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Basal-plane nonlinear susceptibility: A direct probe of the single-ion physics in URu$_2$Si$_2$

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The microscopic nature of the hidden order state in URu$_2$Si$_2$ 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 $\Gamma_3$ magnetic non-Kramers doublet ground state of the U ion can be identified by $\chi_1(T) \propto \chi_3(T)$, where we have determined the constant of proportionality for URu$_2$Si$_2$.

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I. MOTIVATION

Despite tremendous experimental and theoretical efforts over the last quarter-century, the nature of the ordering (“hidden order”) at $T_0 \sim 17.5$ K in the actinide heavy fermion URu$_2$Si$_2$ remains unresolved.1 Clear signatures of Fermi liquid behavior1,2 above $T_0$, and the sharp anomalies in thermodynamic properties1–4 at $T_0$ suggest a Fermi surface instability and thus itinerant behavior.5 However, the high entropy of condensation ($S/T_0 \sim 0.3 R \ln 2$), the Curie-Weiss susceptibility at room temperature,1,2 and the strong Ising anisotropy observed in the magnetic responses3,4 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 URu$_2$Si$_2$ 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 issue.1 Inelastic neutron scattering experiments6,7 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 URu$_2$Si$_2$: the ground-state uranium configuration. Many theories are based on itinerant uranium electrons;11–16 however, these theories have difficulties explaining the high magnetic anisotropy, especially as seen in quantum oscillations.17 Another class of theories assumes localized uranium electrons, of which there are two cases: those based on a $5f^3$ ground state18,19 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 $\Gamma_3$ doublet.25–28 Resolution of the ground-state configuration of the uranium ion in URu$_2$Si$_2$ would provide an important constraint on the theoretical description of its hidden order.

Here we present the nonlinear susceptibility ($\chi_3$) as a probe of the nominal valence of the uranium ion in URu$_2$Si$_2$. In cubic UBe$_{13}$, $\chi_3$ provided strong evidence that the low-lying magnetic excitations are predominantly dipolar ($5f^3$) rather than quadrupolar ($5f^2$) in character.27 We generalize this technique to the tetragonal URu$_2$Si$_2$ system, where the sign of $\chi_3$ 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, $\Gamma_3$, that is magnetic along the $c$ axis but quadrupolar in the basal plane. As both magnetic ($\chi_1$) and quadrupolar ($\chi_\perp \propto \chi_0$) 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; either $5f^2$ can involve low-lying singlets or, in the tetragonal environment appropriate for URu$_2$Si$_2$, it can form a $\Gamma_3$ 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

$$\theta |\pm\rangle = |\pm\rangle,$$

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

$$\theta |\pm\rangle = \mp |\mp\rangle.$$

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 $\Delta$, as in the scenarios considered in Ref. 21 or. 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 $5f^2$ and $5f^3$ configurations at temperatures and fields large
Now on the left-hand side, since
given by its complex conjugate,28
metry. The matrix elements of a time-reversed operator are
non-Kramers doublets, respectively.

\begin{equation}
\langle \alpha | A | \beta \rangle^* = \langle \beta | A | \alpha \rangle = \langle \hat{\alpha} | \Theta A \Theta^{-1} | \hat{\beta} \rangle,
\end{equation}

where \( \Theta | \alpha \rangle = | \hat{\alpha} \rangle \) is the time reversal of state \( | \alpha \rangle \). If we apply this relation to the off-diagonal matrix element \( -| J_- | + \rangle \), then
\begin{equation}
-| J_- | + \rangle^* = +| J_+ | - \rangle = \langle \hat{\neg} | \Theta J_- \Theta^{-1} | \hat{\neg} \rangle.
\end{equation}

Now on the left-hand side, since \( J_+ = J_+ \), we obtain
\( -| J_- | + \rangle^* = +| J_+ | - \rangle \). The action of time reversal on \( J_+ = J_+ - i J_x \) reverses the signs of the angular momentum operators and, as an antiunitary 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
\( | \neg \rangle \rightarrow | + \rangle \) and \( | \neg \rangle \rightarrow | - \rangle \) so that, on the right-hand side of (4), \( \langle \neg | \Theta J_- \Theta^{-1} | \neg \rangle = -\langle J_+ | - \rangle \). Comparing both sides, it follows that
\begin{equation}
-| J_- | + \rangle = -\langle J_+ | - \rangle = 0 \quad \text{(non-Kramers doublet)}.
\end{equation}

with a corresponding relation for \( J_+ \). It follows that the off-diagonal matrix elements of \( J_+ \) vanish for a non-Kramers doublet, giving rise to a resulting Ising anisotropy that is independent of the 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 \( 5 f^3 \) Kramers doublet predominantly in an \( \pm 7/2 \) 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
\begin{equation}
| \pm \rangle = a | \pm 7/2 \rangle + b | \mp 1/2 \rangle + c | \mp 9/2 \rangle.
\end{equation}

In this case, \( | -| J_- | + \rangle |^2 = 5b^2 + 6ac \), 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 0.

