4f-Electron Localization in Ce$_x$La$_{1-x}$MIn$_5$ with $M =$ Co, Rh, or Ir

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The behavior of rare earth and actinide compounds depends largely on the extent to which the f electrons participate in chemical bonding. The evolution from localized to itinerant behavior that gives rise to heavy fermions and quantum criticality is the subject of much theoretical debate [1]. The term “itinerant” refers to electrons that are fully hybridized with the conduction band, giving rise to a “large” Fermi surface (FS) that accommodates the f electrons. Strong fluctuations involving the f-electron spin degrees of freedom cause the resulting composite quasiparticles to have large effective masses and a large Pauli paramagnetic susceptibility. Two qualitatively different models attempt to account for the origin of quantum criticality associated with the development of antiferromagnetic (AFM) order in the low temperature limit. One of these assumes the composite quasiparticles to condense upon formation of a spin-density wave (SDW) [2], involving a translation the large FS in limit. One of these assumes the composite quasiparticles to have large effective masses $f$ electrons, which would then account for the development of a heavy composite Fermi-liquid state as $x \rightarrow 1$. The failure of a composite Fermi-liquid state to form for any $x$ in the case of $M =$ Rh is shown to be inconsistent with theoretical models that propose antiferromagnetism to result from spin-density-wave formation.

The behavior of rare earth and actinide compounds provide an alternative tuning parameter for investigating the factors responsible for quantum criticality. CeMIn$_5$ can be made to lie on either side of the QCP depending on whether $M =$ Co and Ir or $M =$ Rh [6], hence $M$ behaves like a tuning parameter in a qualitatively similar manner to $p$. In the case of $M =$ Co and Ir, a heavy composite Fermi-liquid ground state is thought to exist, which is then unstable to superconductivity at low temperatures. In the case of $M =$ Rh, AFM order is observed, with the magnitude of the moment $\mu = (0.75-0.8)\mu_B/\text{Ce}$ [7] being slightly smaller than that $\mu = 0.92\mu_B/\text{Ce}$ predicted by the crystal field theory of local-
directly supported by the observation that not all of the electrons do not contribute to the FS volume in all series containing Co and Ir).

Electrons remain localized (in contrast to the compounds entirely different FS in (d) being created on entering the structural FS (dotted lines) to be observed. (c) shows the same magnetic fields, enabling the orbits of the original unreconstructed FS to be fragmented, leaving the smaller section intact.

The process of translation (b) causes the larger temperature. The process of translation (b) causes the larger section to be fragmented, leaving the smaller section intact. Quasiparticles may be able to tunnel through the SDW gaps in a magnetic fields, enabling the orbits of the original unreconstructed FS (dotted lines) to be observed. (c) shows the same FS as in (a) in the absence of SDW fluctuations. Instead, the entire FS may be subject to quantum fluctuations, with an entirely different FS in (d) being created on entering the AFM phase, for which Bragg reflection effects are less significant.

FIG. 1. Schematic of the modification of the FS upon formation of AFM order. (a) represents a notional heavy composite FS constructed from two bands, the larger of which may be subject to quantum fluctuations with respect to the translational vector \( \mathbf{Q} \) on approaching a SDW phase transition at zero temperature. The process of translation (b) causes the larger section to be fragmented, leaving the smaller section intact. Quasiparticles may be able to tunnel through the SDW gaps in a magnetic fields, enabling the orbits of the original unreconstructed FS (dotted lines) to be observed. (c) shows the same FS as in (a) in the absence of SDW fluctuations. Instead, the entire FS may be subject to quantum fluctuations, with an entirely different FS in (d) being created on entering the AFM phase, for which Bragg reflection effects are less significant.

ized \( 4f \) electrons [8]. This difference is assumed to be caused by partial Kondo screening, a view that is indirectly supported by the observation that not all of the \( R \ln 2 \) entropy per spin is released above the Néel temperature [9]. However, direct measurements of the FS topology [10], using the dHvA effect, show no significant change in the FS topology or volume over the entire range of \( x \) in \( \text{Ce}_{1-x}\text{La}_{x}\text{RhIn}_5 \), showing conclusively that the \( f \) electrons remain localized (in contrast to the compounds containing Co and Ir).

