Electronic structure of YbFe$_4$Al$_8$ antiferromagnet:
A combined X-ray photoelectron spectroscopy and first-principles study

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Depending on their chemical composition, Yb compounds often exhibit different valence states. Here we investigate the valence state of YbFe$_4$Al$_8$ using X-ray photoelectron spectroscopy (XPS) and first-principles calculations. The XPS valence band of YbFe$_4$Al$_8$ consists of two contributions coming from divalent (Yb$^{2+}$) and trivalent (Yb$^{3+}$) configurations. The determined value of the valence at room temperature is 2.81. Divalent and trivalent contributions are also observed for core-level Yb 4d XPS spectra. We study several collinear antiferromagnetic models of YbFe$_4$Al$_8$ from the first-principles and for comparison we also consider LaFe$_4$Al$_8$ with a fully filled 4f shell. We predict that only Fe sublattices of YbFe$_4$Al$_8$ carry significant magnetic moments and that the most stable magnetic configuration is AFM-C with antiparallel columns of magnetic moments. We also present a Mulliken electronic population analysis describing charge transfer both within and between atoms. In addition, we also study the effect of intra-atomic Coulomb U repulsion term applied for 4f orbitals on Yb valence and Fe magnetic moments.

I. INTRODUCTION

Yb-based compounds exhibit a number of interesting properties that include mixed valence, heavy fermon behavior, Kondo effect, magnetic ordering, and superconductivity [1]. The compound considered in this work, YbFe$_4$Al$_8$, belongs to the ThMn$_{12}$ family of intermetallic compounds with the general formula XT$_4$Al$_8$, where X is the rare-earth or actinide element and T is the transition-metal element [2,3]. Other examples of Yb-based compounds in the XT$_4$Al$_8$ family are YbCr$_4$Al$_8$, YbMn$_4$Al$_8$, and YbCu$_4$Al$_8$ [2], while the isonstructural configuration with Co has not been confirmed. In this section we will introduce the issue of valency of YbFe$_4$Al$_8$ in comparison with other Yb compounds, we will also discuss the issues related to the complex magnetic configuration of YbFe$_4$Al$_8$ and present a model of the crystallographic structure of the considered compound.

A. Valence of Yb-based compounds

One motivation for studying YbFe$_4$Al$_8$ is to determine its valence. Most lanthanides in the metallic state are trivalent, except for Eu and Yb, which are divalent [2,3]. Since Yb has sixteen electrons outside the core, a 4f orbital filled with fourteen electrons is usually stable, and two electrons can participate in the bond. And indeed, a divalent state is observed for metallic Yb [7]. However, the small energy difference observed between the divalent and trivalent states means that Yb in compounds often occurs in the trivalent state or states with valence between two and three.

The set of valence values estimated from measurements for a series of Yb compounds takes on a wide range from two to three [8]. Examples of valence estimates made from measurements are 2.38 for YbFe$_4$Al$_8$ [9], 2.68 for Yb$_2$Si$_2$Al [10], and 2.93 for YbRh$_2$Si$_2$ [11]. Yb compounds with mean valence are usually classified as fluctuating (mixed) or intermediate valence compounds. While fluctuating valence implies dynamic transition processes between two valence states, intermediate valence implies the simultaneous presence of two valence states with specific ratios. It is not uncommon to put the same material into both categories based on similar experimental results, where a well-known example is YbAl$_3$ [12,13]. A valence band, similar to the one observed for YbFe$_4$Al$_8$ [14], consisting of contributions from Yb$^{2+}$ and Yb$^{3+}$ has been seen previously for both materials classified as valence fluctuating, such as YbCu$_2$Si$_2$ [15], YbAl$_2$ [17,18], YbB$_2$ [19], Yb$_2$Pt$_6$Ga$_{15}$ and Yb$_2$Pt$_6$Al$_{15}$ [20], as well as for materials of intermediate valence, such as YbFe$_4$Si$_2$ [21], YbInCu$_3$ [22], YbNi$_{0.8}$Al$_{1.2}$ [23], YbRh$_2$Si$_2$ [11], Yb$_4$Ga$_{24}$Pt$_9$ [24], and Yb$_2$Si$_2$Al [10]. Since our experimental analysis is based...
solely on XPS measurements, we cannot unambiguously resolve the membership of the compound under consideration, YbFe$_4$Al$_8$, in the class of fluctuating or intermediate valence materials. However, previous studies remain consistent that the valence of the considered compound is close to three [2, 4, 15]. Suski cites hard-to-find results of Shcherba et al., indicating for YbFe$_4$Al$_8$ a valence of 3.00(5) [4], which is consistent with the observed slight positive volume deviation of YbFe$_4$Al$_8$ from the trend for a series of mostly trivalent RF$_4$Al$_8$ compounds. As noted by Kummer et al. [25], compounds in which the deviation from trivalence is small are among the most interesting, since in this regime there is a transition from a magnetically ordered ground state to a paramagnetic one.

