HALL EFFECT IN YbXCu₄ AND THE ROLE OF CARRIER DENSITY IN THE
YbInCu₄ VALENCE TRANSITION

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An unrealistically large value of the Gruneisen parameter is required to explain the valence transition which occurs at 42 K in YbInCu₄ as due to a Kondo Volume Collapse. A hint as to the origin of the transition lies in the large change in carrier density which occurs at the transition, from trivalent semimetallic behavior at high temperature to mixed valent metallic behavior at low temperature. In this paper we report measurements of the Hall coefficient \( R_H \) for temperatures in the range 15–300 K for a series of RXCu₄ compounds (\( R = \text{Yb, Lu} \) and \( X = \text{Au, Zn, Cd, Mg, Tl} \)) that form in the cubic \( C15b \) structure. For all \( X \) the Hall coefficients are small (\( \sim 10^{-10} \text{ m}^3/\text{C} \)) so that the transport appears to be metallic. The observation that low carrier density is unique to RInCu₄ leads us to hypothesize that the valence transition (which is also unique to YbInCu₄) is connected with the existence of a quasigap, which is a common feature of the band structure of RXCu₄. The quasigap allows for two competing hybridization states of the \( 4f \) electrons: a small \( T_K \) semimetallic state and a large \( T_K \) metallic state.

Keywords: D. electronic band structure, D. electronic transport, D. heavy fermions.

1. INTRODUCTION

YbInCu₄ has a phase transition at \( T_c = 42 \text{ K} \) [1–3] at which the Yb, which is nearly trivalent at high temperature, becomes strongly mixed valent (\( z = 2.8 \)) at low temperature [1, 4]. The Kondo energy, which is small (\( T_K+ = 25 \text{ K} \)) at high temperature, becomes large (\( T_K- = 500 \text{ K} \)) [4–6] in the low temperature state. Furthermore there is no change in the \( C15b \) crystal symmetry at the transition [7, 8]. Such an "isomorphic" valence transition is fundamentally similar to the \( \alpha-\gamma \) transition in cerium [9, 10], which raises the question whether both transitions have a common origin.

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In the prevailing Kondo Volume Collapse (KVC) Model [10] for the Ce \( \alpha-\gamma \) transition the large change in cell volume at the transition \( (\Delta V/V_0 \approx 0.2) \) causes the Kondo temperature to increase from a value \( T_K+ \sim 100–200 \text{ K} \) in the high temperature (\( \gamma \)) phase to a value \( T_K- \sim 1000–2000 \text{ K} \) in the low temperature (\( \alpha \)) phase. The system gains Kondo condensation energy of order \( kT_K \) at low temperature, but when the temperature becomes greater than \( T_K- \), the system lowers the free energy by converting to the smaller Kondo temperature and taking advantage of the R ln (2J + 1) spin entropy \((J = 5/2 \text{ for Ce}) \) which is liberated for \( T > T_K+ \). This scenario depends not only on the very large (20%) volume change but also on the sensitivity of the Kondo temperature to changes in the cell volume; quantitatively it requires a value of order 50 for the Gruneisen parameter \( \Gamma = -\partial \ln T_K/\partial \ln V \). Such large values of \( \Gamma \) are typical of heavy fermion and mixed valent compounds [11]. For \( \gamma \)-cerium \( \Gamma \) has been estimated [12] to be 25.
from the rate of change of the Curie–Weiss susceptibility parameter $\theta$ with volume; this estimate assumes the relation, valid for the Kondo effect, that $\theta \propto T_K$. For the reasons given above (and as is seen experimentally [12]) $T_c = T_K$, so that $\Gamma$ can also be estimated from the slope of the $\alpha-\gamma$ phase boundary ($1/T_c \partial T_c/\partial P = 2.5$ kbar); given the bulk modulus $B = 200$ kbar [13] this implies $\Gamma = 50$.

