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# Effects of “stuffing” on the atomic and electronic structure of the pyrochlore $\text{Yb}_2\text{Ti}_2\text{O}_7$

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There are reasons to believe that the ground state of the magnetic rare earth pyrochlore  $\text{Yb}_2\text{Ti}_2\text{O}_7$  is on the boundary between competing ground states. We have carried out *ab initio* density functional calculations to determine the most stable chemical formula as a function of the oxygen chemical potential and the likely location of the oxygen atoms in the unit cell of the “stuffed” system. We find that it is energetically favorable in the “stuffed” crystal (with an Yb replacement on a Ti site) to contain oxygen vacancies which dope the Yb 4*f* orbitals and qualitatively change the electronic properties of the system. In addition, with the inclusion of the contribution of spin-orbit-coupling (SOC) on top of the GGA+U approach, we investigated the electronic structure and the magnetic moments of the most stable “stuffed” system. In our determined “stuffed” structure the valence bands as compared to those of the pure system are pushed down and a change in hybridization between the O 2*p* orbitals and the metal ion states is found. Our first-principle findings should form a foundation for effective models describing the low-temperature properties of this material whose true ground state remains controversial.

## I. INTRODUCTION

Pyrochlore materials with the general formula  $\text{A}_2\text{B}_2\text{O}_7$ , where A is a trivalent rare earth ion and B is a transition-metal atom, display a diverse set of physical properties<sup>1</sup>. In the pyrochlore structure, the A and B cations form two distinct interpenetrating lattices of corner-sharing tetrahedra. In such a geometry, the natural tendency to form long-range magnetic order is frustrated and hence these materials have been the subject of considerable theoretical and experimental interest for the last two decades<sup>1</sup>. Some pyrochlores such as  $\text{Ho}_2\text{Ti}_2\text{O}_7$  and  $\text{Dy}_2\text{Ti}_2\text{O}_7$  with large local Ising-like magnetic moments are believed to be long range dipolar<sup>2</sup> “spin-ice” compounds.<sup>3,4</sup>

In comparison to these “classical” pyrochlores, the properties of  $\text{Yb}_2\text{Ti}_2\text{O}_7$  are more debatable. An extensive body of experimental<sup>5–18,43</sup> and theoretical<sup>17,19–26</sup> research have claimed  $\text{Yb}_2\text{Ti}_2\text{O}_7$  states of different nature. It is known to have a ferromagnetic Curie-Weiss temperature of  $\sim 0.65$  K and a first-order transition at  $\sim 0.24$  K<sup>10</sup>. Its properties are dominated by the 4*f*<sup>13</sup> electrons of the  $\text{Yb}^{+3}$  ions which form the A sublattice tetrahedra network, as shown in Fig. 1(a). Large spin-orbit coupling (SOC) and crystal field create a lowest Kramer’s doublet state energetically separated from the first excited doublet by 890 K<sup>27</sup>. The low-energy spin-dynamics as revealed by inelastic neutron scattering<sup>21</sup> can be modelled by an effective pseudospin-1/2 moment<sup>29</sup>. The magnetic interaction of  $\text{Yb}_2\text{Ti}_2\text{O}_7$  has been described in the  $S = 1/2$  subspace by an anisotropic exchange Hamiltonian<sup>16,21</sup> with four independent exchange constants<sup>30</sup>.

Ross et. al<sup>31</sup> have pointed out the role of off-stoichiometry in the difference in ground state properties of this material in various studies, which we must take into account. Generally speaking, it was found that

systems with a single specific heat anomaly between 214 mK and 265 mK<sup>21,32,33</sup> are stoichiometric, whereas systems with broad humps in specific heat<sup>6,21,32</sup> are best described as “stuffed”, with Yb substitution on some Ti sites. Stuffing introduces some new nearest neighbor interactions among the  $\text{Yb}^{+3}$  ions as well as different oxygen environments, which is expected to significantly influence the ground state properties.

