Dual nature of 5f electrons in the isostructural UM₆Si₂ family: from antiferro- to Pauli paramagnetism via hidden order

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Using inelastic x-ray scattering beyond the dipole limit and hard x-ray photoelectron spectroscopy we establish the dual nature of the U 5f electrons in UM₆Si₂ (M = Pd, Ni, Ru, Fe), regardless of their degree of delocalization. We have observed that the compounds have in common a local atomic-like state that is well described by the U 5f² configuration with the Γ₁(1) and Γ₂ quasi-doublet symmetry. The amount of the U 5f³ configuration, however, varies considerably across the UM₆Si₂ family, indicating an increase of U 5f itineracy in going from M = Pd to Ni to Ru, and to the Fe compound. The identified electronic states explain the formation of the very large ordered magnetic moments in UPd₂Si₂ and UNi₂Si₂, the availability of orbital degrees of freedom needed for the hidden order in URu₂Si₂ to occur, as well as the appearance of Pauli paramagnetism in UFe₂Si₂.

A unified and systematic picture of the UM₆Si₂ compounds may now be drawn, thereby providing suggestions for new experiments to induce hidden order and/or superconductivity in U compounds with the tetragonal body-centered ThCr₂Si₂ structure.

In heavy fermion compounds the intricate interplay between the f and conduction electrons has a large impact on ground state properties [1–7]. Herein we study uranium 5f systems with the UM₆Si₂ composition that crystallize in the tetragonal body-centered ThCr₂Si₂ structure whereby M denotes a transition metal. Members of this family exhibit a strong a-c-axis magnetic anisotropy and several of them show long-range magnetic order (e.g. M = Pd, Ni) or remain Pauli paramagnetic (e.g. M = Fe) down to low temperatures [8–16]. URu₂Si₂ is particular. It undergoes two transitions, one into an ordered state at 17.5 K with a considerable loss of entropy (≈0.2 R ln2) and a second one at 1.5 K into a superconducting phase [17–19]. Below 17.5 K ordered magnetic moments of 0.03 μ_B have been measured [20, 21], but the moment is too small to account for the loss of entropy. Therefore, it is believed that the phase below 17.5 K is an electronically ordered state but with an order parameter that is yet unknown and continues to be heavily debated to this day, see Refs. [22–27] and references therein. This is the famous hidden order phase (HO). The application of pressure, however, suppresses the HO phase and a large moment antiferromagnetic (LMAFM) phase develops. At about 5 kbar the ordered magnetic moment rises discontinuously from 0.03 to about 0.4 μ_B [21, 28]. Also, magnetic field acts to suppress the HO state and instead a spin density wave has been observed [29].

In these uranium systems, the 5f electrons are crucial for the ground state formation. This situation raises the question whether a systematic picture can be developed that takes into account both correlation effects and band formation with the 5f states, and at the same time explains consistently the widely varying properties of the UM₆Si₂ compounds. One of the most pressing issues is whether local or atomic-like states can survive the band formation in such metallic systems, or in other words, whether it is meaningful at all to develop models that have atomic multiplet states as a starting point. Otherwise one may be better off using band theory based methods (see Refs. [22–24, 25–27] and references therein). Very recently non-resonant inelastic x-ray scattering (NIXS, or x-ray Raman scattering) beyond the dipole limit revealed that local atomic multiplet states can be identified in URu₂Si₂ [30], which is quite surprising since itineracy and Fermi surface effects do play a role in the HO transition [31–32]. It is now important to investigate whether the other members of the UM₆Si₂ family show multiplets, and if so, whether the atomic multiplet states are the same or different across the isostructural family.

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For our present study we selected $M = \text{Pd, Ni, Ru, Fe}$, with Fe (Pd) being isoelectronic with Ru (Ni). The UPd$_2$Si$_2$ and UNi$_2$Si$_2$ order antiferromagnetically (AF) at $T_N = 136$ and 124 K, respectively [14, 16] with very large ordered moments; 3.37 [8] and 2.3 $\mu_B$ [13] have been reported for UPd$_2$Si$_2$ and 2.7 $\mu_B$, for UNi$_2$Si$_2$ [11]. URu$_2$Si$_2$ is the HO compound exhibiting superconductivity, and UFe$_2$Si$_2$ is a Pauli paramagnet (PP) down to the lowest temperatures [10, 12, 15]. We thus cover a wide range of physical properties while keeping the same U-Si framework and crystal structure ($I4/mmm$). We will apply NIXS at the $O_{4,5}$ edges ($5d \to 5f$) in order to determine the presence and symmetry of possible localized $5f$ states. For measuring the degree of delocalization, we will utilize U$4f$ core-level photoelectron spectroscopy (PES). This is one of the most powerful spectroscopic methods to study hybridization effects in U compounds [33, 34]. Here we apply the hard x-ray version of PES (HAXPES) in order to make use of the larger probing depth and thus to ensure that the signal is representative for the bulk material.

