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Basal-Plane Nonlinear Susceptibility: A Direct Probe of the Single-Ion Physics in URu₂Si₂

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The microscopic nature of the hidden order state in URu₂Si₂ is dependent on the low-energy configurations of the uranium ions, and there is currently no consensus on whether it is predominantly $5f^2$ or $5f^3$. Here we show that measurement of the basal-plane nonlinear susceptibility can resolve this issue; its sign at low-temperatures is a distinguishing factor. We calculate the linear and nonlinear susceptibilities for specific $5f^2$ and $5f^3$ crystal-field schemes that are consistent with current experiment. Because of its dual magnetic and orbital character, a Γ_5 magnetic non-Kramers doublet ground-state of the U ion can be identified by $\chi_1^c(T) \propto \chi_3^c(T)$ where we have determined the constant of proportionality for URu₂Si₂.

PACS numbers:

I. MOTIVATION

Despite tremendous experimental and theoretical efforts over the last quarter century, the nature of the ordering (“hidden order”) at $T_0 \sim 17.5K$ in the actinide heavy fermion URu₂Si₂ remains unresolved¹. Clear signatures of Fermi liquid behavior^{1,2} above T_0 and the sharp anomalies in thermodynamic properties¹⁻⁴ at T_0 suggest a Fermi surface instability and thus itinerant behavior⁵. However, the large entropy of condensation ($\frac{S}{N} \sim 0.3R \ln 2$), the Curie-Weiss susceptibility at room temperature^{1,2} and the strong Ising anisotropy observed in the magnetic responses^{3,4} all point to a localized origin of the key magnetic degrees of freedom that contribute towards the formation of the hidden order state.

A key outstanding issue for URu₂Si₂ is to determine whether its U ion ground-state configuration is predominantly $5f^2$ or $5f^3$. Specific heat, high-temperature susceptibility and even photoemission measurements are unable to resolve this issue¹. Inelastic neutron scattering experiments^{6,7} favor $5f^2$ whereas EELS measurements⁸ are consistent with $5f^3$. While techniques like inelastic x-ray and neutron scattering can successfully resolve the crystal field configurations of $4f$ ions like cerium and praseodymium^{9,10}, these techniques fail for $5f$ ions like uranium due to significantly broader crystal field levels. Our purpose here is to propose a theory-independent test of the base assumptions of the various theoretical proposals for URu₂Si₂: the ground state uranium configuration. Many theories are based on itinerant uranium electrons¹¹⁻¹⁶, however, these theories have difficulties explaining the large magnetic anisotropy, especially as seen in quantum oscillations¹⁷. Another class of theories assume localized uranium electrons, of which there are two cases: those based on a $5f^3$ ground state^{18,19} and those based on a $5f^2$ picture, which can be further subdivided into those relying on singlet ground state configurations²⁰⁻²⁴ or those based on the Γ_5 doublet²⁴⁻²⁶.

Resolution of the ground state configuration of the uranium ion in URu₂Si₂ would provide an important constraint on the theoretical description of its hidden order.

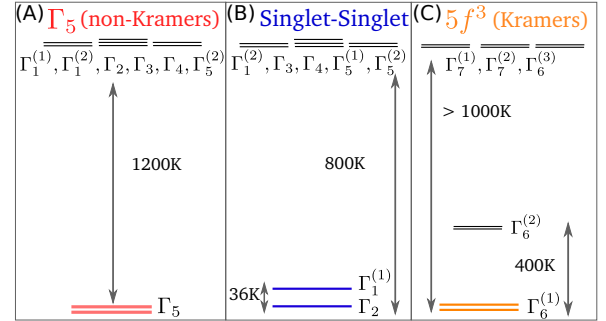


Figure 1: Three possible crystal-field schemes for URu₂Si₂. (A) The $5f^2$ Γ_5 non-Kramers doublet ground-state, with all excited crystal-field states degenerate at 1200 K. (B) Two finely-tuned low-lying singlets scenario (with the two doublets found from DMFT²³), with all other states degenerate at 800 K to reproduce the Van Vleck susceptibility. (C) The $5f^3$ Kramers doublet ground state, with a nearly Ising doublet ground state, $\Gamma_6 = -.91|\pm 7/2\rangle + .42|\mp 1/2\rangle + .05|\mp 9/2\rangle$ chosen to best represent the measured Ising susceptibility, with another, excited Γ_6 doublet at 400K and all other excited doublets above 1000K.

