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Kondo liquid emergence and relocalization in the approach to antiferromagnetic ordering in $CePt_2In_7$

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$CePt_2In_7$ is a heavy fermion system with an antiferromagnetic transition at $T_N = 5.2$ K at ambient pressure. ^{195}Pt Knight shift measurements reveal anomalous behavior below $T^* \sim 40$ K. By comparing the susceptibility and Knight shift data, we extract the individual contributions of the local moments and the heavy electron components to the magnetic susceptibility. Our results confirm the scaling predictions of the standard model, but reveal a surprising result: namely that below 14 K the hybridized quasiparticles begin to "relocalize", an important precursor to their joining the local moments in becoming antiferromagnetically ordered at T_N.

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Competition between different ground states drives much of the interesting physics of solids. A prime example is the case of heavy fermion materials, in which a lattice of nearly localized f-electrons interacts with a sea of conduction electrons, giving rise to rich interplay of ground states associated with competing tendencies toward electron localization versus itineracy.[1,2] In recent years, the phase space between these two extremes has yielded a number of important discoveries, including unconventional superconductivity,[3,4] anomalous behavior in bulk transport and thermodynamic quantities,[5] and unexpected quantum phase transitions with critical fluctuations.[6,7] The development of a new predictive "standard model" for heavy electron materials - a phenomenological two-fluid description, in which two coexisting electronic fluids emerge below a collective hybridization temperature T^*, has changed our physical picture of how this dichotomy manifests itself.[8–11]

Historically, the magnetic behavior of the unpaired spins of the 4f/5f electrons in heavy fermion compounds has been described by a Kondo lattice, in which local moments and conduction electron spins experience an antiferromagnetic exchange interaction.[12] A complete theoretical description of the Kondo lattice remains elusive, particularly in the limit where the intersite coupling between local moments is of the same order of magnitude as the hybridization energy. The two-fluid description[9,10] captures so much of the relevant physics in straightforward fashion that it represents a highly promising new "standard model" that can replace the Doniach model[12] for Kondo lattice behavior.[8–11] It postulates the co-existence of the local moment (LM) f-electron lattice with an itinerant heavy electron Kondo liquid (KL) that emerges through its collective hybridization with the conduction electron sea below a temperature T^*, and attributes the rich variety of observed low temperature behavior to their mutual interaction. The two-fluid model separates the collective excitations of the Kondo lattice from the individual behavior of localized f-spins. The collective behavior below T^* is manifest in the itinerant and global nature of the emergent heavy fluid Kondo liquid, and involves not only hybridization between conduction and f-electrons, as is seen in the optical conductivity,[13] but also nonlocal spin correlations between f-electrons, as is seen in the Knight shift anomaly.[11]

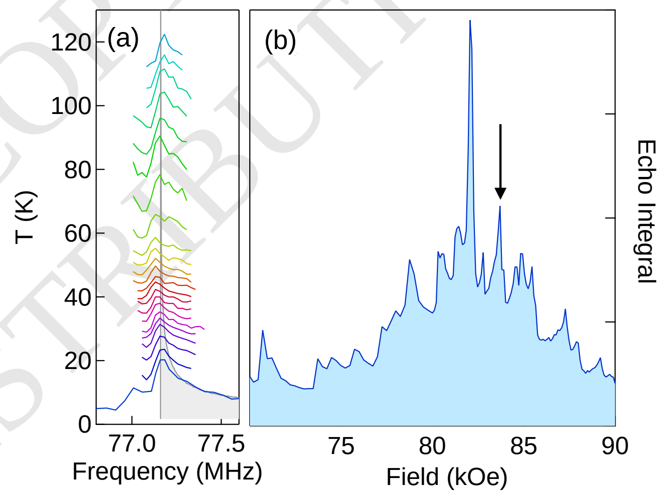

FIG. 1. (color online) (a) Spectra obtained at fixed field of 83.702 kOe showing the powder pattern of the ^{195}Pt as a function of temperature. The filled grey area indicates the theoretical powder pattern as discussed in the text. (b) Field-swept spectrum at fixed frequency of 77.16 MHz measured at 8 K. The majority of the structure arises from the powder pattern of the In(2) site. The black arrow indicates the Pt resonance.