While density functional theory (DFT) has been used to study this system taking the active *f* electrons into account<sup>34</sup>, there is a general need for *ab-initio* calculations to study the effect of off-stoichiometry in this class of materials and to form a basic microscopic understanding of the ground-state properties, which we shall provide here. It is well-known that materials with partially filled *f* orbitals pose serious challenges to DFT calculations, especially of their magnetic properties. Furthermore, the complexity and range of the various possible interactions, as well as the very small energy scales of the exchange Hamiltonian<sup>16,21</sup> put a detailed picture of the magnetic order in the ground state beyond the scope of first-principles calculations. However, one should still start from the atomic and electronic structure suggested by DFT calculations. In particular, an *ab-initio* investigation of the most stable atomic structure in the case of “stuffing” can be very useful information. In addition, the electronic structure and the description of oxygen-vacancy related change in valence states would be pertinent information in building a model for this pyrochlore system.

In this paper, we employ DFT computations to investigate the atomic, electronic and magnetic properties of stoichiometric and stuffed  $\text{Yb}_2\text{Ti}_2\text{O}_7$ . We consider stuffing at various concentrations and find that all the stuffed systems considered are unstable towards formation of oxygen vacancies for a wide range of oxygen chemical potential. The stable vacancy created in the neighborhood

of the substituted cation site leads to significant changes in the structural and electronic properties as compared to the stoichiometric system. We identify  $\text{Ti}^{+3}$  oxidation states as a consequence of the stuffing and note that the Ti atoms do not possess significant magnetic moments. We apply the Hubbard-based DFT+U approach to account for the Coulomb interactions between electrons and find that a minimum value of  $U$  in Yb  $f$  orbitals is required to account for the correct electronic phase of  $\text{Yb}_2\text{Ti}_2\text{O}_7$ .

The paper is organized as follows: After a brief explanation of our computational methods in Sec. II, we present our detailed results in Sec. III and present our conclusions in Sec. IV.

## II. COMPUTATIONAL METHODS

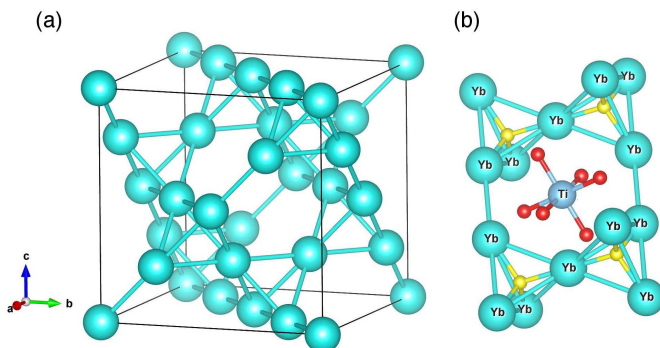


FIG. 1. (a) The pyrochlore crystal structure of  $\text{Yb}_2\text{Ti}_2\text{O}_7$  showing the corner sharing tetrahedral Yb network in a conventional simple cubic lattice (Ti and O atoms have been omitted for clarity). (b) One Yb hexagon with a Ti atom at its center forming part of a  $\{111\}$  Kagome plane. This Ti atom is replaced by an Yb atom in the stuffed system. Also shown are some selected Yb tetrahedra connected to the Kagome plane and perpendicular to it. One of the oxygen atoms the Ti is bonded to (shown in red) is removed to create an Wyckoff  $f$ -site oxygen vacancy. The oxygen atom (shown in yellow) at the center of the Yb tetrahedra is removed to create an Wyckoff  $b$ -site vacancy.

