Electronic structure and magnetism in UGa$_2$: DFT+DMFT approach

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The debate whether uranium 5f electrons are closer to being localized or itinerant in the ferromagnetic compound UGa$_2$ is not yet fully settled. The experimentally determined magnetic moments are large, approximately 3 $\mu_B$, suggesting the localized character of the 5f electrons. In the same time, one can identify signs of itinerant as well as localized behavior in various spectroscopic observations. The band theory, employing local exchange-correlation functionals, is biased toward itinerant 5f states and severely underestimates the moments. Using material-specific dynamical mean-field theory (DMFT), we probe how a less approximate description of electron-electron correlations improves the picture. We present two variants of the theory: starting either from spin-restricted (LDA) or spin-polarized (LSDA) band structure. We show that the L(S)DA+DMFT method can accurately describe the magnetic moments in UGa$_2$ as long as the exchange interaction between the uranium 6d and 5f electrons is preserved by a judicious choice of the spin-polarized double-counting correction. We discuss the computed electronic structure in relation to photoemission experiments and show how the correlations reduce the Sommerfeld coefficient of the electronic specific heat by shifting the 5f states slightly away from the Fermi level.

I. INTRODUCTION

The 5f electrons in actinides and their compounds can be either itinerant and participating in chemical bonds, or localized and not contributing to cohesion. A transition akin to Mott metal–insulator transition occurs in elemental actinide metals between Pu and Am [1]. Although elemental uranium has itinerant 5f electrons, its compounds display both types of 5f states. A traditional way of classifying uranium compounds is by placing them in the Hill plot that relates the critical temperature (magnetic or superconducting) to the nearest neighbor $U$–$U$ spacing [2]. Small $U$–$U$ distances favor superconducting behavior at low temperatures, whereas long-range magnetic order takes place at spacings greater than the so-called Hill limit (3.5 Å).

In UGa$_2$, an intermetallic binary compound with a hexagonal AlB$_2$ structure (space group P6/mmm, Fig. 1), the Ga atoms effectively separate the uranium atoms, increasing the $U$–$U$ distance to 4.0 Å, that is, above the Hill limit. Accordingly, the compound exhibits ferromagnetic order below $T_C = 125$ K with the easy magnetization axis along the [100] direction. Experimental observations establish magnetic moments of approximately 3 $\mu_B$ per U atom in the ferromagnetic phase, using magnetization measurements [3,4] as well as neutron diffraction [5,6]. UGa$_2$ thus exhibits moments and ordering temperature that are larger than typical for ferromagnetic uranium intermetallics [7], which indicates localized 5f electrons. The magnetic behavior can indeed be accurately reproduced by a fully local crystal-field model corresponding to the 5f$^3$ configuration of the U ion [8]. In addition, the observed Sommerfeld coefficient $\gamma = 11$ mJ/mol-K$^2$ [9] is not much enhanced compared to the analogous compound without 5f electrons – LaGa$_2$, displaying $\gamma = 4$ mJ/mol-K$^2$ [10], which testifies against a high density of electronic states at the Fermi level in UGa$_2$, again favoring the localized picture of the 5f electrons. The spectroscopic evidence, on the other hand, is not conclusive about the nature of the 5f states since one can identify spectral features characteristic to localized electrons as well as features typical to itinerant electrons [11–13]. Similarly, the Fermi surface probed by the de Haas–van Alphen effect is not compatible with full 5f localization [9].

The large spin-orbit coupling (SOC), the crystal-field splitting, and the Coulomb interaction between the 5f electrons influence the magnetic moments in a non-trivial manner. This complexity contributes to the fact that the electronic structure of UGa$_2$ is not yet satisfactorily understood. The first-principles band theory based on semi-local approximations to the density-functional theory (DFT) severely underestimates the moments, yielding about 0.6 $\mu_B$ per uranium atom [14,15]. The correlated band theory incorporating an on-site Hubbard interaction term, DFT+U, can successfully model the magnetically ordered states, particularly in insulating compounds with localized 5f electrons [16,18]. In UGa$_2$, it enhances the magnetic moments up to 2.8 $\mu_B$ but the spectroscopic results are not reproduced very well [15,19].
The DFT+$U$ method is a static mean-field approximation and as such it cannot account for the multi-reference character of the 5f shell nor for dynamical many-body effects. These limitations are lifted when DFT is combined with the dynamical mean-field theory (DMFT) \cite{1,2}, which accurately models both itinerant and localized electrons. In this paper, we investigate how the theoretical description of the magnetism and of the electronic structure of UGa$_2$ improves when the DFT+DMFT is applied. We estimate and discuss the effects of the 6d–5f exchange interactions on the 5f magnetic moments, and compare the computed spectral properties with the experimental valence-band photoemission spectra (PES). We also discuss technical matters pertaining to spin-polarized DFT+DMFT solutions.

II. METHOD

The DFT+DMFT method improves upon DFT+$U$ by replacing the static mean-field potential, approximating the Coulomb interaction among the uranium 5f electrons, with an energy-dependent (dynamical) potential (self-energy) \cite{1,2}. This self-energy is computed by solving an auxiliary impurity model – a many-body problem, for which we employ the exact diagonalization. We present two variants of the theory differentiated by the self-energy being inserted (a) into the spin-restricted LDA band structure (we refer to this variant as to LSDA+DMFT). A similar comparison of spin-restricted and spin-polarized parent band structures was performed for ferromagnetic nickel in \cite{23}.

A. General formalism

We start with determination of the first-principles band structure by means of the WIEN2k code \cite{24} using parameters listed in Appendix [x]. Scalar relativistic effects as well as the spin-orbit coupling are included in these WIEN2k calculations \cite{25}. Afterwards, the relevant valence bands are represented by a tight-binding Hamiltonian in the basis of the maximally-localized Wannier functions \cite{26,27}. This Hamiltonian is then used as the parent band structure for the DMFT calculations.

In each iteration of the DMFT self-consistency cycle, the local electronic structure around one shell of the uranium 5f Wannier functions is mapped onto a non-interacting impurity model (Appendix [x]),

\[
\hat{H}_{\text{imp}} = \sum_{mm'mm''} \epsilon_{mm'mm''} \hat{f}_{mm'\sigma}^\dagger \hat{f}_{mm''\sigma} + \sum_j \epsilon_j \hat{b}_j^\dagger \hat{b}_j + \sum_{mm'\sigma \sigma'} \left( J_{m\sigma \sigma'} \hat{f}_{m\sigma}^\dagger \hat{f}_{mm'\sigma} + V_{m\sigma \sigma'} \hat{f}_{m\sigma}^\dagger \hat{f}_{m\sigma} \delta_{\sigma \sigma'} \right),
\]

where $\hat{f}_{m\sigma}$ creates an electron in the 5f shell with magnetic quantum number $m$ and spin projection $\sigma \in \{-1/2,1/2\}$ (eigenvalues of $\hat{s}_z$). The first term in Eq. (1) corresponds to the local Hamiltonian, which describes the 5f shell. It can be decomposed as

\[
\hat{H}_{\text{loc}} = \epsilon_f \hat{f}^\dagger + \hat{\Omega} \cdot \hat{s} - \hat{\Delta}_X,
\]

\[
+ B_{20} \hat{O}_{20} + B_{40} \hat{O}_{40} + B_{60} \hat{O}_{60} + B_{80} \hat{O}_{80},
\]

(2)

where $\epsilon_f$ is the energy of the 5f level, $\hat{\Omega}$ is the strength of the SOC, $\Delta_X$ gives the exchange splitting, and $\hat{O}_{2k}$ and $B_{2k}$ are Stevens operators and the corresponding parameters that characterize the $D_{4h}$ crystal-field potential at the uranium site in UGa$_2$. In general, the parameters $B_{2k}$ can be spin dependent, which we briefly discuss at the end of Appendix [x]. Note that the decomposition introduced in Eq. (2) is only used for the analysis of $\hat{H}_{\text{loc}}$ and has no influence on the DMFT calculations and results.

