Intermediate valence in Yb Intermetallic compounds

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This talk concerns rare earth intermediate valence (IV) metals, with a primary focus on certain Yb-based intermetallics. The ground state is that of a heavy mass Fermi liquid. The d.c. and optical conductivity reflect the existence of a Fermi surface with large effective masses. On the other hand, properties such as the susceptibility, specific heat, valence and spin dynamics that are dominated by the spin fluctuations, which are highly localized, can be understood qualitatively (and sometimes quantitatively) as those of a collection of non-interacting Anderson/Kondo impurities. We will attempt to explain and justify these statements.

Talk at LBL, 12 April 2006

Intermediate Valence Compounds

$CeSn_3$	Fermi liquid (FL)	$YbAgCu_4$, $YbTlCu_4$
$CePd_3$	FL with anomalies	$YbMgCu_4$, $YbAl_3$

High symmetry (cubic) (e.g. fcc, Cu_3Au, C15B)
Hence, isotropic (3D)

Crystal fields unimportant: spin decay rate $k_B T_K/\hbar > k_B T_{cf}/\hbar$
Hence 4f moment degeneracy ($N_J = 2J + 1$) is
$N_J = 6$ (Ce); 8 (Yb)

Ground States:

Moderately heavy Fermi Liquids
(like a Fermi gas but with large effective mass)

Hybridization gap important, but

no antiferromagnetic (AF) correlations

Intermediate Valence (IV) = Nonintegral valence

= Partial occupation of the 4f shell

Yb:	$(5d6s)^3\ 4f^{13}$	$n_f = 1$	trivalent
	$(5d6s)^2\ 4f^{14}$	$n_f = 0$	divalent
$YbAl_3$	$(5d6s)^{2.75}\ 4f^{13.25}$	$n_f = 0.75$	IV

Basic physics:

Highly localized 4f orbital
Hybridization of 4f with conduction electrons
Strong on-site Coulomb interaction U between 4f electrons
preventing multiple occupancy of orbital

Oversimplified single ion model:

Two nearly-degenerate localized configurations
form hybridized w.f.:

$$a\ [4f^{13}(5d6s)^3> + b\ [4f^{14}(5d6s)^2>$$

where $a = \sqrt{n_f}$ and $b = \sqrt{(1 - n_f)}$

Other states $[4f^{12}(5d6s)^4>$, etc., are at very high energy.

Basic behavior of IV metals

High temperature limit: LOCAL MOMENT PARAMAGNET

Integral valence: $n_f \rightarrow 1$ $z = 2+n_f = 3$ Yb $4f^{13}(5d6s)^3$

Curie Law: $\chi \rightarrow C_J/T$ where $C_J = N\, g^2\, \mu_B^2\, J(J+1)/\, 3\, k_B$ $J = 7/2$ (Yb)

Full moment entropy: $S \rightarrow R\, ln(2J+1)$

$\Downarrow$

CROSSOVER

at Characteristic temperature T_K

$\Downarrow$

Low temperature limit: FERMI LIQUID

Nonintegral valence ($n_f < 1$) Yb $4f^{14-nf}(5d6s)^{2+nf}$

Pauli paramagnet: $\chi(0) \sim \mu_B^2\, \rho(\varepsilon_F)$

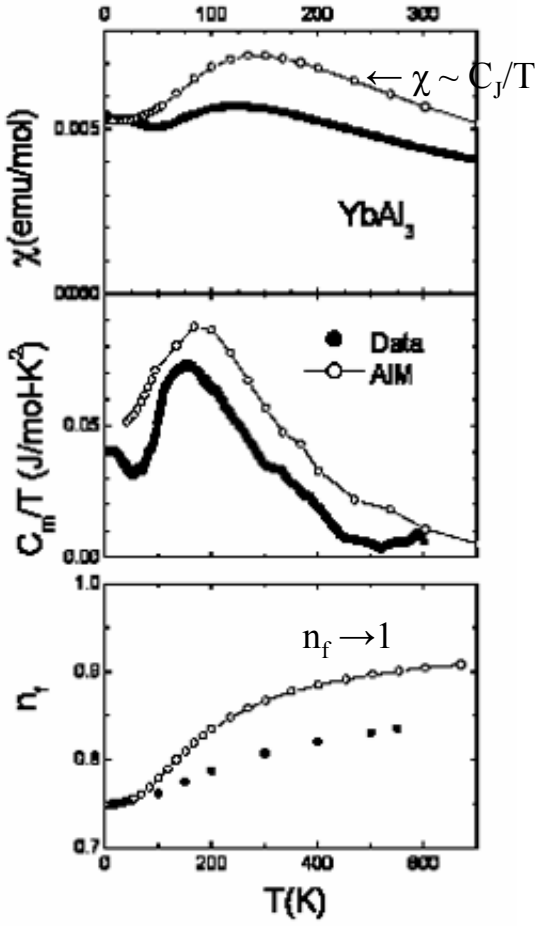
Linear specific heat: $C_v \sim \gamma\, T$

$\gamma = (1/3)\, \pi^2\, \rho(\varepsilon_F)\, k_B^2$

Note: Low T anomalies, relative the AIM, in $\chi(T)$ and $C(T)/T$.

$\chi(0) \rightarrow$

$\gamma \rightarrow$



Cornelius et al, PRL 88 (2002) 117201

FERMI LIQUID BEHAVIOR

A Fermi liquid is a metal where, despite the strong electron-electron interactions, the statistics at low T are those of a free (noninteracting) Fermi gas, but with the replacement m $\rightarrow$ m* (the *effective mass*).

