First-principles investigation of ReO$_3$ and related oxides

M. G. Stachiotti  
Instituto de Física Rosario, Universidad Nacional de Rosario, 27 de Febrero 210 Bis, Rosario (2000), Argentina

F. Corá and C. R. A. Catlow  
The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, United Kingdom

C. O. Rodriguez  
IFLYSIB, Grupo de Física del Sólido, Casilla de Correo 565, La Plata (1900), Argentina
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Electronic-structure calculations are performed, within the local-density approximation to the density-functional theory, using the full-potential linear muffin-tin orbital method to understand the relation between structural and electronic properties of ReO$_3$, WO$_3$, and the stoichiometric tungsten bronze NaWO$_3$. Energy changes associated with small deformations from the cubic phase indicate that ReO$_3$ and the tungsten bronze are stable when cubic while the W ion in WO$_3$ shows a tendency to off-center displacements. The different behavior is explained by examining the band structure of the compounds. Calculated frequencies and eigenvectors of Γ phonons in ReO$_3$ corroborate the existence of high-frequency modes in this crystal which supports a recent theoretical proposal for the interpretation of its electrical resistivity. [S0163-1829(97)03607-2]

I. INTRODUCTION

ReO$_3$ is a transition-metal oxide exhibiting high electrical conductivity. The Bravais lattice is simple cubic ($Pm\bar{3}m-O$), with one formula unit ReO$_3$ per unit cell. Its structure comprises a network of corner-sharing oxygen octahedra, with Re occupying the center of each octahedron (Fig. 1). Among the numerous structures based on MO$_6$ corner sharing (including the perovskitelike compounds) ReO$_3$ is unusual in that the undistorted cubic structure is stable at all temperatures; however, a pressure-induced phase transition was discovered by Razavi, Altounian, and Datars, who observed an anomaly in the Fermi surface when the sample was under pressure. Since then, the nature of this phase transformation has been investigated by different high-pressure experiments.

In contrast to ReO$_3$, the closely related WO$_3$ shows several phase transitions and remains tetragonal up to the melting point: the distorted ReO$_3$ structure of WO$_3$ changes from tetragonal to orthorhombic, monoclinic, triclinic, and monoclinic during cooling. On the other hand, when metal atoms are introduced in the WO$_3$ structure to form insertion compounds (the tungsten bronzes M$_x$WO$_3$), the cubic lattice is again stable for large values of $x$. In the stoichiometric tungsten bronze NaWO$_3$, the Na atom donates its 3$s$ electron to the conduction band making NaWO$_3$ isoelectronic to ReO$_3$. Based on this simple analogy, the stability of the cubic phase in ReO$_3$ could be associated with the occupany of the conduction band, a point examined in this article. Fujimori and Tsuda have also attributed the different structural behavior to the screening effect involving W or Re 5$d$ and O 2$p$ states on the lattice vibrations.

The band structure and Fermi surface of cubic ReO$_3$ were calculated semiempirically by Mattheiss using the Slater-Koster linear combination of atomic orbitals scheme. The tight-binding parameters were adjusted to fit the optical and Fermi surface data. This work found that the valence and conduction bands are mainly composed of O 2$p$ and Re 5$d$ orbitals, respectively. Strong bonding, due to the overlap of those states, contributes to the broadening of the 5$d$ conduction band and leads to metallic conductivity. The Fermi surface is composed of two roughly spherical sheets centered about Γ plus a third sheet that consists of $\langle 100 \rangle$ directed cylinders intersecting at Γ. This remains, to our knowledge, the only theoretical investigation of the electronic structure of ReO$_3$.

