

Warwickites: Electronic Structure and Bonding

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The electronic structure of $\text{Mg}_2\text{Ti}_2\text{B}_2\text{O}_8$, 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 biocahedral 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 $\text{A}_x\text{T}_{4-x}\text{B}_2\text{O}_8$, where A and T are alkaline earth, lanthanide, or transition metals. Their structure⁴ 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 $\text{Mg}_2\text{Ti}_2\text{B}_2\text{O}_8$.⁵ 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 $\text{Mg}_3\text{TiB}_2\text{O}_8$, warwickite itself. $\text{Mg}_2\text{Ti}_2\text{B}_2\text{O}_8$ assumes the same structure, space group $Pnam$, with two formula units in the orthorhombic unit cell ($a = 9.186 \text{ \AA}$, $b = 9.337 \text{ \AA}$, $c = 3.028 \text{ \AA}$). 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

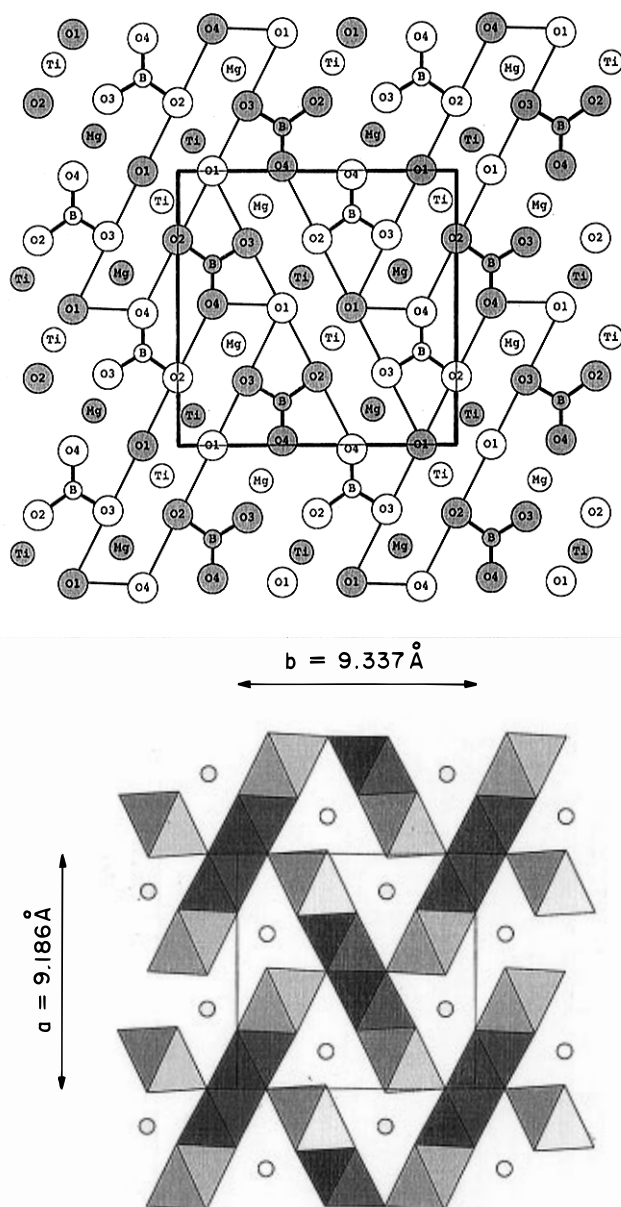


Figure 1. Two projections of the warwickite structure on the ab plane. Top: two layers, one shaded ($z = 0$), the other white ($z = 0.5$), along the c axis. This view emphasizes the borate ions and labels the atoms. Bottom: projection emphasizing the one-dimensional stacks along c . The borons are now shown as isolated open circles.