Here we present the nonlinear susceptibility (χ_3) as a probe of the nominal valence of the uranium ion in URu₂Si₂. In cubic UBe₁₃, χ_3 provided strong evidence that the low-lying magnetic excitations are predominantly dipolar ($5f^3$) rather than quadrupolar ($5f^2$) in character²⁷. We generalize this technique to the tetragonal URu₂Si₂ system, where the sign of χ_3 distinguishes between the two nominal valences $5f^2$ and $5f^3$. The linear and the nonlinear susceptibilities are calculated for specific $5f^2$ and $5f^3$ crystal-field schemes consistent with

recent experiment. In addition we discuss the dual nature of the magnetic non-Kramers doublet, Γ_5 , that is magnetic along the c-axis but quadrupolar in the basal plane. As both magnetic (χ_1^c) and quadrupolar ($\chi_3^\perp \propto \chi_Q$) susceptibilities originate from splitting the same doublet, they will have the same temperature-dependence even outside the single-ion regime.

II. TIME-REVERSAL PROPERTIES OF $5f^2$ AND $5f^3$ CONFIGURATIONS

The two valence configurations $5f^2$ and $5f^3$ are clearly distinguished by their properties under time-reversal. $5f^3$ is always a Kramers doublet; $5f^2$ can either involve low-lying singlets or, in the tetragonal environment appropriate for URu_2Si_2 , it can form a Γ_5 doublet formed from two degenerate orbitals $|x\rangle$ and $|y\rangle$ that are crystal rotations of one another. In a tetragonal environment, these two states are degenerate, so one can construct a magnetic basis $|\pm\rangle = |x\rangle \pm i|y\rangle$. Such a “non-Kramers doublet” possesses a dual orbital and magnetic character; and it can be distinguished from a Kramers doublet through its time-reversal properties. A non-Kramers doublet time reverses according to

$$\theta|\pm\rangle = |\pm\rangle, \quad (1)$$

whereas a Kramers doublet transforms with an additional and all-important minus sign

$$\theta|\pm\rangle = \pm|\mp\rangle. \quad (2)$$

Consider next the case of two almost-degenerate low-lying singlets $|a\rangle$ and $|b\rangle$ that are not related by symmetry, separated by a small crystal field splitting Δ , as in the scenarios considered in²³ or²¹. At temperatures and fields B , $T \gg \Delta$, one can treat this almost-degenerate set of singlets as an accidentally degenerate non-Kramers doublet, defined by the magnetic states $|\pm\rangle = |a\rangle \pm i|b\rangle$. In this way, the properties of a $5f^3$ and $5f^2$ configuration at temperatures and fields large compared to their splitting can be considered as Kramers or non-Kramers doublets respectively.

A distinctive property of non-Kramers doublets is their Ising symmetry, a consequence of their time-reversal symmetry. The matrix elements of a time-reversed operator are given by its complex conjugate²⁸

$$\langle\alpha|A|\beta\rangle^* = \langle\beta|A^\dagger|\alpha\rangle = \langle\tilde{\alpha}|\Theta A \Theta^{-1}|\tilde{\beta}\rangle, \quad (3)$$

where $\Theta|\alpha\rangle = |\tilde{\alpha}\rangle$ is the time-reversal of state $|\alpha\rangle$. If we apply this relation to the off-diagonal matrix element $\langle -|J_-|+\rangle$, then

$$\langle -|J_-|+\rangle^* = \langle +|J_-^\dagger|-\rangle = \langle \tilde{-}|\Theta J_- \Theta^{-1}|\tilde{+}\rangle. \quad (4)$$

Now on the left-hand side, since $J_-^\dagger = J_+$, we obtain $\langle -|J_-|+\rangle^* = \langle +|J_+|-\rangle$. The action of time-reversal on

