

**Electronic and magnetic properties of the different phases of  $\text{Ti}_4\text{O}_7$  from density functional theory**Mariana Weissmann<sup>1,\*</sup> and Ruben Weht<sup>1,2</sup><sup>1</sup>*Gerencia de Investigación y Aplicaciones, CNEA, 1650 - San Martín, Argentina*<sup>2</sup>*Instituto Sabato, Universidad Nacional de San Martín-CNEA, Argentina*

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*Ab initio* calculations using the local spin-density approximation plus Hubbard  $U$  (LSDA+ $U$ ) method have been performed for the three reported phases of  $\text{Ti}_4\text{O}_7$ . Using the experimental structural parameters, we find that the electronic and magnetic properties are qualitatively different for each phase. The low-temperature structure is an antiferromagnetic semiconductor, with bipolarons arranged symmetrically in chains, separated by other nonmagnetic ion chains. The intermediate-temperature structure also contains bipolarons, but in a much more complicated order, in addition to unpaired magnetic  $\text{Ti}^{3+}$  ions and nonmagnetic  $\text{Ti}^{4+}$  ions. It has a smaller band gap than the low-temperature one. The high-temperature structure is metallic, and different distributions of  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  ions can be found that are almost degenerate.

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**I. INTRODUCTION**

$\text{Ti}_4\text{O}_7$  is a member of the homologous series  $\text{Ti}_n\text{O}_{2n-1}$ , which is the Ti family of the Magnéli phases. Its crystalline structures and interesting electronic and magnetic properties have been extensively studied, both experimentally and theoretically, for almost 30 years.<sup>1-8</sup> However, interest in this material has recently reappeared. On the one hand, regarding applications, it was suggested that  $\text{Ti}_4\text{O}_7$  mediates the operation of titanium-oxide resistive switching memories,<sup>9-11</sup> forming or destroying conducting filaments inside the oxide during the switching procedure. On the other hand, a recent paper reported an anomalous state for its intermediate phase, sandwiched between a Fermi liquid and a charge-ordered insulating phase, using photoemission spectroscopy.<sup>12</sup> Here we revisit this problem, calculating the magnetic and electronic properties of the three different phases of  $\text{Ti}_4\text{O}_7$  using *ab initio* methods, and try to clarify some points still under debate, especially regarding the magnetic configurations for the high- and intermediate-temperature phases.

The system is well known to exhibit two consecutive first-order transitions: one in the temperature range of 125–140 K ( $T_{c1}$ ) and the other at about 150 K ( $T_{c2}$ ). At both temperatures, there are strong changes, of orders of magnitude, in the electrical resistivity  $\rho(T)$ . The magnetic susceptibility  $\chi(T)$  only changes at  $T_{c2}$ , being constant and almost negligible below it. Between the low- and intermediate-temperature phases, there is a hysteresis region of around 10 K.

The low-temperature (LT) phase is a semiconductor with a relatively small band gap. Optical measurements originally found a band gap of around 0.25 eV.<sup>13</sup> However, more recently (see Ref. 12), using photoemission spectroscopy, a band gap of only 0.1 eV was found, followed by a broad peak at 0.7 eV. There is a general consensus that it presents chains of dimerized pairs of  $\text{Ti}^{3+}$  (a  $3d^1$  configuration), forming bipolarons, separated from each other by chains of  $\text{Ti}^{4+}$  ( $3d^0$ ). This charge localization has already been noted in earlier works on this material.<sup>3</sup> The schematic structure is shown in Fig. 1 (left).

The high-temperature (HT) phase is conducting and presents no magnetic long-range order, so that the Ti valence

is assumed to be almost uniform at 3.5+; see Fig. 1 (right). Its susceptibility shows a Pauli paramagnetic behavior.