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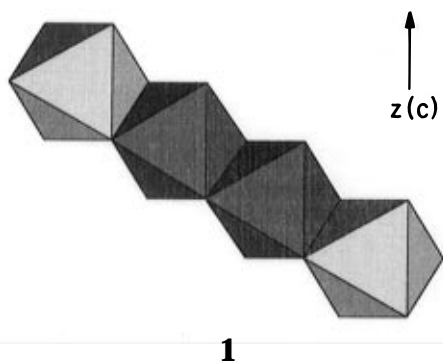
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this group of four edge-sharing octahedra is propagated along the $z(c)$ direction, one of the stacks of the warwickite structure is generated. This stack, of $\text{Mg}_2\text{Ti}_2\text{O}_{10}$ stoichiometry (no charge implied) is shown in two views 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 discussion⁶ 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.⁷ 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.⁸ Their approach is quite similar to ours.

Borate, TiO_6 and MgO_6 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 com-

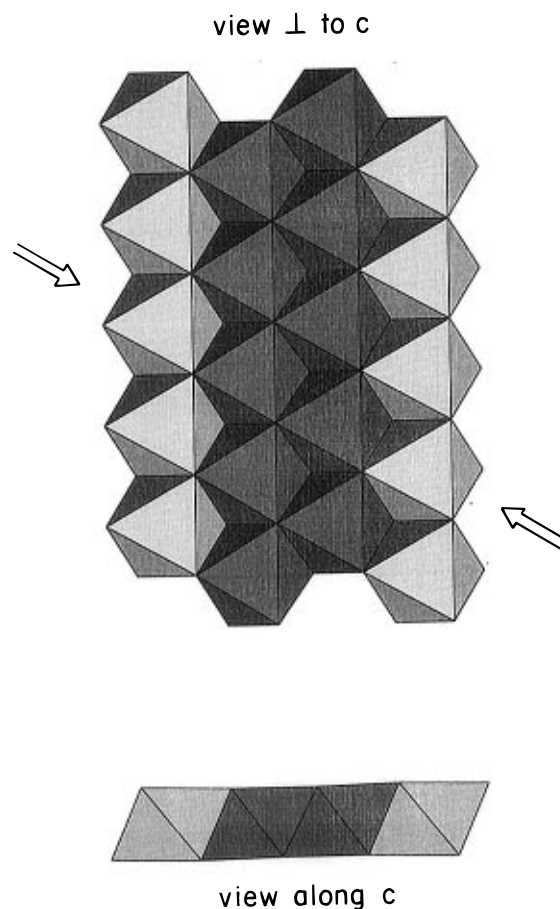


Figure 2. Two views of the one-dimensional stack or ribbon in warwickite. Top: view perpendicular to c and to the ribbon. Bottom: view along c . In either case, the octahedra filled by titaniums are darker, and those filled by magnesium ions are lighter. The arrows point to a strip of 4 octahedra shown in 1.

ponents 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 BO_3^{3-} ion. An interaction diagram for this anion, isoelectronic with even more familiar carbonate, CO_3^{2-} , and nitrate, NO_3^- , is shown on the left side of