Here, we report the results of a dHvA study on the alloy series \( \text{Ce}_{1-x}\text{La}_x\text{MIn}_5 \), that reveals notable differences between \( M = \text{Co} \) and \( \text{Ir} \) and \( M = \text{Rh} \) that occur over the entire range \( 0 < x \leq 1 \). We show that while the \( 4f \) electrons do not contribute to the FS volume in all cases for \( x \leq 0.3 \), significant differences in the quasiparticle scattering emerge. The \( 4f \) electrons reduce the quasiparticle mean free path much more severely for \( M = \text{Co} \) and \( \text{Ir} \) than for \( M = \text{Rh} \), finally becoming itinerant as \( x \to 1 \) only for \( M = \text{Co} \) and \( \text{Ir} \). We then argue that these findings are inconsistent with SDW formation [1], which is a popular scenario for quantum criticality in heavy fermion materials.

The dHvA oscillations are measured using a combination of pulsed and static magnetic fields, using signal detection and \( ^3\text{He} \) refrigeration techniques described elsewhere [10]. In all experiments, the magnetic field \( H = B/\mu_0 \) is applied along the \( c \) axis of the tetragonal unit cell, where a potential change in electronic structure due to metamagnetism is not observed for \( B \leq 50 \) T [11]. Figure 2 shows the dependence of dHvA frequencies \( F_i \) on concentration \( x \) for several different FS sheets for \( M = \text{Co}, \text{Rh}, \) and \( \text{Ir} \). Each frequency \( F_i \) corresponds to a distinct extremal cross section \( A_i \) of the FS in \( k \) space, as determined by the Onsager relation \( F_i = (\hbar/2\pi e)A_i \) [12]. In all cases, \( F_i \) can be seen to depend only very weakly on \( x \) for \( x \approx 0.3 \). This implies that the \( 4f \) electrons provided by the Ce atoms do not contribute significantly to the FS volume at low concentrations (\( x \approx 0.3 \)), and remain essentially localized. In the case of \( M = \text{Co} \) and \( \text{Ir} \), however, all of the dHvA frequencies undergo a significant change between \( x \approx 0.3 \) and \( x = 1 \). These changes indicate that the FS topology undergoes a transformation between \( x \approx 0.3 \) and \( x = 1 \), corresponding to an expansion of the FS volume so as to accommodate \( 4f \) electrons that have now become itinerant [13,14]. In order to enable frequencies from each sheet of the FS to be followed through the range of concentrations where the dHvA effect cannot be observed, additional field-orientation (\( \theta \)-dependent) data are shown for pure \( \text{CeMIn}_5 \) and \( \text{LaMIn}_5 \) with \( M = \text{Co} \) and \( \text{Ir} \). Figure 2: data of Haga et al. [15] are used for the case where \( M = \text{Ir} \) and \( x = 1 \), while similar data for the other limits are published in Refs. [13,16]. While the sizes of each FS sheet vary between the end limits of \( x \), the overall shapes remain unchanged, giving rise to clearly identifiable angular dependences of \( F_i \).

Let us focus initially on the dilute Ce limit: The \( x \) dependence of the effective mass for \( x \approx 0.3 \) is seen to be similar for all \( M \) in Figs. 4(a)–4(c) (though slightly heavier for \( M = \text{Co} \)), being consistent with a scenario in which the Ce atoms behave primarily as isolated Kondo

FIG. 2. A plot of the various frequencies \( F_i \) (in tesla) versus the substituted concentration \( x \) of Ce, for \( M = \text{Co}, \text{Rh}, \) and \( \text{Ir} \) in order of increasing atomic weight. The actual FS cross-sectional areas in \( k \) space can be obtained by applying the Onsager relation. The nomenclature introduced by Shishido et al. [13] is used for the subscripts \( i \).
imurities in the dilute limit [17]. We note that the single-ion Ce Kondo temperature is estimated to be \( T_K = 2 \) K in LaCoIn\(_5\) [18]. Consequently, in magnetic fields above \( \sim 10 \) T, where the effective masses are measured, the degeneracy of the ground state doublet is lifted, causing the Kondo screening to be mostly destroyed. Weakened resonant scattering therefore causes Ce to act mostly as a magnetic impurity for all \( M \) in the very dilute limit [17], causing the dHvA oscillations to be mostly damped by a Dingle scattering term \( R_D = \exp(-\pi/\omega_c \tau) = \exp(-\pi l_c / l) \), where \( l_c = \sqrt{2hf/eB^2} \) is the cyclotron length [12]. Figure 4(d) shows the mean free path \( l \) obtained from an analysis of the field dependence of this damping. Whereas weak scattering in the case of \( M = \text{Rh} \) enables the dHvA effect to be observed for all \( x \) [19], it is sufficiently strong in the case of \( M = \text{Co} \) and \( \text{Ir} \) for \( l \) to become less than the perimeter \( 2\pi l \), of the cyclotron orbit when \( x \approx 0.3 \). This causes the Landau levels to become incoherent, rendering the dHvA effect unobservable [Fig. 4(d)].