The intermediate (IT) phase is still far from being completely understood, with the usual model being that of disordered bipolarons. Marezio *et al.* performed single-crystal x-ray investigations on  $\text{Ti}_4\text{O}_7$  as it went through both transitions.<sup>4</sup> From the determination of the crystalline structures at 120, 140, and 298 K, they estimated the charge of the titanium ions by using the measured (Ti – O) distances and tabulated ionic radii. According to their results, they first suggested that the  $\text{Ti}^{3+} - \text{Ti}^{3+}$  pairs still remain in the intermediate-temperature phase, but without a long-range order. In a later work, Le Page and Marezio<sup>14</sup> revisited the structures of the three different phases. Their low- and high-temperature structures were very similar to the ones previously reported, but they suggested a much more complicated structure for the intermediate phase. They concluded that bipolarons were still present, with a long-range order of Ti valences and the presence of  $\text{Ti}^{3+} - \text{Ti}^{3+}$  pairs.

From the theoretical point of view, a few *ab initio* electronic structure calculations have appeared. In an early work, Eyert and coworkers,<sup>15</sup> using the local density approximation for the density functional theory, found correctly a charge-ordered state in the low-temperature phase and an isotropic occupation for the room-temperature structure. However, all their solutions were metallic, even for the low-temperature phase. Later, Leonov *et al.*<sup>7</sup> added a Hubbard term, working within the local spin-density approximation plus Hubbard  $U$  (LSDA+ $U$ ) formalism, and obtained the correct orbital and charge ordering for the low-temperature phase, remarking on the importance of taking into account the electronic correlations to improve the description of its properties. Liborio *et al.*<sup>8</sup> have also made first-principle calculations on this material, but in this case using the CRYSTAL code, with a Gaussian basis set and the Becke, three-parameter, Lee-Yang-Parr (B3LYP) hybrid exchange functional. They found antiferromagnetic solutions for all three phases.<sup>16</sup> Their results and interpretation of the low-temperature phase coincide with Leonov's and also with our calculations of a localization of the charge, with chains of  $\text{Ti}^{3+} - \text{Ti}^{3+}$  pairs separated by  $\text{Ti}^{4+}$  chains. However, for the intermediate- and high-temperature phases, they found

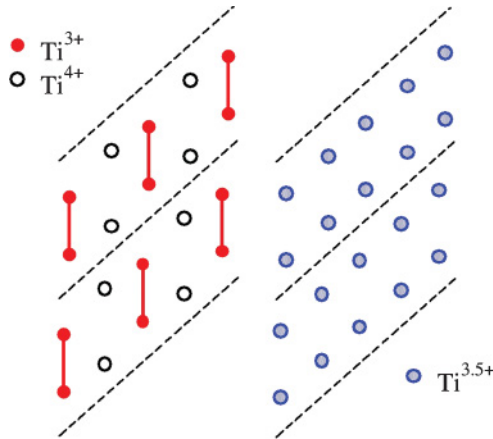


FIG. 1. (Color online) Schematic picture of the crystal structure of  $\text{Ti}_4\text{O}_7$ , showing only the Ti chains that run along the pseudorutile  $c$  axis, for the low- (left) and high- (right) temperature phases.

a magnetic symmetry quite different from our calculations. They found much larger band gaps and all the phases to be antiferromagnetic.

## II. METHOD OF CALCULATION

The unit cell of  $\text{Ti}_4\text{O}_7$  is triclinic and consists of two formula units. However, as we will calculate several crystal structures and magnetic arrangements, all our results will be reported per formula unit (f.u.). We have calculated the magnetic and electronic properties of  $\text{Ti}_4\text{O}_7$  within the density functional theory (DFT),<sup>17</sup> taking into account the electronic correlations on the Ti sites within the LSDA+ $U$  approximation. We have evaluated for the three phases several magnetic orderings using the experimentally determined atomic structures, as reported by Marezio and coworkers in their latest paper.<sup>14</sup> As the *ab initio* calculations do not include temperature, our results show the properties of the different structures at 0 K. Only collinear spins were considered. For the high- and intermediate-temperature phases, we performed fixed spin moment (FSM) calculations to find the lowest-energy ferromagnetic solution.

