High temperature singlet-based magnetism from Hund’s rule correlations

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Uranium compounds can manifest a wide range of fascinating many-body phenomena, and are often thought to be poised at a crossover between localized and itinerant regimes for 5f electrons. The antiferromagnetic dipnictide USb2 has been of recent interest due to the discovery of rich proximate phase diagrams and unusual quantum coherence phenomena. Here, linear-dichroic X-ray absorption and elastic neutron scattering are used to characterize electronic symmetries on uranium in USb2 and isostructural UBi2. Of these two materials, only USb2 is found to enable strong Hund’s rule alignment of local magnetic degrees of freedom, and to undergo distinctive changes in local atomic multiplet symmetry across the magnetic phase transition. Theoretical analysis reveals that these and other anomalous properties of the material may be understood by attributing it as the first known high temperature realization of a singlet ground state magnet, in which magnetism occurs through a process that resembles exciton condensation.
**Results**

**Electron configuration of uranium in UBi$_2$ and USb$_2$.** Unlike the case with stronger ligands such as oxygen and chlorine, there is no unambiguously favored effective valence picture for uranium pnictides. Density functional theory suggests that the charge and spin density on uranium are significantly modified by itinerancy effects\textsuperscript{14,15} (see also Supplementary Note 1), as we will discuss in the analysis below, making it difficult to address this question from secondary characteristics such as the local or ordered moment. However, analyses in 2014–2016 have shown that resonant fine structure at the O-edge ($5d$-$5f$ transition) provides a distinctive fingerprint for identifying the nominal valence state and electronic multiplet symmetry on uranium\textsuperscript{16–19}.

X-ray absorption spectra (XAS) of UBi$_2$ and USb$_2$ were measured by the total electron yield (TEY) method, revealing curves that are superficially similar but quantitatively quite different (Fig. 2a). Both curves have prominent resonance features at $h\nu \sim 100$ and $\sim 113$ eV that are easily recognized as the ‘R1’ and ‘R2’ resonances split by the G-series Slater integrals\textsuperscript{16}. Within models, these resonances are narrowest and most distinct for $5f^4$ systems, and merge as $5f$ electron number increases, becoming difficult to distinguish beyond $5f^5$ (see Fig. 2a (bottom) simulations). The USb$_2$ sample shows absorption features that closely match the absorption curve of URu$_2$Si$_2$\textsuperscript{16}, and are associated with the $J = 4$ ground states of a $5f^4$ multiplet. This correspondence can be drawn with little ambiguity by noting a one-to-one feature correspondence with the fine structure present in a second derivative analysis (SDI, see Fig. 2b).

The R1 and R2 resonances of UBi$_2$ are more broadly separated than in USb$_2$, and the lower energy R1 feature of UBi$_2$ is missing the prominent leading edge peak at $h\nu \sim 98.5$ eV (peak-B), which is a characteristic feature of $5f^2$ uranium\textsuperscript{16,17}. The UBi$_2$ spectrum shows relatively little intensity between R1 and R2, and the higher energy R2 resonance has a much sharper intensity onset. All of these features are closely consistent with expectations for a $5f^4$ multiplet, and the SDI curve in Fig. 2b reveals that the R1 fine structure of UBi$_2$ is a one-to-one match for the $5f^4$ multiplet. We note that a close analysis is not performed for R2 as it is influenced by strong Fano interference (see Supplementary

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**Fig. 1** Singlet ground state magnetism and the ligand cage of U(Bi/Sb)$_2$. a, b The U(Bi/Bi)$_2$ crystal structure is shown with spins indicating the antiferromagnetic structure in UBi$_2$ ($T_N$=180 K) and USb$_2$ ($T_N$=203 K). The uranium atoms have 9-fold ligand coordination with base (S1), middle (S2), and pinnacle (S3) ligand layers as labeled in a with respect to the central uranium atom. c, d In-plane ferromagnetic nucleation regions are circled in c doublet and d singlet ground state magnetic systems. The singlet crystal field ground state has no local moment, causing much of the lattice to have little or no magnetic polarization.
Note 2). The lack of prominent $5f^2$ multiplet features suggests that the $5f^2$ multiplet state is quite pure, and the measurement penetration depth of several nanometers (see Methods) makes it unlikely that this distinction between UHV-cleaved UBi$_2$ and USb$_2$ originates from surface effects. However, the picture for UBi$_2$ is complicated by a very rough cleaved surface, which makes it unlikely that this distinction between UHV-cleaved UBi$_2$ and USb$_2$ (see Supplementary Note 3) find to incorporate at least two non-parallel cleavage planes. Surface oxidation in similar compounds is generally associated with the formation of UO$_2$ ($5f^2$) and does not directly explain the observation of a $5f^2$ state.

