Magnetic Scattering in the 4f-Intermediate Valence Compound CePd$_3$

ICNS 2009

Victor Fanelli
Jon Lawrence, CuiHuan Wang
Andrew D. Christianson, Mark D. Lumsden
Eugene A. Goremychkin, Raymond Osborn
Eric D. Bauer, Kenneth J. McClellan

Los Alamos National Laboratory
University of California - Irvine
Oak Ridge National Laboratory
Argonne National Laboratory
Los Alamos National Laboratory

Work at Los Alamos, supported by NSF, the State of Florida and the US D.O.E.
Work at UC Irvine supported by D.O.E. under Grant No. DEFG03-03ER46036
Intermediate valence metals:

- **Fermi Liquid** ground state that evolves towards a high-\(T\) local moment regime.

The **Anderson lattice model** applicable to these compounds, capturing:

- band-like **coherent character** in the low-\(T\) limit, and
- **local moment** character at high-\(T\)

Physical properties reveal the effects of the lattice coherence.

However ..........

Other properties, depending on spin fluctuations, are better described by the **Anderson impurity model**, despite the magnetic moments sit on a lattice.
Anderson Impurity Model (AIM)

Good semi-quantitative agreement with AIM

\[ \chi_{\text{AIM/NCA}} \]

\[ T = 7 \text{ K} \]

\[ \chi_{\text{AIM/NCA}} \]

\[ E_{i} = 120 \text{ meV} \]

\[ E \sim k_{B}T_{K} \]

\[ \chi(T) = C_{J}/(T + \theta) \]

Non-crossing approx. (NCA)

C. Booth, private communication
**Anderson Lattice Model**

*Spectrum of S(Q, E) for different values of momentum transfer q*

- **Inter-band transitions**: The high energy peak is maximum for q at zone boundary. It shifts to high E with decreasing q.
- **Intra-band transitions**: The low energy peak moves to high E as q increases towards zone boundary.


Motivation

- **magnetic scattering**
  - spectral response
  - dependence over the reciprocal space

- elucidate

- character of the spin fluctuations:
  - Local / coherent?

This Q-dependence has remained an open question

Most of INS performed on polycrystalline samples.

Only four compounds studied by INS on single crystals
Magnetic and non-magnetic Scattering

MAPS spectrometer
7 K, $E_i=60$ meV

$2\pi/a_0$ $(0,k,0)$

- Phonon Scattering dominant
- Magnetic scattering

Multiple Scattering (+ Multi-phonons) and

Non-magnetic Scattering

Represented by “scaled LaPd$_3$”

CePd$_3$ and scaled LaPd$_3$

$E_{\text{transfer}}$ (meV)

Intensity (mb/sr-meV)

Energy transfer $E$ (meV)

Difference should account for magnetic contribution to the scattering
Inelastic Neutron Scattering on CePd$_3$

Distribution of the intensity over momentum transfer space:
- Relatively uniform at room temperature

To explore the Q-dependence
- Look at different regions in Q-space
CePd₃ at 300 K (~½ $T_K$)

Magnetic component of the scattering

- Quasi-elastic Lorentzian
- Q-independent

\[
S_{\text{magn}}(Q, E) = \frac{1}{(1 - e^{-E/k_B T})} f^2(Q) \frac{E A_L}{\pi} \frac{\Gamma}{E^2 + \Gamma^2}
\]

with $\Gamma = 27$ meV

Q-independence implies a **local character** for spin fluctuations as expected for high-$T$ **uncorrelated local moment** limit
**CePd$_3$ at 7 K (Low-T regime)**

Magnetic scattering of CePd$_3$ at four regions in the (k,l) plane

- Variations of intensity ~ 25%
- Similar Inelastic Lorentzians

**Q-dependence not as drastic as expected by Anderson Lattice model**

(NO shift of spectral weight)

Average: $\Gamma = 43.5$ meV

$E_0 = 45$ meV
CePd₃ (Low-T)
Triple-axis spectrometer

Constant-Q scans:
• at the Brillouin **zone boundary** (2.5, 1.5, 0)
• at the Brillouin **zone center** (2, 2, 0)

Again:
Difference between ZB and ZC is **NOT** at all as the pronounced variation predicted by the ALM.
Discussion / Conclusions
Conclusions (i)

1) High-temperature magnetic scattering:
   - Q-independent, quasi-elastic spectrum proving local character of uncorrelated magnetic moments

2) Low-temperature magnetic scattering:
   - Broad inelastic Lorentzian + weak Q-dependence
   - Qualitatively different from ALM predictions

