Peculiarities of U-based Laves phases

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Abstract. This contribution focuses on the structural and physical properties of U-based Laves phases. It starts with the structural description of the different type of Laves phases, followed by a brief description of the factors that affect their stability. The majority of the uranium Laves phases show a weakly paramagnetic behaviour. The reason is the compact structure of the phases that leads to small a U-U spacing as well as very high coordination numbers, regarding both the uranium and the ligands sublattices, which brings a strong hybridization with non-*f* states. However, there are some exceptions of uranium Laves phases that do order magnetically (UFe₂, UNi₂ and the recently discovered U₂Fe₃Ge compound). These exceptions are discussed in more detail in the present manuscript.

1. Introduction

Laves phases are the largest family of intermetallic compounds, with more than 1600 compounds reported in the Pearson's database [1]. They are based in the general formula AB_2 and crystallize with the compact closely related MgZn₂ (C14), MgCu₂ (C15) and MgNi₂ (C36) type structures.

The study of the physical properties of Laves phases, especially of those containing iron and lanthanides, such as terbium, holmium and erbium, has lead to a clear picture of the microscopic magnetic exchange interactions in these materials, mainly due to the separation of the itinerant 3d electrons of the iron atoms from the localized 4f states. The high Curie temperatures observed on this type of compounds (>500 K) arise from the strong Fe-Fe exchange interactions, whereas the large anisotropy observed is a consequence of the strong 4f spin-orbit coupling. In such compounds direct interactions 4f-4f and 4f-3d are negligible but indirect interactions exist, mediated through the 5d electrons. This understanding led to industrial applications of Laves phases on, for example, magneto-optical recording devices [2].

Albeit being a small part of this family of compounds, uranium Laves phases are one of the most widely studied actinide groups. The larger spatial extent of the uranium 5f states leads to physical properties distinct from the lanthanides counterparts. As originally recognized by Hill, uranium

compounds with small U-U closest interatomic distances often show a superconducting, non-magnetic ground state, whereas for large U-U interatomic distances the ground state is normally magnetic and non-superconducting [3]. This behaviour derives from the direct overlap of the *f*-electron wave functions of neighbour uranium atoms, which affects the width of the 5*f* band and, consequently, the occurrence of magnetism via the Stoner criterion [4]. The critical value (called the Hill limit) for uranium compounds was found to be between 0.34 and 0.36 nm. In uranium Laves phases the U-U closest interatomic distances fall in the 0.27-0.35 nm range, below or close to the Hill limit. Therefore, the relationships between formation, structure and magnetic properties of uranium Laves phases have been widely studied in the last decades. The Hill's rule, although very useful, does not take into account the individual details of the density of states, affected also by the 5*f*-ligand hybridization, and several exceptions have been reported [4]. Some uranium Laves phases fall in this category of compounds, making them even more interesting from a fundamental point of view.

As the structural details are crucial for establishing the physical properties of uranium Laves phases, we start with the description of some general characteristics of the different structure types, followed by a brief discussion of the factors affecting their stability. Known uranium Laves phases are then presented, with special emphasis on the characteristics of the magnetic compounds.

2. The Laves phases

2.1. Structural aspects

The unit cells of the three basic Laves phases structure types (MgZn₂, MgCu₂ and MgNi₂) are presented in figure 1a. MgZn₂ and MgNi₂ (C14 and C36, respectively) are both hexagonal structures (space group P6₃/mmc), while MgCu₂ (C15) has a cubic symmetry (space group Fd-3m). All of them show topologically close-packed structures. The three basic Laves structure types are closely related and can be built by a particular stacking of atomic layers. This is clearer when a projection along the cubic <111> direction is adopted to represent MgCu₂-type structure (figure 1b), in order to get a



Figure 1. a) Unit cells of the three basic Laves phases structure types 1–MgZn₂, 2–MgCu₂ and 3–MgNi₂; **b)** Hexagonal setting for the three structure types.

hexagonal setting for all the structure types. In this representation, $MgZn_2$ can be seen as a stacking of ...121212... layers, the $MgCu_2$ -type structure as a ...123123123... sequence and the $MgNi_2$ as a

...121312131213... sequence. The B atoms form capped Kagomé (3.6.3.6) nets, while the A atoms are arranged in two triangular planar nets, above and below the B planes. Figure 2 evidences the different atomic layers sequence for the case of the MgZn₂-type structure (for half of *z*). The three basic Laves structure types correspond to the shortest stacking sequences, which are more stable due to energetic reasons [5]. However, other stacking sequences have been observed in different materials [6,7].



