



Modulated Spin Liquid: A New Paradigm for URu₂Si₂

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We argue that near a Kondo breakdown critical point, a spin liquid with spatial modulations can form. Unlike its uniform counterpart, we find that this occurs via a second order phase transition. The amount of entropy quenched when ordering is of the same magnitude as for an antiferromagnet. Moreover, the two states are competitive, and at low temperatures are separated by a first order phase transition. The modulated spin liquid we find breaks Z_4 symmetry, as recently seen in the hidden order phase of URu₂Si₂. Based on this, we suggest that the modulated spin liquid is a viable candidate for this unique phase of matter.

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The hidden order (HO) phase in URu₂Si₂ is a long-standing problem in condensed matter physics [1], and has recently received renewed attention from both experiment and theory. This metal can be characterized as a moderate heavy fermion with a Sommerfeld coefficient of ~ 180 mJ/mol K². It undergoes a mean-field-like second order phase transition at $T_0 = 17$ K, characterized by a large jump in the specific heat. The amount of entropy quenched at the transition is substantial (≈ 1.38 J/mol K), which is of order 24% of the entropy of a local f doublet. Despite many years of intense investigation, the nature of the hidden order remains controversial. A number of theoretical propositions have been made, which can be divided into itinerant types, where the order parameter originates from delocalized f electrons, and localized types, where it is believed that the local levels of a $U 5f^2$ ion are involved [2,3].

Experimental data show evidence for both itinerant and localized character of the order parameter. Under pressure, the phase diagram evolves from the hidden order phase to an antiferromagnet (AF) [4]. Recent inelastic neutron scattering measurements show that in the HO phase, a resonance occurs at a commensurate wave vector $Q_0 = \frac{2\pi}{a}(1, 0, 0)$ [5,6], which transforms into a strong elastic AF signal for pressures $P \geq 5$ kbar. An inelastic resonance at $Q^* = \frac{2\pi}{a}(1 \pm 0.4, 0, 0)$ occurs in both the HO and AF phases. The compensated nature of this metal leads to several quasinested portions of the Fermi surface, which could account for the Q vectors of these resonances, as well as the formation of a spin density wave [7,8]. Recent STM experiments [9,10] reveal the opening of a gap in the dI/dV characteristic at $\approx T_0$ inside the HO phase. Moreover, careful analyses of specific heat [2] as well as thermal transport [11] have revealed a strong analogy with the superconductor CeCoIn₅. This body of observations, combined with the opening of a Fermi surface gap inferred

from conductivity [12,13], angle resolved photoemission [14], infrared spectroscopy [15,16], and the Hall effect [17] constitute evidence for an itinerant mechanism. The localized viewpoint is based on the observation that under pressure, the first order transition between the HO and AF phases shows no distinct changes in the transport properties. The resistivity, for example, is continuous through the transition [18]. From this observation, one can expect the HO phase to have strong similarities with the AF phase, in particular, a doubling of the unit cell.

In this Letter, we offer a new idea for explaining the mysterious hidden order, which naturally interpolates between the itinerant and localized viewpoints. The idea amounts to the observation that a spin liquid with spatial modulations that break translational symmetry can form via a second order transition with a large jump in the specific heat, while remaining “hidden” to most experimental probes.

The concept of a spin liquid dates from the early work of Fazekas and Anderson that a resonating valence bond (RVB) state might describe frustrated spin systems on a triangular lattice [19]. Subsequent work by Anderson extended this concept to describe high temperature cuprate superconductors [20]. In a seminal paper [21], the uniform spin liquid was understood as being a superposition of bonding and antibonding valence bond singlets, stabilized by quantum fluctuations. This concept has reemerged recently in the context of quantum critical points (QCP) in heavy fermions [22–24]. The common understanding is that the anomalous properties of these metals arise from a competition between the formation of magnetic singlets between localized spins, and the formation of Kondo singlets. Recently, however, a body of experimental observations combined with theoretical insights has concluded that the formation of magnetic singlets is most probably the dominant mechanism for quenching the entropy of the

local f spins [25]. The complexity of actinide ions, under the combined influence of spin-orbit, Hund's rules, and geometric frustration, create the optimal grounds to favor the formation of valence bond singlets that eventually quench the high temperature entropy. A spin liquid can simply be redefined as a regime of localized spins in which the entropy is quenched despite the absence of long range order.

