Localized $f$ electrons in Ce$_x$La$_{1-x}$RhIn$_5$: dHvA Measurements

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Measurements of the de Haas-van Alphen effect in Ce$_x$La$_{1-x}$RhIn$_5$ reveal that the Ce 4$f$ electrons remain localized for all $x$, with the mass enhancement and progressive loss of one spin from the de Haas-van Alphen signal resulting from spin fluctuation effects. This behavior may be typical of antiferromagnetic heavy fermion compounds, despite the fact that the 4$f$ electron localization in CeRhIn$_5$ is driven, in part, by a spin-density wave instability.

Ce and U-based heavy fermion systems display a variety of different ground states, ranging from ordered antiferromagnets to superconductors. There has been considerable effort made to correlate these changes in behavior with changes in the electronic structure, and to identify those characteristics that are universal to all heavy fermion systems. With this goal in mind, de Haas-van Alphen (dHvA) experiments continue to play an important role. They have the potential to yield otherwise inaccessible information on how the 4$f$ or 5$f$ electrons mix with the conduction electrons, and, ultimately, how this determines the electronic ground state.

The heavy fermion compound CeRhIn$_5$ is of special interest to the general understanding heavy fermion systems because, not only does it order antiferromagnetically below $T_N \sim 3.8$ K, but also becomes superconducting ($T_c \sim 2.1$ K) at hydrostatic pressures $p$ exceeding $p_c \sim 16$ kbar. Thus, by changing the experimental conditions, CeRhIn$_5$ displays the two most contrasting types of behavior that are found in heavy fermion systems. A matter of further interest is that both the electronic contribution to the specific heat $\gamma$ and $\Theta_D$ remain largely unchanged for pressures $p < p_c$, and under the application of high magnetic fields $B \leq 50$ T. In addition, the value of the critical applied field that changes or destroys the antiferromagnetic state is highly anisotropic, ranging from 2 T for $B \parallel [100]$ to over 50 T for $B \parallel [001]$. The 2 T transition for $B \parallel [001]$ is known to be from one spiral spin state to a second that persists to $\sim 50$ T.

In this paper, it is shown that the apparent robustness of the electronic structure to large variations of $p$ and $B$ can be attributed to the nearly ideal localized behavior of the 4$f$ electrons in CeRhIn$_5$. dHvA experiments performed throughout the entire Ce$_x$La$_{1-x}$RhIn$_5$ series, (i.e. for $0 < x < 1$) reveal that the Fermi surface topology is nearly independent of $x$, implying that there is virtually no exchange of charge degrees of freedom between the 4$f$ and conduction electrons. This type of behavior may typify antiferromagnetic heavy fermion systems. The progressive loss of one spin from the dHvA signal together with an increase in the quasiparticle effective masses on increasing $x$ indicate that spin fluctuation effects are nevertheless important.

Single crystal samples of Ce$_x$La$_{1-x}$Rh In$_5$, with $0 \leq x \leq 1$ in 12 incremental steps, were grown in In flux. They were etched in a 25% aqueous HCl solution both to remove the residual flux and to reduce them to a size necessary for dHvA measurements. A variety of experimental techniques were used in order to cover a wide range of frequencies and magnetic fields, $B$. Torque magnetometry and field modulation measurements were made in static magnetic fields at the National High Magnetic Field Laboratory (NHMFL), Tallahassee, while pulsed magnetic field measurements in fields of up 50 T were carried out at the NHMFL, Los Alamos (detailed discussions of the techniques are contained in References [66]).

Temperatures in the range $0.45 \leq T \leq 6$ K were used in the measurements. All three techniques yielded similar frequencies for $B$ applied along the principal [100] and [001] axes that were under investigation.

Examples of Fourier transforms of the dHvA data (in the 1/$B$ domain) for $x = 0.05$ and $B$ applied along [100] and for $x = 0.5$ and $B$ applied along [001] are shown in Figs. 1(a) and 1(b) respectively. The presence of many frequencies with signal-to-noise ratios comparable to those measured in pure LaRhIn$_5$ and CeRhIn$_5$ shows that no significant attenuation of the dHvA amplitude results from alloying. This finding is similar to that observed throughout the Ce$_x$La$_{1-x}$B$_6$ series. In contrast to Ce$_x$La$_{1-x}$B$_6$, however, measurements on Ce$_x$La$_{1-x}$RhIn$_5$ (for $0 \leq x \leq 1$), shown in Fig. 2 reveal no significant dependence of the Fermi surface topology on $x$, apart from two small exceptions: First, one very low frequency in LaRhIn$_5$ of $\sim 7$ T, originating from a pocket that occupies less than 1 part in $10^4$ of the Brillouin zone volume, is not present in the alloys. Second, the two distinct but closely spaced frequencies, $f_6$ and $f_7$ (for $B \parallel [001]$) only can be individually resolved for $x \leq 0.95$.

