localized magnetic moments in metals, reservoirs of more electronic ground states and phenomena

- Formation ("survival") of magnetic moments of $T$, $Er$, $Ac$ ions with partially-filled d-or f-electron shells in metal
- Kondo effect
- Reentrant SC due to Kondo effect
- Coexistence of SC and AFM
- Reentrant SC due to FM

Generation of new oscillatory magnetic state that coexists with SC due to SC-FM interaction

- Heavy fermion compounds (cm$^2$/s $\times 10^2$ m$^{-1}$)

- Unconventional SC in heavy fermion compounds

Pairing with $\Delta > 0$, modest in energy gap

Magnetic pairing mechanism

- NFL behavior associated with QCPs
- SC in the vicinity of QCP, magnetic QCP accounted for possibly heavy fermion behavior and SC in Pr$_2$Co$_3$ possibly due to fluctuations of electric quadrupole moment, rather than magnetic dipole fluctuations
* Survey these through electronic, ground states and phenomena
* Emphasis on experiment

* Introduce some ideas and venn some history — useful in our discussion of experiment

* Blackboard, V6's
Outline

1. Moment formation (or "survival") in metal
   - Magnetic moment
   - Experimental observations
   - Friedel-Anderson model
   - Virtual bound state
   - Schrieffer-Wolff transformations
   - Exchange interaction
   - Kondo effect
   - RKKY interaction
   - Competition between Kondo effect and RKKY interaction

2. Localized magnetic moments in conventional SCs
   - Superconductivity w/o localized moments
   - Paramagnetic impurities in SCs
   - Magnetically ordered sublattices in SCs
   - Magnetic field induced SC

3. Valence fluctuations in bo compounds

4. Heavy fermion compounds (primarily f example)
   - Normal state
   - Screeing state (unconventional)
5. Non-Fermi liquid (NFL) behavior near quantum critical points (QCP's)
6. SC near QCP's
7. Heavy fermion behavior and unconventional SC in \( \text{PrOs}\)\(_4\)\(_{12}\) driven by electric quadrupole fluctuations (rather than magnetic dipole fluctuations?)
The system: magnetic moments imbricated within a sea of conduction electrons

- Magnetic moments $\mu$ derived from 1st row transition metal T (3d), lanthanide Ln (4f) activate AC(%) and with partially-filled d/electron shells

- $T$, Ln AC atoms

  substituted for other atoms (low concentration: "impurity")
  e.g., $\text{Al}_{1-x} \text{M}_{x}$, $\text{La}_{1-x} \text{Eu}_{x}$, $\text{Th}_{1-x} \text{U}_{x}$

  component of compound (natural substitute)
  e.g., $\text{Au}_{x} \text{V}$, $\text{Ce}_{x} \text{Al}_{3}$, $\text{V}_{x} \text{Co}_{2-x} \text{Al}_{5}$

- Interactions between localized magnetic moments and conduction electron spins

  Exchange interaction

  $W_{ex} = -2J \sum S_i \cdot \sum S_j$ T (and $J=0$ "quenched")

  $W_{ex} = -2J \sum \frac{S_i \cdot \sum T_j}{(kT+1)}$ $J_{2D} = -2 \sum \sum \left( S_i \cdot S_j - S_i \cdot S - S \cdot S_j \right)$

  in AC and $(S=0, J=\pm S)$
1-exchange interaction parameter

\[ J = J_0 + J \]

\( J > 0 \), Heisenberg

(AFQ)

\( J < 0 \), Hybridization of localized \( d \)-of states and conduction electron states

(Very important!)

Look at magnetic moments in insulators —

How are the fermals (or how do they "survive")

in metal
First row transition metals T atoms: $3d^n 6s^2$

Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn

n 1 2 3 4 5 6 7 8 9 10

(5) (10)

Lanthanide Ln atoms: $4f^m 5d^1 6s^2$ (trivalent - $3^+$)

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Th Yb Lu

n 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

(2) (3) (6) (7) (8) (9)

$\rightarrow 2^+$

$\rightarrow 2^+$

$\rightarrow 2^+$

Actinide Ac atoms: $5f^m 6d^1 7s^2$ (trivalent - $3^+$)

Ac Th Pa U Np Pu ...