We note that even with a clean attribution of multiplet symmetries, it is not at all clear how different the f-orbital symmetries, it is not at all clear how different the f-orbital occupancy will be for these materials, or what magnetic moment should be expected when the single-site multiplet picture is modified by band-structure-like itinerancy$^{10,11}$ (see also Supplementary Note 1). The effective multiplet states identified by shallow-core-level spectroscopy represent the coherent multiplet (or angular moment) state on the scattering site and its surrounding ligands, but are relatively insensitive to the degree of charge transfer from the ligands$^{20}$. Nonetheless, the $5f^2$ and $5f^2$ nominal valence scenarios have very different physical implications. A $5f^2$ nominal valence state does not incorporate multi-electron Hund’s rule physics$^{21,22}$ (same-site multi-electron spin alignment), and must be magnetically polarizable with non-zero pseudospin in the paramagnetic state due to Kramer’s degeneracy (pseudospin $\frac{1}{2}$ for the UBi$_2$ crystal structure). By contrast in the $5f^2$ case one expects to have a Hund’s metal with strong alignment of the 2-electron moment (see dynamical mean field theory (DFT + DMFT) simulation below), and the relatively low symmetry of the 9-fold ligand coordination around uranium strongly favors a non-magnetic singlet crystal electric field (CEF) ground state with $\Gamma_1$ symmetry, gapped from other CEF states by roughly 1/3 the total spread of state energies in the CEF basis (see Table 1). The $\Gamma_1$ state contains equal components of diametrically opposed large-moment $|m_I = +4\rangle$ and $|m_I = -4\rangle$ states, and is poised with no net moment by the combination of spin-orbit and CEF

### Table 1 The CEF energy hierarchy in USb$_2$

| CEF(1) (20/33/33) | CEF(2) (33/33/33) | CEF(3) (50/33/33) | CEF(4) (80/130/130) |
|-----------------|-----------------|-----------------|-----------------|
| $\Gamma_1$ (1)  | 0               | 0               | 0               |
| $\Gamma_2$ (2)  | 10.0            | 11.4            | 12.6            | 38.5 |
| $\Gamma_3$ (1)  | 13.1            | 13.9            | 15.2            | 54.3 |
| $\Delta$CEF(1)  | 27.2            | 30.8            | 37.5            | 106.0 |

The energies in millielectron volts of low-lying $5f^2$ multiplet symmetries are shown for four crystal field parameter sets. Parameters in the first column (CEF(1)) follow the relative energy ordering suggested in ref. 8 (S1 < S2 > S3, as the S1 band is relatively short), and are used for all simulations. The state symmetries are summarized in Supplementary Note 5, which includes an energy level diagram. $\Delta$CEF is defined as the gap between the highest energy $J = 4$ CEF state and the ground state. CEF parameters listed as (S1/S2/S3) for the sites defined in Fig. 1a. These values have units of millielectron volts, and define delta function potentials for Sb atoms in the (S1) base, (S2) middle, and (S3) c-axis pinnacle of the Sb$_9$ cage around each uranium atom. Specifically, the energy parameters indicate the energy added by a single Sb atom to an $m_I = 0$ f-orbital oriented along the U-Sb axis. Source data are provided as a Source Data file.
interactions. This unusual scenario in which magnetic phenomena emerge in spite of a non-magnetic singlet ground state has been considered in the context of mean-field models\textsuperscript{23–26}, and appears to be realized at quite low temperatures (typically \( T < \sim 10 \) K) in a handful of rare earth compounds. The resulting magnetic phases are achieved by partially occupying low-lying magnetic excited states, and have been characterized as spin exciton condensates\textsuperscript{23}.

