



## Why $\text{UF}_x\text{Al}_{12-x}$ phase does not crystallize with $\text{ThMn}_{12}$ -structure type, when $x = 2$ ?

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### ABSTRACT

The crystallographic structure of recently reported orthorhombic  $\text{UF}_2\text{Al}_{10}$  phase, which belongs to the  $\text{YbFe}_2\text{Al}_{10}$ -structure type is different from the well known tetragonal  $\text{UF}_x\text{Al}_{12-x}$  ( $3 < x < 8$ ) having  $\text{ThMn}_{12}$ -structure type. Comparative Density Functional Theory (DFT) study of the relative stability of the orthorhombic  $\text{UF}_2\text{Al}_{10}$  phase with respect to different models of tetragonal  $\text{ThMn}_{12}$ -type structures with the same composition is carried out to explain this unusual phenomenon. It is shown that the fine interplay between the overlapping of  $3d$ -states of Fe and  $5f$ -states of U in the region  $-2.5 \div -0.3$  eV below the Fermi energy dictates the lower total energy of orthorhombic  $\text{UF}_2\text{Al}_{10}$  phase in comparison with tetragonal  $\text{UF}_2\text{Al}_{10}$  phase crystallized in  $\text{ThMn}_{12}$  structure. On the example of  $\text{UF}_2\text{Al}_{10}$  it is also directly demonstrated that DFT calculations in the framework of the Full Potential + Linear Augmented Plane Wave method within the local density approximation may be used for refining the structure of complicate compounds. The calculated equilibrium volume, lattice parameters and atomic Wyckoff positions of  $\text{UF}_2\text{Al}_{10}$  intermetallic compound are in very good agreement with experimental data.

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### 1. Introduction

$\text{AT}_x\text{Al}_{12-x}$  phases (where A = actinide or lanthanide and T = transition-metal) are stable in a wide range of homogeneity region. Among these, the ternary semi-ordered  $\text{UF}_x\text{Al}_{12-x}$  ( $3 < x < 8$ ) phases, possessing  $\text{ThMn}_{12}$  crystallographic structure type, have been a subject of numerous investigations aimed mainly to understand the general magnetic behavior of intermetallic compounds with  $5f$  elements [1–4]. The magnetic behavior of these compounds changes drastically with composition,  $x$  [5]. In a wide range of compositions in these compounds,  $\text{UF}_4\text{Al}_8$  phase in which Fe atoms occupy the  $8f$  position (in Wyckoff notation), and Al atoms occupy the  $8i$  and  $8j$  positions [6], is the most studied.  $\text{NdFe}_2\text{Al}_{10}$  [7] and  $\text{LaCu}_2\text{Al}_{10}$  [8] are another examples of  $\text{AT}_x\text{Al}_{12-x}$  phase that crystallize in  $\text{ThMn}_{12}$  structure.

Recently, a new  $\text{UF}_2\text{Al}_{10}$  intermetallic phase was reported [9–11]. According to the stoichiometry of this phase, it belongs to the line of  $\text{UF}_x\text{Al}_{12-x}$  compounds (having  $x = 2$ ), but the crystallographic structure of this compound is completely different – it possesses the  $\text{YbFe}_2\text{Al}_{10}$ -structure type, and there is no direct group – subgroup relation between their ( $\text{YbFe}_2\text{Al}_{10}$  vs.  $\text{ThMn}_{12}$ -types)

symmetries. Further investigations using magnetic measurements down to 5 K [11] or neutron diffraction down to 3 K [12] have shown that no magnetic ordering exists in the  $\text{UF}_2\text{Al}_{10}$  phase.