There is a great deal of experimental information about dynamical properties of ReO$_3$, but a precise knowledge of the optical modes frequencies at the Brillouin zone center is still missing. The optical bond-stretching modes (Re-O) are observed in the region from 920 to 600 cm$^{-1}$ and those assigned to the angle-bending modes (O-Re-O) are observed below 450 cm$^{-1}$. These modes have been probed by different techniques such as acoustic, electric conductivity, and specific-heat measurements; inelastic neutron scattering and x-ray-absorption spectroscopy. The
only direct observation of optical phonons at the center of the Brillouin zone was made by IR transmission spectroscopy of ReO$_3$ films deposited upon a silicon plate.$^{15}$ Two peaks were found at room temperature at 905 and 315 cm$^{-1}$ and assigned to the IR active stretching and bending modes, respectively, in agreement with the second-order Raman spectrum. Raman spectroscopy studies of tungsten oxides, with the ReO$_3$-like structure, confirm that the stretching and bending modes are expected at 800 and 270 cm$^{-1}$, respectively.$^{16,17}$

In the present article, we report density-functional calculations of ReO$_3$, WO$_3$, and the stoichiometric tungsten bronze NaWO$_3$, performed with the full-potential linear muffin-tin orbital method. In Sec. II we give a description of the computational aspects of our study. The results are presented in Sec. III: the structure optimization and electronic structure and lattice stability in Sec. III A, and the calculation of frequencies and eigenvectors for the optical phonon modes at $\Gamma$ in Sec. III C. Finally, Sec. IV contains a summary and conclusions.

## II. METHOD OF CALCULATION

For the calculation of the electronic structure of the three oxides we used the full-potential (FP) linear muffin-tin orbital (LMTO) code by Methfessel,$^{18,19}$ within the local-density approximation (LDA) and the Hedin-Lundqvist exchange-correlation potential. In the FP-LMTO, no shape approximations are made for either the charge density or the exchange-correlation potential. In the FP-LMTO, no shape approximations are made for either the charge density or the exchange-correlation potential. The participating states are divided into valence, semicore, and core. Core states are those confined within spheres centered on the nuclei. They are treated by solving the radial Schroedinger equation in each iteration, assuming that the wave function is zero on the sphere surface (unfrozen core). Semicore states are those associated with very narrow bands that can, however, spill out of the atomic sphere.

As is customary for a LMTO approach, the basis for the wave function consists of atom-centered Hankel functions, which are augmented by numerical solutions of the radial Schroedinger equation within the nonoverlapping atomic spheres. In the interstitial region the charge density is represented by fitting a linear combination of Hankel functions to the values and slopes on the sphere boundaries. To provide sufficient variational freedom, it is essential in the method to extend the basis using LMTO’s with different localizations. The envelope function decays as $e^{-\kappa r}$, where $-\kappa$ is the kinetic energy of the Hankel function.

The FP-LMTO calculations were performed employing a basis set (presented in Table I) that was found to be optimal for describing the band structure of ReO$_3$. A similar setup was used in the study of the closely related ferroelectric perovskite KTaO$_3$.$^{20}$ In addition, Re 5$s$ and W 5$s$ states have been explicitly included in the separate semicore panel. The choice of muffin-tin (MT) radii was based on the spatial distribution of the self-consistent charge density over the unit cell; this allowed us to attribute charge densities centered at different atoms to their corresponding spheres, leaving only relatively smooth variations of the charge density over the interstitial region. The only exception is Na, whose sphere is enlarged in order to include some interstitial space around it. In the binary oxides, empty spheres (of radius $R_{MT}$=3.2 a.u.) were added at the dodecahedral sites in order to achieve better space filling. The resulting packing parameter ($V_{MT}/V_{total}$) was around 58%. The Brillouin-zone integrations were carried out by the tetrahedron method using 35 irreducible $k$ points (corresponding to $8 \times 8 \times 8$ regular divisions along the $k_x$, $k_y$, and $k_z$ axes, respectively).