In the RVB formalism, the spin liquid can be described within the t - J model [21], which in the limit of half filling reduces to the Heisenberg model, with fermionic spin operators

$$H_0 = J \sum_{\langle i,j \rangle, \sigma\sigma'} \chi_{i\sigma}^\dagger \chi_{i\sigma'} \chi_{j\sigma'}^\dagger \chi_{j\sigma} \quad (1)$$

where $\chi_{i\sigma}^\dagger$ ($\chi_{i\sigma}$) are creation (annihilation) operators for fermions with spin 1/2, charge zero, and gauge charge $+e$, commonly dubbed ‘‘spinons.’’ For simplicity, we restrict ourselves to the square lattice in two dimensions, leaving a three-dimensional generalization more appropriate for URu₂Si₂ to later work. Here $\sigma = \pm$ is the spin index of the SU(2) representation, and spinons are subject to the constraint of one per site: $\sum_{\sigma} \chi_{i\sigma}^\dagger \chi_{i\sigma} = 1$. In the mean-field approximation, the interaction term in (1) can be decoupled in a variety of effective fields to minimize the free energy, including valence bond singlets, $\sum_{\sigma} \langle \chi_{i\sigma}^\dagger \chi_{j\sigma} \rangle$, valence bond ‘‘pairs,’’ $\langle \chi_{i\sigma}^\dagger \chi_{j\bar{\sigma}} - \chi_{i\bar{\sigma}}^\dagger \chi_{j\sigma} \rangle$, or AF order, $\sum_{\alpha\beta} \langle \chi_{i\alpha}^\dagger \sigma_{\alpha\beta} \chi_{i\beta} e^{i\mathbf{Q}\cdot\mathbf{r}_i} \rangle$, with σ the SU(2) spin matrix, and \mathbf{Q} the AF wave vector.

In the RVB theory for cuprate superconductors, uniform valence bond order parameters $\langle \chi_{i\sigma}^\dagger \chi_{j\sigma} \rangle = \phi_0 \delta_{\mathbf{r}_i, \mathbf{r}_j + \mathbf{z}}$ where \mathbf{z} is the index of nearest or next nearest neighbors, or flux phases $\langle \chi_{i\sigma}^\dagger \chi_{j\sigma} \rangle = \phi_0 e^{i\Phi/4n_{ij}}$ where Φ is the flux per plaquette and $n_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/a$ (with a the lattice spacing) is a bond orienting number, are commonly introduced. In the π -flux phase, for example, when a spinon cycles around a plaquette, the circulation of the phase of the order parameter generates a magnetic flux of magnitude π [Fig. 1]. Here we introduce another kind of valence bond order parameter, with real space modulations of the bond centers, which we denote as the modulated spin liquid (MSL):

$$\sum_{\sigma} \langle \chi_{i\sigma}^\dagger \chi_{j\sigma} \rangle = \delta_{i,j+\mathbf{z}} \left\{ \phi_0 + \frac{\phi_0 \mathbf{Q}}{2} \sum_{\pm} e^{\pm i[\theta + \mathbf{Q}\cdot(\mathbf{r}_i + \mathbf{r}_j)/2]} \right\} \quad (2)$$

We see that the value of the bond acquires an oscillating sign from site to site. Since the phase on the bond is not oriented, no flux is generated when a spinon cycles around a plaquette. This order parameter doubles the unit cell associated with the dual lattice of bonds, breaking the Z_4 symmetry of the underlying square lattice [Fig. 1]. Whereas the flux phase is typical of lattices in two dimensions, the MSL can easily be generalized to three dimensions.

