Electronic structure and magnetism of pristine and Fe-doped α-MnO₂ from density-functional theory with extended Hubbard functionals

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We present a first-principles investigation of the structural, electronic, and magnetic properties of the pristine and Fe-doped α-MnO₂ using density-functional theory with extended Hubbard functionals. The onsite U and intersite V Hubbard parameters are determined from first principles and self-consistently using density-functional perturbation theory in the basis of Löwdin-orthogonalized atomic orbitals. Among the ferromagnetic and four types of antiferromagnetic (AFM) orderings for the pristine α-MnO₂ we find the C2-AFM spin configuration to be the most energetically favorable, in agreement with the experimentally observed AFM state. The computed lattice parameters, magnetic moments, and band gaps are overall in good agreement with the experimental ones when both the onsite and intersite Hubbard corrections are included. For the Fe-doped α-MnO₂ two types of doping are considered: Fe insertion in the 2 × 2 tunnels and partial substitution of Fe for Mn. The calculated formation energies show that Fe insertion is energetically favorable, in agreement with experiments. We find that both types of doping preserve the C2-AFM spin configuration of the host lattice. The oxidation state of Fe is found to be 2+ and 4+ in the case of the interstitial and substitutional doping, respectively, while the oxidation state of Mn is 4+ in both cases. This work opens a door for accurate studies of other Mn oxides and complex transition-metal compounds when the localization of 3d electrons occurs in the presence of strong covalent interactions with ligands.

I. INTRODUCTION

Manganese dioxide is an inexpensive and highly reactive material and it has attracted great interest due to its structural diversity with different chemical and physical properties [1]. In particular, α-MnO₂ is made up of 2 × 2 channels due to edge and corner sharing of MnO₆ octahedra along the c axis, and there are two types of oxygen atoms having sp² or sp³ hybridization (see Fig. 1). Such a tunnel-type structure generally can incorporate external cations (e.g. Li⁺, K⁺, NH₄⁺, Ba²⁺, Na⁺, Pt²⁺) [2, 3], transition-metal elements (e.g. Ti, V, Cr, Fe, Co, Ni, Cu, Nb, Ru, Ag) [4–10], rare-earth elements (e.g Ce) [11], and H₂O molecules which can substantially alter its properties. α-MnO₂ has very broad applications, e.g. it is used in Li-, Na-, and Mg-ion batteries [12–14], Zn-air batteries, supercapacitors, electrochemical energy storage systems [15], catalysts in water oxidation [16], and many more [17, 18]. Experimentally, it is reported to be a semiconductor [19] with an antiferromagnetic ordering below TN = 24.5 K, and it crystallizes in a tetragonal crystal structure with space group I4/m (87) [20]. Another experimental study showed that spin glass transition occurs in α-MnO₂ at 50 K due to frustration [21–23].

Many studies seek doping in α-MnO₂ because it has large cavities. The doping enhances the stability of this material [2–10] and thus it allows for potential applications in the range from catalysts to energy storage systems. Generally, two types of doping are considered: i) the interstitial one, where the dopant is placed in the center of the 2 × 2 tunnels, and ii) the substitutional one, where the dopant is partially substituted for Mn atoms [24]. Of particular interest is the Fe-doping of α-MnO₂ because Fe atoms have an atomic radius similar to the one of Mn atoms, and hence Fe can partially substitute Mn or it can easily fit into the cavity. α-MnO₂ doped with Fe is used in industrial processes of preparing cyclohexanone by photocatalytic oxidation process of cyclohexane [25]. This compound is not only cheaper but also it shows highest photo-catalytic activity compared to other catalysts [25]. Moreover, Fe doping of α-MnO₂ makes it better catalyst for oxygen evolution reaction and oxygen reduction reaction and an efficient electrode for Zn–air batteries [26]. However, despite numerous experimental studies of the Fe doping of α-MnO₂ [4, 24, 27, 28, 30] the understanding of the changes in the crystal structure, electronic and magnetic properties, and the oxidation state of Fe and Mn ions is far from being complete. Only a few theoretical studies have attempted to shed more light on this problem [4, 31] since the computational modelling of the pristine and Fe-doped α-MnO₂ is very challenging due to a complex interplay between structural, electronic, and magnetic degrees of freedom.

First-principles simulations of the pristine and Fe-doped α-MnO₂ using density-functional theory (DFT) [32, 33] with local and semi-local exchange-correlation (xc) functionals encounter serious problems due to the presence of localized and partially-filled 3d

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electrons. In particular, local spin-density approximation (LSDA) and spin-polarized generalized-gradient approximation ($\sigma$-GGA) are unable to produce accurate results due to large self-interaction errors for 3d electrons [34, 35]. Therefore, more accurate approaches need to be applied beyond standard DFT. Many methods have been used to study $\alpha$-MnO$_2$ and most of them are based on Hubbard-corrected DFT (DFT+$U$ [36–38]) [14, 39–42] and DFT with hybrid functionals (e.g. HSE06 [43, 44]) [40, 41]. While for hybrid functionals the main bottlenecks are the high computational cost and difficulty to tune the amount of exact exchange, in DFT+$U$ the value of Hubbard $U$ is unknown and often it is chosen empirically which posses ambiguities on the final results of interest, as discussed in the following.

Most DFT-based studies of $\alpha$-MnO$_2$ consider collinear spin configurations: the ferromagnetic (FM) and various types of the antiferromagnetic (AFM) orderings. In the AFM case, magnetic structures such as A2-AFM, C-AFM, C2-AFM, and G-AFM have been studied [10, 16, 39, 40, 45, 46]. On the one hand, DFT with hybrid functionals predicts FM to be lower in energy than AFM [40], thus contradicting to the experimental observation of the AFM state [20]. On the other hand, DFT+$U$ predicts different trends depending on the value of the Hubbard $U$ parameter. In the vast majority of the DFT+$U$ studies of $\alpha$-MnO$_2$, the $U$ parameter is chosen empirically in the range from 1 to 6 eV [39, 40, 45] such that DFT+$U$ reproduces well some experimental property of interest (e.g., the band gap) [47]. However, when selecting $U$ empirically, it is often forgotten to pay attention also to the type of the Hubbard projectors that are used in various electronic-structure codes, as indeed the DFT+$U$ results are extremely sensitive not only to the value of $U$ but also to the type of these projectors [48–50]. Only in one DFT+$U$ study of $\alpha$-MnO$_2$ so far the value of $U$ was computed from first principles (using the constrained DFT) [14], though no information is provided regarding the magnetic ordering used. Therefore, a consistent comparison of the FM and various types of AFM orderings in the pristine and Fe-doped $\alpha$-MnO$_2$ using first-principles Hubbard parameters have not been performed so far. Moreover, in all previous Hubbard-corrected DFT studies only the onsite Hubbard $U$ correction was included, while the intersite Hubbard interactions were fully disregarded even though they are known to be very important in MnO$_2$ polymorphs due to strong Mn(3d)–O(2p) hybridization [50].

In this paper, we present a fully first-principles study of the structural, electronic, and magnetic properties of the pristine and Fe-doped $\alpha$-MnO$_2$ using DFT with extended Hubbard functionals (DFT+$U+V$) [51]. We compute the onsite $U$ and intersite $V$ Hubbard parameters using density-functional perturbation theory (DFPT) [52, 53] in the basis of Löwdin-orthogonalized atomic orbitals. The Hubbard parameters are determined using the self-consistent procedure [53–55] to ensure the full consistency between the crystal and electronic structures. We find that C2-AFM is the most energetically favorable magnetic ordering in the pristine $\alpha$-MnO$_2$ which is in line with the Goodenough-Kanamori rules [56, 57]. The computed formation energy (FE) of the Fe-doped $\alpha$-MnO$_2$ shows that the interstitial doping is energetically favorable in agreement with experiments. The C2-AFM spin configuration is found to be robust with respect to the Fe doping, both interstitial and substitutional. Using the method of Ref. [5] we find that the oxidation state (OS) of Fe is 2+ or 4+ depending on the type of doping (the former corresponds to the interstitial doping while the latter to the substitutional one), while the OS of Mn is 4+ irrespectively of the doping type.

The paper is organized as follows. Section II presents the basics of DFT+$U+V$ and DFPT for computing Hubbard parameters, and Sec. III contains technical details of the calculations. In Sec. IV we present our findings for the structural, electronic, and magnetic properties of the pristine $\alpha$-MnO$_2$ for different types of collinear magnetic orderings, and Sec. V discusses our results for the Fe-doped $\alpha$-MnO$_2$ including the calculation of the FE and OS. In Sec. VI we give our conclusions.