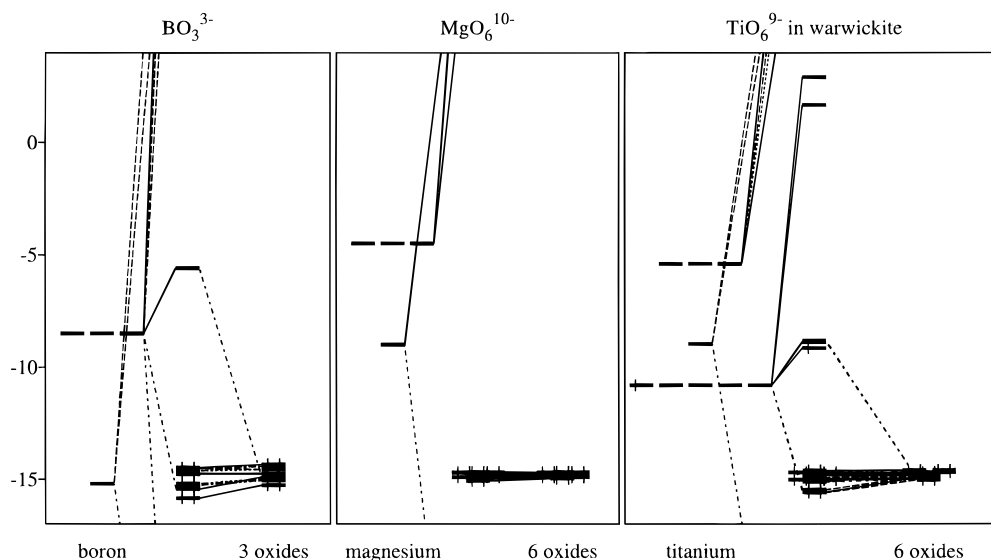
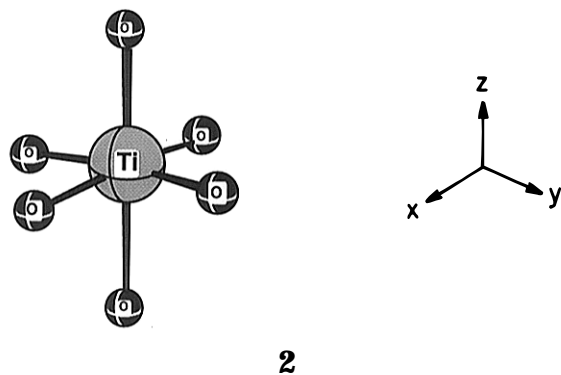


Figure 3. Interaction diagrams forming BO_3^{3-} , MgO_6^{10-} , and TiO_6^{9-} compared in the same energy window.

Figure 3.⁹ At left are the orbitals of a boron atom, at right those of three oxides. Note the substantial gap between filled and unfilled orbitals in the ion—this is a very stable structure. The lowest-lying unfilled orbital in this structure is a B–O π^* orbital, quite localized at the boron.

The point of electronic (and magnetic) interest in this structure is not the boron, however. Neither is it the magnesium, as a calculation on a discrete model MgO_6^{10-} (Figure 3 middle) shows. The geometry of the model is carved out of the solid; the Mg^{2+} ion lies in an approximately octahedral oxygen environment formed by oxygens from five borate groups and one isolated oxide. The Mg s and p orbitals are pushed up very high by the oxide crystal field—outside of the energy window chosen. Both B and Mg environments lead to a significant gap between filled and unfilled levels, and no low-lying orbitals for the electrons responsible for the magnetism of the compound to occupy.

Things are very different at Ti center. Figure 3 (right) shows the interaction diagram forming a TiO_6^{9-} cluster carved out of the solid (i.e., with the distances to oxygens and angles identical with the Ti environment in warwickite). A view of the Ti environment in the crystal, in **2**, barely shows a departure from a perfect octahedron.

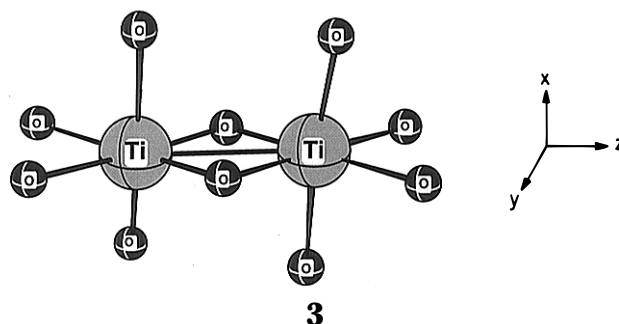


Were the octahedron perfect, we would expect to get a t_{2g} (xz, yz, xy) below e_g ($x^2 - y^2, z^2$) ligand field splitting at Ti. However, all point symmetry is absent in the real crystal geometry, and as Figure 3 (right) shows, there is a small splitting of both the t_{2g} (xy below xz, yz) and e_g (z^2 below $x^2 - y^2$) levels, with the coordinate system as indicated above. The octahedral crystal field is remembered quite well, and the splitting of the important t_{2g} level is less than 0.1 eV. There is one electron in the t_{2g} level, consistent with the Ti^{3+} oxidation state. The magnetic properties of the material will be eventually traced to this electron.