B. Magnetic properties of YbFe$_4$Al$_8$

Although the YbFe$_4$Al$_8$ compound has been known since at least 1976 [2], it attracted the most interest in the first decade of the 21st century [15, 26–31]. This was probably due to its misassignment to the group of RF$_4$Al$_8$ superconducting compounds, like for example ScFe$_4$Al$_8$ ($T_c = 6$ K), YFe$_4$Al$_8$ ($T_c = 6$ K), and YCr$_4$Al$_8$ ($T_c = 4.5$ K) [32, 33]. However, a later study denied YbFe$_4$Al$_8$ membership in the superconducting group [29, 30]. A critical analysis of the presence of a superconductive phase in YbFe$_4$Al$_8$ has led to an explanation of the phenomenon of thermally driven magnetization reversal, sometimes also called negative magnetization [29, 34]. The Néel point of the Fe antiferromagnetic sublattice of YbFe$_4$Al$_8$ is about 140 K [34]. As the temperature decreases, a decrease in magnetization in the external field is observed, and a change in the sign of magnetization occurs when the compensation temperature exceeds 34 K [29, 30]. Andrzejewski et al. concluded that the negative magnetization comes from antiferromagnetic interactions between the magnetic moments on Yb and the canted effective magnetic moments on Fe. The above results for YbFe$_4$Al$_8$ are compared by Andrzejewski et al. with the results for isostructural LuFe$_4$Al$_8$ for which the magnetization observed as a function of temperature is always positive, which the authors relate to the absence of magnetic moments on the Lu sublattice [30]. However, the above explanation of the negative magnetization in YbFe$_4$Al$_8$ is somewhat controversial due to the assumption of the presence of a magnetic moment on Yb atoms, which has not yet been explicitly confirmed, while Suski et al. indicated the absence of a magnetic moment on Yb in the considered compound [27]. Although the magnetic ordering for the Yb sublattice below 8 K was detected with the $^{170}$Yb Mössbauer effect [27, 35] and the effective magnetic moment on Yb ion equal to 4.1 $\mu_B$ was indirectly deduced from the magnetic susceptibility measurements [34], Suski et al. have shown that at temperatures above 200 K the Yb$_{1-x}$Sc$_x$Fe$_4$Al$_8$ alloys follow the Curie-Weiss law with effective magnetic moments of about 7-8 $\mu_B$/f.u. which do not depend on the composition, indicating that all magnetism in this compound is determined by the Fe sublattice [27]. In a subsequent paper, Suski showed that the magnetic susceptibility of YbFe$_4$Al$_8$ is strongly field-dependent, even at temperatures clearly above the antiferromagnetic phase transition, suggesting the existence of a ferromagnetic correlation of unknown origin [36]. Suski, therefore, suggests that ferromagnetic clusters of Fe impurities are responsible for the appearance of negative magnetization in YbFe$_4$Al$_8$, which may mimic the presence of a second magnetic sublattice [36]. This seems likely, given that about 5% of the Fe atoms in the YbFe$_4$Al$_8$ sample may be located at 8i or 8j sites, as shown by Mössbauer effect measurements [31]. Gaczyński et al. suggest that partial disorder leads to interacting antiferromagnetic and spin-fluctuating subsystems [28].

The thermally driven reversal magnetization observed in YbFe$_4$Al$_8$ is also related to the phenomenon of negative magnetoresistivity detected at low magnetic fields in RM$_4$Al$_8$ compounds (including YbFe$_4$Al$_8$) [37]. A proposed explanation for this phenomenon is a combination of the Kondo effect with spin-glass state resulting from crystallographic disturbance [37]. The occurrence of a similar effect, which was the inverse magnetocaloric effect observed in Y$_{1-x}$Gd$_x$Co$_2$ alloys, has been associated with antiferromagnetic or cluster glass behavior [38].

![Diagram of the crystal structure of YbFe$_4$Al$_8$](Image)
C. Crystal structure of YbFe₄Al₈

YbFe₄Al₈ crystallizes in a tetragonal structure of CeMn₄Al₈ type (I4/mmm space group, lattice parameters \(a = 8.712\) and \(c = 5.044\ \text{Å} \)) that is a superstructure of ThMn₁₂ type, see Fig. 1. Lanthanide contraction is the reason that the unit cell volume of YbFe₄Al₈ is one of the smallest among the RF₄Al₈ compounds [2]. YbFe₄Al₈ unit cell consists of 26 atoms (two formula units) [39, 40]. Yb and Fe atoms occupy the 2a and 8f site, respectively, while Al atoms occupy the 8i and 8j positions. As shown in the example of YbCu₄Ga₄, it is also possible to create more complex superstructures in 1-4-8 systems, which require eight non-equivalent atomic positions for a complete description [1].

II. METHODS

A. Experimental details

A polycrystalline YbFe₄Al₈ sample was obtained by induction melting of stoichiometric amounts of elements in an argon atmosphere. Details of the preparation are given in earlier work [15, 29, 30]. X-ray photoelectron spectra were obtained with an Al-K\( \alpha \) source at room temperature using a PHI 5700/660 Physical Electronics Spectrometer. The electron energy spectra were analyzed using a hemispherical mirror analyzer with an energy resolution of approximately 0.3 eV. The Fermi level \(E_F = 0\) was related to a binding energy of Au 4f at 84 eV. All emission spectra were measured immediately after breaking up the sample in a vacuum of \(10^{-9}\) Torr. High vacuum breaking produced clean surfaces free of oxygen and carbon contamination.

