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Entangled origins of the nonmagnetic states of U and Fe atoms in hydrogenated UFeGe

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The experimental ground state of hydrogenated UFeGe (H-UFeGe) is nonmagnetic (NM). This result is not expected since, first, both U and Fe atoms tend to be magnetic in their compounds and, second, the hydrogenation is considered as favorable for magnetism. There are two main scenarios to explain the observation of nonmagnetic U atoms in the U based materials: Pauli paramagnetism of the Stoner type and Kondo-type screening of the atomic 5f moments. We apply the local density approximation (LDA) and LDA+U methods to investigate the origin of the ground state of H-UFeGe. The LDA calculations give in agreement with experiment the NM state as the only self-consistent state. The absence of the magnetic moments of both U and Fe atoms is the result of the U 5f-Fe 3d hybridization. The LDA+U calculations with different U values reveal sensitive competition between NM and magnetic phases. The result of this competition depends nonmonotonously on the value of parameter U. We explain this nonmonotonous behavior by multiorbital nature of the 5f electron contributions to the electron structure of H-UFeGe combined with different responses of different orbitals to the correlation governed by U. Employing constraint calculations we demonstrate that in the magnetic phases the Fe atomic moments can be treated as induced by the U moments. Since the directions of the U and Fe spin moments are opposite, the mechanism of the induction is nontrivial. It includes the spin-projection-dependent charge redistribution and a peculiar influence of the spin polarization on the interatomic hybridization. We compare H-UFeGe with two other materials containing U and Fe atoms and establish important differences.

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I. INTRODUCTION

The 5f-electron systems have been for many decades the subject of intensive investigation because of their highly diverse electronic properties [1–5]. In particular, the magnetic properties of U-based compounds attract considerable attention. Both the type of magnetic structure and the values of the atomic magnetic moments vary widely. There exist also many U compounds with nonmagnetic (NM) ground state. Taking into account that elemental uranium is NM the fact that among U compounds there are materials whose ground state is NM does not appear very surprising. On the other hand, it is very common that atoms of nominally NM transition metals become magnetic (MAG) as constituents of compounds.

There are two main scenarios of the formation of the NM ground state of the U-based materials. One scenario is the Pauli paramagnetism of the type described by the Stoner theory where the kinetic energy wins the competition with the exchange energy leading to vanishing local magnetization [6]. The other, physically more complex, scenario is based on the Kondo-type screening of the U atomic MAG moments by the conduction electrons (see, e.g., a recent publication [7] and references therein). Understanding the nature of the NM ground states of the U compounds is an important problem in the physics of 5f-electron systems.

In this paper, we deal with the ground state of the hydrogenated UFeGe (H-UFeGe) that was experimentally detected to be NM [8]. In the case of H-UFeGe there are two important material-specific aspects relevant to the understanding of the formation of the NM state. The first is the presence of the Fe atoms. Usually Fe atoms in solids carry magnetic moments. This takes place in both elemental Fe and numerous Fe compounds. Therefore considering the ground state of H-UFeGe it is important to understand the absence of the magnetic moments of both U and Fe atoms. This work was partly motivated by a recent study [9] of hydrogenated $U_2(Ni_{1-x}Fe_x)_2Sn$ revealing a nontrivial relation between the magnetic properties of the U and Fe subsystems.

The second aspect is the expectation that hydrogenation stimulates the development of the atomic magnetic moments. A well-known empirical Hill's criterion [10] argues that the decisive factor governing the magnetic properties of the U compounds is the distance between neighboring U atoms. In the spirit of this rule, the hydrogenation, which increases the U-U distances should stimulate the development of the MAG ground state. Indeed, the influence of the hydrogen in the U-based systems on the formation of the MAG state was observed. For instance, UH_3 is magnetic [11,12] although pure U is NM. In the case of H-UFeGe, the hydrogenated material is NM that raises the question why the expectation to find the magnetic ground state does not realize.

We remark that the answer to the question why a given U compound is MAG or NM not only is crucial for the understanding of the physics of this particular material but also contributes to the understanding of the family of the U-based systems as a whole. We will relate our results to the properties of two other materials containing U and Fe atoms: $U_2(Ni_{1-x}Fe_x)_2Sn$ and UFe_2.

The theoretical description of the variety of magnetic properties of the U-based systems within the framework of one universal method remains an unsolved problem. Accordingly, there are many different theoretical approaches employed to deal with magnetic properties of the U compounds. Below we briefly mention some of them.

The parameter-free density functional theory (DFT) calculations provide a very useful basis both for the interpretation of experimental properties of materials and for theoretical developments aiming at more accurate treatment of electronic correlation [13–15]. One of the early developments going beyond DFT is the orbital polarization correction to the DFT methods [16]. It helped to improve the relation between calculated spin and orbital atomic moments. The DFT+U approach [14] is a widely used tool to account for on-site electron correlation beyond the DFT methods. This approach is able to provide the improvements achievable with the orbital polarization correction being, however, a more general and universal theoretical technique [17].

Among the theoretical approaches that go beyond the DFT+U method in the account for electron correlation are the methods emphasizing the importance of the Kondo physics [7]. On the other hand, there are works questioning the relevance of the Kondo scenario in the physics of the 5f electron systems. Thus Zwicknagl *et al.* [18,19] suggest a different viewpoint assuming that a part of the 5f electron states is localized and does not hybridize with conduction electrons while the hybridization of the other 5f states with conduction electron states do exist and is crucial for the properties of the materials. In general, orbital selective behavior as response to the electron correlation is an aspect attracting much attention (see, e.g., a recent publication [20] and references therein).

