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# Irreversible dynamics of the phase boundary in $U(Ru_{0.96}Rh_{0.04})_2Si_2$ and implications for ordering

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We report measurements and analysis of the specific heat and magnetocaloric effect at the phase boundary into the single magnetic field-induced phase (phase II) of $U(Ru_{0.96}Rh_{0.04})_2Si_2$, which yield striking similarities to the valence transition of $Yb_{1-x}Y_xInCu_4$. To explain these similarities, we propose a bootstrap mechanism by which a structural distortion causes an electric quadrupolar order parameter within phase II to become coupled to the $5f$-electron hybridization, giving rise to a valence change at the transition.

The broken symmetry order parameter responsible for the large specific heat anomaly at $T_o \sim 17$ K in $URu_2Si_2$ continues to be of interest owing to its elusive 'hidden' nature [1, 2]. While there has been no clear consensus on the appropriate theoretical description of the 'hidden order' (HO) phase [3, 4, 5, 6, 7, 8, 9, 10, 11, 12], the key properties of the Fermi liquid state, upon which the HO parameter manifests itself, can be understood. Comprehensive de Haas-van Alphen (dHvA) measurements [13] reveal the quasiparticles to have heavy effective masses and Ising spin degrees of freedom [14], indicating that nearly-localized $5f$-electron degrees of freedom contribute to the Fermi liquid. Within an Anderson lattice scheme, hybridization causes the itinerant quasiparticles to acquire the spin and orbital degrees of freedom of a lowest lying crystal electric field $5f^2$-multiplet [15]. In this case, it is a $\Gamma_5$ non-Kramers doublet [6], making the quasiparticles in $URu_2Si_2$ unique among heavy fermion materials, possessing electric quadrupole as well as Ising spin degrees of freedom [14].

On the basis of the dHvA experiments, one can further assert that the HO phase I (that exists at magnetic fields $\mu_0 H \lesssim 35$ T and temperatures $T \lesssim 17$ K [16]) must be explained within the context of an itinerant $\Gamma_5$ quasiparticle model. This is required to account for the survival of $\Gamma_5$ quasiparticles deep within the HO phase [13, 14, 17]. Itinerancy of the $f$-electrons could also be an important factor in making an itinerant electric-quadrupolar order parameter difficult to detect, as proposed for some of the more exotic itinerant models [7, 8, 11, 12]. Given that the HO parameter has defeated attempts at a direct observation, the existence of '$\Gamma_5$ quasiparticles' necessitates an alternative question: can the electric quadrupolar degrees of freedom order within an itinerant $5f$-electron model, and, if so, how might such ordering differ from the established local moment quadrupolar systems such as $UPd_3$ [18]? Until such questions are addressed by a micriscopic theory, an alternative approach to exploring the question of electric quadrupolar order is to tip the balance of the interactions in favor of local moment quadrupolar order of the type seen in $UPd_3$ [6, 18]. In $URu_2Si_2$ this might be achieved in two ways. The first is by Rh-doping, which shifts the spectral weight of the $5f$-electrons away from the Fermi energy [19], weakening the extent to which they hybridize. Rh-doping also inhibits $\mathbf{q}$-dependent itinerant mechanisms by smearing the states at the Fermi surface. The second is by applying strong magnetic fields, which enhance the effect of local correlations in the vicinity of the metamagnetic transition, causing the quasiparticle bandwidth to collapse [21]. The large magnetic susceptibility associated with metamagnetism also strongly favors XY order [20] (in which electric quadrupole 'pseudospins' lie orthogonal to the tetragonal $c$-axis) over Ising antiferromagnetic order [6].

In this paper, we propose that the interplay between an electric quadrupolar order parameter and the extent $V_{fc}$ to which $5f$-electrons hybridize causes the transition into phase II in $U(Ru_{0.96}Rh_{0.04})_2Si_2$ [22] (shown in Fig. 1) to acquire thermodynamic similarities to the valence transition of $YbInCu_4$ [23, 24]. These similarities are evident both in magnetocaloric effect (MCE) and specific heat $C_p(T)$ data. When a more conventional (i.e. non-itinerant) type of electric quadrupolar order [6, 18] occurs, the associated structural distortion can alter $V_{fc}$, which determines both the effective 'Kondo temperature' and the valence state of the system [23, 24, 25].

