Intermediate valence metals: Current issues

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The ground state of rare earth intermediate valence (IV) metals is that of a heavy mass Fermi liquid. The transport, optical conductivity and dHvA signals reflect the existence of a Fermi surface with strongly renormalized 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 show that anomalies exist in some compounds both in the low temperature behavior and in the rate of crossover from Fermi liquid to local moment behavior.

Collaborators

Los Alamos (LANL): Joe Thompson, John Sarrao, Mike Hundley, Eric Bauer
Crystal growth, $\chi(T)$, C(T), $R_H$, $\rho(H)$

NHMFL/LANL Alex Lacerda, Myung-Hwa Jung, Neil Harrison
$\rho(H)$, M(H), dHvA

LBL Corwin Booth $n_i(T)$ (L$_3$ XRA)
Takao Ebihara Crystal growth; dHvA
Andrew Cornelius M(H); dHvA
Peter Riseborough Theory (NCA)

Shizuoka U. Ray Osborn $\chi''(\omega)$ (neutron scattering)

U. Nevada, Las Vegas

Temple U.

IPNS @ ANL

HFBR @ BNL

Ray Osborn

Steve Shapiro
**Intermediate Valence Compounds**

- CeSn$_3$      Fermi liquid (FL)      YbAgCu$_4$, YbTlCu$_4$
- CePd$_3$      FL with anomalies     YbMgCu$_4$, YbAl$_3$
- Ce$_3$Bi$_4$Pt$_3$ Kondo Insulators YbB$_{12}$
- $\alpha$-Ce/$\gamma$-Ce   Valence Transitions YbInCu$_4$

*Archetypal class of solids subject to electron correlations.*

More complex than TM’s (e.g. Pd) or 3D one-band Hubbard Model
Less complex than TM oxides (e.g. high-T$_c$) which have multiple bands, 2D character, possible hidden order, QCP

**Comparison to Heavy Fermions (HF)**

<table>
<thead>
<tr>
<th>IV</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low symmetry (tet, hex)</td>
<td>High symmetry (cubic)</td>
</tr>
<tr>
<td>Anisotropy (sometimes 2D effects)</td>
<td>Isotropic (3D)</td>
</tr>
<tr>
<td>CF doublet ground state: $T_K &lt; T_{cf}$</td>
<td>CF unimportant: $T_K &gt; T_{cf}$</td>
</tr>
<tr>
<td>$N_J = 2J + 1 = 2$</td>
<td>$N_J = 6$ (Ce); 8 (Yb)</td>
</tr>
<tr>
<td>Proximity to QCP: AF correlations</td>
<td>Proximity to Kondo Insulator: Hybridization gap; No AF correlations</td>
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**GROUND STATES:**

- Very heavy FL
- Marginal FL
- HF superconductivity
- Miniscule moment AF (And: first order valence transitions)

*In this talk we focus on IV metals, with FL ground states*
High temperature limit:

**LOCAL MOMENT PARAMAGNET**

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

Curie Law: \( \chi \rightarrow C_J/T \) \( T\chi/C_J \rightarrow 1 \)
\( C_J = N g^2 \mu_B^2 J(J+1)/3 k_B \)
\( J = 7/2 \) (Yb)
\( 5/2 \) (Ce)

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

\( \Downarrow \)

CROSSOVER

at Characteristic temperature \( T_0 \)

\( \Downarrow \)

Low temperature limit:

**FERMI LIQUID**

Nonintegral valence \( (n_f < 1) \)

Yb \( 4f^{14-nf}(5d6s)^{2+nf} \)

Ce \( 4f^{nf}(5d6s)^{4-nf} \)

Pauli paramagnet:

\( \chi(0) \sim \mu_B^2 N(\varepsilon_F) \)

Linear specific heat:

\( S \sim C_v \sim \gamma T \)

\( \gamma = (1/3) \pi^2 N(\varepsilon_F) k_B^2 \)
Example: YbAl$_3$ ground state

Ground state Valence (IV):

YbAl$_3$ \((5d6s)^{2.75} 4f^{13.25}\) \(n_f = 0.75\) IV

Pauli paramagnetism:

YbAl$_3$: \(\chi(0) = 0.005\) emu/mol

Specific heat:

In a Fermi liquid, \(\gamma = \left\{ \pi^2 k_B^2 N_A Z / (3 \ h^3 \pi^2 N/V)^{2/3} \right\} m^*\)

