Localized magnetic moments in metals; reservoirs of novel electronic ground states and phenomena

e.g.,

* Formation ("survival") of magnetic moments of T, Ln, 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 interactions

* Heavy fermion compounds ($m^* \sim 10^2 m_e$)

* Unconventional SC in heavy fermion compounds

Pairing with $L > 0$, nodes in energy gap

Magnetic pairing mechanism

* NFL behavior associated with QCPs
* SC in the vicinity of magnetic QCPs accessed by pressure $\left\{\begin{matrix}\text{AFM's}\\ \text{FM's}\end{matrix}\right.$
* Heavy fermion behavior and SC in $PrOs_4Sb_{12}$

Possibly due to fluctuations of electric quadrupole moments, rather than magnetic dipole fluctuations

* Survey these ~~unusual~~ electronic ground states and phenomena

* Emphasis on experiment

* Introduce some ideas and review some history – useful in our discussion of experiments

* Blackboard, VG's

Outline

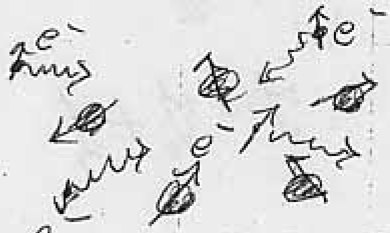
1. Moment formation (or "survival") in metal
    - Magnetic moment
    - Experimental observations
    - Friedel-Anderson model
    - Virtual bound state
    - Schrieffer-Wolff transformation
    - Exchange interaction
    - Kondo effect
    - RKKY interaction
    - Competition between Kondo effect and RKKY interaction
2. Localized magnetic moments in conventional SC's
    - Superconductivity w/o localized moments
    - Paramagnetic impurities in SC's
    - Magnetically ordered sublattices in SC's
    - Magnetic field induced SC
3. Valence fluctuations in Ce compounds
4. Heavy fermion compounds (primarily f-electrons, example of d)
    - Normal state
    - SC'ing 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 $PrOs_4Sb_{12}$; driven by electric quadrupole fluctuations? (rather than magnetic dipole fluctuations?)

The system: magnetic moments imbedded in sea of conduction electrons



* Magnetic moments $\underset{\sim}{\mu}$ derived from —

1st row transition metal T (3d), lanthanide Ln (4f), actinide Ac (5f) ions with partially-filled d or f-electron shells)

* T, Ln, Ac atoms

substituted for other atoms (low concentration: "impurity")

e.g., $Al_{1-x}Mn_x$, $La_{1-x}Ce_xAl_2$, $Th_{1-x}U_x$

component of compound (ordered sublattice)

e.g., Au_4V, $CeAl_3$, UPd_2Al_3

* Interaction between localized magnetic moments and conduction electron spins

Exchange interaction

$$\mathcal{H}_{ex} = -2\mathcal{J}\,\underset{\sim}{S}\cdot\underset{\sim}{s} \quad \text{T ions } (\underset{\sim}{L}=0 \text{ "quenched"})$$

$$\mathcal{H}_{ex} = -2\mathcal{J}\frac{\langle \underset{\sim}{S}\cdot\underset{\sim}{J}\rangle}{J(J+1)}\underset{\sim}{J}\cdot\underset{\sim}{s} = -2\mathcal{J}(g_J-1)\,\underset{\sim}{J}\cdot\underset{\sim}{s}$$

Ln, Ac ions ($\underset{\sim}{L}\neq 0$, $\underset{\sim}{J}=\underset{\sim}{L}+\underset{\sim}{S}$)

J – exchange interaction parameter

$J \sim J_0 + J_1$ $J_0 > 0$ (FM) Heisenberg

$J_1 < 0$ (AFM) Hybridization of localized d- or f-states and conduction electron states
(Very important!)

Look at magnetic moments in insulators –
How are they formed (or how do they "survive")
in metal

First row transition metals T atoms: $3d^n 4s^2$

	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
n	0	1	2	3	4	5	6	7	8	9	10
					(5)					(10)	

Lanthanide Ln atoms: $4f^n 5d\, 6s^2$ (trivalent - 3+)

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
n	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
		(2)	(3)			(6)	(7)						(13)	(14)	
		→ 4+				→ 2+							→ 2+		

valence instabilities
Ce, Pr
Sm, Eu
Tm, Yb
Can have intermediate valence —
"valence fluctuations"

Actinide Ac atoms: $5f^n 6d\, 7s^2$ (trivalent - 3+)

	Ac	Th	Pa	U	Np	Pu	....
n	0	0	2	3			
				(4)			

valence not well defined

(~0.1a) (~0.3a) (~a) a - lattice parameter

NOTE: $r_{4f} < r_{5f} < r_{3d}$ atomic radii

Local moment paramagnetism (insulators)

$$\underset{\sim}{\mu} = -g_J \mu_B \underset{\sim}{J}$$

$$\underset{\sim}{J} = \underset{\sim}{L} + \underset{\sim}{S}$$

$$g_J = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$ Landé g-factor

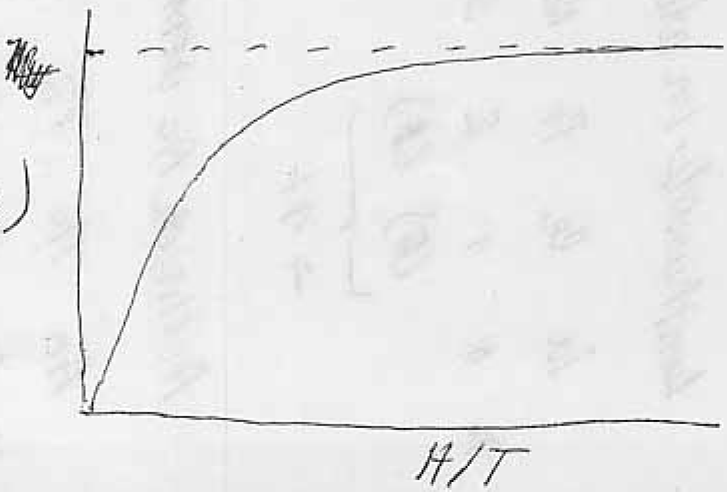
$$\mu_B = \frac{e\hbar}{2mc} = 0.927 \times 10^{-20} \text{ erg/gauss}$$

$$E = m_J g_J \mu_B H \,; \quad m_J = J, J-1, \ldots, -J$$

(2J+1 equally spaced levels)

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

$$B_J(x) = \frac{2J+1}{2J} \operatorname{ctnh}\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \operatorname{ctnh}\left(\frac{x}{2J}\right)$$



$x \ll 1$

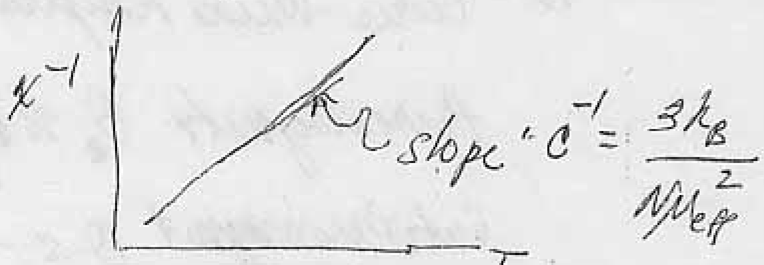
$$\left(N g_J^2 J(J+1)\mu_B^2 / 3k_B T\right) H \approx$$

$$M \approx \left(N\mu_{eff}^2 / 3k_B T\right) H = \chi H$$

$$\boxed{\chi = \frac{M}{H} = \frac{N\mu_{eff}^2}{3k_B T} = \frac{C}{T}}$$ Curie law

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

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



$x \gg 1$

$M \approx g_J J \mu_B$ saturation moment

S, L, J derived from Hund's rules

Ionic configuration $4f^n$ (lanthanide)

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

S = maximum value $\sum_i^n (s_z)_i$

L = maximum value of $\sum_i^n (l_z)_i$ (subject to Pauli principle)