The second term in Eq. (1) corresponds to an effective medium usually referred to as the bath, with which the 5f shell interacts. The operator $\hat{b}_j$ creates an electron in this effective medium. The last term in Eq. (1) accounts for the hybridization of the 5f shell with the bath. In our calculations, the off-diagonal hybridization induced by the non-commutativity of the hexagonal symmetry with the SOC is fully taken into account. The crystal-field splitting of the 5f states is partly due to the crystal-field potential contained in $\hat{H}_{\text{loc}}$ and partly due to the hybridization.

The full interacting impurity model, in which the self-energy is computed, is given by

\[
\hat{H}_{\text{imp}}^{\text{DMFT}} = \hat{H}_{\text{imp}} + \hat{U},
\]

(3)

where $\hat{H}_{\text{imp}}$ is the non-interacting one-electron part shown in Eq. (1) and $\hat{U}$ is the Coulomb repulsion among the 5f electrons,

\[
\hat{U} = \frac{1}{2} \sum_{mm'mm''} \sum_{\sigma \sigma'} U_{mm'mm''} \hat{f}_{mm'\sigma}^\dagger \hat{f}_{mm'\sigma} \hat{f}_{mm''\sigma}^\dagger \hat{f}_{mm''\sigma} - \sum_{\sigma \sigma'} \sum_{\sigma \sigma'} (U_{I - \sigma \sigma'} + \sigma \sigma') \hat{f}_{mm\sigma}^\dagger \hat{f}_{mm\sigma},
\]

(4)

where $U_{mm'mm''}$ is considered in its full spherically symmetric form parametrized by four Slater integrals $F_0 = 2.0$ eV, $F_2 = 7.09$ eV, $F_4 = 4.60$ eV, and $F_6 = 3.36$ eV, which correspond to Coulomb $U = 2.0$ eV and Hund $J = 0.59$ eV. The first integral, $F_0$, is at the upper limit, beyond which the 5f peak in the occupied LSDA+$U$ density of states moves too far from the Fermi level to be compatible with the valence-band photoemission spectra \cite{11,15}. The other three parameters ($F_2$, $F_4$, $F_6$) correspond to the atomic Hartree–Fock values calculated for the $U^{4+}$ ion (5f$^1$ configuration) and then reduced to 80% to mimic screening \cite{28,29}. Note that the unscreened ionic $F_2$ values yield Hund $J = 0.79$ eV, which can be considered as the maximal value for the uranium 5f systems.

The second term in Eq. (4) is the double-counting correction introduced to remove the static mean-field approximation of the 5f–5f Coulomb interaction that is
incorporated in the DFT band structure. We assume the double-counting correction to be spherically symmetric (neither $U_H$ nor $U_X$ depends on the magnetic quantum number $n$), with $U_X = 0$ for the LDA band structure and $U_X \neq 0$ for the LSDA band structure. The numerical values of $U_H$ and $U_X$ are discussed later in Secs. 11C and 11D.

The impurity model, Eq. (3), is solved using the exact diagonalization (Lanczos) method as implemented in our in-house code [32]. The size of the models, which can be solved by this method, is limited due to unfavorable scaling of the computational demands. The impurity models employed in this paper consist of 14 spinorbitals corresponding to the 5f shell and another 42 spinorbitals representing the bath. Of the bath states, $N_b^\sigma = 14$ orbitals have $\epsilon_f$ below the Fermi level (they are nominally occupied) and $N_b^\pi = 28$ orbitals have $\epsilon_f$ above the Fermi level (they are nominally empty). Even these small models are too demanding unless we turn to a reduction of the many-body basis inspired by the work of Gunnarsson and Schönhammer [32,33]. A cutoff $M$ is introduced for each $N$-electron Hilbert space $H_N$, and the diagonalization is performed only in a subspace

$$H_N^{(M)} = \{ f^{N-N_b^\pi-n+m}b^\dagger b^m, 0 \leq m+n \leq M \}. \tag{5}$$

In this notation, $f^{N-N_b^\pi-n+m}$ indicates $N-N_b^\pi-n+m$ electrons in the uranium 5f shell, $b^\dagger b^m$ indicates $m$ electrons in the bath orbitals above the Fermi level, and $b^\dagger b^m$ means $m$ holes in the bath orbitals below the Fermi level. We use $M = 2$ for the cutoff. The convergence with respect to $M$ is discussed in Appendix D.

The impurity solver yields a self-energy $[\Sigma(z)]_{\sigma\pi\sigma'}^{\sigma\sigma'}$, acting in the subspace of 5f spinorbitals, which enters the Dyson equation for the local Green’s function $G(z)$,

$$G(z) = \frac{1}{N} \sum_k [z\hat{I} - \hat{H}_k - \hat{\Sigma}(z)]^{-1}, \tag{6}$$

where $N$ is the number of k points in the Brillouin zone (4096 in our calculations) and $\hat{H}_k$ is the tight-binding Hamiltonian. The local Green’s function determines an updated impurity model (Appendix E), concluding one iteration of the DMFT cycle.

After the DMFT self-consistency is reached, the occupation matrix of the 5f states is evaluated from the 5f block of the local Green’s function,

$$\hat{n}_f = \int_{-E_F}^{E_F} \hat{A}_f(\epsilon) \, d\epsilon, \quad \hat{A}_f(\epsilon) = -\frac{1}{\pi} \text{Im} \hat{G}_f(\epsilon+i0), \tag{7}$$

where the integral runs over all occupied states up to the Fermi energy $E_F$. Knowing the occupation matrix, we can calculate the 5f electron occupation as well as spin and orbital moments as averages of the corresponding operators,

$$n_f = \text{Tr}(\hat{n}_f) \quad \text{and} \quad \langle O \rangle = \text{Tr}(\hat{O} \hat{n}_f). \tag{8}$$

Finally, the Sommerfeld coefficient of the electronic specific heat $\gamma$ is evaluated using the Fermi-liquid formula,

$$\gamma = \frac{\pi k_B^2}{3} \left[ g_f(E_F) \bigg/ Z_f + g_{spd}(E_F) \right], \tag{9}$$

where $g_f(E_F) = \text{Tr} [\hat{A}_f(E_F)]$ is the density of 5f states at the Fermi energy, $g_{spd}(E_F)$ is the density of all other states at the Fermi energy, and $Z_f < 1$ is the average quasiparticle weight in the 5f bands that is estimated from the DMFT self-energy as suggested in [44].

$$\frac{1}{Z_f} = \text{Tr} \left[ \hat{A}_f(E_F) \left( \hat{I} - \frac{d\hat{\Sigma}(\epsilon+i0)}{d\epsilon} \right) \right]_{\epsilon=E_F} \tag{10}$$

All DMFT calculations presented in this paper are performed at temperature $T = 0 \text{ K}$ in order to obtain the ferromagnetic state with saturated magnetic moments.