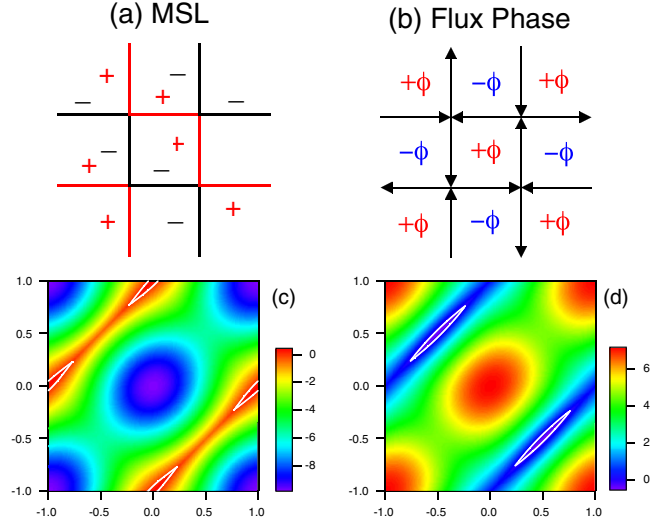


FIG. 1 (color online). The MSL phase (a) and the π -flux phase (b). Note the orientation of the bonds in the latter case. (c),(d) The spinon dispersions for the MSL (bands 1 and 2). Note the breaking of Z_4 symmetry, and the small hole pockets for band 1 and the small electron pockets for band 2 (white curves). The parameters are $t' = 0.1$ and $J_{\text{SL}} = 5$, with $\phi_0 = 2.11$ and $\phi_Q = 1.27$.

The interaction term in (1) can be decoupled as either a spin liquid (SL) or an AF. For given $J \equiv J_{\text{SL}} + J_{\text{AF}}$ we consider J_{SL} and J_{AF} as tuning parameters in our model, which thus acquire a phenomenological character. Considering that the spin liquid can have both a uniform and a modulated component, the corresponding decouplings are performed via Hubbard-Stratonovich transformations on each bond ij , leading to the following Lagrangian:

$$\begin{aligned} \mathcal{L}_0 = & \sum_{i\sigma} \chi_{i\sigma}^\dagger \left(\partial_\tau + \lambda_i + \sigma \sum_z m_{i+\mathbf{z}} \right) \chi_{i\sigma} \\ & - \sum_i \lambda_i + \sum_{\langle i,j \rangle, \sigma} [\varphi_{ij} \chi_{i\sigma}^\dagger \chi_{j\sigma} + \text{c.c.}] \\ & + \sum_{\langle i,j \rangle} \left[\frac{1}{J_{\text{SL}}} |\varphi_{ij}|^2 - \frac{1}{2J_{\text{AF}}} m_i m_j \right]. \quad (3) \end{aligned}$$

Here φ_{ij} is the Hubbard-Stratonovich field introduced for SL decoupling of the bond ij , and m_i arises from the AF decoupling of the site i . In the following, these will be replaced by their constant, self-consistent, mean-field expressions, $\varphi_{ij} = -J_{\text{SL}} \sum_{\sigma} \langle \chi_{i\sigma}^\dagger \chi_{j\sigma} \rangle$ and $m_i = J_{\text{AF}} \sum_{\sigma} \sigma \langle \chi_{i\sigma}^\dagger \chi_{i\sigma} \rangle$. Note that the SL field is defined on the dual lattice, while the AF one is defined on the initial (square) lattice. In general, φ_{ij} can have a nonzero imaginary part, which is the case, for example, in a π -flux phase. Here, we consider real SL fields only, which reflects a symmetry $\varphi_{ij} = \varphi_{ji}$ on each bond. Such a symmetry being incompatible with the occurrence of a magnetic flux, the resulting modulated SL phase is necessarily of a different nature. We introduce the Fourier transformed fields, $\varphi_{\mathbf{q}}$ and $m_{\mathbf{q}}$. Our analysis concentrates onto the three following

mean-field parameters: the uniform SL, $\phi_0 \equiv \varphi_{(0,0)}$, the modulated SL, $\phi_Q \equiv \varphi_{(\pi,\pi)}$, and the Néel AF, $S_Q \equiv m_{(\pi,\pi)}$, noting that (π, π) has a lower free energy than $(\pi, 0)$. In two dimensions, flux phases might still coexist with the present MSL phase, but the study of this phenomenon is beyond the purpose of the present work. The issue of whether a gauge-invariant Lagrangian develops crossovers or phase transitions between the Higgs, confined and Coulomb phases is an old one and much related to the presence of instantons in the system [26]. In the case of the MSL, we argue that the breaking of Z_4 symmetry is enough to ensure a second order transition [27]. This is to be contrasted with the π -flux phase or the possible condensation of the holons with modulations $b_i e^{iQ \cdot r_i}$ [24]. In both of those cases, the order parameter would be sensitive to the effect of gauge fluctuations, and the presence of instantons at finite temperature generates a crossover.