The **specific heat** is linear in temperature $C = \gamma T$

$$\gamma = \{\pi^2 k_B^2 N_A Z/(3 h^3 \pi^2 N/V)^{2/3})\} m^*$$

For simple metals (e.g. K): $\gamma = 2$ mJ/mol-K^2

$m^* = 1.25\ m_e$

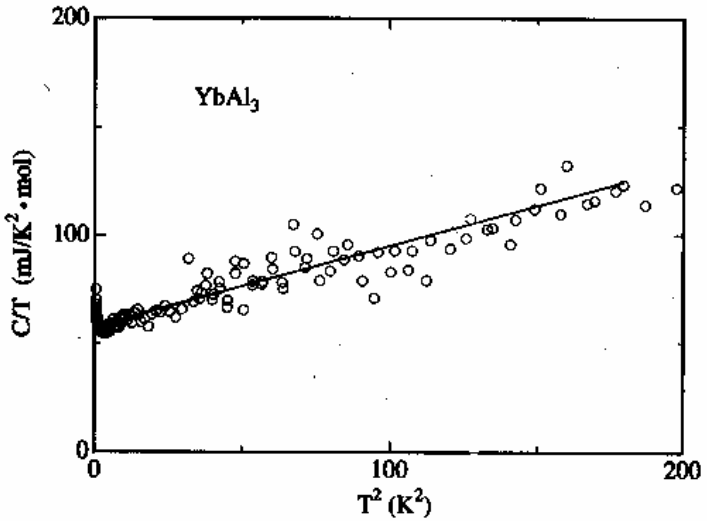
For $YbAl_3$: $\gamma = 45$ mJ/mol-K^2

$m^* \sim 25\ m_e$

$\rightarrow$ "Moderately HEAVY FERMION" compound

The Fermi liquid also exhibits **Pauli paramagnetism:**

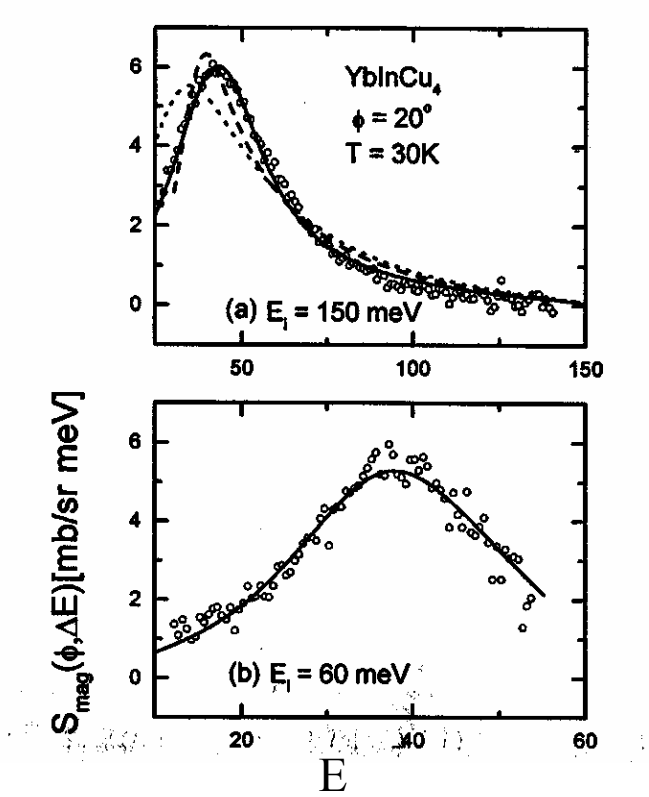
$YbAl_3$: $\chi(0) = 0.005$ emu/mol



C/T vs. T^2 for $YbAl_3$

$\gamma = 45$ mJ/mol-K^2

Ebihara et al
Physica B 281&282
(2000) 754



Spin fluctuation spectra $YbInCu_4$

$YbInCu_4$
Magnetic scattering
S_{mag} vs. E at two incident energies E_i

Lawrence, Osborn et al
PRB 59 (1999) 1134

Lorentzian power spectrum

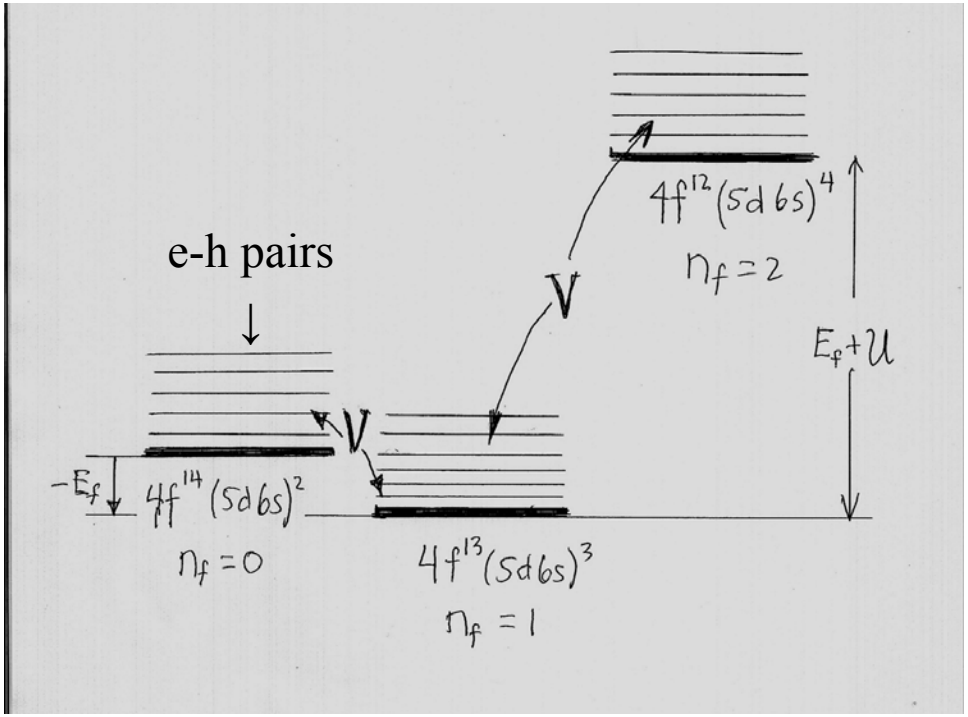
$$S(E) \sim \chi' E P(E) = \chi' E (\Gamma/2)/\{(E - E_0)^2 + \Gamma^2\}$$

Q-dependence: In $YbInCu_4$ (Lawrence, Shapiro et al, PRB 55 (1997) 14467) ***no dependence of Γ or E_0 on Q*** and only a weak (15%) dependence of χ' on **Q**.