The MCE is a convenient tool for studying phase boundaries in a magnetic field [16]. Here, the sample temperature $T$ is recorded while the magnetic field $H$ is swept rapidly under quasi-adiabatic conditions. When an order-disorder transition is crossed, an abrupt change in $T$ reflects the fact that entropy cannot change. A typical MCE measurement for $U(Ru_{0.96}Rh_{0.04})_2Si_2$ is

shown in Fig. 1b. The $T(H)$ curve obtained during the $H$ up-sweep (red line) shows a sudden increase when $\mu_0 H \sim 27$ T, indicating that the system enters an ordered phase: i.e. $T$ must increase in order to conserve entropy. The system then relaxes to equilibrium with the bath until the next phase boundary, exiting phase II, is encountered at $\mu_0 H \approx 38$ T. Now $T$ swings the opposite direction as the ordered phase is abandoned. The observed MCE anomalies are hysteretic, as evident from their dependence on the direction of $H$ sweep, which is a direct consequence of the transition being of first order. Another systematic feature of the data is that the change in $T$ is larger at the high $H$ phase boundary, being consistent with a larger jump in the magnetization [22]. Furthermore, the net magnitude of the swing in $T$ is larger when entering phase II than exiting it. A similar asymmetry is observed in $Yb_{1-x}Y_xInCu_4$ (with $x = 0$), see Fig. 1c.

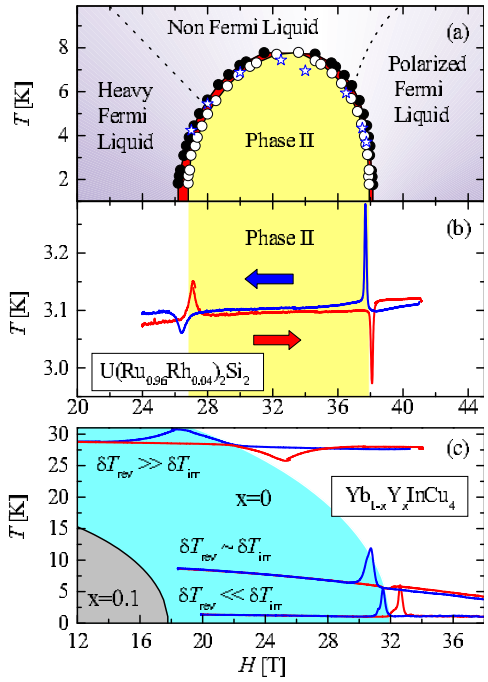


FIG. 1: (a) Phase diagram of $U(Ru_{0.96}Rh_{0.04})_2Si_2$ determined by MCE (circles) and $C_p(T)$ (star symbols). Solid (open) circles indicate the phase boundary exiting (entering) the ordered phase II. The dashed lines represent the approximate Fermi energy scale, as modified by correlations due to metamagnetism [21]. (b) MCE of $U(Ru_{0.96}Rh_{0.04})_2Si_2$, with arrows indicating the direction of $H$ sweep. (c) MCE of $YbInCu_4$, with the changes $\delta T$ in $T$ rescaled $\times 2$.

The total swing $\delta T$ in $T$ in the MCE curve (for a given direction of $H$ sweep) is the sum of reversible $\delta T_{\rm rev}$ and irreversible $\delta T_{\rm irr}$ contributions. $\delta T_{\rm rev}$ always changes sign when the direction of sweep of the magnetic field is changed, while $\delta T_{\rm irr}$ does not, since is entirely due to irreversible (or dissipative) processes. The latter can be associated with the pinning of domain boundaries to the crystalline lattice [26], causing the system to become metastable with its actual state depending on its history. Pinning forces become especially relevant if the order parameter involves charge degrees of freedom, as is known to be the case for valence transitions and electric quadrupolar phases [6, 24]. Figure 2 shows the extracted $\delta T_{\rm rev}$ and $\delta T_{\rm irr}$ for both $U(Ru_{0.96}Rh_{0.04})_2Si_2$ and $Yb_{1-x}Y_xInCu_4$ (with $x = 0$). In the case of $U(Ru_{0.96}Rh_{0.04})_2Si_2$, data is shown only for the upper critical field and the axes have been rescaled to compare the two systems. At higher $T$, $\delta T_{\rm rev}$ dominates the MCE in both materials, but the entropy vanishes as $T \to 0$, $\delta T_{\rm rev}$ must also vanish, causing $\delta T_{\rm irr}$ to dominate in that limit. The latter grows rapidly as $T \to 0$: this is especially clear in the case of $YbInCu_4$ for which a greater range in $T$ can be accessed owing to its high transition temperature.

