Charge Fluctuations and the Valence Transition in Y under Pressure

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We present a dynamical mean field theory study of the valence transition ($f^{14} \rightarrow f^{13}$) in elemental, metallic Yb under pressure. Our calculations reproduce the observed valence transition as reflected in the volume dependence of the $4f$ electrons. The transition is accelerated by heating, and suggests quasiparticle or Kondo-like structure in the spectra of the trivalent end state, consistent with the early lanthanides. Results for the local charge fluctuations and susceptibility, however, show novel signatures uniquely associated with the valence transition itself, indicating that Yb is a fluctuating valence material in contrast to the intermediate valence behavior seen in the early trivalent lanthanides Ce, Pr, and Nd.

The valence state of rare earth atoms in lanthanide compounds has a crucial effect on their physical properties. Determination of the lanthanide valence from first principles and description of the $4f$ electrons has been a long standing challenge due to the duality between their atomic character, stemming from the on-site electron-electron interaction, and the itinerant character, due to the lattice periodicity. Theories based on the two species picture, which treat part of the $4f$ electrons as atomic and $f$ valence orbitals to allow changes of the occupation. We assume the SU(N) symmetric form of the local interaction

$$H_{\text{int}} = \frac{1}{2} U \sum_{i \neq j} \hat{n}_i^f \hat{n}_j^f,$$

(1)

The doped $4f$ holes can move through the crystal by thermally activated hopping with spd bands acting as particle and energy reservoirs, fluctuating valence behavior, or they can move coherently between atomic sites forming a narrow band well known for heavy fermions, intermediate valence behavior. We will discuss how these concepts apply to Yb.

In the present study we start with a self-consistent LDA calculation, transform its one-electron Hamiltonian into an orthogonal Wannier function basis, and then calculate the interaction parameter $U$ as well as the the double counting correction to $H_k^{\text{LDA}}$. Since the valence transition of Yb is of principal interest here, we have to retain the 6s, 6p, and 5d valence orbitals to allow changes of the $f$-shell occupation. We assume the SU(N) symmetric form of the local interaction

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FIG. 1: (Color online) The $f$ shell occupation vs pressure at various temperatures compared to the experimental data (closed symbols). Open symbols are QMC data; the 630 K and 1160 K curves were obtained with CTQMC, and the 1580 K curve with HFQMC at $L = 80$. The consistency of HFQMC with the CTQMC data was checked by $L \rightarrow \infty$ extrapolation of the $L = 80$, 112 and 160 data at 630 K. X-ray absorption edge spectroscopy (XAES) data was taken from Ref. 13, and resonant inelastic x-ray scattering (RIXS) data taken from Ref. 14. Inset shows the interaction $U$ vs. specific volume.

Hirsch-Fye (HFQMC) [11] algorithm and the other using the hybridization expansion continuous time QMC algorithm (CTQMC) [12] as well as an approximate, but computationally efficient Hubbard-I (HI) solver. Extrapolations of the HFQMC results to an infinite number of imaginary time slices $L$ were found to agree within statistical uncertainties with the CTQMC. A $1/L^2$ dependence was used with $L =$ 80, 112, and 160 for the number of $f$ electrons $n_f$ and $L =$ 80 and 112 for the charge fluctuations. However, we point out that especially at the larger $L$ values, the HFQMC calculations had significant difficulties with ergodicity in the midst of the Yb valence transition where large fluctuations in $n_f$ were encountered in the Ising space sampling. The CTQMC method did not encounter such problems.

In Fig. 1 we show the evolution of the $f$-orbital occupation $n_f$ as a function of the specific volume $V$ at various temperatures. Comparison to the experimental x-ray absorption edge spectroscopy (XAES) and resonant inelastic x-ray spectroscopy (RIXS) data shows some underestimation of $n_f$ at lower volumes, possibly originating from the lack of charge self-consistency, which would take into account the correlation driven redistribution of charge between the $f$ and spd orbitals. Overall the DMFT(QMC) results agree reasonably well with the experimental data over the entire pressure range of interest. The ability of DMFT(HI) to produce the valence transition seen in experiment suggests that the physics is essentially related to charge transfer between the $f$ and spd orbitals. At smaller volumes where delocalization of $f$-electrons becomes more important HI overestimates the number of holes in the $4f$ shells. Finally note that the rising $6s$ and $6p$ bands lead to an increase in $n_f$ with compression for the trivalent rare earths [5], so that it is likely that the plateau in the DMFT(QMC) value reached at the smallest volumes in Fig. 1 is indeed near the end of the transition from divalent to trivalent in spite of the fact that $n_f$ is still larger than 13.0.