II. COMPUTATIONAL METHOD

In this section we briefly discuss the basics of DFT+$U+V$ [51, 59] and of DFPT for computing Hubbard parameters [52, 53]. All equations can be easily reduced to DFT+$U$ by simply setting $V = 0$. For the sake of simplicity, the formalism is presented in the framework of norm-conserving (NC) pseudopotentials (PPs) in the collinear spin-polarized case. The generalization to the ultrasoft (US) PPs and the projector augmented wave (PAW) method can be found in Ref. [53]. Hartree atomic units are used.
A. The basics of DFT+$U$+$V$

In DFT+$U$+$V$, an extended Hubbard correction energy $E_{U+V}$ is added to the approximate DFT energy $E_{\text{DFT}}$ [51]:

$$E_{\text{DFT}+U+V} = E_{\text{DFT}} + E_{U+V}. \quad (1)$$

At variance with DFT+$U$ that contains only onsite interactions scaled by $U$, DFT+$U+V$ contains also intersite interactions between an atom and its surrounding ligands scaled by $V$. In the case of pristin and Fe-doped $\text{MnO}_2$, the onsite $U$ correction is needed for the Mn(3d) and Fe(3d) states, while the intersite $V$ correction can be used for Mn(3d)–O(2p) and Fe(3d)–O(2p) interactions [60]. In the simplified rotationally-invariant formulation [38] the extended Hubbard correction energy reads:

$$E_{U+V} = \frac{1}{2} \sum_I \sum_{\sigma m m'} U^I (J_{m m'} - n_{m m'}^{I \sigma}) n_{m m}^{I \sigma},$$

$$- \frac{1}{2} \sum_I \sum_{J \neq I} \sum_{\sigma m m'} V^{IJ} n_{m m'}^{I \sigma} n_{m m}^{J \sigma}, \quad (2)$$

where $I$ and $J$ are the atomic site indices, $m$ and $m'$ are the magnetic quantum numbers associated with a specific angular momentum [$l = 2$ for Mn(3d) and Fe(3d), and $l = 1$ for O(2p)], $U^I$ and $V^{IJ}$ are the effective onsite and intersite Hubbard parameters, and the star in the sum denotes that for each atom $I$ the index $J$ covers all its neighbors up to a given distance.

The generalized occupation matrices $n_{m m'}^{I \sigma}$ are based on a projection of the Kohn-Sham (KS) states on localized orbitals $\phi^I_m (r)$ of neighbor atoms:

$$n_{m m'}^{I \sigma} = \sum_{v, k} f_v^I (\phi^I_{m, v, k} | \phi^I_{m', v, k}), \quad (3)$$

where $v$ and $\sigma$ are the band and spin labels of the KS wavefunctions $\psi^I_{m, v, k} (r)$, respectively, $k$ indicate points in the first Brillouin zone (BZ), $f_v^I$ are the occupations of the KS states, and $\phi^I_{m, v, k} (r) = \phi^I_m (r - R_I)$ are localized orbitals centered on the $I$th atom of type $I$ at the position $R_I$. It is convenient to establish a short-hand notation for the onsite occupation matrix: $n_{m m'}^{I \sigma} \equiv \phi^I_{m, v, k}$, which is used in the standard DFT+$U$ approach [that corresponds to the first line of Eq. (2)]. The two terms in Eq. (2) (i.e., proportional to the onsite $U^I$ and intersite $V^{IJ}$ couplings) counteract each other: the onsite term favors localization on atomic sites (thus suppressing hybridization with neighbors), while the intersite term favors hybridized states with components on neighbor atoms. More details about DFT+$U+V$ can be found in Refs. [51, 61, 62]. Thus, computing $U^I$ and $V^{IJ}$ is crucial to determine the degree of localization of 3d electrons on Mn and Fe sites and the degree of hybridization of these 3d electrons with 2p electrons centered on neighboring O sites. In the next subsection we discuss briefly how these Hubbard parameters can be computed using DFPT.

B. Hubbard parameters from DFPT

In Hubbard-corrected DFT the values of Hubbard parameters are not known a priori, and hence often these values are chosen empirically such that the final results of simulations match some experimental properties of interest. This is, though, fairly arbitrary and, hence, first-principles calculations of Hubbard parameters are essential and highly desirable. In this paper, we compute $U$ and $V$ from a generalized piece-wise linearity condition imposed through linear-response theory [63], based on density-functional perturbation theory (DFPT) [52, 53]. DFPT has proven to be effective for determining Hubbard parameters for a variety of systems with complex magnetic properties [64–67]. Within this framework, the Hubbard parameters are defined as [63]:

$$U^I = (\chi_0^{-1} - \chi^{-1})_{II}, \quad V^{IJ} = (\chi_0^{-1} - \chi^{-1})_{IJ}, \quad (4)$$

where $\chi_0$ and $\chi$ are the bare and self-consistent susceptibilities which measure the response of atomic occupations to shifts in the potential acting on individual Hubbard manifolds. $\chi$ is defined as $\chi_{IJ} = \sum_{\sigma m} (dn^{I \sigma}_{m m} / d\alpha^J_m)$, where $\alpha^J$ is the strength of the perturbation of electronic occupations of the $J$th site, and it is computed at self-consistency of the DFPT calculation, while $\chi_0$ has a similar definition but it is computed before the self-consistent re-adjustment of the Hartree and xc potentials [52]. The response of the occupation matrix is computed in a unit cell as:

$$\frac{dn^{I \sigma}_{m m'}}{d\alpha^J} = \frac{1}{N_q} \sum_{q} \sum_{s} e^{iq\cdot(R_l - R_{l'})} \Delta^J_s n^{I \sigma}_{m m'}, \quad (5)$$

where $q$ is the wavevector of the monochromatic perturbation, $N_q$ is the total number of $q$'s, $\Delta^J_s n^{I \sigma}_{m m'}$ is the lattice-periodic response of atomic occupations to a $q$-specific monochromatic perturbation, $I \equiv (l, s)$ and $J \equiv (l', s')$, where $s$ and $s'$ are the atomic indices in unit cells while $l$ and $l'$ are the unit cell indices, $R_l$ and $R_{l'}$ are the Bravais lattice vectors. The $q$ grid must be chosen dense enough to make the atomic perturbations decoupled from their periodic replicas. More details about this approach can be found in Refs. [52, 53]. It is important to note that the main advantage of DFPT is that it does not require the usage of computationally expensive supercells contrary to the original linear-response formulation of Ref. [63].

Finally, it is very important to remind that the values of the computed Hubbard parameters are strongly dependent on the type of Hubbard projector functions $\phi^I_m (r)$ that are used in Eq. (3). In this work we use the atomic orbitals orthogonalized using the Löwdin method [68, 69]. In fact, it has been shown in previous studies that Hubbard-corrected DFT with this type of Hubbard projectors and respective Hubbard parameters computed using DFPT gives an accurate description of various materials’ properties [70–74]. In particular, in
Ref. [50] we have shown that the most accurate description of the structural, electronic, and magnetic properties of $\beta$-MnO$_2$ is obtained using Löwdin-orthogonalized atomic orbitals as Hubbard projectors.

### III. TECHNICAL DETAILS

All calculations were performed using the QUANTUM ESPRESSO package [75–77]. For the pristine $\alpha$-MnO$_2$, 5 collinear magnetic orderings are considered: FM, AFM, C-AFM, C2-AFM, and G-AFM (see Fig. 2). The first 4 magnetic orderings have unit cells with 24 atoms, whereas G-AFM was modelled using a supercell of size $1 \times 1 \times 2$ containing 48 atoms. For the Fe-doped $\alpha$-MnO$_2$, also 5 collinear magnetic orderings are considered: interstitial (labeled as “A” and “D”) having 25 atoms and substitutional (“B”, “C”, and “E”) having 24 atoms in the simulation cell as shown in Fig. 7.

We have used the xc functional constructed using $\sigma$-GGA with the PBEsol prescription [78]. PPs were chosen based on the SSSP library v1.1 (precision) [79, 80]: we have used mn$_{\text{pbesol-v1.5.uapp.F.UPF}}$ (GBRV library v1.5 [81]), Fe$_{\text{pbesol-n-kjpaw.psl.0.1.UPF}}$ and Fe$_{\text{pbesol-sp-kjpaw.psl.0.2.1.UPF}}$ (Pslibrary v0.3.1 [82]). For metallic ground states, we used the Marzari-Vanderbilt (MV) smearing [83] with a broadening parameter of $2 \times 10^{-2}$ Ry. The crystal structure for all spin configurations was optimized at three levels of theory (DFT, DFT$+U$, and DFT$+U+V$) using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [84] with the convergence thresholds of $10^{-6}$ Ry, $10^{-5}$ Ry/Bohr, and 0.5 KBar for the total energy, forces, and pressure, respectively. For structural optimizations, the $k$ points sampling of the first BZ was done using a uniform Γ-centered mesh of size $4 \times 4 \times 12$ for all spin configurations except G-AFM for which a $4 \times 4 \times 6$ mesh was used. KS wavefunctions and potentials were expanded in plane waves up to a kinetic-energy cutoff of 90 and 1080 Ry, respectively. Total energies were computed using denser $k$ points meshes of size $8 \times 8 \times 24$ and $8 \times 8 \times 12$, respectively, and the KS wavefunctions and potentials were expanded using higher kinetic-energy cutoffs of 150 and 1800 Ry, respectively (to ensure a $\sim$ 1 meV accuracy when comparing the total and formation energies). PDOS was plotted using a Gaussian smearing with a broadening parameter of $4.4 \times 10^{-3}$ Ry.