The aim of this paper is to explain why  $\text{UF}_2\text{Al}_{10}$  compound has  $\text{YbFe}_2\text{Al}_{10}$ -structure type rather than  $\text{ThMn}_{12}$ . Our study is based on comparative analysis of the energies of the  $\text{UF}_2\text{Al}_{10}$  phase belonging to the  $\text{YbFe}_2\text{Al}_{10}$ -structure type and the same phase in different variants of the  $\text{ThMn}_{12}$ -structure type using Density Functional Theory (DFT) calculations. We also investigate the electronic properties including the Density of States (DOS) of these structures to reveal the possible physical reasons for such unexpected behavior of the  $\text{UF}_2\text{Al}_{10}$  phase.

Nowadays DFT became a reliable tool for crystalline, electronic structure and thermodynamic stability research. It can also predict physical and mechanical properties. Recently Söderlind [13] proved that DFT calculations can accurately describe both crystal properties and mechanical properties of  $\alpha$ -U at low temperature. Few other examples of successive application of DFT are the analysis of stability of intermetallic U–Al compounds [14], magnetic behavior of  $\text{UF}_2$  [15], magnetization densities in  $\text{UPTAl}$  [16] and electronic structure of fcc-Th [17].

Usually generalized gradient approximation (GGA) reproduces the experimental situation for the early actinides (Th–Np) with high accuracy [18]. There are, however, cases when the regular DFT approach is not enough, such as strongly correlated materials [19].

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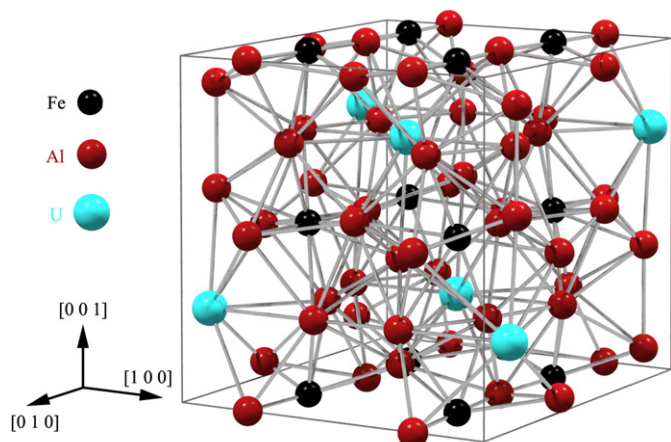


Fig. 1. Crystallographic structure of the  $UFe_2Al_{10}$  compound. The figure was prepared by Powder cell [26] and rendered by POV-ray [27] PC programs.

In these cases the DFT + U method is applied where an orbital-dependent field is introduced which can be shown to give a correction for the self-interaction [20]. DFT + U calculations [18] have large improvement for insulating actinide oxides, as for example  $UO_2$ , and for oxides where the charge ordering is observed [21,22]. Recently using the LDA + U method a periodic charge disproportionation along the  $c$ -axis in the monoclinic structure of  $Fe_3O_4$  was obtained [23]. At the same time, for weakly correlated systems the influence of accounting the Coulomb potential effect (U) is negligible [24].

Another, rather new approach is dynamical mean-field theory (DMFT) + DFT, which is good for weakly correlated metals, strongly correlated metals or Mott insulators [25].

## 2. Analysis of structures and models

### 2.1. $UFe_2Al_{10}$ ( $YbFe_2Al_{10}$ -structure type)

$UFe_2Al_{10}$  compound has an orthorhombic crystallographic structure ( $YbFe_2Al_{10}$ -type,  $Cmcm$  (#63) space group), with uranium