## III. RESULTS

### A. Structure optimization and electronic structure of ReO$_3$

Before analyzing the electronic properties, we have optimized the structure of the oxides examined. For the cubic phase this is a straightforward procedure: since the structure does not contain internal degrees of freedom, the change consists in an isotropic compression or expansion of the unit cell and corresponds to calculating the total energy as a function of the lattice parameter $a$. The results are shown in Table II. The equilibrium lattice constant for ReO$_3$, cubic WO$_3$, and NaWO$_3$ are 3.71, 3.78, and 3.83 Å, respectively. For ReO$_3$, the total energy as a function of volume has the minimum at $V/V_{exp}$=0.969. This difference in the evaluation of the equilibrium volume is typical for a calculation using the local-density approximation. As cubic WO$_3$ has never been observed experimentally, we compare our results with Hartree-Fock calculations.$^{21}$ There is good agreement for the equilibrium lattice constants obtained with the two techniques. For NaWO$_3$ we compare the equilibrium lattice constant with the estimate given by the empirical formula $a=3.7899$ Å + 0.0601 Å×$x$ [valid for Na$_x$WO$_3$ when $x>0.75$ (Ref. 22)] for $x=1$. Results of the calculations reported hereafter make reference to the optimized cubic structure of ReO$_3$. For subsequent reference, we define $a_0$ as the calculated equilibrium lattice constant of ReO$_3$ ($a_0=3.71$ Å).

The calculated bond structure for ReO$_3$ is shown in Fig. 2(a) [Fig. 2(b) is for further reference]. Here and in the following figures the zero of energy is chosen to coincide with the Fermi level of the solid in the case of metallic behavior and the top of the valence band if it is an insulator. The general features are not greatly different from the earlier tight-binding (TB) calculation; there are, however, appre-
calculations, where the top of the valence band at the gap between the conduction and valence bands unlike our have a bandwidth of 2.8 eV. In the TB band structure there is partial change of the specified atom and orbital and allows us to highlight the contributions from the Re and oxygen orbitals of a particular symmetry to each band. The valence band is formed mainly by O 2p states, although they are strongly hybridized with Re 5d orbitals. The conduction band has a dominant contribution from the Re 5d(t_{2g}) orbitals, while the Re 5d(e_g) orbitals lie at higher energy. This trend in the band composition closely resembles that obtained for cubic WO₃ in Ref. 21. The same arguments advanced there apply to the case of ReO₃ treated here: mixing of oxygen and metal states occurs in both valence and conduction bands, but we can clearly distinguish a dominant contribution from the oxygens in the valence band and from the metal in the conduction band (partly occupied in the case of the metallic ReO₃). Regarding the relative energy ordering of the metal e_g and t_{2g} levels, we note that in the conduction band this is as expected for a metal ion in an octahedral field, with the t_{2g} levels at lower energy. The metal contribution in the valence band takes into account the hybridization of its states with the surrounding oxygens. The stabilization arising from this interaction is proportional to the overlap of the corresponding orbitals; this is maximum for the e_g orbitals, which point directly towards the oxygen p states, and the resulting stabilization is such that the e_g levels lie at lower energy than the t_{2g} in the valence band.

In Fig. 4 shows the calculated Fermi surfaces on the k_z=0 and k_x=π/a planes. Two out of the three sheets are closed surfaces centered about Γ, with completely electronlike character. The third is an open surface, with both electronlike and holelike character, and consists of ⟨100⟩ directed cylinders intersecting at Γ. The shape of the three surfaces agrees with the ones obtained by Mattheiss⁷ by adjusting the tight-binding parameters to fit the de Haas-van Alphen data of Marcus.²³

B. Relation between electronic structure and lattice stability of ReO₃, WO₃, and NaWO₃

The electronic band structures for the optimized unit cells of cubic WO₃ and NaWO₃ are shown in Figs. 5(a) and 5(b), respectively; they are very similar to the results of earlier calculations performed on NaWO₃ within the atomic sphere approximation (LMTO) atomic sphere approximation.²⁴ We note that the band structures of the three oxides are topologically very similar (compare with Fig. 2 for ReO₃). Because of the different number of valence electrons per unit cell, the conduction band is empty in WO₃ and half filled in ReO₃ and
the tungsten bronze. The latter two materials are therefore metallic conductors, while the former is an insulator, in agreement with the experimental evidence. This, together with the agreement already mentioned with the experimentally determined Fermi surface for the case of ReO$_3$, reassures that for our case the LDA gives reliable predictions for the band structures. As in ReO$_3$, in both WO$_3$ and NaWO$_3$ the valence bands have a prevalent contribution from the O 2$p$ orbitals and the conduction bands from the metal $t_{2g}$ orbitals.