Scattering in the dilute limit depends on the coupling \( J \) of the \( 4f \) electrons to the conduction electrons, of bandwidth \( W \), and the density of states \( N(\varepsilon_F) = 1/W \), which is thought to be similar for all La\( M \)In\(_5\) compounds. The above differences between \( M = \text{Co} \) and \( \text{Ir} \) and \( M = \text{Rh} \) must be a direct consequence of differences in \( J \), which exist in the small impurity limit. Adopting a simple qualitative analysis based on Doniach’s phase diagram [19], a smaller \( J/W \) in the case of \( M = \text{Rh} \) favors a stronger RKKY coupling strength, \( T_{\text{RKKY}} \approx J^2/W \), compared to the Kondo temperature, \( T_K \approx W \exp(-W/J) \), which is consistent with the formation of AFM order for \( x \approx 0.6 \) [10,20]. A larger \( J/W \) in the case of \( M = \text{Co} \) and \( \text{Ir} \) favors the formation of a heavy composite Fermi-liquid. According to simple percolation arguments based a square lattice of randomly arranged Ce and La atoms [18,21], however, composite quasiparticles cannot move freely throughout the bulk for \( x \leq 0.4 \); possibly explaining why the \( 4f \) electrons appear to remain localized for \( x \leq 0.3 \) in the case of \( M = \text{Co} \) and \( \text{Ir} \). The region \( 0.3 \leq x \leq 1 \) therefore likely corresponds to a highly disordered intermediate state in which the composite Fermi-liquid Landau levels are incoherent, which overlaps with the region of non-Fermi-liquid behavior reported in the electrical transport by Nakatsuji et al. [18] at zero \( B \). After the dHvA signal is lost above \( x = 0.3 \), fully coherent Landau levels are not recovered until \( 0.99 \leq x \leq 1 \), whereupon the \( 4f \) electrons have become itinerant [13,14]. The composite heavy Fermi-liquid state realized as \( x \rightarrow 1 \) is much more susceptible to disorder than the weakly correlated state that exists in the dilute limit. The dHvA effect has thus far not been observed in Ce\(_{0.99}\)La\(_{0.01}\)In\(_5\) for \( M = \text{Co} \) and \( \text{Ir} \) (i.e., with only 1% of the Ce atoms replaced by La).

Given that the compounds with \( M = \text{Co} \) and \( \text{Ir} \) and \( M = \text{Rh} \) occur on opposite sides of the QCP that can be tuned by \( p \) and \( M \) [6], the results of the present study are consistent with the model illustrated in Figs. 1(c) and 1(d), in which the composite fermions break up into their constituent conduction electron and localized \( 4f \)-electron components [1], i.e., the electronic structures are significantly different on either side. The arguments against the AFM forming as the consequence of a SDW instability of the composite quasiparticle FS are therefore rather straightforward.