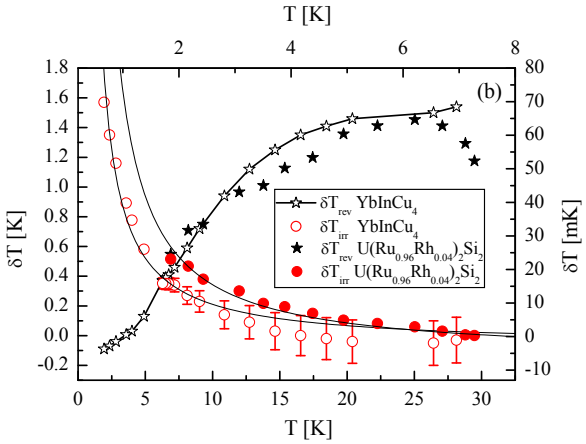


FIG. 2: Irreversible $\delta T_{\rm irr}$ (circles) and reversible $\delta T_{\rm rev}$ (stars) components of the MCE as a function of $T$ for $U(Ru_{0.96}Rh_{0.04})_2Si_2$ (solid symbols) and $YbInCu_4$ (open symbols). The data corresponding to $U(Ru_{0.96}Rh_{0.04})_2Si_2$ ($YbInCu_4$) are linked to the right (left) and upper (lower) axes. The thin lines are fits of $E_p(T)$ to the $\delta T_{\rm irr}$ data while the thick lines are merely guides to the eye.

The similarities between $U(Ru_{0.96}Rh_{0.04})_2Si_2$ and $Yb_{1-x}Y_xInCu_4$ also extend to measurements of the $C_p(T)$. Figure 3 shows $C_p(T)$ for $U(Ru_{0.96}Rh_{0.04})_2Si_2$ and $Yb_{1-x}Y_xInCu_4$ (with $x = 0$ and 0.1) measured at constant $H$ at many different temperatures using the thermal relaxation time method [16] (both during a warm up and cooling down of the sample using a small $\sim$ 1-3% $T$ increment). The first $C_p(T)$ point measured at each $T$ during the warm up yields a larger value (solid symbols) than subsequent points (open symbols), which is consistent with the irreversibilities observed using the MCE. However, neither the first $C_p(T)$ point (as explained above) nor the subsequent points can be used to extract the precise entropy change at the transition. The former includes the energy absorbed by irreversible processes (depinning domain boundaries etc.) in addition to

the equilibrium $C_p(T)$. Once the sample has settled into a new metastable state at each $T$, subsequent measurements have a much reduced effect on its state, leading to a smaller estimate for $C_p(T)$. Type-II superconductors are well known to give rise to a similar irreversible behaviour [27], with the pinned current profile relaxing considerably after the initial thermal cycle.