Similar “Kondo-like” spectral response:
\[ \text{YbAl}_3, \text{(Christianson, PRL, 2006)} \quad \text{YbInCu}_4 \quad \text{(Lawrence, PRB 1997)} \]
\[ \text{CeInSn}_2, \quad \text{(Murani, PRL 2008)} \]
Conclusions (ii)

Possible reasons for the failure of ALM predictions for spin dynamics of IV comp.

a) Band structure more complex than just two hybridized bands. These bands remain to be calculated.

b) There may be significant overlap of the intra-band Fermi Liquid excitations with the inter-band transitions. We are uncertain about the energy scale of the former (above 10 meV?)

c) ALM approximations may require improvements. Some are versions of mean field (MF) approx. which do not necessarily get the excitation energies away from the $\epsilon_F$ correctly.
Conclusions (iii)

3) Evolution with temperature: Agreement with AIM calculations

Excitations in the Anderson lattice are much more like those of an Anderson impurity than has been previously recognized
Thank you!
Anderson Impurity Model (AIM)

Even though RE’s ions sit on a lattice, good semi-quantitative agreement with AIM

High –T LOCAL MOMENT \[\rightarrow\] crossover \[\rightarrow\] Low-T FERMI LIQUID

Curie-Weiss:
\[\chi = C J / (T + \theta)\]
Pauli Paramagnet:
finite \(\chi(0)\)

Integral valence \((n_f \rightarrow 1)\)
Non-integral valence

\begin{align*}
\text{AIM/NCA:} & \quad E_f = 1.0 \text{ eV} \\
& \quad E_r = -0.5547 \text{ eV} \\
& \quad V = 0.1975 \text{ eV} \\
& \quad \Delta_{so} = 0.28 \text{ eV}
\end{align*}

\begin{align*}
\text{AIM/NCA:} & \quad E_f = 120 \text{ meV} \\
& \quad T = 300 \text{ K}
\end{align*}

CePd\textsubscript{3}

Energy transfer \(E\) (meV)

\begin{align*}
\text{Quasi-elastic spectrum} & \quad 2\Gamma \sim k_B T_K \\
\text{Inelastic spin fluctuations,} & \quad E_0 \sim k_B T_K
\end{align*}

\begin{align*}
\text{Non-crossing approx. (NCA)} & \quad C. Booth, private communication
\end{align*}
Smaller Q-Regions

\[ (50-70) \text{ meV} \]

\[ T = 7 \text{ K} \]

<table>
<thead>
<tr>
<th>Q-region</th>
<th>( T ) (K)</th>
<th>( E_0 ) (meV)</th>
<th>( \Gamma ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region 1</td>
<td>7</td>
<td>52.6 ± 0.8</td>
<td>32 ± 1</td>
</tr>
<tr>
<td>Region 2</td>
<td>7</td>
<td>42 ± 5</td>
<td>41 ± 5</td>
</tr>
<tr>
<td>Region 3</td>
<td>7</td>
<td>37 ± 3</td>
<td>44 ± 4</td>
</tr>
<tr>
<td>Region 4</td>
<td>7</td>
<td>46 ± 2</td>
<td>41 ± 4</td>
</tr>
<tr>
<td>average</td>
<td>7</td>
<td>46 ± 3</td>
<td>39.5 ± 4</td>
</tr>
<tr>
<td>all regions</td>
<td>300</td>
<td>0</td>
<td>23.3 ± 0.8</td>
</tr>
</tbody>
</table>
Conclusions (i)

1) High-temperature magnetic scattering:  
   Q-independent quasi-elastic Lorentzian spectrum  
   proving Local character of spin fluctuations for uncorrelated magnetic moments

2) Low-temperature magnetic scattering:  
   (inelastic Lorentzian + weak Q-dependence)  
   Much more like the predictions of the AIM than the ALM.

   Similar “Kondo-like” spectral response:
Conclusions (iii)

3) Low-T magnetic scattering qualitatively different from ALM predictions

“Lattice” predictions

Peak-position decreases with q

CePd$_3$ at low-T, for different Q’s

TOF data

TAS data

- **Q-dependence** not at all as severe as ALM prediction
- **No gap** in the scattering

Band structure more complex than just two hybridized bands.
These bands remain to be calculated.
Values for CePd$_3$ using big Q-regions

<table>
<thead>
<tr>
<th>Q-region</th>
<th>$T$ (K)</th>
<th>$E_0$ (meV)</th>
<th>$\Gamma$ (meV)</th>
<th>$\chi_{DC}$ (10$^{-3}$ emu/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average value</td>
<td>8</td>
<td>45 ± 2</td>
<td>43.5 ± 4</td>
<td>1.93 ± 0.2</td>
</tr>
<tr>
<td>All zones</td>
<td>300</td>
<td>0</td>
<td>26.6 ± 0.7</td>
<td>1.98 ± 0.03</td>
</tr>
</tbody>
</table>
Conclusions (iii)

Low-T magnetic scattering differs from the predictions of the ALM.