It is also important to mention the modern numerical approach of DFT plus dynamical mean-field theory (DFT+DMFT) [15] that has the capacity to describe on a unified basis the broad range of the properties of 5f-electron systems in a material-specific way. However, the DFT+DMFT calculations are rather complex, computer resource intensive and usually require adjusted parameters to describe the properties of specific materials (see, e.g., Ref. [21]). The application of the DFT+DMFT approach to an extensive study of the family of U-based materials remains an important task for the future.

In this paper we apply local density approximation (LDA) and LDA+U methods. To address in a systematic way the problem of the NM state of H-UFeGe we examine the influence of various factors on the theoretical ground state of H-UFeGe. Those factors are spin-orbit coupling (SOC), interatomic hybridization, and electron correlation. Our study shows that both SOC and hybridization are crucial for the formation of the NM state. On the other hand, the calculations reveal the competition between MAG and NM phases whose result sensitively and nonmonotonously depends on the value of parameter U. (In the following, we will supply parameter U with subindex H, coming from Hubbard, to easier distinguish it from the chemical symbol for uranium.) We explain the nonmonotonous behavior by the participation of the multiple U 5f orbitals in the formation of the ground state of the system and different responses of different orbitals to electron correlation parameter U_H.

We investigate the relation between atomic moments of the U and Fe atoms in the MAG phases. In the calculations these moments always appear or disappear simultaneously. Although our calculations provide firm basis for treating the Fe spin moments as induced by the U spin moments, the directions of the moments are opposite to each other. We suggest an explanation of this property relating it to the properties of the spatial spin-density redistribution. The modification of the interatomic hybridization by the electron spin polarization is important for the development of the induced Fe moments comparable in value with the inducing U moments.

As mentioned above, relevant to the present study are the findings of a recent theoretical investigation [9] of hydrogenated $U_2(Ni_{1-x}Fe_x)_2Sn$ also containing U and Fe atoms. We compare present results with the results of Ref. [9] and refer to the properties of UFe_2 containing U and Fe atoms as well. We find that the relation between magnetic moments of the U and Fe atoms differ in all three systems.

The paper is organized as follows. In Sec. II we discuss the method of calculation. Section III is devoted to the results and discussion. Section IV contains the conclusions. Appendix provides an example of calculated occupation matrix of the U 5f electrons illustrating its symmetry.

II. METHOD OF CALCULATION

The calculations are performed with the augmented spherical wave (ASW) method [22–24] and the LDA [25] exchange-correlation potential. The spin-orbit coupling is self-consistently included into consideration. The detailed expression for the SOC can be found in Ref. [9].

The U 5f electron correlation in the U compounds cannot be fully accounted for with the standard DFT approaches as LDA. We will study the effect of the correlation beyond LDA by performing calculations with the LDA+U method [14]. The main idea of the LDA+U approach is to make one-electron potential orbital dependent that is achieved by making energy functional dependent on the occupation matrix of the correlated electrons. The term added to the LDA functional partly accounts for the energy already taken into account by the LDA functional. This double counting should be corrected. The form of the correction term to the energy functional is not unique that leads to different forms of the correction to the one-electron LDA potential. We employ so-called around mean-field (AMF) [26] flavor of the method. For the derivations and discussion of the different forms of the LDA+U corrections we refer the reader to paper by Petukhov *et al.* [27] and references therein.

It was suggested that the AMF form of the method provides a better performance in the case of moderately correlated systems [27–29]. A convenient version of the basis-set invariant [30] LDA+U method was suggested by Dudarev *et al.* [31]. This version of the method was used by Petukhov *et al.* [27]

in their treatment of the corrections to the LDA expressions implemented by us.

The AFM correction to the electron potential has the form [27]

$$V_{m,m'} = -U(n_{m,m'} - \langle n\rangle\delta_{m,m'}). \tag{1}$$

Here n is the orbital density matrix of the correlated atomic states, m and m' are orbital quantum numbers corresponding to the basis of complex spherical harmonics Y_{3m}. Everywhere in the paper we use the z axis as the quantization axis. The diagonal elements $n_{m,m}$ of the orbital density matrix give the occupations of the corresponding m orbitals. $\langle n\rangle$ is the average value of $n_{m,m}$. Examples of the implementation of the n matrix calculation within the DFT methods can be found in Refs. [32,33]. Because of the LDA+U correction [Eq. (1)] to the electron potential, stronger occupied orbitals tend to decrease their energy whereas less occupied orbitals tend to increase their energy.

In Ref. [9] dealing with a related problem, it was obtained that the inclusion of the Fe 3d orbitals in the LDA+U treatment does not change the physical picture importantly. In the present paper we report the results of the calculations where the LDA+U treatment is applied to the U 5f orbitals only.

There is no straightforward reliable method to determine the value of the Hubbard parameter U_H specific for a given material. Even the description of correlation by introducing just one parameter is an approximation. Therefore we decided to perform calculations for an interval of the values of U_H analyzing the trends and relating them to the experimental fact of the NM ground state that we consider as well established.