DFT$+U$ and DFT$+U+V$ calculations were performed using the Löwdin-orthogonalized atomic orbitals as Hubbard projector functions [68, 69]. Hubbard $U$ and $V$ parameters were computed using DFPT [52, 53] as implemented in the HP code [85] which is part of QUANTUM ESPRESSO. Hubbard parameters are listed in Tables I and III, and they will be discussed in detail in the following. We have used uniform Γ-centered $k$ and $q$ points meshes of size $2 \times 2 \times 6$ and $1 \times 1 \times 3$, respectively, for all spin configurations (for the pristine and Fe-doped $\alpha$-MnO$_2$ except G-AFM for which we have used $k$ and $q$ points meshes of size $2 \times 2 \times 4$ and $1 \times 1 \times 2$, respectively. KS wavefunctions and potentials were expanded in plane waves up to a kinetic-energy cutoff of 60 and 720 Ry, respectively, giving the accuracy of computed Hubbard parameters of $\sim$ 0.01 eV. It is important to stress that we have used a self-consistent procedure for the calculation of $U$ and $V$ as described in detail in Ref. [53] which consists of cyclic calculations containing structural optimizations and recalculations of Hubbard parameters for each new geometry.

The total energies of bulk Mn and Fe are required for computing the formation energies for Fe-doped $\alpha$-MnO$_2$. The $\alpha$-phase of bulk Mn consists of 58 atoms in its simplified AFM configuration [86, 87], whereas the most stable Fe structure contains 2 atoms in the $\text{bcc}$ unit cell. The crystal structures of bulk Mn and Fe were optimized at the DFT level (and DFT$+U$ for bulk Fe) using the BFGS algorithm with the convergence thresholds as for the pristine and Fe-doped $\alpha$-MnO$_2$. The optimizations were performed using a uniform Γ-centered $k$ points mesh of size $6 \times 6 \times 6$ for bulk Mn and $8 \times 8 \times 8$ for bulk Fe. KS wavefunctions and potentials for both materials were expanded in plane waves up to a kinetic-energy cutoff of 90 and 1080 Ry, respectively. Total energies were computed using denser $k$ points meshes of size $8 \times 8 \times 8$ for bulk Mn and $12 \times 12 \times 12$ for bulk Fe, while the KS wavefunctions and potentials were expanded up to a kinetic-energy cutoff of 150 and 1800 Ry, respectively. For both materials we have used the MV smearing with a broadening param-

![FIG. 2. Four collinear AFM configurations of $\alpha$-MnO$_2$: (a) A2-AFM, (b) C-AFM, (c) C2-AFM, and (d) G-AFM. Mn atoms with spin-up and spin-down alignments are shown in light brown and blue colors, respectively, while oxygen atoms are shown in yellow color. For FM, all Mn atoms have the same spin alignment (not shown).](image)
magnetic ordering. When using the extended formulation of DFT+V, five collinear magnetic configurations of Mn(3d) states and intersite V between Mn(3d) and O(2p) states are computed in the frameworks of DFT+U and DFT+U+V (PBEsol functional) using Löwdin-orthogonalized atomic orbitals as Hubbard projector functions.

Table I shows self-consistent Hubbard parameters for five collinear magnetic configurations of α-MnO₂ (FM, A2-AFM, C-AFM, C2-AFM, and G-AFM) computed using DFPT in the basis of Löwdin-orthogonalized atomic orbitals as described in Sec. II B. As in the case of β-MnO₂, we find that the value of Hubbard U varies marginally depending on the type of magnetic ordering. When using the extended formulation of DFT+U+V by incorporating also intersite V, the value of U increases slightly due to changes in the electronic screening. In practice, in the DFT+U+V framework the size of the response matrices χ and χ₀ is larger than in the DFT+U case because we compute the response not only of Mn(3d) states but also of O(2p) states. Hence, when inverting these response matrices there is a mixing of all matrix elements including those that describe a coupling of Mn(3d) and O(2p) states, and the final values of U and V are obtained according to Eq. (4).

As can be seen from Table I, the intersite Hubbard V parameters are smaller than the onsite Hubbard U by a factor of 6 – 9. Despite this fact, the relatively small V values turn out to be important to improve the accuracy of various ground-state properties of α-MnO₂ as will be shown in the following, and in analogy with findings for β-MnO₂ [50].

### IV. RESULTS AND DISCUSSION FOR PRISTINE α-MN O₂

#### A. Hubbard parameters

In previous studies it was shown that the values of Hubbard parameters depend on a type of Hubbard projectors, pseudopotentials, oxidation state of transition-metal elements, xc functional, chemical environment, etc. [49, 50, 72, 88, 89]. In particular, in Ref. [50] it is shown for β-MnO₂ that the values of Hubbard U parameters for Mn(3d) states differ by 1.4 – 2.2 eV depending on whether nonorthogonalized or orthogonalized atomic orbitals are used as Hubbard projector functions. Since it was concluded that the highest accuracy is obtained when using orthogonalized atomic orbitals, here we present results obtained using this type of Hubbard projectors.

Table I shows self-consistent Hubbard parameters for five collinear magnetic configurations of α-MnO₂ (FM, A2-AFM, C-AFM, C2-AFM and G-AFM) computed using DFPT in the basis of Löwdin-orthogonalized atomic orbitals as described in Sec. II B. As in the case of β-MnO₂, we find that the value of Hubbard U varies marginally depending on the type of magnetic ordering. When using the extended formulation of DFT+U+V by incorporating also intersite V, the value of U increases slightly due to changes in the electronic screening. In practice, in the DFT+U+V framework the size of the response matrices χ and χ₀ is larger than in the DFT+U case because we compute the response not only of Mn(3d) states but also of O(2p) states. Hence, when inverting these response matrices there is a mixing of all matrix elements including those that describe a coupling of Mn(3d) and O(2p) states, and the final values of U and V are obtained according to Eq. (4).

#### B. Structural properties

α-MnO₂ has a tetragonal crystal structure which is described by two lattice parameters a and c [20]. The detailed comparison of these lattice parameters and the cell volume V at three levels of theory and for different magnetic orderings is presented in Table S1 in the Supplemental Material (SM) [90], while here we discuss briefly only the trends. DFT underestimates the a parameter, while c is very close to the experimental value, and hence overall the cell volume is also underestimated by 3 – 4 %. In contrast, adding the Hubbard U correction leads to a and c which are larger than the experimental ones, and the cell volume is overestimated by 3 – 6 %. The best agreement with the experiments is achieved at the level of DFT+U+V: the optimized a parameter falls in the range of experimental values or slightly overestimated, while c is also slightly overestimated, and the cell volume is within 1 – 3 % compared to experiments. Within DFT+U+V, three types of magnetic orderings (C-AFM, C2-AFM, and G-AFM) give the most accurate predictions of the lattice parameters and the cell volume. Importantly, at all levels of theory we find that the cell remains tetragonal in agreement with experiments and in contrast to previous works that reported a small monoclinic distortion [39, 40]. Such a discrepancy with respect to previous theoretical studies could be due to the fact that in this work we use more stringent computational setup.

To be more specific, we focus on the C2-AFM ordering that was also studied in detail in previous works [39, 40] and because this is the most energetically favorable ordering as will be shown in Sec. IV C. Table II summarizes the crystal structure parameters, bond lengths and angles for this spin configuration that were optimized at
TABLE II. Comparison of experimental and theoretical (computed for C2-AFM using DFT, DFT+$U$, and DFT+$U$+$V$) crystal structure parameters (CSP) for the pristine $\alpha$-MnO$_2$ [see Fig. 2 (c)]: the lattice parameters $a$ and $c$ (in Å), the cell volume $V$ (in Å$^3$), the bond lengths $d_1$ and $d_2$ (in Å), and the bond angles $\theta_1$ and $\theta_2$. DFT and DFT+$U$ structures have lower symmetry, hence the bond lengths $d_1$ (and $d_2$) take multiple values.

![Energetics](https://example.com/energetics.png)

**FIG. 3.** Total energy difference per formula unit (in meV) for five collinear magnetic orderings of the pristine $\alpha$-MnO$_2$ (FM, A2-AFM, C-AFM, C2-AFM, G-AFM) computed at three levels of theory (DFT, DFT+$U$, and DFT+$U$+$V$) using the PBEsol functional. For each case, the Hubbard parameters $U$ and $V$ were computed using DFPT and Löwdin-orthogonalized atomic orbitals, and they are listed in Table I.

C. Energetics

Experimentally it is known that the pristine $\alpha$-MnO$_2$ has an AFM ordering below the Néel temperature of 24.5 K [20], however the precise direction of the atomic magnetic moments is not known. In this respect, computational studies based on DFT could be useful as they might suggest what type of the magnetic ordering is the most energetically stable. In particular, DFT+$U$ predictions are very sensitive not only to the value of $U$ but also to the type of Hubbard projector functions. For example, in Ref. [40] it is reported that for the effective $U \geq 2.0$ eV and when using nonorthogonalized atomic orbitals [95] as Hubbard projector functions the FM ordering is the most energetically favorable compared to all types of the AFM ordering. In contrast, in Refs. [41, 45, 96] it was found that FM is the most energetically stable for the effective $U \gtrsim 4.0$ eV and when using PAW Hubbard projectors. In this work we do not use empirical values of $U$ contrary to previous works, and hence here we do not provide ranges of $U$ for which FM or AFM is the most energetically stable. Instead, we use first-principles Hubbard parameters reported in Table I respectively for each spin configuration and check which one has the lowest energy. We use exactly the same approach as in Ref. [50] for $\beta$-MnO$_2$ (in particular, see the discussion in Sec. IV C of Ref. [50]). Interestingly, we find that using our first-principles values of Hubbard parameters ($U \approx 6-7$ eV and $V \approx 0.7-1.2$ eV, see Table I) and Löwdin-orthogonalized atomic orbitals, three types of the AFM ordering (C-AFM, C2-AFM, and G-AFM) are more energetically favorable than the FM one. This finding clearly underlines that the choice of Hubbard projector functions is as crucial as the values of Hubbard parameters, and hence both should be considered when comparing conclusions from different works. However, one should keep in mind that there are also other differences between this work and previous studies, such as e.g. different pseudopotentials, which could also affect the final DFT+$U(+V)$ predictions [49].