In pure CeRhIn$_5$, there has been some uncertainty about the degree to which the 4$f$ electrons contribute to the Fermi surface. Because the bandstructure cal-
culations on pure CeRhIn$_5$ consider the 4$f$ electrons to be fully itinerant, only if the 4$f$ electron wavefunctions are well mixed with the conduction electrons might one expect to find good agreement between dHvA data and the calculations. Some degree of similarity between the dHvA data and the itinerant 4$f$ electron bandstructure was reported in CeRhIn$_5$. However, the average fractional frequency difference between the calculated and measured values, $\left(F_{\text{Exp}}-F_{\text{BS}}/F_{\text{Exp}}\right)$, is 0.44 for $B||[001]$. Therefore, it is clear from the measurements and calculations in Ref. whether the 4$f$ electrons are itinerant or localized. The results presented in Fig. 2 show that, because of the absence of any strong dependence of the frequencies on $x$, the addition of 4$f$ electrons does not change the Fermi surface volume and therefore they must be almost entirely localized. This conclusion is rigorous since it does not depend on the ability of bandstructure calculations to reproduce experimental data.

A number of Ce-based heavy fermion systems, for example Ce$_6$, CeRu$_2$Si$_2$, CeAl$_2$, and CeCu$_2$Si$_2$, have been shown to exhibit dHvA oscillations at high magnetic fields that appear to be consistent with a localized 4$f$ electron picture. By localized we mean that the high magnetic field dHvA data in these systems are more closely reproduced by bandstructure calculations made on the La analogue compounds than on the completely delocalized bandstructure calculations for the Ce compounds. It is at high magnetic fields, where $f$ electron alignment occurs in these materials, that the dHvA data are often most clear, thereby facilitating a direct comparison between experiment and theory. In cases where this has been studied, it has been concluded previously that all Ce-based heavy fermion compounds exhibit localized $f$ electron behavior upon their alignment by a magnetic field. Owing to the absence of a simple equivalent analogue to La in the case of U, it is difficult to verify in this manner whether this is true in U-based heavy fermion systems.

Several heavy fermion compounds now have been shown to undergo Fermi surface changes at, what is commonly referred to as, the metamagnetic transition field $B_M$. In CeRu$_2$Si$_2$, this change has been associated with what appears to be a transition from itinerant to localized 4$f$ electron behavior at the field where the 4$f$ electrons become aligned. The Fermi surface change in CeCu$_2$Si$_2$ also is likely to be consistent with this picture. In CeIrIn$_5$, on the other hand, dHvA experiments only have been performed at fields below $B_M$ ($\sim 40$ T), where the dHvA results for the fractional frequency differences between measured and fully itinerate calculated band structure frequencies are only 0.15 compared to the 0.44 in CeRhIn$_5$. In addition, at least three U-based heavy fermion systems (UPd$_2$Al$_3$, UPt$_3$ and URu$_2$Si$_2$), in which Fermi surface transformations are observed, have been shown to possess Fermi surfaces at low magnetic fields consistent with the itinerant 5$f$ electron bandstructure.

In this context, CeRhIn$_5$ is interesting because it ex-hibits localized 4$f$ electron behavior at all magnetic fields over which dHvA oscillations are observed, from fields as low as 4 T up to 50 T over a range in which the magnetization never saturates. In this respect, CeRhIn$_5$ exhibits qualitatively the same behavior as CeAl$_2$; another well known strictly antiferromagnetic heavy fermion compound in which the 4$f$ electrons are localized at fields both above and below a magnetic transition. Because their Fermi surfaces do not change on crossing magnetic transitions, the antiferromagnetic heavy fermion systems CePh$_3$ and UCd$_1_1$ also may exhibit the same behavior. The pattern of behavior that emerges here is that a simple almost-localized 4$f$ electron model appears to apply very well to those systems in which the Kondo screening is weak and in which Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions dominate to form a strictly antiferromagnetically ordered ground state; namely CeRhIn$_5$, CeAl$_2$, CePb$_3$, CeB$_5$ and UCd$_1_1$, although dHvA studies only have been possible in CeB$_5$ at fields that greatly exceed $B_M$.

Given that bandstructure calculations on CeRhIn$_5$ predict most of the 4$f$ electron spectral weight to exist at energies between 0.3 and 0.7 eV above the Fermi energy $E_F$, the on-site correlation energy $U_{4f}$ (which is ultimately responsible for their localized behavior), must greatly exceed 0.7 eV. In order for the 4$f$ electrons not to modify the Fermi surface topology in Ce$_x$La$_{1-x}$RhIn$_5$, the singly occupied core 4$f$ electron level $E_{4f}$ must also be lower than $E_F$ by an amount that significantly exceeds the hybridization energy $V$.

