Slow Crossover in $YbX\mathrm{Cu}_4$ Intermediate Valence Compounds

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Abstract

We compare the results of measurements of the magnetic susceptibility $\chi(T)$, the linear coefficient of specific heat $\gamma(T) = C(T)/T$ and $4f$ occupation number $n_f(T)$ for the intermediate valence compounds $YbX\mathrm{Cu}_4$ (X = Ag, Cd, In, Mg, Tl, Zn) to the predictions of the Anderson impurity model, calculated in the non-crossing approximation (NCA). The crossover from the low temperature Fermi liquid state to the high temperature local moment state is substantially slower in the compounds than predicted by the NCA; this corresponds to the "protracted screening" recently predicted for the Anderson Lattice. We present results for the dynamic susceptibility, measured through neutron scattering experiments, to show that the deviations between theory and experiment are not due to crystal field effects, and we present x-ray-absorption fine-structure (XAFS) results that show the local crystal structure around the X atoms is well ordered, so that the deviations probably do not arise from Kondo Disorder. The deviations appear to correlate with the background conduction electron density, as predicted for protracted screening.

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$CePd_3$ SmB_6 $EuPd_2Si_2$ $YbAl_2$
$CeSn_3$:   : $YbAl_3$
Ce metal   :   : $YbCuAl$
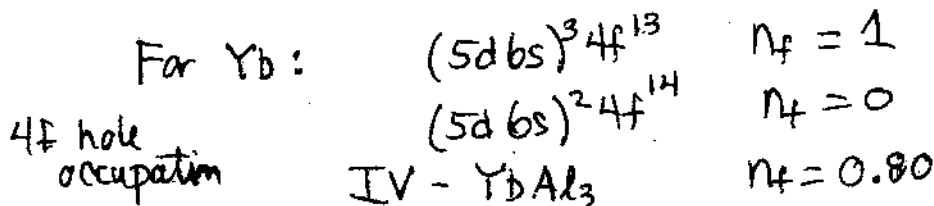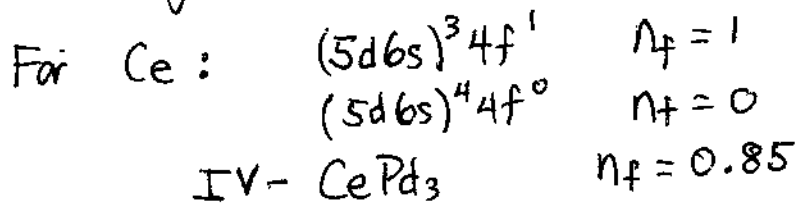 :   :
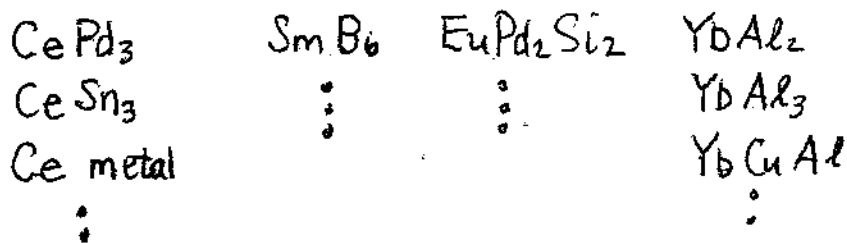
Basic Physics: $4f$ orbital (highly localized)
Hybridizing   with Conduction Electrons
  with   strong Local Coulomb interactions

Archetypal for the study of electron correlations
   in   solids

Intermediate Valence (IV)   Partial Occupation
 = (Homogeneous) Mixed Valence   }   of
 = Non Integral Valence   } $4f$ Shell

     For Ce : $(5d6s)^3 4f^1$ $n_f = 1$
                    $(5d6s)^4 4f^0$ $n_f = 0$
          IV - $CePd_3$ $n_f = 0.85$

     For Yb : $(5d6s)^3 4f^{13}$ $n_f = 1$
                    $(5d6s)^2 4f^{14}$ $n_f = 0$
$4f$ hole
  occupation   IV - $YbAl_3$ $n_f = 0.80$

ANDERSON IMPURITY MODEL (AIM)

This applies to a dilute alloy $La_{1-x}Ce_x$

Nevertheless it describes the zero-order physics of periodic compounds such as $CePd_3$

$$\mathcal{H}_{AI} = \mathcal{H}_0 + \mathcal{H}_f(i)$$

$$\mathcal{H}_0 = \sum_k' \varepsilon_k \hat{n}_k$$

$$\mathcal{H}_f(i) = E_f \hat{n}_f(i) + U\, n_{f\uparrow}(i)\, n_{f\downarrow}(i)$$
$$+ \sum_k' V_{kf}\, C_k^\dagger \hat{f}(i) + cc$$