Our objective is to establish whether the so-called dual nature of $f$-electrons model proposed for the description of both the antiferromagnetic order and heavy fermion properties of UPt$_3$ [35, 36] and UPd$_2$Al$_3$ [37, 38] is also a feasible concept to capture the low-energy electronic structure of the hidden order and Pauli paramagnetic members of the UM$_2$Si$_2$ family, and not only of antiferromagnetic members such as UPt$_2$Si$_2$ [39]. If so, we may be able to draw a systematic picture which in turn can be used to provide a solid basis for the realistic modeling of the HO transition, and to point out further experiments to induce HO or superconductivity in other members of the UM$_2$Si$_2$ family.

I. RESULTS

A. Ground state symmetry with NIXS

In NIXS the directional dependence of the double differential cross-section gives insight to the orbital anisotropy of the ground state, similar to the linear dichroism in x-ray absorption (XAS). Here the direction of the momentum transfer $\vec{q}$ acts similarly to the direction of the electric field vector in XAS. The size of the momentum transfer $|\vec{q}|$ makes the important difference; for large momentum transfers NIXS is governed by multipole selection rules while XAS is governed by dipole selection rules (see Ref. [30] and references therein).

The dominant NIXS signal arises from Compton scattering and the core-level excitations appear as spikes on top (see Fig.S1 in the Appendix). Not all core-levels have a sizable cross-section at $|\vec{q}| = 9.6$ Å$^{-1}$, but the U $O_{4,5}$ core level at 100 eV energy transfer is distinctly visible in all the spectra. The broad Compton background was used for normalizing the spectra of different $\vec{q}$ directions of one compound. In the second step the data of the U $O_{4,5}$ edges of the different compounds were normalized to each other using the isotropic spectra that are constructed from directional dependent $O_{4,5}$ edge data in Fig. 1 as $I_{iso} = (2 I_{\parallel[100]} + I_{\parallel[001]})/3$ [40].

Figure 1 shows the $O_{4,5}$ edge data for $T < 15$ K of UFe$_2$Si$_2$ (a), UNi$_2$Si$_2$ (b), URu$_2$Si$_2$ (c) and UPd$_2$Si$_2$ (d) for $q || [100]$ (blue) and $q || [001]$ (red) measured with energy steps of 0.1 eV (0.2 eV for $M = \text{Ru}$). The size of the data points reflects the statistical error bars. The data were normalized (see above) and a linear background was subtracted. Lastly, the URu$_2$Si$_2$ data were reproduced from Ref. [30].

All four spectra in Fig. 1 exhibit a clear directional dependence (dichroism) and the similarities in magnitude and line shape of the spectra are apparent. The differences between the four compounds are only due to the appearance of the dipole forbidden $M_I$ edges (3$s \to 3d$) of the Ni sample at 112 eV and of the Fe sample at 91 eV. For Ni the $M_I$ edge lies above the higher energy branch of the U $O_{4,5}$ edge but for Fe it coincides with the lower energy branch of the U $O_{4,5}$ edge. These $M_I$ edges also exhibit a dichroism [41] so that in case of UFe$_2$Si$_2$ we mainly rely on the directional dependence of the higher energy branch of the U $O_{4,5}$ edge at 103 eV. Otherwise, the shape of the U $O_{4,5}$ edges seem fairly robust and independent of the compound under investigations.

In Ref. [30] we showed that the multiplet structure of the isotropic NIXS spectrum of URu$_2$Si$_2$ is well reproduced with a U$^{4+}$ 5$f^2$ ansatz. The similarity of the NIXS spectra thus indicates that all the other compounds with $M = \text{Fe, Ni, and Pd}$ show the presence of atomic-like multiplet states, and that these are also 5$f^2$ based.

![Figure 1](image-url)
Fig. 2(a)-(d) shows the difference spectra (dichroism) of the directional dependent NIXS data. Given the similarity of the NIXS spectra in Fig. 1(a)-(d) it does not come as a surprise that the dichroisms of antiferromagnetic UNi₂Si₂ and UPd₂Si₂ agree as well with the one of URu₂Si₂ in the region of the U O₄.5 edge. For the Pauli paramagnet UFe₂Si₂, we also find that the dichroism agrees well with the one the other compounds although we have to restrict the comparison to the U signal at 103 eV in order to avoid the contribution of Fe M₁.