“Lattice” predictions
S(Q,E) for different Q’s

Peak-position decreases with q

Magnetic Intensity spectra:
CePd$_3$ at low-T, for different Q’s

Peak-position increases with q

TOF data
TAS data

• Q-dependence not at all as severe as ALM prediction
• No gap in the scattering
(Overlap of intra- and inter-band transitions?)

Dispersion of the hybridized bands.

The direct gap has a value $2\tilde{\nu}$

Coulomb interaction $U$ renormalizes the parameters $V$ and $E^f$. 

\[
H = \sum_{\mathbf{k}, \sigma} \varepsilon^f_{\mathbf{k}, \sigma} C^+_{\mathbf{k}, \sigma} C^-_{\mathbf{k}, \sigma} + \sum_{\mathbf{i}} \left[ \sum_{\sigma} E^f_{\mathbf{i}, \sigma} f^+_i, \sigma f_i, \sigma + \sum_{\mathbf{k}, \sigma} \left( V^f_{\mathbf{i}, \sigma} C^+_{\mathbf{k}, \sigma} C^-_{\mathbf{k}, \sigma} f_i, \sigma \right) \right] + U f^+_{i, \uparrow} f_{i, \uparrow} f^+_i, \downarrow f_{i, \downarrow}
\]

\[
\omega_{\mathbf{k}}^\pm = \frac{1}{2} \left( \varepsilon^f_{\mathbf{k}} + \tilde{E}^f \pm \sqrt{(\varepsilon^f_{\mathbf{k}} - \tilde{E}^f)^2 + 4 |\tilde{\nu}|^2} \right)
\]
Basic Phenomenological Description

**Low-T FERMI LIQUID**

- Non-integral valence \( n_f < 1 \)

- Pauli Paramagnet
  
  finite \( \chi(0) \sim \mu_B^2 N(\varepsilon_F) \)

- Linear Specific Heat
  
  \( C(T) \sim \gamma T \)

  \( \gamma = \frac{1}{3} \pi^2 N(\varepsilon_F) k_B^2 \)

**High-T LOCAL MOMENT PARAMAGN**

- Integral valence \( n_f \rightarrow 1 \)

- Curie-Weiss: \( \chi = C_J / (T + \theta) \)

- Entropy: \( S_m \rightarrow R \ln(2J+1) \)

---

Basic Phenomenological Description

- **Onset of coherence**
  1. Bloch’s law
  2. $\rho \propto T^2$

- **Scaling**
  
  $1/\chi_0, 1/\gamma, \Gamma, E_0 \propto k_B T_{\text{max}}$

  *Thermodynamic properties are universal function of a scaled temperature $T_{\text{max}}$*
Anderson Impurity Model (AIM)

Even though RE’s sit on a lattice, and are not “impurities”, good agreement with AIM

- Qualitative agreement
- Some quantitative agreement
- Slower crossover than AIM prediction

Non-crossing approx. (NCA)


Calculation: C. Booth, private communication
**Single-crystalline samples**

CePd$_3$ (18 g) LaPd$_3$ (11 g)
Grown by Czochralski method
Annealed at 950°C (6 days)
E. D. Bauer,
C. H. Wang,
K. J. McClellan

YbAl$_3$ (≈ 5 g)*
Grown by self-flux method
A. D. Christianson,
E. D. Bauer

* In the pictures: not the actual set-up used in the experiments reported in this work
Inelastic Neutron Scattering

\[ \vec{Q} = \vec{k}_i - \vec{k}_f \]

\[ E = \frac{\hbar^2}{2 m_N} \left( k_f^2 - k_i^2 \right) \]

Momentum and energy transfer

Triple-axis Spectrometer

Time-of-flight Spectrometer
Inelastic Neutron Scattering
Measuring spin dynamics

Scattering cross section \( \sigma \)
\[
\frac{d^2 \sigma}{d\Omega \, dE} = \frac{k_f}{k_i} \, S(\vec{Q}, E) \]

\textbf{Case of Magnetic Scattering}

\( S_{\text{mag}}(\vec{Q}, E) \)

\( S_{\text{mag}} \): \textit{Fourier Transform of the moment-moment correlation function.}