We calculate the z components of spin m_s^ν and orbital m_o^ν moments of the νth atom as

$$m_s^\nu = \sum_{\mathbf{k}n}^{occ} \int_{\Omega_\nu} \psi^\dagger_{\mathbf{k}n}\sigma_z\psi_{\mathbf{k}n}d\mathbf{r} \tag{2}$$

$$m_o^\nu = \sum_{\mathbf{k}n}^{occ} \int_{\Omega_\nu} \psi^\dagger_{\mathbf{k}n}\hat{l}_z\psi_{\mathbf{k}n}d\mathbf{r}, \tag{3}$$

where a $\psi_{\mathbf{k}n}$ is the spinor wave function of the Kohn-Sham state corresponding to wave vector $\mathbf{k}$ and band index n. The sum is taken over occupied states. The integrals are carried out over νth atomic sphere. We remark that for the crystal structure of the system and magnetic configuration considered in the paper the x and y components of the atomic moments are zero by symmetry. The $\mathbf{k}$ mesh in the Brillouin zone was up to $30 \times 30 \times 30$. The convergence criterion was the stabilization of the energy differences of the NM and MAG states below 10^{-5} Ry.

III. RESULTS AND DISCUSSION

The experiment [8] gives 1.7–1.8 H atoms per formula unit of UFeGe. To preserve translational symmetry we perform calculations assuming two H atoms per formula unit. The crystal structure of the hexagonal ZrBeSi-type characteristic for this level of the H absorption is presented in Fig. 1. The positions of the H atoms were selected on the basis of experimental data for LaNiSnD$_2$ [8]. The hydrogen-free UFeGe has a low-symmetry monoclinic crystal structure.

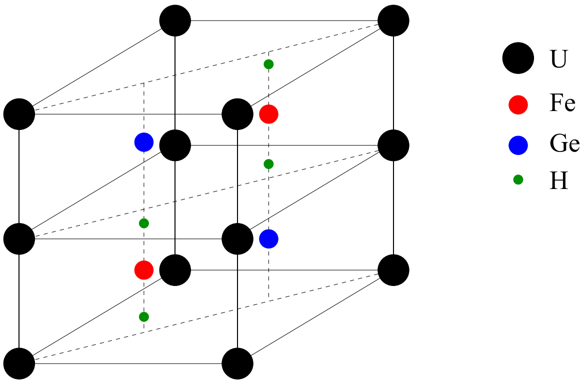

FIG. 1. Crystal structure of H-UFeGe.

The presence of the SOC, by means of the symmetry effects, favors the formation of noncollinear magnetic structures. In some cases the instability of collinear magnetic states becomes inevitable [34]. However, for the hexagonal crystal structure considered in this paper the typical magnetic easy axis is the crystallographic c axis. This is the reason for our choice of the c axis as the direction of the atomic moments [35].

A. LDA calculations

We begin with the discussion of the LDA calculations with the SOC taken into account. The consequences of neglecting SOC will be considered below. The computations started with large atomic moments of 2 μ_B at the U sites converged to the NM state. Thus, important for our study, the result of the LDA calculation is in agreement with experiment concerning the NM nature of H-UFeGe.

Here, it is worth to emphasize the following feature of the DFT-based calculations. If the initial state of the system is chosen NM, the material remains NM during iterations. This property is the consequence of the so-called symmetry constraint [37]. Therefore obtaining a self-consistent NM state does not by itself mean the physical stability of this state. On the other hand, if the calculations started with large atomic moments converge to the NM state, there is a strong basis to treat the NM state as the theoretical ground state of the material. The origin of the physical stability of the NM state in H-UFeGe can be found in the properties of the NM density of states (DOS). As seen in Figs. 2(a), 2(b) the position of the Fermi level, E_F, corresponds to the deep DOS minimum. According to the Stoner picture, a low DOS at E_F contributes to the stabilization of the NM state [6]. The coinciding energy positions of the peaks and deeps of the partial U 5f and Fe 3d DOSs reveal the hybridization of the U and Fe orbitals in the electron states of the material. The common minimum of the U 5f and Fe 3d DOSs close to E_F can be associated with the effective repulsion of the bonding and antibonding states lying, respectively, below and above E_F [38].

To verify the crucial role of the interatomic hybridization for the NM character of H-UFeGe we performed the calculation neglecting the hybridization of the U and ligand orbitals. Technically, this was achieved by setting to zero the matrix