### B. Choice of the tight-binding model

We investigated several tight-binding models $\hat{H}_k$ of increasing size. As the minimal model, we considered one that contains gallium 4s and 4p, and uranium 5f and 6d states. Then we included uranium 7s and finally also 7p states. Various characteristics of these models are listed in Table 1. Although the uranium 7p states are relatively high above the Fermi level, their inclusion makes a sizable difference, in particular to the crystal-field parameters in $\mathbb{H}^{\text{loc}}$ and to the filling of the gallium states.

On the top of that, we found that the LDA+DMFT calculations without the U 7p states converge to the out-of-plane [001] ferromagnetic state, whereas the calculations with the U 7p states predict an in-plane ferromagnetic state. Since the experiments determine UGa$_2$ to be an in-plane ferromagnet [3,4], all results presented in the following sections were obtained in the tight-binding models that include uranium 7s and 7p states.

### C. LDA+DMFT

When the parent band structure is spin-restricted (LDA), we induce the ferromagnetic solution by introducing a small symmetry-breaking magnetic field into the impurity model, Eq. (1), in the first few iterations of the DMFT self-consistency cycle. Afterwards, this field is removed again. Since we do not implement any charge self-consistency, the tight-binding Hamiltonian $\hat{H}_k$ remains unchanged during the whole LDA+DMFT cycle and the spin (and orbital) polarization is introduced only by means of the polarized self-energy applied to the 5f states. This method very likely results in an underestimated spin polarization of the 6d bands. Moreover, the local Hamiltonian $\mathbb{H}^{\text{loc}}$ stays non-polarized as demonstrated in Appendix F that is, no exchange field $\Delta_X$ is induced in $\mathbb{H}^{\text{loc}}$ by the polarized self-energy. Nevertheless,
there should be some exchange field present in $\mathcal{H}_{\text{loc}}$ due to the partially filled and partially polarized 6d bands, and neglecting this exchange certainly means underestimated 5f moments (which is indeed what we observe in Sec. II). We fix this deficiency by introducing an empirical exchange field $\Delta_{fd}$ analogously to the earlier computational studies of rare-earth systems [35, 39]. The magnitude of this field is estimated as $\Delta_{fd} \approx I_{f amalg}[35]$, where $m_f$ is the magnetic moment due to the 6d electrons and $I_{fd}$ is intra-atomic exchange integral. The magnetic moment is approximated by its LSDA value, $m_f \approx 0.24 \mu_B$ (see Table I for the spin-resolved filling of the 6d bands), the exchange integral is estimated by atomic calculations, $I_{fd} \approx 0.15 \text{eV}/\mu_B$ [37]. This yields $I_{f amalg} \approx 36 \text{meV}$ and we explore the LDA+DMFT solutions for $\Delta_{fd}$ varied around this value.

The absence of $\Delta_X$ is a disadvantage of the spin-restricted parent band structure. Its advantage, on the other hand, is that the double-counting correction in Eq. (1) reduces to a single number, $U_H$, since the spin-dependent part, $U_X$, vanishes. One possible approximation to the double counting is the so-called fully localized limit (FLL),

$$U_{H}^{\text{FLL}} = U(n_f - 1/2) - J(n_f - 1)/2,$$

where $n_f$ is the self-consistently determined number of 5f electrons [10, 38]. In our calculations, it turned out that this $U_H^{\text{FLL}}$ severely overestimates the number of 5f electrons, resulting in $n_f \approx 4$. We hence employ an alternative strategy: we choose $U_H$ such that the number of 5f electrons remains close to its LDA value $(n_f = 2.72$, Table I) also in the LDA+DMFT solution to simulate charge self-consistency [39, 40]. This condition implies $U_H \approx 3 \text{eV}$. We note in passing that the FLL formula, Eq. (11), gives 3.93 eV for $n_f = 2.72$, 4.41 eV for $n_f = 3$, and 2.71 eV for $n_f = 2$.

### D. LSDA+DMFT

As discussed above, using spin-restricted LDA as the parent band structure has two deficiencies: underestimated spin polarization of the 6d (and other) bands, and missing exchange field due to 6d moments acting on the 5f electrons. We dealt with the second issue empirically, but we did not address the first one yet. We attempt to do so by using the spin-polarized (LSDA) solution as the parent band structure. This way, all non-5f bands are potentially spin-polarized, which enhances the polarization of the bath and of the bath–5f hybridization in the auxiliary impurity model, Eq. (4), when compared to LDA+DMFT described in Sec. II C.

Although it may seem that the LSDA parent band structure also provides an improved estimate of the local exchange field $\Delta_X$, it is not so, since the LSDA exchange field combines the 6d–5f exchange (tens of meV) with the 5f–5f exchange (about 1 eV). The latter has to be removed by the double-counting correction $U_X$, which we know only approximately. The FLL ansatz for the double counting $U_X$ reads as [10]

$$U_{X}^{\text{FLL}} = E_{\text{FLL}} - E_{\text{FLL}} = J(n_f^\uparrow - n_f^\downarrow),$$

where

$$E_{\text{FLL}} = U(n_f - 1/2) - J(n_f^\uparrow - 1/2),$$

which we find to overcorrect the LSDA 5f–5f exchange. With the LSDA occupation numbers (Table I) and with $J = 0.59 \text{eV}$, the double counting $U_{X}^{\text{FLL}}$ becomes 1.19 eV whereas the LSDA exchange is only $\Delta_X = 0.98 \text{eV}$ (Table I).

Instead of using Eq. (12) or any other similar formula, we again employ the approach introduced in Sec. II C, that is, we select $U_X$ such that $\Delta_{fd} = \Delta_X - U_X \approx I_{f amalg} \approx 36 \text{meV}$. Since $\Delta_X$ is a parameter of the local Hamiltonian, it remains constant during the DMFT self-consistency

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### Table I. Characteristics of several tight-binding models derived from the DFT band structure. All models contain gallium 4s and 4p orbitals, the included uranium orbitals are listed in the first column. The quantities $\zeta$, $\epsilon_f$ and $\Delta_X$ are shown in eV, the crystal-field parameters $B_{mk}$ in meV.

| model           | orbital occupations | local Hamiltonian $B_{mk}$ | $\Delta_X$ | $B_{20}$ | $B_{40}$ | $B_{60}$ | $B_{80}$ |
|-----------------|----------------------|---------------------------|------------|----------|----------|----------|----------|
| nonmagnetic solution |                      |                           |            |          |          |          |          |
| d,f             | 2.79                 | 0.94 0.94 – – 1.51 2.18   | 0.248      | 0.639    | 0 – 0.72 | 0.14 0.00 | 0 – 0.19 |
| s,d,f           | 2.77                 | 0.95 0.95 0.35 – 1.50 2.03 | 0.248      | 0.639    | 0 – 0.69 | 0.12 0.01 | 0 – 0.16 |
| s,p,d,f         | 2.72                 | 1.03 1.03 0.76 0.74 1.39 1.50 | 0.251      | 0.679    | 0 – 2.83 | 0.01 0.00 | 0 – 0.06 |
| ferromagnetic solution [001] |          |                           |            |          |          |          |          |
| s,d,f           | 2.77 2.41 0.37 1.00 0.87 0.35 – 1.49 2.02 | 0.246      | 0.926    | 0.972    | 5.98 0.11 | 0.01 0.00 | 0 – 0.16 |
| s,p,d,f         | 2.72 2.37 0.36 1.08 0.96 0.76 0.74 1.39 1.49 | 0.249      | 0.968    | 0.980    | 3.71 0.01 | 0.00 0.05 |          |
| ferromagnetic solution [210] |          |                           |            |          |          |          |          |
| s,p,d,f         | 2.72 2.34 0.38 1.08 0.95 0.76 0.74 1.34 1.54 | 0.248      | 0.956    | 0.956    | 3.92 0.03 | 0.00 0.04 |          |
iterations as follows from the derivation presented in Appendix C, hence $\Delta_{fd}$ and $U_X$ remain constant as well.