For simple metals (e.g. K): \(\gamma = 2mJ/mol-K^2\) and \(m^* = 1.25m_e\)

For YbAl$_3$: \(\gamma_m = 40mJ/mol-K^2\) and \(m^* = 20m_e\)

\(\rightarrow\) “Moderately HEAVY FERMION” compound

C/T vs. T$^2$ for YbAl$_3$

Ebihara et al
Physica B281&282
(2000) 754
Lorentzian power spectrum

\[ \chi''(Q,E) = (n(E)+1) f^2(Q) \chi'(Q) P(E) \]

\[ P(E) = \left( \frac{\Gamma}{2} \right) \left\{ \left( E - E_0 \right)^2 + \Gamma^2 \right\}^{-1} + \left( E + E_0 \right)^2 + \Gamma^2 \right\}^{-1} \]

\[ f^2(Q) : \text{4f form factor} \]

Q-dependence: In one of the only single x-tal IV metals studied (YbInCu4) (Lawrence, Shapiro et al, PRB55 (1997) 14467) the scattering at five Q in the BZ showed no dependence of \( \Gamma \) or \( E_0 \) on Q and only a weak (15%) dependence of \( \chi' \) on Q.

Q-independent, broad Lorentzian response \( \Rightarrow \)

Primary excitation is a local, highly damped spin fluctuation (oscillation) at characteristic energy \( E_0 = k_B T_0 \)

WHERE IS THE FERMI LIQUID SCATTERING?
Anderson Impurity Model (AIM)

\[
H_{AI} = H_0 + H(i) + V(i)
\]

\[
H_0 = \sum_k \epsilon_k n_k
\]

\[
H_f(i) = \epsilon_f n(i) + U n_f(i) n_{f\dagger}(i)
\]

\[
V(i) = \sum_k V_{kf} c_k^+ f(i) + c.c.
\]

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

**Characteristic features:**

**Kondo Resonance:**

a low energy peak in the renormalized density-of-states (DOS) at

\[
k_B T_K \sim \epsilon_F \exp\{-E_f/(N_j V^2 N(\epsilon_F))\}
\]

**Spin/valence fluctuation:** localized, damped oscillator with characteristic energy \(k_B T_K: \chi'' \sim \chi(T) E \Gamma/((E-E_0)^2 + \Gamma^2)\)

\(E_0 = k_B T_K\)

**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: \((\pi^2 R/3C_J)\chi(0)/\gamma \approx 1 + (1/2J)\)

**VERY MUCH LIKE ACTUAL BEHAVIOR OF IV COMPOUNDS**
**YbAl₃**: Susceptibility, Specific Heat, 4f occupation

Data vs. AIM

### AIM parameters

(Chosen to fit $\chi(0)$, $n_f(0)$ and $\gamma(LuAl₃)$)

- $W = 4.33\,\text{eV}$
- $E_f = -0.58264\,\text{eV}$
- $V = 0.3425\,\text{eV}$
- $T_K = 670\,\text{K}$

### Wilson ratio:

The AIM predicts that the normalized ratio of susceptibility to specific heat should be

$$\left(\frac{\pi^2 R}{3C_J}\right)\frac{\chi(0)}{\gamma} \simeq 1 + \frac{1}{2J} = \frac{8}{7}$$

The experiment gives $1.3-1.4$. 

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Cornelius et al.
PRL88 (2002) 117201
Fits to the AIM: \( n_f(T) \)

- Good quantitative fits for YbAgCu\(_4\) and YbTlCu\(_4\).
- Slow crossover for YbMgCu\(_4\), YbCdCu\(_4\) and YbZnCu\(_4\)

Note: Good quantitative fits for YbAgCu\(_4\) and YbTlCu\(_4\). but **Slow crossover** for YbMgCu\(_4\), YbCdCu\(_4\) and YbZnCu\(_4\)
Fits to the AIM: $\chi(T)$

Symbols: data
Lines: AIM

Note: Good quantitative fits for YbAgCu$_4$ and YbTICu$_4$ but **Slow crossover** for YbMgCu$_4$, YbCdCu$_4$ and YbZnCu$_4$
Low temperature spin dynamics