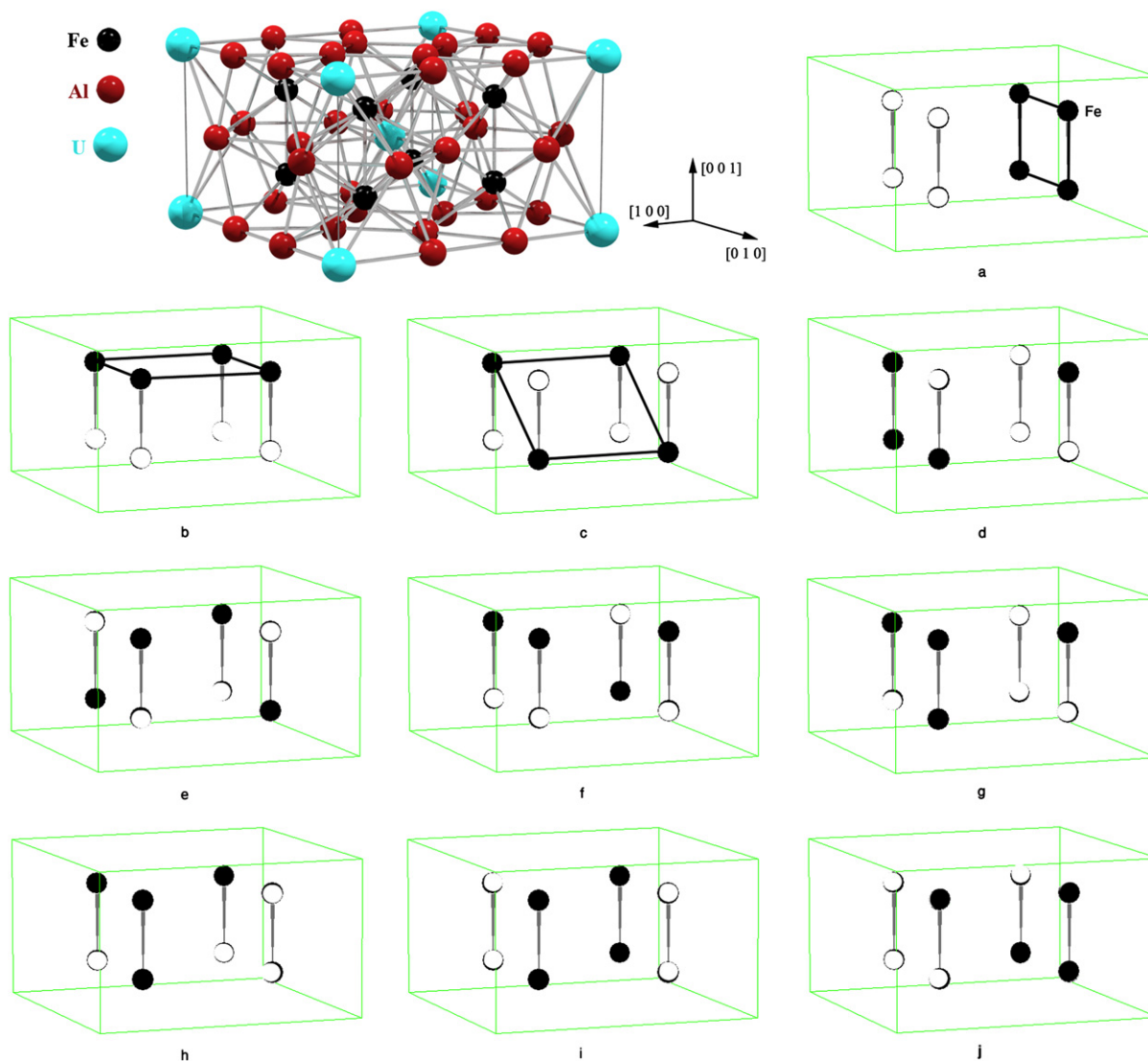


Fig. 2. Hypothetical  $UFe_2Al_{10}$  in  $ThMn_{12}$  crystallographic structure type. Upper-left image is a schematic presentation of the unit cell of the  $UFe_4Al_8$  phase (prepared as Fig. 1); a, b, ..., j: 10 cases of arranging 4 out of 8 atoms. Only 8 atoms (originally Fe atoms in  $UFe_4Al_8$ ) are shown: open circle represents Al atom while black filled circle represents Fe atom. All the rest atoms (both elements and positions) are the same as in  $UFe_4Al_8$ .

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