The calculated $n_f$ values show a sizable temperature dependence both with HI and QMC, particularly at low pressure as is evident in Fig. 1. The general trend is that at higher temperatures, the $f^{13}$ state is favored over the $f^{14}$ state. This trend can be followed down to the lowest studied temperature of 16 K, which is only accessible with HI. We expect this trend would hold at lower temperatures for QMC calculations as well. Temperature dependent measurements of the valence of Yb in YbInCu$_4$ show the same trend ($4f$ occupation decreasing with increasing temperature) [15], with different studies finding a minimum of about 13.1 [16, 17]. The same behavior was found for YbAgCu$_4$ and YbAl$_3$ [18]. The authors of Ref. 18 did not find any significant difference in elemental Yb between the temperatures of 250 K and 25 K; at 250 K Yb should already be strongly divalent and lowering the temperature cannot decrease the valence any further. There is, however, a significant broadening of the spectrum at higher temperature, so we expect that the trend seen in our calculations would be borne out if measurements were carried out at higher temperatures. At high pressure the temperature dependence of $n_f$ becomes weak. The chemical environment of Yb can affect the temperature sensitivity of $n_f$ as well; in fact, the measured valence of Yb in YbGaGe has been recently found to be temperature independent [19], and Yb nearly divalent. This is somewhat a contrast to our result here, where the temperature sensitivity is only near the divalent state. The details of the electronic structure of YbGaGe that causes the Yb valence to be temperature independent are not understood.

The calculated $4f$ spectral densities $A(\omega)$ are shown in Fig. 2, as obtained by direct evaluation of the Green’s function near the real frequency axis for HI, and applying the maximum entropy method [20] to the CTQMC data. At low pressure, there is
a clear spin-orbit-split peak near the chemical potential, which corresponds to the \( f^{14} \rightarrow f^{13} \) excitation. As the pressure is increased, the weight of this double-peak decreases, and the \( f^{13} \rightarrow f^{12} \) excitation appears around 8 eV (≈ \( U \)) below the \( f^{14} \rightarrow f^{13} \) double-peak. While the analytic continuation smears the high energy features of the CTQMC spectra, HI is known to incorrectly reduce the width of the Hubbard bands.

When the valence transition approaches completion as in the HI result (bottom of Fig. 2a), the \( j = 7/2 \) \( f^{14} \rightarrow f^{13} \) peak overlapping the Fermi level shifts increasingly above this energy to become the unoccupied upper Hubbard band for the 4f states, corresponding to the new 4f hole. A close examination of the CTQMC counterpart (Fig. 2c), on the other hand, shows the corresponding \( j = 7/2 \) structure to contain a relatively large peak at the Fermi level with shoulders to either side. Based on the temperature scaling of the Fermi-level peak, we believe it to be a quasiparticle or Kondo-like contribution consistent with increasing delocalization of the 4f hole as volume is reduced, and that the lower shoulders are likely of more Hubbard character. Moreover, any transfer of spectral weight into such a quasiparticle contribution at the expense of the \( f^{13} \rightarrow f^{12} \) Hubbard band would also contribute to a larger DMFT(QMC) \( n_f \) than in DMFT(HI) as is observed. Finally, both the simultaneous existence of two lower Hubbard bands, and the gradual transfer of spectral weight evident in Fig. 2 are fundamental signatures of electron correlation which a single-particle approach such as LDA or LDA+U cannot reproduce.