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

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

{Hund's' rules}

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

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

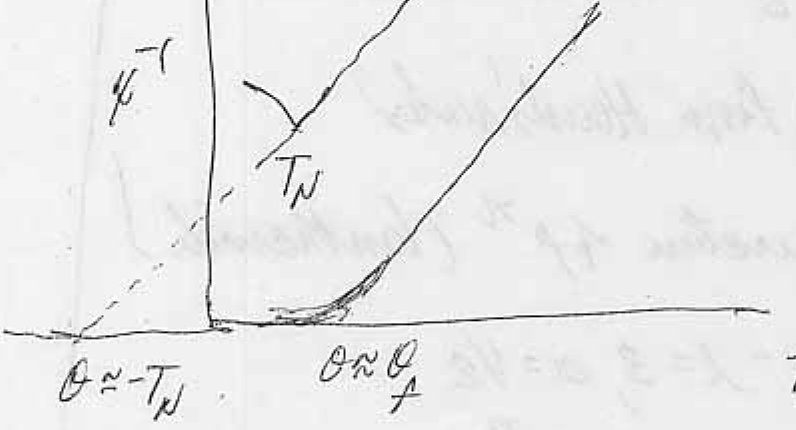
Curie-Weiss law

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

θ – Curie-Weiss temperature

ferromagnets $\theta_c \approx T_c$ (Curie temperature

antiferromagnet $\theta \simeq -T_N$ (Néel temperature)



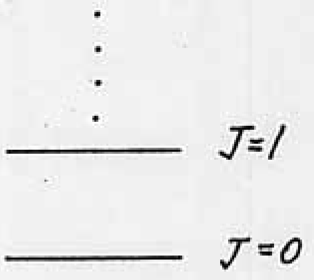
NOTE:

θ is measure of other many-body interactions

e.g., Kondo temperature T_K
valence fluctuation temperature T_0

(2) Van Vleck anomalies in χ due to small multiplet splittings of Sm and Eu –

e.g., Eu^{3+} – $4f^6$



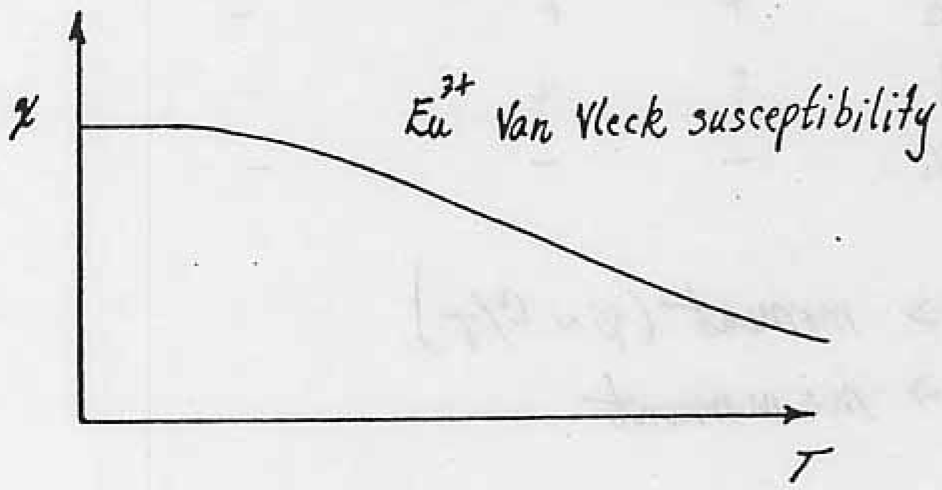
ground state –

$S=3, L=3, J=|L-S|=0$

spectroscopic notation – $^7F_0$

superscript (7) – $2S+1$

subscript (0) – J



Eu^{3+} Van Vleck susceptibility

$k_B T \gg E_1 - E_0 \qquad \chi \sim \dfrac{N|\langle 1|\mu_z|0\rangle|^2}{k_B T}$

$k_B T \ll E_1 - E_0 \qquad \chi \sim \dfrac{2N|\langle 1|\mu_z|0\rangle|^2}{E_1 - E_0}$

relevant for discussing Sm^{2+} –

Heeger ~ '70

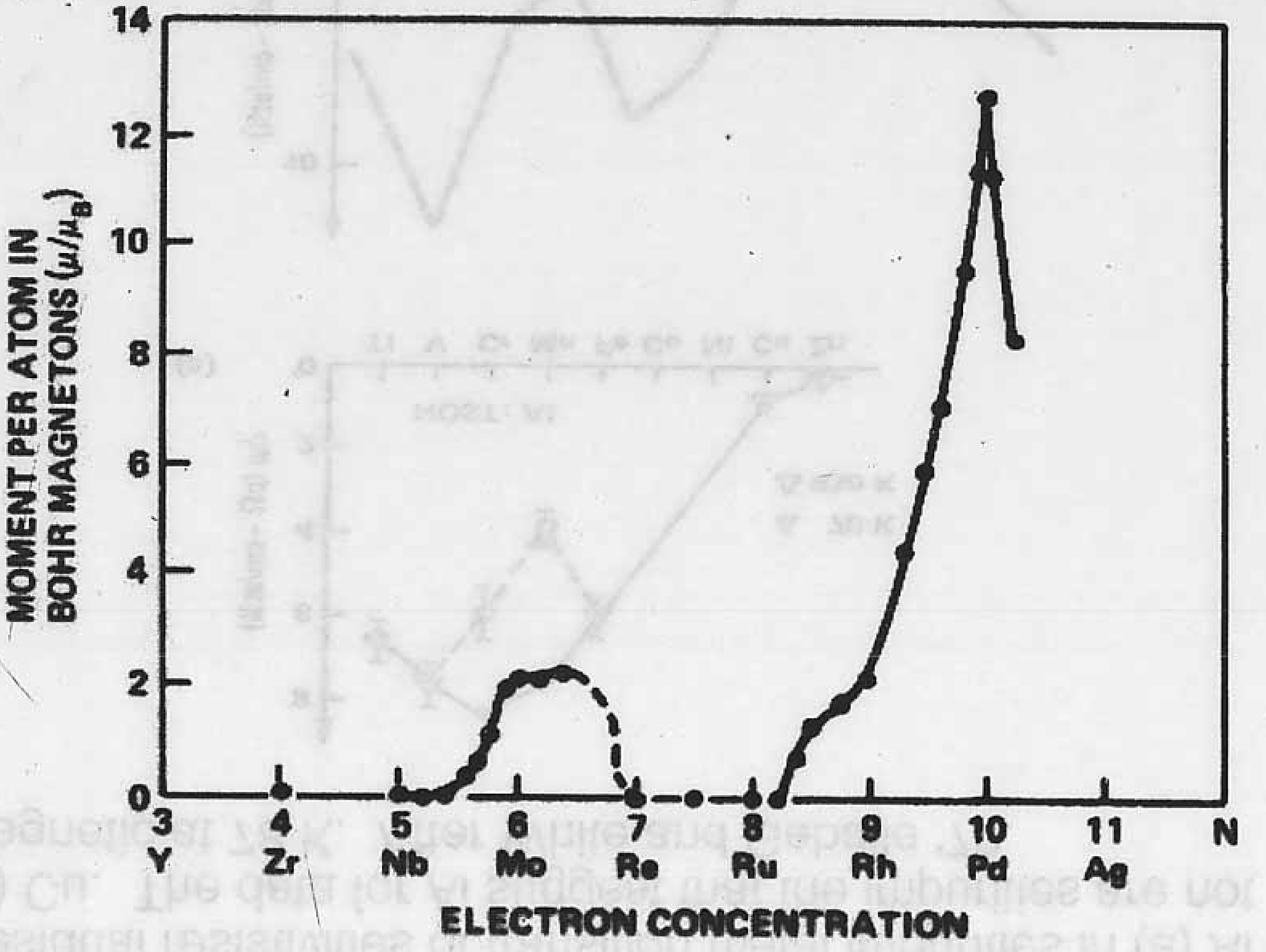
EXAMPLE

host / Solut.	Au	Cu	Ag	Al
Sc				
Ti	—			–
V	?(+)			–
Cr	+	+	+	–
Mn	+	+	+	?
Fe	+	+		–
Co	?	?		–
Ni	—	—		–