Q-independent, broad Lorentzian response $\Rightarrow$

Primary excitation is a local, highly damped spin fluctuation (oscillation) at characteristic energy $E_0 = k_B T_K$

Anderson Impurity Model (AIM)



Highly localized $4f^{13}$ impurity orbital surrounded by a sea of conduction electrons

Nearly degenerate with $4f^{14}$ orbital

Energy separation: E_f

Strong on-site Coulomb interaction U between 4f electrons; $4f^{12}$ orbital at energy $E_f + U$ where $U >> V, E_f$

Hybridization V between configurations: conduction electrons hop on and off the 4f impurity orbital. Hybridization strength

$\Gamma = V^2\rho$ where ρ is the density of final (conduction) states.

Correlated hopping:

when $\Gamma \sim E_f << U$ then

hopping from $4f^{14}$ to $4f^{13}$ is allowed

but hopping from $4f^{13}$ to $4f^{12}$ is inhibited by the large value of U.

Characteristic features:

Mixed valence due to hybridization ($n_f < 1$)

Energy lowering due to hybridization:

$$k_B T_K \sim \varepsilon_F \exp\{-E_f/[N_J V^2 \rho(\varepsilon_F)]\}$$
$$\sim (1 - n_f) N_J V^2 \rho(\varepsilon_F)$$

The factor $(1 - n_f)$ reflects the correlations due to large U

Spin/valence fluctuation: localized*, *damped oscillator
with ***characteristic energy*** $E_0 = k_B T_K$:

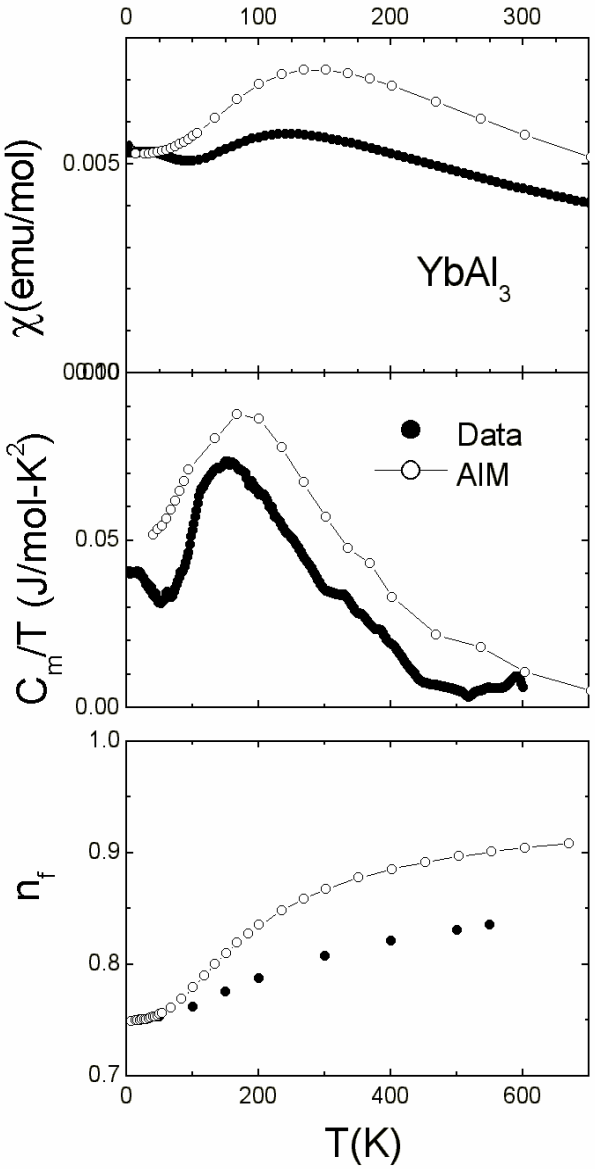
$$\chi'' \sim \chi(T) E \Gamma/((E-E_0)^2 + \Gamma^2)$$

Crossover: from ***Low temperature local Fermi liquid***
(nonintegral valence, Pauli paramagnetism, linear specific heat)
to ***local moment*** behavior for $T > T_K$
(integral valence, Curie law magnetism, R*ln*(2J+1) entropy)

Universality: Properties scale as T/T_K, $E/k_B T_K$, $\mu_B H/k_B T_K$ [Wilson ratio: $(\pi^2 R/3C_J)\, \chi(0)/\gamma \cong 1 + (1/2J)$]

VERY MUCH LIKE ACTUAL BEHAVIOR OF IV COMPOUNDS

Although intended for dilute alloys, (e.g. $Lu_{1-x}Yb_xAl_3$), because the spin fluctuations are local, the AIM describes much of the physics of periodic IV compounds.