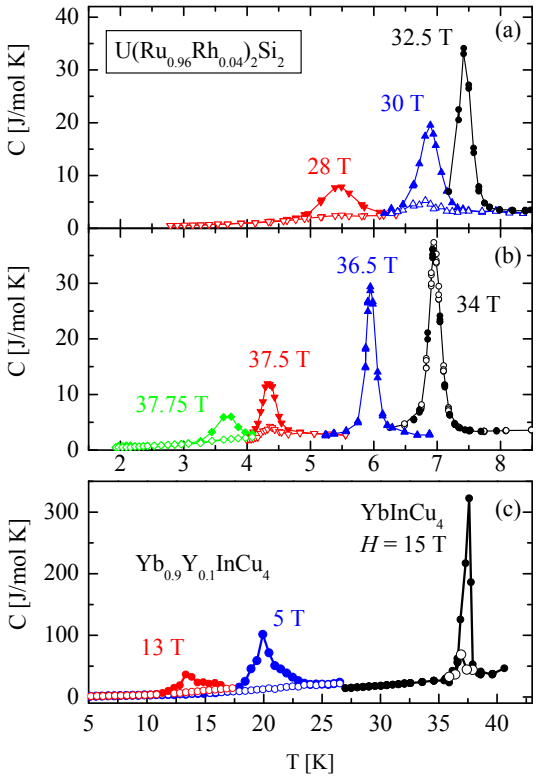


FIG. 3: $C_p(T)$ at different values of $H$ measured on (a) $U(Ru_{0.96}Rh_{0.04})_2Si_2$ for $\mu_0 H < 34$ T, (b) $U(Ru_{0.96}Rh_{0.04})_2Si_2$ for $\mu_0 H \geq 34$ T, and (c) $Yb_{1-x}Y_xInCu_4$(with $x = 0.1$) using a superconducting magnet. Solid symbols represent $C_p$ measured with the first heat pulse on warming-up while open symbols represent the average of subsequent heat pulses.

It is, nevertheless, worth emphasizing the primary difference between $U(Ru_{0.96}Rh_{0.04})_2Si_2$ and $Yb_{1-x}Y_xInCu_4$. The valence instability in $Yb_{1-x}Y_xInCu_4$ is the consequence of a situation whereby the total free energy of the solid develops multiple minima as a function of the volume along with $V_{fc}$ [23, 24]. One can consider the mean value of the hybridization operator as the effective order parameter, although the $f$-electron density is the most natural order parameter to describe a valence transition. Such an order parameter is non symmetry-breaking, making it directly analogous to boiling point of a liquid. The fact that phase II in $U(Ru,Rh)_2Si_2$ occurs only under finite magnetic fields in the vicinity of a metamagnetic crossover [21], around which the correlations are strongly enhanced, indicates that this phase has a different origin to the valence transition in $Yb_{1-x}Y_xInCu_4$ or $Ce_{0.8}Th_{0.1}La_{0.1}$ [23, 24, 25].

Phase II in $U(Ru_{0.96}Rh_{0.04})_2Si_2$ can condense at temperatures that exceed the characteristic Fermi liquid temperature (extrapolated from outside the ordered phase) [21]. This together with the roughly symmetric shape of the phase boundary around the metamagnetic transition is strongly suggestive of local moment ordering. A broken symmetry order parameter involving a structural distortion of the lattice, so as to change $V_{fc}$ within phase II, would provide a very effective bootstrap mechanism for both ensuring its stability and causing the transition to become first order like that in $YInCu_4$. The large changes in sound velocity observed by Suslov *et al.* [28] in pure $URu_2Si_2$ indicate a pronounced magnetoelastic coupling consistent with a lattice distortion. Furthermore, the large redistribution of entropy involved in the formation of phase II indicates that the $5f$-electrons are involved [21], which strongly favors a lattice distortion caused by a electric quadrupolar order parameter as opposed to a charge-density wave.

The possibility of a broken symmetry order parameter being coupled to $V_{fc}$ may have wider appeal than $U(Ru_{0.96}Rh_{0.04})_2Si_2$. For example, an equivalent coupling in $YbRh_2Si_2$ would provide a rather natural explanation as for why the critical field of its unidentified low $T$ ordered phase acquires the physical characteristics of a 'valence fluctuator' quantum critical point [29].

Having established that the $f$-electron valence plays an equally important role in dominating the thermodynamics of both $U(Ru_{0.96}Rh_{0.04})_2Si_2$ and $Yb_{1-x}Y_xInCu_4$, further analysis of the irreversible processes are required in order to understand Fig. 2. The increase in $\delta T_{\rm irr}$ as $T \to 0$ is consistent with the loss of thermal fluctuations, which enable the domain boundaries to overcome pinning forces and undergo creep at finite $T$. Type II superconductors provide a good analogue for understanding creep [30], with the supercurrents sustained by pinned vortices being replaced in the present valence systems by the magnetic currents associated with the difference in magnetization $\Delta M$ between domains. To model the present experimental data, we introduce a phenomenological model for the energy $E_{\rm p} \propto \exp(U_0/k_{\rm B}T) - \exp(U_0/k_{\rm B}T_{\rm o})$ stored due to pinning. Here, $U_0$ is the typical energy of a pinning site [30], while $T_{\rm o}$ is the characteristic ordering temperature introduced to constrain the model so that $E_{\rm p}$ vanishes when $\Delta M$ vanishes. In both systems, the transition temperature $T_{\rm o}$ is optimal (maximum) when $\Delta M = 0$, occurring at $\approx 34$ T in $U(Ru_{0.96}Rh_{0.04})_2Si_2$ (see Fig. 4a) and at $H = 0$ in $Yb_{1-x}Y_xInCu_4$.