Of particular interest is the extent to which this model is predictive, in that it can provide a quantitative explanation of KL emergence in a newly -discovered heavy electron material, and whether it can provide insight into a central question concerning the onset of long range antiferromagnetic order in these materials–does it involve only local moments, or does it represent as well a "relocalization" of itinerant KL quasiparticles? Here we report ^{195}Pt Knight shift data in a new two-dimensional heavy fermion system, $CePt_2In_7$, that answer both questions. $CePt_2In_7$ is antiferromagnetic below T_N= 5.2 K at ambient pressure, and becomes superconducting under pressure.[14,15] We find that in the paramagnetic phase at ambient pressure the Knight shift, K_{ab}, exhibits a dramatic anomaly at $T^*\sim$ 40 K, below which $K_{ab}(T)$ no longer tracks the bulk magnetic susceptibility, $\chi(T)$. The standard model correctly predicts the measured scaling behavior of the temperature dependent KL susceptibility below T^*, while the behavior of the latter below 12K provides direct evidence for the relocalization of KL quasiparticles as the onset of their long-range antiferromagnetic order causes KL scaling to break down.

In the single impurity picture, an isolated f electron in a metal hybridizes with the conduction electrons and forms a singlet below the Kondo temperature, T_K.[16] The two-fluid picture postulates that in a dense Kondo lattice the hybridization occurs collectively through the interaction of neighboring f-electron sites, rather than as individual isolated impurities.[9] The temperature scale for this process is set by $T^*> T_K$, and the hybridization is a continuous process such that for $T < T^*$ the changes in the f-electron degrees of freedom can be described by an order parameter, $f(T)$, that measures the fraction $f(T)$ of the local moments that become part of an itinerant heavy electron Kondo liquid.[8] Although T^* is material dependent, the fraction $f(T)$ is well described for $T < T^*$ by

$$f(T) = f_0\left(1-\frac{T}{T^*}\right)^{3/2}, \qquad (1)$$

where the non-universal constant f_0 measures the effectiveness of the hybridization process. This phenomenology captures well the resistivity, Hall coefficient, specific heat, susceptibility and Knight shift measurements in a broad range of Kondo lattice materials.[9]

Polycrystalline samples of $CePt_2In_7$ were synthesized as described in Ref. 15. The polycrystalline nature of the sample precludes any measurements of the ^{115}In ($I = 9/2$) NMR resonances because the strong electric field gradients and quadrupolar interactions give rise to large variations of the resonant frequencies as a function of orientation in the external magnetic field (see Fig. 1). ^{195}Pt, on the other hand, is spin $I = 1/2$ and has no quadrupolar interactions. The resonant frequency is given by: $\omega = \gamma H_0(1 + K_c \sin^2\theta + K_{ab}\cos^2\theta)$, where $\gamma = 0.9153$ kHz/Oe is the gyromagnetic ratio and θ is the angle between the c-axis and the external field $\mathbf{H}_0$. The only anisotropy in the resonant frequency is given by the Knight shift tensor. Since K_α is on the order of a percent, the Pt spectrum remains relatively sharp.