The directional dependence in the spectra is due to the crystal-field splitting of the Hund’s rule ground state of the U 5f² configuration. It has a total angular momentum J = 4 and is split by the tetragonal (D₁₄h-symmetry) crystalline electric field (CEF) into five singlets and two doublets. J remains a good quantum number even in the intermediate coupling regime of uranium so that the CEF wave functions can be written in terms of J₂ (see eqs. (1)-(7)).

\[ \Gamma_1^{(1)}(\theta) = \cos(\theta) |0\rangle + \sin(\theta) \sqrt{\frac{1}{2}} \left( |+4\rangle + |-4\rangle \right) \]  
\[ \Gamma_1^{(2)}(\theta) = \sin(\theta) |0\rangle - \cos(\theta) \sqrt{\frac{1}{2}} \left( |+4\rangle + |-4\rangle \right) \]  
\[ \Gamma_2 = \sqrt{\frac{1}{2}} \left( |+4\rangle - |-4\rangle \right) \]  
\[ \Gamma_3 = \sqrt{\frac{1}{2}} \left( |+2\rangle + |-2\rangle \right) \]  
\[ \Gamma_4 = \sqrt{\frac{1}{2}} \left( |+2\rangle - |-2\rangle \right) \]  
\[ \Gamma_5^{(1)}(\phi) = \cos(\phi) |\mp 1\rangle + \sin(\phi) |\pm 3\rangle \]  
\[ \Gamma_5^{(2)}(\phi) = \sin(\phi) |\mp 1\rangle - \cos(\phi) |\pm 3\rangle \]

We now calculate the dichroism of the seven CEF states (see Fig. 2(e)-(h)) with the full multiplet code Quanty [42] using the same parameters as in Ref. [30] (see Appendix). For the mixed singlet states Γ₁(θ) (eq. 1 and 2) in panel (e) and the doublet states (eq. 6 and 7) in panel (g) the extreme dichroisms are given for θ and φ equal to 0 and 90°. For other values of θ and φ i.e. in case of J₂ mixtures the dichroism falls in between the dark and light green (red) lines. In contrast, the dichroism of the Γ₂, Γ₃ and Γ₄ singlet states in panel (f) and (h), respectively are given by single lines.

The comparison of the experimental directional dependencies in Fig. 2(a)-(d) and the dichroism of the seven crystal-field states in Fig. 2(e)-(h) shows immediately that for all four UM₂Si₂ compounds investigated, only the Γ₁(≈90°) and the Γ₂ have the correct sign and magnitude to reproduce the difference spectra [13]. In fact, the experimentally observed magnitude is so large that it excludes any other state. This implies that the we can safely conclude that it is the singlet Γ₁(≈90°) or the singlet Γ₂ or, as will be explained below, a quasi-doublet made up of the two that determines the local symmetry in the ground state, and that the four compounds have this result in common.

Additional data were taken at 300 K in order to search for the population of CEF excited states. The open circles at the bottom of each panel in Fig. 1 represent the directional dependence of the 300 K data. We find that the temperature effect is negligible within the error bars of the experiment for all compounds when comparing the open (T = 300 K) with the full circles (T < 15 K). This means that the excited states do not get thermally populated and are quite far away from the Γ₁(90°) or the Γ₂ singlet, or their quasi-doublet ground state. In Ref. [29] we had estimated from the lack of temperature dependence that the states with weak dichroism like the Γ₁(90°), the Γ₃ and Γ₄ must be higher than 150 K (13 meV), whereas states with stronger opposite anisotropy must be even higher in energy (compare Fig. 2(e)-(h)). Only in the case of UPd₂Si₂ the directional dependence seems to have decreased slightly with rising T, hinting towards a smaller CEF splitting with respect to the other compounds.

B. Relative 5f electron count with HAXPES

Figure 3(a) shows the U 4f core-level HAXPES data of UFe₂Si₂, URu₂Si₂, UNi₂Si₂, and UPd₂Si₂ at T = 20 K after subtracting an integral-type (Shirley) background [44] and normalization to the integrated intensity of the U 4f core-level emission lines. The U 4f core level is spin-orbit split by about 10.8 eV (J = 5/2 and 7/2) and the intensity ratio of the spectral weights assigned to the U 4f₅/₂ and U 4f₇/₂ turns out to be about 0.8 for all four compounds which agrees well with the expected value of 6/8 = 0.75. The U 4f core-level data consist of the superposition of several U configurations, each with its own multiplet structure. We may crudely describe the spectra with a triple peak structure at 377.5 (388.3), 380 (390.8), and 384 (394.5) eV for U 4f₇/₂ (U 4f₅/₂) (see Fig. 3(a)).