**Multiplet symmetry from XLD versus temperature.** To address the role of low-lying spin excitations, it is useful to investigate the interplay between magnetism and the occupied multiplet symmetries by measuring the polarization-resolved XAS spectrum as a function of temperature beneath the magnetic transition. Measurements were performed with linear polarization set to horizontal (LH, near \( z \)-axis) and vertical (LV, \( a-b \) plane) configurations. In the case of UBi\(_2\), the XAS spectrum shows little change as a function of temperature from 15 to 210K (Fig. 3a, b), and temperature dependence in the dichroic difference (XLD, Fig. 3b) between these linear polarizations is inconclusive, being dominated by noise from the data normalization process (see Methods and Supplementary Note 4). This lack of temperature dependent XLD is consistent with conventional magnetism from a doublet ground state. The XLD matrix elements do not distinguish between the up- and down-moment states of a Kramers doublet, and so strong XLD is only expected if the magnetic phase incorporates higher energy multiplet symmetries associated with excitations in the paramagnetic state.

By contrast, the temperature dependence of USb\(_2\) shows a large monotonic progression (Fig. 3c, d), suggesting that the atomic symmetry changes significantly in the magnetic phase. The primary absorption peak (\( \hbar \nu = 98.2 \) eV, peak-B) is more pronounced under the LH-polarization at low-temperature, and gradually flattens as temperature increases. The LV polarized spectrum shows the opposite trend, with a sharper peak-B feature visible at high temperature, and a less leading edge intensity at low temperature. This contrasting trend is visible in the temperature dependent XLD in Fig. 3d, as is a monotonic progression with the opposite sign at peak-C (\( \hbar \nu = 100.8 \) eV).

Augmenting the atomic multiplet model for 5\( f^2 \) uranium with mean-field magnetic exchange (AM + MF) aligned to match the \( T_{N'} \sim 200K \) phase transition (see Methods) results in the temperature dependent XAS trends shown in Fig. 3e. The temperature dependent changes in peak-B and peak-C in each linear dichroic curve match the sign of the trends seen in the experimental data, but occur with roughly twice the amplitude, as can be seen in Fig. 3d, f. No attempt is made to precisely match the \( T > 200K \) linear dichroism, as this is influenced by itinerant and Fano physics not considered in the model. The theoretical amplitude could easily be reduced by adding greater broadening on the energy loss axis or by fine tuning of the model (which has been

![Fig. 3](image-url) Temperature dependence of occupied f-electron symmetries. a The R1 XAS spectrum of UBi\(_2\) is shown for linear horizontal (LH) and vertical (LV) polarizations. b The dichroic difference (LH-LV) is shown with temperature distinguished by a rainbow color order (15K (purple), 40K (blue), 80K (green), 120K (yellow), and 210K (red)). c, d Analogous spectra are shown for USb\(_2\). Arrows in d show the monotonic trend direction on the peak-B and peak-C resonances as temperature increases. e, f Simulations for 5\( f^2 \) with mean-field magnetic interactions. g A summary of the linear dichroic difference on the primary XAS resonances of USb\(_2\), as a percentage of total XAS intensity at the indicated resonance energy (\( \hbar \nu = 98.2 \) eV for peak-B, and \( \hbar \nu = 100.8 \) eV for peak-C). Error bars represent a rough upper bound on the error introduced by curve normalization. h The linear dichroic difference trends from the mean field model. Source data are provided as a Source Data file. Shading in g, h indicates the onset of a magnetic ordered moment.
Magnetic ordered moment and the nature of fluctuations. Compared with conventional magnetism, the singlet ground state provides a far richer environment for low temperature physics within the magnetic phase. In a conventional magnetic system, the energy gap between the ground state and next excited state grows monotonically as temperature is decreased beneath the transition, giving an increasingly inert many-body environment. However, in the case of singlet ground state magnetism, the ground state is difficult to magnetically polarize, causing the energy gap between the ground state and easily polarized excited states to shrink as temperature is lowered and the magnetic order parameter becomes stronger. Consequently, within the AM + MF model, many states keep significant occupancy down to $T < 100K$, and the first excited state (derived from the $\Gamma_3$ doublet) actually grows in partial occupancy beneath the phase transition (see Fig. 4b). Of the low energy CEF symmetries (tracked in Fig. 4b), $\Gamma_3$ and $\Gamma_2$ are of particular importance, as $\Gamma_3$ is a magnetically polarizable Ising doublet, and $\Gamma_2$ is a singlet state that can partner coherently with the $\Gamma_1$ ground state to yield a z-axis magnetic moment (see Supplementary Note 5). These non-ground-state crystal field symmetries retain a roughly $1/3$rd of the total occupancy at $T = 100K$, suggesting that a heat capacity peak similar to a Schottky anomaly should appear at low temperature, as has been observed at $T < 50K$ in experiments (see the supplementary material of ref. 10). Alternatively, when intersite exchange effects are factored in, the shrinking energy gap between the $\Gamma_1$ and $\Gamma_3$ CEF states at low temperature will enable Kondo-like resonance physics and coherent exchange effects that are forbidden in conventional magnets.

