

Electronic calculations on the MgTiOBO_3 warwickite: A real-space renormalization approach

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Electronic properties of a warwickite, MgTiOBO_3 , are calculated within the Green's functions formalism, taking into account the crystallographic structure of the system and using a multiorbital basis to represent the Hamiltonian. The many body problem is considered through an alloy analog approximation for the intra-atomic interaction at the titanium sites by using real-space renormalization techniques. Local and total density of states reflect the one-dimensional character of the structure and its insulating nature. The metal-nonmetal transition is also analyzed as a function of the charge doping. [S0163-1829(97)04031-9]

I. INTRODUCTION

The interest in low-dimensional systems has been largely increased since the first evidences of quantum confinement properties exhibited by semiconductor nanostructures with very important industrial applications. On the other hand, the discovery of high temperature superconductivity in copper oxides and the attempts of understanding the role played by the (two-dimensional) cuprate planes have opened a new class of investigations on strongly correlated low-dimensional systems. In particular, a family of oxyborates named warwickites, was recently characterized from the magnetic point of view. Titanium warwickites were identified via magnetization, ac susceptibility and x-ray measurements, as belonging to a family of inorganic, one-dimensional, disordered magnetic systems.¹ Magnetic properties of Vanadium warwickites have been theoretically and experimentally studied by Continentino *et al.*;² they have shown that this borate structure presents an ac susceptibility which can be described by a power law over up to 40 K, above which it follows a Curie Weiss law.

The warwickites are formed by substructures, similar to ribbons extending along the c axis of an orthorhombic crystalline structure, weakly connected to each other, and containing boron atoms in the space between them. Each ribbon is formed by edge-sharing oxygen octahedra in a four column group, with divalent and trivalent metal ions inside. For the MgScOBO_3 warwickite, Norrestam³ has shown that the transition metal preferentially occupies the two inner octahedra, while the Mg ions are preferably located inside the two outer ones (see Fig. 1). More recently, Matos *et al.*⁴ have presented a theoretical investigation of the electronic structure of the MgTiOBO_3 warwickite, based on an extended Hückel molecular orbital calculation.⁵ They concluded that the electronic band structure of the crystal is basically one-dimensional near the Fermi level which is located inside a Ti-3d band. The 1D character of the band structure was shown to be independent of the particular arrangement of Ti

and Mg ions among the octahedra units; when different occupation patterns were considered, only small changes were seen in the density of states due to weak metal-metal interactions between adjacent ribbons. Even though the molecular orbital calculation was clarifying, some of the most interesting properties of the warwickite, i.e., its magnetic behavior and its insulator nature, cannot be understood within a one-electron approach. For a proper understanding of the electronic properties of the system, it is essential to incorporate in the theoretical framework an adequate description of the electronic correlations in the transition metal sites, which we know could change completely the description of the band structure by, e.g., opening a Mott gap near the Fermi level.

In this work we present a multiorbital tight-binding cal-

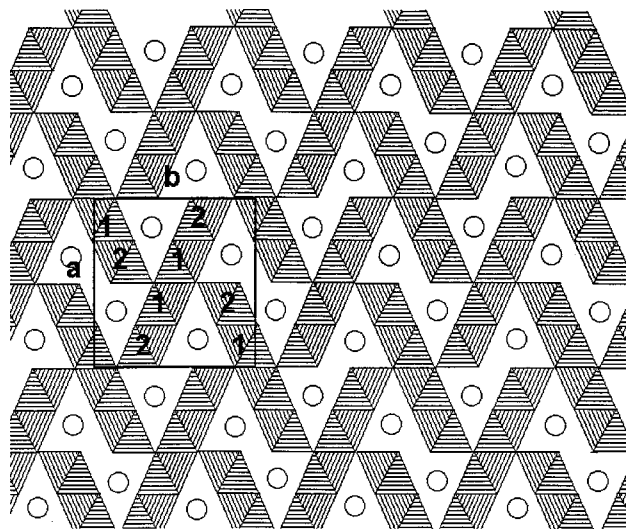


FIG. 1. Schematical view of the structure of the warwickites projected in the plane (001). The numbers 1 and 2 represent the sites where the metallic ions are located, a and b are the sides of the unitary cell, and the open circles are the boron ions (adapted from Ref. 3).

ulation developed to describe the main electronic properties of the Ti warwickite. We follow the Green's functions formalism and adopt real spatial renormalization techniques to simplify the representation of the real, more intricate, crystalline lattice. Intrasite electron repulsion terms are treated through the "chain approximation" of a Green function cumulant expansion. For simplicity, we have assumed the Ti atoms occupying the two inner octahedra, according to the more probable pattern found in the Sc warwickite.