A systematic change becomes apparent when comparing the 4f core-level spectra of the four compounds: from Pd → Ni → Ru → Fe the higher energy spectral weight at 384 (394.5) eV of the U 4f₇/₂ (U 4f₅/₂) core level loses spectral weight to the benefit of the peak at 377.5 (388.5) eV. The change in spectral weights cannot be due to different crystal structures, different multiplets or different ground-state symmetries because the four compounds are isostructural and it was shown in the previous section that all four compounds have the same ground-state symmetry arising out of an U⁺⁵ 5f² configuration. It can therefore only be due to a change in the 5f-shell occupation. To be more specific, it must be due to a successive increase of the number of the f electrons in the 5f-shell occupation. In accordance with the sequence Pd → Ni → Ru → Fe.

The justification for this interpretation of increasing 5f shell filling from M = Pd to Fe is given in Fig. 3(b)
which shows the U 4f core-level HAXPES data of UCd$_{11}$ (red line) and UPd$_3$ (blue line). Again the data are normalized to the integrated intensity (note the larger y-scale in comparison to panel (a) to accommodate the strong UCd$_{11}$ signal). UCd$_{11}$ is an example for an intermetallic U compound that has adopted the 5f$^3$ configuration [35] and it shows a simple U 4f core-level spectrum with peaks at A (U 4f$_{7/2}$) and A’ (U 4f$_{5/2}$) with hardly any satellites. UPd$_3$, on the other hand is an intermetallic U compound that is quite localized and well described by the U 5f$^2$ configuration [40]. It shows a pronounced double peak structure B (B’) and C (C’) for U 4f$_{7/2}$ (U 4f$_{5/2}$) with some minor, third contribution A (A’), very much in agreement with Fujimori et al. [34].

For a better comparison we overlaid the spectrum of URu$_2$Si$_2$ in Fig. 3(b). This clearly reveals that URu$_2$Si$_2$ is intermediate valent because the spectrum contains the A, B, C (A’, B’, C’) structure of the U 5f$^2$ and U 5f$^3$ features. The peak positions in UPd$_3$ and UCd$_{11}$ are not precisely the same as in UM$_2$Si$_2$ compounds which can be attributed to the different chemical environment of the U atoms. We further know from a configuration interaction analysis of PES data of e.g. cerium compounds [47][49] that the higher f-shell filling has an overproportional higher spectral weight, so that, without attempting a quantitative analysis, we can further state that the amount of the 5f$^2$ configuration in the initial state must be significant. Another look at Fig. 3(a) lets us then conclude that the U 5f$^3$ contribution increases successively from the two antiferromagnets UPd$_2$Si$_2$ and UNi$_2$Si$_2$ to the hidden order compound URu$_2$Si$_2$, and to the Pauli paramagnet UF$_2$Si$_2$.

II. DISCUSSION

In NIXS all four compounds exhibit multiplets that are well described with the U 5f$^2$ local symmetry i.e. the multiplets survive even the itineracy in the Pauli paramagnetic state in UF$_2$Si$_2$. Hence, irrespective of the degree of itineracy, the U 5f$^2$ configuration determines the local symmetry. This gives credit to our previous findings of U 5f$^2$ multiplets in the hidden order compound URu$_2$Si$_2$ [30]. Together with the local symmetry contributions, all four compounds have to be classified as intermediate valent; their ground states are mixtures of the U 5f$^2$ and U 5f$^3$ configurations. The overall presence of multiplets implies that the dual nature of f electrons not only exists among the antiferromagnetic members, it also persists in the most itinerant members of the UM$_2$Si$_2$ family.

