Warwickites: Electronic Structure and Bonding

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The electronic structure of Mg$_2$Ti$_2$B$_2$O$_8$, a warwickite with Mg in the outer octahedra, Ti in the inner ones, is studied with approximate molecular orbital calculations. A chemical construction of the band structure, density of states, and bonding of this material begins with molecular octahedral and biocatahedral models and then proceeds through a one-dimensional ribbon to the full three-dimensional solid. There is weak Ti–Ti interaction in this material, both direct and through bridging oxygens. Warwickite is very much one-dimensional, such interaction as there is being confined to the ribbons.

The warwickites are a class of mixed metal borates of the general formula A$_x$T$_{4-x}$B$_2$O$_8$, where A and T are alkaline earth, lanthanide, or transition metals. Their structure contains borate (BO$_3^{3-}$) and isolated oxide ions (O$_2^{-}$) which are arranged so as to form distorted octahedral environments for the metals. The octahedral coordination polyhedra share edges to form one-dimensional ribbons four octahedra wide, which then interconnect to form the full three-dimensional structure.

Our interest in these oxides was stimulated by the synthesis and properties of an unusual warwickite Mg$_2$Ti$_2$B$_2$O$_8$. If we assume the normal oxidation states of B$^{3+}$, O$_2^{-}$, and Mg$^{2+}$, we reach a 3$^+$ oxidation state for Ti, or a d$^1$ configuration. The material in fact exhibits interesting magnetic properties, which stimulated us to look at its electronic structure.

**Warwickite Structure.** Because the structure is of some complexity, it is important to become familiar with its intricacies. The original mineral structure solved was Mg$_3$TiB$_2$O$_8$, warwickite itself. Mg$_2$Ti$_2$B$_2$O$_8$ assumes the same structure, space group Pnam, with two formula units in the orthorhombic unit cell (a = 9.186 Å, b = 9.337 Å, c = 3.028 Å). Figure 1 shows two projections of the warwickite structure on the ab plane.

In the representation at top we see clearly the borate groups, each containing three of the four distinct oxygens in the structure, (O2, O3, O4). The fourth oxide ion (O1) is isolated. All the oxides, those from the borates together with O1, form the outer framework of the stack of octahedral chains; each octahedron is then filled by a metal atom. These stacks are outlined at top in Figure 1 but are more clearly visible in the projection at bottom. One can see the stacks connect by sharing O1, but the octahedral nature of the stacking modules is not easily perceived in these “head-on” projections.

Let's look next at the one-dimensional stacks in warwickite. One building unit (there are several ways to choose these) of the stacks is shown in 1. The representation shows four octahedra sharing edges. If
this group of four edge-sharing octahedra is propagated along the z(c) direction, one of the stacks of the warwickite structure is generated. This stack, of Mg₂Ti₂O₁₀ stoichiometry (no charge implied) is shown in two views in Figure 2.

There is a further detail of the structure that needs to be discussed. In the warwickite structure there are two symmetry-related “inner” octahedra in the ribbon and two “outer” ones. The A and T cations are usually disordered among the inner and outer octahedra. Because there is some evidence for the Ti's preferring the inner octahedra (and Mg's the outer ones) in the structure under discussion and because we need translational symmetry in our computations, we have simply assumed full occupancy of inner octahedra by Ti, outer ones by Mg.

With the geometrical structure in hand, let us build up the electronic structure of this material. All the calculations we report in the sequel, for discrete molecules or extended structures, are of the extended Hückel type. The parameters of this semiempirical molecular orbital procedure are given in the Appendix. The reader’s attention is directed to incisive and comprehensive theoretical studies of octahedral metal-centered oxide frameworks of varying dimensionality by Whangbo, Canadell, and co-workers. Their approach is quite similar to ours.

**Borate, TiO₆ and MgO₆ Modules**

While we could look at the full crystal electronic structure at once, we find instructive a chemical building process. By looking at the zero-dimensional components of the structure, model molecules, we will be able to understand more deeply the full electronic structure of the material.