Cornelius et al
PRL 88 (2002) 117201

Comparison to AIM
$YbAl_3$: Susceptibilty, Specific Heat, 4f occupation

AIM parameters

(Chosen to fit $\chi(0)$, $n_f(0)$ and $\gamma(LuAl_3)$)

W = 4.33eV
E_f = -0.58264eV
V = 0.3425eV
T_K = 670K

Comparison to AIM (continued)

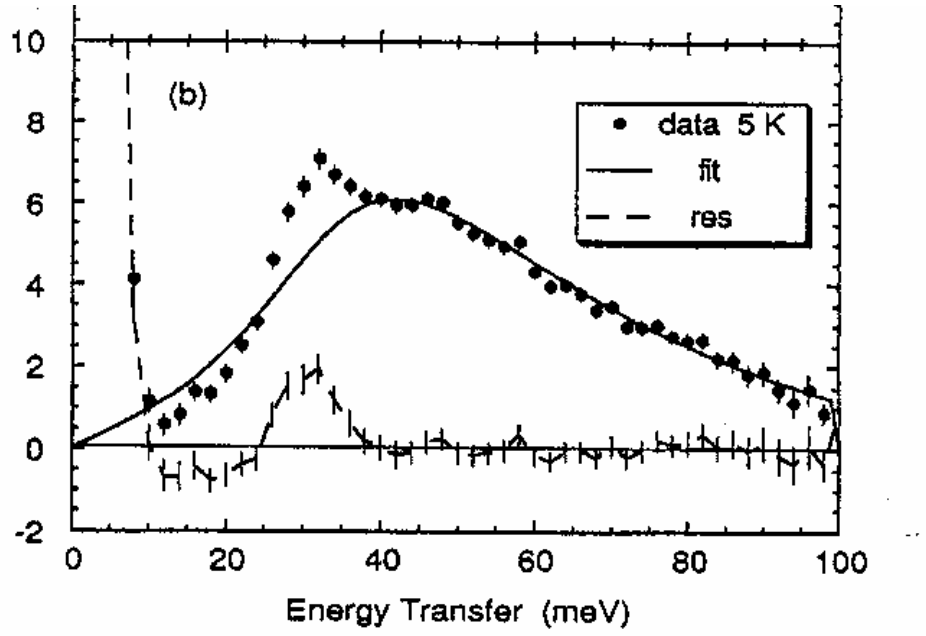
Murani, PRB 50 (1994) 9882

Low temperature spin dynamics
Neutron scattering:

At low temperature the neutron scattering exhibits an inelastic (IE) q-independent Kondo peak:

$\chi''(E) = \Gamma E / ((E- E_0)^2 + \Gamma^2)$

representing the strongly damped local excitation.



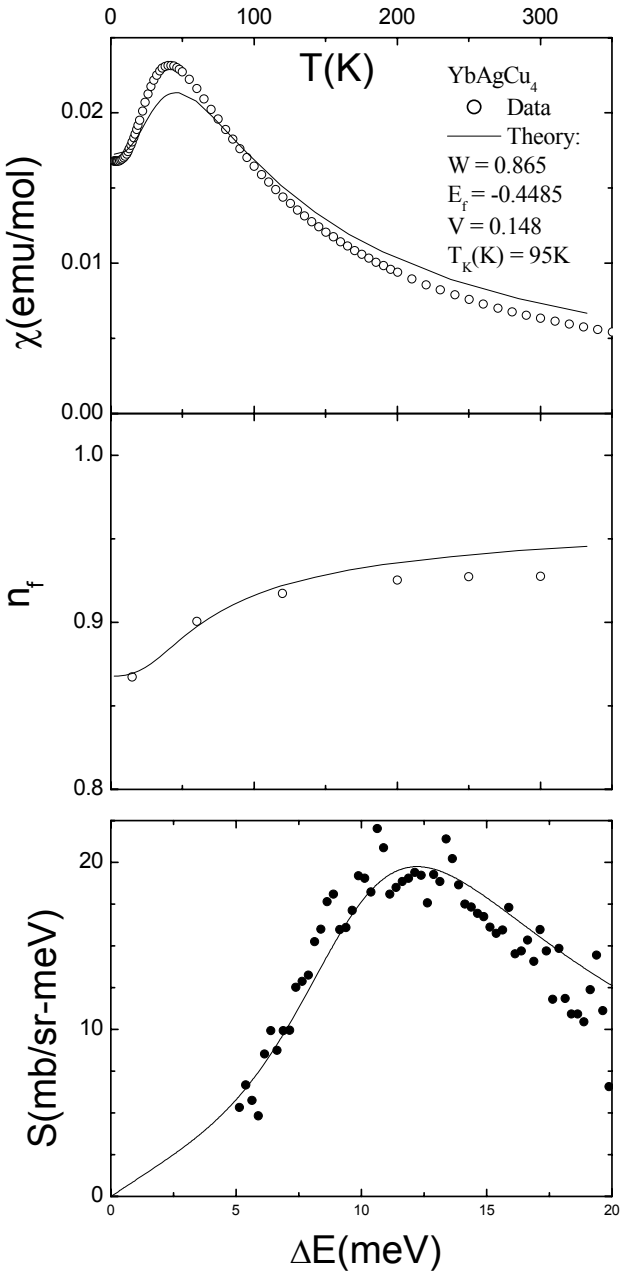
For the low-T Lorentzian power function seen in $YbAl_3$, experiment gives

$E_0 = 40$meV and $\Gamma = 25$meV

while the AIM calculation gives

$E_0 = 40$meV and $\Gamma = 22$meV

The experiment also exhibits a crossover to quasielastic behavior that is expected in the AIM



Fits to the AIM for $YbAgCu_4$:

O data

___ AIM

Excellent quantitative fits!

Lawrence, Cornelius, Booth, et al

Overall agreement with AIM (NCA):

Two parameters (E_f, V) chosen to fit $\chi(0)$ and $n_f(0)$
(plus one parameter for background bandwidth, chosen to agree with linear coefficient of nonmagnetic analogues $LuAl_3$ and $LuAgCu_4$)

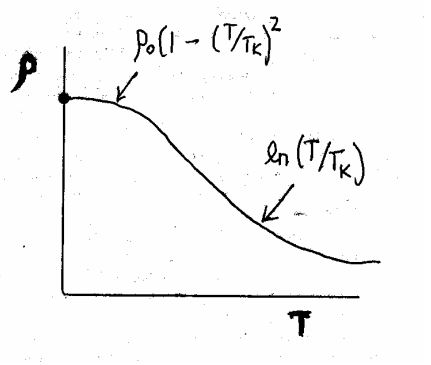
$YbAgCu_4$: Good quantitative fits to the T dependence of χ and n_f
and to the low T neutron spectrum

$YbAl_3$: Fits neutron spectral parameters at T = 0
Fits specific heat coefficient to 20%
It predicts the temperatures T_{max} of the maxima in susceptibility and specific heat to within 20%.