A. Singlets and quasi-doublets

The symmetry of the 5f$^2$ ground state is, according to our experiment, a singlet state so that the question arises how this is understood within the context of the antiferromagnetic ground states of UPd$_2$Si$_2$ and UNi$_2$Si$_2$ with very large ordered moments. After all, only the $\Gamma_{1}^{(1,2)}$ doublets carry a moment but none of the singlet states do (see Table I). The NIXS data, however, can also be described with two singlets states close in energy, i.e. with a quasi-doublet consisting of the $\Gamma_1^{(1)}$ (≈90°) and $\Gamma_2$ nearby in energy. Here the $\Gamma_1^{(1)}$ has a large $J_z = +4$ and $-4$ component and the $\Gamma_2$ is a pure $J_z = +4$ and $-4$ state and a quasi-doublet consisting of these two may carry an induced moment. Actually, in the UM$_2$Si$_2$ structure,
reached. The range of magnetic moment values are listed
normalized to the integrated intensity. (a) of UFe
quasi-doublets consisting of Γ^{1,2}(θ) with URu
photoelectron spectroscopy (HAXPES) data (h
FIG. 3. Background corrected U 4f core level hard x-ray
normalized to the integrated intensity. (a) of UFe_2Si_2 (green),
URu_2Si_2 (black), UNi_2Si_2 (blue) and UPd_2Si_2 (orange), and
(b) of the reference compounds UCd_{11} (red line) and UPd_3 (blue line) with URu_2Si_2 (gray filling) for comparison. Note
the expanded y-scale in (b).

TABLE I. Possible ordered magnetic moments μ_ord for the respective crystal-field states and of the quasi-doublets Γ^{1,2}(θ) & Γ_2 and Γ_3 & Γ_4 (third column).

| CEF states | μ_ord of singlet states | μ_ord of quasi-doublet |
|------------|------------------------|------------------------|
| Γ^{1,2}(θ) | 0                      | 0-4μ_B                 |
| Γ_2        | 0                      | 0-2μ_B                 |
| Γ_3        | 0                      |                        |
| Γ_4        | 0                      |                        |
| Γ^{1,2}(θ) | 0-3μ_B                 |                        |

Our NIXS results reveal that the ground-state symmetry is that of the Γ^{1(1)} or the Γ_2 singlet, or the Γ^{1(1)} & Γ_2 quasi-doublet. Such a quasi-doublet can generate induced moments of up to 4μ_B (see Table1), thus naturally accommodating the large ordered moments that were observed in UPd_2Al_3 [8] and UNi_2Si_2 [11]. Even the value of 3.37μ_B [8] could be explained by such a quasi-doublet. We would like to note that the idea of using a quasi-doublet to induce magnetic moments and long range AF magnetic order is not unrealistic. Such an induced magnetic moment scenario has been proposed to explain the magnetic moments in the moderate heavy-fermion compound UPd_2Al_3 with the dual nature of f electrons explaining the heavy bands and dispersive magnetic singlet-singlet excitations mediating the superconducting pairing [37] [38] [50].

Another important aspect of having a quasi-doublet is that it allows for the degeneracy needed for a hidden order to occur in URu_2Si_2. Here, we argue that the orbital degrees of freedom rather than spin form the driving force for the phase transition. Furthermore, it should be mentioned that the Ising like anisotropy of the static susceptibility is compatible with a quasi-doublet consisting of these two states [51].

B. f-d hybridization strength

We need to look at the hybridization process between the 5f and the conduction band electrons in order to explain the increase of the U^{3+} 5f^3 spectral weight in the sequence M = Pd(AF) → Ni(AF) → Ru(HO) → Fe(PP).

Figure 1(a)-(d) show the result of density functional theory (DFT) calculations in the non-magnetic phase using FPLO [52] (see Appendix). The partial density of states (DOS) of U 5f for J = 5/2 and 7/2, the U 6d, the transition metal 3d or 4d, respectively, and the Si 3p partial DOS are displayed. We observe first of all that there are transition metal d states (colored green (Fe), black (Ru), blue (Ni), and orange (Pd)) present in the energy region where the U 5f_{5/2} (colored red) is located, i.e. around the Fermi level. The amount is appreciable for the Fe compound, and gets smaller for the Ru and Ni, and is tiny for the Pd. In addition, a closer look reveals that the width of the U 5f_{5/2} band is the largest for the Fe compound and the smallest for the Pd, with the Ru and Pd in between. All together, this indicates that the mixing or hybridization between the transition metal d and the U 5f is the strongest for the Fe, and decreases for the Ru and Ni, and is the weakest for the Pd. This trend is fully consistent with the U 4f HAXPES result in that the U 5f^3 contribution decreases successively from the Pauli paramagnet UFe_2Si_2 via the hidden order compound URu_2Si_2 to the two antiferromagnets UNi_2Si_2 and UPd_2Si_2.