$J_- = J_x - iJ_y$ reverses the signs of the angular momentum operators, and as an anti-unitary operator, takes the complex conjugate of the coefficient $-i$; it thus follows that $\Theta J_- \Theta^{-1} = -J_+$. The time-reversal of the non-Kramers states is given by $|\tilde{-}\rangle = |+\rangle$ and $|\tilde{+}\rangle = |-\rangle$ so that on the right-hand side of (4), $\langle \tilde{-}|\Theta J_- \Theta^{-1}|\tilde{+}\rangle = -\langle +|J_+|-\rangle$. Comparing both sides, it follows that

$$\langle -|J_-|+\rangle = -\langle +|J_-|-\rangle = 0, \quad (\text{non-Kramers doublet}) \quad (5)$$

with a corresponding relation for J_+ . It follows that the off-diagonal matrix elements of J_\pm vanish for a non-Kramers doublet, giving rise to a resulting Ising anisotropy that is independent of crystal structure.

By contrast, for a Kramers doublet, the additional minus sign in the transformation of the states removes the constraint on the off-diagonal matrix elements. To see how this works for URu_2Si_2 , suppose that the f-configuration is a $5f^3$ Kramers doublet predominantly in an $|\pm 7/2\rangle$ state. The presence of a tetragonal symmetry will add and subtract units of $\pm 4\hbar$, so that the crystal field ground-state will take the form

$$|\pm\rangle = a|\pm 7/2\rangle + b|\mp 1/2\rangle + c|\mp 9/2\rangle \quad (6)$$

In this case, $|\langle -|J_+|+\rangle|^2 = 5b^2 + 6ac$, so perfect Ising anisotropy is only obtained when $5b^2 + 6ac = 0$, i.e if the tetragonal crystal fields that mix the two configurations are fine-tuned to zero.

However if the ground-state is a non-Kramers doublet of the form

$$|\pm\rangle = a|\pm 3\rangle + b|\mp 1\rangle \quad (7)$$

then an Ising anisotropy follows for arbitrary mixing between the $|\pm 3\rangle$ state and the $|\mp 1\rangle$ state. Thus the observed Ising anisotropy in URu_2Si_2 either results from a finely-tuned $5f^3$ state, or from a $5f^2$ state with a real or an effective non-Kramers doublet ground-state. The challenge is to distinguish these scenarios. We now show that this can be done by measuring the nonlinear susceptibility to a transverse field (perpendicular to the Ising axis).

Kramers and non-Kramers states differ in their response to a transverse field. If we integrate out the high-lying crystal field excitations in the presence of a transverse field in the x-direction, the remaining effective Hamiltonian will contain off-diagonal terms of the form

$$\mathcal{H}_{eff}(B) = \begin{pmatrix} 0 & \Delta E(B) \\ \Delta E(B) & 0 \end{pmatrix} \quad (8)$$

Now for a Kramers doublet, applying (3), we obtain

$$\begin{aligned} \langle +|\mathcal{H}_{eff}(B)|-\rangle &= -\langle +|\Theta \mathcal{H}_{eff}(B) \Theta^{-1}|-\rangle \\ &= -\langle +|\mathcal{H}_{eff}(-B)|-\rangle \end{aligned} \quad (9)$$

so the off-diagonal matrix elements of $\mathcal{H}_{eff}(B)$ must be an odd function of B , taking the form

$$\Delta E_K(B) = gB + \frac{1}{3!}\gamma B^3. \quad (10)$$

Here $\gamma \sim 1/\Delta_{VV}^2$ is a consequence of third order perturbation theory, where Δ_{VV} is the gap to excited crystal field states, and γ can have either sign. Physically, this means that a Kramers doublet can develop dipole and octupole components, but has no quadrupolar response. By contrast, for a non-Kramers doublet, applying (3), we obtain

$$\langle +|\mathcal{H}_{eff}(B)|-\rangle = \langle +|\Theta\mathcal{H}_{eff}(B)\Theta^{-1}|-\rangle = \langle +|\mathcal{H}_{eff}(-B)|-\rangle \quad (11)$$

so the off-diagonal matrix elements of \mathcal{H} are even in field, where the leading order term is quadrupolar

$$\Delta E_{NK}(B) = \frac{1}{2}qB^2. \quad (12)$$

Here $q \sim 1/\Delta$, since this results from second-order perturbation theory. We note that our use of the term “quadrupolar” here refers to the magnetic quadrupole $\pm q$ associated with a non-Kramers doublet which couples quadratically to a field in the basal plane. The quadrupolar character of the doublet means that it is also split linearly by a strain field η , $\Delta E_{NK} = a\eta + \frac{1}{2}qB^2$, so that the quadrupolar strain susceptibility $-\partial^2 F/\partial\eta^2$ is proportional to the quadrupolar spin susceptibility.