Two- and Four-Octahedra Strips. Let us consider the models for the two inner Ti-centered octahedra and the complete four-octahedron strip. We address the following questions: (1) What is the extent of Ti–Ti interaction in the inner core? (2) Do the outer Mg-centered octahedra affect the Ti–Ti interaction?

The general outlook here is that of orbital interaction affecting magnetism.¹⁰ 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^1-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 experience¹¹ we know that the bridging oxygens provide a coupling pathway. So it is interesting to see what happens in the inner octahedron pair, a $\text{Ti}_2\text{O}_{10}^{14-}$ 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 systems⁷ 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 $\text{Ti}_2\text{O}_{10}^{14-}$ 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 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 $\text{Ti(II)}-\text{Ti(II)}$.

Experimentally, this warwickite is described as a one-dimensional random-exchange Heisenberg antiferromagnetic chain,² i.e., in the spin Hamiltonian describing the system

$$H_{ij} = -\sum_{i<j} J_{ij} S_i \cdot S_j$$

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

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(9) For the orbitals of AB_3 molecules see: Gimarc, B. *Molecular Structure and Bonding*; Academic Press: New York, 1979; Chapter 3.

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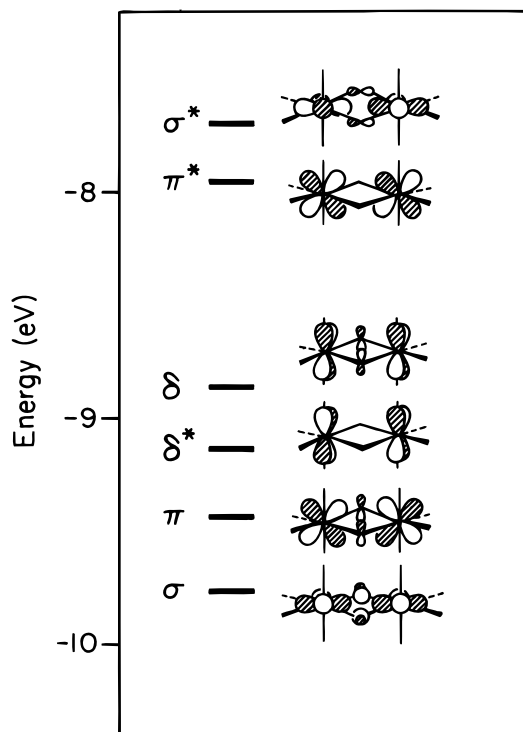


Figure 4. The t_{2g} block (six orbitals in all) of a Ti_2O_{10} unit carved out of the warwickite structure.

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 σ , π , and δ 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_2O_{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 δ^* is below δ . This is a well-understood phenomenon,⁷ the result of only δ (and not δ^* , 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 d^1-d^1 dimer of interest to us. The two levels competing for the pair of electrons are σ and π , 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 σ vs π 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} bioctahedral 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.