The physics is dominated by the

KONDO RESONANCE

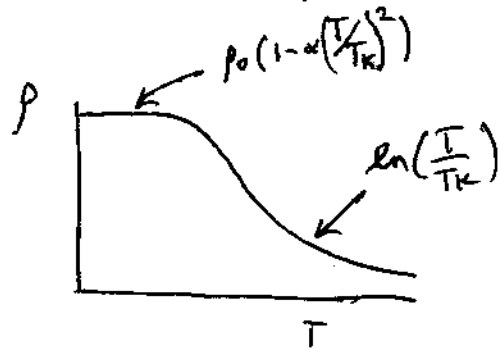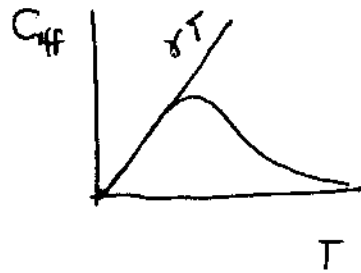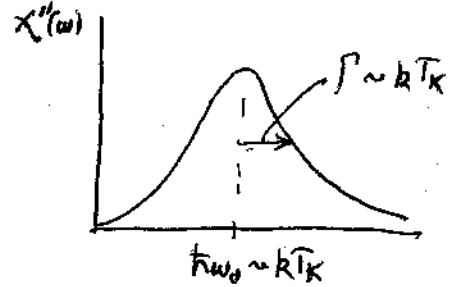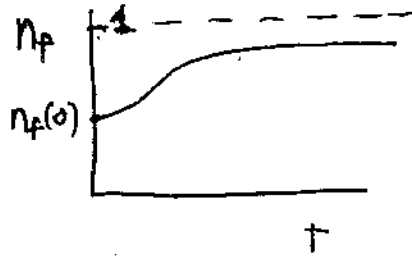Peak in renormalized f-density of states at low energy $\sim kT_K$

where $\quad kT_K \sim W e^{-E_f/N_J V^2 \rho}$

$$N_J = 2J + 1$$

Basic Predictions of AIM

$$\chi(0) \sim N_f(\varepsilon_F) \sim 1/T_K$$

$$C = \gamma T \qquad \gamma \sim N_f(\varepsilon_F) \sim 1/T_K$$

χ vs T: $T_m \sim T_K$

n_f vs t: 1, $n_f(0)$

$\chi''(\omega)$: $\Gamma \sim k T_K$, $\hbar \omega_0 \sim k T_K$

C_{4f} vs T: γT

ρ vs T: $\rho_0 \left(1 - \alpha \left(\frac{T}{T_K}\right)^2\right)$, $\ell n\left(\frac{T}{T_K}\right)$
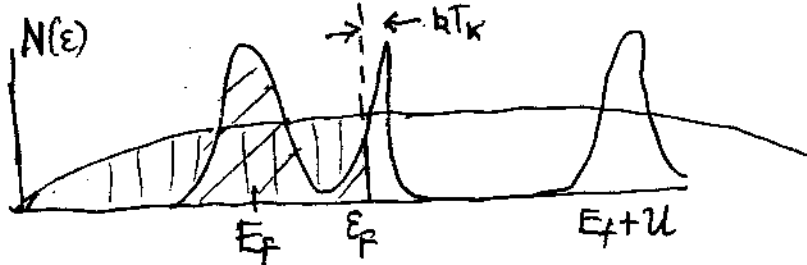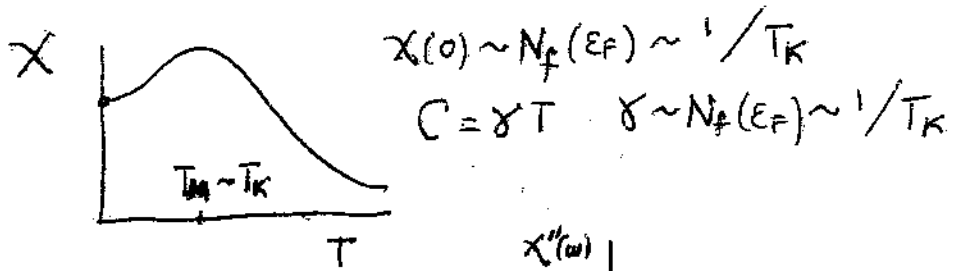
UNIVERSALITY:

Properties Scale
as

T/T_K

$\hbar \omega / k T_K$

etc.