As can be seen in Fig. 3, C2-AFM is the most energetically favorable spin configuration at all levels of theory. However, at the levels of DFT+$U$ and DFT+$U$+$V$, C2-AFM has larger energy difference compared to C-AFM and G-AFM. This shows that Hubbard-corrected DFT stabilizes C2-AFM more than standard DFT. It is worth mentioning that DFT+$U$ and DFT+$U$+$V$ show similar trends for the energetics of the pristine $\alpha$-MnO$_2$, hence the intersite $V$ corrections turn out to be no so crucial contrary to what is the case for $\beta$-MnO$_2$ [50]. However, it will be shown in the following that for the Fe-doped $\alpha$-MnO$_2$ the intersite Hubbard corrections are crucial to stabilize the C2-AFM spin configuration of the host lattice. Finally, we note that the C2-AFM ordering is consistent with the Goodenough-Kanamori rules [56, 57].
even though the bond angles are not 90° and 180° as required by the latter (see Table II).

D. Magnetic moment

Figure 4 shows a comparison of the magnetic moments on Mn atoms in the pristine α-MnO$_2$ as measured in experiments and as computed using three levels of theory for five magnetic orderings. The magnetic moments were determined using the projection method, i.e. by computing the onsite occupation matrix ($I = J$) using Eq. (3) and then by taking a difference between the spin-up and spin-down components. It can be seen from Fig. 4 that DFT underestimates the magnetic moments by about 29 – 36% depending on the type of the magnetic ordering. DFT+$U$ provides the closest agreement with experiments with magnetic moments being underestimated by 6 – 15%, while DFT+$U$+$V$ gives magnetic moments that fall in the range between the DFT and DFT+$U$ predictions. This result is not surprising, since the onsite $U$ correction localizes the 3$d$ electrons on the Mn atoms and reduces the hybridization with the ligand states, and thus the magnetic moments are increased. Instead, within DFT+$U$+$V$ the hybridization with ligands is partially restored while still preserving the localized nature of the 3$d$ electrons, and as a consequence the magnetic moments are slightly decreased.

For our best candidate (i.e. C2-AFM) with our best approach (DFT+$U$+$V$) the computed magnetic moment is 3.31 $\mu_B$ which differs from the experimental ones by 16 – 18%. Thus, there is definitely a room for improvements, and this could be possibly achieved by including also the Hund’s $J$ interactions [97–99], but this goes beyond the frames of this study.

E. Band gap

Pristine α-MnO$_2$ is a semiconductor, but the exact value of the band gap is difficult to determine experimentally since it is hard to synthesize pure samples without dopants. Noticeable works are Refs. [19, 101, 102] that reported experimental band gap values in the range from 1.61 to 2.1 eV. Previous computational studies reported quite scattered values of band gaps depending on the method used. For example, in Ref. [40] the HSE06 functional was used that predicted FM as the ground state with the respective band gap of 2.2 eV. In the same work, the authors used DFT+$U$ with the empirical $U = 1.6$ eV and nonorthogonalized atomic orbitals as Hubbard projectors predicting C2-AFM to be the most energetically stable with the band gap of 0.94 eV. In another DFT+$U$ study [39], empirical $U = 2.8$ eV and $J = 1.2$ eV with PAW Hubbard projectors were used giving the band gap of 1.33 eV for C2-AFM. Finally, in the DFT+$U$ study of Ref. [103] the empirical $U = 3.9$ eV was used for C2-AFM giving the gap of 0.70 eV. Hence, in all these studies the band gap values lie outside the experimental range.

Figure 5 shows a comparison of band gaps computed using DFT, DFT+$U$, and DFT+$U$+$V$ for five magnetic orderings of the pristine α-MnO$_2$. We can see that on average DFT underestimates the band gaps the most, followed by DFT+$U$ and then by DFT+$U$+$V$. As in the case of β-MnO$_2$, the band gap is very sensitive to the type of the magnetic ordering [50]. Here we find that DFT+$U$+$V$ again provides the most accurate band gaps, with C-AFM, C2-AFM, and G-AFM having band gaps that fall in the range of the experimental values. In particular, the band gap for the C2-AFM ordering, which is the most energetically stable, is 1.72 eV which is very close to the lower bound of the known experimental values (1.61 – 1.65 eV). Definitely, the narrowing down of the experimental range of band gaps is needed in order to further assess the predictive accuracy of DFT+$U$+$V$.

![Figure 4](image-url) Magnetic moment (in $\mu_B$) on Mn atoms in the pristine α-MnO$_2$ for five collinear magnetic orderings (FM, A2-AFM, C-AFM, C2-AFM, G-AFM) computed at three levels of theory (DFT, DFT+$U$, and DFT+$U$+$V$) using the PBEsol functional. For each case, the Hubbard parameters $U$ and $V$ were computed using DFPT and are listed in Table I. The experimental magnetic moments are 3.94 – 4.04 $\mu_B$ [100] and 4.04 $\mu_B$ [22] and they are indicated with horizontal dashed lines.

![Figure 5](image-url) Band gap (in eV) in the pristine α-MnO$_2$ for five collinear magnetic orderings (FM, A2-AFM, C-AFM, C2-AFM, G-AFM) computed at three levels of theory (DFT, DFT+$U$, and DFT+$U$+$V$) using the PBEsol functional. The experimental band gaps (1.61 eV [19], 1.65 eV [101], and 2.10 eV [102]) are indicated with horizontal dashed lines.
F. Projected density of states

Figure 6 shows the spin-resolved PDOS and total DOS for five magnetic orderings of the pristine α-MnO₂ computed at three levels of theory. The spin-up (upper part) and spin-down (lower part) components of the PDOS are shown on each panel in Fig. 6 and they were obtained by summing over all atoms of the same type. Mn1 and Mn2 correspond to Mn atoms with the opposite spin polarizations in the AFM cases. In general, the trends for α-MnO₂ are very similar to those that were observed for β-MnO₂ [50].

In the DFT case, we see that the Mn(3d) states are very delocalized due to large self-interaction errors, and they hybridize strongly with the O(2p) states. The exact shape of the PDOS varies depending on the type of magnetic ordering. However, qualitatively the PDOS for various AFM types are very similar and differ mainly by the magnitude of the band gap and details in the dispersion of the valence and conduction bands. The top of the valence bands is of a mixed Mn(3d) and O(2p) character, while the bottom of the conduction bands is dominated by the Mn(3d) states.

The PDOS at the DFT+U level of theory differs strongly from the DFT one. As in the case of β-MnO₂, the application of the Hubbard U correction pushes the occupied Mn(3d) states to lower energies while the empty Mn(3d) states are pushed to higher energies. As a consequence, the top of the valence bands becomes of a pure O(2p) character, while the bottom of the conduction bands becomes of a mixed Mn(3d) and O(2p) character. As in Ref. [40] we find that for FM the empty e_g states in the spin-up channel overlap with the empty t_2g and e_g states in the spin-down channel in the DFT case, while in DFT+U these empty states in the spin-down channel are shifted to higher energies and there is an energy gap between these states and the empty e_g states in the spin-up channel. For AFM, the trends are the same and they apply to Mn1 and Mn2 atoms which have opposite spin polarizations. Finally, within DFT+U+V the PDOS looks very similar to the one computed using DFT+U. One of the major differences is that the band gap is larger in DFT+U+V than in DFT+U, as was discussed in Sec. IV E, and the energy separation between the groups of empty bands is somewhat smaller in DFT+U+V.

We are not aware of any valence- or conduction-band spectra measured in the x-ray photoelectron spectroscopy (XPS) and x-ray absorption near-edge structure (XANES) experiments for the pristine α-MnO₂. Hence, at this stage we cannot validate the accuracy of the computed spin-polarized PDOS. However, these results are valuable for the further discussions when considering the Fe-doped α-MnO₂. In particular, our goal is to understand where the Fe(3d) states are located and whether the semiconducting character of α-MnO₂ is preserved after doping. All this is discussed in Sec. V F.

![Figure 6](image_url)
V. RESULTS AND DISCUSSION FOR FE-DOPED α-MNO₂

In this section we discuss structural, electronic, and magnetic properties of the Fe-doped α-MnO₂. We examine two types of doping, namely the interstitial one (FeMn₈O₁₆) and the substitutional one (FeMn₇O₁₆). For the former case we consider two spin configurations (labeled as “A” and “D”), while for the latter we consider three cases (“B”, “C”, and “E”). These spin configurations are based on the C2-AFM and FM magnetic orderings of the pristine α-MnO₂, since the former is the most energetically stable one while the latter is also often considered in various studies. All these five cases of Fe-doped α-MnO₂ differ by the variations in the chemical environment for Fe atoms and are schematically represented in Fig. 7. We also note that the configurations A, B, and C have the FM ordering, while D and E have the ferrimagnetic (FiM) ordering.