n 0 0 0 2 3

(4) Valence not well defined

($v_0, 1a$) ($v_0, 3a$) (na) $a$-lattice parameter

NOTE: $\nu < \nu < \nu$ Atomic radius

$4\nu < 5\nu < 6\nu$
local moment paramagnetism (mottites)

\[ M = -g_J M_B \frac{J}{J} \]

\[ J = \frac{L + S}{2} \]

\[ g_J = 1 + \frac{J(J+1) - (L+1)}{2J(J+1)} \]

\[ M_B = \frac{e\hbar}{2mc} = 0.927 \times 10^{-20} \text{ erg/gauss} \]

\[ E = M \frac{g_J M_B}{J} H; \quad M_J = J, J-1, \ldots, -J \]

\[ 2J+1 \text{ equally spaced levels} \]

\[ M = M(\mu_B B(x), x = g_J M_B H/\hbar B T) \]

\[ B(x) = \frac{2J+1}{2J} \coth \left( \frac{(2J+1)x}{2J} \right) - \frac{1}{2J} \coth \left( \frac{x}{2J} \right) \]

\[ q_{\gamma J}(M_B) \]

\[ M(\mu_B) \]

\[ H/T \]
\[ x \ll 1 \]

\[ \mu_{eff} = \left( N / J \right) H \]

\[ M = (N \mu_{eff}^2 / 3k_B T) H = x M \]

\[ x = \frac{M}{N \mu_{eff}^2 / 3k_B T} = \frac{C}{T} \quad \text{(Curie law)} \]

\[ C = N \mu_{eff}^2 / 3k_B \quad \text{(Curie constant)} \]

\[ \mu_{eff} = \gamma \left[ J(J+1) \right]^{1/2} \mu_B \quad \text{effective moment} \]

\[ \frac{M_{sat}}{x} = x^{-1} \]

\[ \text{slope, } \frac{1}{C} = \frac{3k_B}{N \mu_{eff}^2} \]

\[ M \approx \gamma J / \mu_B \quad \text{saturated moment} \]

\[ A, J \text{ derived from Hund's rules} \]

Ionic configuration \( 4f^7 \) (lanthanides)

4f electrons - \( l = 3 \), \( s = 1/2 \)

\[ S = \text{maximum value } \sum_{i=1}^{n} \left( \frac{S_i}{2} \right) \]

\[ L = \text{maximum value } \sum_{i=1}^{n} \left( S_i / 2 \right) \quad \text{(subject to Pauli principle)} \]
$T = 1/2 \text{ for } N < V$

$T = L + S \text{ for } N \geq V$

Fermi's rule

\[ s = \frac{1}{2}, L = 3, J = L - S = \frac{5}{2} \]

Curie-Weiss law

\[ \chi = v \mu_{\text{eff}}^2 / 3k_B (T - \theta) \]

\( O \) - Curie-Weiss temperature

Ferromagnet: \( O \propto T \) (Curie temperature)

Antiferromagnet: \( O \propto -T \) (Néel temperature)

\( T_N \)

\( T \)

\( \theta \) - Néel temperature

Note:

\( \theta \) is a measure of other magnetic interactions

E.g., Néel temperature, \( T_N \)

\( \theta \) is a measure of magnetic interactions

E.g., Néel temperature, \( T_N \)
(2) Van Vleck anomalies in $\chi$ due to small multiplet splittings of Sm and Eu -

e.g., $\text{Eu}^{3+} \rightarrow 4f^{6}$

ground state -

$S = 3, \, L = 3, \, J = 1/2 - S = 0$

spectroscopic notation - $7F_0$

superscript $(7) - 2S+1$

subscript $(0) - J$

Eu$^{3+}$ Van Vleck susceptibility

\[
\chi \propto \frac{N(1/14z10)^2}{k_B T} \quad k_B T \gg E_1 - E_0
\]

\[
\chi \propto \frac{2N(1/14z10)^2}{E_1 - E_0} \quad k_B T \ll E_1 - E_0
\]

relevant for discussing Sm$^{2+}$
<table>
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<th>Metal</th>
<th>Au</th>
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<td>?</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

+ → moment (Q ≈ o/T)
- → no moment
The average magnetic moment of Fe impurities in 4d metals and alloys as determined from the magnetic susceptibility. After Clogston et al. '62.
After White and Ceballe '79:

(b) Cu. The data for Al suggest that the impurities are not residual resistivities of transition metal impurities in (a) Al and

Host: Cu

\( \Delta \rho (\Omega \cdot \text{cm}) \)

\( \Delta \rho (\Omega \cdot \text{cm}) \)

Host: Fe, Cr, Mn, Co, Ni, Cu, Zn

After Ceballe host: Cu

Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

Magnetic at 78 K.
After Rizzuto, 74.