Figure 2. Atomic layers sequence for the MgZn₂-type structure.

The close relation between the three Laves structure types is also evident from the observation of the next-nearest-neighbours coordination spheres (figure 3). The magnesium atoms have similar environments in all the Laves structure types, with a point group 3m (in the case of the cubic system this symmetry exists on the special projection along [111]). Each magnesium atom is surrounded by 16 atoms, with an atomic environment of the $12^{5.0}4^{6.0}$ type (according to the Villars and Daams notation [8]). On the other hand, the 3d metals have two basic distinct types of next-nearest-neighbours environments, consisting of six A and six B atoms arranged in distorted icosahedras of the $12^{5.0}$ type. The main difference between them is a position exchange between one A and one B atom.



Figure 3. Next-nearest-neighbours coordination in the Laves phases.

In the cubic MgCu₂-type structure all the coordinates are fixed and, consequently, the interatomic distances can be calculated directly from the cell parameters. In contrast, the hexagonal MgZn₂ and MgNi₂-type structures have sites with x and z free coordinates, and therefore the interatomic distances can only be correctly calculated after the structure refinement.

2.2. Factors affecting the stability

Geometric and electronic factors are known to determine the existence and stability of the Laves phases. Many reviews were dedicated to this subject and models based on these factors have been developed to predict which particular Laves polytype should be more stable for a certain composition [9-13]. Nevertheless, a recent paper has showed that there is not yet a valid, complete and consistent description for all the Laves phases [5]. Therefore, here we present only a brief overview of the factors that affect the occurrence of a Laves phase.

As stressed before, Laves phases are compact close-packed structures composed by larger A and smaller B elements, with the general formula AB₂. However, homogeneity ranges deviating from this stoichiometry are sometimes observed: figure 4a shows the isothermal section of the ternary U–Fe–Sn phase diagram at 750°C [14], where exists an (α) UFe₂-based solid solution, crystallizing in the Laves MgCu₂-type structure. This solid solution extends up to the 3U:8Fe:1Sn composition and single-crystal structure refinements indicated that tin partially substitutes both uranium and iron in their positions [14]. Thus, albeit usually the 1:2 composition ratio is the most stable, Laves phases may have homogeneity ranges on both sides of the ideal stoichiometric composition.



Figure 4. Isothermal sections of the systems: a) U-Fe-Sn at 750°C [14]; b) U-Fe-Al at 850°C [15].

On the hard spheres model, the closest packing is obtained for the ideal $r_A/r_B = (3/2)^{1/2} \approx 1.225$ ratio. However, deviations from this ideal value are frequently observed. As an obvious example, figure 4b presents the isothermal section of the ternary U-Fe-Al system at 850°C [15], where three extended solid solutions, $UAl_{2-x}Fe_x$, $UFe_{1+x}Al_{1-x}$ and $UFe_{2-x}Al_x$, crystallize in the MgCu₂, MgZn₂ and MgCu₂ structure types, respectively. Aluminium and iron metallic radii are quite different so there is some ability of the atoms to contract or expand to achieve the ideal ratio. The mutual size adjustments of the





component atoms A and B are also evidenced in figure 5, where the difference of the atomic diameters for a coordination number 12 (D_A and D_B), and the atomic diameters in the cubic actinide Laves

phases (d_A and d_B), are plotted versus the r_A/r_B atomic ratio [16]. A higher contraction and expansion of the A atom, when compared with the B atom, is observed, suggesting that it is mostly the B sublattice that controls the overall stability and size of the Laves phase. Real size r_A/r_B ratios of Laves phases were found to vary between 1.05 and 1.70 [5].