A. Hubbard parameters

In the previous DFT+U studies of the Fe-doped α-MnO₂ [4, 31], the value of Hubbard U for Mn(3d) states was chosen empirically and it was assumed to be exactly the same as in the pristine α-MnO₂. Here we show that when U is computed from first principles, its value for Mn(3d) states changes due to the Fe doping, since the latter leads to changes in the crystal and electronic structure. Indeed, from Table III we can see that on average the U parameter for Mn(3d) states is increased by a fraction of an eV compared to the pristine α-MnO₂ case. Moreover, there is no longer just one global value of U for all Mn sites in the structure, instead there are slightly different U values for different Mn sites. This is because the introduction of Fe in the α-MnO₂ host lattice leads to structural distortions which break the equivalence of the Mn sites. This approach was also used in Refs. [64, 70] to determine the site-dependent Hubbard parameters in perovskites due to the presence of oxygen vacancies.

The Hubbard U parameter for Fe(3d) states is in the range from roughly 5.6 to 7.0 eV depending on the method used (DFT+U or DFT+U+V) and on the type of the spin configuration. These values are larger than the value of 5.11 eV which is obtained for the bulk Fe. This shows once again that U is not transferable and it is sensitive to changes in the chemical environment.

The intersite Hubbard V parameters for the Mn–O and Fe–O couples are also listed in Table III. We can see that V for Mn–O did not change substantially with respect to V values in the pristine α-MnO₂ case, and they span approximately the same range. Moreover, the V values for Fe–O are similar to those for Mn–O. In order to assess the importance of intersite Hubbard corrections for the Fe-doped α-MnO₂, in the following sections we present the ground-state properties computed using DFT+U and DFT+U+V with the respective sets of self-consistent Hubbard parameters.

B. Structural properties

Doping of α-MnO₂ with Fe leads to structural distortions (see Table S2 in SM [90]). From our calculations we find that in the case of A type doping the lattice preserves the tetragonal symmetry at all levels of theory, while for the B, C, and D types of doping the lattice has a very small monoclinic distortion. In the case of the E type doping, the the optimized structure has a triclinic cell at the levels of DFT+U and DFT+U+V, while at the DFT level the cell is monoclinic. We are aware of only one experimental study of the Fe-doped α-MnO₂ [4] showing that the lattice preserves the tetragonal symmetry like in the pristine α-MnO₂. This seems to suggest that the A type is the most likely spin configuration in the case of the interstitial doping. However, in order to understand better this aspect, further high-accuracy experimental investigations of different types of doping of α-MnO₂ are needed in order to resolve possible monoclinic (or triclinic) distortions.

For what concerns the crystal structure parameters, we also observe different trends. In the case of the interstitial doping (A and D), Fe atoms residing in the centers of the 2 × 2 channels form bonds with the nearest four O atoms (see Fig. S1 in SM [90]). Our calculations show that this leads to the reduction of the a and b lattice parameters by ~2% with respect to the pristine α-MnO₂ case, while the c lattice parameter is increased by ~4% (at the DFT+U and DFT+U+V levels of theory). In the case of the substitutional doping (B, C, and E), all lattice parameters are increased by ~1% (at the DFT+U and DFT+U+V levels of theory). In contrast, the experimental lattice parameters for the Fe-doped α-MnO₂ are a_{exp} = b_{exp} = 9.83 Å and c_{exp} = 2.86 Å [4] meaning that there are no noticeable changes with respect to the pristine case [1–3]. It should be noted that the uncertainties in the experimental crystal structure parameters are relatively large, and hence more accurate experiments are needed to detect possible small changes in the crystal structure due to doping.

We analyzed also the bond lengths and angles for the A and D types of doping (see Fig. S1 and Table S3 in SM [90]). We find that due to the Fe doping some Mn–O bonds contract and some expand, and they cover a range of about 1.8 – 2.1 Å. The Fe–O bonds are symmetrical in the A type and they have different lengths in the D type (in the range 2.1 – 2.2 Å). The bond angles Mn–O–Mn are also distorted and their exact values are listed in Table S3 in SM [90]. Finally, the O–Fe–O angles are 90° in the A type and they deviate slightly from 90° in the D type, while the Fe–O–Mn angles are in the range 123 – 126°. We are not aware of any experimental data for the bond angles and lengths in the Fe-doped α-MnO₂, hence we cannot verify the accuracy of these predictions.
C. Energetics

As in the case of the pristine α-MnO₂ (see Sec. IV C), we compare the total energies of various spin configurations in the case of the Fe-doped α-MnO₂. It is important to note that since the number of atoms in the simulation cell is not the same for the interstitial and substitutional doping, we can compare the total energies only for spin configurations having the same number of atoms.

As can be seen from Table IV which is for the interstitial doping, the trends are different at different levels of theory. DFT predicts the D type to be more energetically favorable than the A type, while DFT+U predicts the opposite trend. Hence, the onsite Hubbard U correction for Mn(3d) and Fe(3d) states influences significantly the overall energetics of the system. Interestingly, when the intersite Hubbard V correction for Mn–O and Fe–O couples is also included, the trend reverses back to the one found in DFT. This shows that intersite Hubbard interactions play a decisive role in stabilizing back the D type in the presence of localized 3d electrons residing on Mn and Fe atoms. Hence, the delicate balance between the onsite localization and intersite hybridization due to covalent bonding is captured by DFT+U+V but not by DFT+U. Instead, in DFT these two effects are poorly described and apparently there is a cancellation of errors which might explain why the D type turns out to be the most energetically stable as in DFT+U+V. Therefore, our most accurate level of theory DFT+U+V predicts that the D type is more energetically favorable than the A type. This is physically sound since the doping of C2-AFM α-MnO₂ with Fe is likely to preserve the C2-AFM character of the host; in contrast, switching to the FM character would require swapping spins on half of the Mn atoms which has high energetic cost and hence it is less likely.

In the case of the substitutional doping we find that all levels of theory predict the E type to be the most energetically favorable, as can be seen in Table V. Interestingly, for this type of doping the onsite Hubbard U correction alone is able to capture the right energetics of the system at variance with the case of the interstitial doping. Thus, again we find that doping of C2-AFM α-MnO₂ with Fe preserves the C2-AFM character of the host when making a partial substitution of Mn for Fe.

| Method  | HP  | Atoms          | Magnetic ordering |
|---------|-----|----------------|-------------------|
|         |     | A              | B                | C              | D              | E              |
| DFT+U   | U   | Mn 7.01 – 7.10 | 6.65 – 6.72       | 6.65 – 6.72    | 6.54 – 7.02    | 6.46 – 6.48    |
|         | Fe 5.92                       | 6.03                  | 6.02                  | 5.58                  | 5.94                  |
| DFT+U+V | U   | Mn 7.24 – 7.60 | 6.85 – 6.95       | 6.88 – 6.96    | 6.78 – 7.37    | 6.62 – 6.73    |
|         | Fe 5.86                       | 6.95                  | 6.94                  | 5.69                  | 6.58                  |
|         | V   | Mn–O 0.82 – 1.23 | 0.75 – 1.16       | 0.75 – 1.18    | 0.69 – 1.25    | 0.64 – 1.18    |
|         |     | Fe–O 0.53       | 1.03 – 1.37       | 1.05 – 1.37    | 0.54 – 0.63    | 0.75 – 1.28    |

TABLE III. Self-consistent Hubbard parameters (HP) in eV computed using DFPT (see Sec. II B) for five magnetic orderings of the Fe-doped α-MnO₂: A, B, C, D, and E. The onsite U for Mn(3d) and Fe(3d) states and intersite V for Mn(3d)–O(2p) and Fe(3d)–O(2p) interactions are computed in the frameworks of DFT+U and DFT+U+V (PBEsol functional) using Löwdin-orthogonalized atomic orbitals as Hubbard projector functions.

| Magnetic ordering | DFT   | DFT+U | DFT+U+V |
|-------------------|-------|-------|---------|
| A                 | 0.855 | 0     | 0.254   |
| D                 | 0     | 0.072 | 0       |

TABLE IV. Total energy difference (in eV) in the case of the interstitial doping Fe₃Mn₁₆O₁₆ (A and D). The zero of energy corresponds to the lowest-energy structure within each level of theory.

FIG. 7. Five collinear spin configurations for the Fe-doped α-MnO₂. A and D correspond to the interstitial doping, while B, C, and E correspond to the substitutional doping. Light brown and blue colors correspond to Mn atoms with spin-up and spin-down alignments, respectively, while light green color corresponds to the Fe atom with the spin-up alignment. The oxygen atoms are shown in yellow color.
D. Formation energy

In order to gain more insights about the most likely spin configuration of the Fe-doped α-MnO$_2$, in this section we discuss the formation energy (FE). By definition, FE of a compound is the energy required for making this compound from its constituents. In the case of the interstitial doping of α-MnO$_2$, FE is computed as [104, 105]:

\[ E_f = E(\text{FeMn}_8\text{O}_{16}) - E(\text{Mn}_8\text{O}_{16}) - E(\text{Fe}), \]

where \( E(\text{FeMn}_8\text{O}_{16}) \) and \( E(\text{Mn}_8\text{O}_{16}) \) are the total energies of the Fe-doped and pristine α-MnO$_2$ containing 25 and 24 atoms in the simulation cell, respectively, while \( E(\text{Fe}) \) is the total energy per atom of the bulk Fe. All total energies in Eq. (6) are computed consistently within the same level of theory (except for the DFT+U+V case where we used the DFT+U total energy for bulk Fe since the intersite Fe–Fe Hubbard interactions are very small and hence were neglected). As can be seen from the results reported in Table VI, DFT predicts positive FE for both types of the interstitial doping (A and D) which means that the formation of the compound FeMn$_8$O$_{16}$ is unlikely, which contradicts to experiments. In contrast, both DFT+U and DFT+U+V predict negative FE which means that the formation of the compound is favorable in line with the experimental reports [27, 28]. Within DFT+U, FE for the A type turns out to be negative and larger by absolute value than for the D type, and hence the former is more favorable. Instead, within DFT+U+V, D type turns out to be more favorable. These findings are consistent with the analysis of the total energy differences in Table IV. Hence, again we find that the most accurate level of theory (DFT+U+V) predicts the D type to be the most likely spin configuration for the interstitial Fe doping of α-MnO$_2$.