The most strongly bound chemical unit in the structure is the BO₃³⁻ ion. An interaction diagram for this anion, isoelectronic with even more familiar carbonate, CO₃²⁻, and nitrate, NO₃⁻, is shown on the left side of Figure 3. Interaction diagrams forming BO₃³⁻, MgO₆¹⁰⁻, and TiO₆⁹⁻ in warwickite compared in the same energy window.
The general outlook here is that of orbital interaction affecting magnetism. If the splitting between two levels—that splitting resulting from direct orbital overlap or through-bond coupling—is small, then the ground state is likely to be high-spin. In the case of our d^3-d^1 dimer, high-spin means a triplet ground state. If the splitting is large, then the electrons are likely to be "antiferromagnetically coupled", and the consequence is a low-spin dimer, a singlet ground state here.

The shortest Ti–Ti separation in warwickite is 2.73 Å. This is in the region where there is some metal–metal overlap, though perhaps more of the diffuse 4s, 4p orbitals than the 3d. Also, from previous experience we know that the bridging oxygens provide a coupling pathway. So it is interesting to see what happens in the inner octahedron pair, a TiO_12^{14−} model carved out of the solid, as in 3.

A word is in order here on the coordinate systems. In the warwickite structure the Ti–Ti vector does not lie along any single coordinate axis. The molecule is distorted, not possessing the idealized D_{2h} symmetry characteristic of two perfect edge-sharing octahedra. At the same time we have in hand a detailed analysis of the bonding in such systems with the specific coordinate system indicated in 3, i.e., the Ti–Ti vector along z, the two Ti and six oxygens (in ideal D_{2h} symmetry) in the yz plane.

To benefit from the previous analysis, we have reoriented the TiO_12^{14−} fragment from the solid into as close an orientation as we get to an idealized bioctahedron. The calculation gives a "t_{2g}" block of six levels (Figure 4), with a total "bandwidth" of approximately 2 eV. The lowest level of this band is approximately 2 eV. The lowest level of this band is separated by only 0.3 eV from the next higher one. The magnitude of this splitting is small, close to the borderline which would separate a certain low-spin state from a high-spin one. We will have to await better calculations to make a decision on what is the ground state of the molecule. At low temperatures it is likely to be a singlet, i.e., an antiferromagnetically coupled Ti(III)–Ti(III).

Experimentally, this warwickite is described as a one-dimensional random-exchange Heisenberg antiferromagnetic chain, i.e., in the spin Hamiltonian describing the system

\[ H_{ij} = -\sum_{i<j} J_{ij} S_i S_j \]

the exchange integral J_{ij} is negative and varies randomly along the chain.

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(9) For the orbitals of AX_2 molecules see: Gimarc, B. Molecular Structure and Bonding; Academic Press: New York, 1979; Chapter 3.
Let’s discuss these $t_{2g}$ levels in somewhat greater detail. In the orientation of the dimer shown in 3, each octahedron has its individual $t_{2g}$ set made up of $y^2 - z^2$, $xz$, and $xy$ orbitals. These are of $\sigma$, $\pi$, and $\delta$ pseudo-symmetry with respect to the Ti–Ti axis. If only metal–metal through-space interaction mattered, we’d get a splitting of the resulting dimer MO’s $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$. The argument here is nothing sophisticated, just that bonding levels come below antibonding ones, and that the extent of bonding is a function of the overlap, which in turn is such that $\sigma > \pi > \delta$.

Whether one looks at the symmetrized Ti$_2$O$_{10}$ model or the “real” dimer cut out of the solid, the only essential change from a simple metal–metal overlap determined level ordering is that $\delta^*$ is below $\delta$. This is a well-understood phenomenon, the result of only $\delta$ (and not $\delta^*$, by symmetry) interacting with the appropriate symmetry bridging O 2p orbitals.

The small orbital pattern change caused by the bridging oxygens is of little consequence to the d1–d1 dimer of interest to us. The two levels competing for the pair of electrons are $\sigma$ and $\pi$, in-phase, bonding combinations of $y^2 - z^2$ and $xz$, respectively. Their splitting is a consequence of direct, through-space Ti–Ti interactions, and the differential in $\sigma$ vs $\pi$ overlap.