We used the WIEN2K code,<sup>18</sup> which is an implementation of the full potential, linear augmented plane waves (FP-LAPW) method. The calculations were scalar relativistic, with the parameters listed in Ref. 19.

In the case of oxides, as was also evaluated by Eyert *et al.*<sup>15</sup> for  $\text{Ti}_4\text{O}_7$  itself, it is well known that it is necessary to correct the very small (or negligible) band gap given by the DFT. For this purpose, we have used the LSDA+ $U$  (Ref. 20) method for the Ti- $d$  orbitals, with a fixed  $U = 0.4$  Ry. This value of  $U$  was selected after performing calculations for the three different phases varying  $U$ . For  $U = 0.4$  Ry, the energies of the three phases differ by less than a hundredth of eV, as shown in Fig. 2, and this is the order of magnitude of the experimental transition temperatures. A similar value of  $U$  has been used in our previous work<sup>21</sup> to study the rutile and anatase phases of  $\text{TiO}_2$ , and was also obtained by Calzado *et al.*,<sup>22</sup> using *ab initio* embedded cluster methods to study a reduced rutile surface.

In the operation of resistive switching memory devices,  $\text{Ti}_4\text{O}_7$  will also compete with structures of  $\text{TiO}_2$  with oxygen

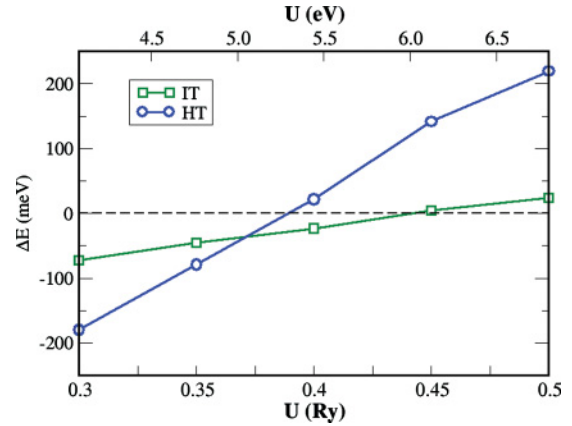


FIG. 2. (Color online) Lowest energy/f.u. for the intermediate- and high-temperature phases as a function of  $U$ , taking as zero the values for the low temperature case.

vacancies. For the sake of comparison, we calculated  $\text{Ti}_4\text{O}_7$  in the anatase structure (one unit cell with a missing oxygen) and in the rutile structure (unit cell doubled along  $c$  with a missing oxygen) without relaxing the unit cell size of each material. Of course, this is only a first approximation as such a large concentration of vacancies in a periodic structure would certainly increase the optimal cell size in each case. Also, by restricting this calculation to small cell sizes, the oxygen vacancies are ordered. In the case of anatase, two Ti atoms share a vacancy and the system is not magnetic, while in the case of rutile, there are no shared vacancies and the system becomes magnetic. This problem has already been extensively discussed in a previous paper.<sup>23</sup> The important fact here is that for the same value of  $U$  used in our calculations, the total energies per f.u. are considerably higher (see Table I) than those for the Magnéli phases. When there is a large number of oxygen vacancies, they redistribute themselves to form the Magnéli structures, where each Ti atom has six oxygen neighbors.

## III. RESULTS

The results of the calculations are shown in Table I. Although the three phases have very similar-looking structures, with only small changes in cell volume and small displacements of the atoms, the lowest-energy configuration for each of them has different electronic and magnetic characteristics. In fact, the low-temperature structure is clearly an antiferromagnetic insulator with an energy gap of around 0.7 eV, which is certainly higher than the value recently reported,<sup>12</sup> but lower than the one obtained by Liborio *et al.*<sup>8</sup> (1.5 eV). This structure has the Ti ions forming two types of neighboring chains. One of them is dimerized (bipolarons), with distances  $\text{Ti}_1 - \text{Ti}_1 = 3.14$  Å and  $\text{Ti}_1 - \text{Ti}_3 = 2.80$  Å, while the other is not. The dimerized titanium ions have local magnetic moments of  $\pm 0.62 \mu_B$  and are usually represented as  $\text{Ti}^{3+}$ , while the ions on the other line are not magnetized and represent  $\text{Ti}^{4+}$ . There is also a stable ferromagnetic configuration and a nonmagnetic one, both higher in energy and with a very small, almost vanishing, gap for the nonmagnetic state. It is worth mentioning that the magnitude of the ionic magnetic