It is worth noticing that the scheme adopted does not describe the full-warwickite crystal, rather, it restricts the study to an isolated ribbon. Although each ribbon interacts with the others through the boron and some of the oxygen atoms, the model adopted is a good approximation for the electronic properties at the Fermi level, as reported by Matos *et al.*⁴

II. THEORY

The Hamiltonian taken to describe the crystal is one of the Hubbard type and contains contributions of oxygen, titanium, and magnesium atoms. The orbitals we consider are O-2*p* (*p_x*, *p_y*, and *p_z*), Ti-3*d* (*d_{xy}*, *d_{yz}*, *d_{xz}*, *d_{x²-y²}*, and *d_{z²}*), and Mg-3*s*. The O-2*s*, Ti-4*s* and -4*p*, and Mg-3*p* orbitals were not included in our calculation since they do not contribute to the density of states around the Fermi level.⁴ To this multiorbital description, it is important to incorporate the electronic interaction terms on the transition metal sites. The Hamiltonian then takes the form

$$H = \sum_{i,\alpha,\sigma} E_i^\alpha c_{i,\alpha,\sigma}^\dagger c_{i,\alpha,\sigma} + \sum_{i,j,\alpha,\beta,\sigma} V_{i,j}^{\alpha,\beta} c_{i,\alpha,\sigma}^\dagger c_{j,\beta,\sigma} + U_{\text{Ti}} \sum_{i,\alpha,\sigma}' n_{i,\sigma}^\alpha n_{i,\sigma}^\alpha + Y_{\text{Ti}} \sum_{i,\alpha,\beta,\sigma,\sigma'}' n_{i,\sigma}^\alpha n_{i,\sigma'}^\beta, \quad (1)$$

where *i* and *j* denote atomic positions, α and β orbitals, and U_{Ti} and Y_{Ti} are titanium electron-electron repulsion terms, both related to the same atom (intrasite) but involving either one single *d* orbital (U_{Ti}) or two different *d* orbitals (Y_{Ti}) in that atom. The symbol Σ' indicates a summation restricted to the titanium sites. The operator $c_{i,\alpha,\sigma}^\dagger$ creates an electron on site *i*, in the α orbital, with spin σ . The matrix element $V_{i,j}^{\alpha,\beta}$ corresponds to the hopping energy between orbitals α and β , belonging, respectively, to atoms *i* and *j* considered to be first neighbors. For the hopping integrals we use parameters of the extended Huckel method, the same ones used in a former study of the warwickite.⁴ These are given by the well known formula $V_{ij}^{\alpha,\beta} = k S_{ij}^{\alpha,\beta} (H_{i,i}^{\alpha,\alpha} + H_{j,j}^{\beta,\beta})/2$, where $S_{ij}^{\alpha,\beta}$ corresponds to the overlap integral and *k* is a constant. The hopping matrix elements are then proportional to the overlap integrals. The diagonal elements $H_{i,i}^{\alpha,\alpha}$ are taken as⁶ $E_{\text{O}}^{p's} = -14.8$ eV, $E_{\text{Ti}}^{d's} = -10.8$ eV, and $E_{\text{Mg}}^s = -9.0$ eV. We have done some calculations including the Ti-4*s* orbitals in order to study their influence in the present approach. Their effect on the total Ti density of states is negligible over a sufficiently wide range of energy around the Fermi level, confirming the molecular orbital result of Ref. 4. This "repulsion" of Ti-4*s* states is due to the large overlap between Ti-4*s* and O-2*p* orbitals, a consequence of the more extended Ti-4*s* orbitals as compared to Ti-3*d*.

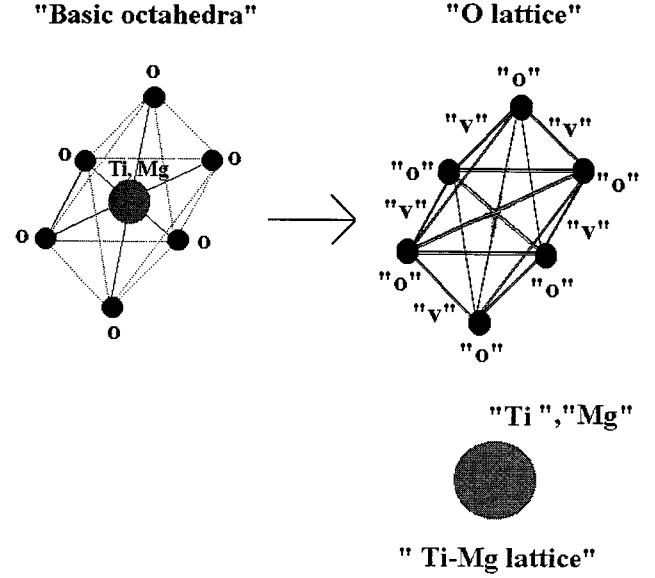


FIG. 2. Schematic representation of the renormalization scheme adopted in the calculation of the effective locator and hopping elements for both effective lattices described in the text. Full dots represent oxygen atom whereas gray dots describe Mg and Ti elements. The symbols "O," "Ti," "Mg," and "V" are used to represent renormalized Green's functions and hoppings, respectively.