The Ti–Ti interaction thus appears to be small, but significant. How would the situation vary with a change in Ti–Ti distance, which might be induced, for instance, by anisotropic application of pressure or a change in crystal structure? To answer this question, we took an idealized D$_{2h}$, biocahedral structure and varied the Ti–Ti distance in it while keeping all Ti–O separations, bridging and terminal, at 2.0 Å. The geometrical distortion may be alternatively viewed as a purely angular one (the Ti–O–Ti angles varying symmetrically, the O–Ti–O angles tied to these by a constraint of planarity). The plot of Figure 5 uses the Ti–O–Ti angle as the horizontal coordinate, to maintain continuity with a previous discussion.

As in our earlier analysis of Cl and PH$_2$ bridged biocahedra, one moves from a region where metal–metal separations are short (small Ti–O–Ti angle) and through-space Ti–Ti interactions dominate, to a region where the metals are far apart, and indirect (through bridging oxygens) interactions are stronger. Inside the former region, the level order is $\sigma < \pi < \delta^* < \pi^* < \sigma^*$ (at very short Ti–Ti distances $\delta$ goes below $\delta^*$). In the latter region, the level ordering is complex (but can be understood), and the levels are split by little.

The $\sigma$–$\pi$ splitting, important for determining the ground state of the molecule, does not vary monotonically with Ti–O–Ti angle. But it is nowhere greater than 0.4 eV. The system is precarious poised between high and low spin possibilities at all Ti–O–Ti angles.

Next we added the two outer octahedra, containing the Mg$^{2+}$ ions. The model molecule is Mg$_2$Ti$_2$O$_{18}$$^{26}$. The results are not shown here, but we can summarize them by saying that very little change takes place in the critical “Fermi-level” $t_{2g}$ region. The “miniband” of six mainly Ti-based $t_{2g}$ levels has the same “bandwidth” as for the two inner-octahedra model.

**One-Dimensional Ribbon Sublattice.** In the structure of warwickite the strip of four octahedra propagates along the c axis into a one-dimensional ribbon. In defining a model for this strip, we need to consider whether to include the set of borate ions that contribute O2, O3, and O4 to the Ti and Mg environment. While the O–B bonding is strong, the molecular model calculations clearly indicate that the extra electrons reside in Ti orbitals. So we have chosen to exclude, in the interest of simplicity, the borates. We did keep the specific oxygens (taken as O$^{2-}$) the borates contribute to sheathe the strip.
This leaves us with a ribbon of $\text{Mg}_2\text{Ti}_2\text{O}_{10}$ stoichiometry. The band structure and density of states (DOS) of this ribbon is shown in Figure 6, in a small energy window.

Note from the analysis of the contributions to the DOS that all the states in this window are primarily Ti 3d. Further analysis shows that the lower six bands are of “$t_{2g}$”, and the upper four bands of Ti “$e_g$” character. There is a small amount of oxygen and virtually no magnesium character in the “$t_{2g}$” bands.

The six “$t_{2g}$” energies at any $k$ point correspond to the six “$t_{2g}$” levels of the dimer we have analyzed before. Why are they split apart more than the six “$t_{2g}$” levels of the dimer model? If one examines the geometry of the full ribbon, one sees not only that is there a Ti–Ti bioctahedron of the type we have chosen but also that each Ti is engaged in two further edge-sharing interactions with the next unit cell. One involves another Ti at a distance identical by symmetry to the one within the unit cell (2.733 Å). The other one is to a Ti only a little further away (3.028 Å). The geometrical arrangement is shown in 4.

The significance of these other interactions is that if the direct Ti–Ti interactions are at the edge of being significant, as we think they are, the bandwidth of the one-dimensional warwickite ribbon should be somewhat greater than the splitting of the Ti “$t_{2g}$” block in the $\text{Ti}_2\text{O}_{10}$ model. A comparison of Figures 4 and 6 shows this is indeed so.

The dispersion of the bands in the ribbon is such as to overcome the small (0.5 eV or less) splittings among the individual dimer unit levels. So instead of six levels, a single “$t_{2g}$” band results; one-sixth of that band would be filled in a low-spin nonmagnetic ribbon.