We perform Spin-GGA and Spin-GGA+U computations using plane-wave basis set (cutoff of 520 eV) with the projected augmented wave methodology<sup>35</sup> used to describe the wavefunctions of the electrons as implemented in the VASP package<sup>36–39</sup>. We use the Perdew-Burke-Ernzerhof (PBE) formulation of the exchange correlation functional<sup>40</sup>. The  $4s$ ,  $3d$ ,  $3p$  electrons of titanium and the  $2s$ ,  $2p$  electrons of the oxygen were treated as valence electrons. For ytterbium, the  $4f$ ,  $6s$  as well as the semi-core  $5s$ ,  $5p$ ,  $4s$  electrons were included.  $\text{Yb}_2\text{Ti}_2\text{O}_7$  belongs to the space group  $\text{Fd}\bar{3}\text{m}$  (227) with Yb and Ti

both forming a lattice of corner sharing tetrahedra. The Yb tetrahedral network is shown in Fig. 1(a). There are two types of oxygen in the unit cell, one in the Wyckoff  $f$ -site, and the other type in the Wyckoff  $b$ -site at the center of the Yb tetrahedra. We consider simulation cells with 2, 4 and 8  $\text{Yb}_2\text{Ti}_2\text{O}_7$  formula units (f.u.) to study the role of stuffing and oxygen vacancy stability at various concentrations. The stoichiometric system consists of four ytterbium atoms in a 22-atom primitive unit cell. For the Yb  $f$ -orbitals in these systems, we vary the parameter  $U$  between 0 and 6 eV to see its effect on the electronic structure, and use values of 0, 0.8 and 1 eV for the on-site exchange  $J$ . We use  $U = 2$  eV and  $J = 0.8$  eV for the Ti  $3d$  orbitals. Changing the values of  $U$  and  $J$  for Ti does not have a significant effect on the system properties. For all other systems, we fix the values of  $U$  and  $J$  at  $U_{\text{Yb}} = 6$  eV,  $J_{\text{Yb}} = 1$  eV,  $U_{\text{Ti}} = 2$  eV and  $J_{\text{Ti}} = 0.80$  eV.

All the stuffed systems are structurally relaxed until the forces were converged to less than 10 meV/Å for each ion. The stuffed systems have additional Yb atoms substituting Ti atoms at the center of the hexagon in the  $\{111\}$  Kagome plane (Fig. 1(b)). We create vacancies in the stuffed systems by removing an oxygen atom either in the Wyckoff  $f$ -site (neighbor of this Ti atom) or in the Wyckoff  $b$ -site (center of the Yb tetrahedron) to study their stability and their effect on the electronic structure.

The Brillouin zones for the stoichiometric systems with 2  $\text{Yb}_2\text{Ti}_2\text{O}_7$  f.u. in the computational cell, and its stuffed variants (with and without an oxygen vacancy) were each sampled with a  $7 \times 7 \times 7$   $k$ -point grid. By increasing the  $k$ -point sampling up to  $9 \times 9 \times 9$  for selected systems, we found the energy converged to within 0.20 meV/atom. The Brillouin zone of the 4  $\text{Yb}_2\text{Ti}_2\text{O}_7$  f.u. systems were sampled with up to  $6 \times 6 \times 3$   $k$ -point grids and that of the 8  $\text{Yb}_2\text{Ti}_2\text{O}_7$  f.u. systems were sampled with  $3 \times 3 \times 3$   $k$ -point grids.

In the 2 and 4 f.u. systems, we included SOC to accurately represent the electronic structure. Symmetry was turned off altogether when SOC was included, except during the ionic relaxation cycles which were carried out without SOC taken into consideration. SOC in these systems generate anisotropies including the Dzyaloshinsky-Moriya (DM) interaction between nearest neighbor Yb ions. Even though SOC in  $4f$  orbitals is strong, its overall effect is weak, as can be seen from the values of the exchange parameters in the anisotropic exchange Hamiltonian<sup>16,21</sup>. Therefore, structural relaxation without including SOC is justifiable. SOC was not included in computing the oxygen vacancy stability in the 8  $\text{Yb}_2\text{Ti}_2\text{O}_7$  f.u. systems.