At low temperature the neutron scattering exhibits an inelastic (IE) q-independent Kondo peak:
\[ \chi''(E) = \frac{\Gamma E}{((E- E_0)^2 + \Gamma^2)} + \text{anti-Stokes} \]
representing the strongly damped local excitation. For YbAl\(_3\) the parameters of the low temperature peak are \( E_0 = 40\)meV and \( \Gamma = 25\)meV which compare favorably to the AIM values \( E_0 = 40\)meV and \( \Gamma = 25\)meV

For YbAgCu\(_4\) the parameters of the AIM fit \( E_0 = 11\)meV and \( \Gamma = 7\)meV are equal to the measured values

Overall agreement with AIM (NCA):
Two parameters (\( E_f, V \)) chosen to fit \( \chi(0) \) and \( n_f(0) \)

YbAgCu\(_4\): Fits T dependence of \( \chi \) and \( n_f \)
    and low T neutron spectral parameters
YbTlCu\(_4\): Fits T dependence of \( \chi \) and \( n_f \)
YbAl\(_3\): Fits neutron spectral parameters at T = 0
    Fits specific heat coefficient to 20%
    Fits \( T_{\text{max}} \) for \( \chi \) and \( \gamma=C/T \) to 20%
BUT: AIM predictions evolve more rapidly with temperature than
the data for YbMgCu\(_4\), YbCdCu\(_4\) and YbAl\(_3\) and there are low-T anomalies in the latter compound.
TRANSPORT BEHAVIOR OF IV COMPOUNDS

The AIM predicts a finite resistivity at $T = 0$ (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.

In YbAl$_3$ this occurs below the “coherence temperature”

$$T_{\text{coh}} \sim 40K$$

Two theoretical approaches to the Fermi Liquid

Band theory: Itinerant 4f electrons (LDA) with correlations:

a) LDA + U, or
b) Add Kondo physics through Renormalized Band Method

Anderson Lattice Model: Localized 4f electrons

a) Ignore intersite contributions


b) Large $N_J = 2J+1$ methods

Georges et al, PRL 85 (2000) 1048


c) Dynamic Mean Field


Ebihara et al

The de Haas van Alphen experiment measures oscillations in the magnetization as a function of inverse magnetic field.

The frequency of the oscillations is determined by the areas $S$ of the extremal cross sections of the Fermi surface in the direction perpendicular to the applied field.

$$ M = A \cos(2\pi F/H) $$

$$ F = \frac{hc}{2\pi e} S $$

The temperature dependence of the amplitude determines the effective mass $m^*$

$$ A = \frac{1}{\sinh(Q m^* T/H)} $$

where $Q$ is a constant
For IV compounds LDA gives the correct extremal areas!

One-electron band theory (LDA) treats 4f electrons as itinerant. It correctly predicts the topology of the Fermi surface as observed by dHvA.

But: **LDA strongly underestimates the effective masses!**

LDA badly overestimates the 4f band widths and consequently strongly underestimates the effective masses:

\[
\text{LDA: } m^* \sim m_e \\
\text{dHvA: } m^* \sim 15-25m_e
\]

LDA also tends to make Yb compounds (including YbAl\(_3\)!!) be divalent. Large masses and intermediate valence can be obtained by LDA + U
(For YbAl\(_3\) the correct valence was obtained by forcing the 4f level energy in the LDA)
ANDERSON LATTICE

For a periodic IV compound the appropriate model is

\[ H = \sum_{k} \varepsilon_k n_k + \sum_i \{ E_f n_{fi} + U n_{fi\uparrow} n_{fi\downarrow} + \sum_k [V_{kf} c_{ki}^+ f_i + cc] \} \]

This leads to a coherent band structure with (renormalized) hybridized bands near the Fermi energy. The bands exhibit a hybridization gap; 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 away with increasing temperature:

For very low T << T_K
Fully hybridized bands

For T ~ T_K,
No gap
Incoherent Kondo resonances

For T >> T_K
Local moments uncoupled from band electrons

Spin dynamics should exhibit:

Fermi liquid scattering across \( \varepsilon_F^* \)
Q-dependent gap scattering, peaking at Zone Boundary

THESE HAVE NOT OBSERVED IN ANY IV METAL!!
**Optical conductivity**

**BEST EVIDENCE FOR THE HYBRIDIZATION GAP AND ITS RENORMALIZATION WITH TEMPERATURE**

**High temperature:**
Normal Drude behavior:

\[ \sigma'(\omega) = \left(\frac{ne^2}{m_b}\right) \left\{ \frac{\tau}{(1 + \tau^2 \omega^2)} \right\} \]