For the interpretation of the calculated partial DOS, one can look whether the hybridization trend of Fe-Ru-Ni-Pd is reflected by the U-U distances a or the U-
transition metal distances $d_{U,TM}$ across this set of compounds. If so, the $f$-$d$ hopping integral may play an important role. However, the trend of $a$, from small to large, goes as Fe, Ni, Ru and Pd (see e.g. Fig S2 in the Appendix). The trend for $d_{U,TM}$ is, from small to large, Ni, Fe, Ru and Pd. In other words, already the opposite order of the Ni and Ru compounds in both, $a$ and $d_{U,TM}$ does not favor an interpretation of hopping integral driven systematics. What is clearly forming a trend in the calculations is the energy position of the $d$ states relative to the U 5$f$. In going from $M = Fe$ to Ru to Ni, and to Pd, we observe that the $d$ states are moving to more negative energies and thus farther away from the U 5$f$ levels. This strongly suggests that, in terms of a many body model such as an Anderson impurity or lattice model, it is the 5$f$ level position $\epsilon_f$ that provides the crucial parameter when comparing this UM2Si2 series.

Valence band HAXPES has been used to check whether these DFT predictions are valid. Figure 4(e)-(h) shows the spectra of the four compounds. In order to compare the DFT results to the experiment, we calculate the valence band spectra by multiplying each of the partial DOS by their respective shell-specific photoionization cross-section at 5945 eV photon energy as derived from from Refs. [3] and by the Fermi function to include only the contributions from the occupied states, followed by a broadening to account for the experimental resolution and intrinsic broadening, and their summation. This was done for all the partial DOS included in the calculation (not only the ones shown in Figure 4(a)-(d)). The results are displayed in Figure 4(e)-(h) (black lines). The comparison with valence band HAXPES data confirms the validity of the DFT predictions; the general agreement between experiment and theory is very good. There are deviations in the U 5$f$ regions where the calculated intensities are higher than in the experiment since correlation effects were neglected in the DFT, but the line shape and positions of the silicon, transition metal, and uranium non-$f$ bands are well reproduced. This validates the hybridization picture offered by the DFT calculations, and in turn, provides a consistent reasoning for the increase of the 5$f^2$ spectral weight in the sequence $M = Pd(AF) \rightarrow Ni(AF) \rightarrow Ru(HO) \rightarrow Fe(PP)$.

C. Dual nature of the 5$f$ electrons

The above findings are very much compatible with the dual-nature idea of $f$ electrons in uranium heavy fermion compounds [35]. On one hand, we have observed in NIXS the local atomic multiplet structure of the U 5$f^2$ configuration in the UM2Si2 system. On the other hand, we have noticed from HAXPES the intermediate valent character of U in UM2Si2, and that the U 5$f^3$ weight increases from Pd to Ni to Ru to Fe. Thus with increasing $f$-$d$ hybridization the magnetic moments get suppressed until eventually an intermediate valent Fermi liquid state with enhanced Pauli paramagnetism is reached, thereby
showing the impact of the itinerant part. Two of the 5f electrons remain localized and form atomic multiplet states whereas a third electron is effectively delocalized with an accordingly renormalized mass.

An important finding is that the four compounds share the same multiplet states for the 5f² configuration, namely the Γ_1(4)(≈90°)/Γ_2 quasi-doublet. This allows us to draw a Doniach-like phase diagram in which the temperature T is plotted versus an effective interaction J, a quantity that is determined by the f-d hopping integral V and the f energy ε_f [5] and that can be associated with the degree of delocalization of the third electron. For small J magnetic order prevails, whereas for large J a Kondo-like screened (intermediate valent) state forms that is well described in terms of a Fermi liquid (FL) with enhanced Pauli paramagnetism. In the transition region a quantum critical point (QCP) and non-Fermi liquid (NFL) scaling occurs that is often hidden by a superconducting (SC) dome [4][54]. In Fig. 3(i) the Pd member of the family is placed the most to the left because it has the largest ordered moment, followed by the Ni compound that also resides in the AF regime. URu₂Si₂, however, is placed very close to or at the QCP since it is the only compound of the family that exhibits superconductivity and hidden order. UF₂₂Si₂, finally, is located on the Kondo-like screened side (PP) to the right of the QCP where the physical properties follow FL scaling.

The application of pressure is known to push URu₂Si₂ into the AF regime [21][28] i.e. pressure reduces the itinerant part, and in our picture, reduces J. This may seem counterintuitive since pressure will decrease distances and hence increase V so that J becomes larger since it is proportional to V²/ε_f [5]. However, we know pressure will stabilize the f² configuration with its smaller ionic radius at the expense of the f³. This is reflected in this description by the increase of ε_f whereby ε_f is positive to denote that the f² configuration is lower in energy than the f³. Hence, J is decreased with pressure because ε_f increases more strongly than V². With this in mind, we now speculate what applying pressure to UF₂₂Si₂ will do. Our expectation is that J will also be reduced and thus drives the compound into the superconducting-hidden order regime.