ANDERSON LATTICE (AL)

For a periodic IV compound we use AL model

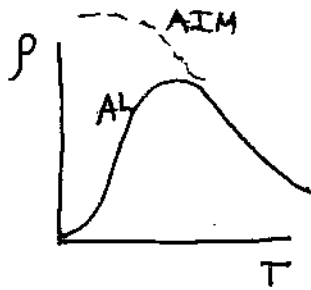$$\mathcal{H} = \mathcal{H}_0 + \sum_i \mathcal{H}_f(i)$$

Key Effect: "Coherence"

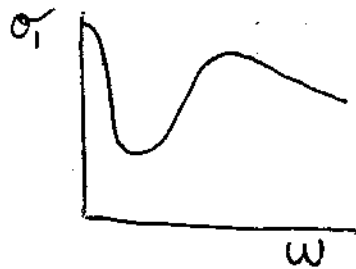The f-resonance becomes a renormalized band, giving Bloch states at $T \ll T_K$

Hybridization Gap Δ is believed to be important

$\mathcal{E}_F \; E_f$
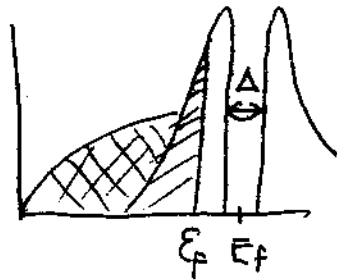
Coherence is seen clearly in electron transport, which depends crucially on the periodicity of the scattering potential

Resistivity
Vanishes

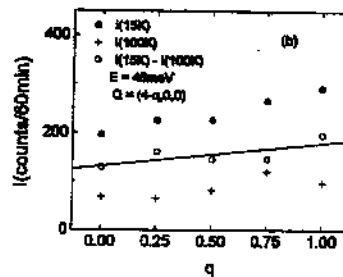Optical Conductivity:
Drude Response
Large m^*

Fermi Surface
dHvA
sees
bands with
heavy
mass m^*

The spin dynamics of IV periodic compounds
are very similar to the predictions of AIM:

a) Very little Q - dependence
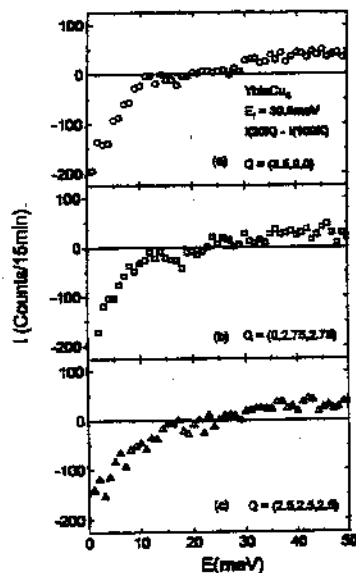
Weak (10%) increase
of $\chi(Q)$ from zone center
to zone boundary

b)   Lorentzian Power Spectrum
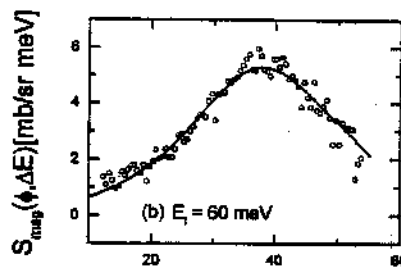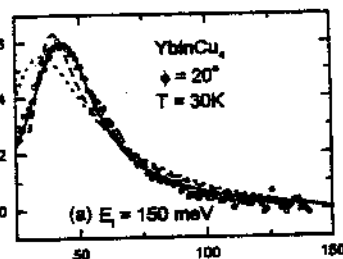
$$\chi''(Q,\omega) = (n(\omega)+1)\, f^2(Q)\, \chi'(Q)\, \omega\, P(\omega)$$

$$P(\omega) = \left(\frac{\Gamma}{2\pi}\right)\left[\frac{1}{(\omega-\omega_0)^2+\Gamma^2} + \frac{1}{(\omega+\omega_0)^2+\Gamma^2}\right]$$

THERMODYNAMICS:

As a consequence of the similarity of $\chi''(Q\omega)$ of periodic IV compounds to the AIM predictions those properties $(\chi(T), n_f(T), C(T))$ which are dominated by the spin fluctuations are qualitatively similar to predictions of AIM