Various hosts. Dashed lines: free ion value $2\sqrt{5} (s+1)^{1/2}$

Effective magnetic moments of transition metal ions in

$\Delta Zn + Cd$

$\times Mo$

$+ Ag$

$\triangle Cu$

$\circ Au$
Friedel-Anderson model

Non-degenerate orbital state in conduction band

\[ H = E \sum_{\sigma} n_{\sigma 1} + V \sum_{\sigma} n_{\sigma 2} \quad \text{where } \sigma = \pm 1 \]

\[ E_{1} + (E+V) \]

1st 2nd
Electron electron

\[ \langle n_{\sigma} \rangle \leq 1 \quad \text{Haven't allowed for orbital degeneracy} \]

\[ (d (L=2); 2(2) + 1 = 5; f (L=3); 2(3) + 1 = 7) \]

\[ E_{F} \]

Constant interaction

\[ V = \left( \frac{1}{2} \phi_{x_{1}} \phi_{x_{2}} \right) \int \frac{e^{2}}{r_{1} - r_{2}} \phi_{x_{1}} \phi_{x_{2}} \, d\tau_{1} \, d\tau_{2} \]
Mixing interaction

\[ H_{\text{mix}} = \frac{\hbar}{\epsilon} \sum C_{\sigma}^* C_{\sigma} + \frac{\hbar}{\epsilon} \sum C_{\sigma} C_{\sigma}^* \]

\[ C_{\sigma}^* \text{ destroys localized electron with spin } \sigma \]
\[ C_{\sigma} \text{ creates conduction electron with wave vector } k \text{ and spin } \sigma \]

\[ \Rightarrow \Delta = \frac{1}{\sigma} = \frac{\pi}{\hbar} \frac{1}{\epsilon} \left( NCE_{\text{el}} \right) \approx \frac{\pi}{\hbar} \left( \frac{1}{NCE_{\text{el}}} \right) \]

**NOTE:** \( \Delta \) increases with \( \left\{ \right. \)
\( (1) \frac{1}{\epsilon} \frac{1}{NCE_{\text{el}}} \)
\( (2) NCE_{\text{el}} \)

Local density of states

\[ N_{\text{el}}(E) = \frac{1}{\pi} \frac{\Delta}{(E-E_{\text{el}})^2 + \Delta^2} \]

Nonmagnetic state

Friedel-Anderson picture of nonmagnetic d-level impurity state in metal
"Remnant state" or "virtual bound state" (VBS)

Magnetic moment: \( M = (\Delta, \frac{1}{2}) \mu_B = 0 \)

Magnetic state

If sufficiently large \( \Rightarrow \) magnetic state

Criterion for magnetic moment: For symmetric case

\[
\frac{\pi A}{V} < 1
\]

magnetic

Demagnetization

leads to noninteger moments

Increase \( \Delta \) further \( \Rightarrow \) decrease \( (E - E_F) \) further

\( \Rightarrow \) nonmagnetic solution \( \langle n_{\frac{1}{2}} \rangle = \langle n_{\frac{1}{2}} \rangle \)}
Phase boundary
\[ \langle \eta_{x} \rangle \neq \langle \eta_{y} \rangle \] magnetic solution
\[ \langle \eta_{x} \rangle = \langle \eta_{y} \rangle \] non-magnetic solution

Non-magnetic when
\[ 1 \geq V N_{0} \langle C_{F} \rangle = \frac{V}{U} \sin^{2}(\pi \langle \eta \rangle) \]

\[ \frac{\pi A}{U} \]

\[ 0 \quad 0.5 \quad 1.0 \quad \langle \eta \rangle \]

\[ \text{Magnetic} \quad \text{Non-magnetic} \]

\[ \Rightarrow \text{localization most probable near middle of solute transition metal series} \]

Explains Table of moment formation of 3d solute in Au, Cu, Ag, Al (ordering increasing MP at)
Most favorable case for magnetism

\[ \frac{E - E_c}{U} = \ln 2 \] (symmetric case)

\[ \Rightarrow \text{magnetic solutions when } \frac{\pi A}{U} < 1 \]

Second order phase transition

Transition

\( 0 \) (a) Fe dissolved in 2nd row transition metal alloy host

\( A_x B_{1-x} \text{Fe}_x \) which has minimum near Mo

\( \text{Pd}_{1-x} \text{Fe}_x \) is special case (Pd nearly magnetic)

\( 0 \) (b) Transition metal solute in Au, Ag, Al

\( \text{La}_{1-x} \text{Ce}_x, \text{Y}_{1-x} \text{Ce}_x \) under pressure?