Before we draw some conclusions about the magnetism of the material, let us take the short step to the full structure.

**Electronic Structure of Warwickite**

The band structure of warwickite, with its full $\text{Mg}_4\text{Ti}_4\text{B}_4\text{O}_{16}$ unit cell, is shown in Figure 7. Along the lines of the previous analysis we can zoom in on the Fermi level region. For comparison, we have repeated in an inserted panel the one-dimensional ribbon band structure.

Note first that we have a doubling of each “$t_{2g}$” band: this is the result of there being two ribbons in the full three-dimensional warwickite structure. The very small splitting of the two components of each band is the first indication of the one-dimensional nature of this material. A second indication is the tiny dispersion of the bands along the $\Gamma$–$X$ and $\Gamma$–$Y$ edges of the Brillouin zone. And finally, and most convincingly, note how the $t_{2g}$ bands of the three-dimensional material along $\Gamma$–$Z$ match the same bands of the one-dimensional model ribbon. There are some new bands between $-3$ and $-7$ eV in the three-dimensional material; these are the B–O $\pi^*$ orbitals which could not appear in the ribbon, for there we excluded the borons from the model.

Figure 8 shows the DOS of three-dimensional warwickite, along with Ti 3d and boron contributions to it. In view of the previous discussion, it is not surprising that this DOS is much like that of the one-dimensional ribbon, except where boron states come in. It might be worthwhile to mention here the rather different charges on the oxygens, those bonded to the borons (see numbering of oxygens in Figure 1) bearing charges as follows: $-0.977$ (O2), $-1.130$ (O3), $-1.276$ (O4). The isolated O1 has a computed charge of $-0.956$.

The Fermi level for four electrons per unit cell, one electron per Ti, comes in a region of a reasonably high DOS. But there are several bands within 0.5 eV of the Fermi level. We have no good way of predicting from these approximate molecular orbital calculations whether these materials will be conducting, or magnetic semiconductors, or Peierls-distorted semiconductors. Experimentally, one knows that the warwickite is mag-
the energy range of to it of boron and Ti 3d states. The boron states contribute in the resulting density of states (solid line) and the contributions to it of boron and Ti 3d states. The boron states contribute in the energy range of −3 to −7 eV; they are absent in the one-dimensional ribbon sublattice, whose density of states is given in the rightmost panel. The Fermi level is marked by a dashed horizontal line around −10 eV.

The several bands which spread around the Fermi level tend to broaden when we go from the left panel to the right, while the band width decreases. Note that, for the three last calculations, the DOS and the Ti contributions to it are in fact very similar. For Ti−Mg−Ti−Mg and Ti−Mg−Mg−Ti the distances between Ti atoms in the unit cell are bigger than 5 Å, therefore intracell Ti−Ti interactions are negligible. The band width that remains is set by the inter-cell Ti−Ti interactions (see discussion above), which is still there. The large Ti−Ti separation is responsible for the band structure being essentially the same as for the Mg3−TiB2O8 ribbon.

Though there are some differences in the details of the band structure, we can see that the changes are not appreciable; the important general features are preserved in the four different filling patterns; the “$t_{2g}$” and “$e_g$” band widths vary by less than 1 eV and the Fermi level stays, in all cases, close to the bottom of the “$t_{2g}$” band.

We have also analyzed the energetics of the different filling patterns of Ti and Mg atoms, by calculating the total electronic energy per unit cell for each case. The results are shown in Table 1.

Given the one-dimensional nature of the electronic structure of the material, we started the analysis by comparing the band structures of idealized one-dimensional ribbons with the filling patterns specified in Figure 8. The four first panels show the total and Ti 3d projected DOS, with the first one corresponding to the usual occupancy, Mg−Ti−Ti−Mg. For comparison we show, in the last panel, the density of states of the Mg3−TiB2O8 warwickite, with the single Ti atom occupying one of the inside octahedra.

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The structure we have calculated assumes a certain ordered filling of the octahedra—magnesiums in the outside one, titaniums in the central polyhedra. In fact, the exact pattern of filling is not easily determined. So we have studied some alternative variants, the four distinct patterns arising from filling four octahedra by two Ti and two Mg and keeping a four octahedra translational repeat unit. These are illustrated in Figure 9.