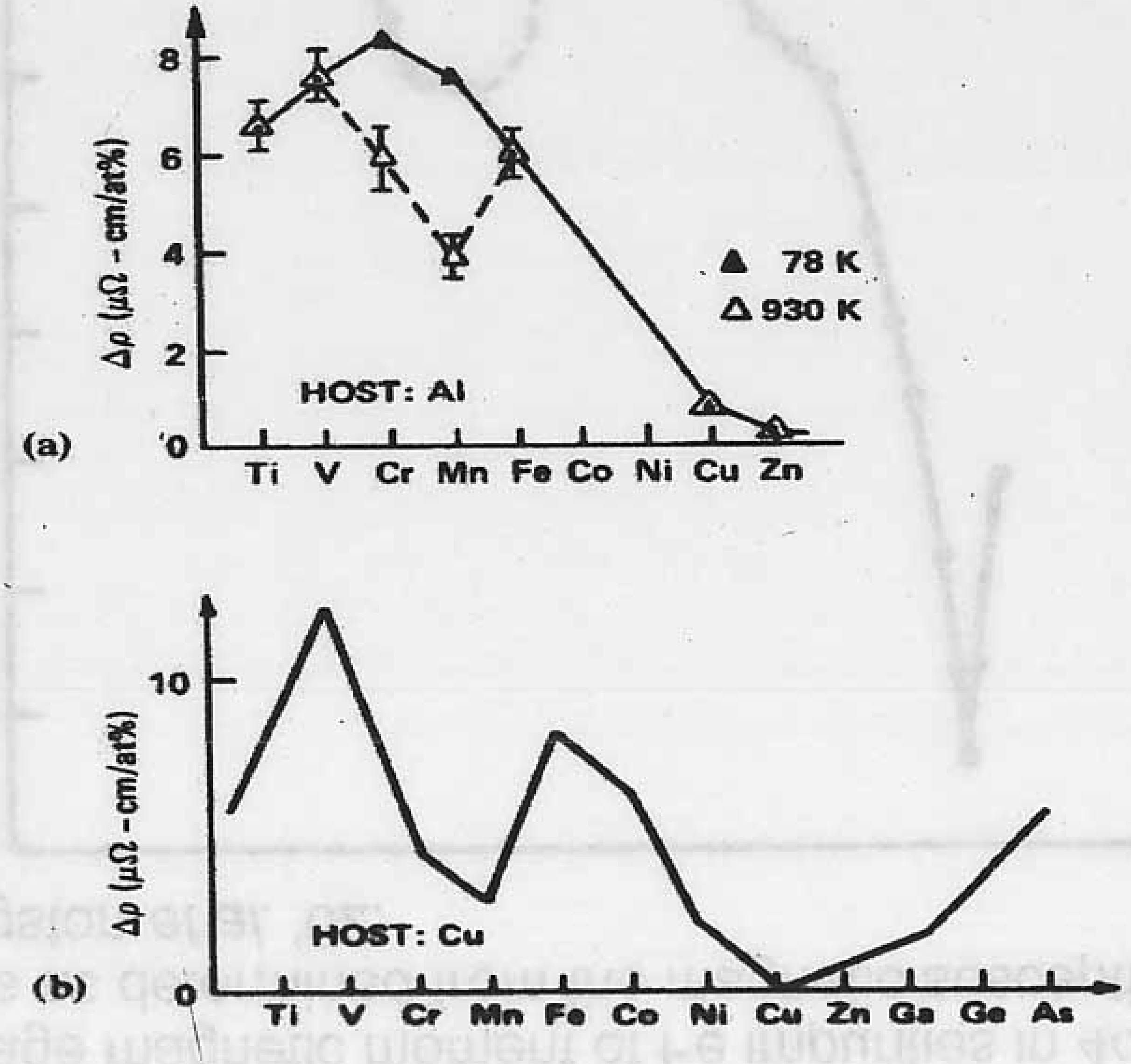
+ ⇒ moment ($\chi \sim C/T$)

– ⇒ no moment

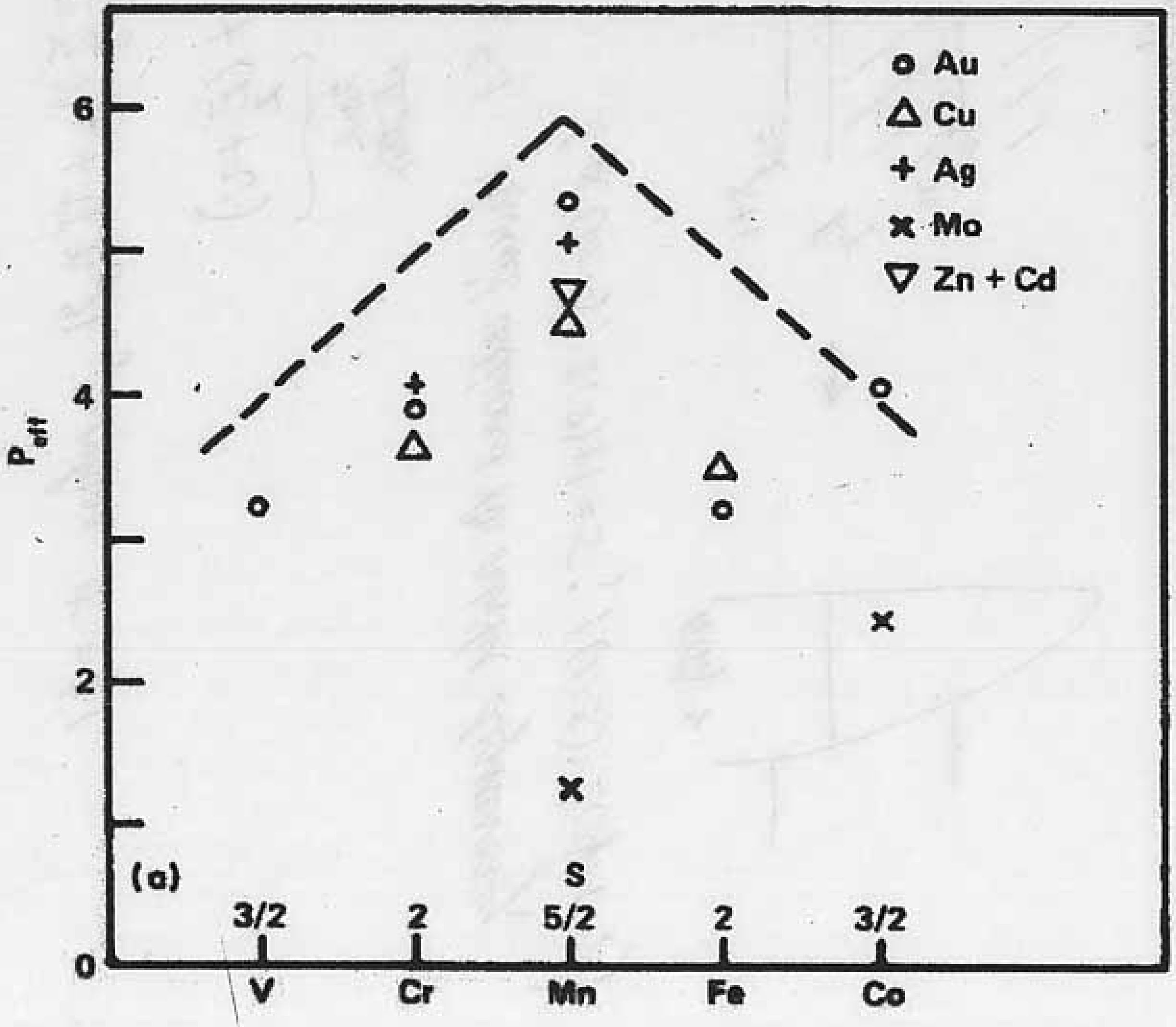
The average magnetic moment of Fe impurities in 4d metals and alloys as determined from the magnetic susceptibility. After Clogston *et al.* ‘62.



Residual resistivities of transition metal impurities in (a) Al and (b) Cu. The data for Al suggest that the impurities are not magnetic at 78 K. After White and Geballe '79.



Effective magnetic moments of transition metal ions in various hosts. Dashed line: free ion value $2[S(S+1)]^{1/2}$. After Rizzuto '74.