The valence transition in YbInCu$_4$ also can be viewed as a competition between a low temperature state with a large Kondo condensation energy and a high temperature state with a large spin entropy ($J = 7/2$ for Yb). However, the change in cell volume at the valence transition in YbInCu$_4$ is so small ($\Delta V/V_0 \sim 0.005$) [3, 5, 8] that to drive a change in $T_K$ from 25 K to 500 K would require an unphysically large value ($\sim 4000$) of the Gruneisen parameter. Since it has been determined experimentally [4] for YbInCu$_4$ that $T_c \sim T_K$, we estimate $\Gamma = - (B/T_c) \partial T_c/\partial P = 56$ where we have used $\partial T_c/\partial P = - 2$ K kbar$^{-1}$ [14] and $B = 1120$ kbar [15]. Hence, while it is reasonable to speak of the YbInCu$_4$ valence transition as a "Kondo Collapse", it is not a "Volume Collapse" driven by a large change in cell volume as for Ce.

In addition to the issue of the relation between the phase transitions in Ce and YbInCu$_4$, a further question is why the valence transition is unique to YbInCu$_4$ in the larger set of YbXCu$_4$ compounds ($X =$ Ag, Au, Pd etc. [16]) that grow in the same C15b crystal structure. A clue to the origin of the transition comes from the observation that the compounds RInCu$_4$, where R is a heavy rare earth, are semimetals with low carrier density and large Hall coefficients [17]. In a recent study [4] of YbIn$_{1-x}$Ag$_x$Cu$_4$ alloys, we have shown that the Hall coefficients $R_H$ in LuAgCu$_4$, YbAgCu$_4$ and in the low temperature state of YbInCu$_4$ have values ($\sim 10^{-10}$ m$^3$/C) typical of ordinary metals, but $R_H$ is anomalously large ($\sim 0.3-1.7 \times 10^{-9}$ m$^3$/C) in LuInCu$_4$ and in the high temperature state of YbInCu$_4$ ($\sim 4-8 \times 10^{-9}$ m$^3$/C). Hence the carrier density changes at the phase transition; this changes the density of states at the Fermi level $N(\epsilon_F)$ and consequently changes the Kondo temperature $T_K \sim \exp[-|E_F - \epsilon_F|/(2J + 1)\Delta]$ which depends sensitively on $N(\epsilon_F)$ through the 4f-conduction hybridization strength $\Delta = V_{4f}^2 N(\epsilon_F)$ as well as on $\Delta = (E_F - \epsilon_F)$, the distance from the Yb 4f level to the Fermi level and the degeneracy $(2J + 1 = 8$ for Yb). Our hypothesis is that specific features of the RInCu$_4$ band structure allow for two nearly degenerate states: a metallic state with strong hybridization and a semimetallic state with weak hybridization.

In this paper we report measurements of the Hall coefficient $R_H$ for a set of C15b YbXCu$_4$ and LuXCu$_4$ compounds ($X =$ Au [16], Zn, Cd [18], Ti [18], Mg). The results show that the Hall coefficients have small values characteristic of normal metals in every case. This means that low carrier density is unique to RInCu$_4$. This observation allows us to hypothesize that the valence transition (which is also unique to YbInCu$_4$) is connected with the existence of a quasigap, which is a common feature in the band structure [19, 20] of C15b RInCu$_4$ compounds.

### 2. EXPERIMENTAL DETAILS

Polycrystalline samples of RXCu$_4$ ($R =$ Yb, Lu and $X =$ Cu, Zn, Ti, Mg) were prepared by heating the starting materials in evacuated tantalum tubes which were then sealed in evacuated quartz tubes and heated to 1150°C for 12 h, cooled to 800°C and held at that temperature for 7 days. Single crystal samples of RCoCu$_4$ ($R =$ Yb, Lu) and of YbXCu$_4$ ($X =$ Zn, Ti and Mg) were also grown in fluxes by the method outlined in [3]. Using conventional X-ray diffraction we established that all these samples crystallize in the C15b structure. The Hall coefficients were measured using a He-flow cryostat for temperatures in the range 15–325 K. The samples were shaped into thin plates of typical dimension $0.5 \times 2 \times 3$ mm. The Hall voltage was measured in fields of $\pm 1 T$ at various fixed temperatures using an LR400 resistance bridge and an operating frequency of 16 Hz. Small misalignment voltages were compensated electronically and the magnetoresistance was cancelled by reversing the polarity of the field. The Hall voltage was linear in applied field for $H \leq 1 T$.