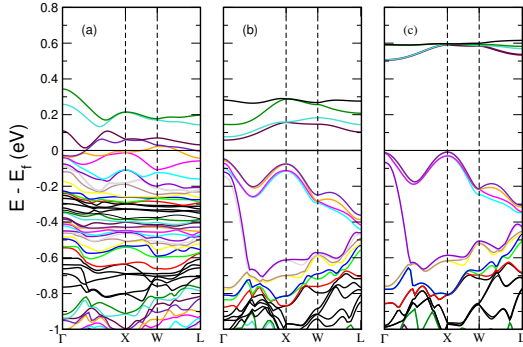


FIG. 2. Electronic band structure of  $\text{Yb}_2\text{Ti}_2\text{O}_7$  calculated using Spin-GGA + U + SOC method, for various values of U and J in Yb  $f$  orbitals, shown along the crystal high symmetry lines. We use in (a)  $U = 0$  eV,  $J = 0$  eV, which gives us a metallic ground state. In (b), we use  $U = 3$  eV,  $J = 0.7$  eV, which opens a small gap. In (c), we use  $U = 6$  eV,  $J = 1$  eV.

### III. ATOMIC, ELECTRONIC AND MAGNETIC STRUCTURE

#### A. Pure pyrochlore $\text{Yb}_2\text{Ti}_2\text{O}_7$ crystal

For  $4f$  electrons of the  $\text{Yb}^{+3}$  ions, SOC is strong and should be considered before crystal field effects. The thirteen  $f$  electrons should have spin  $S = 1/2$  and angular momentum  $L = 3$  according to Hund's rule. The fourteen-fold degeneracy is lifted by SOC leading to eight-fold degenerate  $J = 7/2$  states and six-fold degenerate  $J = 5/2$  states. The crystal field further splits the  $J = 7/2$  states into four Kramer's doublet and the ground state can be described by an effective  $S = 1/2$  pseudospin. The thirteen electrons fill this manifold creating one empty conduction band. Thus, we expect as many  $4f$ -character bands near the Fermi level as there are Yb atoms in the computational unit cell. The stuffed systems will be expected to have more conduction bands than the stoichiometric system.

In Fig. 2(a), we plot the bands for stoichiometric  $\text{Yb}_2\text{Ti}_2\text{O}_7$  with four Yb atoms in the unit cell. We find that for low correlations in the  $4f$  orbitals, the ground state is metallic. This differs from the experimental result that  $\text{Yb}_2\text{Ti}_2\text{O}_7$  is an insulator which is either dark red in color or clear transparent<sup>41</sup>. A moderate value of  $U \sim 3$  eV is needed to open up a gap in the electronic spectrum, which we show in Fig. 2(b). Once the system becomes an insulator, the qualitative features do not change with the value of U. For large correlation ( $U = 6$  eV,  $J = 1$  eV), we find in Fig. 2(c) a direct band gap of 0.52 eV. This is close to that in a previous study<sup>34</sup> with the same  $U$  and  $J$  values where the band gap was found to be 0.6 eV. The ground state is that a single  $4f$  hole at each Yb site, occupying one of the conduction bands

in Fig. 2(b or c) and the O  $2p$  occupied sites shown as the valence states in the same figures. The anisotropic superexchange interaction between Yb ions is driven by a virtual hopping<sup>29</sup> between these levels.

It may be noted that a previous DFT work<sup>42</sup>, in which the  $f$  electrons were frozen in the core during the calculations, found the difference between the conduction band minimum (CBM) and valence band maximum (VBM) to be 3.34 eV. In our work, that corresponds to the difference of 3.25 eV between the valence band maximum and the empty Ti  $3d$  states (shown later in Fig. 5).