PROTRACTED SCREENING

Nevertheless, a recent prediction for the Anderson Lattice (using $1/d$, d = spatial dimension) is that the moment "unbinds" more slowly in the Anderson Lattice than in the Anderson Impurity Model. That is, the <u>crossover</u> from Fermi Liquid behavior at low T to local moment behavior at high T is slower:
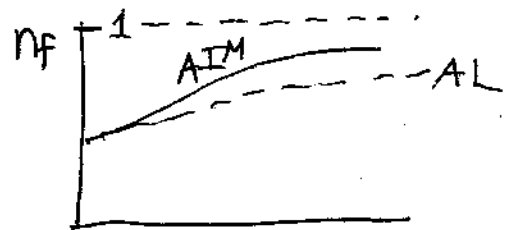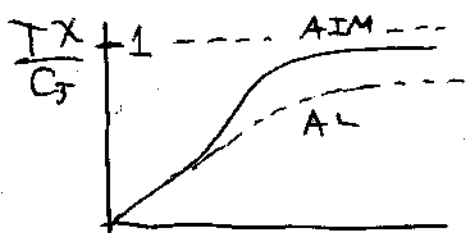
$Yb\underline{X}Cu_4$: Testbed for Slow Crossover

$\underline{X} = Ag, In, Mg, Tl, Zn, Cd$

Common crystal structure (C 15 b)

High Quality Flux-Grown Crystals (Fisk, Sarrao)

Common background bandstructure, phonons etc.

Broad range of T_K, $n_f(0)$

We measure
$\begin{cases} \chi(T) & \text{SQUID : (Thompson)} \\ C(T) = \gamma T & \text{(Hundley)} \\ n_f(T) & L_3 \text{ x-ray absorption} \\ & \text{(Lawrence, Booth)} \\ \chi''(Q, \omega) & \text{(Lawrence, Osborn)} \end{cases}$

For $\chi(T)$ & $C(T)$ the measurements are routine and errors are well controlled.

Use NCA to calculate properties of AIM
(Riseborough)

Include known spin orbit splitting 1.3eV
but ignore crystal field splitting

(because $kT_K \gg \Delta_{cf}$)

$2J+1=6$

Δ_{so}

$2J+1=8$
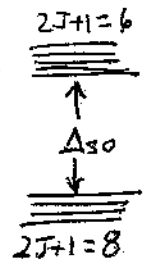
Three parameters:

E_f f-level position

V f/conduction hybridization

W : Background bandwidth $e^{-E^2/W^2} / \sqrt{\pi W}$

Since $\chi, C, n_f, \chi''(\omega)$ are only affected by
states within $\max\{T, T_K\}$ of ε_{Fermi}
we fix W to give correct background band
density of states which we determine
using free electron formula from the specific
heat coefficient of nonmagnetic $Lu\,X\,Cu_4$

[The (5d 6s)³ bands of $Lu\,X\,Cu_4$ are
essentially similar to the band that the
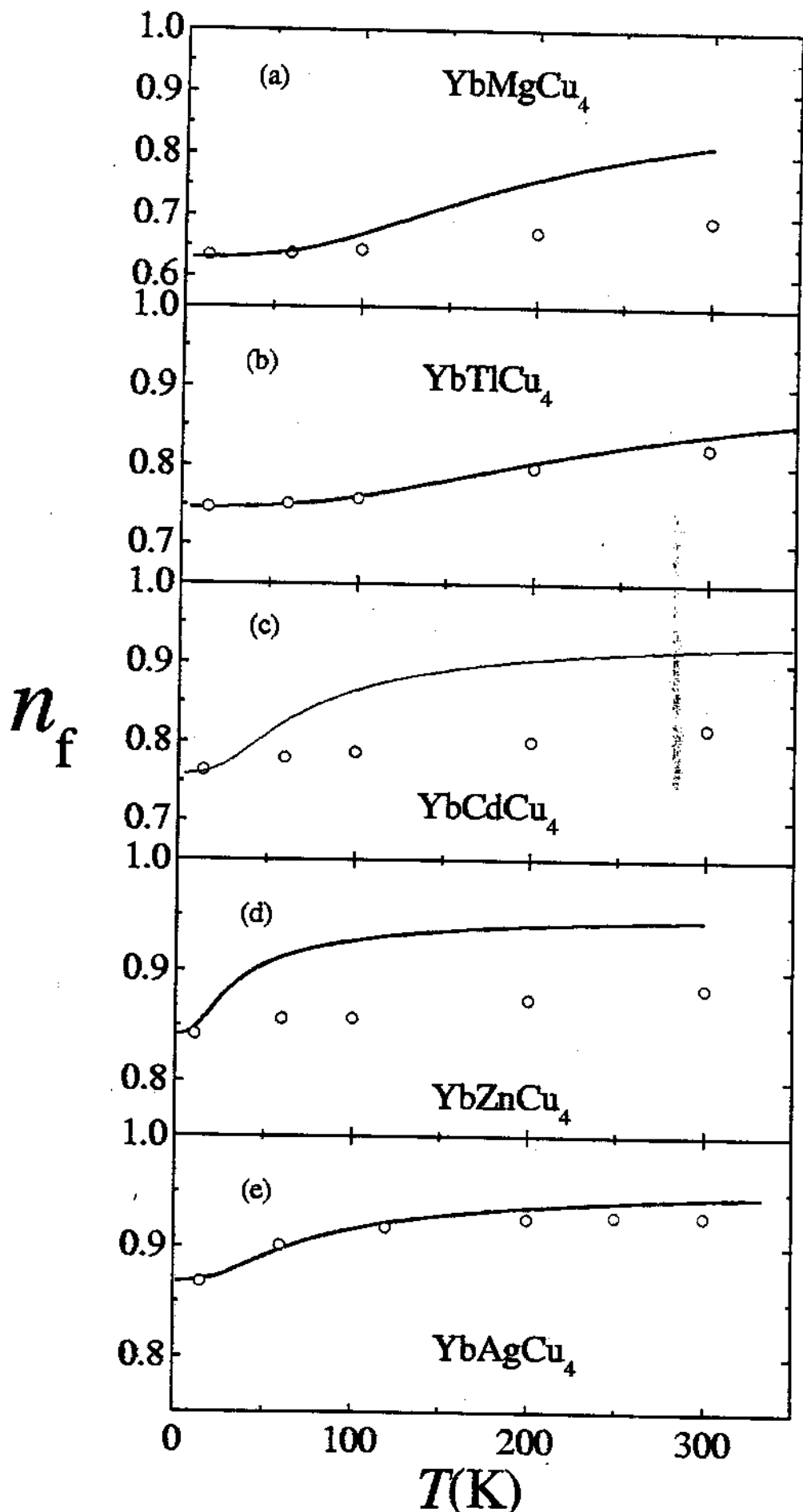4f electron in $Yb\,X\,Cu_4$ hybridizes with]