But the AIM predictions evolve more slowly with temperature than the data and there are low temperature anomalies in the susceptibility, specific heat and the neutron spectrum.

TRANSPORT BEHAVIOR OF IV COMPOUNDS

The AIM predicts a finite resistivity at T = 0 due to unitary scattering from the 4f impurity.



In an IV compound, where the 4f atoms form a periodic array, the resistivity must vanish.

(**Bloch's law**)

Typically in IV compounds

$\rho \sim A\,(T/T_0)^2$

This is a sign of Fermi Liquid "coherence" among the spin fluctuations.

$YbAl_3$ ρ vs T^2

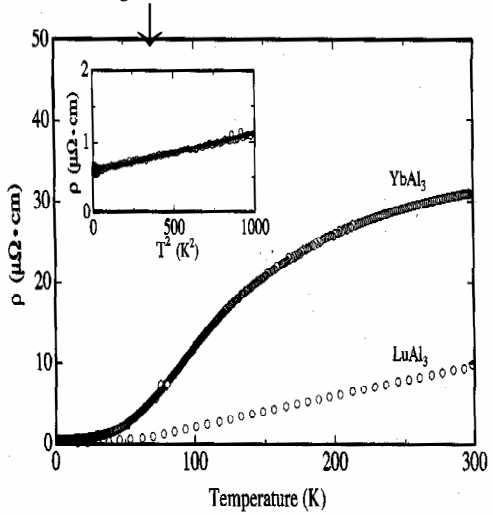


Fig. 1. Temperature dependence of the electrical resistivity of $YbAl_3$ and $LuAl_3$. The inset shows the T^2-dependence of the resistivity.

Ebihara et al
Physica B 281&282 (2000) 754

While the AIM is qualitatively good (and sometimes quantitatively, e.g. $YbAgCu_4$)
for χ (T), $C_v(T)$, $n_f(T)$ and $\chi''(\omega;T)$
to get correct transport behavior and to determine the Fermi surface

Coherent Fermi Liquid behavior $\Rightarrow$ Theory must treat 4f lattice

Two theoretical approaches to the Fermi Liquid State

Band theory: Itinerant 4f electrons: Calculate band structure in the LDA.

One-electron band theory (LDA) treats 4f electrons as itinerant;

it does a good job of treating the 4f-conduction electron hybridization.

It correctly predicts the topology of the Fermi surface.

But: **Band theory strongly underestimates the effective masses!**

LDA: $m^* \sim m_e$ dHvA: $m^* \sim$ 15-25 m_e

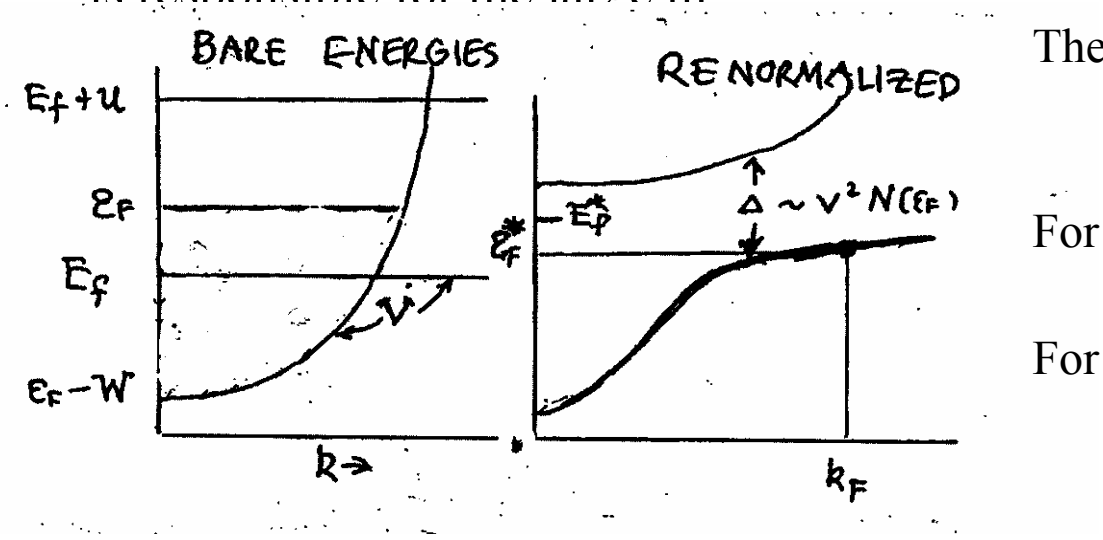
And, it can't calculate the temperature dependence.

Anderson Lattice Model: Localized 4f electrons

Put 4f electrons, with AIM interactions (E_f, V, U), on each site of a periodic lattice.
This loses the details of the Fermi surface
but gets the effective masses and the T-dependence correctly.

Bloch's law is satisfied for both cases.