#### B. The stuffed $\text{Yb}_2\text{Ti}_2\text{O}_7$ with oxygen vacancy

To study the stability of oxygen vacancies in stuffed  $\text{Yb}_2\text{Ti}_2\text{O}_7$  We compare the energies of  $\text{Yb}_{2+x}\text{Ti}_{2-x}\text{O}_{7-\delta}$  with Yb stuffing concentration of 25 % ( $x = 1/2$ ) and 12.5 % ( $x = 1/4$ ) with the corresponding " $\delta = 0$ " states. We expect our description to be quantitatively accurate for high stuffing concentrations or for microscopic clusters of stuffing in the crystal, and qualitatively meaningful in the dilute regime. To create these systems we replace Ti atoms at sites labeled in Fig. 1(b) by Yb atoms. Due to the substitution of a +4 Ti ion with a +3 Yb ion, it is reasonable to expect one oxygen atom bonded to the cation in this site to leave. While there are direct evidences of Yb stuffing<sup>31,41</sup>, oxygen vacancy, which seems quite plausible given general oxidation state arguments, has been either assumed or argued for indirectly<sup>43</sup> based on a Ti valence change. To find the stability of creation of oxygen vacancy, we compute:

$$F = [F_V - F_0 + \mu_O] / N_u, \quad (1)$$

where  $F_V$  is the free-energy of the stuffed unit cell with an oxygen vacancy,  $F_0$  is the free-energy of the stuffed no-vacancy unit cell,  $\mu_O$  is the oxygen chemical potential, and  $N_u$  is the number of Yb octahedra included in our computational unit cells.

We use the following computational cells in our stability computations. 25 % Yb stuffing and one oxygen vacancy in the 22-atom (2 f.u.) unit cell creates a system with the chemical formula  $\text{Yb}_{2+x}\text{Ti}_{2-x}\text{O}_{7-x}$  ( $x = 1/2$ ). To create a unit cell with the chemical formula  $\text{Yb}_{2+x}\text{Ti}_{2-x}\text{O}_{7-x/2}$ , we replace two Ti atoms with a Yb atom each, and remove one oxygen atom. This creates a stuffing concentration of 25 % ( $x = 1/2$ ) in the 44-atom (4 f.u.) unit cell and 12.5 % ( $x = 1/4$ ) in the 88-atom (8 f.u.) unit cell. To find the possible range of  $\mu_O$ , we first note that the value is bounded from above by the chemical potential of formation of the triplet  $\text{O}_2$  molecule,

$$\mu_O < \mu_{\text{O}_2}/2 = -4.917 \text{ eV}.$$

To find the lower limit, we assume that  $\mu_O$  is the same in the gas phase and in the stuffed pyrochlore. Then

the chemical potentials of the elements in the stuffed pyrochlore are constrained by:

$$(2+x)\mu_{\text{Yb}} + (2-x)\mu_{\text{Ti}} + 7\mu_{\text{O}} = \mu_{\text{Yb}_{2+x}\text{Ti}_{2-x}\text{O}_7}.$$

To stop phase separation into  $\text{Yb}_{\text{bulk}}$  and  $\text{Ti}_{\text{bulk}}$ , the chemical potentials of Yb and Ti themselves must satisfy inequality constraints:

$$\begin{aligned}\mu_{\text{Yb}} &< \mu_{\text{Yb}}^{\text{bulk}} = -1.231 \text{ eV}, \\ \mu_{\text{Ti}} &< \mu_{\text{Ti}}^{\text{bulk}} = -7.898 \text{ eV}.\end{aligned}$$