- \(m_b\) is the bare band mass
- \(\tau\) is the relaxation time.

\[ \Downarrow \]

CROSSOVER

\[ \Downarrow \]

**Low temperature:**

1) IR absorption peak from transitions across hybridization gap
2) *Very* narrow Drude peak. Both \(m\) and \(\tau\) renormalized.

\[ m_b \to \lambda m_b = m^* \quad \tau \to \lambda \tau = \tau^* \]

\[ \sigma'(\omega) = ne^2 \left\{ \frac{\tau^*}{m^*} \right\} \frac{1}{(1 + \tau^{*2} \omega^2)} \]

Okamura, Ebihara and Namba, cond-mat/0208006

**RENORMALIZATION COMPLETE BELOW** \( T_{coh} = 40K \)**
Assuming frequency-dependent scattering
\[ \sigma(\omega) = \frac{ne^2}{mb} \left[ \gamma(\omega) - i\omega \right]^{-1} \]
then the mass enhancement
\[ m^* = \lambda m_b \]
\[ \lambda(\omega) = -\text{Im}[\gamma(\omega)]/\omega \]
is both frequency and temperature dependent

For YbAl$_3$ this procedure gives $m^* \sim 25-30$, comparable to the dHvA masses.
CePd$_3$ optical conductivity

Development of renormalized Drude with decreasing temperature is connected with a transfer of spectral weight over large (eV) energy scales.

Observation of the full renormalized Drude response requires microwave conductivity measurement (using resonant cavity)

Assuming frequency-dependent scattering

\[ \sigma(\omega) = \left( \frac{ne^2}{m_b} \right) \left[ \gamma(\omega) - i\omega \right]^{-1} \]

then the mass enhancement

\[ m^* = \lambda m_b \]

\[ \lambda(\omega) = -\text{Im}[\gamma(\omega)]/\omega \]

is both frequency and temperature dependent

For YbAl$_3$ this procedure gives $m^* \sim 25-30$, comparable to the dHvA masses.
Two energy scales and slow crossover in the Anderson Lattice

While the transport behavior and the Fermi surface (dHvA) are affected by Fermi liquid coherence, we have seen that experimental quantities such as the specific heat, susceptibility, valence and spin dynamics are qualitatively in good accord with the predictions of the AIM over a broad range of temperature. This reflects highly localized spin/valence fluctuations.

Nevertheless, recent theory for the Anderson Lattice suggests that the behavior of these latter quantities can differ in two ways from the predictions of the AIM:

1) Non-universal low temperature scale for coherence and/or Low temperature anomalies

![Graphs showing non-universal low temperature scale for coherence and/or Low temperature anomalies.](Image)

Antoine Georges et al, PRL 85 (2000) 1048

2) Slow crossover from Fermi Liquid to Local Moment

![Graphs showing slow crossover from Fermi Liquid to Local Moment.](Image)


Theory predicts that these differences become magnified when the conduction electron or hole density is low.
Slow crossover in YbAl$_3$

We have seen that slow crossover in $\chi(T)$ and $n_f(T)$ occurs for YbXCu$_4$
It has been correlated to electron density $n_e = 1/R_H e$ determined from the Hall coefficient (Lawrence et al, PRB 63 (2001) 054427)

YbAgCu$_4$, YbTlCu$_4$  $n_e > 1\text{e/atom}$  No slow crossover
YbMgCu$_4$, YbZnCu$_4$  $n_e < 1\text{e/atom}$  Slow crossover

For YbAl$_3$

$n_e = 1/R_H e = 0.5 \text{e/atom}$
slow crossover is observed for entropy, susceptibility and 4f occupation number

Symbols: expt. Data
Lines: AIM

Cornelius et al
PRL88 (2002) 117201
Low temperature form factor and susceptibility anomalies in CePd$_3$

The neutron form factor measures the spatial distribution of magnetization around the Ce or Yb site.

At high T the form factor has the same Q (or r) dependence $f^2(4f;Q)$ as the 4f radial function. (Solid line)

In CePd$_3$ at low T a more diffuse 5d component $f^2(5d;Q)$ is present:
\[ f^2(Q) = a^2 f^2(4f) + (1-a^2) f^2(5d) \] (Dashed line)

The 5d contribution gives rise to an anomalous increase in the low temperature (T < 50K) susceptibility over and beyond the Kondo peak (which is near 150K).
Low temperature anomalies in YbAl$_3$

Above 40K the **susceptibility** and **specific heat** correspond qualitatively to the predictions of the AIM. Below 40K, **anomalies** are observed. These anomalies are destroyed rapidly by alloying (Bauer et al) indicating the importance of lattice coherence in the anomalies.