B. Computational details

The second part of this paper will present the results of computations performed under density functional theory (DFT). The YbFe₄Al₈ model was investigated using the full-potential local-orbital scheme (FPLO version 18.00-52) [41, 42]. The use of the full potential approach is particularly important for 4f-electron compounds, for which the results are strongly dependent on the quality of the potential [11]. The second important element of our method is the treatment of relativistic effects in the full 4-component formalism. The use of a fully relativistic method (accounting for spin-orbit coupling) significantly improves the description of 4f electrons characterized by a large spin-orbit coupling. For the exchange-correlation potential, we chose the generalized gradient approximation (GGA) with the Perdew-Burke-Érnzerhof (PBE) parametrization [43]. For elements containing 4f electrons, it is worth investigating how the results might be affected by the inclusion of an additional Coulomb U term of intra-atomic repulsion to the energy functional, described by the GGA + U method [44]. In the present work, we used the fully-localized limit of the LSDA+U (GGA+U) proposed by Czyżyk and Sawatzky [45], which is also known as the atomic limit. The effect of the value of the parameter U on the obtained results in the range from 0 to 10 eV has been investigated. Previously, a similar LDA + U(4f) approach was adopted for YbFe₄Sb₁₂ [46, 47]. Furthermore, our previous experience with modeling alloys containing 3d elements shows that including the LDA+U correction for 3d atoms has very little effect on the position of the 3d band [46, 47], so to simplify the model we have not included this correction. The calculations were performed on a \(20 \times 20 \times 20\) k-mesh with a density accuracy of \(10^{-6}\). The site geometry optimization was performed with a force accuracy of \(10^{-3}\) eV Å⁻¹. Details of the geometry optimization will be presented in the next section. Drawings of the crystalline and antiferromagnetic structures were made using the VESTA code [50].

III. RESULTS AND DISCUSSION

The properties of YbFe₄Al₈, such as the thermally driven magnetization reversal, magnetism of Yb ions, non-trivial valence and antiferromagnetic configuration motivated us to perform studies that we hope will resolve some of the ambiguities. In our previous work on YbFe₄Al₈ we investigated its magnetic and transport properties [15, 29, 30]. Here we will extend the analysis of X-ray photoelectron spectra presented before [15]. The analysis of the valence band will be followed by the interpretation of selected core-level spectra. In the second part of the work, we will present the results of first-principles calculations focusing on the structural and magnetic properties of the system.

A. X-ray photoelectron spectroscopy

1. Valence band spectrum

While for divalent metallic Yb we observe a rather simple valence band with a 2F spin-orbit doublet [7], Yb compounds with a mean valence, between two and three, reveal a valence band composed of two parts associated with different states before photoemission [52]. Such binary valence band spectra have been observed before for YbFe₄Sb₁₂ [21] and YbInCu₄ [22], for example. As we see in Fig. 2, the valence band of YbFe₄Al₈ also consists of two contributions, from divalent (Yb²⁺) and trivalent (Yb³⁺) configurations. The divalent part (Yb²⁺) is characterized by a doublet derived from the final state 4f¹³, while the trivalent part (Yb³⁺) is characterized by a multiplet derived from the final state 4f¹². The distance separating the two parts, which in this case is just under 6 eV, is interpreted as the intra-atomic correlation.
energy [52]. However, we see that the divalent part does not resemble a doublet. This is because XPS measurements using a source with an energy of about 1.5 keV are sensitive to surface effects, resulting in the appearance of a second doublet shifted by about 1 eV toward higher binding energies [11]. Depending on the mutual shift of the doublets, a structure of four or three peaks may appear. A structure similar to the triple one seen in Fig. 2 has been observed, for example, for Yb2Pt6Al15 [20]. A one way to discard the signal from the surface would be to use hard X-rays with photon energy on the order of a few keV [20]. Alternatively, also reducing the energy of the source allows to determine the impact of the surface [11]. However, the small difference in their mutual position (on the order of 0.2 eV) does not allow us to distinguish them as easily as in the case of the divalent part of the valence band. In addition to the beam energy, the observed valence band spectrum is also affected by the temperature. For example, XPS valence bands measured for YbInCu4 at temperatures of 10 and 150 K showed that at a lower temperature the trivalent contribution decreases and the divalent contribution increases, which is naturally due to the decrease in mean valence (of 0.1 in this case) [22].