We have not explicitly incorporated the *p* states of the Mg atoms ($E_{\text{Mg}}^{3p's} = -4.5$ eV), since the oxygen-crystal field acts on the Mg-*p* energy by pushing it far above the Fermi level. For this reason the bonding between O and Mg orbitals has been considered by taking into account a renormalized energy value for the Mg *s* orbitals. As the boron atoms are strongly bounded to the neighbor oxygen atoms and do not contribute significantly to the electronic structure near the Fermi level, the electronic properties of the warwickite can be studied on the ribbon.

Isolated oxygen octahedra, containing Ti or Mg ions in the interstitial sites were considered primarily as being the basic units of the structure. To describe the warwickite, we define two distinct renormalized lattices: one formed by renormalized oxygen octahedra (the "oxygen lattice"), in which the original hoppings between oxygen and transition metal atoms (O-Ti, O-Mg) are replaced by effective hopping integrals between "dressed oxygen" atoms (O-O), and another lattice (the "Ti-Mg lattice") made of dressed Ti and Mg atoms where the new effective hopping interaction terms are obtained after a decimation of the oxygens. Figure 2 illustrates, schematically, the first decimation step used in the construction of both effective lattices.

The Green's functions corresponding to the undressed atoms are

$$g_{\text{O(Mg)}}^\alpha(\omega) = \frac{1}{\omega^+ - E_{\text{O(Mg)}}^\alpha}, \quad (2)$$

with $\omega^+ = \omega + i\eta$, $\eta = 0^+$, and α denoting a *p*, or *s* orbital of the O and Mg atom, respectively. For the Ti sites, the undressed Green functions are obtained by defining the operators⁷ which diagonalize the titanium atomic Hamiltonian with the intrasite *e-e* interaction,

$$A_{i,\sigma;\alpha,\beta,\gamma}^r = c_{i,\sigma}^r n_{i,\sigma}^{r,\alpha_r} \prod_{m \neq r=1}^5 n_{i,\sigma}^{m,\beta_m} n_{i,\sigma}^{m,\gamma_m}, \quad (3)$$

where m stands for the band indices, and with α , β_j , and γ_j assuming two values, 1 and 2, such that,

$$n_{i,\sigma}^{m1} = n_{i,\sigma}^m, \quad n_{i,\sigma}^{m2} = 1 - n_{i,\sigma}^m. \quad (4)$$

In a two-band scheme proposed previously by Anda,⁷ the undressed locators are obtained by calculating self-consistently the mean value of different occupation number operators of both bands. By performing an approximation in the actual five-band problem, we calculate the Ti Green function replacing the mean values of products of occupation operators by products of mean values of occupation operators,

$$g_{i,\sigma}^m(\omega) = \sum_{\alpha,\{\beta\},\{\gamma\}} \frac{\langle n_{i,\sigma}^{m,\alpha} \rangle \prod_{n \neq m=1}^5 \langle n_{i,\sigma}^{n,\beta_n} \rangle \langle n_{i,\sigma}^{n,\gamma_n} \rangle}{\omega^+ - E_{\alpha,\{\beta\},\{\gamma\}}}, \quad (5)$$

where $E_{\alpha,\{\beta\},\{\gamma\}}$ is calculated on the basis of the electronic occupation of each one of the five d bands and $\langle \rangle$ stands for a mean value calculated on the ground state of the system. As an example, it is easy to show that for the configuration corresponding to only one occupied band with two electrons (spin up and down) $E = E_{\text{Ti}} + U$, whereas for the case of three half full occupied bands $E = E_{\text{Ti}} + 3Y$, and for one full and two half-full occupied, the energy is given by $E = E_{\text{Ti}} + U + 2Y$. The titanium occupation number, n_{Ti}^α , is solved self-consistently and we assume, for simplicity, an identical mean value for the five d orbitals.