With W fixed, V & E_f can be uniquely determined
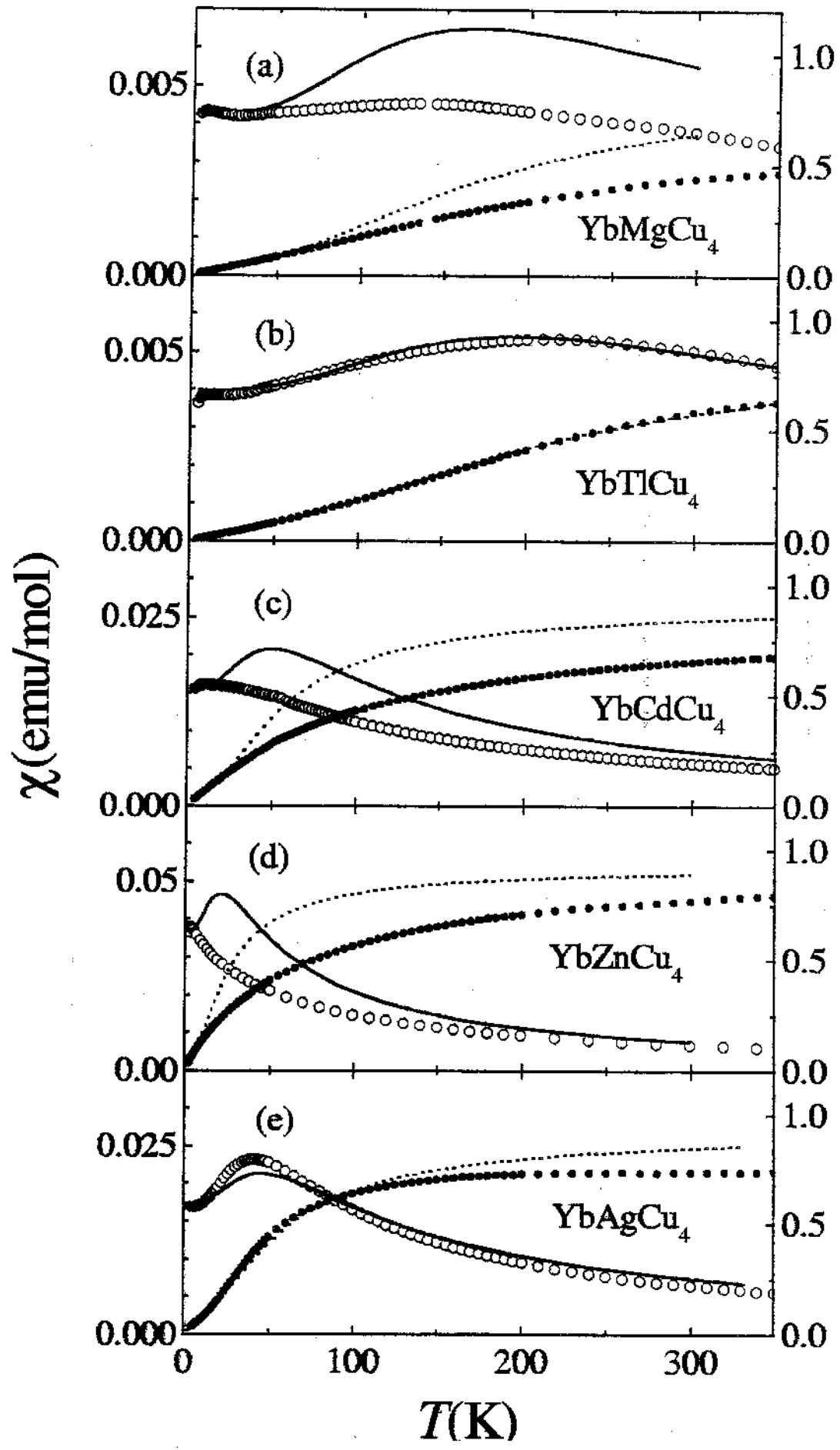from measurement of $\chi(0)$ & $n_f(0)$