The measured valence band spectra can be used to determine valence. For this purpose, the relative intensity \( \eta \) is determined from the formula:

\[
\eta = \frac{I^{(2+)}}{I^{(2+)} + I^{(3+)}}.
\]

where \( I^{(2+)} \) and \( I^{(3+)} \) are the integral intensities [11]. The determined value of \( \eta \) is affected by the choice of background correction [22] and the difficulty in separating the surface and volume contributions. Assuming that surface and the volume components of the divalent contribution are equal, we obtain \( \eta \) equal to 0.315. Although the relationship \( v = 3 - \eta \) is usually used to determine the valence \( v \) from the relative intensities in Yb compounds, Kummer et al. have shown that a more accurate result can be obtained using the cubic function

\[
v(\eta) = 3 - 0.55\eta - 0.01\eta^2 - 0.44\eta^3.
\]

Thus, for YbFe4Al8 at room temperature, the determined valence value is 2.81. The effect of surface contributions on the result can be minimized in the future by performing the hard x-ray photoemission spectroscopy (HAXPES) measurements [20]. Using the example of YbFe3Sb12, Okane et al. have shown that low-temperature soft-x-ray synchrotron radiation photoemission spectroscopy (SRPES) can also be very helpful in the valence band analysis of Yb compounds [54].

2. Core level spectra Yb 4d, Fe 2p, and Al 2p

The mean valence of YbFe4Al8 also affects its core-level states. As can be seen in Fig. 3 the core-level

![Fig. 2: Valence band of YbFe4Al8 measured by X-ray photoelectron spectroscopy at room temperature using Al Kα source with photon energy 1487.6 eV. The experimental result is compared with the multiplet structure of the 4f13 → 4f12 transition calculated by Gerken [51].](image-url)
spectrum of the Yb 4d orbital is relatively complex and consists of parts derived from the Yb$^{3+}$ and Yb$^{2+}$ configurations. The Yb 4d spectrum can be interpreted based on theoretically predicted multiplets calculated for Yb$^{3+}$ and Yb$^{2+}$ by Ogasawara et al. The divalent doublet consists of spin-orbit split levels, while the trivalent multiplet arises from more complex 4d-4f Coulomb-exchange interactions resulting from incomplete 4f shell occupancy. The measured spectrum reveals that the contributions from the divalent doublet are rather small, confirming that the valence of the compound is closer to three. This also agrees with the result deduced for the valence band. The presented Yb 4d spectrum can also be compared with the results for Yb metal and other Yb compounds. This comparison confirms the nature of the spectrum similar to the trivalent state of Yb with a smaller divalent contribution. For mixed-valence compound YbInCu$_4$, it has been observed that the intensity of the 4d$_{5/2}$ valent peak around 182 eV strongly decreases with decreasing temperature, which was associated with an increase in valence. Whereas for the mixed-valence alloy (Lu$_{1-x}$Yb$_x$)$_3$Rh$_4$Ge$_{13}$ [58] it has been shown that the peak associated with the Yb$^{3+}$ state located around 185 eV increases significantly with increasing Yb concentration.

The spin-orbit split doublet of asymmetric Fe 2p lines having Doniach-Sunjic shape resembles the corresponding result for pure iron [59] and also shows none of the chemical shifts and charge-transfer satellites characteristic of iron oxides [60], see Fig. 4(a). The determined spin-orbit coupling of Fe 2p doublet (about 13 eV) is similar to the value observed in pure Fe. The position of the Al 2p peak (-72.6 eV) observed in Fig. 4(b) is similar to that of pure metal Al (-72.7 eV). The observed spectral line broadening we ascribe to spin-orbit splitting and differences in level positions for the two non-equivalent Al positions present in the compound. Relativistic atomic calculations, to be presented later, show that the spin-orbit splitting between the Al 2p$_{1/2}$ and Al 2p$_{3/2}$ states is equal to 0.44 eV.

### B. First-principles calculations

#### 1. Theoretical models for Yb and DFT results for XFe$_4$Al$_8$ compounds

Although DFT-based models perform quite well in predicting a range of properties of many rare-earth compounds [61], the single-electron nature of local density approximation (LDA), which does not adequately take correlation into account, severely limits the quality of results obtained for mixed-valence Yb-based compounds [62]. As a result, the LDA (LDA + U) framework yields to a single divalent-type Yb 4f valence band [63, 64], instead of a complex two-part divalent/trivalent band as observed from spectroscopy. The successful step toward overcoming this barrier was made in a paper analyzing the effect of pressure on Yb properties, which used LDA-based Quantum Monte Carlo (QMC) methods to determine the valence and to model the valence band of Yb [62]. An alternative approach to modeling the valence band of Yb compounds is the single-impurity Anderson model (SIAM) [11]. This method, although it leads to a two-part 2+/3+ valence band, is based on the approximation of Yb as an impurity, so it is also not applicable to modeling Yb compounds from first-principles.

Earlier DFT results for YbFe$_4$Al$_8$ were presented in 2019 by Wang et al., in a review paper on RFe$_4$Al$_8$ compounds [65], in which, among other things, the authors calculate lattice parameters of YbFe$_4$Al$_8$ (8.703 and 5.049 Å), spin magnetic moment on Fe (1.559 $\mu_B$), elastic constants, phonon spectra, bulk, shear, and Young’s modulus. Their calculations are based on the full potential (FP) projector augmented wave (PAW) approach.
FIG. 5: Considered antiferromagnetic configurations of spin magnetic moments on Fe sites for YbFe₄Al₈: AFM-A (a), AFM-C (b), and AFM-G (c).

with Perdew-Burke-Ernzerhof (PBE) approximation. In this work, we will improve their model by using a fully relativistic approach and considering an antiferromagnetic configuration. Previously, the antiferromagnetic configuration of Fe sublattices was also considered in the works of Grechnev et al. on RFe₄Al₈ superconductors (R = Sc, Y, Lu) [66–68].