The calculation of FE for the interstitial type of doping requires knowledge of the total energy of bulk Mn, \( E(\text{Mn}) \). While this quantity can be easily computed at the DFT level of theory, we did not manage to converge the DFT+U calculations for bulk Mn (possibly due to the complex magnetic properties of this material) [86, 87]. For this reason, we could not compute FE of FeMn$_7$O$_{16}$ at the levels of DFT+U and DFT+U+V. However, in the SM [90] we present a discussion of computing FE using the method of Ref. [6] which is based on mixing total energies computed at different levels of theory.

E. Magnetic moment

The magnetic moments on Mn and Fe atoms for the Fe-doped α-MnO$_2$ computed at different levels of theory for five spin configurations are shown in Fig. 8. We are not aware of any experimental reports of magnetic moments for the Fe-doped α-MnO$_2$, hence we present the analysis based on a comparison with the magnetic moments in the pristine α-MnO$_2$ (see Sec. IV D).

By comparing Figs. 4 and 8 we can see that there are no big changes in the magnetic moments on Mn atoms after the Fe doping. We observe an increase on average only by \( \sim 0.2 \mu_\text{B} \) in the case of DFT+U and DFT+U+V, and negligible changes in the case of DFT. Moreover, we still see the same trends as in the case of the pristine α-MnO$_2$: DFT and DFT+U give the smallest and the largest magnetic moments, respectively, while DFT+U+V gives magnetic moments that fall in-between the DFT and DFT+U predictions.

The magnetic moments on Fe atoms are very similar within DFT+U and DFT+U+V, in contrast to the magnetic moments on Mn atoms which have larger differences between DFT+U and DFT+U+V. This is due to the fact that Mn atoms have stronger covalent bonding with ligands [55], and hence the magnetic moments are affected stronger by the intersite Hubbard V correction.

![Figure 8](image_url)

**FIG. 8.** Magnetic moment (in \( \mu_\text{B} \)) on Mn and Fe atoms in the Fe-doped α-MnO$_2$ for five collinear magnetic orderings (A, B, C, D, and E) computed at three levels of theory (DFT, DFT+U, and DFT+U+V) using the PBEsol functional. For each case, the Hubbard parameters \( U \) and \( V \) were computed using DFPT and are listed in Table III.

| Magnetic ordering | DFT | DFT+U | DFT+U+V |
|------------------|-----|-------|---------|
| A                | 1.36| -2.00 | -1.33   |
| D                | 0.50| -1.93 | -1.58   |

TABLE VI. Formation energy (in eV) in the case of the interstitial doping FeMn$_8$O$_{16}$ (A and D).

| Magnetic ordering | DFT | DFT+U | DFT+U+V |
|------------------|-----|-------|---------|
| A                | 1.36| -2.00 | -1.33   |
| D                | 0.50| -1.93 | -1.58   |

TABLE V. Total energy difference (in eV) in the case of the substitutional doping FeMn$_7$O$_{16}$ (B, C, and E). The zero of energy corresponds to the lowest-energy structure within each level of theory.

| Magnetic ordering | DFT | DFT+U | DFT+U+V |
|------------------|-----|-------|---------|
| B                | 0.802| 0.296 | 0.357   |
| C                | 0.798| 0.287 | 0.313   |
| E                | 0    | 0     | 0       |

| Magnetic ordering | DFT | DFT+U | DFT+U+V |
|------------------|-----|-------|---------|
| B                | 0.802| 0.296 | 0.357   |
| C                | 0.798| 0.287 | 0.313   |
| E                | 0    | 0     | 0       |
FIG. 9. Spin-resolved PDOS and total DOS for five collinear magnetic orderings of the Fe-doped α-MnO₂ (A, B, C, D, and E) computed using the PBEsol functional within (a) DFT+U, and (b) DFT+U+V. For each case the Hubbard parameters $U$ and $V$ were computed using DFPT and are listed in Table III. Upper panels correspond to the spin-up components, while lower panels correspond to the spin-down components. The zero of energy corresponds to the Fermi energy (in the case of metallic ground states) or top of the valence bands (in the case of insulating ground states).

tions. Within DFT, the values of magnetic moments on Fe atoms are scattered (for different spin configurations) much more than in the case of DFT+U and DFT+U+V (in particular, note the difference between the A and E types). This is due to the failure of DFT with standard functionals to describe accurately the electronic and magnetic properties of Fe due to large self-interaction errors for 3$d$ electrons. Interestingly, the scattering of magnetic moments on Mn atoms in the case of DFT is much smaller than for Fe. Finally, it would be desirable to have the experimental data for the magnetic moments on Mn and Fe in the Fe-doped α-MnO₂ which would allow us to check the accuracy of computational predictions of this work.

F. Projected density of states

After the Fe doping of α-MnO₂ the electronic structure of this material changes significantly as can be seen in Figs. S3 (a) and (b) that show the spin-resolved PDOS and total DOS computed using DFT+U and DFT+U+V. We note in passing that the PDOS of the Fe-doped α-MnO₂ computed using DFT is unreliable [like in the case of the pristine α-MnO₂, see Fig. 6 (a)] due to the overdelocalization of 3$d$ electrons of Mn and Fe atoms (see Fig. S2 in SM [90]). As can be seen from Fig. S3, the doped material turns out to be a (half-)metal for all spin configurations except the E type which shows a semiconducting behavior with a small band gap of 0.21 eV in the case of DFT+U and 0.56 eV in the case of DFT+U+V. From the experimental side, we are aware of Ref. [107] that reports a band gap of 0.30 eV at low Fe concentrations (5 mol%). It is important to note, though, that a significant amount of water was accumulated in the tunnels of the Fe-doped α-MnO₂ samples in Ref. [107], hence the band gap value reported above might not be very accurate. Nonetheless, both DFT+U and DFT+U+V predict a band gap for the E type which is qualitatively consistent with the finding of Ref. [107]. In contrast, for the D type we do not find a band gap, though the DOS at the Fermi level is extremely small (see also Fig. S3 in SM [90]). Therefore, since it is not known which type of doping is dominant in the samples of Ref. [107] (interstitial or substitutional), our DFT+U+V calculations for the two best candidates (D and E types) can be considered as satisfactory. Obviously, more experiments on the accurate band gap determination in the Fe-doped α-MnO₂ are needed.

Of particular interest is to analyze the position of the Fe(3$d$) states in the spin-resolved PDOS of the Fe-doped α-MnO₂. As can be seen in Fig. S3, in the case of the interstitial doping (A and D) these states appear around −6.5 eV and 3.5 eV in the spin-up and spin-down channels, respectively, while in the case of the substitutional doping they appear around −8.5 eV and 2.5 eV in the spin-up and spin-down channels, respectively. This information could be useful when interpreting the XPS and XANES spectra to determine which type of doping is present in the samples. DFT+U and DFT+U+V predict similar position and shape of the peaks due to Fe(3$d$) states in the PDOS; the main differences are mainly around the Fermi level (for the A, B, C, and D types) or top of the valence bands (for the E type) as can be seen in Fig. S3 in SM [90]. Finally, we note that the empty Fe(3$d$) states in the spin-down channel have negligible
hybridization with the O(2p) states, while in the spin-up channel the hybridization of the occupied Fe(3d) states with the O(2p) states is very small. Thus, the intersite V correction for the Fe–O couples is not so important when describing the relative position of the Fe(3d) and O(2p) states, while it is relevant for the Mn–O couples which show stronger hybridization especially for the lowest conduction bands.

G. Oxidation state

The OS of Mn and Fe in the Fe-doped α-MnO₂ is actively discussed in the experimental literature [4, 24, 27, 28, 30]. In Refs. [4, 24, 27, 30] it is reported that there is a mixture of two types of Mn with the OS of 4+ and 3+. It is argued that Mn³⁺ is present due to the appearance of the oxygen vacancies after the Fe doping. The OS of Fe is also reported to be 4+ and 3+, with Fe⁴⁺ being present also due to the oxygen vacancies [4], while in Ref. [28] it is argued that the OS of Fe is exclusively 3+. Computational studies could be useful to verify these experimental findings and enrich them.

