Symmetry and magnetism of UFe$_5$Al$_7$

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We report symmetry analysis and first-principles density-functional-theory (DFT) calculations of the magnetic structure in UFe$_5$Al$_7$. Two results can be considered as most significant. First, we show that the magnetic structure of UFe$_5$Al$_7$ is noncollinear. This is an important modification of the magnetic phase diagram suggested previously. The noncollinearity is a consequence of the interplay between the symmetry of the magnetic crystal and the spin-orbit coupling. Second, we show that the DFT reproduces a drastic difference in the magnetic structure of UFe$_5$Al$_7$ and UFe$_4$Al$_8$ compounds. This difference appears mainly as a result of a strong variation of the angle between the crystallographic b axis and the $8f$ Fe moments under the influence of the replacement of one of the Al atoms by the Fe atom. The influence of the orbital polarization correction is discussed.

I. INTRODUCTION

The compounds UFe$_x$Al$_{12-x}$ are characterized by a drastic change of the magnetic properties with variation of the composition. They crystallize in a tetragonal-body-centered ThMn$_{12}$-type structure and have a congruent melting range from $x=3.8$ to $x=5.8$.[1] This permits a systematic experimental study of single crystals with different compositions.[2] Magnetization, Mössbauer, ac-susceptibility, and specific heat measurements as well as the results of earlier neutron diffraction experiments[3,4] were used in Ref. 2 to suggest a magnetic phase diagram of the system. Three different ranges of composition were found to have different magnetic behavior: $x<4+\delta_1$, $4+\delta_1<x<5-\delta_2$, and $x>5-\delta_2$. In this paper we will refer to these ranges as first, second, and third composition regions, respectively. Here δ_1 and δ_2 are small positive numbers.

The stoichiometric compound UFe$_4$Al$_8$ belongs to the first composition region. The magnetic structure of UFe$_4$Al$_8$ was determined by neutron diffraction measurements[3] and appeared to be very unusual. The magnetic structure of the Fe sublattice is close to collinear antiferromagnetic, with a weak canting leading to a ferromagnetic component. On the other hand, the U sublattice is ferromagnetic with magnetic moments almost orthogonal to the Fe moments. The origin of the unusual magnetism of UFe$_4$Al$_8$ was explained in Ref. 5 on the basis of symmetry analysis and first-principles calculations in the framework of density functional theory (DFT).

In the second region two magnetic phase transitions were observed, revealing the formation of two different magnetic structures in different temperature intervals.[2] Presently, no

neutron diffraction experiment has been performed for compounds within this composition range. In the third composition region there is again one magnetic phase transition. The magnetic structure of the compounds of the third region was suggested in Refs. 2 and 4.

A remarkable feature of this series of compounds is a radical difference between the magnetic structures in different composition ranges. For example, the value of the magnetization per formula unit varies from 1.6μ_B in UFe$_4$Al$_8$ to 7.5μ_B in UFe$_5$Al$_7$. According to the scheme suggested in Ref. 2 the complex magnetic structure of UFe$_4$Al$_8$ is replaced in the case of UFe$_5$Al$_7$ by a simple collinear ferromagnetic configuration (Fig. 1).

In the present paper we report the theoretical study of the magnetism of UFe$_5$Al$_7$ and provide an explanation of the strong variation of the magnetic properties within the series.

II. CRYSTAL STRUCTURE AND SYMMETRY ANALYSIS

In UFe$_5$Al$_7$ four Fe atoms occupy the $8f$ sites and one additional Fe atom per formula unit replaces one of the four Al atoms in the $8j$ positions. The additional Fe atoms are not completely ordered. In the present study we, however, neglect this structural disorder and assume the translational periodicity of the positions of the fifth Fe atoms. In Table I we present the symmetry operations of the crystal structure thus obtained.