The hopping matrix elements representing the effective interactions between the renormalized atoms (see Fig. 2) were calculated by taking into account symmetry properties of the distinct atomic orbitals considered in our model. The dressed Green functions for Ti, Mg, and O atoms are obtained through the solution of a Dyson equation.⁷ For the case of the effective Ti-Mg lattice, we solve a 5×5 matricial Dyson equation to get the renormalized Green functions of the transition metals, $\tilde{G}_{\text{Ti,Ti}}$. It can be written as

$$\tilde{G}_{\text{Ti,Ti}} = \tilde{g}_{\text{Ti}} + \tilde{g}_{\text{Ti}} \sum_{\text{ox.sites},\mu} \tilde{T}_{\text{Ti,Ox}_i}^\mu \tilde{G}_{\text{Ox}_i,\text{Ti}}, \quad (6)$$

where $\mu = x, y, \text{ and } z$, defines the direction of the binding along the structure, and the hopping matrices are

$$\tilde{T}_{o,1}^x = \begin{pmatrix} o & t_1 & o \\ o & o & t_1 \\ o & o & o \\ t_2 & o & o \\ t_3 & o & o \end{pmatrix}, \quad \tilde{T}_{o,1}^y = \begin{pmatrix} t_1 & o & o \\ o & o & o \\ o & o & t_1 \\ o & t_2 & o \\ o & t_3 & o \end{pmatrix},$$

$$\tilde{T}_{o,1}^z = \begin{pmatrix} o & o & o \\ t_1 & o & o \\ o & t_1 & o \\ o & o & o \\ o & o & t_4 \end{pmatrix}, \quad (7)$$

with t_1 , t_2 , t_3 , and t_4 being the corresponding nonzero hopping energies between Ti d orbitals and O p orbitals of distinct symmetries. The values for the hopping elements t_i 's are related to those previously defined, and therefore are obtained from an extended Hückel molecular orbital parameters.⁵ They result to be $t_1 = 2.74$ eV, $t_2 = 3.05$ eV, $t_3 = 3.648$ eV, and $t_4 = 1.734$ eV. In Eq. (6), the undressed locators \tilde{g}_{Ti} and \tilde{g}_0 are 5×5 and 3×3 diagonal matrices, respectively. The resulting dressed Green's functions are given by

$$\tilde{G}_{\text{Ti,Ti}} = \begin{pmatrix} \gamma_1 & o & o & o & o \\ o & \gamma_1 & o & o & o \\ o & o & \gamma_1 & o & o \\ o & o & o & \gamma_2 & \gamma_3 \\ o & o & o & \gamma_3 & \gamma_2 \end{pmatrix}, \quad (8)$$

with the γ 's being

$$\gamma_1 = \frac{g_{\text{Ti}}}{1 - 4g_{\text{Ti}}g_{\text{O}}t_1^2}, \quad (9)$$

$$\gamma_2 = \frac{g_{\text{Ti}}[1 - 2g_{\text{Ti}}g_{\text{O}}(t_4^2 + 2t_3^2)]}{1 - g_{\text{Ti}}g_{\text{O}}(4t_2^2 + 2t_4^2 + 4t_3^2 - 8t_2^2)}, \quad (10)$$

and

$$\gamma_3 = \frac{4g_{\text{Ti}}^2g_{\text{O}}t_2t_3}{1 - g_{\text{Ti}}g_{\text{O}}(4t_2^2 + 2t_4^2 + 4t_3^2 - 8t_2^2)}. \quad (11)$$

The original undressed Ti Green's functions have been replaced by dressed Ti locators which together with the Mg ones relate the effective Ti-Mg lattice. By applying an equivalent procedure, it is possible to obtain the renormalized oxygen Green functions, $\tilde{G}_{\text{O,O}}$ associated to the "oxygen lattice." The effective oxygen lattice can be considered as being formed by sharing-edges renormalized octahedras whereas, the effective Ti-Mg lattice is a simpler one defined by ribbons constituted by four sites occupied by dressed Ti and Mg atoms in the two central columns, and on the external ones, respectively.

In order to obtain the local electronic density of state corresponding to different sites of the original system, matricial Green's function equations of motion of different sizes must be evaluated. In the case of the effective Ti-Mg lattice, a system of 12 equations has to be solved, whereas for the O effective lattice a system of 30 is necessary. Finally, the diagonal Green's functions are calculated by applying a real-space renormalization technique⁸ by successive decimations of dressed lattice points displayed along a one-dimensional chain laying in the warwickite c direction. These points correspond to previously renormalized unit cells which, when

displayed together, form the full ribbon structure. The recursive equations used in the renormalization procedure of the effective 1D chain are