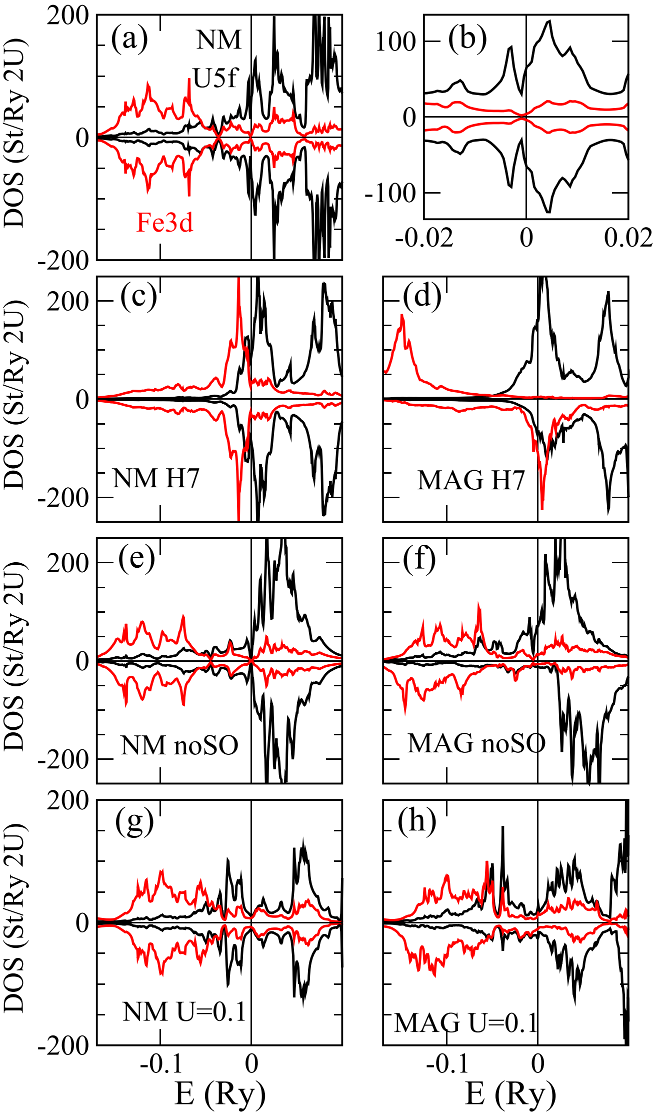

FIG. 2. The partial spin-projected U 5f (black lines) and Fe 3d (red lines) DOSs. The curves above (below) the abscissa axis correspond to the positive (negative) spin projection. The energy origin is at the Fermi level. (a) NM phase. (b) The same as (a) but zoomed in the energy region about E_F. (c) NM phase calculated with neglected U-Fe hybridization. (d) MAG phase calculated with neglected U-Fe hybridization. (e) NM phase calculated with neglected SOC. (f) MAG phase calculated with neglected SOC. (g) NM phase calculated with LDA+U method and $U_H = 0.1$ Ry. (h) MAG phase calculated with LDA+U method and $U_H = 0.1$ Ry.

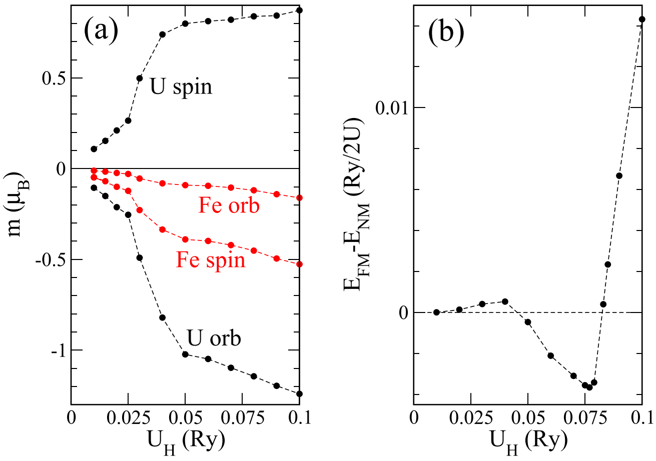

FIG. 3. (a) Calculated spin and orbital moments of the U and Fe atoms as functions of Hubbard parameter U_H. The direction of the U spin moment is chosen as positive. (b) Energy difference between MAG and NM states as a function of U_H.

elements between corresponding basis functions. The NM DOS obtained in this case [Fig. 2(c)], in contrast to the DOS from the full calculation [Fig. 2(a)], shows no hybridization-caused common behavior of the U 5f and Fe 3d DOSs as well as absence of their joint minimum at E_F. In contrast to the full calculation, in this case the MAG self-consistent state does exist [Fig. 2(d)]. The obtained spin moments of the U and Fe atoms are parallel to each other and have values of 1.07 and 2.41 μ_B, respectively. These results prove the crucial importance of the interatomic hybridization for obtaining the NM ground state. We remark that in all other calculations considered in the paper the number of the U 5f electrons is close to three while in the calculation with neglected interatomic hybridization it is about 1.9 showing again that the role of the hybridization is critical.

Next we examine how the neglect of the SOC [Figs. 2(e), 2(f)] influences the physical picture. In contrast to the calculation with SOC taken into account [Fig. 2(a)], and in analogy to the calculation with neglected hybridization [Fig. 2(d)], the self-consistent MAG state in this case was obtained [Fig. 2(f)]. The spin magnetic moments of the U and Fe atoms are antiparallel and equal to 1.12 and 0.06 μ_B, respectively. The energy of the MAG state is lower by 1.6 mRy/U than the energy of the NM state also calculated without SOC. The strong influence of the SOC on the electronic structure and the disagreement with experiment of the nonrelativistic calculation show that the account for the SOC is essential for obtaining a realistic description of the system.

B. LDA+U calculations

The LDA+U calculations allow us to investigate how the accounting the 5f electron correlation beyond LDA influences the physical picture. For U_H below 0.05 Ry, similar to the LDA calculation, we did not obtain a self-consistent MAG state. However, the situation changes importantly for larger U_H values. Now the self-consistent MAG state exists and its energy can be compared with the energy of the NM state. The values of the atomic magnetic moments as a function of U_H are shown in Fig. 3(a). The magnetic moments of both U and Fe appear simultaneously and the directions of their spin moments are always opposite. The attempts to start calculations with parallel U and Fe spin moments resulted in flipping of the Fe moment. The U_H dependencies of the atomic moments are monotonous. The magnitudes of the moments increase with increasing U_H. However, the detailed character of the dependencies differ considerably in different U_H intervals. Focusing on the U spin moment we obtain a moderately fast increase in the interval 0.01–0.025 Ry, a fast increase in the interval 0.025–0.04 Ry, and a rather slow further increase above 0.04 Ry. Similar behavior we see in the U_H dependence of the U orbital moment. As expected on the basis of the third

Hund's rule, the direction of the U orbital moment is opposite to the direction of the U spin moment. The Fe spin moment is about half of the U spin moment and has opposite direction. The Fe orbital moment is small corresponding to a relatively small SOC of the Fe 3d states.