On sweeping the magnetic field, $E_{\rm p}$ manifests itself as an irreversible (hysteretic) contribution to the magnetization $\delta M_{\rm irr}$ [31]. This energy must be released as heat as soon as the phase boundary is crossed, giving rise to the irreversible contribution $\delta T_{\rm irr}$ to the MCE. Upon making a rather simple assumption that $\delta T_{\rm irr} \propto E_{\rm p}$, fits of $E_{\rm p}(T)$

in Fig. 2 reproduce the experimental data rather well for both $U(Ru_{0.96}Rh_{0.04})_2Si_2$ and $Yb_{1-x}Y_xInCu_4$, yielding $U_0 = 1 \pm 0.3$ K for both systems. Time-dependent magnetization measurements of $Yb_{1-x}Y_xInCu_4$ (with $x = 0.1$) in Fig. 4b provide rather direct evidence for metastability and creep, revealing that, after cooling the sample part way through the transition, the magnetization changes slowly under a constant $H$ and $T$, having an approximate logarithmic time dependence. The large critical fields prevent an equivalent study from being made on $U(Ru_{0.96}Rh_{0.04})_2Si_2$.

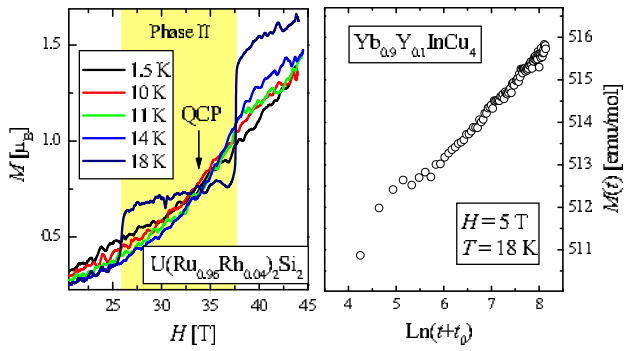


FIG. 4: (a) magnetization as a function of field at several temperatures for the $U(Ru_{0.96}Rh_{0.04})_2Si_2$ sample. (b) Relaxation of the magnetization for the $Yb_{0.9}Y_{0.1}InCu_4$ sample at $\mu_0 H = 5$ T and $T = 18$ K plotted as an stretched exponential.

In summary, we have shown that the irreversible properties of the first order phase transition into the field-induced phase (phase II) of $U(Ru_{0.96}Rh_{0.04})_2Si_2$ are very similar to that associated with the valence transition of $Yb_{1-x}Y_xInCu_4$. This suggests that the broken symmetry order parameter responsible for phase II is coupled to a change in valence, or equivalently $V_{fc}$. Given that the low $H$ Fermi liquid of $URu_2Si_2$ (in which field-induced phase II also occurs [22]) is consistent with a lowest energy $\Gamma_5$ doublet [14], it is reasonable to expect some form of antiferroquadrupolar order. We propose that the collapse of the quasiparticle bandwidth associated with metamagnetism [21] favors field-induced local moment electric quadrupolar ordering in $URu_2Si_2$ [6] over the itinerant phases, which is further favored in $U(Ru_{0.96}Rh_{0.04})_2Si_2$ by Rh-doping. A local moment ordering within phase II lends itself more easily to the established local spectroscopic probes such as NQR and resonant x-ray scattering [18], as well as magnetoelastic techniques such as magnetostriction and thermal expansion which have yet to be performed at the high magnetic fields necessary to access phase II.

The itinerant order parameter responsible for the low $H$ HO phase in pure $URu_2Si_2$, in contrast, may lend itself more accessible to probes that are more suitable for studying itinerant quasiparticles, such as the dHvA effect. Such probes have already revealed the Zeeman splitting of quasiparticle with Ising spin degrees of freedom [14], but could in principle be extended to studying the equivalent splitting of electric quadrupolar degrees of freedom by applying uniaxial strain in the appropriate X or Y direction.

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