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The Fermi level is shown by the dashed line crossing the lower "t_{2g}" bands. The additional contribution to the upper, "e_g", Ti 3d bands and for the ribbon.

The titanium contribution to it for the 3D warwickite occupation pattern. Figure 10 shows the total DOS and WrightiteTi distances in angstroms.

Table 1. Total Electronic Energies per Unit Cell for Ti and Sc Warwickites in Different Filling Patterns

<table>
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<th>Mg–Ti–Ti–Mg</th>
<th>Mg–Mg–Ti–Ti</th>
<th>Mg–Ti–Mg–Ti</th>
<th>Ti–Mg–Mg–Ti</th>
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<td></td>
<td>2.73</td>
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<tr>
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<td>2.84</td>
<td>3.25</td>
<td>5.16</td>
<td>8.14</td>
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</table>

* All calculations are for the ribbon. Energies are in electronvolts relative to the most stable configuration, and Ti–Ti distances in angstroms.

Figure 10. Density of states of the three-dimensional warwickite and the ribbon, both for the occupation pattern Ti–Ti–Mg–Mg. The filled curves show the total titanium contribution to the DOS. The Fermi level is shown by the dashed line crossing the lower "t_{2g}" bands.

example, chosen at random, the Ti–Ti–Mg–Mg occupation pattern. Figure 10 shows the total DOS and the titanium contribution to it for the 3D warwickite and for the ribbon.

Note the similarity between the band structures. The additional contribution to the upper, "e_g", Ti 3d bands in the three-dimensional calculation comes from the boron atoms. In general, the electronic structure of the ribbon and the three-dimensional structure are similar to each other in the way they are in the Mg–Ti–Ti–Mg warwickite (see Figure 8).

Our calculations thus indicate that the warwickite would remain mainly one-dimensional in its electronic structure, even if different occupation patterns of metal filling were to occur.

Conclusion

We have investigated the electronic structure of the Mg_2Ti_2B_2O_8 warwickite by using the extended Hückel approach molecular orbital method. The analysis of the complete three-dimensional structure of the material was approached by following a chemical building process in which calculations are done first on separate subunits. This analysis of individual parts of the structure was useful in understanding some basic electronic properties of the system.

One of the important subunits is the one formed by two edge-sharing oxygen octahedra centered by two Ti atoms. The study of this molecular unit has shown that in the warwickite Ti–Ti interactions are weak, leading to a small splitting of the two molecular orbitals which compete for the two electrons of the d^1–d^3 configuration.

As a consequence, the separation between low-spin and high-spin states will be small. Better calculations must be performed to determine the true ground state of the molecule or of the extended systems.

The next important subunit is the one-dimensional infinite ribbon, formed by four edge-sharing O octahedra with two Ti's and two Mg's at the centers, running along the c axis of the rhombohedral unit cell. By comparing the band structure and density of states of the ribbon with those of the complete three-dimensional system, we have shown that the warwickites are essentially one-dimensional in nature, with all important electronic features described by the ribbon substructure. The detailed analysis was done by considering one particular filling order of metal atoms inside the oxygen octahedra, the Mg–Ti–Ti–Mg one, experimentally found to be more likely to occur. But the effect of different filling patterns was analyzed, as well. No significant changes were noted in the conclusions obtained previously.

The one-dimensional nature of the titanium warwickite, indicated by our computations, is in accordance with the experimental observations of the magnetic behavior of the system.

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Appendix

Table 2. Parameters Used in the Extended Hückel Calculations

<table>
<thead>
<tr>
<th>atom</th>
<th>orbital</th>
<th>H_{ii} (eV)</th>
<th>C_1^a</th>
<th>C_2^a</th>
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<td>1.1</td>
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<tr>
<td></td>
<td>2p</td>
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</tbody>
</table>

* Coefficient in double-ζ expansion of 3d function.

All calculations were performed using the program YAEHMOP, developed by G. Landrum at Cornell. The parameters used in the calculations are given in Table 2. They were all taken from a standard set except for the Ti parameters, which were obtained from a recent study of ferroelectrics.12

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