Using the above inequality constraints and the computed value  $\mu_{\text{Yb}_{(2+x)}\text{Ti}_{(2-x)}\text{O}_7} = -79.395 \text{ eV}$ , the allowable energy of the oxygen chemical potential is

$$-9.210 \text{ eV} < \mu_{\text{O}} < -4.917 \text{ eV}.$$

As shown in Fig. 3, we find that the pyrochlore struc-

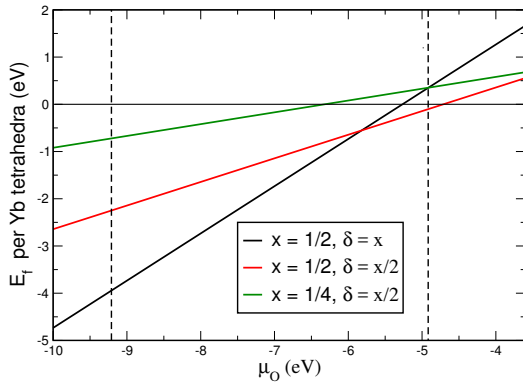


FIG. 3. Free energy of the oxygen vacancy process in stuffed  $\text{Yb}_2\text{Ti}_2\text{O}_7$  for 25 % and 12.5 % Yb stuffing. Three different types of unit cells with chemical formula  $\text{Yb}_{2+x}\text{Ti}_{2-x}\text{O}_{7-\delta}$  are shown and their free energies are compared with those of the corresponding stuffed structures with no oxygen vacancy. The vacancies are at Wyckoff  $f$ -sites. The limits of oxygen chemical potential is shown by dotted lines. We use  $U_{\text{Yb}} = 6 \text{ eV}$ ,  $J_{\text{Yb}} = 1 \text{ eV}$ ,  $U_{\text{Ti}} = 2 \text{ eV}$ ,  $J_{\text{Ti}} = 0.8 \text{ eV}$ .

tures at all stuffing concentrations considered will create an oxygen vacancy over a wide range of possible oxygen chemical potential. There has recently been direct experimental evidence of Yb stuffing on to Ti sites<sup>43</sup> using atomically resolved energy-dispersive x-ray spectroscopy (EDX) along with indirect evidence of oxygen vacancies by observing changes in Ti valence using electron energy loss near-edge structure (ELNES) spectra. We further find that the Wyckoff  $f$ -site oxygen vacancy is more stable than the Wyckoff  $b$ -site vacancy by 0.4 eV per Yb tetrahedra so we do not consider the latter in further discussions. If Ti cations outside the pyrochlore phase are created by the synthesis process which produces off-stoichiometric ratios of Yb and Ti, the oxygen ions will react to produce a stable  $\text{TiO}_2$  phase.

The replacement of Ti atoms with Yb and the removal of an oxygen atom cause the stuffed Yb to move away from the vacant oxygen site, displacing it from the center of the Kagome hexagon. The Yb-Yb bond length in the ideal system is 3.57 Å. For  $x = 1/2$ , the Yb-Yb distance between the center of the hexagon and the two Yb corners its shifted away from is 3.78 Å. The Yb-Yb distance between the center and the two corners its pulled towards is 3.48 Å. The various Yb-O bond lengths for this new Yb atom are found to be between 2.14 Å and 2.32 Å, which is shorter than the Yb-O bond length of 2.51 Å at the Wyckoff  $f$ -site but longer than the Ti-O bond length of 1.94 Å. In contrast to the 4*f* orbitals of  $\text{Yb}^{3+}$  where the ground state changes from metallic to insulating as the value of Hubbard  $U$  crosses a threshold, the role of  $U$  in Ti 3*d* orbitals is found to be minimal in determining the character near the Fermi level. We show the electronic band structure of the stuffed pyrochlore  $\text{Yb}_{2+x}\text{Ti}_{2-x}\text{O}_{7-x/2}$  ( $x = 1/2$ ), which we earlier found to be stable, in Fig. 4(b). We repeat Fig. 2(c) in Fig. 4(a) for comparison. There are ten Yb 4*f* conduction bands in Fig. 4(b). Due to the oxygen vacancy caused by stuffing, the mostly O 2*p* valence bands just below the Fermi level are missing. Effectively, the O 2*p* energy bands are thus pushed down compared to those in the stoichiometric system. The band gap compared to the stoichiometric system is widened, to 1.02 eV.