For the spin-independent part of the double-counting correction, we choose $U_H = 3.3$ eV. This value is 0.3 eV larger than in LDA+DMFT because the average position of the 5f level is approximately 0.3 eV higher in the ferromagnetic LSDA solution compared to the non-magnetic LDA solution (Table II).

III. RESULTS

A. Magnetic moments

The method outlined in the preceding sections is not entirely self-contained – there are several semi-empirical parameters, such as the Coulomb parameters $F_k$, the double-counting correction $U_H$, and the exchange field $\Delta_{fd}$. Especially the exchange field was estimated only roughly and hence we decided to explore a range of values around this estimate.

In Figure 2 we show how the magnetic moments depend on $\Delta_{fd}$ in the LDA+DMFT calculations when $\Delta_{fd}$ is applied in plane, along the [210] direction, which corresponds to the [210] ferromagnetic state [41]. The orbital and spin contributions to the magnetic moment are antiparallel as expected for 5f filling smaller than 7. At $\Delta_{fd} = 0$ meV, the total magnetic moment is clearly underestimated (1.76 $\mu_B$), which confirms our earlier reasoning that some exchange field has to be introduced. As the exchange field increases, the magnetic moment quickly increases too, it reaches 2.75 $\mu_B$ at $\Delta_{fd} = 35$ meV, at which point it is already very close to the saturation value $\approx 2.88 \mu_B$. The quick saturation of the moments is a convenient feature – an inaccuracy in estimating the realistic value of $\Delta_{fd}$ translates to only a minor uncertainty of the computed magnetic moments. The moments and 5f filling in Table II.

Analogous calculations were performed also for the exchange field $\Delta_{fd}$ applied along the out-of-plane [001] direction. In this case, the ferromagnetic state parallel to the exchange field is stable only above some critical value of $\Delta_{fd}$, see Fig. 3. Above this value, the magnetic moment very quickly saturates, much faster that in Fig. 2. For

| $U_H$ | $\Delta_{fd}$ (meV) | $m_S$ | $m_L$ | $m_{tot}$ | $n_f$ | $\gamma$ |
|-------|--------------------|------|------|-----------|------|--------|
| LSDA  | [210] 35 | 1.96 | 2.79 | 0.65 | 2.72 | 24.5 |
| LSDA  | [001] 35 | -2.00 | 2.89 | 0.70 | 2.72 | 21.2 |
| LDA+DMFT | [210] 3.0 | -1.85 | 4.60 | 2.75 | 2.76 | 8.2 |
| LDA+DMFT | [001] 3.0 | -1.91 | 4.87 | 2.96 | 2.74 | 7.7 |
| LSDA+DMFT | [210] 3.3 | -1.66 | 4.15 | 2.30 | 2.82 | 7.2 |
| LSDA+DMFT | [001] 3.3 | -1.59 | 3.89 | 2.12 | 2.80 | 7.5 |
| experiment | | | | | 3.07 | 11.0 |

In Figure 3 we show how the magnetic moments depend on $\Delta_{fd}$ in the LDA+DMFT calculations when $\Delta_{fd}$ is applied along the [210] direction (red) and to the [001] direction (green) when the exchange field $\Delta_{fd}$ is applied along the [001] direction and the LDA+DMFT calculations are started from the LDA solution with $\Sigma(z) = 0$. The orbital and spin moments (not shown) behave similarly as in Fig. 2.
smaller values of $\Delta_{fd}$, the DMFT iterations converge to a nearly in-plane state with just a small out-of-plane tilt of the magnetic moments. For a range of $\Delta_{fd}$ values we get two stationary solutions, one nearly in-plane and the other out-of-plane, depending on the starting point of the DMFT iterations. Figure 3 shows calculations that were started at a given $\Delta_{fd}$ from the LDA state with $\Sigma(z) = 0$. The transition from the in-plane to out-of-plane state then occurs at $\Delta_{fd} \approx 2.2$ meV. Calculations starting from the [001] ferromagnetic state converge to the out-of-plane state already at $\Delta_{fd} \gtrsim 0.6$ meV (not shown).

Unfortunately, we cannot determine which of the two stationary states found for $\Delta_{fd}$ between 0.6 meV and 2.2 meV is the ground state because we cannot reliably evaluate the total energy in our LDA+DMFT implementation. For the same reason, we cannot estimate the magneto-crystalline anisotropy energy. We can, however, conclude that the response of the magnetic moments to $\Delta_{fd}$ as observed in LDA+DMFT is consistent with the experimental finding that the easy axis is oriented in plane. Starting from the paramagnetic state ($\Delta_{fd} = 0$) and cooling down, the system always ends up in the in-plane state, since the moments exhibit an instability toward in-plane direction. Increasing in-plane moment increases in-plane $\Delta_{fd}$, which stabilizes the in-plane state further.

The magnetic moments computed using LSDA+DMFT, with the spin-dependent part of the double-counting correction $U_X$ varied to reproduce the same range of $\Delta_{fd}$ as explored above, are presented in Figs. 4 and 5 for the in-plane and out-of-plane orientation of the LSDA polarization. As in the LDA+DMFT, the total magnetic moments relatively quickly saturate with increasing $\Delta_{fd}$, and the saturation is again faster in the [001] state than in the [210] state. Surprisingly, the saturated values of the total moments are noticeably smaller than in the corresponding LDA+DMFT calculations, by 15% in the case of the [210] ferromagnet and by 30% in the case of the [001] ferromagnet (compare with Figs. 2 and 3).

We expected the opposite, since the LSDA parent band structure is certainly more polarized than the LDA parent band structure – besides $\Delta_{fd}$ that is the same in both approaches by construction, the LSDA has all non-5f bands spin split, which results in an enhanced polarization of the hybridization function. Intuitively, this should have induced a larger polarization in the 5f shell but the calculations show that it does not.

The difference in the computed moments could in principle be due to a difference in fillings of the 5f shell between the LDA+DMFT and LSDA+DMFT solutions, but this is not the case either. The 5f filling in both methods is very close as can be checked in Table I where we summarize our results for the realistic setting of the exchange field $\Delta_{fd}$. We speculate that the inaccurate LSDA+DMFT moments come from some artifact of the static LSDA approximation, possibly from an artificially broken symmetry. One suspect feature is the strong spin dependence of the crystal-field parameters $B_{kq}$ in the local Hamiltonian shown in Appendix C. Another feature, for which we do not have a clear explanation and which is likely to be related to the LSDA solution as well, is the jump in magnetic moments near $\Delta_{fd} = 30$ meV in Fig. 4.