2. Antiferromagnetic configurations, geometry optimization, and site preferences

TABLE I: Crystallographic data for YbFe₄Al₈ as optimized with the FPLO code. The lattice parameters for antiferromagnetic configuration AFM-C are $a = 12.306$ Å and $c = 5.019$ Å, see Fig. 5(b), whereas for basic non-magnetic configuration (NM) lattice parameters are $a = 8.702$ Å and $c = 5.019$ Å.

| AFM-C sg. Fmmm (69) | NM sg. I4/mmm (139) |
|---------------------|---------------------|
| **Yb** | 0 | 0 | 0 | Yb 2a | 0 | 0 | 0 |
| Fe$_{up}$ | -1/4 | 0 | -1/4 | Fe 8f | 1/4 | 1/4 | 1/4 |
| Fe$_{dn}$ | 0 | -1/4 | -1/4 | Al 8i | 0.3307 | 0 | 0 |
| Al$_1$ | 0.1693 | 0.1693 | 0 | Al 8j | 0.2784 | 1/2 | 0 |
| Al$_2$ | 0.3896 | -0.1104 | 0 |

Although it is confirmed that there are two magnetic Fe sublattices in the YbFe₄Al₈, the exact type of antiferromagnetic configuration is not known. The powder neutron diffraction at 4 K for the isostructural compound CaFe₄Al₈ has shown that the magnetic moments on the Fe atoms form antiparallel chains oriented along the c-direction and slightly canted from the axis [69], which can be described as a canted AFM-C configuration. Since the FPLO code only allows the calculation of collinear magnetic configurations, we consider for the YbFe₄Al₈ simplified collinear AFM-C model. As the initial lattice parameters, we take the values 8.714 and 5.026 Å measured for YbFe₄Al₈ [2]. Since the literature does not provide atomic positions for the studied compound, we take initial positions from the isostructural CaFe₄Al₈ (neutron powder data, $T = 4$ K) [69]. As a result of optimizing the lattice parameters and atomic positions, we obtain the AFM-C structure presented in Table I. AFM-C structure can be further reduced to a form with only one Fe sublattice, which results we also present in Table I. We see that the optimized lattice parameters (8.702 and 5.019 Å) are in very good agreement with the experimental results (8.714 and 5.026 Å) [2].

In addition, we have prepared two more models of antiferromagnetic configurations, AFM-A and AFM-G, and compared them in terms of the total energy in order to identify the most favorable and hence the most stable structure at the lowest temperature, see Fig. 5. The AFM-A configuration proven to be unstable, difficult to converge, and its total energy was considerably higher than for the other two. In contrast, the AFM-C configuration is 0.7 eV f.u.$^{-1}$ more stable than AFM-G, so results presented from now on will be based on the AFM-C configuration unless otherwise noted.

On the sidelines of the work to prepare structural models, we decided to answer the question of the preference of Fe atoms to occupy particular sites in crystal structure. For this purpose, we prepared three YbFe₄Al₈ structures in which Fe atoms occupied the 8f, 8i, or 8j sites. In agreement with the experiment [39, 40], our calculations show that Fe atoms prefer to occupy the 8f sites and that the structures with Fe occupying the 8j and 8i sites are higher in energy by 0.58 and 0.97 eV/Fe atom, respectively. The calculated values are relatively high [70], indicating a rather strong preference for Fe to occupy sites 8f.

3. Effect of on-site Coulomb repulsion $U$ on Yb $4f$ orbital

LDA+$U$ calculations for YbFe$_4$Sb$_{12}$ showed that the on-site Coulomb repulsion $U$ significantly affects the position of the Yb $4f$ states in the valence band [46, 47]. In the following, we would like to determine whether the effect that the correction induces is beneficial, against the
previously presented valence band measurements. For this purpose we examine how the properties of YbFe₄Al₈ change as U applied to 4f orbitals increases from 0 to 10 eV. In Fig. 6 we see that the valence band region of the densities of states (DOS) is dominated by two spin-orbit split peaks of Yb 4f states. As a result of the aforementioned limitations of the GGA/GGA + U method, we observe only a single 4f doublet rather than a complex 2+3+ binary spectrum as in the XPS measurement presented earlier. We observe, that as U increases the Yb 4f states shift toward lower energies. Also as U increases, the occupancy of orbital Yb 4f increases, while the occupancy of orbital Yb 5d decreases, see Fig. 7 which shows the close relationship these two orbitals. The occupancy of the 4f orbital for bare GGA is equal to 13.53, which is closest to the experimental value about 13.2 at 300 K. Given the above, we conclude that the most appropriate approximation for the description of YbFe₄Al₈ is the GGA model without the on-site Coulomb repulsion U. Therefore, the detailed results presented below will be based specifically on GGA (PBE).