### 3. RESULTS AND ANALYSIS

The Hall coefficients $R_H$ of YbXCu$_4$ and LuXCu$_4$ compounds are shown in Fig. 1. The Hall coefficients of LuXCu$_4$ for $X =$ Cu, Zn, Cd, Mg are weakly temperature dependent, small ($\sim 0.3-1.7 \times 10^{-10}$ m$^3$/C) and negative. (For LuTiCu$_4$, $R_H$ is even smaller in magnitude, but positive below 25 K; the latter may be extrinsic behavior.) For YbXCu$_4$ there are four formula units in a cell of side 7.1 Å, so that in sample one-band model a Hall coefficient of $- 1 \times 10^{-10}$ m$^3$/C corresponds to 5.6 electrons per formula unit. This suggests that these LuXCu$_4$ compounds are good metals. The Hall coefficients of the YbXCu$_4$ compounds are also relatively small, being in the range $[-1-10] \times 10^{-10}$ m$^3$/C (with the exception of YbZnCu$_4$ where $R_H$ reaches the value $- 20 \times 10^{-10}$ m$^3$/C at the lowest temperatures). As for other Yb compounds [21], the temperature dependence of $R_H$ observed in YbXCu$_4$ is not due to changes in the carrier density, but is associated with skew scattering [22] from the Yb 4f electrons which give a temperature dependence of the form $R_H(T) = R_0(T) + \beta \chi(T) \rho(T)$.
where $\chi$ is the susceptibility, $\rho$ is the resistivity and $\beta$ is a constant. While we defer such an analysis to a later publication [23], here we note that for X = Au [16], Zn [23] and Cd [18] the susceptibility increases with decreasing temperature, so that the results shown in Fig. 1 imply that $\beta$ is negative, as is often found [21] in Yb compounds. YbMgCu$_4$ [23] and YbTlCu$_4$ [18] show broad susceptibility maxima, characteristic of mixed valent compounds; Fig. 1 then implies that $\beta$ is negative for YbMgCu$_4$ but positive for YbTlCu$_4$. The background (non-4f) contributions $R_B(X)$ can be estimated from the high temperature asymptotic values (where $\chi$ is small); these lie close to the values for the corresponding LuXCu$_4$ compounds. Our basic result is, then, that the RXCu$_4$ compounds for R = Yb, Lu and X = Au, Zn, Cd, Mg and Tl have Hall coefficients that are more than an order of magnitude smaller than the values seen in semimetallic LuInCu$_4$ and the high temperature state of YbInCu$_4$, which suggests that the RXCu$_4$ compounds are all good metals.

4. DISCUSSION

We now consider whether the bandstructure of RXCu$_4$ supports our hypothesis that the phase transition in YbInCu$_4$ is connected intimately with the high temperature semimetallic behavior and in addition which features of the bandstructure yield our basic result that semimetallic behavior appears to be unique to RhCu$_4$ in the class of RXCu$_4$ compounds in the C15b structure. Bandstructures have been reported for RhCu$_4$ (R = Yb, Lu) [19] and for RAgCu$_4$ (R = Yb, Lu) YbAuCu$_4$ and YbPdCu$_4$ [20]. A sketch of the non-4f density of states common to all cases studied is given in Fig. 2. A large peak due to Cu-3d and X-3d states resides 2–6 eV below the Fermi level $\epsilon_F$. For most cases the Fermi level lies in a smaller double-peak due to Cu-p, d and X-p, d states, which is of maximum magnitude ~1–3 states/eV-atom and of width ~1.5 eV. This is separated by a quasigap (of very low density of states) of width 0.5–1 eV from a peak of width 3 eV and magnitude ~5 states/eV-atom due primarily to R-5d states and secondarily to Cu-3s, p states. For the Yb compounds, the calculations [19, 20] treat the Yb 4f electrons as band states (as opposed to frozen core states) which forces a partial occupancy (of...
order 13.6) for the 4f state; the Fermi level lies near the
top of this 4f band. The Fermi level moves progressively
from the bottom (low energy side) of the double-peak p, d
structure for YbPdCu4, to the middle for YbAgCu4,
LuAgCu4 and YbAuCu4 and then to the top (high energy
side) for YbInCu4. Given the similarity of the density of
states in all cases and given this trend in the position of
the Fermi level it is clear that rigid band concepts apply
at least qualitatively. The Fermi level pushes up through
the p, d double-peak as the X atom moves to the right in
the Periodic Table.