The nonlinear susceptibility, χ_3 , is defined as the cubic term in the magnetization

$$M = \chi_1 B + (1/3!)\chi_3 B^3 + \dots \quad (13)$$

in the direction of the applied field (B), so that $\chi_3 = \partial^3 M/\partial B^3 = -\partial^4 F/\partial B^4$. If we take the free energy $F(B) = -T \ln \left(2 \cosh[\beta \Delta E(B)] \right)$ and do a high-temperature expansion, we find

$$\begin{aligned} F(B) &= -T \ln \left\{ 2 \left[1 + \frac{1}{2} \left(\frac{\Delta E(B)}{T} \right)^2 + \frac{1}{4!} \left(\frac{\Delta E(B)}{T} \right)^4 \right] \right\} \\ &\sim -\frac{1}{2} \frac{[\Delta E(B)]^2}{T} + \frac{1}{12} \frac{[\Delta E(B)]^4}{T^3}. \end{aligned} \quad (14)$$

Using expressions (10) and (12), we obtain

$$\begin{aligned} \chi_3^{NK} &= \frac{3q^2}{T}, & (\text{Non-Kramers doublet}) \\ \chi_3^K &= \frac{4g\gamma}{T} - \frac{3g^2}{T^3} & (\text{Kramers doublet}). \end{aligned} \quad (15)$$

We note that the quadrupolar response of the non-Kramers doublet leads to a positive $\chi_3^{NK} > 0$, whereas its Kramers counterpart is negative at the lowest temperatures where the $1/T^3$ term dominates. Thus the different time-reversal properties of a $5f^3$ Kramers doublet and a $5f^2$ non-Kramers doublet (or an effective non-Kramers doublet composed of two low-lying singlets) can be experimentally distinguished by the sign of the nonlinear susceptibility at low temperatures. However, it is important that the U remain in the single-ion regime, which we define as the region above the coherence temperature

where the moments remain unquenched. If γ is positive there is a crossover temperature scale, $T_x \sim \sqrt{\frac{3g}{4\gamma}}$, where χ_3^\perp changes sign (but if γ is negative then $\chi_3^\perp < 0$ for all T). Therefore, provided the single-ion regime continues to sufficiently low temperatures, one can identify the magnetic state of the U ion from the sign of the basal-plane nonlinear susceptibility. This experiment may require dilution studies to extend the single-ion regime down to sufficiently low temperatures.

III. χ_3 FOR SPECIFIC $5f^2$ AND $5f^3$ SINGLE-ION SCHEMES

In order to illustrate the above results in detail, we have calculated the linear and nonlinear susceptibilities within three distinct crystal-field schemes: (i) non-Kramers doublet, (ii) a “pseudo”-non-Kramers doublet given by two closely spaced singlets and (iii) a Kramers doublet. These three scenarios are chosen to reproduce the high temperature behavior: the Ising anisotropy, moment and van Vleck susceptibilities. We assume that the maximum in χ_1^{c2} results from the Kondo effect, and thus we are not considering “three-singlet” crystal field schemes²¹.

The three crystal-field scenarios that we consider here (cf. Fig. 1) are:

- (A) **Non-Kramers doublet:** $5f^2$ ($J=4$) Γ_5 :

$$|\Gamma_5 \pm\rangle = a|\pm 3\rangle + b|\mp 1\rangle, \quad (16)$$

where a, b are adjustable parameters. For simplicity, all other crystal field states (five singlets and one doublet) have been placed at 1200K to reproduce the magnitude of the van Vleck susceptibility; however, the behavior of the linear and non-linear susceptibilities are relatively insensitive to the exact arrangement of the excited states.