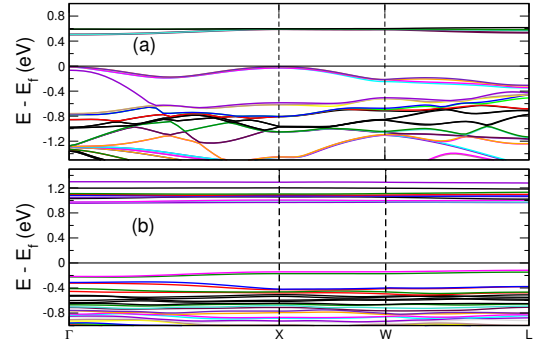


FIG. 4. (a) Electronic band structure of stoichiometric  $\text{Yb}_2\text{Ti}_2\text{O}_7$  calculated using Spin-GGA +  $U$  + SOC method (Fig 2(c) repeated). Electronic band structure of  $\text{Yb}_{2+x}\text{Ti}_{2-x}\text{O}_{7-x/2}$  ( $x = 1/2$ ), shown along the crystal high symmetry lines. The vacancy is in the Wyckoff  $f$ -site. The ten energy bands around the Fermi level are 4*f* in character. Results are for  $U_{\text{Yb}} = 6 \text{ eV}$ ,  $J_{\text{Yb}} = 1 \text{ eV}$ ,  $U_{\text{Ti}} = 2 \text{ eV}$ ,  $J_{\text{Ti}} = 0.8 \text{ eV}$ .

To show the full impact of off-stoichiometry, Fig. 5 compares the density of states (DOS) of the stoichiometric crystal with the stuffed ( $x = 1/2$ ) crystal having an oxygen vacancy. The states near the Fermi surface are Yb 4*f* whereas the valence states are a mixture of O 2*p* and Yb states. As a consequence



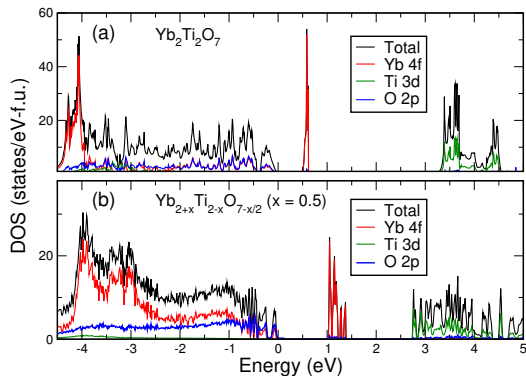


FIG. 5. (a) Total and atom-projected density of states (DOS) of  $\text{Yb}_2\text{Ti}_2\text{O}_7$  and (b)  $\text{Yb}_{2+x}\text{Ti}_{2-x}\text{O}_{7-x/2}$  at  $x = 1/2$  calculated using Spin-GGA + U + SOC. It can be seen that stuffing and oxygen vacancy modify the states between -5 eV and 0 eV, which arise from Yb 4f and O 2p. Yb 4f states make up the sharp peaks in the DOS that form the conduction bands, and are narrower in the stoichiometric system. The states between 2.5 and 5 eV are primarily Ti 3d with some O 2p character. The Fermi energies are set to zero. Results are for  $U_{\text{Yb}} = 6$  eV,  $J_{\text{Yb}} = 1$  eV,  $U_{\text{Ti}} = 2$  eV,  $J_{\text{Ti}} = 0.8$  eV.

of removal of an oxygen atom, the Ti atom near the vacancy acquire a +3 valence character. The increased hybridization between Ti 3d states and O 2p states show up in the stuffed crystal between 2.5 and 5 eV (Fig. 5 (b)). Change in Yb-O bond length caused by the defects increases Yb-O hybridization which shows up as an increased density of states below the Fermi level.