"Squeeze" at \text{Th}?
"Virtual bound state" of transition metal impurity in metallic host

Friedel sum rule (based on scattering theory)

\[ Z = \frac{e}{\pi} \sum (2L+1) \eta_L (k_F) \]

\( \eta_L \) phase shift of scattering particle

\( Z \) charge differential between solute and metallic host

\[ \Delta \rho = \frac{4 \pi n_i}{ne^2 k_F} \sum (2L+1) \sin^2 (\eta_L - \eta_{L+1}) \]

If only one phase shift is large

\( \eta_L (k_F) = \pi \frac{7}{2} (2L+2) = \pi \frac{7}{2} (4L+2) \)

\[ \Rightarrow \Delta \rho = \frac{4 \pi n_i}{ne^2 k_F} (2L+1) \sin^2 \left( \frac{\pi \frac{7}{2}}{4L+2} \right) \]

For \( Z = 5 \), \( \eta_L = \frac{5 \pi}{4(2)+2} = \frac{\pi}{2} \sin (\pi/2) = 1 \)

\( \Delta \rho \max \)

As \( Z \) increases, VBS sinks into Fermi sea

\( \Delta \rho \) goes through maximum when centroid of VBS at \( E_F \)

One peak for nonmagnetic VBS / two peaks for magnetic VBS (Pauli)
Effect of mixing interaction on the magnetic state

\[ V_{el} \]

(1) broadens localized states
(2) allows electron transfer between localized state and conductive electron states

Matrix element of perturbing Hamiltonian between two levels results in repulsion of the two levels from one another (levels "repel" each other)

Dashed line in figure - after repulsion
The exact Fermi level, electron flows from \( \uparrow \) state to \( \downarrow \) state

Result in spin polarization of conduction electrons opposite to impurity moment

Antiferromagnetic interaction
\[
V_{ex} = -2\Phi \frac{S}{N}
\]

Where

\[
Y = -\frac{kpe \ell^2 V}{\varepsilon (\varepsilon + V)} < 0
\]

For \( V \gg \varepsilon_0 \)

\[
Y = -kpe \frac{\ell^2}{\varepsilon_0}
\]

Schröder-Wolf transformation

\[
E = \frac{F_p - \varepsilon}{\varepsilon}
\]
Bound state (a) and resonance, or virtual bound state, (b) formed when energy $E_o$ of a localized state lies below (a) or within (b) the continuum of free electron states. After White and Geballe '79.
Density of states associated with a magnetic impurity (Anderson model).
Two ways in which an impurity may be nonmagnetic:

(a) $E_0$ far from $E_F$ and (b) $E_0 = E_F - U/2$. 

Diagram: 
- (a) shows a line at $E_0$ with a shaded region indicating a deviation from an idealized energy distribution.
- (b) shows a line at $E_0$ with a shaded region indicating a different deviation from an idealized energy distribution.

$\frac{dN}{dE}$ and $\frac{dE}{dN}$ are shown as arrows, with $dN$ and $dE$ relationships indicated.
Anderson model -

Consider nondegenerate orbital state ($S = \frac{1}{2}, L = 0$) (not appropriate for RE's - return to this later)

\[ \Delta = \pi \langle V_{k\sigma}^2 \rangle N(E_F) \]

\[ N_f(E_F) = \frac{1}{\pi} \frac{\Delta}{E_f^2 + \Delta^2} \]

\[ \mathcal{H} = \sum_{k\sigma} \epsilon_k n_{k\sigma} \]

\[ \mathcal{H}_f = \sum_{k\sigma} E_k n_{k\sigma} + U n_f n_{\uparrow} n_{\downarrow} \]

\[ U = \int |\phi_f(r)|^2 \frac{e^2}{r_{12}} |\phi_f(r)|^2 d^3r \]

\[ \mathcal{H}_{sf} = \sum_{k\sigma} V_{k\sigma} (c^+_{k\sigma} c_{f\sigma} + c^+_{f\sigma} c_{k\sigma}) \]

\[ V_{k\sigma} = \langle \phi_f(r) | H_I | \phi_f(r) \rangle \]