\( S_{\text{mag}} \) \textit{Related to the imaginary part of the} dynamic susceptibility \( \chi \)

\[
S_{\text{mag}}(\vec{Q}, E) = \frac{1}{\pi} \left[ \frac{1}{1 - e^{-E/k_B T}} \right] \chi''(\vec{Q}, E)
\]

\[
\chi''(Q, E) \propto f^2(Q) \frac{E \chi_{DC} \Gamma_Q}{2\pi} \left( \frac{1}{(E - E_{0,Q})^2 + \Gamma_Q^2} + \frac{1}{(E + E_{0,Q})^2 + \Gamma_Q^2} \right)
\]

\textbf{Magnetic form factor} \hphantom{a} \textbf{Power-spectrum}
Inelastic Neutron Scattering on YbAl$_3$

Measurements at 300 K, 100 K and 8 K

on time – of – flight spectrometer

(no non-magnetic analog compound)
**Intensity** = (Magn. Comp.) + (Non-magn. Comp)

Assuming: (Non-magn) = 3 Gaussian peaks + elastic peak

We have not measured INS on a non-magnetic counterpart compound

居然没有测量非磁性对称化合物的INF
\textbf{YbAl}_3 \textit{magnetic scattering}

\begin{equation*}
E_i = 60 \text{ meV}
\end{equation*}

\begin{equation*}
E_i = 120 \text{ meV}
\end{equation*}

\begin{align*}
\text{(Magn.)} &= I - \text{(Non-magn)} \\
\text{(Magn.)} &= I - \text{(Non-magn)}
\end{align*}

\text{Temp-scale 3-Gaussian}

\text{Check use Lorentzian}

\text{If good agreement}

\text{Temp-scale Non-magnetic}

\text{Temp-scale Non-magnetic}
Magnetic and non-magnetic Scattering

\[ E_i = 120 \text{ meV}, \quad T = 8 \text{ K} \]

\[ I = MS + M f^2(Q) + BQ^2 \]

Ei = 120 meV, T = 8 K

Intensity color map E vs k

Non-magnetic scattering
Represented as a “scaled LaPd\textsubscript{3}”
CePd\textsubscript{3} and scaled LaPd\textsubscript{3}

CePd\textsubscript{3} and LaPd\textsubscript{3}

Energy transfer E (meV)
Intensity (mb/sr-meV)

Energy transfer E (meV)
Intensity (mb/sr-meV)
Polycrystalline average (i)

- Integrate on a large portion of the reciprocal space

**CePd₃** on MAPS, $T = 8\, \text{K}$, $E_i = 120\, \text{meV}$

- Plot intensity $I$ vs. $Q$ for different ranges of energy transfer
- Analyze Intensity as composed by 3 contributions for the scattering:

$$I = MS + BQ^2 + M f^2(Q)$$

- **Multiple scattering**
- **Single phonon scattering**
- **Magnetic scattering**

$f^2(Q)$: magnetic form factor for Ce 4f orbital

**Assumption:**

$MS$ and $M$ are $Q$-independent
Polycrystalline average (ii)

- **Non-magnetic scattering** from LaPd$_3$
- **Magnetic scattering** $I = MS + BQ^2 + Mf^2(Q)$

### Scale factor

$$\text{scale factor} = \frac{\sigma^{(\text{CePd}_3)}_{\text{coh}}}{\sigma^{(\text{LaPd}_3)}_{\text{coh}}}$$

### Energy Transfer vs. Intensity

- **LaPd$_3$**
  - $E = 15-20$ meV
  - $E = 15-25$ meV
  - $E = 25-35$ meV
  - $E = 35-45$ meV
  - $E = 55-65$ meV
  - $E = 75-85$ meV

- **CePd$_3$**
  - $I = MS + BQ^2$
  - $E = 120$ meV
  - $T = 8$ K
  - $k_i // [100]$

### Magnetic Scattering

- $BQ^2$ dominant $< 30$ meV
- $Mf^2(Q)$ dominant above phonon cutoff

### Obtain MS, B

- **LaPd$_3$**
  - $Q (\text{Å}^{-1})$

- **CePd$_3$**
  - $Q (\text{Å}^{-1})$

Polycrystalline average (iii)

$T = 8 \text{ K}$: Inelastic Kondo-like magnetic scattering:

maximum between 50 and 60 meV, (same scale of $T_K \sim (500-600) \text{ K}$).