TABLE I. Input parameters W, E_f and V for the AIM calculation; the calculated Kondo temperature T_K; and the theoretical and experimental values of the specific heat coefficient γ, the Wilson ratio $\mathcal{R}$ and the neutron lineshape parameters E_0 and Γ.

Compound	W (eV)	E_f (eV)	V (eV)	T_K (K)	γ ($\frac{mJ}{mol-K^2}$)	$\mathcal{R}$	E_0 (meV)	Γ (meV)
YbTlCu$_4$	1.286	-0.50146	0.2195	514	32.1	1.26	54.0	31.2
				Expt:	24.2	1.67	38.8	32.3
YbMgCu$_4$	1.005	-0.1897	0.128	500	36.7	1.22	44.6	23.4
				Expt:	53.3	0.84	31.9	34.5
YbInCu$_4$	1[1]	-0.7442	0.232	299	41.3	1.44	41.6	25.9
				Expt:	41.3[1]	1.44[1]	41.6	13.5
YbCdCu$_4$	0.929	-0.17576	0.098	127	120.4	1.40		
				Expt:	165.6	1.02		
YbAgCu$_4$	0.865	-0.4485	0.148	95	137.9	1.29	11.3	7.1
				Expt::	198.9	0.89	9.8[2]	6.0[2]
YbZnCu$_4$	1.213	-0.1984	0.1038	60	296.8	1.33	5.0	4.1
				Expt:	370	1.07	7.4	6.1

Notes: 1) The values of W are deduced from the specific heat of the corresponding LuXCu$_4$ compound and the experimental specific heat coefficients have been corrected for the non-4f contribution by subtracting the specific heat coefficient of the LuXCu$_4$ compound. Since the groundstate of LuInCu$_4$ is semimetallic[19] and does not serve for these estimates, we have arbitrarily set $W = 1$eV and we have subtracted a corresponding amount (8.7mJ/molK^2) from the specific heat coefficient. 2) For comparison to theory these values should be increased by 10% to account for the fact that the neutron scattering sample had a Kondo temperature that is 10% smaller than the sample used to measure χ and n_f.

(a) YbMgCu$_4$

(b) YbTlCu$_4$

(c) YbCdCu$_4$

(d) YbZnCu$_4$

(e) YbAgCu$_4$

χ(emu/mol)

$(\mu_{eff})^2 = T\chi/C_J$

T(K)

SLOW CROSSOVER CONFIRMED

In each case (except $YbTlCu_4$) the data crosses over more slowly than the AIM prediction.

The degree of slowness increases in the sequence $X = Tl, Ag, Cd, Zn, Mg$. This trend does not correlate with T_K or $n_f(0)$. It does appear to correlate with the Hall constant of $LuXCu_4$. The latter is a measure of the conduction electron density in the background band: In a one-band model

$$n = 1/eR_H$$

	$T_K(K)$	$n_f(T=0)$	$R_H(T=0)$ m^3/C	$n = 1/R_He$ e/cm^3
$YbMgCu_4$	500	0.64	-1.8×10^{-10}	3.5×10^{22}
$YbZnCu_4$	60	0.84	-1.0	6.2
$YbCdCu_4$	127	0.76	-0.8	7.8
$YbAgCu_4$	95	0.87	-0.6	1.04×10^{23}
$YbTlCu_4$	514	0.75	<0.1	$>6 \times 10^{23}$

The crossover becomes slower as the background conduction electron density decreases

(This is a basic feature of theory.)