↑ one electron Hamiltonian
Kondo effect

Kondo effect developed to explain resistivity minimum phenomenon first observed in nominally pure noble metals such as Au in 30's and 70's and later in 3d solids in metals

E.g., Cu$_{1-x}$Fe$_x$, Cu$_{1-x}$Mn$_x$, Au$_{1-x}$Fe$_x$

\[ P \sim \frac{T_{min}}{T} \]

Kondo calculated spin dependent scattering of conduction electrons \( s \) by paramagnetic impurity \( \uparrow \) and \( \downarrow \) via exchange interaction for \( J < 0 \)

 Obtained

\[ \rho = \rho_m \left[ 1 + 2N(E_F) \right] \ln \left( T/T_F \right) + \ldots \]

\[ \rho_m = \frac{\pi m N(E_F)}{e^2 N} n f^2 s(s+1) \]
Basic potential scale with $T_K$

\[ \Delta p \]

\[ \ln T \]

\[ -2 \]

\[ T \]

\[ k = \frac{c}{T+D}; \quad \Delta n \approx T K \]

\[ \Delta c \]

\[ T_K \]

\[ T \]

Physical picture

Many body effects start as $T$ decreases below $T_K$

AFM screening of $S$ by AF of conduction electrons

Zeol transition metal (Cr, V, Mn, Fe, Ni), e.g., $A_{1-x}Fe_x$

4f lanthanide (Ce, Pr, Yb), e.g., $La_{1-x}Ce_xAl_2$

5f actinide ($U$), e.g., $Th_{1-x}U_x$
Series diverges at "Kondo temperature" $T_K$.

$T_K \sim T \exp(-1/\mathcal{N}_{EF})/\mathcal{Y}_1$ (Thermodynamic T-scale)

Concentration dependence at $T_{\text{min}}$

$\rho(T) = \rho_{\text{host}}(T) + \rho_{\text{imp}}(T)$

$\rho_{\text{host}}(T) = \rho_0 + \alpha T$ \quad $T \ll \Theta_D$

$\rho_{\text{imp}}(T) = \beta x (1 - \delta \ln T)$

$\Rightarrow \rho(T) = \rho_0 + \alpha T^m + \beta x (1 - \delta \ln T)$

$\frac{d\rho}{dT} = m\alpha T^{m-1} - \frac{\beta x}{T_{\text{min}}} = 0$

$T_{\text{min}}$

$\Rightarrow T_{\text{min}}^m = \left(\frac{\beta x}{m\alpha}\right)x \Rightarrow T_{\text{min}} \propto x^\frac{1}{m}$

Blind $\Rightarrow m = 5 \Rightarrow T_{\text{min}} \propto x^{\frac{1}{5}}$

$\text{Bunimov} \Rightarrow \text{m=5} \Rightarrow T_{\text{min}} \propto x^{\frac{1}{5}}$

$\text{Note: } T_K \text{ is not at } T_{\text{min}}.$
**T-dependent Kondo (Abrikosov-Suhl) resonance**

\[ e.g., Ce^{3+} \]

\[
\eta(E) = \frac{\eta_{K}\sqrt{\nu E}}{3k_{B}(T-\Theta)} - \frac{\Theta}{\beta} = 0.5 \beta T_{K}, \quad \beta = 3.4
\]

\[
\rho(T) \sim k_{B} T \rightarrow "Kondo minimum"'
\]

**T \gg T_{K}**: Local moment

\[
\eta(T) \sim \frac{N_{eff}^{2} \nu}{3k_{B}(T-\Theta)}
\]

**T \ll T_{K}**: Many body slight ground state

Local Fermi liquid, \( T_{F} \sim T_{K} \)

\[
\eta(T), \sigma(T)/T \sim \text{const} \times N(E_{F})\nu/k_{B}
\]

\[
\rho(T) \sim \rho(0) [1 - (T/T_{K})^{2}]
\]

NOTE: Magnetic \( T \gg T_{K} \)

Nonmagnetic \( T \ll T_{K} \)

\[
\frac{R_{w}}{\sigma_{1}/\sigma_{0}} \quad \text{(Wilson-Furmanski ratio)}
\]

\[
R_{w} = \frac{8\pi^{2}}{\xi_{1}/\xi_{0}} = 2.855
\]