TABLE I. Number of formula units (f.u.) per unit cell used in the calculations, total energy per formula unit given in each case with respect to the lower-energy magnetic configuration, total magnetic moment per f.u. [with antiferromagnetic (AFM) and nonmagnetic (NM) configurations as indicated], and band gaps for the different Magnéli structures. For comparison, anatase and rutile structures with one vacancy were calculated, using small unit cells and therefore ordered vacancies. In these cases the energy of the Magnéli low temperature phase is taken as zero.

| Case              | f.u./cell | Energy/f.u.<br>eV | Moment/f.u.<br>$\mu_B$ | gap<br>eV |
|-------------------|-----------|-------------------|------------------------|-----------|
| Magnéli low $T$   | 2         | 0.000             | 0.0 (AFM)              | 0.75      |
|                   | 2         | 0.127             | 2.0                    | 0.53      |
|                   | 2         | 0.374             | 0.0 (NM)               | 0.00      |
| Magnéli int $T$   | 10        | 0.000             | 0.0                    | 0.30      |
|                   | 10        | 0.000             | 0.4                    | 0.30      |
|                   | 10        | 0.072             | 2.0                    | 0.00      |
| Magnéli high $T$  | 2         | 0.000             | 0.75                   | 0.00      |
|                   | 2         | 0.010             | 0.0 (AFM)              | 0.20      |
|                   | 2         | 0.022             | 2.0                    | 0.00      |
|                   | 2         | 0.150             | 0.0 (NM)               | 0.00      |
| Anatase with vac. | 1         | 1.35              | 0.0                    | 0.20      |
| Rutile with vac.  | 1         | 1.85              | 2.0                    | 0.10      |
|                   | 1         | 1.95              | 0.0                    | 0.25      |

moments remains almost unchanged in the ferromagnetic ordering, showing that they are linked to the local structure around each Ti ion. In fact, the average distance between the Ti ion and its six neighboring oxygen atoms is larger than 2 Å for the dimerized  $\text{Ti}^{3+}$  ions, but less than 2 Å for those in the other chain,  $\text{Ti}^{4+}$ , with no local magnetic moment.

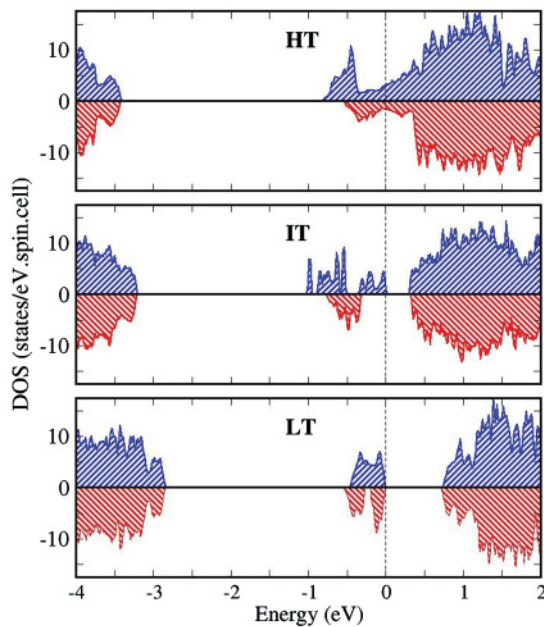


FIG. 3. (Color online) Densities of states of the three different Magnéli phases. The Fermi energy is taken as zero. Positive and negative values correspond to majority and minority spins, respectively. States near the Fermi level for the LT phase belong to the  $\text{Ti}^{3+}$  ions.