4. Relativistic atomic energies

Figure 8 shows the calculated relativistic atomic energies, which represent the broadest picture of the electronic structure covering all energy levels of YbFe₄Al₈. Since these are obtained before the self-consistent cycle, they may change after the calculations converge. The results are presented in three consecutive ranges and where readability is maintained, energy levels are assigned to individual orbitals. The levels shown in the top graph do not appear in the results of XPS measurement using a standard X-ray source such as Al-Kα, with a photon energy of 1486.6 eV. The lowest level at -61 keV belongs the most strongly bound electron Yb 1s. The middle panel shows the binding energy range typical of an Al-Kα source such as the one used in the experimental part of this work, while the bottom panel covers the energy range from -120 eV to the Fermi level. The calculated levels for Yb 4d (-183.1 and -173.9 eV), Fe 2p (-706.5 and -694.0 eV), and Al 2p (-69.9 and -69.5 eV) are in good agreement with the measured XPS spectra showed before. The differences are due to Coulomb exchange interactions with the valence band levels, effect of spin polarization, and in case of Al nonequivalent atomic positions in the unit cell. Finally, the part of the XPS spectrum, which covers the area of a few eV around the Fermi level can be interpreted more accurately on the self-consistently calculated valence band structure. For all-electron methods, like FPLO, accurate positions of the core-electrons energy levels in the range up to about 200 eV of binding energy can be also obtained from self-consistent calculations.

5. Densities of states

We will start the valence band analysis by presenting the density of states in the range of a few eV around the Fermi level, see Fig. 9. In this region, the most important contributions come from the Yb 4f and Fe 3d orbitals. 13.53 4f electrons, as determined by Mulliken electron population analysis, uniformly fill the two spin channels. However, as a result of spin-orbit splitting, the 4f states split into two narrow bands with energies of about -0.2 and -1.6 eV. The observed spin-orbit doublet resembles the divalent part of the XPS spectrum, compare Fig. 2. However, in the PBE picture we do not
FIG. 8: The relativistic atomic energies for YbFe₄Al₈ as calculated using FPLO18 in a fully relativistic approach.

observe the second trivalent Yb 4f component present in the XPS spectrum below -5 eV.

Since we are considering a model with the antiferromagnetic ordering of moments on Fe atoms, red and blue colors are used to draw 3d contributions from Fe sublattices with opposite spin polarizations. As can be seen in Fig. 8, the DOSs of the two Fe sublattices are polarized in opposite directions and their resulting spin magnetic moment is fully compensated. In the occupied region, the characteristic maxima of the Fe 3d orbitals are located at about -0.8 eV, just between the split Yb 4f bands. For clarity, the figure does not show contributions from the less occupied valence orbitals, e.g., Yb 5d or Al 3s and 3p. A more complete list of which can be found in the next section of this paper on Mulliken analysis.

6. Density of states at the Fermi level and electronic specific heat coefficient γ

The density of states at the Fermi level [DOS(E_F)] is 9.4 states eV⁻¹ f.u.⁻¹ and consists mainly of contributions from Yb 4f (2.5 states eV⁻¹ f.u.⁻¹) and Fe 3d (3.0 states eV⁻¹ f.u.⁻¹). The DOS(E_F) calculated here is relatively close to the values calculated earlier for the antiferromagnetic phases ScFe₄Al₈, LuFe₂Al₄, and YFe₄Al₈ equal to about 14.5 states eV⁻¹ cell⁻¹ [60] and to a calculated DOS(E_F) value for YbFe₄Sb₁₂ equal to 31 states eV⁻¹ f.u.⁻¹ [40].

In the Sommerfeld model, the electronic specific heat coefficient γ is determined from DOS(E_F) according to the equation \( \gamma = \frac{1}{2} \pi^2 k_B^2 \text{DOS}(E_F) \) [71], where \( k_B \) is Boltzmann constant. For YbFe₄Al₈ this leads to γ equal to 22.2 mJ mol⁻¹ K⁻², which is much lower than experimental γ values for isostructural compounds YFe₂Al₉ (60 mJ mol⁻¹ K⁻²) and LuFe₄Al₈ (75 mJ mol⁻¹ K⁻²) [32, 72]. However, the underestimation of γ is a recognized weakness of the DFT method, resulting from the neglect of spin fluctuations and many-body effects in low-energy excitations [73]. Moreover, the γ value of 22.2 mJ mol⁻¹ K⁻² calculated for YbFe₄Al₈ is more than twice the value of 9.1 mJ mol⁻¹ K⁻² that we obtained for another compound containing lanthanides and 3d-metal (Y₀.₉Tio₁.₀Co₂) [74]. The difference is due to the absence of the 4f contribution in the latter case and the slightly higher filling of the 3d shell in Co than in Fe.