- (B) **Finely Tuned Singlets :** $5f^2$ ($J = 4$) with two low-lying singlets separated by a gap, $\Delta = 36K$. We use the singlets, Γ_2 and Γ_1 proposed by Haule and Kotliar²³:

$$\begin{aligned} |\Gamma_2\rangle &= \sqrt{\frac{1}{2}}(|4\rangle - |-4\rangle) \\ |\Gamma_1\rangle &= \frac{\cos \phi}{\sqrt{2}}(|4\rangle + |-4\rangle) - \sin \phi |0\rangle, \end{aligned} \quad (17)$$

where $\phi = .23\pi$. Again, all excited crystal field states have been placed at the same energy, here 800K, to reproduce the Van Vleck term, and again the results are quite insensitive to the exact arrangement of the excited states.

- (C) **Kramers doublet:** $5f^3$ ($J = 9/2$) $\Gamma_6^{(1)}$:

$$|\Gamma_6^{(1)} \pm\rangle = a|\pm 7/2\rangle + b|\mp 1/2\rangle + c|\mp 9/2\rangle, \quad (18)$$

where b and c describe the small admixture of $|\mp 1/2\rangle$ and $|\mp 9/2\rangle$ chosen to reproduce the anisotropy of the susceptibility at room temperature. We require that we simultaneously satisfy the requirement of perfect Ising anisotropy and the correct c-axis moment of $3.5\mu_B$; as we discuss in the Appendix, for the Ising state with $5b^2 + 6ac = 0$, this is only satisfied with a low-lying crystal-field excitation at 110 K that is inconsistent with current neutron scattering results¹. We have chosen a compromise solution to illustrate the $5f^3$ configuration (see Appendix for details) with a crystal-field scheme that is compatible with experiment¹. This doublet is not a pure Ising doublet, but has a transverse moment $|\langle -|J_+|+\rangle| = .55\mu_B$, giving a c-axis anisotropy of $1/50$.

Based on the high-temperature linear susceptibilities (Fig. 2), these three scenarios are practically indistinguishable. The nonlinear susceptibility (Fig 3), χ_3^\perp , clearly distinguishes the three cases: the non-Kramers doublet has a clear $+1/T$ dependence, the finely tuned singlets have a $+1/T$ dependence at high temperatures that turns over to become a constant at zero temperature, resulting in a maximum at $T \approx 2\Delta$, where Δ is the separation of the singlets. This temperature is significantly higher than the quenching of the linear susceptibility, χ_1^c at $T \approx .25\Delta$. By contrast, the Kramers doublet has a strong $-1/T^3$ dependence that should dominate at temperatures much smaller than the crystal field splitting, $T \ll \Delta_{VV}$.

Of course, these are only single-ion calculations, and in URu_2Si_2 we only expect single-ion physics to hold for $T > T^* \equiv 70\text{K}$ with $(1/T \rightarrow 1/(T - \theta_{CW}))$, making it difficult to distinguish the fine-tuned singlets from a true non-Kramers doublet. In the dilute limit, $\text{U}_x\text{Th}_{1-x}\text{Ru}_2\text{Si}_2$ ($x \leq .07$), the single-ion physics extends to much lower temperatures, down to 10K. Below this temperature, the Curie-like single-ion behavior is replaced by a critical logarithmic temperature dependence, $-\log T/T_K$, where $T_K \approx 10\text{K}$ ²⁵. This physics has been attributed to two channel Kondo criticality, although magnetization studies show fine differences from the single impurity two-channel Kondo model²⁹ that may be due to the fact that two-channel impurities are never really in the idealized dilute limit.

IV. DUALITY OF THE Γ_5 DOUBLET

As Γ_5 is a magnetic non-Kramers doublet, it is protected by a combination of both time-reversal and tetragonal crystal symmetry, $(|\pm\rangle = |x\rangle \pm i|y\rangle)$, and it thus possesses a dual magnetic and orbital character. This means that the c-axis moment is magnetic (both dipolar and octupolar), while the basal plane moment is quadrupolar ($\mathcal{O}_{xy}, \mathcal{O}_{x^2-y^2}$). As magnetic and quadrupolar moments