In spite of the fact that the 4$f$ electrons are almost entirely localized in CeRhIn$_5$, the effects of spin fluctuations (excitations involving only spin degrees of freedom) are clearly important. This is seen in Fig. 3 by the progressive increase in the effective mass across the series and in Fig. 3(a) by the progressive loss of one spin direction from the dHvA signal. A complete single spin dHvA signal is observed for $x \geq 0.4$, when the logarithm $ln[A_q/\sqrt{q}]$ of the amplitude $A_q$ of each dHvA harmonic divided by the square root of the harmonic index $q$ falls on a straight line. We note that this is near the concentration of Ce where the series first exhibits antiferromagnetism. This type of behavior recently was observed in Ce$_x$La$_{1-x}$B$_6$ and the sign of the dominant spin channel was further found to be consistent with the model of Edwards and Grewe. According to their model, the high magnetic field phase of a heavy fermion system is similar to that of a field-induced ferromagnet. The spin-down electrons have effective masses that are more greatly enhanced by spin fluctuations and suffer from disorder scattering, causing them to no longer contribute to the dHvA signal. In the present case, the 4$f$ moments are only partially aligned in the range of measurement fields used.

The variation in the effective mass $m^*$ on increasing $x$ from the single impurity limit ($x \to 0$) to the impurity lattice limit ($x = 1$), has yet to be understood. The model of Gor’kov and Kim, which considers two-
impurity terms, appeared to explain a quadratic dependence in Ce$_{1-x}$La$_x$B$_6$ over a limited range of $x$. This model cannot, however, account for the non-monotonic dependence of $m^*$ on $x$ observed in Ce$_{1-x}$La$_x$RhIn$_5$ displayed in Fig. 3. Were the magnetic interactions between the 4$f$ electrons only of the nearest neighbor RKKY type, one would normally expect the establishment of long range antiferromagnetic order in pure CeRhIn$_5$ to compete with the Kondo-like screening interactions that give rise to strongly enhanced effective masses. It can be seen that there is only a slight increase in $m^*$ near $x = 0.4$ where the onset of antiferromagnetism occurs in the series. The dramatic increase in $m^*$ for $x \geq 0.9$ suggests that additional terms need to be incorporated into the lattice model.

Neutron diffraction experiments recently have shown the periodicity of the magnetic structure perpendicular to the CeIn$_3$ planes is incommensurate, evidencing the existence of a spin-density wave (SDW) [23]. This could imply that, in addition to RKKY interactions, Fermi surface nesting plays an important role in causing the 4$f$ electrons to behave in a localized fashion. While we would expect RKKY interactions to be especially important within the CeIn$_3$ planes, Fermi surface nesting could help stabilise long range order perpendicular to the planes. One particularly novel aspect of this observation is that the localised spins that accompany SDW ordering could help stabilise long range order perpendicular to the planes [21].

The possible involvement of Fermi surface nesting indicates that the balance between itinerant and localized 4$f$ electron nature in CeRhIn$_5$ may be somewhat delicate.

In summary, on performing a dHvA study across the Ce$_{1-x}$La$_x$RhIn$_5$ series, the near insensitivity of the Fermi surface topology to $x$ implies that the 4$f$ electrons are almost entirely localized. The increase in the effective masses together with the disappearance of one spin contribution to the dHvA signal on increasing $x$ do, however, indicate that spin fluctuation effects are important. The virtual insensitivity of $T_N$ and $\gamma$ to $p$, for $p < p_c$, implies that the localised 4$f$ electron picture survives for $p < p_c$, but then gives way to a more abrupt Fermi surface change for $p > p_c$ accompanying the onset of superconductivity. Such a Fermi surface change could be consistent with the finding, in other superconducting heavy fermion systems (CeCu$_2$Si$_2$, UPd$_2$Al$_3$, UPt$_3$, URu$_2$Si$_2$, and CeIn$_3$), where the dHvA data for $B < B_M$ are more consistent with an itinerant $f$ electron bandstructure.

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FIG. 1. Fourier transform of dHvA signals in Ce$_x$La$_{1-x}$RhIn$_5$, (a) for 4 < $B$ < 14.5 T aligned along the [100] axis at $T \approx 1.30$ K and $x = 0.05$, and (b) for 20 < $B$ < 30 T aligned along the [001] axis at $T \approx 1.43$ K and $x = 0.5$. The frequency labels are the same as in [11] and the data are shown in the insets.

FIG. 2. The principal dHvA frequencies in Ce$_x$La$_{1-x}$RhIn$_5$ plotted versus $x$, (a) for $B$ applied along [100] and (b) for $B$ applied along [001].

FIG. 3. Concentration dependence of the effective masses of various dHvA frequencies for (a) 4 < $B$ < 14.5 T aligned along [100] and (b) 20 < $B$ < 30 T aligned along [001]. The effective masses are obtained by fitting only to the temperature dependent term in the Lifshitz-Kosevich formula.

FIG. 4. A plot of $\ln[A_q/\sqrt{q}]$ versus harmonic index $q$ for the $F_3$ frequency, for which several harmonics could be observed. The dHvA signal is dominated by a single spin for $x \geq 0.5$, evidenced by the straight lines.