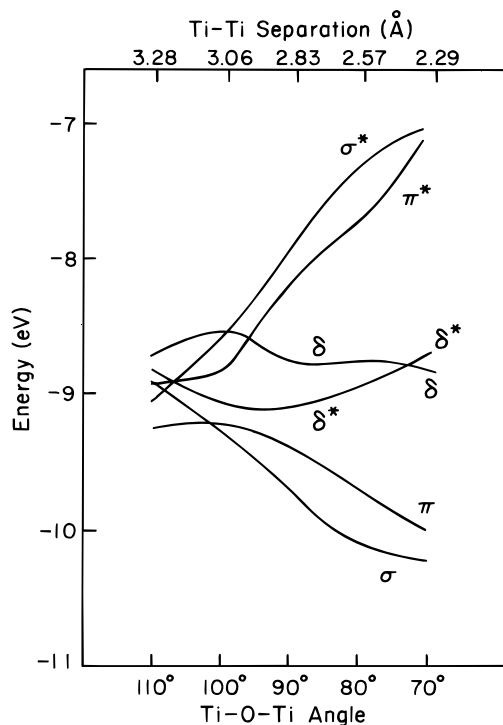


Figure 5. The six t_{2g} orbitals of an idealized bioctahedral Ti_2O_{10} molecule as a function of Ti-O-Ti angle. A (nonlinear) Ti-Ti separation scale is indicated at the top. At the smallest Ti-O-Ti angles, therefore short Ti-Ti separations, direct Ti-Ti bonding dominates, with the level ordering $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$. At larger Ti-O-Ti angles coupling through the bridging oxygens becomes important. In the warwickite structure, the Ti-O-Ti angle is near 90°.

As in our earlier analysis of Cl and PH_2 bridged bioctahedra,⁷ 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 $\sigma < \pi < \delta^* < \delta < \pi^* < \sigma^*$ (at very short Ti-Ti distances δ goes below δ^*). In the latter region, the level ordering is complex (but can be understood), and the levels are split by little.

The σ - π 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 precariously 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 $Mg_2Ti_2O_{18}^{26-}$. 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 B-O 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.

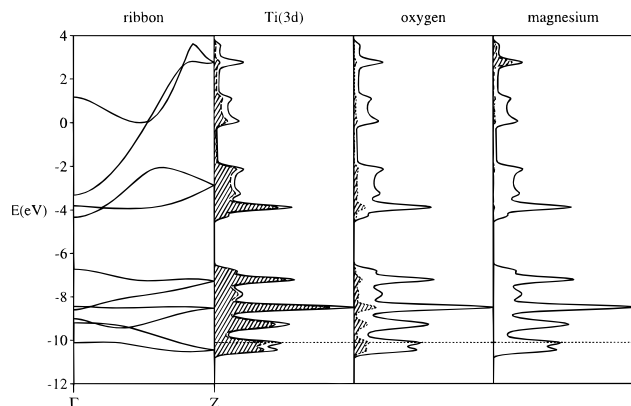
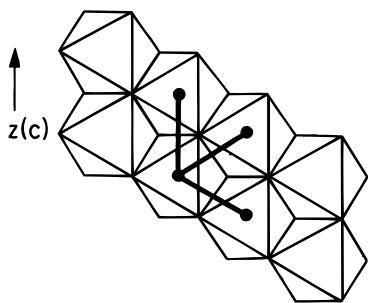


Figure 6. Band structure (left-hand panel) of a one-dimensional ribbon cut out of warwickite, stoichiometry $\text{Mg}_2\text{Ti}_2\text{O}_{10}^{10-}$. The three panels at right show the total density states that result (solid line) and shade in contributions of Ti 3d, all oxygen, and all Mg orbitals. The Fermi level is indicated by a horizontal line in the DOS diagrams. It is clear that in the energy window shown we are in the Ti 3d block—the six lower bands are “ t_{2g} ”, the four upper ones “ e_g ”.

This leaves us with a ribbon of $\text{Mg}_2\text{Ti}_2\text{O}_{10}^{10-}$ 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 there is a Ti–Ti biotetrahedron 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.