First, the differences in behavior between \( M = \text{Co} \) and \( \text{Ir} \), on one hand, and \( M = \text{Rh} \), on the other, in the limit \( x \rightarrow 1 \) are consistent with different bare interaction strengths in the dilute limit. This suggests that differ-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{A comparison of the FSs of the pure La (open symbols) and Ce (filled symbols) compounds for \( M = \text{Co} \) (a) and \( M = \text{Ir} \) (b), made by means of angle-dependent studies, where \( \theta \) is angle between of \( H \) and the tetragonal \( c \) axis. Data for \( M = \text{Ir} \) and \( x = 1 \) are taken from Haga et al. [15].}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{A plot of the dependence of the quasiparticle effective masses \( m^*_i \) on \( x \) for the various FS cross sections observed in \( M = \text{Co} \) (a), \( \text{Rh} \) (b), and \( \text{Ir} \) (c), obtained from fitting the \( T \) dependence of the dHvA amplitudes for \( 20 \leq B < 40 \) T, \( 10 < B < 20 \) T, and \( 25 < B < 45 \) T, respectively. The symbols refer to the different frequencies identified in Figs. 2 and 3. (d) \( l \) for the \( F_{\rho 2} \) frequency as a function of \( x \) for \( M = \text{Co} \), \( \text{Rh} \), and \( \text{Ir} \).}
\end{figure}
quences in the degree of hybridization between the 4f- and conduction electrons in the AFM state is predetermined by the differences in J in the dilute limit.

Second, a SDW in CeRhIn$_5$ would have to condense from a composite Fermi-liquid state of the type that exists in CeCoIn$_5$ and CeIrIn$_5$. There is, however, no evidence that such a state is ever realized to any extent in Ce$_{1-x}$La$_x$RhIn$_5$, with or without AFM order (which is realized for $x \approx 0.6$ [10,20]). The SDW would cause such a composite quasiparticle FS to become fragmented by Bragg reflection upon formation of the AFM Brillouin zone in the manner depicted schematically in Fig. 1(b): orbitals smaller than the AFM Brillouin zone would remain mostly unaffected while larger orbits could be recovered upon the tunneling of quasiparticles through the SDW gap, $\Delta$, in a magnetic field (dotted line). This tunneling (often referred to as magnetic breakdown [12]) can occur provided $\hbar \omega_c e_F \approx \Delta^2$; here, $\hbar \omega_c = \hbar e B/m^*$ is the cyclotron energy and $e_F = \hbar e F/m^*$ is the effective Fermi energy. This inequality would have to be satisfied in CeRhIn$_5$ to account for the observation of dHvA frequencies (e.g., from the $\beta$ orbit) [13] that exceed the frequency $F_{MBZ} = 4780$ T corresponding to the cross-sectional area of the AFM Brillouin zone [22,23]. The SDW model is disproved in Ce$_{1-x}$La$_x$RhIn$_5$ by virtue of the fact that all of the observed dHvA frequencies are consistent with a FS in which the 4f electrons remain localized. The AFM order therefore cannot form as a consequence of a SDW instability of a composite heavy Fermi-liquid in the manner depicted in Fig. 1(b).

Any Bragg reflection that occurs must therefore occur between conduction electrons and a localized lattice of 4f electrons. Uncoupled conduction electrons with lighter effective masses, $m^* = eB/\omega_c$, and therefore larger kinetic energies, $e_F$, cause the weaker Bragg reflection in this case to be more vulnerable to magnetic breakdown, i.e., $\hbar \omega_c e_F \gg \Delta^2$. This perhaps explains why evidence for Bragg reflection is seldom observed in dHvA experiments on AFM ordered heavy fermion materials [5,23,24], in contrast to genuine SDW materials where such evidence is abundant [3,25].

The picture that emerges is therefore one in which a weak relative coupling, $J/W$, predisposes the 4f electrons in Ce$_{1-x}$La$_x$RhIn$_5$ to be localized for all $x > 0$, including the dilute limit where AFM order cannot form. The AFM order must therefore be driven by RKKY exchange interactions between 4f electrons that are predisposed to be localized by a small $J/W$, causing $T_K/T_{RKKY} = (W/J)^2 \exp(-W/J)$ to be small. The present results further suggest that 4f-electron localization is the primary driving factor for quantum criticality in the $p,M$ phase diagram of Ce$_{1-x}$La$_x$MIn$_5$ rather than the AFM order parameter. The close correspondence between antiferromagnetism and 4f-electron localization appears to be qualitatively similar to that observed between ferromagnetism and f-electron localization reported in systems such as CeRu$_2$Si$_2$ [26], where ferromagnetism is induced by a magnetic field by way of metamagnetism. Metamagnetism has also been proposed as a source of quantum critical behavior [27].

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