An intuitive description of the MSL phase, compared to other possible SL phases, can be obtained from finite size versions of our model. For two sites and $J_{AF} = 0$, the effective mean-field Hamiltonian (3) can be decomposed into bonding and antibonding eigenmodes, $H_{12} = \frac{|\varphi_{12}|^2}{J_{SL}} + \varphi_{12} \sum_{\sigma} (\chi_{A\sigma}^\dagger \chi_{A\sigma} - \chi_{B\sigma}^\dagger \chi_{B\sigma})$, with $\chi_{B\sigma} \equiv \frac{1}{\sqrt{2}}(\chi_{1\sigma} + \chi_{2\sigma})$ and $\chi_{A\sigma} \equiv \frac{1}{\sqrt{2}}(\chi_{1\sigma} - \chi_{2\sigma})$. These modes are reminiscent of the singlet, and the $S_z = 0$ triplet, which diagonalize the initial two sites, Hamiltonian (1). Invoking the saddle-point self-consistent relation for φ_{12} , we find a ground state energy, $\langle H_{12} \rangle = -\frac{|\varphi_{12}|^2}{J_{SL}}$. The $\pm \varphi_{12}$ degeneracy reflects the $U(1)$ local gauge symmetry of the Hamiltonian (1), which is invariant with respect to the transformation $\chi_{2\sigma}^\dagger \rightarrow -\chi_{2\sigma}^\dagger$. The ground state of the mean-field effective model can therefore arbitrarily be chosen as a bonding or an antibonding mode. Because of this gauge symmetry, for the two sites model, all SL mean-fields are equivalent and mimic the energy splitting between a singlet ground state and one of the triplet excited states. This equivalence does not hold anymore for bigger systems, where the number of sites (i.e., the number of local gauge symmetries) becomes smaller than the number of bonds. In the MSL case on the square lattice, however, the bonding and antibonding character oscillates from site to site, since the sign of the hopping parameter, φ_{ij} , is oscillating.

The MSL can be considered as the true RVB parent of the AF phase. It can also be viewed as a liquid phase of dimers, where a resonance moves between different dimer coverings of the lattice. In three dimensions, the liquid phase of dimers can coexist with the breaking of translational invariance.

In the remainder of the Letter, we discuss the compatibility of the MSL with the HO phase in URu₂Si₂, and its relation to the AF phase. To proceed, we solve a simpler model where the conduction electrons are ignored, and the f electrons are treated as a single orbital on a square lattice with $Q = (\pi, \pi)$. The resulting free energy per site, allowing for the coexistence of both phases, can be written as

$$F = -\frac{k_B T}{N} \sum_{k,i} \ln[1 + e^{-\beta \omega_i(k)}] + \frac{2(\phi_0^2 + \phi_Q^2)}{J_{SL}} + \frac{S_Q^2}{J_{AF}} \quad (4)$$

where $\beta = 1/(k_B T)$, N is the number of sites, i runs over the two bands (each of which are Kramers degenerate), and the spinon dispersions $\omega_i(k)$ are given by

$$\omega_i(k) = \frac{\phi_0}{2} (\epsilon_k + \epsilon_{k+Q}) - \mu_f \pm \sqrt{\frac{\phi_0^2}{4} (\epsilon_k - \epsilon_{k+Q})^2 + (\phi_Q \epsilon_{k-Q/2}^{NN})^2 + 16S_Q^2} \quad (5)$$

with

$$\epsilon_k = -2[\cos(k_x a) + \cos(k_y a)] - 4t' \cos(k_x a) \cos(k_y a) \quad (6)$$

and μ_f the chemical potential of the f electrons adjusted so that the system is at half filling. Here, t' represents the next nearest-neighbor contribution to ϕ_0 . For ϕ_Q , only near neighbor bonds are considered (with ϵ^{NN} the first term of the previous equation), and to obtain a real field, the quantity θ in (2) is set to $\pi/2$. We minimize the free energy using Powell's method, and use a root finder to determine μ_f for each choice of (ϕ_0, ϕ_Q, S_Q) [28].