In general, the presence of magnetic structure lowers the symmetry of the crystal since not only the atomic positions but also the directions of the atomic moments must be invariant under the action of symmetry operations. The sym-
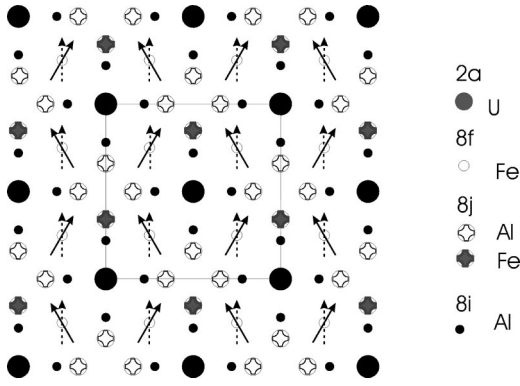
FIG. 1. Magnetic structure of the UFe_5Al_7 compound. The moments of the U ($2a$ site) and the Fe atoms in the $8j$ site always point along the y axis. In the collinear structure (proposed in Ref. 1) the Fe on the $8f$ sites (dotted, white arrows) also point along the y axis; in the noncollinear structure, the $8j$ Fe moment (solid line, white arrows) deviation from y axis follows from the symmetry analysis.

metry operations of the collinear ferromagnetic structure with the atomic moments parallel to the y axis (Fig. 1) are collected in Table I.[6] The symmetry group of the ferromagnetic state is a subgroup of the symmetry group of the nonmagnetic state (Table I). Note that the replacement of one of the Al atoms by the Fe atom does not destroy the equivalence of the four Fe atoms in the $8f$ positions.

Next we discuss an important question of the stability of the collinear magnetic configuration in UFe_5Al_7. In Refs. 5 7, and 8 an intimate connection between the symmetry properties of the system and the stability of the magnetic structure has been shown. The following criterion was formulated: *A collinear magnetic configuration of a given type of atoms cannot be stable if this state is not distinguished by*

TABLE I. Generators of the symmetry group of nonmagnetic and collinear ferromagnetic UFe_5Al_7. In the ferromagnetic case only operations C_{2y} and $m_{yz}R$ survive. The restrictions these operations impose on the moment direction are collected in the third column.

Operation	Transposition of the $8f$ Fe atoms $i \leftrightarrow j$	Restriction on magnetic moments U and Fe atoms[a]
C_{2y}	$1 \leftrightarrow 3; 2 \leftrightarrow 4$	$\begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}_i = \begin{pmatrix} -m_x \\ m_y \\ -m_z \end{pmatrix}_j$
$m_{yz}R$	$1 \leftrightarrow 4; 2 \leftrightarrow 3$	$\begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}_i = \begin{pmatrix} -m_x \\ m_y \\ m_z \end{pmatrix}_j$
R	no	

[a]For the U and $8j$ Fe atoms $i=j$; for the $8f$ Fe sublattice i and j according to the column "Transposition of the $8f$ Fe atoms."
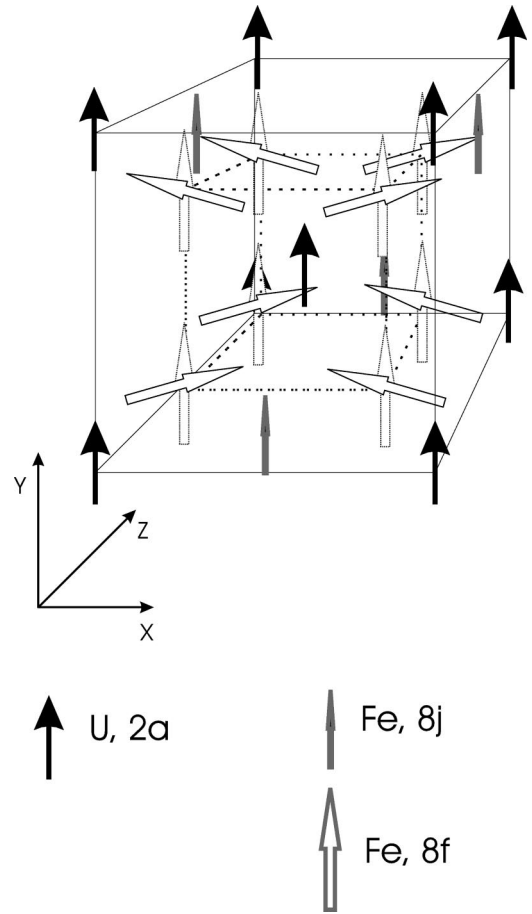

FIG. 2. Projection of atomic positions and Fe $8f$ moments on the xy plane. The collinear (dashed-line arrows) and the noncollinear (solid-line arrows) magnetic structures have the same symmetry.