Fig. 1(b) show a field-swept spectrum at fixed frequency. The signal is spread out over a broad range of fields, and exhibits several singularities associated with particular orientations. The dominant contribution to the spectrum is from the In(2) sites with $\nu_z = 2.5$ MHz, and $\eta = 0.4$. The singularity at 83.7 kOe corresponds to the ^{195}Pt resonance. Fig. 1(a) shows the same ^{195}Pt resonance obtained by sweeping frequency at fixed field. The spectrum at 6 K reveals a peak at roughly 77.16 MHz with a high frequency tail. This shape is characteristic of a spin $I = 1/2$ nucleus with an anisotropic magnetic shift. The powder pattern is given by $\mathcal{P}(\omega)d\omega = d\Omega/|\nabla\omega|$, where Ω is the solid angle. The shaded grey area indicates the theoretical spectrum for $K_{ab} = 0.71\%$ and $K_c = 1.3\%$. The singularity or "horn" corresponds to $\theta = 90^\circ$ and is given by $\omega = \gamma H_0(1 + K_{ab})$. By tracking the temperature dependence of this horn, one can measure anisotropic Knight shift even though the sample is a polycrystalline powder.[17] This procedure can give rise to a slight overestimate ($\sim 0.01\%$) of K_{ab} due to the fact that the actual spectrum is given by a convolution of $\mathcal{P}(\omega)$ with the intrinsic lineshape of the nucleus.

From the spectra in Fig. 1(b) we extract the temperature dependence of the Knight shift in the ab direction, K_{ab} (Figure 2). For $T \gtrsim 40$ K, $K_{ab}(T)$ is proportional to the bulk magnetic susceptibility, $\chi(T)$. The inset shows K_{ab} versus χ with temperature as an implicit parameter. The negative value of the hyperfine coupling B_{ab} = -1.15(7) kOe/μ_B and the large orbital contribution $K^0_{ab} = 0.89\%$ are typical for transition metals such as ^{195}Pt.[18] The relatively small magnitude of the coupling suggests that the Pt is only weakly coupled to the Ce spins, which is not surprising as the Pt site is located between Ce-In(1) layers.[15] The magnetic susceptibility is only weakly dependent on field, and the anomalous behavior below 40 K is essentially field independent.[19] It is important to note that the Knight shift is measured along the ab direction whereas the susceptibility is reported for polycrystalline samples. However, previous investigations of Knight shift anomalies in single crystals reveals little or no difference in the anisotropy of the anomaly.[11,19]

In the majority of solids, the Knight shift is proportional to the magnetic susceptibility. If there is a single type of spin, such as the conduction electrons in a metal, or a local electron moment in an insulator, then the hyperfine coupling between the electron spin and the nucleus gives rise to a static shift of the nuclear resonance frequency and hence a linear Knight shift. Knight shift anomalies, in which the Knight shift, K, is not linearly proportional to the magnetic susceptibility, χ, are ubiquitous in heavy fermion compounds. The origin of the anomalous behavior in these materials is the emergence of a second component of the magnetic susceptibility from the Kondo liquid. The hyperfine Hamiltonian is given by $\hat{\mathcal{H}}_{\rm hyp} = \gamma\hbar\mathbf{I}\cdot\left(\mathbb{A}\cdot\hat{\mathbf{S}}_c + \mathbb{B}\cdot\hat{\mathbf{S}}_f\right)$, where $\mathbf{I}$ is the nuclear spin, γ is the nuclear gyromagnetic ratio, $\mathbb{A}$ is an on-site hyperfine tensor interaction to the itinerant electron spin, $\mathbf{S}_c$, and $\mathbb{B}$ is a transferred hyperfine tensor to the localized f spins, $\mathbf{S}_f$.[11] In this case, K and χ are given by:

$$K = (A + B)\,\chi_{\rm KL} + B\chi_{\rm LM} \qquad (2)$$

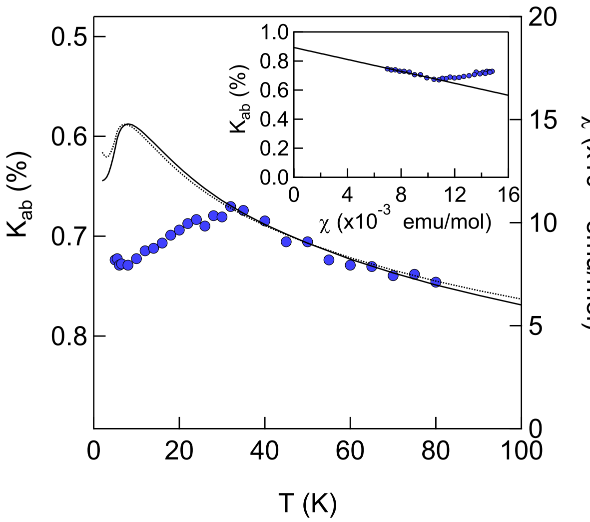

FIG. 2. (color online) The planar Knight shift, K_{ab} (●), and the powder susceptibility, χ (solid, dotted lines), versus temperature. The solid (dotted) line was measured in 0.5 T (7.0 T). INSET: K_{ab} versus χ, showing a change in slope at T^*. The solid line is a fit to the high temperature data with $A_{ab}=$ -1.15(7) kOe/μ_B and $K^0_{ab}=0.89(1)$ %.

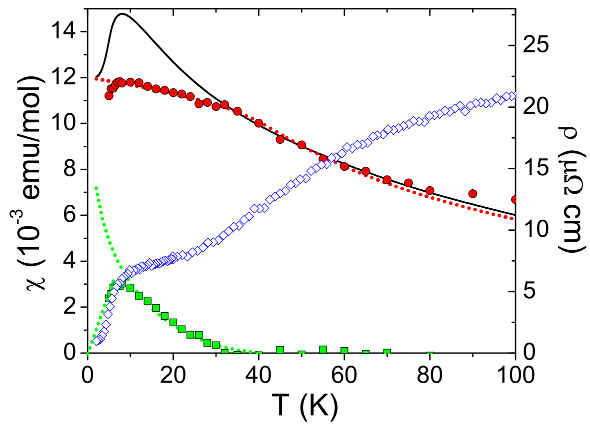

FIG. 3. (color online) The total susceptibility (solid line), the susceptibility of the local moments, χ_{LM} (●,red), and the susceptibility of the Kondo liquid component, χ_{KL} (■, green), and the resistivity (◇, blue) versus temperature. The dotted lines are fits to to χ_{LM} and χ_{KL} using the expressions given in the text. $T_0=12$ K is identified as the temperature where the data no longer coincide with the universal scaling predicted by the solid lines.

$$\chi = 2\chi_{\rm KL} + \chi_{\rm LM}, \tag{3}$$

where $\chi_{\rm KL}$ and $\chi_{\rm LM}$ are the KL and LM susceptibilities respectively, and are linear combinations of the correlation functions $\langle S_cS_c\rangle$, $\langle S_cS_f\rangle$, and $\langle S_fS_f\rangle$.[11] Above T^*, $\chi_{\rm KL}=0$ and $K=B\chi_{\rm LM}=B\chi$, reflecting linear behavior of a system that is dominated by local moment physics (see Inset of Fig. 2). The total magnetic susceptibility is given by the LM susceptibility alone and described by a Curie-Weiss form, $\chi_{LM}=C/(T+T^*)$, where C is a constant. Below T^*, $\chi_{\rm KL}=f(T)(R\ln 2/2T^*)R_W(1+\ln(T^*/T))$, where the Wilson ratio $R_W=2$ and the intrinsic entropy of the Kondo liquid approaches $R\ln 2$ at T^*.[20] For the LM susceptibility, we choose a modified Curie-Weiss form, $\chi_{LM}=(1-f(T))C/(T+\theta(T))$ with a temperature dependent $\theta(T)=(1-f(T))T^*$. This assumes that the local moments and their exchange interaction are both reduced by the factor $1-f(T)$ due to hybridization. At this point the local moments and conduction electrons have begun to hybridize, but retain both local and itinerant character and thus both $\chi_{\rm KL}$ and $\chi_{\rm LM}$ contribute to K with different weights (assuming $A\neq B$). The logarithmic growth of $\chi_{\rm KL}$ reflects the coherent nature of the KL state, and is consistent with the mass enhancement observed via the Sommerfeld coefficient of KL specific heat, which is related to the susceptibility via the Wilson ratio.[8] The magnetic shift arising from the Kondo liquid,

$$K_{\rm KL}=(A-B)\chi_{KL}(T), \tag{4}$$

is given by $K-B\chi$, and has been shown experimentally to scale as T/T^* up to two decades below T^*.[11]