If we extend the Anderson impurity model by having f-electron sites on a lattice, then the model involves *level crossing*: a narrow 4f band at an energy E_f below the Fermi level ε_F degenerate with and hybridizing (with matrix element V) with a wide conduction band whose density of states is ρ. In the absence of Coulomb correlations (U = 0) the hybridization and resulting level repulsion leads to a band structure with a hybridization gap of order $\Delta = N_J V^2 \rho$. The Coulomb interaction U inhibits the hopping when the site has the wrong occupation. This leads to an effective hybridization Hamiltonian with renormalized parameters, that are smaller than the bare parameters: $V_{eff} = (1-n_f)^{1/2} V$ and $U_{eff} = 0$. This gives rise to a coherent band structure with renormalized hybridized bands near the Fermi energy. The bands exhibit a hybridization gap Δ_{eff}; the indirect gap is of order T_K. The Fermi level lies in the high DOS region due to the large admixture of 4f states. The large DOS is responsible for the large m*



The structure renormalizes back to the bare energies with increasing temperature:

For very low $T << T_K$, fully hybridized bands.

For $T >> T_K$, local moments uncoupled from band electrons.

Optical conductivity

BEST EVIDENCE FOR THE HYBRIDIZATION GAP AND ITS RENORMALIZATION WITH TEMPERATURE

High temperature:

Normal Drude behavior:

$\sigma'(\omega) = (ne^2/m_b)\{\tau / (1 + \tau^2\omega^2)\}$

m_b is the bare band mass, τ is the relaxation time. Scattering from local moments.

$\Downarrow$

CROSSOVER

$\Downarrow$

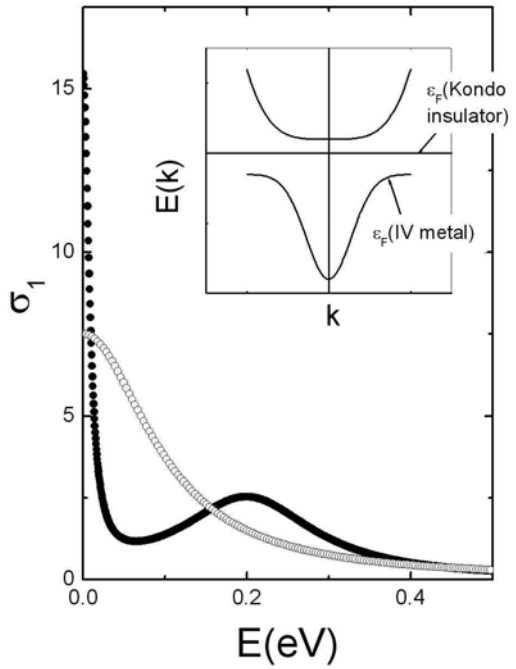
Low temperature:

1) IR absorption peak from vertical (Q = 0) transitions across hybridization gap

2) *Very* narrow Drude peak. Both m and τ renormalized:

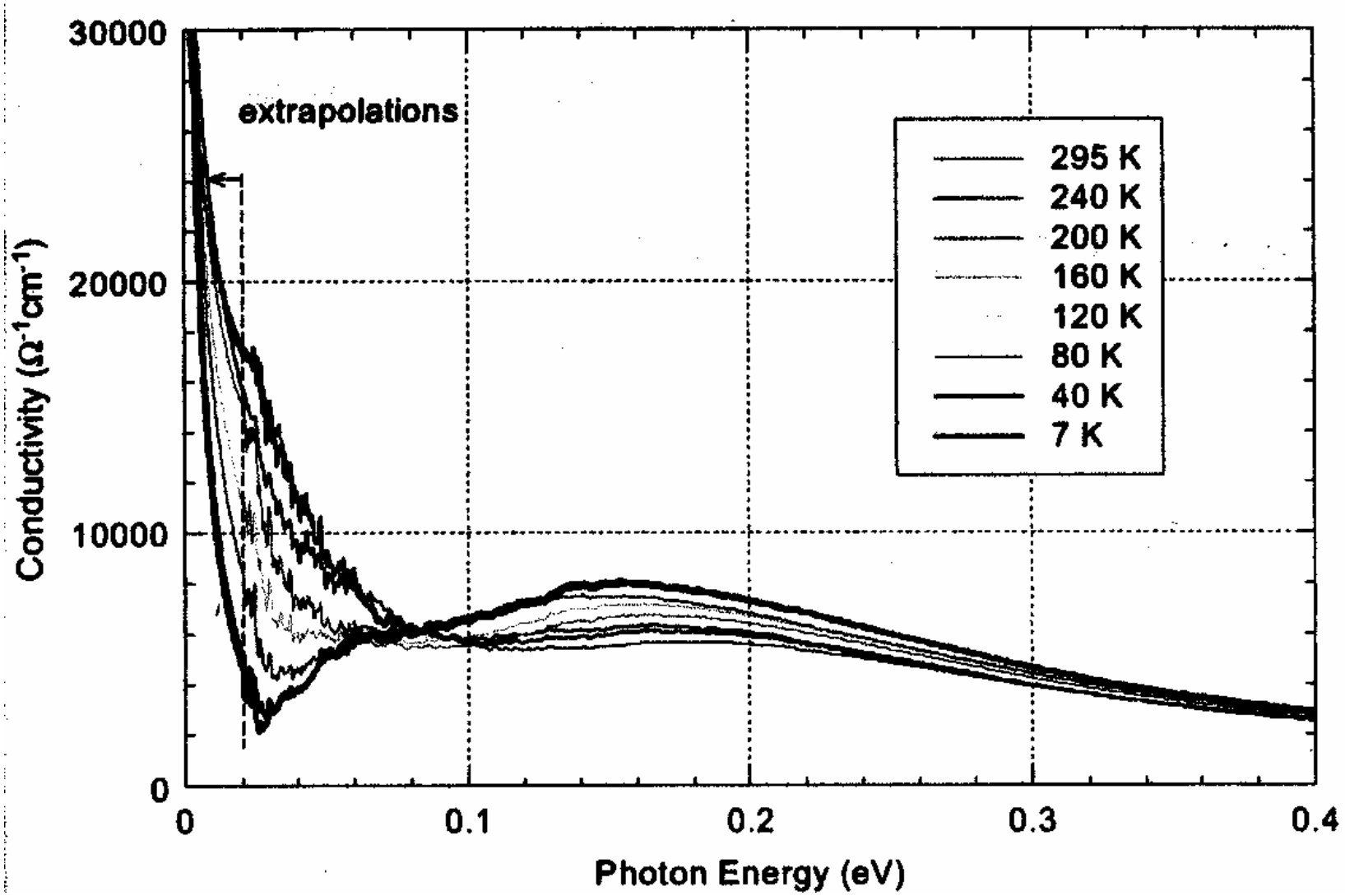
$m_b \rightarrow \lambda\, m_b = m^*$ $\qquad$ $\tau \rightarrow \lambda\, \tau = \tau^*$