$$\tilde{G}'_{o,o} = [\tilde{\Gamma} - \tilde{Z}_{o,1}\tilde{Z}_{1,o} - \tilde{Z}_{o,\bar{1}}\tilde{Z}_{\bar{1},o}]^{-1}\tilde{G}_{o,o}, \quad (12)$$

$$\tilde{Z}'_{o,1} = [\tilde{\Gamma} - \tilde{Z}_{o,1}\tilde{Z}_{1,o} - \tilde{Z}_{o,\bar{1}}\tilde{Z}_{\bar{1},o}]^{-1}\tilde{Z}_{o,1}\tilde{Z}_{1,2}, \quad (13)$$

$$\tilde{Z}'_{o,\bar{1}} = [\tilde{\Gamma} - \tilde{Z}_{o,1}\tilde{Z}_{1,o} - \tilde{Z}_{o,\bar{1}}\tilde{Z}_{\bar{1},o}]^{-1}\tilde{Z}_{o,\bar{1}}\tilde{Z}_{\bar{1},\bar{2}}, \quad (14)$$

with

$$\tilde{G}_{o,o} = [\tilde{\Gamma} - \tilde{G}_{o,o}\tilde{T}_{o,o}]^{-1}\tilde{G}_{o,o}, \quad (15)$$

and

$$\tilde{Z}_{o,1(\bar{1})} = \hat{G}_{o,o}\tilde{T}_{o,1(\bar{1})}. \quad (16)$$

Notice that $\tilde{Z}_{1,2}$ and $\tilde{Z}_{\bar{1},\bar{2}}$ follow the same recursive relations defined in Eqs. (13) and (14) since $\tilde{Z}_{1,2} = \tilde{Z}_{o,1}$ and $\tilde{Z}_{\bar{1},\bar{2}} = \tilde{Z}_{o,\bar{1}}$. The above equations define an iterative procedure which is implemented until a fixed point is attained for the Green function. At this point the effective interaction between distant renormalized elements of the structure goes to zero. The local density of states can be obtained by taking the imaginary part of the renormalized locator.

The position of the Fermi energy, E_F , and the occupation numbers at the Ti sites are obtained self-consistently by solving the following charge balance coupled equations:

$$2 \int_{-\infty}^{E_F} \left[\sum_{\alpha=1}^5 \rho_{\text{Ti}}^{\alpha}(\omega) + \rho_{\text{Mg}}(\omega) + \sum_{\beta=1}^3 \sum_{i=1}^5 \rho_{\text{O}_i}^{\beta}(\omega) \right] d\omega = Q, \quad (17)$$

and

$$\sum_{\alpha=1}^5 2 \int_{-\infty}^{E_F} \rho_{\text{Ti}}^{\alpha}(\omega) d\omega = n_{\text{Ti}}, \quad (18)$$

where $\rho_i^{\beta}(\omega)$ corresponds to the local electronic density of states of each atom i and orbital β , and Q is the number of electrons per unit cell which was taken to be equal to 31 for unit cell in the case of the isolated ribbon. This number corresponds to the situation in which each oxygen atom retain six electrons (full p -orbital occupation), whereas the Ti-III remains like 3 d^1 . The factor 2 appearing in both integrals takes into account the spin degeneracy. It is worth noticing that for the isolated ribbon we have five oxygens atoms (each one has a particular atomic neighborhood) rather than four which would be the full-warwickite value since two oxygen atoms are shared with neighborhood ribbons. Otherwise, by changing the Q value it is possible to investigate the change in the electronic properties and in particular the metal-nonmetal transition with doping.

III. RESULTS

We present here the results obtained for the calculated local density of states on different sites of the warwickite-ribbon lattice following the iterative scheme described above (we have added an imaginary part equal to 10^{-1} eV in the real frequencies). Figure 3 shows the local density of states