symmetry when compared to states with infinitesimal deviation of the magnetic moments. This means that if there exists a deviation of magnetic moments from the collinear directions which does not disturb any of the symmetry operations of the collinear structure, such a deviation must take place. To study the stability of the collinear ferromagnetic structure in UFe_5Al_7 on the basis of this criterion we consider the restrictions imposed by the symmetry operations of the collinear magnetic configuration on the atomic moments. For the U and Fe $8j$ moments we have $m_x=0$ and $m_z=0$. Therefore these moments preserve their initial direction along the y axis. For the $8f$ Fe atoms, the deviation of the magnetic moments from the y axis does not disturb the symmetry of the initial structure if the x and z components of the moments fulfill the conditions summarized in the third column of Table I and illustrated in Fig. 2. Therefore the stability of the collinear structure proposed for the UFe_5Al_7 in Refs. 2 and 4 is improbable and a deviation of the magnetic moments from the y axis must take place. Note that the x and z components of different atoms compensate (Fig. 2); the total moment of the crystal preserves the direction parallel to the y axis. The value of the deviation angle cannot be predicted on the basis of symmetry arguments and needs a concrete calculation with account for various interactions influencing the forma-

tion of the magnetic structure.

III. CALCULATIONAL RESULTS AND DISCUSSION

The calculations were carried out using the augmented-spherical-wave (ASW) method modified to account for the noncollinear magnetic structure and relativistic interactions as described in Refs. 9 and 10. The experimental lattice parameters[2] $a = 868.51$ pm and $c = 501.67$ pm were used in the calculations with internal parameters units of a for the $8i$ positions $\alpha = 0.344$ and for the $8j$ positions $\beta = 0.2805$.

The results reported in the paper were obtained in the calculations with 131 points in the first Brillouin zone. A test calculation with 330 points gave for the collinear ferromagnetic structure a deviation in energy of less than 0.2 mRy per formula unit.

A. Collinear ferromagnetic state

Calculation for the collinear ferromagnetic structure proposed in Ref. 2 resulted in a self-consistent magnetic state with the total energy 23.4 mRy per formula unit lower than the energy of the nonmagnetic state. A characteristic feature of the density of states (DOS) of the ferromagnetic state [Figs. 3(e)–3(h)] compared to the nonmagnetic DOS [Figs. 3(a)–3(d)] is a strongly decreased density of states at the Fermi level.

The calculated values of the magnetic moments are collected in Table II. The calculated value of the magnetization per formula unit is in reasonable agreement with experiment although exceeds somewhat the experimental value.

As usual for U atoms, the spin and orbital moments are antiparallel. The values of two moments are close to each other, which results in a small total moment on the U sites. The Fe moments are larger than the U moment, revealing a primary role of the Fe atoms in the magnetism of the compound.

The Fe moments are parallel to the U total moment. This agrees with the results of the neutron diffraction measurements.[4] The calculated $8j$ Fe moment is larger than the $8f$ Fe moment, which agrees with the estimations of the hyperfine fields obtained from the Mössbauer measurement.[11] We explain the higher moment of the $8j$ Fe atoms by a higher number of Fe neighbors in the first coordination sphere compared with the $8f$ site (correspondingly 4 and 3).

Comparison of the values of the moments shows that the theoretical Fe moments are larger than the values estimated in neutron diffraction measurement.[4] On the other hand, the calculated U moment is smaller than the experimental value; this is a rather typical feature of the DFT calculations.