$\sigma'(\omega) = ne^2\,[\tau^*/m^*]\,\{1/(1 + \tau^{*2}\omega^2)\}$



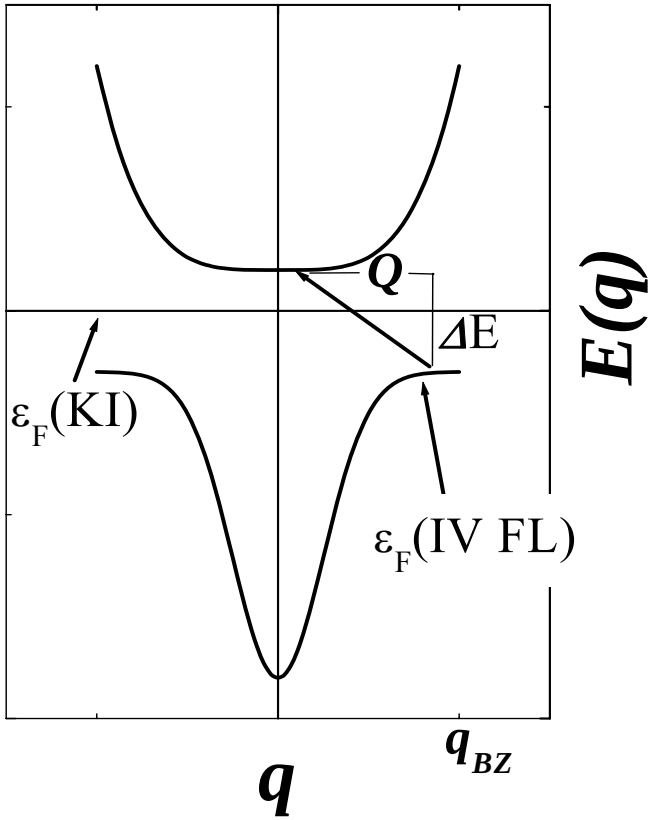
Optical conductivity $YbAl_3$

Okamura et al, J Phys Soc Japan 73 (2004) 2045

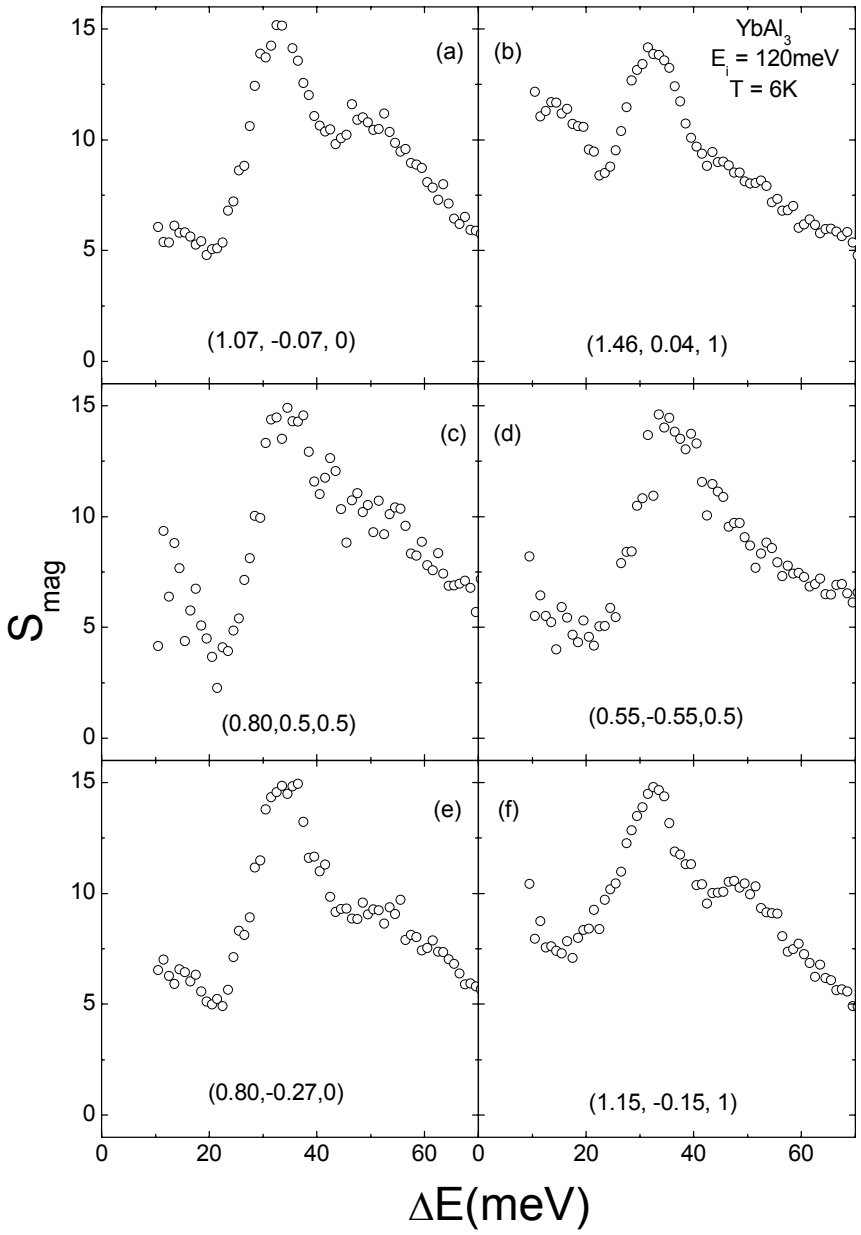


Neutron Scattering

Both interband (across the gap) and intraband (Drude-like scattering near the Fermi energy) are expected in the neutron scattering, but in this case excitations at energy transfer ΔE can have finite momentum, transfer $\boldsymbol{Q}$.



