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Noncollinear magnetism of the UFe_xAl_{12-x} series: ab initio calculations

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The UFe_xAl_{12-x} series was the object of a systematic experimental study in single crystals with different compositions [Phys. Rev. B **60**, 9494 (1999)]. Several experimental technics were used to suggest a magnetic phase diagram of the system. Three different ranges of composition were found to have different magnetic behaviour: $x < 4 + \delta_1$, $4 + \delta_1 < x < 5 - \delta_2$, and $x > 5 - \delta_2$. Here δ_1 and δ_2 are small positive numbers. The UFe_4Al_8 and UFe_5Al_7 compounds belong to two different regions of the phase diagram. DFT calculations and symmetry analysis for these two compounds [Phys. Rev. B **60**, R 6961 (1999); **65**, 94413 (2002)] contributed to the understanding of the origin of the complex magnetic behaviour of the series. In order to complete the systematic study of the series we report calculations of magnetic properties for $UFe_{4.5}Al_{7.5}$. The latter compound belongs to the third and the most interesting region of the phase diagram with two magnetic phase transitions. Based on this ab initio study, we discuss the proposed phase diagram.

Introduction The UFe_xAl_{12-x} series has shown to be very interesting as the magnetic behaviour of its compounds changes drastically with composition [1]. The combination of extensive experimental results lead to a proposal of a phase diagram with three composition regions: $x < 4 + \delta_1$, $4 + \delta_1 < x < 5 - \delta_2$, and $x > 5 - \delta_2$, δ_1 and δ_2 small positive numbers.

Previous theoretical studies [2, 3] were performed on two compounds of the series belonging to different composition regions: UFe_4Al_8 and UFe_5Al_7. These studies confirmed the complexity of the structures and described successfully the transition from a small to a large ferromagnetic component from the UFe_4Al_8 compound to the UFe_5Al_7. The purpose of the present work is to extend these studies to the third region of composition, intermediate between the previous two, and rediscuss the whole series based on these new results.

The compound $UFe_{4.5}Al_{7.5}$ belongs to the intermediate region. The magnetic structure proposed for this compound in the low temperature region consists in three magnetic sublattices, formed respectively by U atoms, Fe atoms on the 8f positions and Fe atoms on the 8j positions. According to this proposal, both Fe sublattices are noncollinear but with different canting angles; with increasing temperature the Fe 8j sublattice undergoes a phase transition and orders collinearly.

Symmetry analysis As for the cases of UFe_4Al_8 [3] and UFe_5Al_7 [2], symmetry analysis allows the prediction of the magnetic structure of the $UFe_{4.5}Al_{7.5}$ compound. For the UFe_4Al_8 compound all the

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Table 1 Generators of the symmetry group of collinear ferromagnetic $UFe_{4.5}Al_{7.5}$. The restrictions these operations impose to the moments direction are collected in the third column. (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").

operation	transposition of the 8f Fe atoms $i \leftrightarrow j$	restriction on magnetic moments U and Fe atoms
C_{2y}	$\begin{pmatrix} 1 \leftrightarrow 6 \\ 2 \leftrightarrow 5 \\ 3 \leftrightarrow 8 \\ 4 \leftrightarrow 7 \end{pmatrix}$	$\begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}_i = \begin{pmatrix} -m_x \\ m_y \\ -m_z \end{pmatrix}_j$
$m_{yz}R$	$\begin{pmatrix} 1 \leftrightarrow 7 \\ 2 \leftrightarrow 8 \\ 3 \leftrightarrow 5 \\ 4 \leftrightarrow 6 \end{pmatrix}$	$\begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}_i = \begin{pmatrix} -m_x \\ m_y \\ m_z \end{pmatrix}_j$
R	no	

Fe atoms in the 8f sites are equivalent [3]. In UFe_5Al_7 an extra Fe atom per formula unit, corresponding to two Fe atoms per unit cell, replaces two Al atoms in 8j sites but the Fe atoms on the 8f sites remain equivalent to each other [2]. In the case of $UFe_{4.5}Al_{7.5}$ there is only one extra Fe atom per unit cell and therefore a larger number of inequivalent sites: there are two nonequivalent U atoms with 8 or 9 Fe atoms as nearest neighbours, two different Fe atoms in 8f sites and another in an 8j site.

In Table 1 we present the symmetry operations for the symmetry group of the ferromagnetic structure of the $UFe_{4.5}Al_{7.5}$ system and the restrictions imposed on the moments' directions. The second column of Table 1 shows the interchange of the 8f Fe atoms due to each of the symmetry operations.

The U atoms and the Fe atoms on the 8j positions must have their moments along the y-axis (third column); the Fe atoms in 8f positions are in two nonequivalent sites. The moments of equivalent 8f Fe atoms, interchanged by the symmetry operations on the second column, are related by the conditions collected in the third column (for example the m_x of the first Fe atom in an 8f site must be equal to $-m_x$ of sixth Fe atom on the same site) which leads to a noncollinear structure with a antiferromagnetic projection along the x- and z-axis and a ferromagnetic projection along y-axis. These symmetry conditions mean that the ferromagnetic configuration and the noncollinear configuration just described have the same symmetry properties.

For the analysis of the magnetic structure of the $UFe_{4.5}Al_{7.5}$ compound we adopt the same symmetry criteria already used for the UFe_4Al_8 and UFe_5Al_7 [2, 3], which states that if a collinear structure has the same symmetry properties as a noncollinear configuration, the probability of the ground state being described by the collinear system is zero. Therefore we expect a magnetic structure with two noncollinear sublattices constituted by the two nonequivalent Fe atoms in the 8f positions. The exact values of the canting angles must be determined by the DFT calculations, however our symmetry analysis shows that the crystal has a collinear ferromagnetic ordering of the 8j Fe atoms, in disagreement with the previously proposed phase diagram [1].