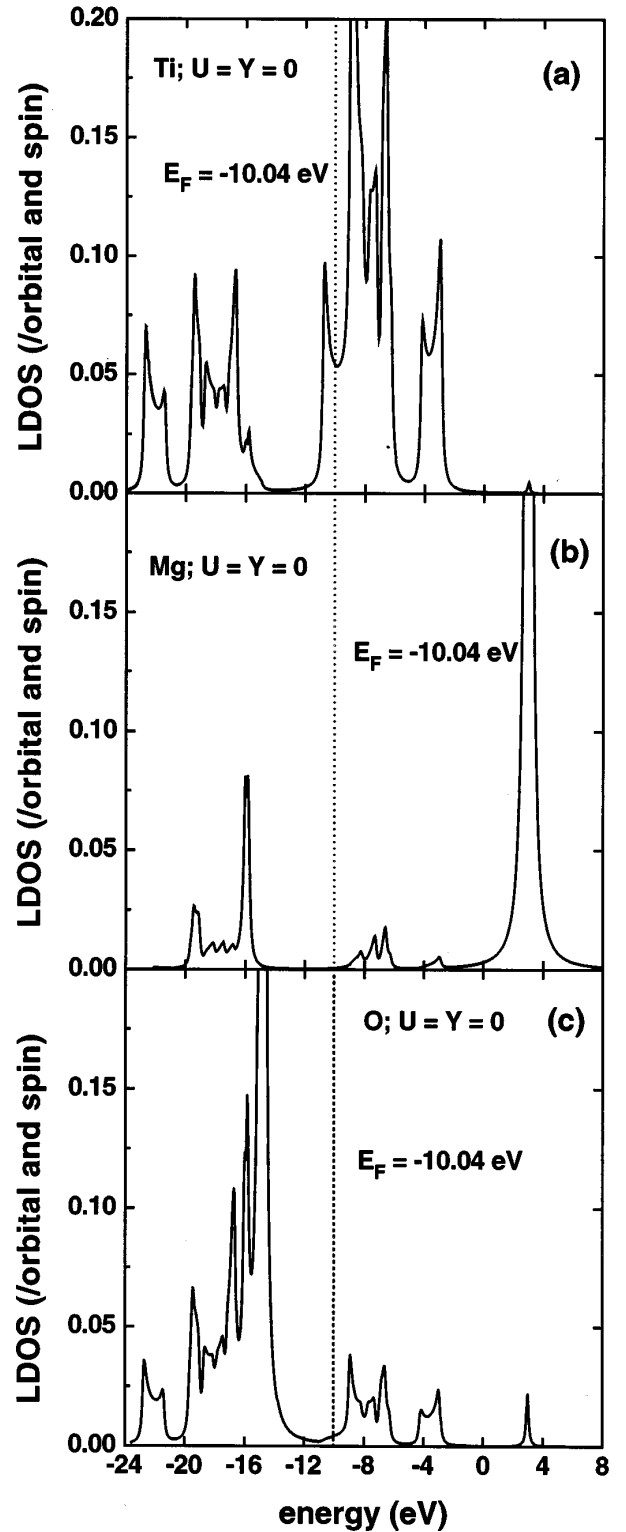


FIG. 3. Local density of states for the warwickite elements: (a) Ti, (b) Mg, and (c) O atoms. Results are presented for all the orbitals considered in the theoretical description and for the case of U and Y equal to zero. The position of the Fermi energy is denoted by a dotted line in the figures.

at the different atoms as a function of energy, neglecting all $e-e$ interaction ($U_{\text{Ti}} = Y_{\text{Ti}} = 0$). These results exhibit a very good agreement with the local and total density of states obtained previously using the extended Hückel molecular orbitals scheme⁴ in which all the orbitals of the Mg, Ti, and O