Remarkably, in contrast to monotonous dependence on U_H of the magnetic moments the energy difference between MAG and NM phases $\Delta E = E_{\mathrm{MAG}} - E_{NM}$ is not monotonous [Fig. 3(b)]. Most importantly, the difference $\Delta E(U_H)$ changes sign with the variation of U_H. This reveals the competition between NM and MAG phases. The experiment shows that in reality the NM state wins. The presence of the close in energy NM and MAG phases can be the source of strong magnetic fluctuations.

Under the influence of U_H, the DOS changes compared to the LDA DOS. To analyze the transformation of the electronic structure we plot in Figs. 2(g), 2(h) the DOSs for NM and MAG phases calculated with $U_H = 0.1$ Ry. We begin with the comparison of the NM DOSs [Figs. 2(a), 2(g)]. As expected, the occupied part of the U 5f DOS shifts under the influence of U_H to lower energies whereas the empty part moves to higher energies. The comparison of the NM and MAG DOSs calculated with $U_H = 0.1$ Ry reveals strong changes due to spin polarization in the MAG case. The number of the spin-up U 5f states below E_F distinctly increases while the number of the spin-down states in this energy region decreases. However, the total spin-summed DOSs differ in the NM and MAG cases less dramatically and the numbers of the 5f electrons are in both cases rather close to each other. This is an important factor that helps to understand why despite the strong difference in the spin-projected DOSs the total energies of the NM and MAG phases are in competition.

Analyzing the impact of parameter U_H on the crystal electron states it is important to take into account that these states are mixtures containing contributions of both U 5f orbitals experiencing influence of parameter U_H and conduction-electron orbitals not subjected to the direct influence of U_H. The resulting effect of U_H on a crystal electron state depends on the relation between contributions of different atomic orbitals. The larger is the contribution of the 5f orbitals, the stronger is the response of the state to the U_H term. The contributions of conduction electron orbitals, on the contrary, make the electron state more resistant to the influence of U_H. The orbital compositions of the crystal electron states depend on the crystal field effects (CFE) governing the interatomic hybridization. Although the same parameter U_H is used in our calculations for all U 5f orbitals these orbitals respond differently since they hybridize differently with conduction electron orbitals. The orbital-dependence of the response can be enhanced by choosing different values of U_H for different 5f orbitals, a popular concept in the discussion of the effect of electron correlation. To gain a deeper insight into the response of the 5f orbitals to different physical factors we analyze below the properties of the partial $(m\sigma)$ DOSs corresponding to given orbital m and spin σ quantum numbers.

C. Properties of the $(m\sigma)$ resolved partial U 5f DOSs

We start with the analysis of the symmetry properties of the U 5f occupation matrix $n_{(m\sigma),(m'\sigma')}$ whose diagonal elements determine the properties of the partial $(m\sigma)$ DOSs. We consider the following four cases. (i) The highest symmetry of $n_{(m\sigma),(m'\sigma')}$ corresponds to the NM case with neglected SOC. Here both the complex conjugation operator K responsible for the time reversal in spinless problems and spin-projection reversal operator given by the Pauli matrix σ_y are separate symmetry operations of the problem. As a result there are the following relations between elements of the occupation matrix:

$$n_{(m\sigma),(m'\sigma')} = n^*_{(-m\sigma),(-m'\sigma')} \tag{4}$$

$$n_{(m\sigma),(m'\sigma')} = n_{(m,-\sigma),(m',-\sigma')}. \tag{5}$$

Here the asterisk denotes complex conjugation. The symmetry with respect to the product $K\sigma_y$ leads to the relation

$$n_{(m\sigma),(m'\sigma')} = n^*_{(-m,-\sigma),(-m',-\sigma')}, \tag{6}$$

which is a direct consequence of Eqs. (4), (5).

Respectively, we have the relation between partial $(m\sigma)$ DOSs:

$$\mathrm{DOS}(m,\sigma) = \mathrm{DOS}(|m|,|\sigma|). \tag{7}$$

Since in this case the $(m\sigma)$ DOSs are invariant to the change of the signs of m and σ, both the orbital moment corresponding to the contributions with a given σ and the spin moment corresponding to the contributions with a given m are zero. (ii) For the MAG phase calculated with neglected SOC, only K remains a symmetry operation. Respectively, the symmetry properties of the occupation matrix reduce to Eq. (4) and, therefore,

$$\mathrm{DOS}(m,\sigma) = \mathrm{DOS}(|m|,\sigma). \tag{8}$$

In contrast to previous case, the DOSs corresponding to different spin projections σ are different. As a result, the spin moment of the atom is nonzero while orbital moments still vanish for both values of σ. (iii) In the NM relativistic case the time-reversal operation takes the form of the product $K\sigma_y$. As a consequence, we obtain the symmetry relation given by Eq. (6) and

$$\mathrm{DOS}(m,\sigma) = \mathrm{DOS}(-m,-\sigma). \tag{9}$$

Respectively, both atomic spin and atomic orbital moments vanish, as it must be for a NM system. However, in contrast to the nonrelativistic case each spin channel σ has a nonzero orbital moment. These two orbital moments have opposite directions and compensate each other exactly. (iv) Finally, in the relativistic MAG case the symmetry with respect to the time reversal is broken leading to nonzero spin and orbital atomic moments. There still remain the symmetry properties of the occupation matrix that follow from the crystal symmetry operations: spatial rotations and reflections. As a consequence of this symmetry many elements of the occupation matrix are zero, which reflects the hybridization properties of the 5f orbitals with each other in the given crystal environment. An example of the calculated occupation matrix is given in the Appendix.