Results and discussion The calculations were carried out using augmented spherical waves (ASW) method modified to account for the noncollinear magnetic structure and relativistic interactions [4] within the ASA and LDA aproximations [5]. The experimental lattice parameters [1] $a = 869.7$ pm, $c = 502.79$ pm were used in the calculations with internal parameters units of a for the 8i positions $\alpha = 0.344$ and for the 8j positions $\beta = 0.289$. The results reported in the paper were obtained in the calculations with 144 points in the first Brillouin zone.

Table 2 Calculated magnetic moments for the $UFe_{4.5}Al_{7.5}$ compound. 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_1 2a		−1.64	1.96	0.32
U_2 2a		−1.66	1.93	0.27
Fe_1 8f		1.50	0.08	1.58
Fe_2 8f		1.44	0.10	1.54
Fe 8j		1.73	0.08	1.81
M				7.44
unconstrained				
U_1 2a		−1.61	1.94	0.33
U_2 2a		−1.63	1.88	0.25
Fe_1 8f	11.7°	1.50	0.08	1.58
Fe_2 8f	18.2°	1.43	0.08	1.51
Fe 8j		1.72	0.08	1.80
M				7.16
magnetization measurement [1]				
M				5.5

We first performed calculations constraining the magnetic structure to a collinear ferromagnetic order. The results are collected in Table 2. The values obtained for the moments are intermediate between the values for the UFe_4Al_8 [3] and UFe_5Al_7 [2] but closer to the latter. The total moment is larger than the value determined by the magnetization measurements [1]. However the experimental value for the $UFe_{4.5}Al_{7.5}$ compound is somewhat lower than the values determined for compounds of the same region therefore we suspect that the correct value of the total moment of $UFe_{4.5}Al_{7.5}$ is higher than the reported and closer to the value determined by the calculations.

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 [6]. The Fe atoms in the 8f sites closer to the 8j Fe atom have a slightly larger moment than the other 8f Fe atoms at a larger distance. We explain the higher moment of the 8j Fe atoms by a higher number of the Fe neighbours in the first coordination sphere (correspondingly 4) compared with the two different 8f sites (2 or 3 nearest neighbours).

The symmetry analysis of the compound indicates that the magnetic structure is not collinear so we performed calculations allowing all the moments to rotate. The results are collected in Table 2. As expected the Fe atoms in the 8f positions deviate from direction defined by the U and 8j Fe moments, both in the x- and z-directions, although the x- and z-components of the moment of different atoms cancel each other. The canting angle has different values for the two nonequivalent 8f Fe atoms, which results in a larger ferromagnetic component of the 8f Fe atoms with a higher number of Fe neighbours. The unconstrained noncollinear state has a total energy that is about 3.2 mRy/f.u. lower than the energy of the constrained collinear state.

Phase diagram of UFe_xAl_{12-x} The values of the magnetic moments determined by the calculations for the three compounds studied by this method are in reasonable agreement with the values determined by the magnetization measurements (Table 2, Refs. [2, 3]).

The calculations correctly predict a strong increase on the magnetization from the region of $x < 4 + \delta_1$ to the $x > 5 - \delta_2$ due an increase of the average atomic Fe moments and a decrease of the canting angles of the 8f Fe atoms.

The increase is related to the occupancy by Fe atoms of the 8j positions which have a higher number of Fe nearest neighbours and therefore a higher magnetic moment then the 8f sites. The

occupancy of 8j sites by Fe atoms in $UFe_{4.5}Al_{7.5}$ also creates 8f positions with different number of Fe nearest neighbours, 2 and 3, resulting in a slightly higher moment in the latter site than in the first. The Mössbauer measurements [6] of the hyperfine field agree with the dependency of the Fe magnetic moment on the number of Fe nearest neighbours.

There are substantial differences between the compounds of the three composition regions. In all the three regions the Fe atoms in the 8f positions have noncollinear structures but the calculated values of the canting angle are different (measured relatively to the U moments direction): 82° for UFe_4Al_8 [3], 15° for UFe_5Al_7, and 12° and 18° for the two inequivalent 8f Fe atoms in $UFe_{4.5}Al_{7.5}$. In the case of UFe_4Al_8, the symmetry properties do not allow a deviation of the moments towards the z-direction. The canting angle towards the c-direction for the UFe_5Al_7 and the $UFe_{4.5}Al_{7.5}$ is very small, less than 1°.

The canting angles of $UFe_{4.5}Al_{7.5}$, are between the values calculated for UFe_4Al_8 and UFe_5Al_7 but closer to the UFe_5Al_7 value. The canting angle of the 8f Fe atom with 3 Fe nearest neighbours in $UFe_{4.5}Al_{7.5}$ is similar to that of 8f Fe atom in UFe_5Al_7. This suggests a dependency not only on the magnetic moment but also of the canting angle on the number of nearest neighbours and complex hybridization between the 8j and 8f Fe atoms.

In the composition region of Fe content, x, between 4 and 5 atoms per formula unit two magnetic transitions were detected. According to the Mössbauer results [6], all the atoms order at the same temperature. It is also expected that the U atoms order at this temperature. In Ref. [1] it was suggested that the lower transition temperature corresponds to a reorientation of the noncollinear moments of 8j and 8f Fe atoms with more than 2 nearest neighbours [1, 7]. We have seen however that the 8j Fe moments have a collinear structure at low temperatures. Therefore we expect the transition not to be related with the 8j Fe atoms but to at least some of the 8f atoms.

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