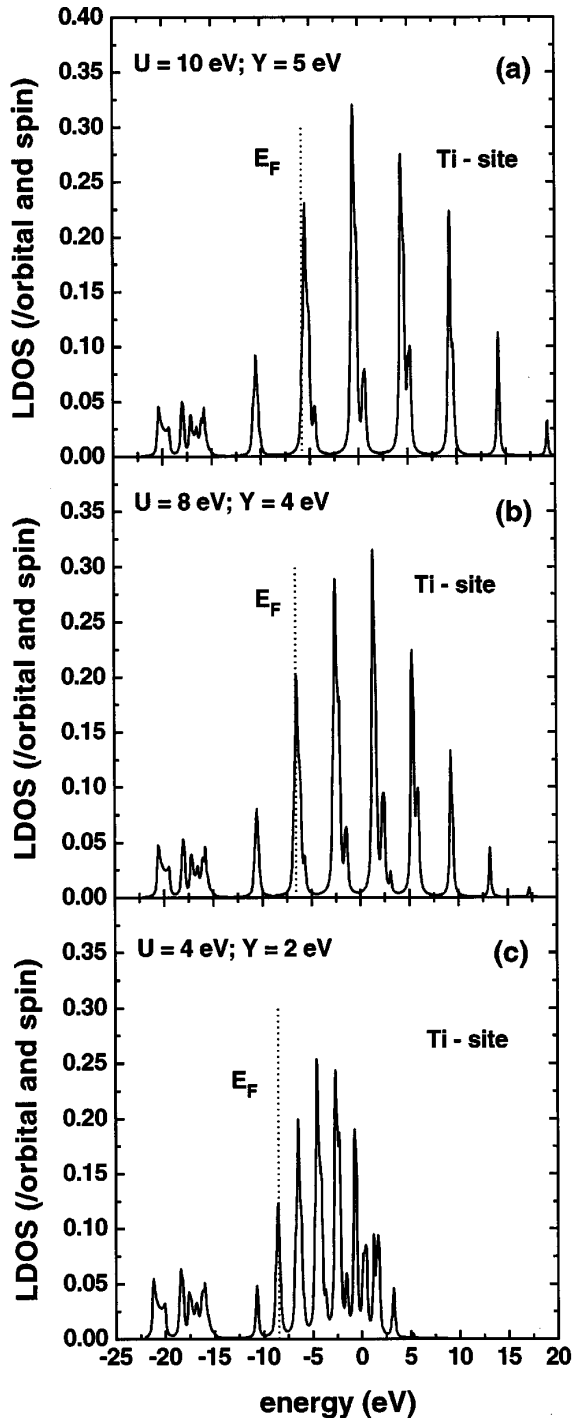


FIG. 4. Local density of states for the Ti site in the warwickite system. Results are present for all the orbitals considered and are for the case of (a) $U=10.0$ eV and $Y=5.0$ eV; (b) $U=8.0$ eV and $Y=4.0$ eV; and (c) $U=4.0$ eV and $Y=2.0$ eV. The positions of the Fermi energy are denoted by dotted lines in the figures.

were included. The sequence of peaks and gaps are quite the same in both results reflecting the one-dimensional nature of the total density of states in the energy range close to the Fermi level.

The effects of the electronic correlation on the Ti density of states can be seen by studying the Ti local density of states for a particular pair of U and Y values; this is presented in Fig. 4. The value of U was estimated from the

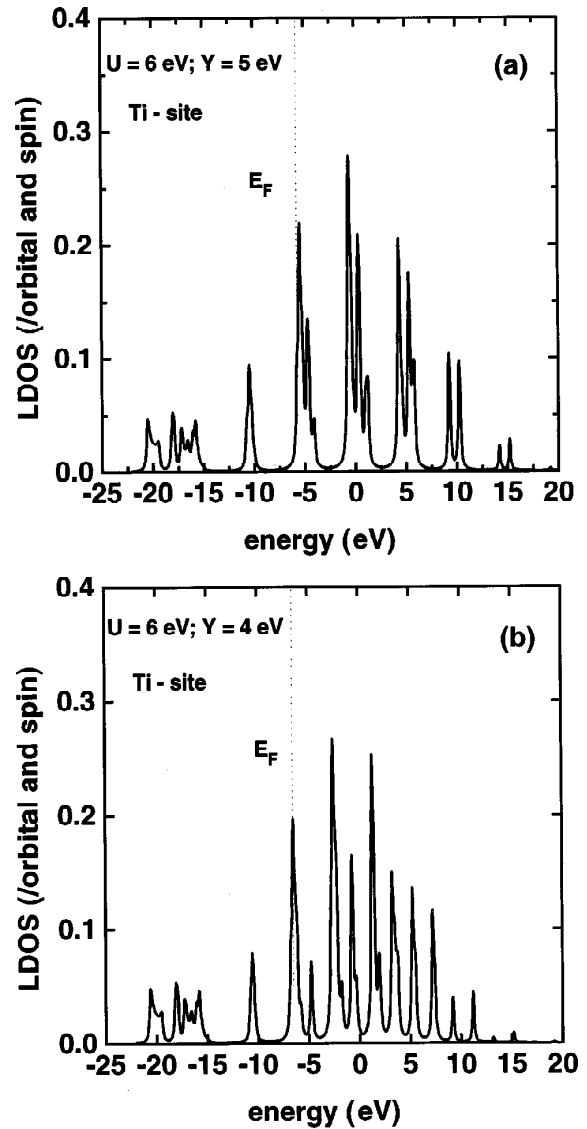


FIG. 5. Local density of states for the Ti site in the warwickite system as in Fig. 4 but for $U=6.0$ eV and (a) $Y=5.0$ eV and (b) $Y=4.0$ eV. The positions of the Fermi energy are denoted by dotted lines in the figures.

electronegativity energy associated to the metallic Ti, whereas the Y value was arbitrarily considered to be equal to $U/2$. By changing the U and Y value, it is possible to analyze the changes on the Fermi energy value and the gap next to the Fermi level; as the values of U and Y increase a sequence of peaks and gaps appears. It can be clearly noticed that the distance between successive peaks in the density of states is proportional to the value of Y , as expected. In fact, the features of the electronic density of states are very sensitive to the inclusion of electronic correlations showing, unambiguously, that a correct description of the present problem must take into account these terms in the Hamiltonian of the problem. The system is an insulator as reported experimentally. From the theoretical point of view the insulator character is a result of the interplay between localization due to disorder and electronic correlation. A small reduction of the Fermi energy produced by doping would localize it on the correlation gap and the crystal would be a pure Mott insulator. Figure 5 shows the results for the Ti local density of states