In this work we do not consider oxygen vacancies in the Fe-doped α-MnO₂, but we can compare what is the OS of Mn and Fe for different types of doping (interstitial and substitutional). The determination of OS is, in general, not a trivial task [108–110]. In particular, using the Löwdin occupations as a proxy for determining the OS could be often misleading [74, 109]. Here we use the projection-based method of Ref. [5] that has proven to be effective for determining the OS of transition-metal elements in various complex materials [74, 111]. The main idea is based on the count of the eigenvalues of the site-diagonal occupation matrix [see Eq. (3)] that are close to unity. Using this approach and our DFT+U+V’ data for the C2-AFM pristine α-MnO₂ we find that the OS of Mn is 4+, which agrees with the nominal OS. In Table S4 in SM [90] we report the eigenvalues of the site-diagonal occupation matrix for the D and E types of the Fe-doped α-MnO₂. We find that in both cases the OS of Mn is 4+, while the OS of Fe is 2+ in the D type and 4+ in the E type. These findings are physically sound and could be interpreted as follows. In the D type doping, where dopant ions reside in the 2 × 2 tunnels, Fe gives away 2 electrons from the 4s shell, and hence 6 electrons remain in the 3d shell in the high-spin state, d⁵(↑)d⁰(↓). In contrast, in the E type doping, where the dopant ions partially substitute Mn atoms, Fe tries to adapt itself to the local chemical environment and hence it has the same OS as Mn, i.e. 4+. As a consequence, in this case Fe gives away 2 electrons from the 4s shell and 2 electrons from the 3d shell, and thus only 4 electrons remain in the 3d shell in the high-spin state, d⁴(↑)d⁵(↓). To be more precise, Fe does not give away fully some electrons, but it shares them with O atoms by creating covalent bonds, and as a consequence there are fractional occupations of those levels (i.e. the eigenvalues of the occupation matrix have fractional values between 0 and 1) [5]. Obviously, the chemistry of the Fe-doped α-MnO₂ will change in the case when there are oxygen vacancies (see e.g. Ref. [30]), and this will be the topic of future investigations.

VI. CONCLUSIONS

We have presented a first-principles study of the structural, electronic, and magnetic properties of the pristine and Fe-doped α-MnO₂ using DFT with extended Hubbard functionals. The onsite and intersite Hubbard parameters were computed self-consistently using DFPT in the basis of Löwdin-orthogonalized atomic orbitals.

We found that the C2-AFM spin configuration is the most energetically favorable one (compared to the FM and other types of the AFM magnetic orderings) in the pristine α-MnO₂ and that it is robust with respect to the substitutional and interstitial doping with Fe. The computed crystal structure properties and the band gap of the pristine α-MnO₂ are in good agreement with experiments, while the magnetic moments are somewhat underestimated. The oxidation state of Fe in the two types of doping is found to be different: it is 2+ in the case of the interstitial doping, and 4+ in the case of the substitutional doping. The oxidation state of Mn is 4+ in the pristine and all types of the Fe-doped α-MnO₂. The semiconducting character of α-MnO₂ is preserved in the case of the substitutional doping (E type), while the material becomes metallic with a vanishing DOS at the Fermi level in the case of the interstitial doping (D type). This work paves the way for future studies of α-MnO₂ doped not only with Fe but also other transitional-metal elements or cations in the presence of oxygen vacancies or under strain. Finally, the data used to produce the results of this paper are available in the Materials Cloud Archive [112].

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Supplemental Material for

“Electronic structure and magnetism of pristine and Fe-doped α-MnO$_2$ from density-functional theory with extended Hubbard functionals”

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S1. CRYSTAL STRUCTURE PROPERTIES, PROJECTED DENSITY OF STATES, AND POPULATION ANALYSIS FOR THE PRISTINE AND FE-DOPED α-MnO$_2$

| Magnetic ordering | CSP | DFT | DFT+U | DFT+U+V |
|-------------------|-----|-----|-------|---------|
| FM                |     |     |       |         |
| $a$ (Å)           | 9.71| 9.93| 9.84  |         |
| $c$ (Å)           | 2.94| 2.95| 2.92  |         |
| $V$ (Å$^3$)       | 267.47| 291.14| 282.34|         |
| $\Delta V$ (%)    | -2.56| 6.06| 2.86  |         |
| A2-AFM            |     |     |       |         |
| $a$ (Å)           | 9.71| 9.86| 9.81  |         |
| $c$ (Å)           | 2.84| 2.94| 2.91  |         |
| $V$ (Å$^3$)       | 267.5| 285.42| 279.83|         |
| $\Delta V$ (%)    | -2.55| 3.98| 1.94  |         |
| C-AFM             |     |     |       |         |
| $a$ (Å)           | 9.66| 9.81| 9.76  |         |
| $c$ (Å)           | 2.83| 2.93| 2.90  |         |
| $V$ (Å$^3$)       | 264.44| 281.55| 276.76|         |
| $\Delta V$ (%)    | -3.66| 3.98| 0.82  |         |
| C2-AFM            |     |     |       |         |
| $a$ (Å)           | 9.66| 9.85| 9.78  |         |
| $c$ (Å)           | 2.83| 2.93| 2.91  |         |
| $V$ (Å$^3$)       | 263.91| 284.61| 278.26|         |
| $\Delta V$ (%)    | -3.86| 3.68| 1.37  |         |
| G-AFM             |     |     |       |         |
| $a$ (Å)           | 9.69| 9.83| 9.78  |         |
| $c$ (Å)           | 2.82| 2.92| 2.90  |         |
| $V$ (Å$^3$)       | 265.16| 282.57| 277.41|         |
| $\Delta V$ (%)    | -3.40| 2.94| 1.06  |         |

TABLE S1. Crystal structure parameters (CSP) of the pristine α-MnO$_2$ (see Fig. 1 in the main text): lattice parameters $a$ and $c$ (in Å), volume $V$ (in Å$^3$) corresponding to the 24-atoms unit cell and its deviation $\Delta V$ (in %) from the experimental value 274.5 Å$^3$ of Ref. [1]. All theoretical predictions preserve the tetragonal symmetry (hence $a = b$ and we report only $a$). The results are presented for five collinear magnetic orderings (FM, A2-AFM, C-AFM, C2-AFM and G-AFM) computed at three level of theory (see Fig. 2 in the main text): DFT, DFT+U, and DFT+U+V (PBEsol functional). Hubbard-corrected results are obtained using Löwdin-orthogonalized atomic orbitals as Hubbard projector functions and the respective Hubbard parameters (see Table I in the main text). The experimental CSP for the pristine α-MnO$_2$ (tetragonal structure) are $a_{\exp} = 9.75$ Å, $c_{\exp} = 2.86$ Å, and $V_{\exp} = 272.0$ Å$^3$ according to Ref. [2]; $a_{\exp} = 9.84$ Å, $c_{\exp} = 2.86$ Å, and $V_{\exp} = 276.9$ Å$^3$ according to Ref. [3]; $a_{\exp} = 9.79$ Å, $c_{\exp} = 2.86$ (2.87) Å, and $V_{\exp} = 274.1$ (274.5) Å$^3$ according to Ref. [1].
TABLE S2. Crystal structure parameters (CSP) of the Fe-doped α-MnO$_2$: lattice parameters $a$, $b$, and $c$ (in Å), angles $\alpha$, $\beta$, $\gamma$ (in degrees), and the volume $V$ (in Å$^3$). The results are presented for five collinear magnetic orderings (A, B, C, D, and E - see Fig. 7 in the main text) computed at three level of theory: DFT, DFT+$U$ and DFT+$U$+$V$ (PBEsol functional). Hubbard-corrected results are obtained using L"owdin-orthogonalized atomic orbitals as Hubbard projector functions and the respective Hubbard parameters (see Table III in the main text). The experimental CSP for the Fe-doped α-MnO$_2$ are $a_{\text{exp}} = 9.83$ Å, $b_{\text{exp}} = 9.83$ Å, $c_{\text{exp}} = 2.86$ Å, and $V_{\text{exp}} = 276.4$ Å$^3$ [4].

| Magnetic ordering | CSP | a (Å) | b (Å) | c (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) | V (Å$^3$) |
|-------------------|-----|-------|-------|-------|-------------|-------------|-------------|---------|
| A                 | a   | 9.49  | 9.68  | 9.62  |             |             |             |         |
|                   | b   | 9.49  | 9.68  | 9.62  |             |             |             |         |
|                   | c   | 2.84  | 3.07  | 3.03  |             |             |             |         |
|                   | $\alpha$ | 90.00 | 90.00 | 90.00 |             |             |             |         |
|                   | $\beta$ | 90.00 | 90.00 | 90.00 |             |             |             |         |
|                   | $\gamma$ | 90.00 | 90.00 | 90.00 |             |             |             |         |
|                   | V   | 255.80| 287.29| 280.38|             |             |             |         |
| B                 | a   | 9.70  | 9.94  | 9.86  |             |             |             |         |
|                   | b   | 9.69  | 9.95  | 9.87  |             |             |             |         |
|                   | c   | 2.83  | 2.96  | 2.93  |             |             |             |         |
|                   | $\alpha$ | 90.00 | 90.00 | 90.00 |             |             |             |         |
|                   | $\beta$ | 90.00 | 90.00 | 90.00 |             |             |             |         |
|                   | $\gamma$ | 89.81 | 89.79 | 89.87 |             |             |             |         |
|                   | V   | 266.30| 292.73| 284.81|             |             |             |         |
| C                 | a   | 9.68  | 9.96  | 9.87  |             |             |             |         |
|                   | b   | 9.70  | 9.94  | 9.86  |             |             |             |         |
|                   | c   | 2.83  | 2.96  | 2.93  |             |             |             |         |
|                   | $\alpha$ | 90.00 | 90.00 | 90.00 |             |             |             |         |
|                   | $\beta$ | 90.00 | 90.00 | 90.00 |             |             |             |         |
|                   | $\gamma$ | 89.75 | 89.54 | 89.87 |             |             |             |         |
|                   | V   | 253.80| 281.92| 276.41|             |             |             |         |
| D                 | a   | 9.63  | 9.89  | 9.84  |             |             |             |         |
|                   | b   | 9.64  | 9.87  | 9.77  |             |             |             |         |
|                   | c   | 2.83  | 2.94  | 2.91  |             |             |             |         |
|                   | $\alpha$ | 90.00 | 89.86 | 89.79 |             |             |             |         |
|                   | $\beta$ | 90.00 | 89.50 | 89.40 |             |             |             |         |
|                   | $\gamma$ | 90.21 | 90.09 | 89.88 |             |             |             |         |
|                   | V   | 262.36| 286.89| 280.14|             |             |             |         |