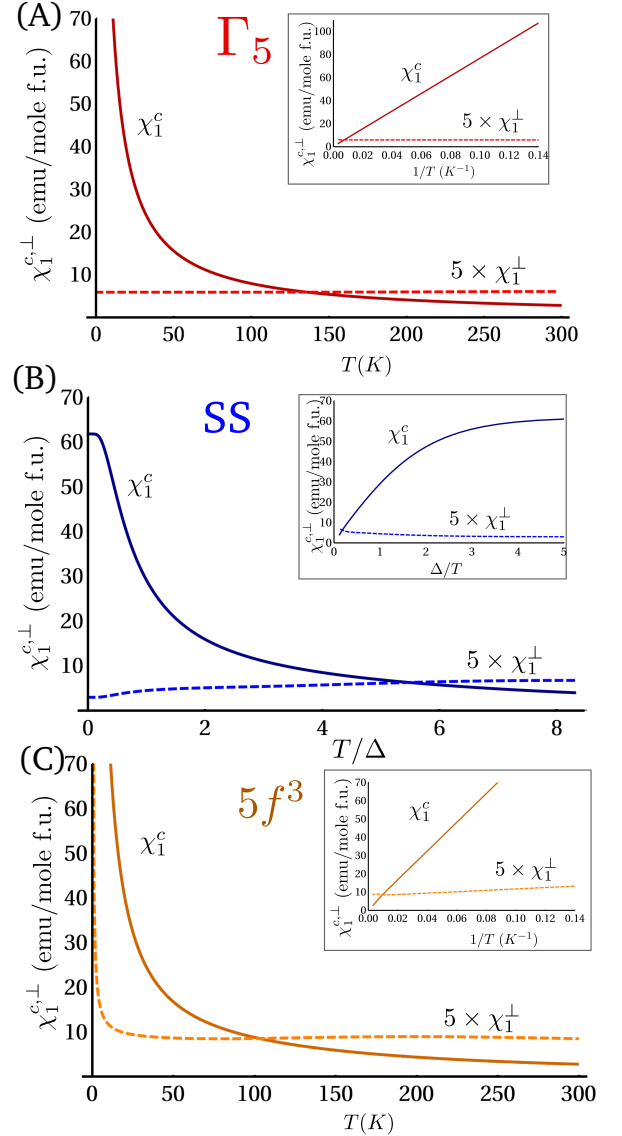


Figure 2: Linear susceptibilities for the three crystal field schemes with the c-axis and basal plane susceptibilities given by solid and dashed lines respectively. The basal-plane susceptibility is multiplied by five. (a) Γ_5 ground-state. Inset shows the anisotropic Curie behavior. (b) Finely-tuned singlets. Here the temperature has been rescaled by the gap, $\Delta = 36\text{K}$ between the two singlets. Inset shows the $1/T$ dependence of the magnetic susceptibility at temperatures larger than the gap Δ . (c) $5f^3$ Kramers doublet scenario. Inset shows Curie behavior of susceptibility in both the c-axis and basal plane.

result in linear and quadratic field splittings, respectively

$$\Delta(B_c, B_\perp) = g_f \mu_F B_c + \frac{1}{2} \alpha \chi_{VV} B_\perp^2, \quad (19)$$

they will appear in the linear and nonlinear susceptibilities respectively, as the nonlinear susceptibility is proportional to the quadrupolar susceptibility for the Γ_5 dou-

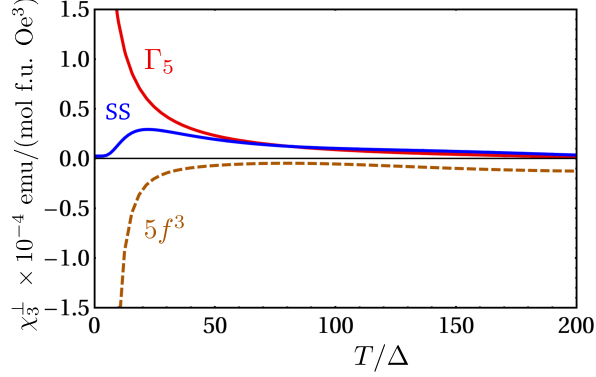


Figure 3: The basal-plane nonlinear susceptibility, χ_3^\perp for the three scenarios, where all three are plotted versus the inverse temperature rescaled as Δ/T , where $\Delta = 36K$ is the gap for the singlet scenario. The Γ_5 is given in solid red, the finely-tuned-singlet scenario in solid blue, and the $5f^3$ Kramers doublet scenario in dashed orange. Note that only the singlet scenario has a strong non-monotonic temperature-dependence, with a maximum around $T = \Delta$. The Γ_5 scenario has a strong, positive Curie-dependence, while the $5f^3$ is dominated by a negative $-1/T^3$ term.