Critical behavior at the Néel transition should also differ, as the phase transition in a singlet-ground-state magnet is only possible on a background of strong fluctuations. Measuring the ordered moment as a function of temperature with elastic neutron scattering (Fig. 4c) reveals that the UBi$_2$ moment follows a trend that appears consistent with the $\beta = 0.327$ critical exponent for a 3D Ising system. The order parameter in UBi$_2$ has a sharper onset that cannot be fitted sufficiently close to the transition point due to disorder, but can be overlaid with an exponent of $\beta = 0.19$, and may resemble high-fluctuation scenarios such as tricriticality ($\beta = 0.25^{28,29}$). This sharp onset cannot be explained from the AM + MF model (blue curve in Fig. 4c), as mean field models that replace fluctuations with a static field give large critical avoided – see Methods). However, it is difficult to compensate for a factor of two, and the discrepancy is likely to represent a fundamental limitation of the non-itinerant mean field atomic multiplet model. Indeed, when the competition between local moment physics and electronic itinerancy is evaluated for USb$_2$ with dynamical mean field theory (DFT + DMFT), we find that the uranium site shows a non-negligible $\sim 25\%$ admixture of $5f^1$ and $5f^3$ configurations (Fig. 4a).
exponents such as $\beta = 0.5$ and unphysically high temperature transitions in systems where fluctuations are important. Another approach to evaluate the importance of fluctuations is to lower the Néel temperature by alloying with non-magnetic thorium (Th), as $U_{1-x}Th_xSb_2$ (see Fig. 4d), thus quenching thermal fluctuations at the phase transition. Performing such a growth series reveals that the magnetic transition can be suppressed to $T_N \sim 100$ K, but is then abruptly lost at $x \sim 0.7$, consistent with the need for fluctuations across a CEF gap of $k_B T_N \sim 10 \text{ meV}$, which matches expectations from theory for the energy separation between $\Gamma_1$ and $\Gamma_5$ (see Table 1 and Methods).

**Discussion**

In summary, we have shown that the USb$_2$ and UBi$_2$ O-edge XAS spectra represent different nominal valence symmetries, with USb$_2$ manifesting 5f$^2$ moments that are expected to create a Hund’s metal physical scenario, and UBi$_2$ showing strong 5f$^1$–like symmetry character. The CEF ground state of a paramagnetic USb$_2$ Hund’s metal is theoretically predicted to be a robust non-magnetic singlet, creating an exotic setting for magnetism that resembles an excion condensate, and is previously only known from fragile and low temperature realizations. Neutron diffraction measurements are found to quench magnetism beneath the Neel transition, and suppressing thermal magnetism. Neutron diffraction measurements show a relatively sharp local moment onset at the transition, consistent with the importance of fluctuations to nucleate the singlet-based magnetic transition, and suppressing thermal fluctuations in a doping series is found to quench magnetism beneath $T_N \sim 100$ K.

Taken together, these measurements are consistent with a single crystal magnetic energy hierarchy that yields an anomalously large number of thermally accessible degrees of freedom at low temperature ($T_\text{c} \sim 100 $K), and provides a foundation for explaining the otherwise mysterious coherence effects found in previous transport, heat capacity, and ARPES measurements at $T_\text{c} < 100$ K.

**Methods**

**Experiment.** The samples of UBi$_2$ and USb$_2$ were top-posted in a nitrogen glove-box and then transferred within minutes to the ultra high vacuum (UHV) environment. The samples were cleaved in UHV and measured in-situ, with initial U O-edge spectra roughly 30 minutes after cleavage. The UV-XAS measurements were performed in the MERISX (BL4.0.3) in the Advanced Light Source with base pressure better than $4 \times 10^{-10}$ Torr. The switch between linear horizontal polarization (LH-pol) and linear vertical polarization (LV-pol) is controlled by an elliptically polarizing undulator (EPU) and keep precisely the same beam spot across the monochromator. The penetration depth of VUV light set by the mean free path of low energy ($\sim 10$ eV) secondary electrons escaping from the material following each core hole decay is typically unknown (within $\sim 30\%$) with coarse estimates from density functional theory.