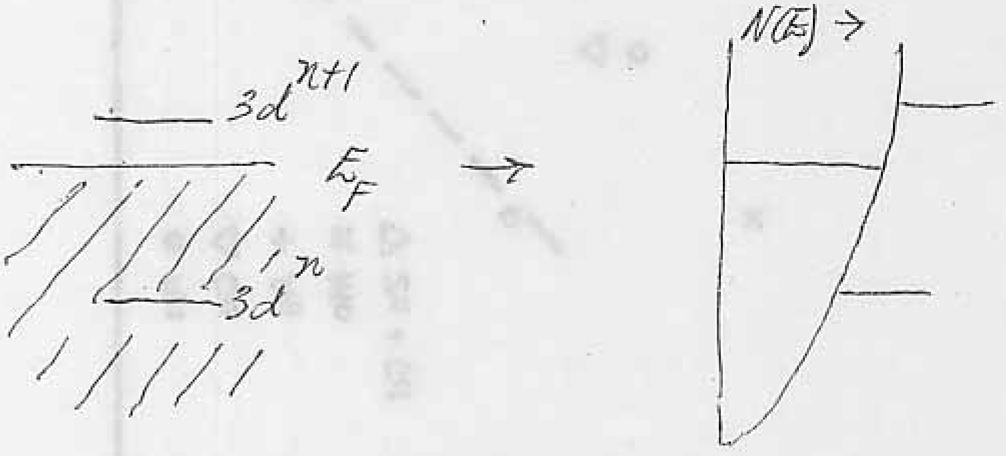
Friedel -Anderson model

Nondegenerate orbital state in conduction band

$$\mathcal{H}_{loc} = E_l \sum_\sigma n_\sigma + U n_\sigma n_{-\sigma} \quad \text{where } \sigma = \pm 1$$

$$= \underbrace{E_l}_{\substack{\text{1st}\\ \text{electron}}} + \underbrace{(E_l + U)}_{\substack{\text{2nd}\\ \text{electron}}}$$

$\langle n_\sigma \rangle \le 1$ Haven't allowed for orbital degeneracy
(d (L=2): 2(2)+1 = 5 ; f (L=3): 2(3)+1 = 7)



Coulomb interaction

$$U = \int |\varphi_l(r_1)|^2 \frac{e^2}{r_1 - r_2} |\varphi_l(r_2)|^2 \, d\tau_1 \, d\tau_2$$

Mixing interaction

$$\mathcal{H}_{mix} = V_{k\ell} \sum_{\underset{\sim}{k}\sigma} \left(c^{*}_{\underset{\sim}{k}\sigma} a_{\sigma} + a^{*}_{\sigma} c_{\underset{\sim}{k}\sigma} \right)$$

$c^{*}_{\underset{\sim}{k}\sigma} a_{\sigma}$ destroys localized electron with spin σ
creates conduction electron with wave vector $\underset{\sim}{k}$ and spin σ

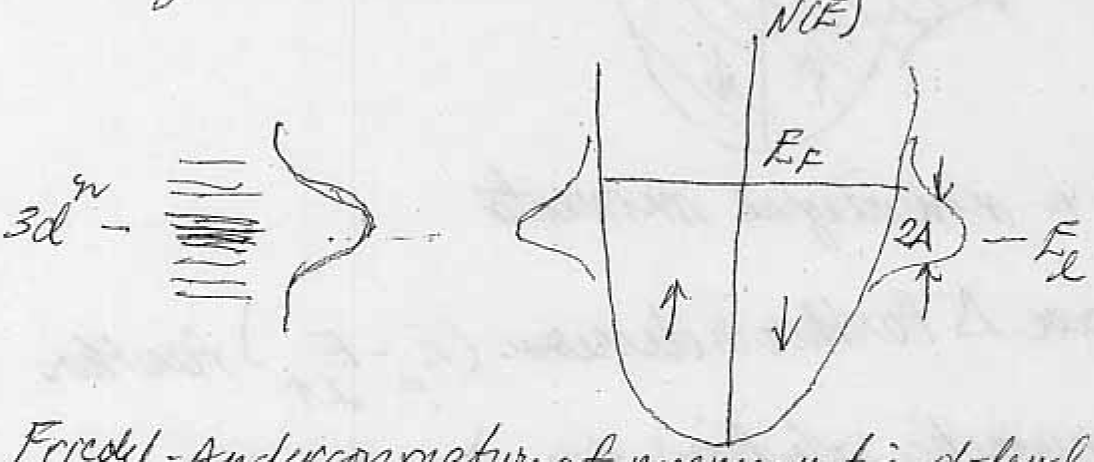
$$\Rightarrow \quad \boxed{\Delta = \frac{1}{\tau} = \pi |V_{k\ell}|^2 N(E_\ell) \approx \pi |V_{k\ell}|^2 N(E_F)}$$

NOTE: Δ increases with $\begin{cases} (1)\ |V_{k\ell}|^2 \\ (2)\ N(E_F) \end{cases}$

Local density of states

$$N_{\ell\sigma}(E) = \frac{1}{\pi} \frac{\Delta}{(E - E_{\ell\sigma})^2 + \Delta^2}$$

Nonmagnetic state



Friedel-Anderson picture of nonmagnetic d-level impurity state in metal

"Resonant state" or "virtual bound state" (vbs)

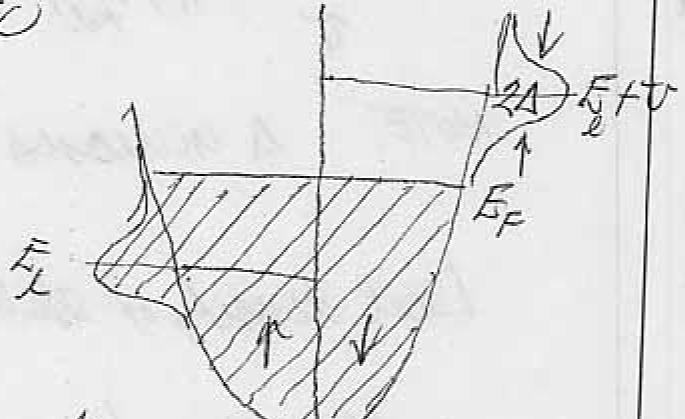
Magnetic moment: $\mu = (\langle n_\uparrow\rangle - \langle n_\downarrow\rangle)\mu_B = 0$

Magnetic State

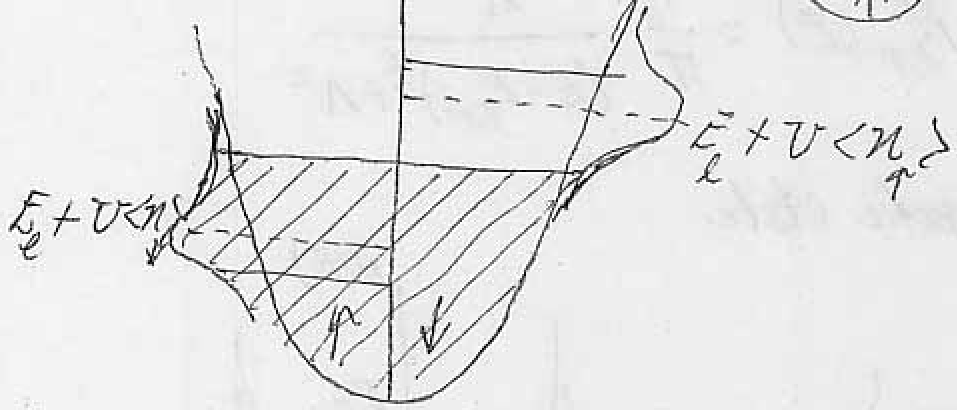
V sufficiently large ⇒ magnetic state

Criterion for magnetic moment for symmetric case

$\boxed{\pi\Delta/V < 1}$ magnetic



Demagnetization



Leads to nonintegral moments

Increase Δ further or decrease ($E_F - E_{l\uparrow}$) further

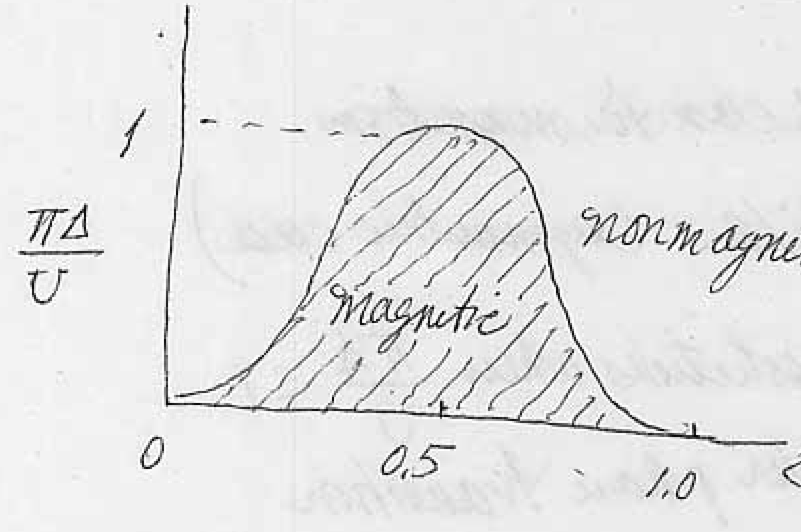
⇒ nonmagnetic solution $\langle n_{l\uparrow}\rangle = \langle n_{l\downarrow}\rangle$