blet; $\alpha\chi_{VV} = \frac{(g\mu_B)^2}{\Delta_{VV}} \langle \Gamma_5 + |J_x^2| \Gamma_5 - \rangle$. Thus the linear c-axis susceptibility and the nonlinear basal plane susceptibility are predicted to have the same temperature dependence - albeit with different coefficients. Taking the above splitting, the free energy is given by $F = -\frac{\eta}{2}\Delta^2$, where $\eta = \chi_1^c/(g\mu_B)^2$ is found in c-axis field, $F = -\frac{1}{2}\chi_1^c B_c^2$. In a basal plane field,

$$F = -\frac{\alpha^2 \chi_{VV}^2 \chi_1^c(T)}{8(g\mu_B)^2} B_\perp^4, \quad (20)$$

which implies that the basal plane nonlinear susceptibility

$$\begin{aligned} \chi_3^\perp(T) &= -3 \frac{\partial^4 F}{\partial B_\perp^4} = \frac{\alpha^2 \chi_{VV}^2}{(g\mu_B)^2} \chi_1^c(T) \\ &= 1.2 \times 10^{-6} \text{ (T - f.u.)}^{-1}, \end{aligned} \quad (21)$$

will always share the temperature dependence of the linear c-axis susceptibility, where we have used the crystal field parameters for the Γ_5 doublet scenario (A), which have been fit to the linear susceptibility of the real material. This shared temperature dependence is a result of the duality of the non-Kramers doublet and will hold not only in the single-ion limit, but in the critical dilute and dense limits. The Kramers doublet does not have this duality, as we can see from the different temperature dependences even in the single-ion case. The finely tuned singlets will only exhibit this duality down to the gap temperature ($\sim 36K$).

V. V. DISCUSSION AND CONCLUSIONS

Our treatment up to this point has assumed isolated single-ion behavior, determined by a nominal and integral f-valence. In reality the 5f state is not a purely integral valence state, but its magnetic properties do reflect a nominal integral valent configuration. The reasoning behind this is somewhat subtle and now deserves discussion.

One of the important concepts that comes to our aid, is the distinction between the *nominal* integral valence that determines the magnetic properties and the *microscopic* valence measured by high energy spectroscopic probes³⁰. To illustrate this point, consider the case of a nominal $5f^3$ configuration, undergoing valence fluctuations into a $5f^2$ singlet,

$$5f^3 \rightleftharpoons 5f^2 + e^-$$

In the isolated atomic limit, such a state is $|5f^3 : \sigma\rangle$, but once valence fluctuations are included, this state is then described by a Varma-Yafet wavefunction³¹ of the form

$$|\sigma^*\rangle = (1 + \sum_k \alpha_k c_{k\alpha}^\dagger f_\alpha) |5f^3 : \sigma\rangle, \quad (22)$$

where the second term describes the virtual excitation of an f-electron into the conduction sea in a partial wave state with the same spin-orbit coupled angular momentum as the f-state. The important point here, is that while the valence is reduced below its nominal value, so that here $n_f^* = 3 - \delta$, since valence fluctuations conserve total angular momentum, they do not renormalize the magnetic moment. For this reason, the magnetic moment of an isolated Anderson impurity is unaffected by significant departures from integral valence³². The above arguments will of course also apply if the nominal configuration is a $5f^2$ non-Kramers doublet and $n_f = 2 + \delta$. The important point is that valence fluctuations do not renormalize the magnetic moment so that a single-ion treatment can be used to describe the susceptibility in the region that Curie behavior is observed. It also means that susceptibility measurements of any kind can only determine the nominal, not the microscopic valence of the ion.

There is in fact a lot of circumstantial evidence that these kinds of arguments apply to URu_2Si_2 . In particular:

- In the dilute limit, the magnetic susceptibility follows a Curie Weiss form down to $10K$, giving us an estimate for the single-ion Kondo temperature $T_K \sim 10K$. In concentrated case, single-ion behavior continues down to about $100K$, which is still a small scale more characteristic of a system close to integral valence than a strongly mixed valent system.
- STM measurements do indicate admixture between the f-electrons and the conduction electrons. In-

deed, coherent tunneling into the f-states is observed on the Si layers of URu_2Si_2 , indicating that the renormalized f-states extend to the silicon orbitals^{33,34}.