In Fig. 4(a) we show the $(m\sigma)$ DOSs obtained for the NM system with neglected SOC. As discussed above the time-reversal symmetry leads in this case to the invariance of the

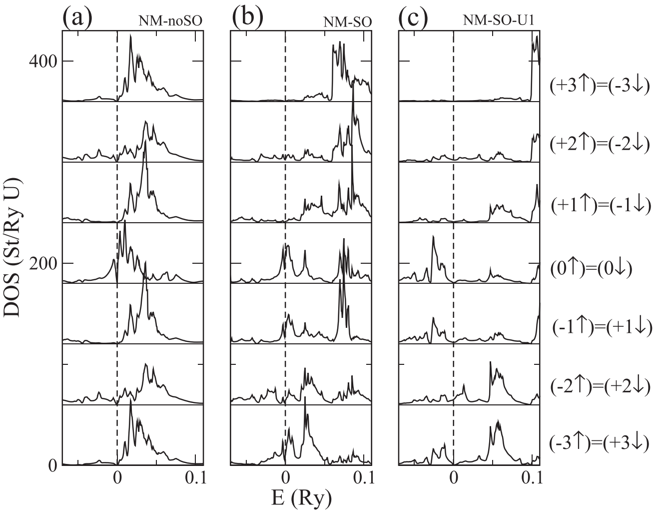

FIG. 4. $(m\sigma)$-projected DOSs of the NM phases. (a) LDA calculation without SOC. (b) LDA calculation. (c) LDA+U calculation with $U_H = 0.1$ Ry. In each panel there are seven curves corresponding to seven values of quantum number m. For better visual comprehension the curves are shifted with respect to each other along the ordinate axis. The symmetry relation between spin-up and spin-down DOSs is given to the right from (c).

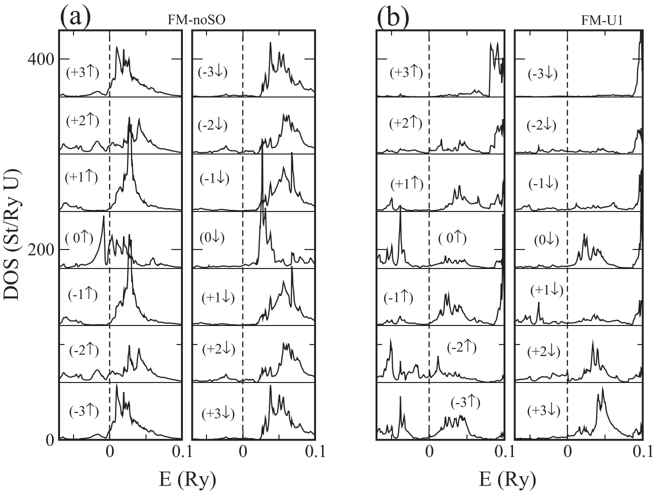

FIG. 5. $(m\sigma)$-projected DOSs of the MAG phases. (a) LDA calculation without SOC. (b) LDA+U calculation with $U_H = 0.1$ Ry. For better visual comprehension the curves are shifted with respect to each other along the ordinate axis.

curves with respect to the change of the signs of m and σ. The energy intervals occupied by different m orbitals are roughly the same. The difference of the curves is the result of the CFE.

The account for the SOC [Fig. 4(b)] leads to strong change of the NM $(m\sigma)$ DOSs. The curves are now invariant with respect to simultaneous change of the signs of both m and σ. The influence of the SOC competes with the influence of the CFE. We see that for $\sigma = +1$ (spin-up orbitals) with increasing m there is the trend to the shift of the $(m\sigma)$ DOS to higher energies. This is an expected consequence of the SOC. On the other hand, there are features that do not follow a simple rule of monotonous m dependence. For instance, there are peaks around E_F for m equal to -3, -1, and 0 in contrast to $m = -2$ DOS where there is no clearly formed peak in this energy region. The coexistence of such features reflects the competition between influences of SOC and CFE. Since the simultaneous change of the signs of m and σ does not change the $(m\sigma)$ DOS the corresponding trends are present also in the $(m\sigma)$ DOSs for the spin-down orbitals.

The account for the electron correlation governed by parameter U_H brings into competition one additional source of influence. It tends to lower the energies of higher occupied orbitals and increase the energies of lower occupied orbitals. Indeed, taking the case of $U_H = 0.1$ Ry [Fig. 4(c)] as an example we see that the DOS at E_F decreases. The peaks of the occupied states lie now below E_F whereas the empty peaks are at distinct energy distance above E_F. In this case the effects of correlation compete with the influences of SOC and CFE. This is seen for instance in the $m = 0$ DOS that has peaks in both occupied and empty parts of the DOS.