Phase boundary

$\langle n_{l\uparrow}\rangle \neq \langle n_{l\downarrow}\rangle$ magnetic solution

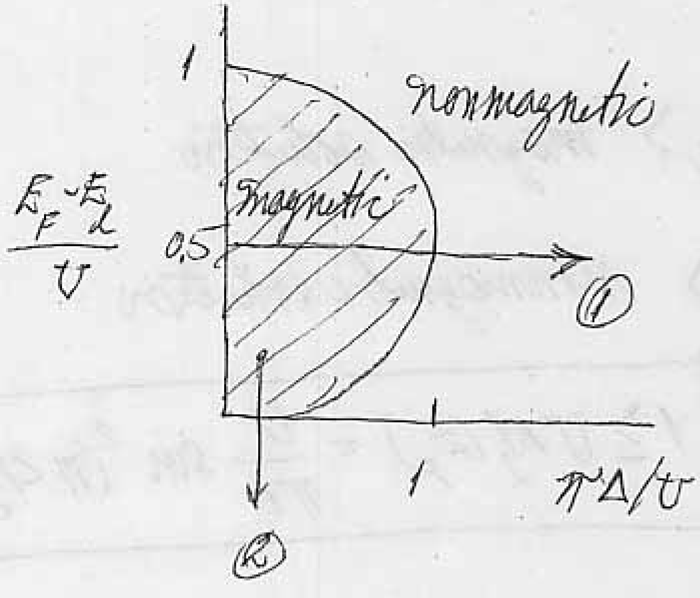
$\langle n_{l\uparrow}\rangle = \langle n_{l\downarrow}\rangle$ nonmagnetic solution

Nonmagnetic when $\boxed{1 \geq U N_l(E_F) = \frac{U}{\pi\Delta}\sin^2(\pi\langle n_l\rangle)}$



⇒ localization most probable near middle of solute transition metal series

Explains Table of moment formation of 3d solute in Au, Cu, Ag, Al (order of increasing $N(E_F)$)



Most favorable case for magnetism

$E_F - E_d = U/2$ (symmetric case)

⇒ magnetic solutions when $\frac{\pi\Delta}{U} < 1$

second order phase transition

Transitions

① (a) Fe dissolved in 2nd row transition metal alloy hosts

$\Delta \propto N(E_F)$ which has minimum near Mo

$Pd_{1-x}Fe_x$ is special case (Pd nearly magnetic)

(b) Transition metal solutes in Au, Cu, Ag, Al

② $La_{1-x}Ce_x$, $Y_{1-x}Ce_x$ under pressure } "squeeze" out f-electrons

$(La_{1-y}Th_y)_{1-x}Ce_x$

"Virtual bound state" of transition metal impurity in metallic host

Friedel sum rule (based on scattering theory)

$$Z = \frac{2}{\pi}\sum_L (2L+1)\,\eta_L(k_F)$$

η_L phase shift of scattering particle

Z charge differential between solute and metallic host

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

If only one phase shift is large

$$\eta_L(k_F) = \pi z/2(2L+2) = \pi z/(4L+2)$$

$$\Rightarrow \quad \Delta\rho = \frac{4\pi n_i}{ne^2 k_F}(2L+1)\sin^2\left(\frac{\pi z}{4L+2}\right)$$

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

$\Delta\rho$ max.

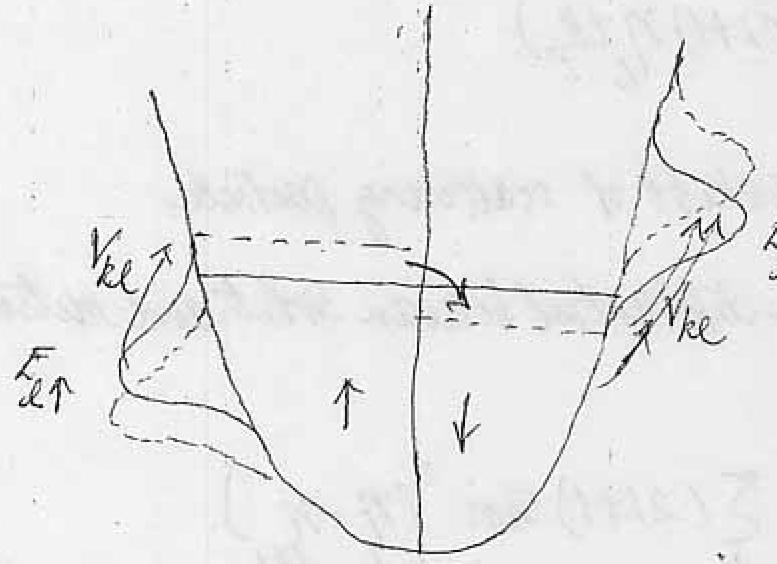
As increase z, vbs sinks into Fermi sea

$\Delta\rho$ goes through maximum when centroid of vbs at E_F

One peak for nonmagnetic vbs / two peaks for magnetic vbs (↑ and ↓)

Effect of mixing interaction on the magnetic state

$V_{k\ell}$ { (1) broadens localized states
(2) allows electron transfer between localized state and conduction 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 lines in figure - after repulsion