The intergap excitations, whose intensities are proportional to the joint (initial and final) density of states (DOS), should be biggest for zone boundary $\boldsymbol{Q}$ which connects regions of large 4f DOS. The energy for this case is the indirect gap. For smaller Q, the spectrum should be more like the optical conductivity (Q = 0), i.e. on the scale of the direct gap.



Christianson et al, PRL 96 (2006) 117206

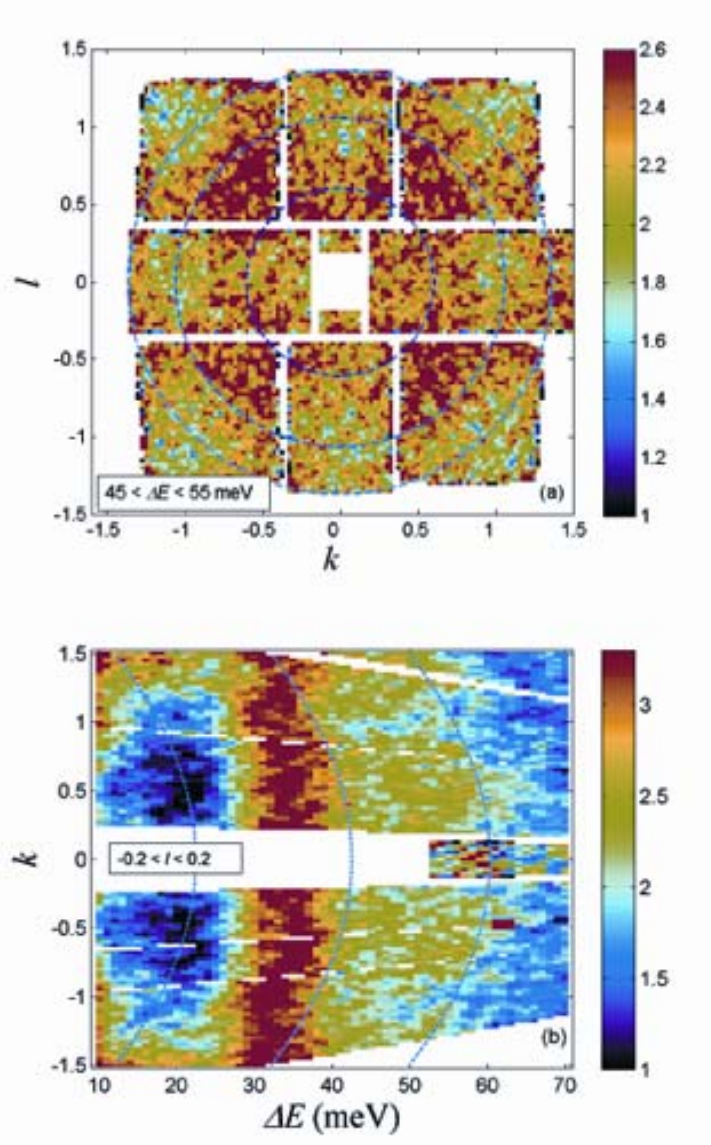
Neutron scattering $YbAl_3$

The low temperature magnetic scattering shows two features:

1) A broad feature near $E_1 = 50$ meV, which energy is essentially $k_B T_K$. This is most intense for zone boundary ***Q***.

2) A narrow feature near $E_2 = 30$ meV, the energy of the deep minimum in the optical conductivity. This is independent of Q.

Neutron scattering $YbAl_3$: Q dependence



Christianson et al, PRL 96 (2006) 117206

This plot integrates over the $E_1 = 50$ meV intergap excitation at various positions in the Q_K, Q_L scattering plane. Peak intensity occurs near

$$(Q_K,Q_L) = (1/2, 1/2)$$

i.e. at the zone boundary,

This Q-dependence is as expected for intergap transitions in the Anderson lattice

This plot integrates over Q at $Q_L = 0$. The band of constant color near $E_2 = 32$ meV means that the excitation is independent of Q along the Q_K direction.

Such an excitation does not occur in the theory of the Anderson lattice. It corresponds to a localized excitation in the middle of the hybridization gap – like a magnetic exciton.

Conclusions

Properties of IV compounds such as the susceptibility, specific heat, temperature-dependent valence and Q-integrated neutron scattering line shape, which are dominated by highly localized spin fluctuations, fit qualitatively and sometimes quantitatively to the Anderson impurity model.

Properties that are highly sensitive to lattice order – d.c. transport (resistivity), optical conductivity – require treatment of the lattice periodicity. Band theory gets the shape of the Fermi surface correctly, but can't get the large mass enhancements or the temperature dependence. Anderson lattice theory gets the mass enhancements and the temperature dependence but forsakes the Fermi surface geometry. It predicts key features of the optical conductivity and the neutron scattering, in particular that there will be a hybridization gap, with intergap transitions strong for momentum transfer $\boldsymbol{Q}$ at the zone boundary.

However, there are many anomalies: the susceptibility and specific heat are enhanced at low T relative the models, and evolve more slowly with temperature than expected based on the AIM. In addition, there appears to be a localized excitation in the hybridization gap that is also not predicted by the models.