With only the isotropic Heisenberg exchange (without SOC) the magnetic moments in the pyrochlore geometry are frustrated. The presence of SOC removes the frustration. However, the anisotropic coefficients in the exchange Hamiltonian evaluated experimentally<sup>16,31</sup> by fitting neutron scattering excitation data are exceedingly small, being of the order of 0.1 meV and less. Our computation methods were accurate to within 0.2 meV/atom. Predictably, we found all the states we considered as starting points (spin-ice, all-in/all-out, (100) ferromagnetic, (100) antiferromagnetic, (111) ferromagnetic and (111) antiferromagnetic) to be degenerate.

We find that the total magnetic moment per Yb atom in the stoichiometric system to be  $0.86 \pm 0.005 \mu\text{B}$  and the orbital magnetic moment per Yb atom to be  $0.25 \pm 0.007 \mu\text{B}$ . In the non-stoichiometric systems, we find the total magnetic moment per Yb atom to be  $0.92 \pm 0.02 \mu\text{B}$  and orbital magnetic moment per Yb atom to be  $0.24 \pm 0.02 \mu\text{B}$ . These magnetic moments compare well to recent to experimental findings<sup>18</sup> where they were measured to be  $0.87(2) \mu\text{B}$ , and are different from a previous DFT calculation<sup>34</sup>. There was no noticeable magnetic moment

in the Ti atoms even as there was a change in oxidation state due to the oxygen vacancy.

The magnetic moments were calculated using VASP non-self-consistent routines including the effect of SOC where the charge density was kept fixed during the non-collinear calculations. It is also possible to include non-collinear SOC in a fully self-consistent way. When we do that, the magnetic moments change significantly. In the stoichiometric system, we find total magnetic moment per Yb atom to be  $0.28 \mu\text{B}$  and orbital magnetic moment to be  $0.53 \mu\text{B}$ . This suggests a rotation of the orbital and spin expectation values with respect to each other.

#### IV. CONCLUSIONS

The atomic and electronic structure of stoichiometric and stuffed  $\text{Yb}_2\text{Ti}_2\text{O}_7$  are investigated using density functional calculations within the GGA+U scheme and including spin-orbit coupling. Through our stability computations, we show that once there is substitution of a  $\text{Yb}^{+3}$  in a  $\text{Ti}^{+4}$  site (the stuffed system), it is energetically favorable to contain oxygen vacancy defects in the Wyckoff *f*-sites, leading to stable oxygen deficient materials characterized by a change in Ti valence state from  $\text{Ti}^{+4}$  to  $\text{Ti}^{+3}$ . Stuffing and oxygen vacancy defects cause changes in the Ti-O and Yb-O bond lengths which create a different hybridization character. The O 2p valence bands are pushed down and the band gap is increased. We find the electronic phase and the band gap of  $\text{Yb}_2\text{Ti}_2\text{O}_7$  to be dependent on the value of correlation *U* in the Yb *f* orbitals. We notice no significant magnetic moment in the Ti atoms in the defect system. The magnetic moments of the Yb atoms were calculated and found to be reasonably close to measured values. Off-stoichiometry introduces a magnetic moment in the substituted lattice sites which have different exchange pathways as compared to the Yb tetrahedra in the stoichiometric system. This, combined with oxygen vacancy and structural distortion is likely to destroy long range magnetic order. While the GGA+U scheme seems to work reasonably well, it is known for its limitations in *f*-electron systems. However, our revealed atomic structure of the “stuffed” compound, in particular the stability of the oxygen vacancies, is expected to be correct since its determination involves quite large energy differences between it and the other competing structures.

Note added: When our lengthy computations were finished and we were preparing this manuscript for submission, we became aware of the recently published experimental paper Ref. 43, whose EDX and EELS based findings are consistent with our ab-initio findings and point to the role of disorder in determining the ground-state properties of  $\text{Yb}_2\text{Ti}_2\text{O}_7$ . In this latest form of the present paper, we have discussed and compared our findings to those of Ref. 43 in detail throughout the manuscript.

## V. ACKNOWLEDGMENTS

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