For the intermediate-temperature phase, the unit cell is larger, as reported in a later work by Le Page and Marezio.<sup>14</sup> It contains 40 Ti atoms, with half of them having an average distance to their neighbor oxygens larger than 2 Å. Those acquire a local magnetic moment in all the calculations, while the others do not. Even considering only collinear spins, it is not easy to find the lowest-energy configuration of the 20 spins, because there are more than one million of them. However, one can imagine a similar scenario as that of the low-temperature phase, and assume that magnetic ions that are close to each other form bipolarons. In fact, this was already suggested by Le Page and Marezio in Ref. 14, where Ti pairs with distance of less than 3 Å from each other are shown connected with bold black lines in their Fig. 1. We identified eight pairs of this type and only four unpaired magnetic Ti ions (polarons). The total energy of this magnetic ordering is slightly lower than the ferromagnetic one, which is half metallic, and antiferromagnetic one described by Liborio *et al.*<sup>8</sup> The four unpaired magnetic Ti spins can be set parallel or antiparallel, but as they are far apart from each other, the two magnetic structures are degenerate within our calculation error of 1 m Ry, as seen in Table I. The system presents a smaller gap than the low-temperature case, and the local magnetic moments are somewhat smaller, between 0.5 and 0.6  $\mu_B$ .

The high-temperature phase presents several almost degenerate electronic and magnetic structures. For example, there are two pairs of  $\text{Ti}^{3+}$  that are close to each other but related by symmetry,  $\text{Ti}_1 - \text{Ti}_1 = 2.92$  Å and  $\text{Ti}_2 - \text{Ti}_2 = 2.94$  Å. To be able to reverse one of these spins and, therefore, find out if bipolarons are present, the unit cell has to be changed and, therefore, new magnetic configurations appear. The lowest-energy one is metallic and magnetic. The fixed-spin-moment procedure was used to obtain the lowest energy for ferromagnetic alignment, but not all spin results are equal; they range from 0.1 to 0.4  $\mu_B$ . There is also a stable magnetic structure with bipolarons and a small gap of 0.17 eV, but it is slightly higher in energy. In this last case, all the Ti atoms are paired but the pairs are all different, with their local magnetic moments ranging from 0.1 to 0.4  $\mu_B$ . Possibly for this reason, the valence of the Ti atoms is usually set as +3.5. The distance  $\text{Ti}_1 - \text{Ti}_1$  is smaller than  $\text{Ti}_1 - \text{Ti}_3$  (2.89 and 3.02 Å, respectively), which is opposite to what happens at the low temperature. Also, the unit cell volume is 0.4% smaller than that of the low-temperature structure.<sup>14</sup>

#### IV. CONCLUSIONS

The results shown in the previous section indicate that the differences in the crystalline structure of the three Magnéli phases of  $\text{Ti}_4\text{O}_7$  can account for their different electronic and magnetic properties. The low-temperature phase is clearly dimerized with  $\text{Ti}^{3+} - \text{Ti}^{3+}$  pairs, and a bonding that favors an antiferromagnetic configuration. The stable configuration of the high-temperature phase is, according to our calculations, a ferromagnetic metal with a rather low magnetic moment (of around 0.2  $\mu_B/\text{Ti}$ , on average). That low value of magnetic moment and the presence of several quasidegenerate magnetic solutions would make the material behave as a paramagnet due to temperature disorder. The intermediate-temperature phase has a much larger unit cell, coexisting polarons, bipolarons,

and nonmagnetic Ti ions. It is not disordered, but has a more complicated symmetry. It is a semiconductor with a very small band gap and smaller magnetic moment per Ti. That explains why the resistivity changes with respect to the high-temperature phase and also why the magnetic susceptibility becomes zero below  $T_{c2}$ .

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