Figures 4 and 5 show the computed magnetic moments as functions of the exchange field $\Delta_{fd}$ for a fixed spin-independent part of the double-counting correction $U_H$. Although the employed values of $U_H$ are not fixed in Secs. II C and II D, it is useful to analyze the sensitivity of the magnetic moments to changes of $U_H$ or, equivalently, to changes of the 5f filling $n_f$. This sensitivity is illustrated in Fig. 6 for the [210] ferromagnetic state calculated with the LDA+DMFT method. The [001] ferromagnetic
FIG. 6. The computed LDA+DMFT magnetic moments plotted as functions of the 5f filling \( n_f \) that is varied by changing the double-counting correction \( U_H \). The exchange field \( \Delta_{Jd} = 35 \text{ meV} \) was applied along the [210] direction. The value \( U_H = 3.0 \text{ eV} \) employed throughout the paper is marked by the orange stripe.

state and the results of the LSDA+DMFT method behave analogously. The magnetic moments increase toward the experimentally determined value with increasing \( n_f \) but this route to improved agreement with experiments does not have a solid physical backing. Moreover, it would come at the cost of worsened agreement with the spectroscopic measurements, since increased \( U_H \) would push the uranium 5f states to too large binding energies.

B. Valence-band spectroscopy

Two measurements of valence-band photoemission spectra of UGa\(_2\) can be found in the literature, the ultraviolet photoemission spectrum \( [11] \) (UPS, shown in the left panel of Fig. 7) and the soft-x-ray photoemission spectrum \( [12] \) (SX-PES, shown in the middle panel of Fig. 7). The UPS was measured on sputter-deposited films at room temperature, that is, in the paramagnetic phase. The maximum intensity was observed just below the Fermi level with a long tail extending toward higher binding energies. The SX-PES was measured on a freshly cleaved single crystal at \( T = 20 \text{ K} \), that is, well below the Curie temperature. The spectrum shows a narrow peak slightly below the Fermi level accompanied with two broader features at \(-0.5 \text{ eV} \) and \(-1.0 \text{ eV} \), and an even broader hump can be discerned at \(-2.8 \text{ eV} \).

The two spectra are clearly different and the difference cannot be ascribed to the lower resolution of the UPS spectra. The magnetic order is also unlikely to cause such large changes, we certainly do not see any evidence of that in DFT+DMFT calculations (not shown), and the experiment does not detect any changes either \( [12] \). The more probable source of the differences is the probing depth of the two experiments. The UPS used incident photons with energy \( 40.8 \text{ eV} \) (He II line), SX-PES used \( 800 \text{ eV} \) (synchrotron radiation), and hence the photoelectrons are emitted from deeper layers in the bulk of the sample in the SX-PES measurements.

Since our calculations do not include any surface effects, they should be closer to the SX-PES data. In Figure 7 we show our theoretically estimated photoelectron spectra at the appropriate photon energies, calculated for the [210] ferromagnetic phase with the LDA+DMFT method \( (\Delta_{Jd} = 35 \text{ meV}, \text{ but the spectra are not sensitive to variations of the 6d–5f exchange field}) \). The spectra are constructed as linear combinations of the orbital-resolved densities of states (DOS) weighted with photoionization cross sections listed in \( [13] \). According to these cross sections, the 5f DOS has by far the largest weight for both 40.8 eV and 800 eV photon energies, and hence these photoemission measurements probe mainly the 5f states.

The computed spectra display a main peak at \(-0.15 \text{ eV} \) and a satellite at \(-0.8 \text{ eV} \). The satellite has a considerably smaller intensity than the features seen in the SX-PES and as such the theory appears to be closer to the UPS spectra. The \(-0.5 \text{ eV} \) and \(-2.8 \text{ eV} \) features observed in SX-PES do not show up in the theoretical UPS, but there are distinct peaks appearing at nearby energies in the LDA+DMFT total DOS (Fig. 7). They originate from orbitals that have small photoionization cross sections. These peaks are due to hybridized \( 6d \) and \( 4p \) bands at \(-0.5 \text{ eV} \), and mainly \( 4p \) bands at \(-2.4 \text{ eV} \). The distinct feature outside the range probed by photoemission, at \(-7.6 \text{ eV} \), is due to Ga 4s. The fact that SX-PES sees a signal where the theory places \( 4p \) bands may be an indication that the theory underestimates the hybridization between Ga 4p and U 5f states. If the hybridization was stronger, some U 5f DOS would possibly appear at the position of the Ga 4p states, but that is just a speculation at this point.

Photoemission experiments access only the occupied part of the spectrum. The unoccupied part could be probed by inverse photoemission (we are not aware of any such experiment being performed to date) or by x-ray absorption spectroscopy (we discuss recent x-ray absorption measurements at the uranium M\(_{4,5}\) edges in UGa\(_2\) elsewhere \( [13] \)). In Figure 8, we analyze the complete (occupied and unoccupied) 5f DOS from a theoretical perspective. We compare the LDA+DMFT result with the DOS computed for a spherically symmetric \( 5f^3 \) ion, since three is the closest integer value to the computed average 5f filling \( n_f \) \( (\text{Table} \ [11]) \) and the probability of finding the 5f shell in the \( 5f^3 \) configuration predicted by LDA+DMFT is large, namely \( 83\% \). See Appendix \( [12] \), Eq. \( (D1) \), for the meaning of the fluctuating number of 5f electrons. We can achieve a very close correspondence of the ionic and LDA+DMFT densities of states when the Coulomb \( U \) in
FIG. 7. Experimental photoelectron spectra (black line) from [11] (left panel) and from [12, 42] (middle panel) are compared to the LDA+DMFT estimate of the spectra (green line). A Gaussian broadening (FWHM 0.2 eV) is added to simulate the instrument resolution. The LDA+DMFT total DOS, subject to the same broadening, is shown for comparison (dotted line). In the right panel, we plot the orbital-resolved DOS without broadening (5f in red, sum of all others in dotted blue). All theoretical lines correspond to the [210] ferromagnet ($\Delta_{\text{fd}} = 35$ meV).

FIG. 8. The uranium 5f DOS in the [210] ferromagnet from the LDA+DMFT method ($\Delta_{\text{fd}} = 35$ meV) in the top panel is compared to the DOS from an atomic calculation (5f$^3$ state) in the bottom panel (black lines). The parameter $F_0 = U$ was reduced in the atomic calculation to mimic the screening effects incorporated in the LDA+DMFT method. The $j = 5/2$ components of the 5f DOS are shown in red.

Figure 9 illustrates that the Fermi level cuts right through the 5f bands in LSDA, which is accompanied by a high density of states at the Fermi level and, subsequently, by a large Sommerfeld coefficient of the electronic specific heat $\gamma$. Indeed, LSDA predicts $\gamma > 20$ mJ/mol K$^2$ (Table I), which is at odds with the experimental value 11 mJ/mol K$^2$ [9]. In DFT+DMFT (and in LSDA+U as well), the 5f states move away from the Fermi level toward higher binding energies and the coefficient $\gamma$ is re-
IV. CONCLUSIONS

We have studied the electronic structure and magnetic properties of the ferromagnetic compound UGa$_2$ using the DFT+DMFT method, and compared our results with more approximate electronic-structure methods. We have found that our implementation of the DFT+DMFT method reproduces the experimentally observed large magnetic moments as well as the sign of the magnetocrystalline anisotropy energy, when the exchange interaction between uranium 6d and 5f states is included in a semi-empirical manner. This is done either in the form of an extra potential acting on the 5f states or in the form of a spin-polarized double-counting correction. We have compared two formulations of the DFT+DMFT method, one keeping the non-5f states spin restricted (LDA), and the other allowing their spin polarization (LSDA). Of the two, the LDA-based variant was found to provide more consistent results. It is a future work to investigate how the semi-empirical approach to the 6d–5f exchange could be improved toward a fully first-principles method.