The MAG case [Fig. 5] adds the factor of the spin polarization: the occupied peaks of the spin-up DOSs move further towards lower energies while corresponding spin-down peaks are now above the E_F. The spin polarization leads to a considerable redistribution of the electrons between 5f orbitals. However, the total occupation of the 5f orbitals, n_{5f}, changes relatively weakly. In all cases presented in Figs. 4 and 5, n_{5f} is close to three electrons. For $U_H = 0.1$ Ry the difference between NM and MAG cases is ≈0.05 electrons, for $U_H = 0.05$ Ry it is only ≈0.005 electrons. Relatively small change of the n_{5f} despite considerable difference in the occupation of individual atomic orbitals is an important factor in the energy competition between NM and MAG phases signifying relatively small change in the total 5f electron density due to spin polarization.

Different behavior of the U 5f orbitals reflecting their different hybridization with conduction electron states is an important feature in the formation of the properties of the U-based materials. In this respect it is worth mentioning the suggestion of Zwicknagl *et al.* [18,19] that the many-body effects can lead to the enhancement of the role of this factor resulting in vanishing hybridization with the conduction electron states of some of the 5f orbitals. According to Zwicknagel *et al.* such a renormalized hybridization gives the basis for the explanation of the heavy-fermion properties of the 5f materials that is an alternative to the Kondo scenario based on strong effective interaction of the 5f and conduction electrons.

The properties of the $(m\sigma)$ DOSs discussed above suggest an explanation of the nonmonotonic behavior of $\Delta E(U_H)$ revealing the competition between the NM and MAG phases. Microscopically the nonmonotonous behavior can be explained by a large number of electron bands participating in the transformation of the electron structure under the influence of parameter U_H. These contributing electron states have different orbital composition. Although the transformation of a selected electron state can be expected to be monotonous with increasing U_H, the quantitative characteristics of the transformations are different for different states. This difference leads to the change in the relative energy positions of the electron states and, therefore, in the change of their occupations and contributions to the total energies. These complex processes are different for different phases and are the origin of the nonmonotonous U_H dependence of $\Delta E(U_H)$.

D. Relation between U and Fe moments

After we have established the magnitudes of the atomic moments and their U_H dependence in the MAG states of H-UFeGe [Fig. 3(a)], there are two questions about the relation between U and Fe moments we would like to address. First, can the magnetism of one type of atoms be considered as primary and the magnetism of the other as induced? To remind, the MAG moments of U and Fe appear simultaneously with variation of U_H and have clear correlation in the character of their U_H dependencies. Quantitatively, the value of the Fe spin moment is about a half of the value of the U spin moment. Second, why the directions of the U and Fe spin moments are opposite. We will briefly relate our findings to the corresponding properties of two other materials, hydrogenated U_2Fe_2Sn and UFe_2, containing U and Fe atoms.

To address the first question we performed the following constrained calculation. We started with self-consistent MAG state obtained with $U_H = 0.1$ Ry and imposed the restriction that at the beginning of each iteration the spin-up and spin-down potentials of the Fe atoms are averaged and made equal to each other. The self-consistent calculation under this constraint resulted in the MAG state with atomic spin moment of the U atoms equal to $0.55\,\mu_B$ and Fe spin moment equal to $-0.06\ \mu_B$. So, the U spin moment reduced its value by ≈40% while the Fe spin moment dropped by about one order of value. These results allow us to draw the following conclusions. First, the U moment although reduced assumes rather large value that shows that the U subsystem remains magnetic without supporting influence of the Fe moments. The small value of the Fe moment shows that it is induced by the U moments. The fact that the Fe spin moment obtained in this constraint calculation is much smaller than the moment obtained in unconstrained calculation reveals important enhancing role of the Fe on-site exchange interaction in the unconstrained calculation. This enhancement is switched off by the condition of equal spin-up and spin-down potentials. Also, the back influence of the enhanced Fe moment of the unconstrained calculation on the U moment is substantial.

On the other hand, if we impose the constraint of equal spin potentials on the U atoms leaving Fe potentials unconstrained, the whole system converges to the NM state. This shows again that the magnetism of the U atoms plays a leading role and the magnetism of the Fe atoms is induced.

The facts that the self-consistent MAG states can be obtained only for antiparallel directions of the spin moments of the U and Fe atoms and that the values of the moments strongly influence each other show that the system cannot be classified as possessing well-defined atomic moments, even for the U_H values where the magnetic solution exists. Indeed, for the well-defined atomic moments it is expected that, first, the self-consistent MAG states exist for arbitrary relative directions of the moments and, second, the values of the moments in these states do not change much. Therefore, the mapping of such a MAG material onto the Heisenberg or Ising Hamiltonian of interacting atomic moments may appear a rather crude approximation. The peculiar nature of the U atomic moments is an important aspect of the physics of the U-based materials. In this respect it is useful, as an example, to refer to the detailed experimental study [39] of magnetic excitations in U_2Pt_2Si that has shown the essential localized-itinerant duality of the U moments despite their large values of $\approx 2\ \mu_B$.

It is instructive to discuss the relation between magnetism of the U and Fe atoms in other two materials containing these type of atoms. The constrained calculations for U_2Fe_2Sn, similar to those discussed above, were performed in Ref. [9] within the framework of the study of hydrogenated $U_2(Ni_{1-x}Fe_x)_2Sn$. The result from Ref. [9] was different from the present result for H-UFeGe: none of the atomic moments, neither U nor Fe, survives if the potential of the other atomic type is spin averaged. Therefore in U_2Fe_2Sn none of the moments can be treated as induced by the other. They exist only supporting each other. On the other hand, our calculations for UFe_2 [40] show that the U moments are induced by the Fe moments that exist also in the case of spin-average constraint on the U atoms. The opposite, however, is not true: without Fe moments the U moments vanish. Thus, in different U-based materials the relation between U and Fe moments can be very different. It expectedly depends on the relative content of the U and Fe atoms but also on other chemical and structural aspects since in both H-UFeGe and U_2Fe_2Sn the numbers of the U and Fe atoms are equal to each other.