We extract the two components, χ_{KL} and χ_{LM} from the Knight shift and the susceptibility, and our best fit determines the single free parameter $f_0=1$ (Fig. 3). The emergence and growth of the KL component is well fit by the two-fluid model down to 12 K. The experimentally determined values for $f(T)=\chi_{\rm KL}/(1+\ln(T^*/T))$ and $1-f(T)$ are shown in Fig. 4, along with the prediction from the two-fluid model (Eq. 1). Surprisingly, instead of continuing to increase to unity as predicted by Eq. 1, $f(T)$ turns over and a simple extrapolation of its linear downward slope suggests would approach zero at $T=0$ in the absence of long range antiferromagnetic order. For sufficiently low temperatures, one expects this scaling will be cut short by the influence of long range order (antiferromagnetism or superconductivity) on the hybridization process. In the case of $CePt_2In_7$, we find this happens at a surprisingly high temperature ($\sim 2.7T_N$), with $f(T)$ reaching a maximum value of ~ 0.6 at $\sim 0.35T^*$(14K), and decreasing linearly with temperature down to ~ 0.4 at $T_{\rm N}=0.13T^*$ (5.2K). Physically this indicates that below 12 K collective hybridization begins to reverse as the local moments begin the process of reducing their entropy through antiferromagnetic order, while the KL quasiparticles begin to relocalize. This trend is also evident in the relatively small value of $(T_1T)^{-1}$ at the In(1) site, suggesting that the f-electrons in $CePt_2In_7$ are only weakly hybridized.[15,21]

Antiferromagnetic order and collective hybridization may be viewed as competing LM states, just as itinerant behavior and localization are competing KL states. We see that at $T_{\rm N}$ a substantial fraction of KL quasipar-

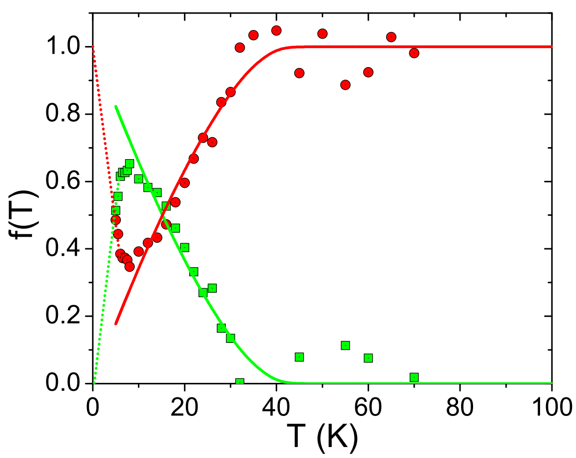

FIG. 4. (color online) The heavy electron fraction, $f(T)$ (■, green), and the local moment fraction, 1-$f(T)$ (●, red), versus temperature. The solid lines are the theoretical expressions as discussed in the text, and the dotted lines are linear fits to the low temperature data.

ticles remain itinerant; it is tempting to assume that the relocalization process proceeds linearly with temperature as the material becomes antiferromagnetic, with all KL quasiparticles ordering antiferromagnetically at $T = 0$. It remains to be seen what fraction of these relocalize and join the local moments in becoming part of the antiferromagnetic state. What is clear is that since a superconducting state emerges with pressure, it follows that as pressure increases some KL quasiparticles must not localize easily and superconductivity wins the competition with antiferromagnetism for their low temperature ordered state. The antiferromagnetic ordering process is likely driven by a combination of strong intersite direct exchange interactions between the moments, and their coupling to the KL quasiparticles which are also likely coupled antiferromagnetically. Indeed, both T_1^{-1} (at the In(3) site) and resistivity measurements (see Fig. 3) indicate that antiferromagnetic fluctuations develop around 12 K.