TABLE S3. Crystal structure parameters (CSP) for the A and D types of the Fe-doped α-MnO$_2$ at the levels of DFT, DFT+$U$, and DFT+$U$+$V$. Bond lengths are shown for Mn–O and Fe–O couples, and the angles $\theta_1$–$\theta_3$ and $\phi_1$–$\phi_4$ are shown in Fig. S1.
FIG. S1. Bond angles in the Fe-doped α-MnO$_2$ for the A type (left panel) and D type (right panel) spin configurations (see Fig. 7 in the main text). Light brown and blue colors correspond to Mn atoms with spin-up and spin-down alignments, respectively, while light green color corresponds to the Fe atom with the spin-up alignment. The oxygen atoms are shown in yellow color.

FIG. S2. Spin-resolved PDOS and total DOS (left panels) and its zoom (right panels) for five collinear magnetic orderings of the Fe-doped α-MnO$_2$ (A, B, C, D, and E) computed using standard DFT (PBEsol functional). The zero of energy corresponds to the Fermi energy.

FIG. S3. Zoomed-in spin-resolved PDOS and total DOS for five collinear magnetic orderings of the Fe-doped α-MnO$_2$ (A, B, C, D, and E) computed using DFT+U (left panels) and DFT+U+V (right panels) with the PBEsol functional. For each case, the Hubbard parameters $U$ and $V$ were computed using DFPT. The zero of energy corresponds to the Fermi energy (in the case of metallic ground states) or top of the valence bands (in the case of insulating ground states).
TABLE S4. Population analysis data for the 3d shell of Mn and Fe atoms in the Fe-doped α-MnO₂ computed using DFT+U (PBEsol functional). Two doping types are considered: interstitial (D) and substitutional (E). This table shows the eigenvalues of the site-diagonal occupation matrix for the spin-up ($\lambda^+_i$, $i=1,5$) and spin-down ($\lambda^-_i$, $i=1,5$) channels, Löwdin occupations \( n = \sum_i (\lambda^+_i + \lambda^-_i) \), and the oxidation state (OS). For the sake of simplicity we dropped the atomic site index \( I \) from all quantities reported here. The eigenvalues are written in the ascending order (from left to right) for each spin channel. The eigenvalues written in bold are considered as being such that correspond to fully occupied states and thus are taken into account when determining the OS according to Ref. [5].

| Doping | Element | $\lambda^+_1$ | $\lambda^+_2$ | $\lambda^+_3$ | $\lambda^+_4$ | $\lambda^+_5$ | $\lambda^-_1$ | $\lambda^-_2$ | $\lambda^-_3$ | $\lambda^-_4$ | $\lambda^-_5$ | \( n \) | OS |
|--------|---------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-------|----|
| D type | Mn1     | 0.57           | 0.61           | 0.99           | 1.00           | 1.00           | 0.06           | 0.09           | 0.13           | 0.27           | 0.29           | 4.99  | 4+ |
|        | Mn2     | 0.55           | 0.86           | 1.00           | 1.00           | 1.00           | 0.04           | 0.07           | 0.09           | 0.18           | 0.25           | 5.01  | 4+ |
|        | Mn3     | 0.55           | 0.86           | 1.00           | 1.00           | 1.00           | 0.04           | 0.07           | 0.09           | 0.18           | 0.25           | 5.01  | 4+ |
|        | Mn4     | 0.57           | 0.61           | 0.99           | 1.00           | 1.00           | 0.06           | 0.09           | 0.11           | 0.27           | 0.29           | 4.99  | 4+ |
|        | Mn5     | 0.06           | 0.10           | 0.28           | 0.30           | 0.56           | 0.61           | 0.99           | 1.00           | 1.00           | 5.00  | 4+ |
|        | Mn6     | 0.04           | 0.07           | 0.09           | 0.18           | 0.25           | 0.55           | 0.85           | 1.00           | 1.00           | 1.00           | 5.01  | 4+ |
|        | Mn7     | 0.06           | 0.10           | 0.11           | 0.28           | 0.30           | 0.56           | 0.61           | 0.99           | 1.00           | 1.00           | 5.00  | 4+ |
|        | Mn8     | 0.04           | 0.07           | 0.09           | 0.18           | 0.25           | 0.55           | 0.85           | 1.00           | 1.00           | 1.00           | 5.01  | 4+ |
|        | Fe      | 0.97           | 0.99           | 1.00           | 1.00           | 1.00           | 0.02           | 0.02           | 0.03           | 0.15           | 0.94           | 6.12  | 2+ |
| E type | Mn1     | 0.58           | 0.59           | 0.99           | 1.00           | 1.00           | 0.07           | 0.10           | 0.11           | 0.28           | 0.29           | 5.00  | 4+ |
|        | Mn2     | 0.58           | 0.59           | 0.99           | 0.99           | 1.00           | 0.07           | 0.10           | 0.11           | 0.28           | 0.29           | 5.00  | 4+ |
|        | Mn3     | 0.58           | 0.59           | 0.99           | 1.00           | 1.00           | 0.07           | 0.10           | 0.11           | 0.28           | 0.29           | 5.00  | 4+ |
|        | Mn4     | 0.07           | 0.09           | 0.11           | 0.28           | 0.29           | 0.58           | 0.60           | 0.99           | 1.00           | 1.00           | 5.00  | 4+ |
|        | Mn5     | 0.07           | 0.10           | 0.11           | 0.29           | 0.29           | 0.58           | 0.59           | 0.99           | 1.00           | 1.00           | 5.00  | 4+ |
|        | Mn6     | 0.07           | 0.10           | 0.11           | 0.28           | 0.29           | 0.58           | 0.59           | 0.99           | 1.00           | 1.00           | 5.00  | 4+ |
|        | Mn7     | 0.07           | 0.10           | 0.11           | 0.28           | 0.29           | 0.58           | 0.59           | 0.99           | 1.00           | 1.00           | 5.00  | 4+ |
|        | Mn8     | 0.78           | 0.99           | 1.00           | 1.00           | 1.00           | 0.09           | 0.12           | 0.18           | 0.30           | 0.37           | 5.80  | 4+ |

TABLE S5. Formation energy (in eV) in the case of the interstitial doping FeMn₈O₁₆ (A and D) computed using the method of Ref. [6].

S2. FORMATION ENERGY

In this section we present the formation energy (FE) computed using the method of Ref. [6]. The main idea is based on mixing total energies computed using different levels of theory. For example, in the DFT+U framework the FE for the interstitial and substitutional doping can be defined as:

$$E_f = E_{DFT+U}(\text{FeMn}_8\text{O}_{16}) - E_{DFT+U}(\text{Mn}_8\text{O}_{16}) - E_{DFT}(\text{Fe}),$$  \hspace{1cm} (S1)

$$E_f = E_{DFT+U}(\text{FeMn}_7\text{O}_{16}) - E_{DFT+U}(\text{Mn}_8\text{O}_{16}) - E_{DFT}(\text{Fe}) + E_{DFT}(\text{Mn}).$$  \hspace{1cm} (S2)

Here, the total energies of the pristine and Fe-doped α-MnO₂ are computed at the level of DFT+U, while the total energies of bulk Fe and Mn are computed at the level of DFT. Equations S1 and S2 can be used also in the DFT+U+V framework by replacing the DFT+U total energies by the DFT+U+V ones, and by keeping the DFT total energies for bulk Fe and Mn. The resulting FE are shown in Tables S5 and S6. It can be seen that all FE are positive at all levels of theory which means that the formation of the doped structure is unfavorable which contradicts to experiments. Therefore, we find that the method of Ref. [6] is not suitable for the purposes of computing FE for the Fe-doped α-MnO₂.

| Magnetic ordering | DFT | DFT+U | DFT+U+V |
|------------------|-----|-------|---------|
| A                | 1.36| 1.50  | 2.18    |
| D                | 0.50| 1.58  | 1.92    |

TABLE S5. Formation energy (in eV) in the case of the interstitial doping FeMn₈O₁₆ (A and D) computed using the method of Ref. [6].
| Magnetic ordering | DFT  | DFT+U | DFT+U+V |
|------------------|------|-------|---------|
| B                | 2.23 | 1.59  | 1.83    |
| C                | 2.23 | 1.59  | 1.79    |
| E                | 1.43 | 1.30  | 1.47    |

TABLE S6. Formation energy (in eV) in the case of the substitutional doping FeMn$_7$O$_{16}$ (B, C, and E) computed using the method of Ref. [6].

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