Besides the magnetic properties, we have also modeled the valence-band photoemission spectra on the basis of the DFT+DMFT density of states. We were not able to fully explain the differences between the two published photoemission experiments [11, 12] but we could understand how the electron-electron correlations move the 5f states slightly away from the Fermi level, which is in accord with both photoemission spectra as well as with the observed small Sommerfeld coefficient of the electronic specific heat. With the aid of the DFT+DMFT method, it is thus possible to reconcile large magnetic moments and a small Sommerfeld coefficient with the 5f spectral density in the close vicinity of the Fermi level.

Our calculations indicate a close-to-localized uranium 5f states in UGa$_2$. From the comparison to the experimental photoemission spectra we deduce that the tendency to localization is probably slightly overestimated in our theoretical description. Such a tendency is to be expected for the employed impurity solver that implements a form of expansion around the atomic limit.

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Appendix A: Parameters of DFT calculations

To perform all DFT calculations presented in this paper, we employed the WIEN2k package \cite{24} that implements linearized augmented plane-wave method and its extensions. It combines a scalar-relativistic description with spin-orbit coupling \cite{25}. All calculations were performed at the experimental lattice constants $a = 4.213\ \text{Å}$ and $c = 4.020\ \text{Å}$, reported in \cite{3}, with the following parameters: the radii of the muffin-tin spheres were $R_{\text{MT}}(U) = 2.80\ a_B$ for uranium atoms and $R_{\text{MT}}(Ga) = 2.25\ a_B$ for gallium atoms, the Brillouin zone was sampled with 6137 k points (900 k points in the irreducible wedge), and the basis-set cutoff $K_{\text{max}}$ was defined with $R_{\text{MT}}(Ga) \times K_{\text{max}} = 10.0$. The default basis set with local orbitals for semicore states (U 6s, 6p, and Ga 3d) was used in all cases.

TABLE III. The orbital and spin magnetic moments in uranium 5f shell, $m_S$ and $m_L$ (in $\mu_B$), the total magnetic moment in the unit cell $m_{\text{tot}}$ (in $\mu_B$), the occupation of 5f shell $n_f$, and the Sommerfeld coefficient $\gamma$ (in mJ/mol-K$^2$). The 5f magnetic moments and the 5f filling correspond to the atomic (muffin-tin) spheres.

| direction | $m_S$ | $m_L$ | $m_{\text{tot}}$ | $n_f$ | $\gamma$ |
|-----------|------|------|-----------------|------|---------|
| LDA       | -    | -    | -               | 2.45 | 43.9    |
| LSDA [100]| -1.82| 2.67 | 0.57            | 2.51 | 24.7    |
| LSDA [210]| -1.82| 2.64 | 0.54            | 2.50 | 26.7    |
| LSDA [001]| -1.86| 2.72 | 0.57            | 2.50 | 22.5    |

Our largest tight-binding models, that is, those actually used in all cases.

The moments and the filling of the 5f shell correspond to the atomic (muffin-tin) spheres. Since there are no gaps in the spectrum above the Fermi level, disentanglement was necessary \cite{44}. We used 62 Bloch states on input, which were necessary \cite{44}. We used 62 Bloch states on input, which corresponds to the energy window from $-10\ eV$ to $24\ eV$. (Our largest tight-binding models, that is, those actually used for the DMFT calculations, have 48 Wannier functions). The frozen inner window extended to $6\ eV$ (3 eV for the smallest model listed in Table I), going higher meant that the centers of the Wannier functions started drifting away from the atomic centers, which is undesirable in our application that assumes the Wannier functions to be atomic-like. In the model used for the DMFT calculations, the original WIEN2k bands were represented perfectly up to $6\ eV$ above the Fermi level, the match was still very good up to approximately $12\ eV$, and above that the correspondence quickly deteriorated.

Appendix B: Construction of the impurity model

Here we discuss how the parameters of the finite impurity model, Eq. (4), are found so that the model matches the effective medium (the bath) as closely as possible. The impurity Hamiltonian has the form a block matrix

$$
\mathbb{H}_{\text{imp}} = \begin{pmatrix}
\mathbb{H}_{\text{loc}} & V_1 & V_2 & V_3 & \cdots \\
V_1^\dagger & \mathbb{H}^{(1)}_{\text{bath}} & 0 & 0 & \cdots \\
V_2^\dagger & 0 & \mathbb{H}^{(2)}_{\text{bath}} & 0 & \cdots \\
V_3^\dagger & 0 & 0 & \mathbb{H}^{(3)}_{\text{bath}} & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix},
$$

(B1)

where all blocks are $14 \times 14$ square matrices. The local Hamiltonian $\mathbb{H}_{\text{loc}}$ contains a strong spin-orbit coupling which does not commute with the hybridization function that follows the crystal symmetry. Therefore, the problem cannot be simplified to diagonal matrices.

If there is only one bath block, all three matrices $\mathbb{H}_{\text{loc}}, \mathbb{H}_{\text{bath}}$ and $V$ can be determined by comparing the large $z$ asymptotics of the local block of the impurity Green’s function,

$$
G_{\text{loc}}(z) = \left[ zI - \mathbb{H}_{\text{loc}} - \sum_i V_i (zI - \mathbb{H}_{\text{bath}}^{(i)})^{-1} V_i^\dagger \right]^{-1},
$$

(B2)

to the asymptotics of the bath Green’s function defined as

$$
G(z) = \left[ G_f^{-1}(z) + \Sigma(z) \right]^{-1}.
$$

(B3)

Here $G_f(z)$ is the 5f block of the local Green’s function $G(z)$ from Eq. (4). We refer the reader to \cite{32} for details. For larger impurity models, like Eq. (B1), this strategy leads to an unsolvable set of polynomial equations for the $14 \times 14$ square matrices. To overcome the problem, we combine two shorter asymptotic expansions, one for the Green’s function as before, and one for the hybridization function.

The asymptotic expansion of the local block of the impurity Green’s function $G_{\text{loc}}(z)$ starts as

$$
G_{\text{loc}}(z) = \frac{1}{z} + \frac{\mathbb{H}_{\text{loc}}}{z^2} + O(z^{-3}),
$$

(B4)

and the analogous expansion of the hybridization function

$$
\Delta_{\text{imp}} = zI - \mathbb{H}_{\text{loc}} - G_{\text{loc}}^{-1}(z)
$$

(B5)
starts as
\[ \Delta_{\text{imp}} = \sum_i \mathbb{V}_i (zI - \mathbb{H}^{(i)}_{\text{bath}})^{-1} \mathbb{V}_i^\dagger = \]
\[ \sum_i \left[ \frac{\mathbb{V}_i \mathbb{V}_i^\dagger}{z} + \frac{\mathbb{V}_i \mathbb{H}^{(i)}_{\text{bath}} \mathbb{V}_i^\dagger}{z^2} \right] + O(z^{-3}). \] (B6)

From the other side, the bath Green’s function, Eq. (B3), reads in the spectral representation as
\[ \mathcal{G}(z) = \int \frac{\hat{A}(\epsilon)}{z - \epsilon} \, d\epsilon, \] (B7)
where we introduced the spectral density
\[ \hat{A}(\epsilon) = \frac{\mathcal{G}(\epsilon - i0) - \mathcal{G}(\epsilon + i0)}{2\pi i}. \] (B8)