7. Mulliken electronic population analysis

In YbX₄Al₈ compounds, the valence of Yb ions is strongly dependent on the transition metal. For example, the Yb ion is divalent in YbMn₄Al₈ and possibly in a mixed state in YbCr₄Al₈ and YbCu₄Al₈ [57]. The previous results suggest that Yb ion in YbFe₄Al₈ is close to trivalent [35, 75]. However, the valence determined
for YbFe$_4$Al$_8$ from the relative intensity of divalent and trivalent peaks in XPS valence band is 2.81 at room temperature, suggesting occupancy of Yb 4f orbitals close to 13.2. As shown by the measurements [22], mean valence of the Yb compound may decrease with temperature, suggesting that the Yb 4f occupancy in YbFe$_4$Al$_8$ may be above 13.2 close to 0 K.

Tables II and III show the results of the Mulliken electronic population analysis [76]. The application of Mulliken’s approach is possible because the basis of the FPLO code is the method of linear combination of atomic orbitals. For YbFe$_4$Al$_8$, we observe that the charge taken from the Yb and Fe sites (-0.65 and -0.10) is transferred to the Al sites (+0.12 and +0.14). The excess electron number for Yb (-0.65) is very different from -2 or -3, values one would expect for a divalent or trivalent configurations. This is due, among other things, to the fact that first-principles calculations involve a much larger basis than assumed by the conventional valence model (e.g. polarization orbitals Yb 6s and 6p) and also allow fractional occupancy of individual orbitals. Similarly large differences between nominal valence and the calculated occupancy are typically observed in DFT calculations. For Yb in YbFe$_4$Al$_8$ we observe fractional occupation of orbital 4f (13.53) and low occupations of orbitals 5d (1.17) and polarization orbitals 6s and 6p (0.36 and 0.32). For Fe sites, with regard to the ground state electronic configuration of a neutral Fe atom (3d$^6$ 4s$^2$), we observe an increase in the occupation of the 3d orbital while depopulating the 4s orbital.

For comparative analysis, we chose LuFe$_4$Al$_8$, a compound containing a filled 4f shell with a much more stable and simpler to predict electronic structure. The calculated occupancy of the 4f orbital for LuFe$_4$Al$_8$ is 13.96, which is almost the maximum. For LuFe$_4$Al$_8$ we observe a similar picture of charge transfer as for YbFe$_4$Al$_8$, but with a significant difference at the position of the 4f element (charge transfer -0.88 for Lu versus -0.65 for Yb). Comparing in more details the occupation of Yb and Lu, we see that at the cost of over-occupation of Yb 4f orbital (above 13.0), the other three Yb orbitals under consideration (5d, 6s, and 6p) are depopulated compared to LuFe$_4$Al$_8$. Of particular importance is the underoccupancy of the Yb 5d orbital, which leads to a positive deviation of volume from the trend observed for trivalent RF$_4$Al$_8$ compounds. While experiments have shown that the type of transition metal affects the valence of Yb in YbM$_4$Al$_8$ compounds [35], the change of the 4f element between YbFe$_4$Al$_8$ and LuFe$_4$Al$_8$ compounds shows no significant effect on the occupancy of Fe and Al orbitals. However, the greatest changes in electron structure occur on the 4f elements themselves, see Table III.

### 8. Spin and orbital magnetic moments

In the last section we will focus on the detailed analysis of magnetic moments. For YbFe$_4$Al$_8$, the calculated spin magnetic moments on antiferromagnetically oriented Fe sublattices are equal to 1.523 $\mu_B$ and compensate each other. The additional orbital contributions occurring on the Fe atoms are 0.037 $\mu_B$/Fe atom. Since no magnetic moments have been measured for YbFe$_4$Al$_8$ so far, our result can at best be compared with moments experimentally obtained for LuFe$_4$Al$_8$. Neutron diffraction studies at 1.5 K have shown that for LuFe$_4$Al$_8$ the magnetic moments on the Fe atoms are 1.8(2) $\mu_B$ [40]. We can see that the value of the total magnetic moment (spin plus orbital) on the Fe atom for YbFe$_4$Al$_8$ equal to about 1.6 $\mu_B$ is within the range of accuracy of the measurement for LuFe$_4$Al$_8$ [40]. The calculated spin magnetic moments on Fe in YbFe$_4$Al$_8$ (1.523 $\mu_B$) are significantly lower than the corresponding values for bcc Fe (2.16 $\mu_B$) calculated under the same theoretical model, as well as compared to the experimental value for bcc Fe (1.98 $\mu_B$ [77]). The calculated orbital magnetic moments on Fe in YbFe$_4$Al$_8$ (0.037 $\mu_B$/Fe atom) and in bcc Fe (0.045 $\mu_B$/Fe atom) are comparable. However, both of these values are reduced from the experimental value for bcc Fe (0.086 $\mu_B$) [77]. Underestimation

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**TABLE II: Excess electron number for YbFe$_4$Al$_8$ and LuFe$_4$Al$_8$ compounds calculated using FPLO18 in a fully-relativistic approach.**

| formula\site | Yb/Lu | Fe | Al1 | Al2 |
|--------------|-------|----|-----|-----|
| YbFe$_4$Al$_8$ | 0.65  | -0.10 | 0.12 | 0.14 |
| LuFe$_4$Al$_8$ | 0.88  | -0.08 | 0.14 | 0.17 |