Thus while there is mixed valence, single-ion magnetic physics is observed.

One method to directly determine the microscopic valence of the U ions is from the branching ratios of two core-level d-states⁸. The quoted microscopic valence determined by these methods is $n_f = 2.6\text{--}2.8$, which would suggest a nominal valence of 3 ($5f^3$) with a Kramers doublet. Such measurements would at first sight seem to make a magnetic determination of the nominal valence unnecessary. However, recent theoretical work suggests that the microscopic valence determined by these methods requires a more accurate many body treatment of the spin-orbit coupling in the f-states, which can give substantial corrections to the inferred microscopic valence³⁵.

In conclusion, we have proposed a bench-top experimental probe that can determine the nominal U valence configuration in URu_2Si_2 , distinguishing between a $5f^2$ configuration that is naturally Ising-like and a $5f^3$ Kramers configuration that is fine-tuned close to the Ising limit. Using a single ion approximation valid at high temperatures, we have shown the basal plane non-linear susceptibility for a $5f^2$ non-Kramers or singlet-singlet ground-state is *always positive*, whereas the Kramers ground state turns negative at low temperatures. In the dilute limit, we have used the duality of the non-Kramers doublet to predict a temperature-independent ratio between the basal plane non-linear susceptibility and the c-axis linear susceptibility; if found this will provide direct confirmation of the Γ_5 doublet. The non-linear susceptibility of concentrated URu_2Si_2 was last measured twenty years ago^{4,36}; measurements were only conducted for $T < 25\text{K}$, well below the single-ion temperature regime. A set of new measurements over an extended and higher temperature range in both the dilute and the concentrated limits has the potential to add much insight to this problem. Resolution of the uranium single-ion ground state in URu_2Si_2 will provide crucial insight into the origin of its hidden order, providing an important constraint on future microscopic theories.

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VI. APPENDIX

Here we explain the details of choosing a representative state for the $5f^3$ configuration. The strong spin-orbit cou-

pling means that $J = 9/2$, and in a tetragonal field, the crystal field Hamiltonian contains five free parameters,

$$H = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 O_4^4 + B_6^4 O_6^4, \quad (23)$$

where O_l^m are the Stevens operators³⁷. There are three Γ_6 doublets that mix $J_z = 9/2, 7/2$ and $1/2$ states and two Γ_7 doublets that mix $J_z = 3/2$ and $5/2$, which between them have eight free parameters, so the problem is grossly overconstrained. In order to find a set of parameters, B that have the correct c-axis moment, high temperature anisotropy and van Vleck susceptibility, we performed a simulated annealing search of the space of B 's. We found that it is possible to find a state with nearly zero transverse moment, $|\langle -|J_+|+\rangle| = .01\mu_B$. This finely tuned state has a positive $\chi_3^\perp(T)$ at low temperatures due to the lack of basal plane moment. However, this state also requires the existence of a low-lying doublet at 110K that is inconsistent with neutron scattering¹ and gives an entropy of greater than $R \log 4$ at room temperature. And even in this case, $\chi_3^\perp(T)$ is negative over some regime of temperature, so the sign of $\chi_3^\perp(T)$ is still a good indicator of $5f^3$ behavior.

Figure 4: (Color online) Comparing possible $5f^3$ states: a finely tuned Ising state, $.14|\pm 9/2\rangle + .39|\pm 1/2\rangle - .91|\mp 7/2\rangle$ (purple, darker) and a more generic compromise state $.05|\pm 9/2\rangle + .42|\pm 1/2\rangle - .91|\mp 7/2\rangle$ (orange, lighter). (A) The linear susceptibilities both look similar at high temperatures, though the absence of a basal plane moment can be seen at low temperatures. (Inset) Crystal field scheme for the finely-tuned state. (B) The finely-tuned state has a low-lying doublet at 110K that makes the low temperature entropy much larger. (C) The nonlinear susceptibility looks the same above 100K, but the lack of basal plane moment gives a positive contribution to the finely-tuned state that resembles the Γ_5 upturn. However, the negative $\chi_3^{\perp}(T)$ above 100K clearly indicates the $5f^3$ nature.

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