We would like to note that already in 1993 Endstra et al. [12] sorted the members of the UM₂Si₂ family into a Doniach-like phase diagram. The same sequence was suggested, but this was merely based on semiquantitative band structure calculations of the hybridization strength. Which local atomic like states are active were not known, and moreover, the issue whether the UM₂Si₂ members have the same multiplet states in common was not even considered. Our experimental findings justify the use of a Doniach-like phase diagram since a common quasi-doublet scenario can be established for the local states together with the observation of strongly varying 5f count across the family. Of utmost importance is the fact that the particular quasi-doublet scenario made of J = 4 states allows for the large span of properties across the UM₂Si₂ family, namely to cover antiferromagnetism with very large ordered moments, hidden order and superconductivity, as well as Pauli paramagnetism.

III. CONCLUSION

The dual nature of the 5f electrons in four isostructural compounds with very different ground state properties, namely UPd₂Si₂ (AF), UNi₂Si₂ (AF), URu₂Si₂ (HO), and UF₂₂Si₂ (PP) has been shown. The NIXS data of the U O₄.5 edge reveal multiplets of the localized U 5f² configuration in all four compounds, irrespective of the degree of itineracy, and the directional dependence of NIXS unveils that the different collectively ordered (or non-ordered) ground states form out of the same symmetry. The symmetry is determined by the singlet states Γ₁(4)(≈90°) or Γ₂ of the U 5f² Hund’s rule ground state, so that only an induced-type of order with a quasi-doublet consisting of these two singlet states can explain the large ordered moment of the antiferromagnetic members of the family. The comparison of the 4f core-level HAXPES data is meaningful because the four compounds have the same local ground-state symmetry. It reveals the change of the itinerant character within the family. The relative 5f-shell filling increases successively when going from M = Pd(AF) → Ni(AF) → Ru(AF) → Fe(PP) so that a comprehensive picture is proposed, namely the sorting of the UM₂Si₂ compounds into a Doniach-like phase diagram.

IV. APPENDIX

A. Sample Preparation

The URu₂Si₂ single crystals used for HAXPES were grown by the Czochralski method in a tetra-arc furnace in San Diego from high purity starting elements (depleted uranium –3N, Ru –3N, Si –6N). Single crystalline URu₂Si₂ used for the NIXS experiment was grown with the traveling zone method in the two-mirror furnace in Amsterdam under high-purity (6N) argon atmosphere. Single crystals of UM₂Si₂ with M = Fe, Ni, and Pd were grown in Wroclaw by Czochralski pulling technique in ultra-pure Ar atmosphere using a tetra-arc furnace. The starting components were high-purity elements (natural uranium –3N, Fe –3N, Ni –4N, Pd –4N, and Si –6N). All single crystals were checked x-ray Laue diffraction for thers single-crystalline nature.

Polycrystalline UPd₃ sample of 1 g was synthesized in Dresden by arc melting stoichiometric amounts of uranium metal (natural, foil, Goodfellow, 99.98 wt.%) with palladium metal (shot, Chempur, 99.99 wt.%) under a protective atmosphere of argon gas. The melted button was then placed into an alumina crucible and sealed into a tantalum tube. The sample was heated to 1400°C...
within 6 hours, annealed for additional 6 hours and subsequently furnace cooled to room temperature. The single phase nature of the sample was deduced from the analysis of powder XRD data. Single crystals of UCd$_{11}$ were grown from Cd flux. Uranium and cadmium pieces in the molar ratio U: Cd = 1:133 were placed in an alumina crucible and sealed under vacuum in a silica ampoule. The ampoule was heated to 600$^\circ$C, held at that temperature for 20 hours, then slowly cooled at 2$^\circ$C/hr. to 400$^\circ$C, whereupon the excess Cd flux was removed via a centrifuge.