The effect of the valence electron concentration per atom, e/a or VEC, on the stability of the Laves phases was already recognized by Laves and Witte in one of their original papers [17]. Magnesiumbased Laves phases usually only occur for valence electron concentrations between 1.33 and 2.2 electrons/atom (figure 6) [17]. However, in transition metals Laves phases the e/a value (defined as the number of *d*-electrons per atom) can exist in a broad range, from 3.4 to 8 [18]. Therefore, for different Laves series different VEC ranges must be considered. This is most probably due to the importance of the electronic structure details on the stability of the Laves phases.



Figure 6. Homogeneity ranges of the different magnesium-based Laves phases as a function of the valence electron concentration [17].

In Laves phases, the larger A element is usually an electropositive metal (such as alkali, alkaline earth, lanthanide, actinide or early transition metal), while the smaller B element is generally a less electropositive transition metal (like those from the VII, VIII, or IB groups). However, the increase of the electronegativity difference between the A and B atoms usually leads to polar compounds where typically the B atoms form networks with lower coordination numbers, when compared to those existing in the Laves phases. A good example is the $CaAl_{2-x}Zn_x$ system, where the polarity increase occurs due to the larger electronegativity of zinc (when compared to aluminium). The terminal $CaAl_2$ and $CaZn_2$ compounds crystallize in the Laves MgCu₂-type structure and in the orthorhombic $CeCu_2$ structure type, respectively, but an intermediate MgNi₂-type Laves phase was also observed [19].

Each of the geometric and electronic factors discussed above cannot determine alone the stability of the Laves phases, but altogether they can give strong hints on their existence for a certain composition or composition range.

3. Uranium Laves phases

Several binary and ternary uranium Laves phases have been reported in the literature. Figure 7 presents, up to our best knowledge, the binary and ternary uranium Laves phases studied until now. There is a strong domination of the $MgZn_2$ and $MgCu_2$ -type structures, with only three examples of uranium compounds crystallizing in the $MgNi_2$ -type (the UAl₂ being reported to exist in this form only at high pressures [20]). Notwithstanding that many of ternary reported uranium Laves phases, in particular those based on the binary compounds, can be considered as pseudo-binary Laves phases, it is evident that there is still a lot of exploratory work to be done. Considering the factors that affect the Laves stability, it is obvious that other uranium Laves phases should still exist.

The majority of the uranium Laves phases are weakly paramagnetic. The reason is the compact structure of the phases that leads to small a U-U interatomic spacing, as well as very high coordination numbers, regarding both the uranium sublattice and the B ligands, which leads to a strong hybridization with non-*f* states. On one side, this character can be qualitatively justified by the Hill



Figure 7. Uranium-based Laves phases and respective structure types.

picture, due to the low inter-uranium distances. But on the other side, the Hill-limit view brings new problems to understand the exceptions of uranium Laves phases, which do order magnetically, as UFe_2 , UNi_2 and the recently discovered U_2Fe_3Ge compound. These exceptions are discussed below in more detail.

3.1. UFe₂

UFe₂ was one of the first uranium ferromagnetic compounds discovered [21]. It crystallizes in the cubic MgCu₂-type structure, with the U-U spacing ≈ 0.306 nm, i.e below the Hill limit. Detailed magnetization studies made on stoichiometric UFe₂ single crystals show that this compound has a Curie temperature of T_C = 162 K and a saturation magnetization of 1.09 µ_B/f.u. along the [111] easy axis [22]. Neutron diffraction experiments, using both polarised and unpolarised neutrons, indicated that the macroscopic moment is mainly coming from the iron atoms (0.6 µ_B/Fe) [23]. However, it also showed that a very small moment exists in the uranium atoms ($\approx 0.01 \mu_{B}/U$, figure 8), which resulted from the cancelation of the spin (-0.22 µ_B) and orbital (0.23 µ_B) contributions due to their antiparallel arrangement.



Figure 8. UFe₂ magnetic scattering amplitude on the uranium sublattice as a function of sin θ/λ [23]. The solid circles are deduced from the Bragg reflections coming from the Usublattice only. The middle curve is the best fit, corresponding the to moments given in the text.