The asymptotic expansion of the bath Green’s function is obtained by expanding the denominator in Eq. (B7),
\[ \mathcal{G}(z) = \sum_{n=0}^\infty \frac{M_n}{z^{n+1}}, \quad M_n = \int e^n \hat{A}(\epsilon) \, d\epsilon, \] (B9)
where \( M_n \) are moments of the spectral density. The spectral density \( \hat{A}(\epsilon) \) is a hermitian matrix and hence its moments are hermitian matrices as well. We immediately see that
\[ \mathbb{H}_{\text{loc}} = M_1. \] (B10)

The spectral representation of the hybridization function corresponding to \( \mathcal{G}(z) \), that is, of \( \Delta(z) = zI - M_1 - \mathcal{G}^{-1}(z) \), can be written as
\[ \Delta(z) = \int \frac{\mathcal{B}(\epsilon)}{z - \epsilon} \, d\epsilon, \] (B11)
where the spectral density is defined as
\[ \mathcal{B}(\epsilon) = \frac{\Delta(\epsilon - i0) - \Delta(\epsilon + i0)}{2\pi i}. \] (B12)

Now we split the support of \( \mathcal{B}(\epsilon) \) to as many segments as many \( \mathbb{H}^{(i)}_{\text{bath}} \) blocks we wish (or can afford) to have,
\[ \Delta(z) = \sum_i \Delta_i(z), \quad \text{where} \quad \Delta_i(z) = \int_{\epsilon_i}^{\epsilon_{i+1}} \frac{\mathcal{B}(\epsilon)}{z - \epsilon} \, d\epsilon \] (B13)
with \( \epsilon_i < \epsilon_{i+1} \), and we pair each \( \Delta_i \) with one summand in Eq. (B6). The splitting can be arbitrary or it can be guided by an insight into the structure of the hybridization function – the individual \( \mathbb{H}^{(i)}_{\text{bath}} \) blocks can be aligned with groups of bands. In UGm2, the hybridization below the Fermi level comes mainly from Ga 4s and 4p bands, and in the first \( \approx 6 \) eV above the Fermi level it is dominated by U 6d bands.

The asymptotic expansion at the individual intervals reads as
\[ \Delta_i(z) = \sum_{n=0}^\infty \frac{N_{n,i}}{z^{n+1}}, \quad N_{n,i} = \int_{\epsilon_i}^{\epsilon_{i+1}} e^n \mathcal{B}(\epsilon) \, d\epsilon. \] (B14)

Comparing Eqs. (B6) and (B14), the blocks of \( \mathbb{H}^{(i)}_{\text{imp}} \) can be written in terms of the moments \( N_{n,i}^{(i)} \) as
\[ \mathbb{V}_i = \mathbb{V}_i^\dagger = \sqrt{N_{0,i}^{(i)}}, \] (B15a)
\[ \mathbb{H}^{(i)}_{\text{bath}} = \mathbb{V}^{-1}_i N_{1,i}^{(i)} (\mathbb{V}_i^\dagger)^{-1}, \] (B15b)
which, together with Eq. (B10), concludes the construction of the impurity model \( \mathbb{H}^{(i)}_{\text{imp}} \) from the local Green’s function \( \mathcal{G}(z) \). Optionally, we can diagonalize the blocks \( \mathbb{H}^{(i)}_{\text{bath}} \) to make their interpretation more straightforward and to arrive at the form of the impurity model used in Eq. (1). The corresponding transformations are
\[ \mathbb{H}^{(i)}_{\text{bath}} \rightarrow C_i^{-1}\mathbb{H}^{(i)}_{\text{bath}}C_i, \quad \mathbb{V}_i \rightarrow \mathbb{V}_i C_i, \] (B16)
where \( C_i \) are the appropriate unitary matrices and the new \( \mathbb{V}_i \) are no longer hermitian. By construction, the eigenvalues of \( \mathbb{H}^{(i)}_{\text{bath}} \) are confined to intervals \( (\epsilon_i, \epsilon_{i+1}) \).

For the purpose of their actual evaluation, the moments are expressed in terms of contour integrals in the complex plane. Using the path segments sketched in Fig. 10 we have
\[ M_1 = \frac{1}{2\pi i} \left[ \int_{L_-} - \int_{L_+} \right] z \mathcal{G}(z) \, dz \]
\[ = \frac{1}{2\pi i} \left[ \int_{C_-} - \int_{C_+} \right] z \mathcal{G}(z) \, dz, \] (B17)
\[ N_{n,i}^{(i)} = \frac{1}{2\pi i} \left[ \int_{C_-(i)} - \int_{C_+(i)} \right] z^n [zI - M_1 - \mathcal{G}^{-1}(z)] \, dz \]
\[ = \frac{1}{2\pi i} \left[ \int_{C_-(i)}^{} - \int_{C_+(i)}^{} \right] z^n [zI - M_1 - \mathcal{G}^{-1}(z)] \, dz, \] (B18)

FIG. 10. Contours in the complex plane used for integration of the moments \( M_1 \) (dashed blue) and \( N_{n,i}^{(i)} \) (red). Line segments are denoted as \( L_\pm \), half circles as \( C_\pm \).
where the integral over the (dashed blue) circle \( C = C_\gamma \cap C_\delta \) encloses the entire support of \( h(x) \) and the integrals over the (red) circles \( C^{(i)} = C^{(i)}_\gamma \cap C^{(i)}_\delta \) enclose the intervals \((\epsilon_i, \epsilon_{i+1})\). During the DMFT calculations, the self-energy is thus evaluated along the circles \( C \) and \( C^{(i)} \), and also along one additional semicircle in the upper half plane to compute the number of electrons in the primitive cell and to adjust the Fermi level. An alternative to the circle \( C \), which serves for evaluation of \( \Sigma_{\text{loc}} = M_1 \), is described in Appendix C.

In the DFT+DMFT calculations of UGa$_2$ discussed in the paper, we used three intervals \((\epsilon_i, \epsilon_{i+1})\), namely \((-10, 0)\) eV, \((0, 6)\) eV and \((6, 12)\) eV. The hybridization above 12 eV was discarded, since our tight-binding Hamiltonians do not accurately represent the original DFT bands that far above the Fermi level (Appendix A).

