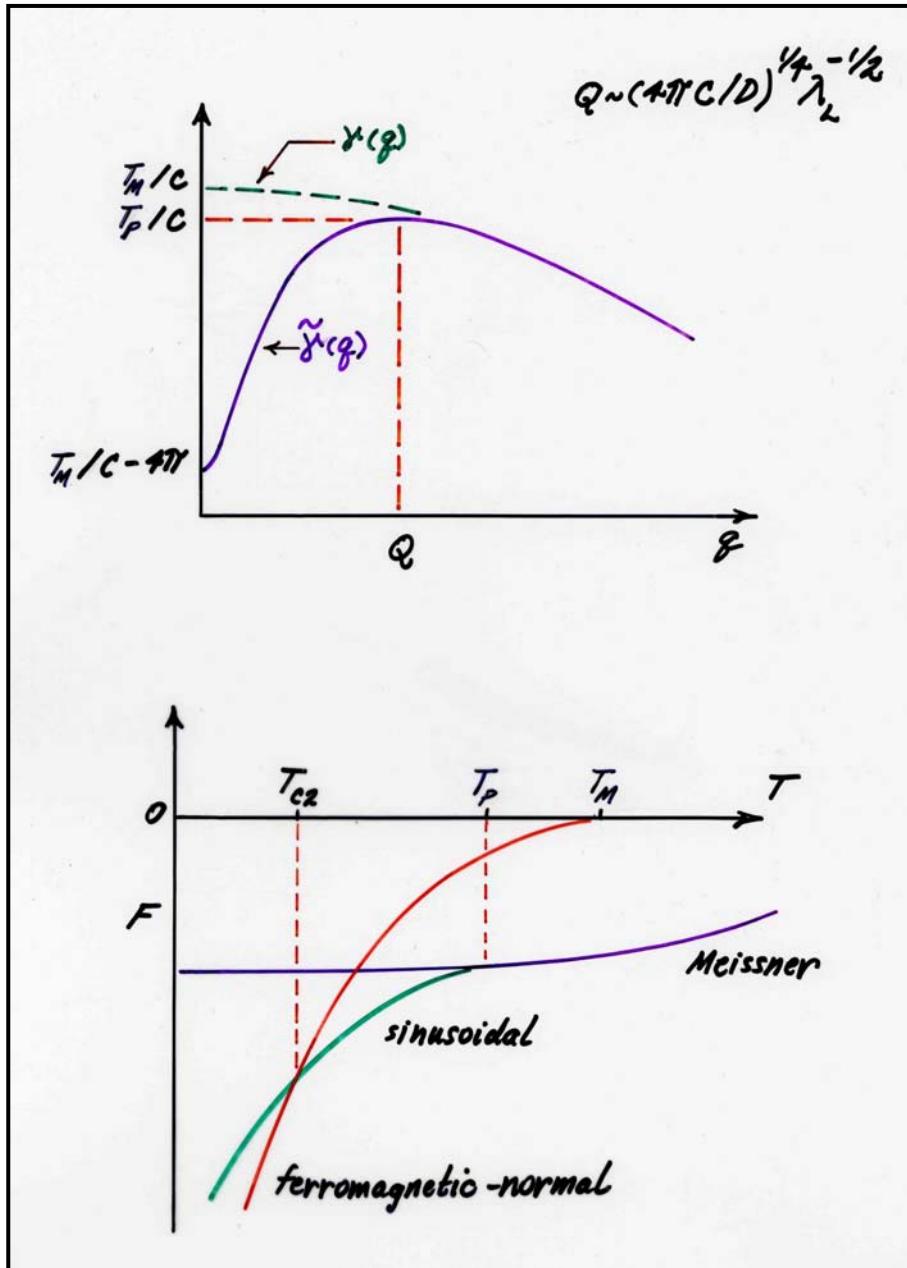
$\tilde{\chi}(q)$  maximum at  $Q \sim (4\pi C/D)^{1/4} \lambda^{-1/2}$

SC screens exchange interaction at long wavelengths

$\Rightarrow$  AFM, SC for  $T_{c2} \leq T \leq T_p < T_n$  (2nd order)

FM for  $T \leq T_{c2}$  (1st order)

# Oscillatory magnetic state in FM SCs



**END**

# Superconductivity

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- Conventional superconductivity

Electron pairs (Cooper pairs) –  $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$

$S = 0$  (singlet)

$L = 0$  (s-wave)

Pairing mechanism — electron-phonon interaction

$$T_c \approx \theta_D \exp(-1/N(E_F)V)$$

Isotropic energy gap  $\Delta(\mathbf{k}) = \Delta$

“Activated” behavior;

$$\text{e.g., } C_e(T) \sim \exp(-\Delta/T)$$

# Superconductivity

- Unconventional superconductivity

Electron pairs ( $L > 0$ )

$S = 1$  (triplet)  $\Rightarrow L = 1$  (p-wave)

$S = 0$  (singlet)  $\Rightarrow L = 2$  (d-wave)

Pairing mechanism – AFM spin fluctuations

Anisotropic energy gap  $\Delta(\mathbf{k}) \neq \Delta$

$\Delta(\mathbf{k})$  vanishes at points or lines on Fermi surface

“Power Law” behavior;

e.g.,  $C_e(T) \sim T^n$  ( $n = 2$ , line nodes;  $n = 3$ , point nodes)