A major iron contribution to the UFe₂ magnetic properties was also observed by ⁵⁷Fe Mössbauer spectroscopy. Figure 9 shows the Mössbauer spectra of UFe2 at 4.2 K and 300 K [24]. Below T_C two magnetically non-equivalent iron atoms, with internal magnetic hyperfine fields at 4.2 K of ≈3 T and ≈ 3.8 T, are observed, confirming the [111] direction as the easy magnetization axis [24].



The low iron moment observed in UFe₂ (much smaller than in α -Fe), together with the reduced uranium spin moment (when compared with the free-ion values), was explained by the strong hybridization between the iron 3d states and the uranium 5d and 5f states [25]. However, albeit the small U-U spacing and the consequent strong 5f-5f overlap, finite uranium magnetic spin moments are observed. The uranium spin moments order antiparallel to the iron moments, and electronic band structure calculations indicate that they are most probably induced by iron, through the 5f-3dhybridization [25,26].

The itinerant character of the ferromagnetism in UFe₂ was confirmed through high-pressure magnetization and magnetic susceptibility measurements [27,28]. A strong negative dependence of the spontaneous magnetic moment and Curie temperature with the increasing temperature is observed, a behaviour similar to that observed for pure 3d metals.

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Variations of the UFe₂ stoichiometry composition were found to strongly influence the magnetic properties. A large spread of magnetic parameters, as spontaneous magnetization and Curie temperature, was reported on the early studies of UFe₂, is likely due to possible small offstoichiometry of the samples. The study of Fe sub-stoichiometric samples show that the Laves structure persists down to UFe_{1.7} and that the magnetic properties vary linearly with variations in stoichiometry [22]. A recent work made on iron over stoichiometric samples prepared by splat cooling confirms this trend [29]. The Laves phase structure can accommodate up to 0.3 of excess iron, while the Curie temperature is enhanced up to ≈220 K (figure 10 [29]). ⁵⁷Fe Mössbauer spectroscopy shows

that the iron atoms occupying the uranium sublattice have higher magnetic hyperfine fields than those in the regular iron sites [29].

3.2. UNi₂

The UNi₂ compound crystallizes in the hexagonal MgZn₂-type structure. Recent crystal structure results from single crystal XRD refinements have confirmed that the U-U closest interatomic distances are very small ($d_{U-U} \approx 0.303$ nm), and therefore below the Hill limit [30].



UNi₂ is a weak itinerant ferromagnet, with $T_C \approx 20$ K [31]. This compounds has a very low spontaneous magnetic moment, $\mu_S = 0.08 \mu_B/f.u.$, and a very strong easy-plane magnetic anisotropy ($\mu_0 H_A > 25$ T) [32]. Polarized neutron diffraction experiments have shown that the magnetic moments are essentially located on the uranium atoms [33] (and consequently its ferromagnetism is mainly caused by the 5*f* electrons). The 5*f* form factor shows a maximum at about sin θ / $\lambda = 0.2$ Å⁻¹ (figure 11), which was the first clear evidence of the large orbital contribution to the magnetization in an itinerant ferromagnet and is consistent with the observed huge magnetic anisotropy in this compound [33].

The itinerant character of the UNi_2 magnetism was evidenced by several experimental results, as the T² dependence of the spontaneous magnetization [34], the weakly dependent paramagnetic susceptibility above 60 K [35], the very small magnetic entropy connected with the magnetic ordering [32] and the strong negative pressure dependence of the saturation magnetization and Curie temperature [27]. Electronic band structure calculations are consistent with these results [36],



Figure 12. Calculated density of states of UNi₂ [36].

sustaining the itinerant character of the UNi₂ magnetism and its 5*f* origin. A high density of the 5*f* states at the Fermi level was calculated (figure 12), leading to a Stoner product larger than 1 and instability of the paramagnetic state toward ferromagnetism [36]. Also photoemission spectroscopy results confirm the high density of the 5*f* states close to the Fermi level [37]. Comparing with the off-stoichiometric UFe_x Laves phases it is interesting to note that small excess of nickel leads to the decrease of T_c , i.e. just opposite to UFe₂ with the dominant 3*d* magnetism [38].