As temperature increases, it evolves towards a quasielastic Lorentzian

Scattering cross sections

<table>
<thead>
<tr>
<th>Cross sections</th>
<th>$\sigma_{\text{coh}}$ (barns)</th>
<th>$\sigma_{\text{isc}}$ (barns)</th>
<th>$\sigma_{\text{coh}}^{\text{inel}}$ (barns)</th>
<th>$\sigma_{\text{lab}}$ (barns)</th>
<th>$\sigma_{\text{coh}}$ (fm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>8.53</td>
<td>1.13</td>
<td>9.66</td>
<td>8.94</td>
<td>8.24</td>
</tr>
<tr>
<td>Ce</td>
<td>2.94</td>
<td>0</td>
<td>2.94</td>
<td>0.63</td>
<td>4.84</td>
</tr>
<tr>
<td>Pd</td>
<td>4.39</td>
<td>0.093</td>
<td>4.48</td>
<td>6.9</td>
<td>5.91</td>
</tr>
<tr>
<td>LaPd$_3$</td>
<td>21.70</td>
<td>1.409</td>
<td>23.10</td>
<td>29.54</td>
<td>25.97</td>
</tr>
<tr>
<td>CePd$_3$</td>
<td>16.11</td>
<td>0.279</td>
<td>16.38</td>
<td>21.33</td>
<td>22.57</td>
</tr>
</tbody>
</table>

Ratio $(\text{CePd}_3/\text{LaPd}_3)$: 0.742 0.198 0.709 0.720 0.869
Comparison Triple-axis vs Time-of-flight spectrometers

**(a)** $\text{CePd}_3$

$\begin{align*}
E_i &= 14.7 \text{ meV} \\
T &= 12 \text{ K}
\end{align*}$

Zone Center (2, 2, 0)

- • CePd$_3$ + sample can
- ○ Empty sample can
- ▲ CePd$_3$

Energy transfer $E$ (meV)

Intensity per mcu

**(b)** $\text{CePd}_3$

$\begin{align*}
E_i &= 120 \text{ meV} \\
T &= 7 \text{ K} \\
k_i &= [1 \ 0 \ 0]
\end{align*}$

Zone 1 (h, 0.5, 0)

- • CePd$_3$ + sample can
- ○ Empty sample can
- ▲ CePd$_3$

Energy transfer $E$ (meV)

Intensity (mb/sr-meV)

**(c)** $\text{CePd}_3$

$\begin{align*}
E_f &= 14.7 \text{ meV} \\
T &= 12 \text{ K}
\end{align*}$

Zone Center (2, 2, 0)

$\text{Ef} = 14.7 \text{ meV}$

Energy transfer $E$ (meV)

$h$ component

9 hs. of beam

12 hs. of beam
Measuring on Triple-axis spectrometer

**HB3 Triple axis spectrometer** $T = 12\ K$, $E_f=14.7\ meV$

**TAS has higher background**, and lesser statistics:
- Maxwell profile of the reactor ($\sim 70\ meV$)
- Larger amount of aluminum “in the beam”

**Constant Q- scans:**

(a) Energy-scan at the Brillouin zone boundary, and (b) at the Brillouin zone center

The magnetic intensity from TOF measurements (green line) is also included for comparison.
Alternative Method to Obtain the Non-magnetic Scattering
L_{III} X-ray absorption spectrum

Spectra correspondent to divalent and trivalent Yb absorptions

Estimation for the spectrum of particle-hole excitations for a basic scheme of hybridized bands

\[ S(\tilde{Q}, E) \propto \int dE' f(E') \left( 1 - f(E') \right) D(E', E'+E; \tilde{Q}) \]

Hybridized bands \( \omega^+ \) and \( \omega^- \)

Spectra for intraband (lines) and interband (circles) excitations for momentum transfer in the range between 0 and \( Q = Q_{\text{ZB}} \).
Magnetic Susceptibility

Bulk measurements and $\chi$ obtained from INS

![Graph showing magnetic susceptibility of $YbAl_3$ and $CePd_3$.]
Oscillation of Magnetic Intensity

$T = 7\, \text{K}$

Variations of order 20%

$S_{\text{magn}}$

Energy transfer $E$ (meV)

MAPS
$E_1 = 120\, \text{meV}$
$T = 7\, \text{K}$

$\Gamma = (58 \pm 10)\, \text{meV}$
$E_0 = (35 \pm 6)\, \text{meV}$
$\chi_{\text{DC}} = (2.1 \pm 0.2) \times 10^{-3}\, \text{emu/mol}$

Region 2 ($h, 0.5, 0.5$)

$\Gamma_2 = (70 \pm 10)\, \text{meV}$
$E_2 = (100 \pm 20)\, \text{meV}$

$\chi_{\text{DC}} = (2.5 \pm 0.5) \times 10^{-4}\, \text{emu/mol}$

$L_N$

Operated by Los Alamos National Security, LLC for the U.S. Department of Energy’s NNSA