Since one of our purposes is to understand the difference in the magnetic states of UFe$_5$Al$_7$ and UFe$_4$Al$_8$ compounds, we performed the calculation of UFe$_5$Al$_7$ in a magnetic configuration similar to that of UFe$_4$Al$_8$: The moments of the four Fe $8f$ atoms were arranged in a type-G antiferromagnetic structure and directed along the x axis, being orthogonal to the U moment and the moment of the fifth Fe atom. The total energy of this structure is about 4.5 mRy/f.u. higher
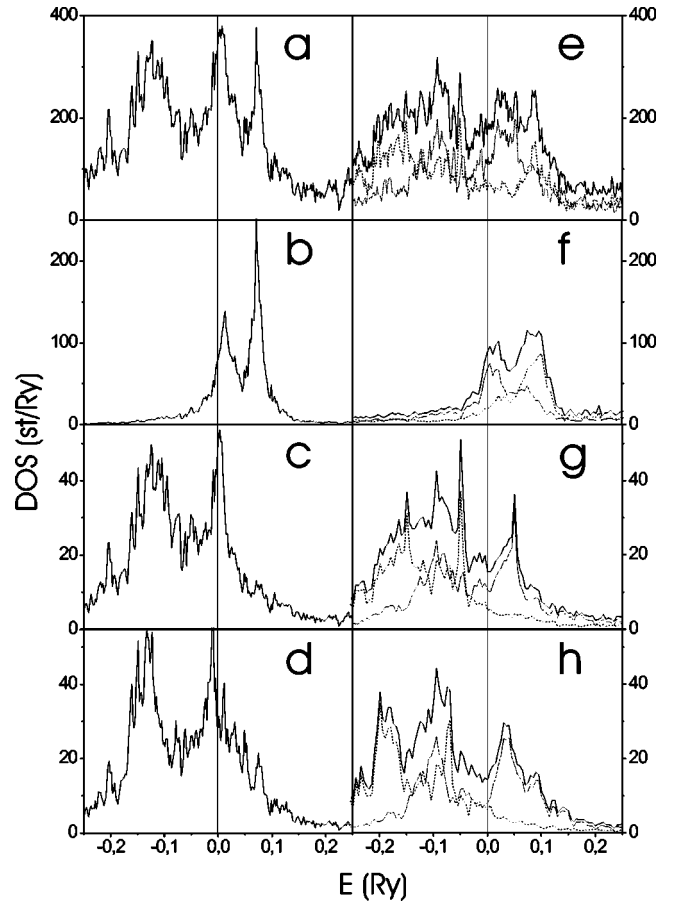

FIG. 3. DOS of the nonmagnetic (right panels) and collinear ferromagnetic (left panels) states of UFe$_5$Al$_7$: (a) and (e) total DOS, (b) and (f) U $5f$ DOS, (c) and (g) $8f$ Fe $3d$ DOS, and (d) and (h) $8j$ Fe $3d$ DOS. The total DOS is given per formula unit, the partial DOS per atom. The energy origin is at the Fermi energy. In the ferromagnetic case, the dashed (dotted) line shows spin-up (spin-down) contribution.

than for the collinear ferromagnetic configuration. This confirms the experimental result that the magnetic state of UFe$_5$Al$_7$ is drastically different from the magnetic state of UFe$_4$Al$_8$. In this magnetic configuration the value of the Fe $8f$ moments (Table II) is close to the value obtained for UFe$_4$Al$_8$ and is substantially smaller than the corresponding moment in the collinear ferromagnetic state. It is remarkable that the fifth Fe moment, although orthogonal to other Fe moments, practically did not decrease compared with the ferromagnetic configuration. The spin and orbital components of the U moment, although decreased, are still much larger than in UFe$_4$Al$_8$.[5]

B. Noncollinear magnetism of UFe$_5$Al$_7$

The symmetry analysis performed in Sec. II shows that the collinear ferromagnetic structure proposed in Ref. 2 in UFe$_5$Al$_7$ cannot be stable: the moments of the $8f$ Fe atoms must deviate from the y axis. To verify this prediction we performed an unconstrained calculation with all magnetic moments allowed to deviate from the initial directions.

TABLE II. Calculated magnetic moments. Values of the spin orbital and total moments are given in μ_B per atom. M is the magnetization in μ_B per formula unit.

	Canting angle	Spin	Orbital	Total
Collinear ferromagnetic				
U 2a		-1.72	1.83	0.11
Fe 8f		1.49	0.08	1.58
Fe 8j		1.83	0.08	1.92
M				8.35
Collinear antiferromagnetic				
U 2a		-1.28	1.50	0.22
Fe 8f	90°	1.36	0.07	1.43
Fe 8j		1.69	0.07	1.76
M				1.98
Unconstrained				
U 2a		-1.70	1.79	0.09
Fe 8f	15°	1.49	0.07	1.56
Fe 8j		1.81	0.08	1.90
M				8.02
Fe 8j nonmagnetic				
U 2a		-1.25	1.38	0.13
Fe 8f	54°	1.38	0.06	1.45
M				4.8
OPC correction (1 mRy)				
U 2a		-1.86	2.44	0.57
Fe 8f	10.7°	1.49	0.08	1.58
Fe 8j		1.83	0.09	1.92
M				8.77
Magnetization measurements[a]				
M				7.46
Neutron diffraction measurements[b]				
U 2a				0.86
Fe 8f				1.1
Fe 8j				1.26

[a]Reference 2.
[b]Reference 4.