However, if the ground state is a non-Kramers doublet of the form
\begin{equation}
| \pm \rangle = a | \pm 3 \rangle + b | \mp 1 \rangle,
\end{equation}
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 \( URu_2Si_2 \) results either from a finely tuned \( 5 f^3 \) state or from a \( 5 f^2 \) 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
\begin{equation}
\mathcal{H}_{\text{eff}}(B) = \begin{pmatrix}
0 & \Delta E(B) \\
\Delta E(B) & 0
\end{pmatrix}.
\end{equation}

Now for a Kramers doublet, applying (3), we obtain
\begin{align}
( +| \mathcal{H}_{\text{eff}}(B) | - ) &= - ( + | \Theta \mathcal{H}_{\text{eff}}(B) \Theta^{-1} | - ) \\
&= - ( + | \mathcal{H}_{\text{eff}}(-B) | - ),
\end{align}
so the off-diagonal matrix elements of \( \mathcal{H}_{\text{eff}}(B) \) must be an odd function of \( B \), taking the form
\begin{equation}
\Delta E_K(B) = g_B + \frac{1}{3!} \gamma B^3.
\end{equation}

Here \( \gamma \sim 1/\Delta_{VV}^2 \) is a consequence of third-order perturbation theory, where \( \Delta_{VV} \) is the gap to excited crystal-field states, and \( \gamma \) 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
\begin{align}
( +| \mathcal{H}_{\text{eff}}(B) | - ) &= + ( + | \Theta \mathcal{H}_{\text{eff}}(B) \Theta^{-1} | - ) = ( + | \mathcal{H}_{\text{eff}}(-B) | - )
\end{align}
so the off-diagonal matrix elements of \( \mathcal{H} \) are even in field, where the leading order term is quadrupolar:
\begin{equation}
\Delta E_{NK}(B) = \frac{1}{2} q B^2.
\end{equation}

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 \( \eta \), \( \Delta E_{NK} = a \eta + \frac{1}{2} q B^2 \), so that the quadrupolar strain susceptibility \( -\partial^2 F/\partial \eta^2 \) is proportional to the quadrupolar spin susceptibility.

The nonlinear susceptibility, \( \chi_3 \), is defined as the cubic term in the magnetization
\begin{equation}
M = \chi_3 B + (1/3!) \chi_3 B^3 + \ldots
\end{equation}
in the direction of the applied field \( B \), so that \( \chi_3 = \partial^3 M/\partial B^3 = -\partial^2 F/\partial \eta^2 \). If we take the free energy \( F(B) = -T \ln \{ 2 \cosh[\beta \Delta E(B)] \} \) and do a high-temperature expansion, we find
\begin{align}
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} \left( \frac{\Delta E(B)}{T} \right)^2 + \frac{1}{12} \left( \frac{\Delta E(B)}{T} \right)^4.
\end{align}

Using expressions (10) and (12), we obtain
\begin{equation}
\chi_3^{NK} = \frac{3q^2}{T} \quad \text{(non-Kramers doublet)},
\end{equation}
\begin{equation}
\chi_3^K = \frac{4g\gamma}{T} - \frac{3g^2}{T^3} \quad \text{(Kramers doublet)}.
\end{equation}

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 \( 1/T^2 \) term dominates. Thus the different time-reversal properties of a \( 5 f^3 \) Kramers doublet and a \( 5 f^2 \) 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 \( \gamma \) is positive, there is a crossover temperature scale, \( T_0 \sim \sqrt{\frac{3 \Delta}{4\pi}} \), where \( \chi_1^2 \) changes sign (but if \( \gamma \) is negative, then \( \chi_1^2 < 0 \) 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. \( \chi_3 \) FOR SPECIFIC 5\( f^2 \) AND 5\( f^3 \) 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) a 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 \( \chi_3^2 \) results from the Kondo effect, and thus we do not consider “three-singlet” crystal-field schemes.