The success of the two-fluid picture and the straightforward physical picture contained therein clearly reveal a rich spectrum of behavior in the Kondo lattice materials. The relocalization of KL quasiparticles is a significant precursor to their ordering antiferromagnetically, while a simple extrapolation of the downward slope of $f(T)$ suggest that at ambient pressure all of the KL quasiparticles will become antiferromagnetic ordered by $T = 0$.

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[1] Z. Fisk, D. W. Hess, C. J. Pethick, D. Pines, J. L. Smith, J. D. Thompson, and J. O. Willis, Science, **239**, 33 (1988).
[2] P. Coleman, C. Pepin, Q. M. Si, and R. Ramazashvili, J. Phys.: Condens. Matter, **13**, R723 (2001).
[3] C. Petrovic, P. G. Pagliuso, M. F. Hundley, R. Movshovich, J. L. Sarrao, J. D. Thompson, Z. Fisk, and P. Monthoux, J. Phys. Cond. Mat., **13**, L337-L342 (2001).
[4] J. L. Sarrao, L. A. Morales, J. D. Thompson, B. L. Scott, G. R. Stewart, F. Wastin, J. Rebizant, P. Boulet, E. Colineau, and G. H. Lander, Nature, **420**, 297 (2002).
[5] J. Custers, P. Gegenwart, H. Wilhelm, K. Neumaier, Y. Tokiwa, O. Trovarelli, C. Geibel, F. Steglich, C. Pepin, and P. Coleman, Nature, **424**, 524 (2003).
[6] O. Stockert, E. Faulhaber, G. Zwicknagl, N. Stüßer, H. S. Jeevan, M. Deppe, R. Borth, R. Küchler, M. Loewenhaupt, C. Geibel, and F. Steglich, Phys. Rev. Lett., **92**, 136401 (2004).
[7] T. Park, M. J. Graf, L. Boulaevskii, J. L. Sarrao, and J. D. Thompson, Proc. Nat. Acad. Sci., **105**, 6825 (2008).
[8] S. Nakatsuji, D. Pines, and Z. Fisk, Phys. Rev. Lett., **92**, 016401 (2004).
[9] Y.-F. Yang, Z. Fisk, H.-O. Lee, J. D. Thompson, and D. Pines, Nature, **454**, 611 (2008).
[10] Y.-F. Yang and D. Pines, Phys. Rev. Lett., **100**, 096404 (2008).
[11] N. J. Curro, B. L. Young, J. Schmalian, and D. Pines, Phys. Rev. B, **70**, 235117 (2004).
[12] S. Doniach, Physica, **91B**, 231 (1977).
[13] K. S. Burch, S. V. Dordevic, F. P. Mena, A. B. Kuzmenko, D. van der Marel, J. L. Sarrao, J. R. Jeffries, E. D. Bauer, M. B. Maple, and D. N. Basov, Phys. Rev. B, **75**, 054523 (2007).
[14] E. D. Bauer, V. A. Sidorov, H. Lee, N. Kurita, F. Ronning, R. Movshovich, and J. D. Thompson, J. Phys.: Conf. Ser., **200**, 012011 (2010).
[15] N. apRoberts Warren, A. P. Dioguardi, A. C. Shockley, C. H. Lin, J. Crocker, P. Klavins, and N. J. Curro, Phys. Rev. B, **81**, 180403 (2010).
[16] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, 1993).
[17] N. J. Curro, T. Imai, C. P. Slichter, and B. Dabrowski, Phys. Rev. B, **56**, 877 (1997).
[18] A. M. Clogston and V. Jaccarino, Phys. Rev., **121**, 1357 (1961).
[19] N. J. Curro, B. Simovic, P. C. Hammel, P. G. Pagliuso, J. L. Sarrao, J. D. Thompson, and G. B. Martins, Phys. Rev. B, **64**, 180514 (2001).
[20] Y. feng Yang, N. J. Curro, Z. Fisk, D. Pines, and J. D. Thompson, (2010), 1005.5184.
[21] Y.-F. Yang, R. Urbano, N. J. Curro, and D. Pines, Phys. Rev. Lett., **103**, 197004 (2009).