The Fermi level for LuInCu4 lies in the quasigap
[19], which can also be understood as a consequence of
rigid band motion: in the calculation for YbInCu4 the Yb
atoms are formally in the $4f^{14-n}(5d, 6s)^{2+n}$ configuration with $n = 0.4$ and contribute 13.6 4f electrons and
therefore 2.4 5d and 6s electrons to the valence band,
whereas for LuInCu4 the Lu atoms are in the $4f^{14}(5d, 6s)^3$ configuration and hence contribute 0.6
more (5d, 6s) electrons to the valence band, pushing the
Fermi level up into the quasigap. Closer examination
[19] shows the LuInCu4 is a semimetal, with a closed
hole sheet around the X point and a closed electron
sheet around the X point, with the number of electrons
equal to the number of holes (0.04 per formula unit).

We note that the Hall coefficient of LuInCu4 (which is
$-60 \times 10^{-16}$ m$^3$/C at low temperature [4]) suggests in
a one band model that there are 0.09 electrons per
formula unit.

There is an important difference between the
expected 4f states of YbInCu4 and those calculated in
the band structure: the strong intraatomic correlations
cause the 4f states to be highly localized and description
of them as a simple band at the Fermi level is
inappropriate. Nevertheless, the difference between the
high temperature and low temperature electronic con-
figurations of YbInCu4 is similar to the difference
between the electron configurations of LuInCu4 and
YbInCu4 in the band calculations in the following
respect: the Yb changes from a mixed valent
$4f^{13.2}(5d, 6s)^{2.8}$ configuration at low temperature to a
trivalent $4f^{13}(5d, 6s)^3$ configuration at high temperature.

The observed change in the carrier density at the phase
transition suggests that the extra electrons contributed to
the valence band at high temperatures push the
Fermi level up into the quasigap, just as occurs for
LuInCu4. This provides justification for our hypothesis
that by a small increase in electron count (≈0.1–0.2)
the system can move the Fermi energy in such a
manner as to decrease significantly the density of
states $N(\varepsilon_F)$ and hence decrease the 4f-conduction
hybridization strength $\Delta = V_{\text{Kr}}^2 N(\varepsilon_F)$ in such a manner
as to cause a large decrease in the Kondo temperature
$T_K \sim \exp [- |E_F - \varepsilon_F|/(2J + 1)\Delta]$. It is this feature of the

bandstructure which allows for the phase transition in
YbInCu4, as opposed to the sensitivity of the Kondo
temperature to changes in cell volume as in Ce.

For X atoms which are in columns of the Periodic
Table to the left of In, the Fermi level of YbXCu4 and
LuXCu4 should be located in the p, d double-peak with a
healthy density of states and concomitant metallic beha-
vor. As reported here for X = Au, Cd, Zn and Mg and as
reported elsewhere [16] for X = Pd and Ag the YbXCu4
and LuXCu4 compounds for these X appear to be good
metals. The small Hall coefficients seen in LuTiCu4
and YbTiCu4 suggest that these are also good metals.
This means that position of the Fermi level can't be
determined simplistically from the column of the X
element in the Periodic Table. The positive value of the
skew scattering coefficient in YbInCu4 may, however,
be an indication of significant differences between
RTiCu4 and the other RXCu4.

Our hypothesis, which in a straightforward way links
the experimental behavior to features of the band-
structure, is compelling and general. We are currently
measuring the resistivity, susceptibility, specific heat and
$L_1$ X-ray absorption spectra of the YbXCu4 compounds
[23]. This should allow us to determine whether the
Kondo temperature and valence can be related to the
position of the Fermi level relative the quasigap as
required by our hypothesis. More detailed tests of the
hypothesis will require such measurements as photo-
emission, de Haas van Alphen (dHvA) and optical
absorption to establish the background band structures
and the position of the renormalized f bands.

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