### Appendix C: Asymptotics of the bath Green’s function and the local Hamiltonian

At each \( k \) point, the tight-binding Hamiltonian \( \hat{H}_k \) can be divided into four blocks,

\[
\hat{H}_k = \begin{pmatrix}
\hat{H}^f_k & \hat{T}_k \\
\hat{T}_k^\dagger & \hat{H}^{spd}_k
\end{pmatrix},
\]

and the 5f block of the lattice Green’s function can be written as

\[
\hat{G}^f_k(z) = \left[ z \hat{I} - \hat{H}^f_k + \hat{\Sigma}(z) - \hat{T}_k (z \hat{I} - \hat{H}^{spd}_k)^{-1} \hat{T}_k^\dagger \right]^{-1} \hat{G}^\text{loc}(z),
\]

Its asymptotic expansion reads as

\[
\hat{G}^f_k(z) = \frac{\hat{I}}{z} + \frac{\hat{T}_k + \hat{\Sigma}(\infty)}{z^2} + O(z^{-3}),
\]

where \( \hat{\Sigma}(\infty) \) is the static part of the self-energy, which is the leading term of the expansion \( \hat{\Sigma}(z) = \hat{\Sigma}(\infty) + O(z^{-1}) \). For the bath Green’s function, Eq. (B3), we need only the local element,

\[
\hat{G}_f(z) = \frac{1}{N} \sum_k \hat{G}^f_k(z)
\]

\[
= \frac{\hat{I}}{z} + \frac{N^{-1} \sum_k \hat{H}^f_k + \hat{\Sigma}(\infty)}{z^2} + O(z^{-3}),
\]

respectively its inverse,

\[
\hat{G}^{-1}_f(z) = z \hat{I} - \frac{1}{N} \sum_k \hat{H}^f_k - \hat{\Sigma}(\infty) + O(z^{-1}).
\]

Inserting this expression into the definition of the bath Green’s function, Eq. (B3), yields

\[
\hat{G}(z) = \frac{\hat{I}}{z} + \frac{1}{z^2} \frac{1}{N} \sum_k \hat{H}^f_k + O(z^{-1}).
\]

The self-energy cancels out from the first moment of the corresponding spectral density, and the moment thus equals to the local block of the tight-binding Hamiltonian,

\[
M_1 = \frac{1}{N} \sum_k \hat{H}^f_k = \hat{H}^{\text{loc}},
\]

throughout the whole DMFT self-consistency loop.

To extract the individual contributions to the Hamiltonian shown in Eq. (B2), we can exploit the orthogonality of operators \( \hat{I}, \hat{\tilde{\sigma}} \cdot \hat{s}, \hat{\tilde{s}} \) and \( \hat{\sigma}_{\text{loc}} \) as \( 14 \times 14 \) matrices. We can write

\[
\epsilon_f = \text{Tr}(\hat{H}^{\text{loc}})/14,
\]

\[
\Delta^\sigma_{\text{loc}}(z) = \text{Tr}(\hat{\sigma}_{\text{loc}} \hat{H}^{\text{loc}}) / \text{Tr}(\hat{\sigma}_{\text{loc}}), \hspace{0.5cm} \alpha = x, y, z,
\]

\[
\zeta = \text{Tr}(\hat{\tilde{\sigma}} \cdot \hat{s} \hat{\tilde{\sigma}} \cdot \hat{s}) / \text{Tr}(\hat{\tilde{\sigma}} \cdot \hat{s} \hat{\tilde{\sigma}} \cdot \hat{s}),
\]

\[
B_{\sigma\sigma'} = \text{Tr}(\hat{\sigma}_{\text{loc}} \hat{\sigma}_{\text{loc}}) / \text{Tr}(\hat{\sigma}_{\text{loc}} \hat{\sigma}_{\text{loc}}).
\]

In the case of spin-polarized electronic structure, spin-dependent crystal-field parameters can be introduced as

\[
B_{\sigma\sigma'} = \text{Tr}(\hat{\sigma}_{\text{loc}} \hat{\sigma}_{\text{loc}}) / \text{Tr}(\hat{\sigma}_{\text{loc}} \hat{\sigma}_{\text{loc}}),
\]

\[
B_{\sigma\sigma'} = \text{Tr}(\hat{\sigma}_{\text{loc}} \hat{\sigma}_{\text{loc}}) / \text{Tr}(\hat{\sigma}_{\text{loc}} \hat{\sigma}_{\text{loc}}).
\]

The spin dependence of the crystal-field parameters derived from the LSDA band structure is substantial, which is illustrated in Table IV. Note that we do not attempt to remove the 5f self-interaction from the crystal-field potential [43, 46]. Nevertheless, the spin dependence would not disappear even if we did [46].

| \( B_{20} \) | \( B_{40} \) | \( B_{60} \) | \( B_{80} \) |
|---|---|---|---|
| ferromagnetic solution [001] | | | |
| restricted | 3.72 | 0.0061 | -0.0043 | -0.052 |
| spin ↑ | 1.75 | -0.0024 | 0.0017 | -0.107 |
| spin ↓ | 5.68 | 0.0146 | -0.0100 | 0.003 |
| ferromagnetic solution [210] | | | |
| restricted | 3.92 | 0.0262 | -0.0011 | -0.044 |
| spin ↑ | 1.54 | 0.0111 | -0.0154 | -0.009 |
| spin ↓ | 6.30 | 0.0414 | 0.0133 | -0.079 |

TABLE IV. Crystal-field parameters \( B_{\sigma\sigma'} \), Eq. (C8e), derived from the LSDA tight-binding Hamiltonian (s.p.d.f model). Spin-restricted parameters \( B_{\sigma\sigma'} \) computed from Eq. (C8d) are the same as shown in Table I.
Appendix D: Convergence of the impurity-model solution with the size of the many-body basis

As indicated in Sec. IIIA, we cannot diagonalize the impurity model in the complete Fock space, only in reduced subspaces \( \mathcal{H}_N^{(M)} \), defined in Eq. (3), where \( N \) is the number of electrons in the model (its filling) and \( M \) is a cut-off parameter. Analyzing the convergence of the complete DMFT solution with respect to \( M \) is computationally very demanding. Hence, we limit this Appendix to selected intermediate quantities, evaluation of which does not involve computing the self-energy. In particular, we diagonalize the auxiliary impurity model corresponding to the [210] ferromagnetic LDA+DMFT solution, obtained for \( \Delta_{fd} = 35 \text{ meV} \) and presented in Sec. III for different settings of the cut-off parameter \( M \). The crudest approximation is \( M = 0 \) that does not allow any hops of electrons between the 5f shell and the bath, and thus corresponds to the Hubbard-I approximation. The best approximation we consider is \( M = 3 \), one step better than the setting employed in the main text.

Figure 11 shows the \( M \)-dependence of the ground-state energy \( E_0 \) for fillings \( N \) around the overall grandcanonical ground state which is located at \( N = 17 \). The differences between the \( M = 2 \) and \( M = 3 \) basis sets are very small (less than 70 meV), which indicates that \( M = 2 \) is indeed a sensible choice. The differences are even smaller (less than 30 meV) for energy gaps \( E_0(N \pm 1) - E_0(N) \) that determine the positions of the main peaks in the valence-band spectra like those plotted in Fig. 8.

Furthermore, we present the 5f occupation number \( N_f = \text{Tr}(\hat{N}_f \hat{\rho}) \), where \( \hat{\rho} \) is the grandcanonical density matrix of the impurity model, together with its fluctuation

\[
\Delta N_f = \sqrt{\text{Tr}(\hat{N}_f^2 \hat{\rho}) - N_f^2} \tag{D1}
\]

as functions of the cut-off \( M \) in Fig. 12. Both these quantities again change very little when \( M \) is increased from \( M = 2 \) to \( M = 3 \), which represents another reassurance that \( M = 2 \) is good enough.

Note that \( N_f \) should be the same number as \( n_f \) defined in Eq. (8) and listed in Table II which follows from the DMFT embedding condition. In our DMFT calculations, they are not the same, \( N_f \) is approximately 0.2 larger than \( n_f \), which is a consequence of the approximate finite impurity model (discrete bath) being used instead of the exact infinite impurity model (continuous bath). This is roughly the same discrepancy as we observed earlier when we applied this method to the ferromagnetic nickel [47]. In principle, the situation could be improved by adding more bath orbitals, but in practice, it is computationally prohibitive at present.

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