To correct Fermi level, electrons flow from
↑ states to ↓ states

Results in spin polarization of conduction electrons opposite to impurity moment

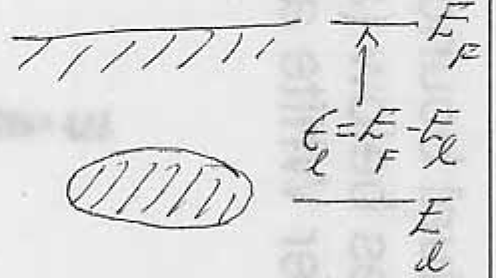
Antiferromagnetic interaction

$$\mathcal{H}_{ex} = -2J \underset{\sim}{S} \cdot \underset{\sim}{s}$$

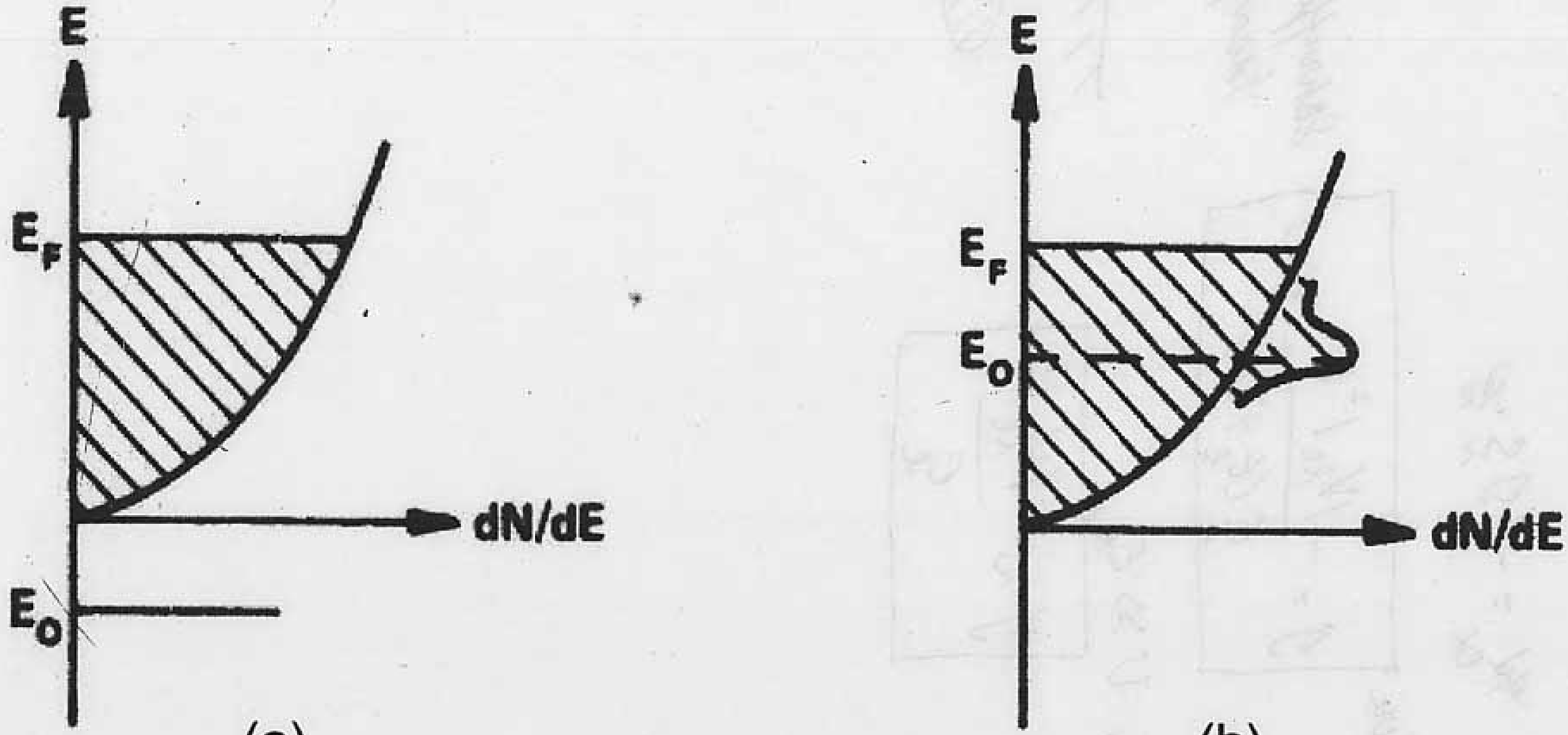
where $\boxed{J = -\frac{|V_{kl}|^2 U}{\epsilon_l(\epsilon_l + U)} < 0}$ Schrieffer-Wolff transformation

For $U \gg \epsilon_l$,

$$\boxed{J \sim -\frac{|V_{kl}|^2}{\epsilon_l}}$$



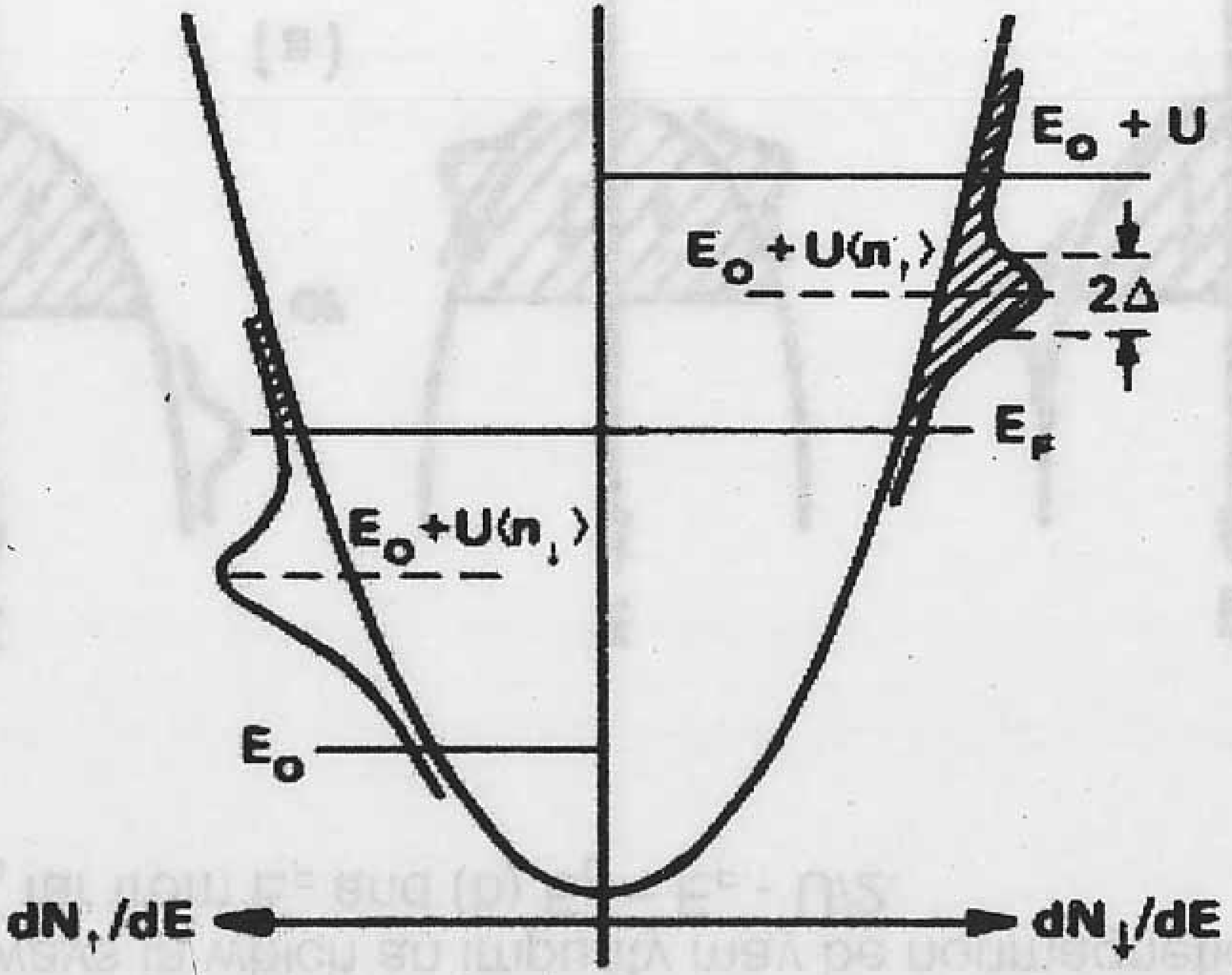
Bound state (a) and resonance, or virtual bound state, (b) formed when energy E_o of a localized state lies below (a) or within (b) the continuum of free electron states. After White and Geballe '79.