In Fig. 1, we show the spinon dispersions for the MSL case. Note the pronounced breaking of Z_4 symmetry, which has been recently detected in the HO phase from susceptibility measurements [29]. A large part of the Fermi surface (as defined when ϕ_Q is zero) is gapped upon ordering [1], which gives a natural explanation for the amount of entropy quenched, and is consistent with the Hall [17], thermal conductivity [11], and quantum oscillation [30] data that suggest that 90% of the carriers disappear at the transition. The dispersion for the AF phase is very similar, except in our simplistic approximation, a full energy gap occurs once $S_Q > t' \phi_0/2$. We also find that the order parameters in each phase have similar magnitude. One can tune between the two phases by varying J_{AF} relative to J_{SL} , as shown in Fig. 2. Note that ϕ_0 and ϕ_Q are quasidegenerate and condense at almost the same T . They would be equal if $t' = 0$. Above their condensation temperature, the free energy goes as $-2k_B T \ln(2)$, which is just the free energy for a local f doublet. S_Q condenses as J_{AF} increases, via a first order transition for low T , changing to a second order transition at higher T . In the AF phase, all three order parameters are at first nonzero, with ϕ_Q eventually disappearing (at low T , we find a finite ϕ_0). The competition between the modulated component (ϕ_Q) and the AF order (S_Q) that gives rise to the first order behavior is obvious from Fig. 2. This reproduces the qualitative features of the experimental phase diagram under pressure where a first order transition occurs between the HO and AF phases. Note that since both orders double the

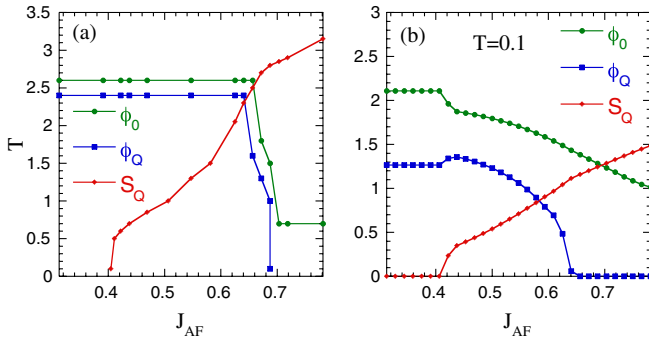


FIG. 2 (color online). (a) Mean-field phase diagram in the (T, J_{AF}) plane from (4) for a square lattice model with $t' = 0.1$ and $J_{SL} = 5$. Below the circles curve (green), ϕ_0 turns on and below the squares one (blue), ϕ_Q condenses. S_Q condenses below the diamonds curve (red). For low T this is a first order transition, at higher T a second order one. Note the coexistence of the two phases for intermediate J_{AF} . (b) Variation of ϕ_0 , ϕ_Q , and S_Q as a function of J_{AF} for $T = 0.1$.

unit cell, no noticeable feature is expected to be seen in the electrical conductivity at this transition.

Since the spinons disperse, any inclusion of a Kondo hybridization will introduce an itinerant Fermi surface. Moreover, from this more complete theory, we expect that the MSL phase will be stabilized near a Kondo breakdown QCP [24], reflecting the localization of the two $5f$ electrons per U site due to strong Coulomb forces. At the localization transition, the two $5f$ electrons decouple from the conduction electrons to form a spin liquid. The effective hybridization is renormalized to zero at the QCP. The tunneling experiments confirm the opening of a hybridization gap at $\approx T_0$ between heavy and light holelike bands [9,10]. We interpret the hybridization gap as the effective hybridization between the spinons and the conduction electrons. Note that the spinons are very difficult to observe; they can be detected by transport only when they hybridize with the conduction electrons. This could explain why the heavy band seems to disappear above T_0 .

Inelastic neutron scattering experiments show an inelastic resonance at a commensurate wave vector $Q = \frac{2\pi}{a} \times (1, 0, 0)$ in the HO phase [6], which becomes an elastic peak in the AF phase. Our theory also has an inelastic resonance at Q_{AF} since the AF state has a higher free energy in the HO phase. We speculate that the incommensurate peaks are due to nesting of the spinon Fermi surface.

In conclusion, the modulated spin liquid is an interesting phase of matter which has many properties compatible with the hidden order phase in URu_2Si_2 . The hidden nature of our order parameter simply relies on the fact that a spin liquid is hardly detectable if no long range symmetry is broken. We believe that it is a viable candidate for the solution of this long-standing mystery.

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