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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 Ti_2O_{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

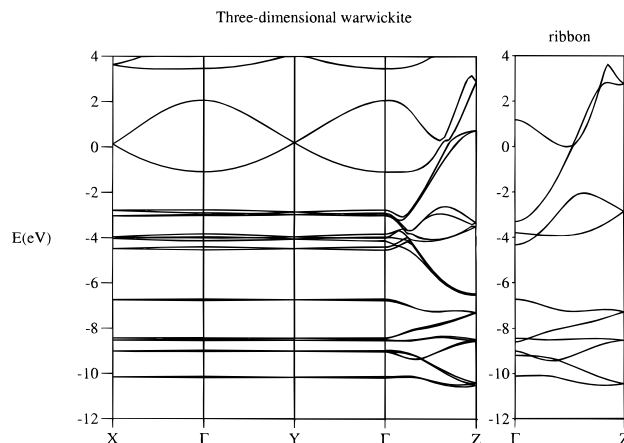


Figure 7. Band structure of three-dimensional warwickite. Note the significant dispersion only along the Γ – Z direction. The calculated Fermi level (not marked) is in the region of the lowest band, below -10 eV. For comparison, the rightmost panel shows the very similar dispersion of the bands in the one-dimensional ribbon sublattice.

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 Γ – X and Γ – Y edges of the Brillouin zone. And finally, and most convincingly, note how the t_{2g} bands of the three-dimensional material along Γ – 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 π^* 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-

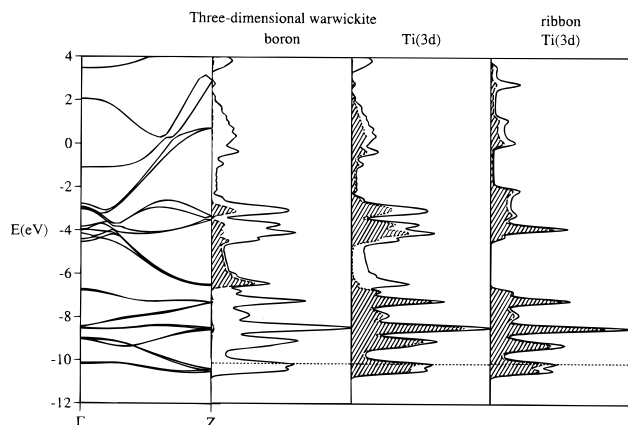


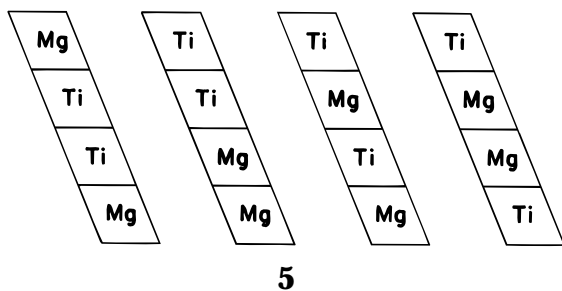
Figure 8. In the leftmost panel the band structure of three-dimensional warwickite along the Brillouin zone direction of most dispersion, Γ – Z , is repeated. The two central panels show the resulting density of states (solid line) and the contributions to it of boron and Ti 3d states. The boron states 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.

netic, characterized, as we mentioned, as a random exchange antiferromagnetically coupled quasi-one-dimensional material. Further calculations of the magnetism, including electron interaction explicitly, are in progress.

We do conclude, without ambiguity, that the warwickites will be very much one-dimensional. And we have attained a good chemical and physical understanding of the bonding in this interesting group of materials.

Alternative Occupation Patterns of the Octahedra

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 5.



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 5. The results are shown in Figure 9.

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 Mg₃TiB₂O₈ warwickite, with the single Ti atom occupying one of the inside octahedra.

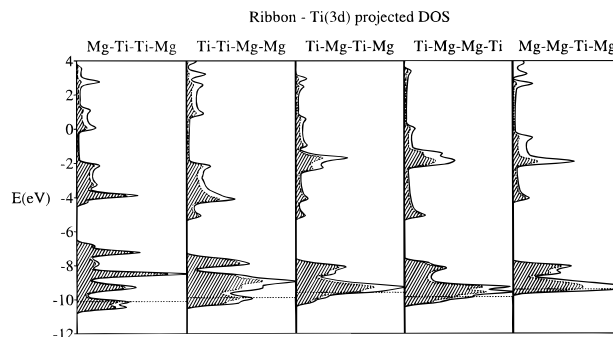


Figure 9. Leftmost panel repeats the total DOS and the Ti(3d) contributions to it of the warwickite ribbon with the usual occupancy Mg–Ti–Ti–Mg. The next three panels show the density of states of the ribbon with different filling patterns for the two Ti's and the two Mg's. The patterns are indicated above each panel. The rightmost panel shows the density of states for the ribbon with one Ti and three Mg atoms. The filling order is also indicated above the panel. The dotted line shows the Fermi level in each case.