B. Experiment

The NIXS measurements were performed at the High-Resolution Dynamics Beamline P01 of the PETRA-III synchrotron in Hamburg, Germany. The end station has a vertical geometry with twelve Si(660) 1 m radius spherically bent crystal analyzers that are arranged 3×4 matrix and positioned at scattering angles of 2$\theta$≈150$^\circ$, 155$^\circ$, and 160$^\circ$. The final energy was fixed at 9690 eV, the incident energy was selected with a Si(311) double monochromator, and the overall energy resolution was ≈0.7 eV. The scattered beam was detected by a position sensitive custom-made Lambda detector based on a Medipix3 chip. A sketch of the scattering geometry can be found in Ref. [55]. The averaged momentum transfer was $|\vec{q}|=(9.6 \pm 0.1)$ Å$^{-1}$ at the U O$_{4.5}$ edge. The crystals were mounted in a Dynaflow He flow cryostat with Al-Kapton windows.

The HAXPES experiments were carried out at the beamlines P09 and P22 of the PETRA-III synchrotron in Hamburg, Germany [56, 57]. The incident photon energy was set at 5945 eV. The valence band spectrum of a gold sample was measured in order to determine the Fermi level $E_F$ and the overall instrumental resolution of 300 meV. The excited photoelectrons were collected using a SPECS225HV electron energy analyzer in the horizontal plane at 90$^\circ$. The sample emission angle was 45$^\circ$. Clean sample surfaces were obtained by cleaving the samples in situ in the cleaving chamber prior to inserting them into the main chamber where the pressure was ≈10$^{-10}$ mbar. The measurements were performed at a temperature of 20 K.

C. Simulation

The simulations include the spin-orbit as well as Coulomb interactions with atomic values from the Cowan code. The Slater integrals 5f-5f and 5d-5f were reduced in order to account for screening effects in the solid [58, 59]. A reduction of 50% reproduces the energy dependence of the multiplet excitations of the U O$_{4.5}$-edges of the U$_2$Si$_2$. The $J$ = 4 multiplet forms the ground state for all finite values of spin-orbit coupling and Coulomb interaction. The relative contributions of the orbital angular momenta $L$ = 3, 4, and 5 are 1%, 14%, and 85% for the present ratio of spin-orbit coupling and Coulomb interaction. A Gaussian broadening of 0.7 eV accounts for the instrumental resolution and a Lorentzian broadening of 1.3 eV for life-time effects. In addition some asymmetry due to the metallicty of the samples has been described by using a Mahan-type line shape with an asymmetry factor of 0.18 and an energy continuum of 1000 eV.

D. DFT calculation

Density functional theory based calculations were performed using the full-potential non-orthogonal local orbital code (FPLO v.18.00.52) employing the local density approximation (LDA) and including spin-orbit coupling (fully relativistic calculation). A grid of 15×15×15 k-points and 5000 energy points (about 1 point every 8 meV) have been used for the calculation of the band structure and density of states (DOS).

V. SUPPORTING INFORMATION

Compton: Figure 5 show the experimental NIXS spectra of UFe$_2$Si$_2$ (a), UNi$_2$Si$_2$ (b), URu$_2$Si$_2$ (c) and UPd$_2$Si$_2$ (d) over a wide energy range with a coarse

FIG. 5. Experimental wide energy scans at $T < 20$ K covering the peak of the Compton signal of (a) UFe$_2$Si$_2$, (b) UNi$_2$Si$_2$, (c) URu$_2$Si$_2$ and of (d) UPd$_2$Si$_2$; red and blue denote the two different directions of the momentum transfer $\vec{q}$. The data of different momentum directions are scaled to the Compton peak. The URu$_2$Si$_2$ data in panel (c) were acquired in a previous experiment on a different beamline with a larger step size [50, 60] and were averaged over several directions of $\vec{q}$. 
energy step size of 0.5 eV (even larger for URu$_2$Si$_2$) for different directions of the momentum transfer $\vec{q}$, $q_y[100]$ (blue) and $q_y[001]$ (red). The URu$_2$Si$_2$ data were obtained in a previous experiment (see Ref. [30, 60]) and here only $<q>$ averaged signal is shown. The dominant signal arises from Compton scattering and the core-level excitations appear as spikes on top.

**Properties:** Figure 6 summarizes the lattice constants, U transition metal (TM) distances, structure, and ground state properties of the UM$_2$Si$_2$ compounds surrounding URu$_2$Si$_2$.

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**TABLE 6.** Section of the periodic table for the UM$_2$Si$_2$ compounds providing the crystallographic structure, the lattice constants, the U–transition metal distances, the ground state properties AF for antiferromagnetic, PP for Pauli paramagnetic, HO for hidden order, SC for superconducting, as well as the temperatures at which the respective transitions take place [8–10, 12–16].

| 3d | 4d | 5d |
|----|----|----|
| Fe | Ru | Os |
| Co | Rh | Ir |
| Ni | Pd | Pt |

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