In agreement with the symmetry analysis, the unconstrained calculation for UFe_5Al_7 has shown that the U and Fe 8j moments keep their direction parallel to the y axis. On the contrary, the Fe 8f moments deviate from the y axis by 15°. The x and z components of the Fe 8f moments become nonzero; however, as predicted by the symmetry analysis they sum to zero (Fig. 1). The calculated total magnetization is now closer to the experimental magnetization (Table II).

These calculations successfully reproduce the drastic difference in the magnetization of UFe_5Al_7 and UFe_4Al_8 established experimentally. We have shown that in both compounds the 8f Fe moments form a canted noncollinear configuration but with very different canting angles: 15° for UFe_5Al_7 and 74° for UFe_4Al_8.[5] Although it is clear that the difference in the magnetism of UFe_4Al_8 and UFe_5Al_7 compounds is caused by the replacement of one of the Al atoms by an Fe atom, there are two different aspects of the influence of this replacement on the magnetic configuration. First, the chemical nature of Al and Fe is very different. Another aspect is a large magnetic moment on the fifth Fe atom.

To separate the influence of these two factors we performed model calculations keeping the fifth Fe moment nonmagnetic. Both canting angles and the values of the moments (Table II) are intermediate between UFe_4Al_8 and UFe_5Al_7.

These results show that already a nonmagnetic fifth Fe atom influences the exchange interactions in the compound. The magnetic moment on the fifth Fe atom strengthens the trend to a large total ferromagnetic component in UFe_5Al_7 in contrast to the small ferromagnetic component in UFe_4Al_8.

IV. CALCULATIONS WITH THE ORBITAL POLARIZATION CORRECTION

The value of the U orbital moment is usually underestimated within the local spin density approximation (LSDA) scheme. A possible method to improve agreement with experiment is the inclusion of the orbital polarization correction[12,7] (OPC) term into the Hamiltonian of the problem. We used the OPC term in the form $\hat{H}_{orb} = I_{orb} L \hat{l}_z$,[12,7] where I_{orb} is a parameter, L is the value of the atomic orbital

moment, and $\hat{l}_z$ is the operator for the projection of the angular momentum on the local atomic z axis. The purpose of this term is to simulate the effect of Hund's second rule.

Surprisingly, in the case of UFe$_4$Al$_8$ the OPC was not able to improve the agreement with experiment: For small values of the OPC parameter both the size of the U moment and the canting of the Fe moments decrease under influence of the OPC. For an OPC parameter of about 1 mRy the U moment and the canting angle jump to large values which far exceed the experimental values.[5] This suggests that the form of the correction is not adequate to account for the complex magnetic structure with two almost orthogonal magnetic sublattices and the induced nature of the U magnetism.

To study the effect of the OPC on the magnetic state of UFe$_5$Al$_7$ we performed calculations with two values of the OPC parameter, 0.5 and 1 mRyd. In this case a usual result of an increased orbital U moment is obtained for both values of the parameter.

The use of the OPC makes the difference between the calculated and measured magnetization somewhat larger.

V. CONCLUSIONS

We reported symmetry analysis and first-principles DFT calculations of the magnetic structure in UFe$_5$Al$_7$. The following two results can be considered as most significant. First, we have shown that the magnetic structure of UFe$_5$Al$_7$ is noncollinear. This is an important modification of the magnetic phase diagram suggested in Ref. 2. The noncollinearity is a consequence of the interplay between the symmetry of the magnetic crystal and the spin-orbit coupling.

Second, we have shown that the DFT reproduces the drastic difference in the magnetic structure of UFe$_5$Al$_7$ and UFe$_4$Al$_8$ compounds. This difference appears mainly as a result of the strong variation of the angle between the y axis and the $8f$ Fe moments under the influence of the replacement of one of the Al atoms by an Fe atom. The influence of the orbital polarization correction is discussed to make the picture of the magnetism in UFe$_5$Al$_7$ more complete. We obtained good agreement with experiment in the value of the magnetization per formula units. There is, however, a substantial difference between theoretical and experimental estimations of the values of individual atomic moments. Further theoretical and experimental efforts are needed to understand the origin of this difference.

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