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 Mg₃TiB₂O₈ 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.

In general the extended Hückel method is too simple to compute reliably total energies, but it often gives relative energies reasonably well. In the case at hand there seems to be a reasonable correlation of total energy with short Ti–Ti separation; the Mg–Ti–Ti–Mg filling pattern is most stable, followed by Mg–Mg–Ti–Ti. Direct Ti–Ti interaction is stabilizing.

For the MgScOBO₃ warwickite, for which it was experimentally found that the most probable arrangement is Mg–Sc–Sc–Mg,⁶ we obtain results similar to those of the Ti warwickite. As seen in Table 1, the most stable arrangement is the one with the two transition metals occupying the inner octahedra.

Our total energy calculations are, therefore, consistent with the known structures of the warwickites.

In the three-dimensional warwickite, the number of chemically different ways that four Ti's (and four Mg's) can occupy the available positions in the two ribbons inside the unit cell is much bigger. We have investigated some of these patterns and the results show that the warwickite remains basically one-dimensional in nature. To illustrate this, we have taken one specific

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

	Mg–Ti–Ti–Mg	Mg–Mg–Ti–Ti	Mg–Ti–Mg–Ti	Ti–Mg–Mg–Ti
E_{total}	[0]	0.73	1.11	1.10
$d(\text{Ti–Ti})$	2.73	3.14	5.02	7.91
	Mg–Sc–Sc–Mg	Mg–Mg–Sc–Sc	Mg–Sc–Mg–Sc	Sc–Mg–Mg–Sc
E_{total}	[0]	0.52	0.50	1.08
$d(\text{Sc–Sc})$	2.84	3.25	5.16	8.14

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

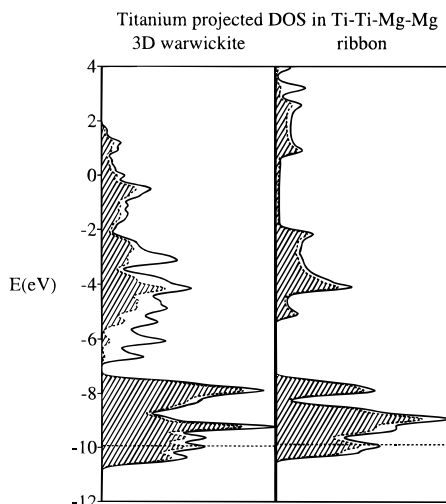


Figure 10. Density of states of the three-dimensional warwickite and the ribbon, both for the occupation pattern Ti–Ti–Mg–Mg. The filled curves show the total titanium contribution to the DOS. The Fermi level is shown by the dashed line crossing the lower “ t_{2g} ” bands.

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 $\text{Mg}_2\text{Ti}_2\text{B}_2\text{O}_8$ warwickite by using the extended Hückel approximate 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^1 configuration.

Table 2. Parameters Used in the Extended Hückel Calculations

atom	orbital	H_{ii} (eV)		C_1^a	C_2^a	
Ti	3d	–10.81	4.55	1.4	0.421	0.784
	4s	–8.97	1.075			
	4p	–5.4	1.075			
Mg	3s	–9	1.1			
	3p	–4.5	1.1			
O	2s	–32.3	2.275			
	2p	–14.8	2.275			
B	2s	–15.2	1.3			
	2p	–8.5	1.3			

^a Coefficient in double- ζ expansion of 3d function.

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

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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