POSSIBLE PROBLEMS

① Systematic Error in n_f

② Crystal fields may slow the crossover

③ "Kondo Disorder":

Yb in a disordered environment sees a different V & hence different T_K than in the bulk.

$$X(T) = \int X(T_K; T) \, P(T_K) \, dT_K$$
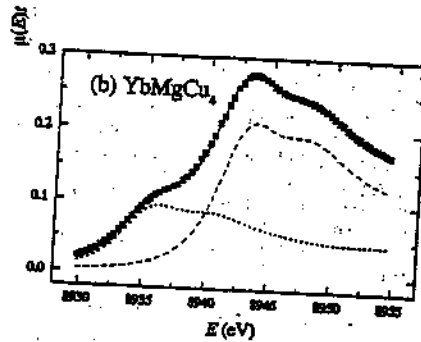
This can spread out the crossover

FIG. 7. Example of absorption data and fits to the divalent and trivalent components of the Yb L_{III} edge.

For $n_f(T)$ we use L_3 x-ray absorption:

$$h\nu + |\cdots 2p^6 \cdots (6s^2 5d^{n_f}) 4f^{14-n_f}\rangle$$

$$\longrightarrow a|\cdots 2p^5 \cdots 6s^2 5d^1 4f^{14}\rangle + b|\cdots 2p^5 \cdots 6s^2 5d^2 4f^{13}\rangle$$

$$\text{weight } (1-n_f) \qquad\qquad \text{weight } n_f$$

Assumptions:

a) $4f^{14}$ and $4f^{13}$ final states have identically shaped absorption edges ("replicate splitting")

b) Matrix elements for the two transitions are identical so final state weight reflects the initial state weight.

While this means we don't understand the systematic error, this is _the_ standard method for determining n_f in IV compounds

To see whether crystal fields matter we do inelastic neutron scattering.

Key sources of systematic error:

(a) Since we're using Time-of-Flight neutron scattering we need large (50g) samples which means polycrystalline samples. Hence any Q dependence is averaged out. Fortunately (we think) there is very little Q-dependence so this works in our favor (better statistics)

(b) Correct subtraction of nonmagnetic background.

Usual assumption: Use nonmagnetic $Lu \overline{X} Cu_4$ to determine factor by which high Q scattering (which is entirely nonmagnetic) scales to low Q (where magnetic scattering is strongest).

This assumption is not perfect! The multiple scattering dominates the low Q response but it is stronger for Yb than for Lu...