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

(a) Non-Kramers doublet: 5\( f^2 \) (\( J = 4 \)) \( \Gamma_5 \),

\[
|\Gamma_5\pm\rangle = a|\pm 7/2\rangle + b|\mp 1/2\rangle + c|\mp 9/2\rangle,
\]

where \( a \) and \( b \) are adjustable parameters. For simplicity, all other crystal-field states (five singlets and one doublet) have been placed at 1200 K 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: 5\( f^2 \) (\( J = 4 \)) with two low-lying singlets separated by a gap, \( \Delta = 36 \) K. We use the singlets, \( \Gamma_2 \) and \( \Gamma_4 \), proposed by Haule and Kotliar,

\[
|\Gamma_2\rangle = \frac{1}{\sqrt{2}}(4|\mp 4\rangle - |\pm 4\rangle - \sin \phi |0\rangle),
\]

where \( \phi = 0.23\pi \). Again, all excited crystal-field states have been placed at the same energy, here 800 K, to reproduce the van Vleck term, and again, the results are quite insensitive to the exact arrangement of the excited states.

(c) Kramers doublet: 5\( f^3 \) (\( J = 9/2 \)) \( \Gamma_6 \),

\[
|\Gamma_6\pm\rangle = a|\pm 7/2\rangle + b|\mp 1/2\rangle + c|\mp 9/2\rangle,
\]

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 consistent with current neutron scattering results. We have chosen a compromise solution to illustrate the 5\( f^3 \) configuration (see Appendix for details) with a crystal-field scheme that is compatible with experiment. This doublet is not a pure Ising doublet but has a transverse moment \( |\pm J_z| \) = 0.85\( \mu_B \), 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), \( \chi_3^2 \), 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 \( \Delta \) is the separation of the singlets. This temperature is significantly higher than the quenching of the linear susceptibility, \( \chi_1^2 \) at \( T \approx 0.25\Delta \). By contrast, the Kramers doublet has a strong \(-1/T^3 \) dependence that should dominate at temperatures much lower than the crystal-field splitting, \( T \ll \Delta_{VV} \).

Of course, these are only single-ion calculations, and in URu\(_2\)Si\(_2\) we only expect single-ion physics to hold for \( T > T^{\star} \approx 70 \) K with \( [1/T \to 1/(T - \theta_{VV})] \), making it difficult to distinguish the fine-tuned singlets from a true non-Kramers doublet. In the dilute limit, \( U_{\text{U}, \text{Th}} \sim \text{URu}_2\text{Si}_2 \) (\( x \leq 0.07 \)), the single-ion physics extends to much lower temperatures, down to 10 K. Below this temperature, the Curie-like single-ion behavior is replaced by a critical logarithmic temperature dependence, \( -\log T/T_K \), where \( T_K \approx 10 \) K. This physics has been attributed to two-channel Kondo criticality, although magnetization studies show fine differences from the single-impurity two-channel Kondo model, which may be due to the fact that two-channel impurities are never really in the idealized dilute limit.
As $\Gamma_5$ is a magnetic non-Kramers doublet, it is protected by a combination of both time-reversal and tetragonal crystal symmetry, $\langle \pm | x \rangle = \langle x | \pm | y \rangle$, 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 ($O_{xy}$, $O_{x'c''}$). As magnetic and quadrupolar moments result in linear and quadratic field splittings, respectively,

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

they will appear in the linear and nonlinear susceptibilities, respectively, as the nonlinear susceptibility is proportional to the quadrupolar susceptibility for the $\Gamma_5$ doublet; $\alpha \chi_{VV} = -\frac{(g \mu_B)^2}{\Delta}$.

**IV. DUALITY OF THE $\Gamma_5$ DOUBLET**

As $\Gamma_5$ is a magnetic non-Kramers doublet, it is protected by a combination of both time-reversal and tetragonal crystal symmetry, $(\pm | x \rangle = \langle x | \pm | y \rangle)$, 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 ($O_{xy}$, $O_{x'c''}$).

**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 valence 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 probes.\ To illustrate this point, consider the case of a nominal 5\textit{f}^3\ configuration, undergoing valence fluctuations into a 5\textit{f}^2 singlet,
\[
5\textit{f}^3 = 5\textit{f}^2 + e^−.
\]
In the isolated atomic limit, such a state is [5\textit{f}^3 : \sigma], but once valence fluctuations are included, this state is then described by a Varma-Yafet wave function\ of the form
\[
|\sigma^+⟩ = \left[1 + \sum_k \alpha_k c_k^† f_\alpha \right]|5\textit{f}^3 : \sigma⟩,
\]
where the second term describes the virtual excitation of an \textit{f} electron into the conduction sea in a partial-wave state with the same spin-orbit-coupled angular momentum as the \textit{f} state. The important point here is that while the valence is reduced below its nominal value, so that here \textit{n}_f^1 = 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 valence.\ The above arguments will of course also apply if the nominal configuration is a 5\textit{f}^2 non-Kramers doublet and \textit{n}_f^2 = 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 where Curie behavior is observed. It also means that susceptibility measurements of any kind can only determine the nominal, and not the microscopic, valence of the ion.