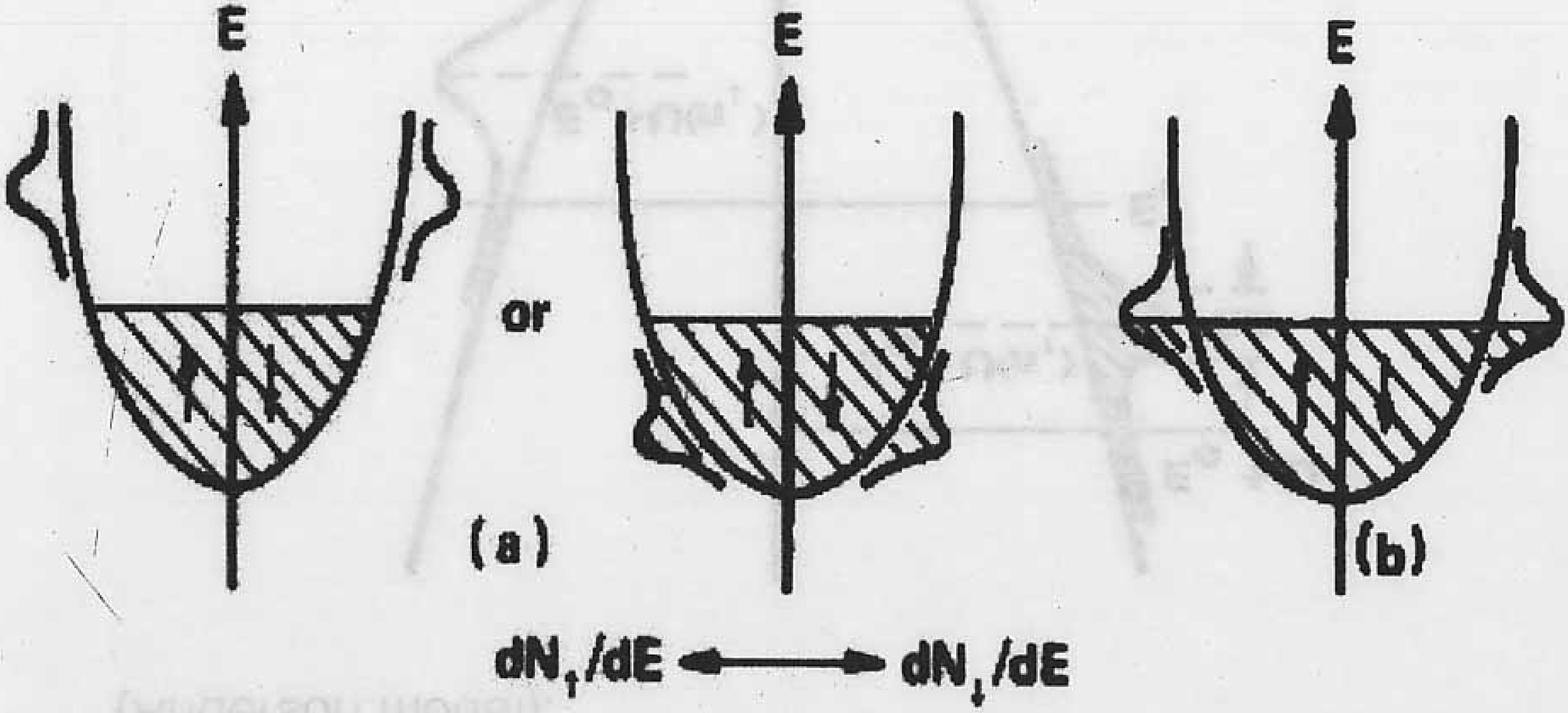
(a)

(b)

Density of states associated with a magnetic impurity (Anderson model).

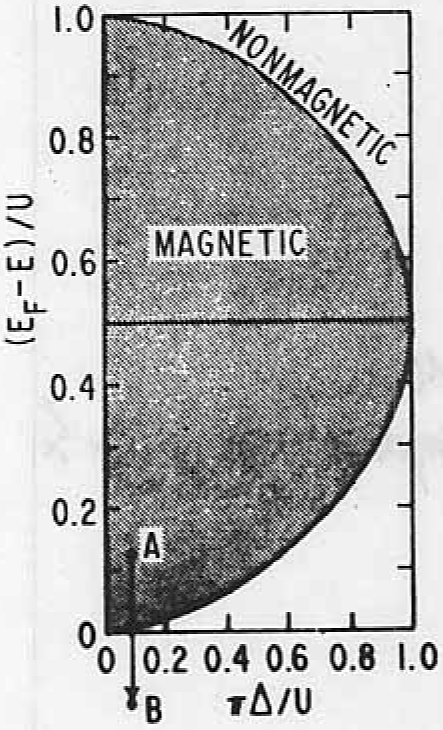


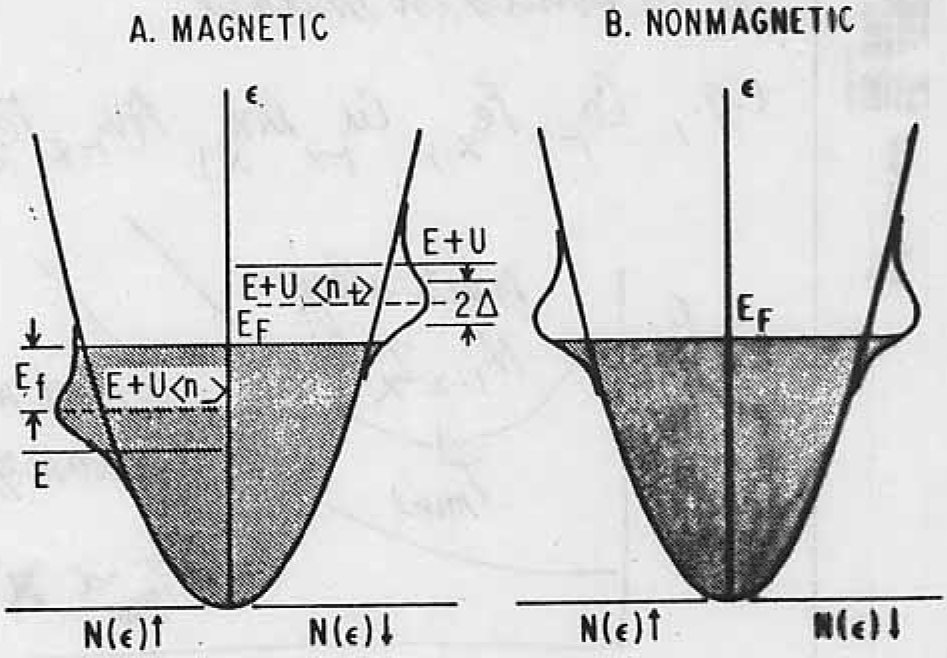
Two ways in which an impurity may be nonmagnetic:
(a) E_o far from E_F and (b) $E_o = E_F - U/2$.



Anderson model —

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





$$\Delta = \pi \langle V_{kf}^2 \rangle N(E_F)\ ; \quad N_f(E_F) = \frac{1}{\pi}\,\frac{\Delta}{E_f^2 + \Delta^2}$$

$$\mathcal{H}_k = \sum_{k\sigma} \epsilon_k n_{k\sigma}$$

$$\mathcal{H}_f = \sum_{\sigma} E_f n_{f\sigma} + U n_{f\uparrow} n_{f\downarrow} \qquad n_f = c^+_{f\sigma} c_{f\sigma}$$

$$U = \int |\phi_f(r_1)|^2 \frac{e^2}{r_{12}} |\phi_f(r_2)|^2 \, d\tau_1 \, d\tau_2$$

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

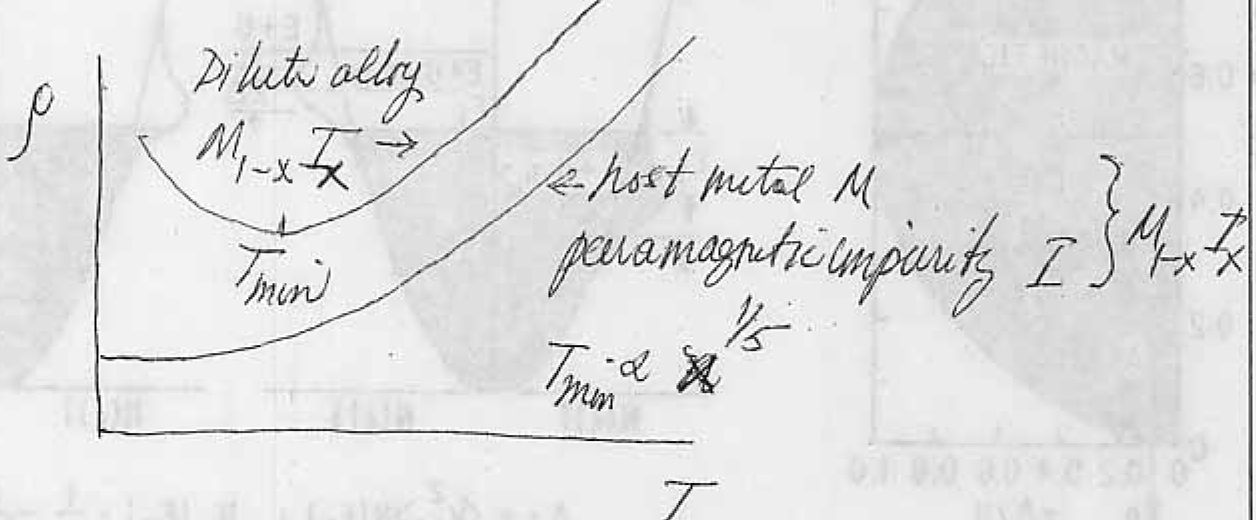
$$V_{kf} = \langle \phi_f(r) | H | \phi_k(r) \rangle$$