So systematic error is not well understood
Nevertheless...
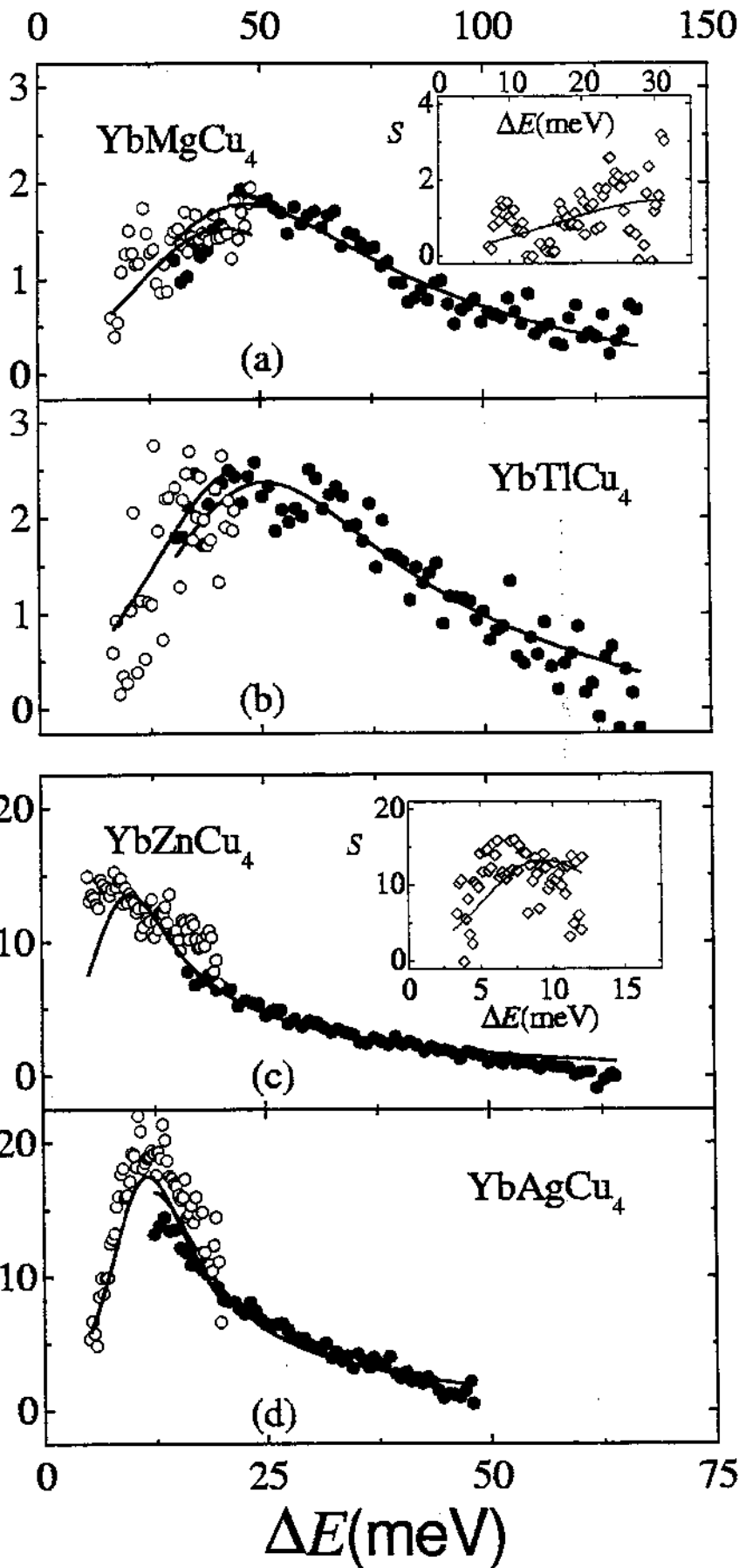
The conclusion is that no sharp crystal fields are present; in each case the spectrum can be fit with a single - Lorentzian broadened power spectrum.

This statement is independent of the systematic error

(But the systematic error does affect the measured values of E_0 & Γ.

(a) YbAgCu₄ Ag K edge

T=15 K

data
fit

(b) YbCdCu₄ Cd K edge

FT of $k^3 \chi(k)$

r (Å)
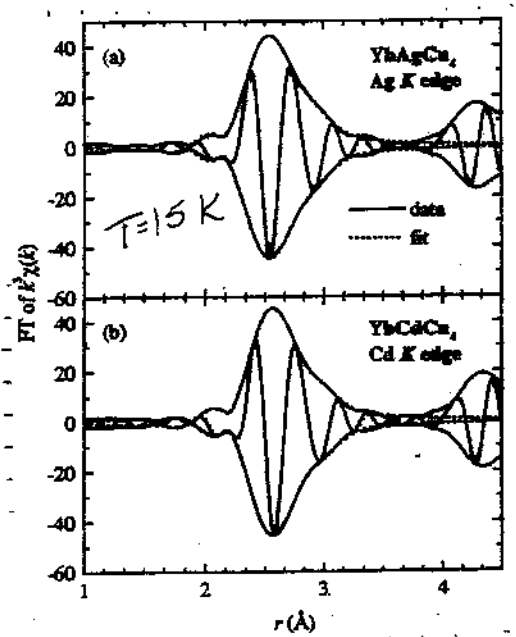
(Booth) X = Ag, Cd, In, Tl

KONDO DISORDER

XAFS on the X-atom Kshell Sensitive to X/Cu site interchange (the predominant kind of disorder in these compounds).

The XAFS can be fit very well assuming no site disorder; furthermore the linewidths (which measure bond length disorder) have the small values characteristic of well-ordered compounds

CONCLUSION

- The $4f$ occupation number $n_f(T)$ and effective moment $T\chi/C_J$ cross over from the Fermi Liquid state to the high temperature local moment regime more slowly than predicted by the Anderson Impurity Model.

- The crossover appears to become slower as the electron density in the background band decreases.

- The results accord with predictions for the $S = \frac{1}{2}$ Anderson Lattice, based on the $1/d$ approximation.

- A question for theory: How does the effect depend on $N_J = 2J + 1$?

- We have ruled out crystal fields and Kondo Disorder (except, perhaps, for $Yb\,Zn\,Cu_4$) as sources of the effect

- Unknown systematic error in $n_f(T)$ is a potential problem — However the slow crossover is clearly present in $\chi(T)$ for which there is no systematic error