The O-edge XAS curves observed under LH-pol and LV-pol polarization are normalized to set the lowest energy excitation to 10 meV, a round number that is approximately comparable to room temperature ($T_\text{c} \sim 100$ K), and provides a foundation for describing the properties of the system in terms of a thermally weighted single-atom multiplet state ensemble. The specific values of individual $\zeta_i$, $\eta_i$ terms are unimportant in this approximation, however their signs must match the antiferromagnetic structure in Fig. 1, and the sum of the absolute value of neighbor terms must equal $I_{\text{CEF}} \sim \eta_{ij} |I_{\text{CEF}}| = 43$ meV to yield a magnetic transition at $T_\text{c} = 203$ K. When considering the doped case of $U_{1-x}Th_xSb_2$, the expectation value $\zeta_{ij} \eta_{ij}$ is effectively reduced by weighting in the appropriate density of magnetic moments in Th sites.

The CEF energy hierarchy has not been fine tuned. Perturbation strengths are scaled to set the lowest energy excitation to 10 meV, a round number that roughly matches the lowest $\zeta_{ij} \eta_{ij}$ value at which a magnetic transition is observed in $U_{1-x}Th_xSb_2$. This assignment gives a total energy scale for crystal field physics that is approximately comparable to room temperature (SCRF-$k_{\text{B}} T_\text{c}$), as expected for this class of materials, and the associated orbital energies were found to correspond reasonably (within $\sim 30\%$) with coarse estimates from density functional theory. The crystal field parameters are listed in the first column of Table 1.

The temperature low ordered moment of $M = 1.90 \mu_B$ seen by neutron scattering is matched by downward-renormalizing the moment calculated in the mean field model to 62% (see Fig. 4d shading). Within density functional theory (DFT) models, the consideration of itinerant electronic states provides a mechanism to explain most of this discrepancy. In DFT simulations, the spin component of the magnetic moment is enhanced to $M_{\text{CEF}} - k_{\text{B}} T_\text{c}$, larger than the maximal value of $M_{\text{CEF}} - k_{\text{B}} T_\text{c}$ that we find in the 5f$^2$ ($T_\text{c} = 4$) atomic multiplet picture. This larger DFT spin moment is directly opposed to the orbital magnetic moment of $M_{\text{CEF}}$. The observation that the magnetism is enhanced by an order of magnitude in USb$_2$ compared to the lowered moment expected from DFT calculations likely results from the breakdown of the mean field approximation in the U-rich limit.
moment, resulting in a smaller overall ordered moment. The ordered moment in the multiplet simulation could alternatively be reduced by strengthening the crystal field, but this is challenging to physically motivate, and has the opposite effect of reducing the spin moment to \( M_S < 1 \mu_B \).

**Density functional theory + dynamical mean field theory (DFT + DMFT).** The combination of density functional theory (DFT) and dynamical mean-field theory (DMFT), as implemented in the full-potential linearized augmented plane-wave method (FLAPW), was used to describe the competition between the localized and itinerant nature of 5f-electron systems. The correlated uranium 5f electrons were treated dynamically by the DMFT local self-energy, while all other delocalized spd electrons were treated on the DFT level. The vertex corrected one-crossing approximation was adopted as the impurity solver, in which full atomic interaction matrix was taken into account. The Coulomb interaction \( U = 4.0 \text{ eV} \) and the Hund’s coupling \( J = 0.57 \text{ eV} \) were used for the DFT + DMFT calculations.

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**Author contributions**

L.M., R.B., Y.X., E.K., and H.H. carried out the XAS experiments with support from J.D., Y.-D.C., and J.R.J.; neutron measurements were performed by S.R. and N.P.B. with support from Y.Z., X.Z., and J.W.L.; STM measurements were performed by I.G. with guidance from P.A.; high-temperature samples were synthesized by S.R. and S.R.S. with guidance from N.P.B.; multiplet simulations were performed by L.M. with guidance from L.A.W., and DFT + DMFT simulations were performed by C.-J.K. with assistance from Y.W. and guidance from G.K.; J.M., L.B., Y.X., P.A., N.P.B., and L.A.W. participated in the analysis, figure planning, and draft preparation; L.A.W. was responsible for the conception and the overall direction, planning, and integration among different research units.
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