↑ 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 40's and later for 3d solutes in metals

e.g., $Cu_{1-x}Fe_x$, $Cu_{1-x}Mn_x$, $Au_{1-x}Fe_x$



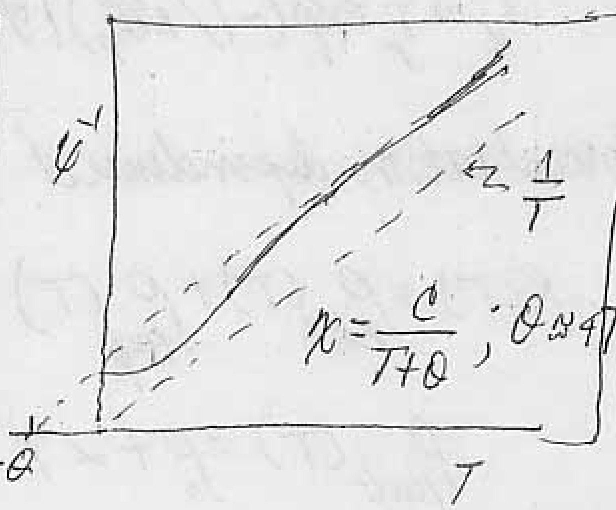
Kondo calculated spin dependent scattering of conduction electrons ($\underset{\sim}{s}$) by paramagnetic impurity ions ($\underset{\sim}{S}$) via exchange interaction for $\mathcal{J}<0$

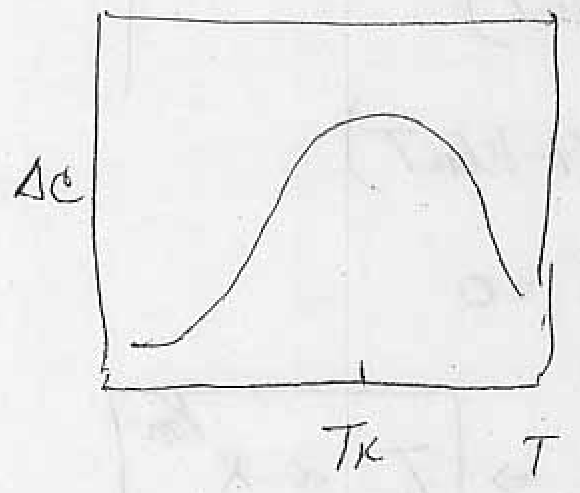
Obtained

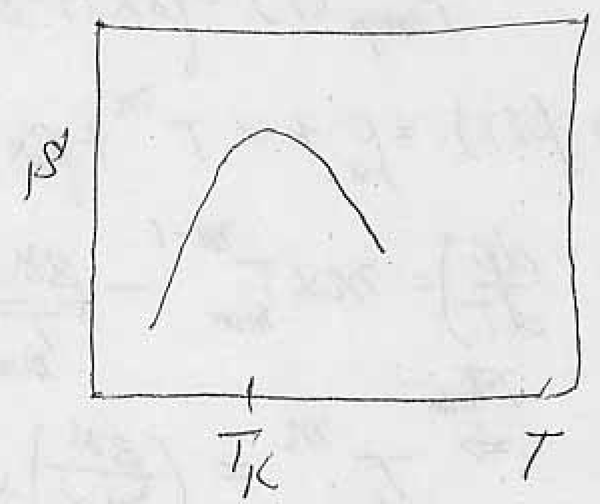
$$\rho = \rho_m^B \left[1 + 2N(E_F)\mathcal{J}\ln(T/T_F) + \ldots\right]$$

$$\rho_m^B = \frac{\pi m N(E_F)}{e^2 \hbar N} n \mathcal{J}^2 S(S+1)$$

Basic properties scale with T_K







Physical picture

Many body singlet forms as T decreases below T_K

AFM screening of $\underset{\sim}{S}$ by $\underset{\sim}{s}$'s of conduction electrons ($\underset{\sim}{S}\cdot\underset{\sim}{s}$,

Systems

3d transition metal (Cr, V, Mn, Fe, Ni); e.g., $Cu_{1-x}Fe_x$
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

$$T_K \sim T_F \exp(-1/N(E_F)|J|)$$

Thermodynamic T-scale

$$C_V = T f_c(T/T_K)$$

$$\chi \sim \mu_B^2 f_\chi(T/T_K)$$

Concentration dependence of T_{min}

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

$$\rho_{host}(T) = \rho_0 + \alpha T^m \qquad T \ll \Theta_D$$

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

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

$$\left.\frac{d\rho}{dT}\right)_{T=T_{min}} = m\alpha T_{min}^{m-1} - \frac{\beta\gamma x}{T_{min}} = 0$$

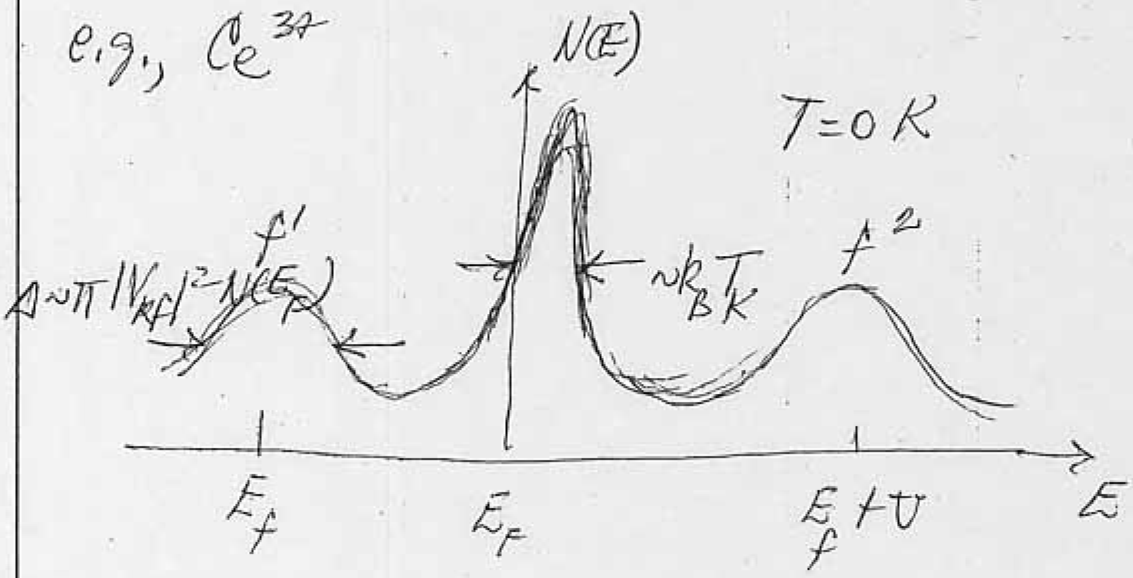
$$\Rightarrow T_{min}^m = \left(\frac{\beta\gamma}{m\alpha}\right) x \Rightarrow \boxed{T_{min} \propto x^{1/m}}$$

Bloch-Grüneisen $\Big\}$ $m = 5 \Rightarrow T_{min} \propto x^{1/5}$

NOTE: T_K is not at T_{min}!

T-dependent Kondo (Abrikosov - Suhl) resonance

e.g., Ce^{3+}



$T \gg T_K$: Local moment

$$\chi(T) \sim \frac{N\mu_{eff}^2}{3k_B(T-\theta)} \qquad -\theta_p = \beta T_K,\ \beta = 3\text{-}4$$

$\rho(T) \sim \ln T \rightarrow$ "Kondo minimum"

$T \ll T_K$: Many body singlet ground state

Local Fermi liquid, $T_F^* \sim T_K$

$\chi(T),\ C(T)/T \sim \text{const} \propto N(E_F) \sim 1/T_K$

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

$R_W = \dfrac{\delta\chi/\chi}{\delta\gamma/\gamma} = 2$ for $S = \frac{1}{2}$

Wilson-Sommerfeld ratio

free electron gas; $R_W = 1$

NOTE: magnetic $T \gg T_K$

nonmagnetic $T \ll T_K$