3.3. U_2Fe_3Ge

U₂Fe₃Ge is a recently discovered compound [39,40], which crystallizes in the Mg₂Cu₃Si-type structure, an ordered variant of the MgZn₂-type, where the iron atoms fully occupy the 6*h* sites and the germanium atoms are located at the 2*a* sites. The nearest-neighbour U-U distances in this compound are very small (\approx 275 nm), well below the sum of the uranium metallic radii and analogous to those found in α -U.

Similarly to the UFe₂ and UNi₂ cases, U₂Fe₃Ge has the shortest U-U spacing lower than the Hill limit, and was not expected to order magnetically. However, studies on polycrystalline samples indicate the ferromagnetic behaviour, with $T_C = 55$ K and a spontaneous magnetization $M_{sp} = 0.85 \mu_B/f.u.$ at T = 2 K, values higher than those found in UNi₂. The conjecture that iron has sizeable ordered moments similar to UFe₂ can be discarded due to ⁵⁷Fe Mössbauer spectroscopy results, exhibiting zero or very small magnetic hyperfine splitting (figure 13, the upper limit for iron moments can be estimated as $0.1 \mu_B$).



Figure 13. 57 Fe Mössbauer spectra of U₂Fe₃Ge collected at different temperatures.

This compound was also studied by different experimental techniques on single crystalline samples. Electrical resistivity measurements show a metallic-like behaviour with a change in the slope at T_c, typical of a ferromagnetic material. Applying the Kadowaki-Woods relation, a moderate γ -value of 47 mJ/mol U K² can be deduced from the low temperature resistivity data, in good agreement with the $\gamma = 48$ mJ/mol U K² obtained from the specific heat results. This Sommerfeld coefficient value does not deviate from the values typical for other uranium Laves phases, and proves its broad-band character. The Curie temperature and magnetization decreasing with hydrostatic pressure are reminiscent of the UFe₂ behaviour, which could point to the 3*d* origin of magnetic order, but similar data for UNi₂ do not differ substantially and therefore only a general itinerant character of magnetism can be concluded for this compound. Quantitative comparison of the logarithmic pressure derivatives of T_c, $\delta \ln T_c/d p$, which equals to -3.2 Mbar⁻¹ in UFe₂ and -6.7 Mbar⁻¹ in UNi₂[41], and is about -7.4

Mbar⁻¹ in U₂Fe₃Ge, points to the similarity with the the 5*f* ferromagnet UNi₂. The specific heat data, where no prominent feature at T_c was found (figure 14), agrees with the magnetic itinerant picture for U₂Fe₃Ge.



Figure 14. Specific heat as a function of temperature of U_2Fe_3Ge for zero magnetic field and the field of 1 T. The lack of any clear anomaly around T = 50 K proves the strongly itinerant nature of ferromagnetism.

Electronic structure of U₂Fe₃Ge was calculated in the conventional (von Barth-Hedin) local spindensity approximation (LSDA) which is often believed to be valid for itinerant metallic systems [42]. Relativistic version [43] of the full-potential LAPW method [44] was used. The calculations were performed using the experimental lattice parameters. Surprisingly both uranium ($\mu_L = 0.83 \ \mu_B$, $\mu_S = -0.56 \ \mu_B$) and iron ($\mu_L = -0.08 \ \mu_B$, $\mu_S = -1.01 \ \mu_B$) carry sizeable magnetic moments in a stable ferromagnetic solution. To investigate whether the calculations leading to the large iron moments can have a realistic background, the same type of calculation was performed for its weakly paramagnetic isotype U₂Fe₃Si. Indeed, here the method fails to reproduce the non-magnetic state, yielding ($\mu_L = 0.53 \ \mu_B$, $\mu_S = -0.32 \ \mu_B$) for uranium and ($\mu_L = -0.06 \ \mu_B$, $\mu_S = -0.63 \ \mu_B$) for iron.

The reasons why LSDA is not adequate in apparently a band system remain unclear, adding one more enigma to the U-based Laves phases. In fact, there is a growing evidence that LSDA and its semi-local generalized gradient approximation (GGA) substantially overestimate the exchange splitting in itinerant systems (e.g. $ZrZn_2$) as they can not properly account for the long-range longitudinal spin-fluctuations [45]. The ``beyond LSDA'' calculations that properly resemble the Moriya's spin-fluctuation theory [46] are needed.

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