Thus far we have shown a gradual emptying of the 4f shell with applied pressure and the corresponding changes in the single-particle spectra interpreted in terms of the relative abundance of \( f^{13} \) and \( f^{14} \) configurations in the system. We now present an analysis of the associated local charge fluctuations in Yb. In Fig. 3a we compare the local charge fluctuations in Yb, defined through the mean square deviation of the \( f \)-occupation \( \langle \delta \hat{n}_f^2 \rangle \); \( \delta \hat{n}_f = \hat{n}_f - n_f \), with those in Ce, Pr and Nd [21]. While Ce, Pr and Nd show a monotonic increase of \( \langle \delta \hat{n}_f^2 \rangle \) with pressure, the charge fluctuations in Yb exhibit a local maximum around 27 Å\(^3\)/atom where \( n_f \approx 13.5 \). Evaluating the thermal expectation in a basis of \( \hat{n}_f \) eigenstates yields \( \langle \delta \hat{n}_f^2 \rangle = w_{13}(1-w_{13}) \), if we assume only \( f^{13} \) and \( f^{14} \) configurations have significant weight \( (w_{13}+w_{14} = 1) \), and thus a peak in the midst of the valence transition \( w_{13} = 0 \rightarrow 1 \). On the other hand, if a single \( f^n \) configuration predominates \( (w_n \sim 1) \) but then loses weight to \( f^{n+1} \) and \( f^{n+1} \) states due to growing hybridization under compression, one will see a monotonic increase in \( \langle \delta \hat{n}_f^2 \rangle \). It would appear likely that the behavior seen in Fig. 3a for Yb is a combination of both effects, while that of Ce, Pr, and Nd is primarily the latter delocalization behavior.
is the case for Ce, Pr, and Nd where are rather rare since they are usu-
ally suppressed by the onsite Coulomb repulsion, as correlated metals are rather
energy charge excitations. 

Comparison of two-orders of magnitude smaller than imaginary time charge correlations for revealed in the inset of Fig. 4 where we compare the charge susceptibility. The origin of this behavior is maxima at about the same volume, however, the in-
the local charge susceptibility with both having their 
tuations with pressure is mirrored by an increase of 

We find that the initial increase of the charge fluctu-
ations at high pressure are short lived (rapid 

doing into the atomic-like 4f shell can therefore explain both the (local) maxima in and the second mechanism, growing hybridization with its concomitant 4f delocaliz-

likelihood suggests that pressure affects metallic Yb ess-
entially in two ways which can, to a first approxima-
tion, be looked at separately: hole doping of the 

To gain more insight we further evaluate the local charge susceptibility \( \chi^{(1)} \) (Fig. 3b), obtained from the imaginary-time correlation function

\[
\chi^{(1)} = \int_0^\beta d\tau \chi(\tau), \quad \chi(\tau) = \langle \delta n_f(\tau) \delta n_f(0) \rangle. \tag{2}
\]

We find that the initial increase of the charge fluctuations with pressure is mirrored by an increase of the local charge susceptibility with both having their maxima at about the same volume, however, the in-
crease of \( \langle \delta n_f^2 \rangle \) at high pressure is not reflected in the charge susceptibility. The origin of this behavior is revealed in the inset of Fig. 4 where we compare the imaginary time charge correlations for \( V=13.6 \) and \( 29.0 \) \( \text{Å}^3/\text{atom} \). While the magnitude of the charge fluctuations is about the same (\( \tau = 0 \) intercepts), the fluctuations at high pressure are short lived (rapid decay with increasing \( \tau \)) leading to a relatively lower susceptibility. In Fig. 4 we show the corresponding physical susceptibilities on the real frequency axis, imaginary parts of which characterizes the density of charge excitations.

\[
\chi(\tau) = \frac{1}{\pi} \int_0^\infty d\omega \frac{e^{-\tau\omega} + e^{-(\beta-\tau)\omega}}{1-e^{-\beta\omega}} \chi^{(2)}(\omega) \tag{3}
\]

Comparison of \( \chi(\tau) \) and \( \chi^{(2)}(\omega) \) shows that slowly decaying fluctuations are, as expected, related to low energy charge excitations.

Low energy local charge excitations in strongly correlated metals are rather rare since they are usually suppressed by the onsite Coulomb repulsion, as is the case for Ce, Pr, and Nd where \( T\chi^{(1)} \) is nearly two-orders of magnitude smaller than \( \langle \delta n_f^2 \rangle \) over the volume range of Fig. 4b [21]. Existence of such exci-
tations and the corresponding maxima in \( \chi^{(1)} \) vs \( V \) and \( \langle \delta n_f^2 \rangle \) vs \( V \) curves distinguishes this fluctuating valence behavior of Yb from the intermediate valence behavior of the other studied lanthanides. The calculated local charge susceptibility provides a clear physical meaning to the earlier reports of near degeneracy of 2+ and 3+ valence states in Yb [1]. There is also a direct connection to the experimental observation of the unusual pressure-volume curve of Yb, namely the compressibility of the electronic sub-
system is proportional to its charge susceptibility. It is plausible to expect that the maximum of local \( \chi^{(1)} \) vs \( V \) leads to softening of the entire electronic liquid, although the effect will be to some extent masked by the presence of \( spd \) bands.

Our local charge fluctuation and susceptibility results suggest that pressure affects metallic Yb ess-
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