The anomalies occur on the same temperature scale $T_{coh}$ as the fully renormalized optical conductivity and the Fermi liquid $T^2$ resistivity. We note $T_{coh} \sim n_f T_K/(2J+1)$

However, in YbAl$_3$, there is **no form factor anomaly** -- the magnetization density is that of the 4f orbital at all temperatures (solid lines).
New peak in low temperature spin dynamics

We have seen that for most temperatures and energies the magnetic neutron scattering in YbAl$_3$ follows the predictions of the AIM, with a Lorentzian power spectrum with $E_0 = 40\text{meV}$ and $\Gamma = 25\text{meV}$

At low $T$, there is an additional narrow peak with $E_0 = 30\text{meV}$ and $\Gamma = 5\text{meV}$ This peak vanishes above 50K, and hence appears to be a property of the fully coherent ground state.

Magnetotransport anomalies

Anomalies in the Hall coefficient and magnetoresistance are observed in this same temperature range.

Since $R_H \sim 1/ne$ this suggests a change in carrier density. The onset of coherent Fermi liquid behavior appears to involve a change in the Fermi surface.

Cornelius et al
PRL 88 (2002) 117201
High field dHvA shows that the effective masses for $H//<111>$ decrease substantially for $H > 40\,\text{T}$. This field is much smaller than the Kondo field $B_K = kT_K/gJ\mu_B$ required to polarize the f electrons, but is of order $k_B T_{\text{coh}}/\mu_B$.

A field of this magnitude also suppresses the low temperature susceptibility anomaly.

It is as though that the system exhibits a crossover from a anomalous high mass Fermi Liquid state to a non-anomalous moderately enhanced Fermi liquid state for $\mu_B H > k_B T_{\text{coh}}$. 
The low temperature anomalies in the susceptibility and specific heat are very sensitive to alloy disorder, and disappear for alloy concentrations as small as \( x = 0.05 \) in \( \text{Yb}_{1-x}\text{Lu}_x\text{Al}_3 \). Apparently the enhanced masses observed below \( T_{\text{coh}} \) are very sensitive to lattice coherence.
Summary

The Kondo temperature $T_K \sim 500 \text{K}$ sets the main scale for the crossover from local moment behavior to nonmagnetic behavior in IV compounds. At high $T$ the behavior is that of uncorrelated Kondo impurities; the AIM works qualitatively (sometimes quantitatively) for $\chi(T), n_f(T)$ and $\chi''(\omega)$.

Below a lower temperature scale for the onset of coherence ($T_{coh} \sim 30-50 \text{K}$)

The following should occur in all compounds:

1) The resistivity shows $T^2$ behavior. All compounds

2) Onset of fully renormalized mass in the optical conductivity Direct observation: CePd$_3$
   Extrapolation: YbAl$_3$; YbFe$_4$Sb$_{12}$

3) Onset of fully developed hybridization gap CePd$_3$; YbFe$_4$Sb$_{12}$; YbAl$_3$

4) Large effective masses in dHvA CeSn$_3$, CeNi, YbAl$_3$

5) Anomaly in the Hall coefficient CeBe$_{13}$, CePd$_3$, CeSn$_3$, YbAl$_3$
   indicating a change in carrier density.

6) FL scattering and Q-dependent gap scattering expected in $\chi''(Q,\omega)$ Not observed for any compound

The following anomalies occur in some, but not all, compounds:

7) New peak in $\chi$ CePd$_3$, YbAl$_3$ (Maybe CeSn$_3$, not YbAgCu$_4$)

8) New peak in $C/T$ YbAl$_3$

9) New peak in the spin dynamics: YbAl$_3$, (Maybe CeNi; not YbAgCu$_4$)

10) $5d$ contribution to the form factor CePd$_3$ (Maybe CeSn$_3$, not YbAl$_3$)

11) Suppression of dHvA mass at $B \sim k_B T_{coh}/\mu_B << B_K = k_B T_K/g\mu_B$ YbAl$_3$

12) Slow crossover from low temperature Fermi liquid to high temperature paramagnet YbAl$_3$, YbMgCu$_4$
   (not YbAgCu$_4$, YbTlCu$_4$)