The next question we discuss is the physical mechanism responsible for opposite directions of the inducing U and induced Fe spin moments in H-UFeGe. The first guess might be the interatomic hybridization between U and Fe orbitals that transfers spin polarization from the U atoms to the Fe atoms. However, the hybridization is expected to be stronger between the orbitals with the same spin projection and therefore should lead to parallel spin moments. Indeed, in the nonrelativistic calculation [Fig. 2(f)] there is no hybridization between spin-up and spin-down orbitals. In the relativistic case [Fig. 2(h)] we see signatures of stronger hybridization in the DOSs corresponding the same spin projection: for example the common peak positions at ≈0.04 and ≈0.055 Ry below E_F for the spin-up DOSs of the U 5f and Fe 3d electrons for $U_H = 0.1$ Ry. We suggest that the mechanism responsible for the opposite directions of the atomic moments is spin-dependent spatial charge redistribution. The U spin moment makes the spin-up potential in the U atomic region deeper than the corresponding spin-down potential. This deep potential attracts additional spin-up electron density into U atomic volume making the region outside the U atom, in particular the atomic volumes of the Fe atoms, poorer on the spin-up electron density. Thus the sign of the spin density at the Fe site will be negative leading to the negative direction of the Fe spin moment. This mechanism resembles some features of the prominent Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism used in particular to explain complex processes in the 4f systems (see, e.g., Ref. [41] and recent publication Ref. [42]).

If the hybridization does not play a decisive role, why does larger U spin moment increasing with increasing U_H lead to larger Fe spin moment? Here there are the following two aspects. First, larger U moment means deeper spin-up potential and, respectively, enhanced impact on the negative spin density at the Fe sites. Second and probably more important, the occupied spin-down Fe 3d states are now at energies where there is no peaks of the spin-down U 5f DOS that reduces the Fe 3d-U 5f hybridization in the spin-down channel. Because of reduced interatomic hybridization the intra-atomic Hund exchange interaction becomes more efficient leading to increased magnitudes of the Fe spin moments. It is worth to remark that here there is an interesting analogy to the conclusion by Zwicknagl *et al.* that 5f electron correlation leads to reduced hybridization of a part of the U 5f states with conduction electron states.

IV. CONCLUSIONS

The experimental ground state of H-UFeGe is NM. This result is not expected since, first, both U and Fe tend to be magnetic in their compounds and, second, the hydrogenation is considered as favorable for magnetism. The two possible scenarios of vanishing moment at the U sites are the Pauli paramagnetism of the Stoner type and the Kondo-type screening of the U 5f moment. We apply the LDA and LDA+U methods to investigate the origin of the NM state of H-UFeGe. We obtain the U 5f-Fe 3d hybridization as an important physical factor. The LDA+U calculations reveal the presence of sensitive competition between NM and MAG phases. The variation of parameter U_H in the interval from 0–0.1 Ry results in the nonmonotonous behavior of the difference $\Delta E(U_H)$ of the energies of the MAG and NM phases. The sign of $\Delta E(U_H)$ changes several times reflecting the competition of the two phases. Remarkably, in contrast to $\Delta E(U_H)$ the U_H dependence of the magnetic moments is monotonous. We explain the nonmonotonous behavior of the energy difference as the consequence of the participation of multiple U 5f orbitals in the formation of the ground-state properties. We investigate the response of the U 5f orbitals to various physical factors. The response of different orbitals to the correlation strength U_H varies because of their different hybridization with conduction electrons governed by the CFE.

We establish the essential role of the interatomic hybridization and SOC in the stabilization of the experimental NM state. Considering the MAG phase we demonstrate that the Fe moments can be treated as induced by the U_H moments. Both types of atomic moments appear and disappear simultaneously. We explain how these characteristics of the moments coexist with the opposite directions of the inducing U spin moment and induced Fe spin moment. We compare the properties of the U and Fe moments in H-UFeGe with their properties in U_2Fe_2Sn and UFe_2 obtaining important differences in all three cases.

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APPENDIX: EXAMPLE OF THE CALCULATED OCCUPATION MATRIX

Below, as an example, we show the spin-up block of the occupation matrix $n_{m,m'}$ calculated for nonmagnetic H-UFeGe with SOC taken into account. The zero elements of the matrix are consequences of the symmetry of the lattice. In the ASW method the occupation matrix of a given atom consists of two contributions [29]: one coming from the basis functions centered on the atom and the second from the tails of the functions centered on the other atoms. We show the first type of the contribution,

$$\begin{pmatrix} 0.21 & 0 & 0 & 0.04 & 0 & 0 & -0.01 \\ 0 & 0.27 & 0 & 0 & -0.05 & 0 & 0 \\ 0 & 0 & 0.16 & 0 & 0 & 0.05 & 0 \\ 0.04 & 0 & 0 & 0.21 & 0 & 0 & -0.02 \\ 0 & -0.05 & 0 & 0 & 0.10 & 0 & 0 \\ 0 & 0 & 0.05 & 0 & 0 & 0.14 & 0 \\ -0.01 & 0 & 0 & -0.02 & 0 & 0 & 0.05 \end{pmatrix}.$$

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