**TABLE III: The Mulliken electronic population analysis for YbFe$_4$Al$_8$ and LuFe$_4$Al$_8$ compounds calculated using FPLO18 in a fully-relativistic approach. Notation of lattice sites of AFM-C structure according to Table II.**

| site          | 6s | 5d | 6p | 4f |
|---------------|----|----|----|----|
| YbFe$_4$Al$_8$ |   |    |    |    |
| Yb            | 0.36 | 1.17 | 0.32 | 13.53 |
| LuFe$_4$Al$_8$ |   |    |    |    |
| Lu            | 0.43 | 1.33 | 0.39 | 13.96 |

| site          | 4s | 3d | 4d | 4p |
|---------------|----|----|----|----|
| YbFe$_4$Al$_8$ |   |    |    |    |
| Yb            | 0.65 | 6.73 | 0.11 | 0.42 |
| LuFe$_4$Al$_8$ |   |    |    |    |
| Lu            | 0.64 | 6.74 | 0.11 | 0.42 |

| site          | 3s | 3p | 3d |
|---------------|----|----|----|
| YbFe$_4$Al$_8$ |   |    |    |
| Yb            | 1.16 | 1.73 | 0.28 |
| LuFe$_4$Al$_8$ |   |    |    |
| Lu            | 1.15 | 1.75 | 0.28 |

| site          | 3s | 3p | 3d |
|---------------|----|----|----|
| YbFe$_4$Al$_8$ |   |    |    |
| Yb            | 1.12 | 1.75 | 0.30 |
| LuFe$_4$Al$_8$ |   |    |    |
| Lu            | 1.12 | 1.77 | 0.31 |
of the orbital magnetic moment for transition metals is considered as one of the weaknesses of GGA and LDA. For YbFe$_4$Al$_8$ we do not observe any magnetic moments on the Yb and Al sites. Since the calculations based on the AFM-C model with a single Yb position cannot account for a possible antiferromagnetic ordering on Yb atoms, we prepared an alternative structural model with two non-equivalent Yb positions in addition to two non-equivalent Fe positions. The calculations for this model, however, led to identical results as presented for a simpler model with a single Yb position, showing no magnetic moments on the Yb atoms. However, it is worth noting the limitations of our DFT model, which lead to a description of the Yb 4$f$ valence states that is inconsistent with the results observed in XPS and thus can affect the obtained magnetic state of Yb ions. In conclusion, although the results of our calculations indicate the absence of a magnetic moment on Yb ions, calculations within a more advanced theoretical model than the one used in this work are needed to unambiguously resolve the question of the magnetic state of Yb ions in YbFe$_4$Al$_8$.

IV. SUMMARY AND CONCLUSIONS

We have investigated the valence state of YbFe$_4$Al$_8$ using X-ray photoelectron spectroscopy and first-principles calculations. We interpreted XPS measurements of the valence band and selected core-levels based on previously predicted theoretical energy level multiplets. We have identified that the XPS valence band of YbFe$_4$Al$_8$ consists of two contributions coming from divalent (Yb$^{2+}$) and trivalent (Yb$^{3+}$) configuration. The YbFe$_4$Al$_8$ valence is determined from the relative intensity of divalent and trivalent peaks is 2.81 at room temperature.

The second part of the paper consisted of first-principles calculations performed using a full-potential local-orbital scheme (FPLO). Since atomic positions of YbFe$_2$Al$_{10}$ are not available in the literature, we performed full structure optimization and presented the resultant complete structural model. Due to the antiferromagnetic arrangement of magnetic moments revealed in the YbFe$_4$Al$_8$ compound, we considered several collinear antiferromagnetic configurations (AFM-A, AFM-C, and AFM-G), of which AFM-C was found to be the most stable. The AFM-C configuration is characterized by the arrangement of magnetic moments on Fe in the form of antiparallel chains. The calculations predicted no magnetic moments at the Yb and Al sites and showed that the antiparallel moments at the Fe chains completely compensate. Mulliken analysis showed that the charge taken from the Yb and Fe sites is transferred to Al and that the fractional occupation of the 4$f$ orbital is about 13.5 (at 0 K), although the valence deduced from the XPS spectra suggests an occupation closer to 13.2 (at 300 K). The calculated valence band densities of states presenting a spin-orbit split Yb 4$f$ doublet stand in opposition to the complex XPS spectrum consisting of a divalent doublet and a trivalent multiplet of Yb 4$f$ states. In order to more accurately describe the valence band and resolve the magnetism of Yb ions, calculations beyond the GGA must be performed.

ACKNOWLEDGMENTS

We acknowledge the financial support of the National Science Centre Poland under the decision DEC-2018/30/E/ST3/00267. Part of the computations was performed on the resources provided by the Poznań Supercomputing and Networking Center (PSNC). We thank Paweł Lesniak and Daniel Depcik for compiling the scientific software and administration of the computing cluster at the Institute of Molecular Physics, Polish Academy of Sciences. We thank Justyna Rychły and Justyna Snarski-Adamski for reading the manuscript and useful comments.

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