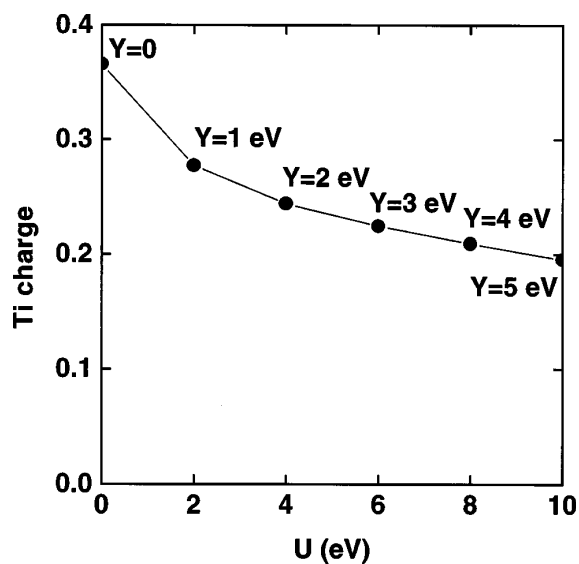


FIG. 6. Dependence of the Ti charge on the Ti-intersite correlation value.

by considering a fixed value of U (6.0 eV) and two values of the Ti intrasite interactions between different orbitals (parameter Y). As mentioned before, the sequence of gaps in the local density of states depends on this electronic interaction value since electronic states are shifted for higher energy values as it increases.

The dependence of the Ti charge on the U and Y parameters of the Hamiltonian is displayed in Fig. 6. It is interesting to point out here that from a chemical study of the compound it was previously stated that each Ti atom contributes with one electron to the warwickite structure; this leads to a charge content of 0.2 electrons per orbital and spin which is only achieved for high values of the electronic interactions, U and Y . It seems from our theoretical results that the self-consistent calculation of the Ti charge could be properly used to better understand the electronic properties of the crystal.

To simulate different doping in the warwickite-ribbon lattice, which can be obtained substituting, for instance, the boron atoms by Be, we have studied the shift of the Fermi level as the net charge is increased. As the typical density of states exhibits a sequence of gaps and peaks in the range of energy that we are interested in, a sequence of steplike features is expected with doping. This is clearly illustrated in Fig. 7 for a particular pair of parameters ($U=6.0$ eV and $Y=5.0$ eV). Although this can be considered as a general behavior, the width and height of the steps would depend on

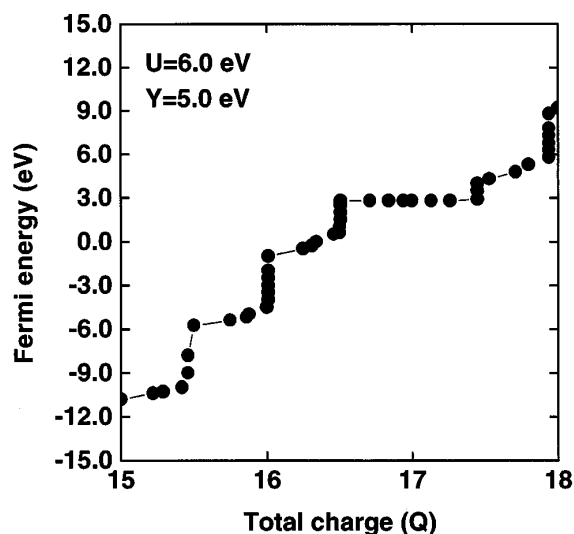


FIG. 7. Fermi energy as a function of the system charge for $U=6.0$ eV and $Y=5.0$ eV.

the set of parameters (U and Y) adopted. This theoretical prediction could be investigated, for instance, by measuring the specific heat of Ti warwickites or by photoemission experiments. Unfortunately, to the best of our knowledge, no data have been reported in the literature up to the present.

IV. CONCLUSIONS

We have presented a detailed study of the electronic properties of Ti warwickite, by performing a multiorbital calculation within a real-space renormalization scheme. We have shown that a proper description of the system requires the incorporation of the electronic interaction at the transition-metal sites. Moreover, the insulating nature of the compound is properly described and the metal-nonmetal transition is studied by performing a direct self-consistent calculation of the Fermi level for different doping situations. Interest in this family of compounds continues to grow due to its intrinsically one- and two-dimensional magnetic and crystallographic characteristics.

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