There is, in fact, a lot of circumstantial evidence that these kinds of arguments apply to URu$_2$Si$_2$. In particular,

\begin{enumerate}
\item[(1)] In the dilute limit, the magnetic susceptibility follows a Curie Weiss form down to 10 K, giving us an estimate for the single-ion Kondo temperature \textit{T}_K \sim 10 K. In the concentrated case, single-ion behavior continues down to about 100 K, which is still a small scale more characteristic of a system close to integral valence than a strongly mixed valent system.
\item[(2)] STM measurements do indicate admixture between the \textit{f} electrons and the conduction electrons. Indeed, coherent tunneling into the \textit{f} states is observed on the Si layers of URu$_2$Si$_2$, indicating that the renormalized \textit{f} states extend to the silicon orbitals.
\end{enumerate}

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 \textit{d} states.\ The quoted microscopic valence determined by these methods is \textit{n}_f = 2.6−2.8, which would suggest a nominal valence of $3\ (5\textit{f}^3)$ with a Kramers doublet. Such measurements would, at first glance, 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 \textit{f} states, which can give substantial corrections to the inferred microscopic valence.\ In conclusion, we have proposed a benchtop experimental probe that can determine the nominal U valence configuration in URu$_2$Si$_2$, distinguishing between a 5\textit{f}^2 configuration that is naturally Ising-like and a 5\textit{f}^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 nonlinear susceptibility for a 5\textit{f}^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 nonlinear susceptibility and the \textit{c}-axis linear susceptibility; if found, this will provide direct confirmation of the \Gamma_5\ doublet. The nonlinear susceptibility of concentrated URu$_2$Si$_2$ was last measured 20 years ago;\ measurements were only conducted for $T < 25 K$, 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 into this problem. Resolution of the uranium single-ion ground state in URu$_2$Si$_2$ will provide crucial insight into the origin of its hidden order, providing an important constraint on future microscopic theories.

\section*{ACKNOWLEDGMENTS}

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\section*{APPENDIX}

Here we explain the details of choosing a representative state for the 5\textit{f}^3 configuration. The strong spin-orbit coupling means that $J = 9/2$, and in a tetragonal field, the crystal-field Hamiltonian contains five free parameters,
\[
H = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^2 O_4^2 + B_6^4 O_6^4.
\]
where $O_n^m$ are the Stevens operators.\ There are three $\Gamma_6$ doublets that mix $J_\perp = 9/2, 7/2$, and 1/2 states and two $\Gamma_7$ doublets that mix $J_\perp = 3/2$ and 5/2, which, between them, have eight free parameters, so the problem is grossly overconstrained. In order to find a set of parameters $\mathbf{B}$ that have the correct \textit{c}-axis moment, high-temperature anisotropy, and van Vleck susceptibility, we performed a simulated annealing search of the space of \textit{B}s. We found that it is possible to find a state with nearly zero transverse moment, $|−|J_\perp + 1⟩| = 0.01 \mu_\text{B}$. This finely tuned state has a positive $\chi_3^\perp(T)$ at low temperatures due to the lack of basal-plane moment, see Fig. 4(a) and 4(c). However, this state also requires the existence of a low-lying doublet at 110 K that is inconsistent with neutron scattering and gives an entropy of greater than $R \log 4$ at room temperature, see Fig. 4(b). 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 5\textit{f}^3 behavior.
FIG. 4. (Color online) Comparing possible 5$f^3$ states: a finely tuned Ising state, $0^+|±9/2⟩ + 0.39|±1/2⟩ - 0.91|±7/2⟩$ [purple (darker) line]; and a more generic compromise state, $0^+|±9/2⟩ + 0.42|±1/2⟩ - 0.91|±7/2⟩$ [orange (lighter) line]. (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 110 K that makes the low-temperature susceptibilities both look similar at high temperatures, though the absence of a basal-plane moment can be seen at low temperatures. (c) The nonlinear susceptibility looks the same above 100 K, but the lack of a basal-plane moment gives a positive contribution to the finely tuned state that resembles the $γ_3$ upturn. However, the negative $χ''(T)$ above 100 K clearly indicates the 5$f^3$ nature.

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36We note that in Fig. 2 of Ref. 4, there is a constant negative $χ_3$ for fields along the $a$ axis. This contribution is most likely not a single-ion response and may well be a feature associated with the heavy electron fluid. Dilution experiments and measurements over an extended temperature range will help to resolve this issue, and in the dense limit, subtracting the ThRu$_2$Si$_2$ nonlinear susceptibility should isolate the uranium contribution.