The charge density in ReO$_3$ was investigated experimentally by x-ray structural analysis. An anisotropic charge distribution was found around the Re atom, which was attributed to the $\pi$ bond formed by Re 5$d$($t_{2g}$) and O 2$p$ electrons. This experiment also indicated that the thermal vibrations of the oxygen atoms were remarkably anisotropic at every temperature: the amplitude of the oxygen vibration towards Re is in fact much smaller than in the perpendicular direction, towards the empty spaces of the perovskite-like structure. These structural features of the solid are evident in Fig. 6(a), where we show the calculated valence charge density of ReO$_3$ in the (001) plane. The metal and oxygen positions marked in Fig. 6(a) serve as a reference for Figs. 6(b) and 6(c).

FIG. 5. Band structure of (a) cubic WO$_3$ and (b) stoichiometric tungsten bronze NaWO$_3$.

FIG. 6. (a) Valence charge density of ReO$_3$ and (b) and (c) difference between the self-consistent charge density for the metals and WO$_3$ in the (100) plane: (b) ReO$_3$ and (c) NaWO$_3$. Continuous, dashed, and dot-dashed lines correspond to positive, negative, and zero densities, respectively; the interval between consecutive isodensity lines is 0.0015 a.u. (e/bohr$^3$).

The electronic charge densities for WO$_3$ and NaWO$_3$ are very similar to the one shown in Fig. 6(a) for ReO$_3$. To highlight the differences we have compared the valence density of both metals with that obtained for WO$_3$. Figure 6(b) reports the difference between ReO$_3$ and WO$_3$ in the (100) plane. In both cases we have employed the equilibrium lattice parameter of ReO$_3$ ($a_0$). Given the similarity in the band structures, this procedure can be considered as equivalent to integrating the density of the half-filled conduction band in ReO$_3$ (showing also a minor charge redistribution arising from the different potentials of the two crystals); this map is therefore showing the distribution of the electron responsible for the metallic conductivity of ReO$_3$. The corresponding difference density map for NaWO$_3$ is shown in Fig. 6(c). In ReO$_3$ the conduction electron is well localized in a $t_{2g}$ orbital on the metal center; this is not the case in the bronze, where the electron is delocalized over the whole structure. In both cases we observed a depopulation of the metal $e_g$ orbital. The plane selected in Fig. 6 does not contain Na ions; the increased density at the corners of Fig. 6(c), with respect to Fig. 6(b), therefore is not directly associated with the Na nuclear region. The Na cations in the bronze increase the polarization of the oxygen ions in the direction perpendicular to W-O, as can be seen in Fig. 6(c).
In the study of the lattice deformations we are interested in understanding the different behaviors of the three materials and not their absolute properties. For this reason we did not consider completely optimized structures, but used an idealized description in which the oxygen sublattice is fixed in its undistorted cubic position. The lattice parameter chosen was $a_0$ in every case. Only ferroelectric displacements of the transition metal along the principal crystallographic directions have been examined: results are shown in Fig. 7, where the total energy is reported for displacements of the transition metal sublattice along the [001] (right panel) and [111] (left panel) directions. These movements correspond to displace the B ion towards a corner ([001]) or towards a face ([111]) of its coordination octahedron (see Fig. 1). For ReO$_3$ and the bronze, the cubic structure remains favored over the displaced ones and the potential wells have an essentially parabolic shape. On the contrary, the cubic structure in WO$_3$ is unstable when the transition metal is displaced, in both the [001] and [111] directions; the equilibrium position for W is along the [111] direction, and a local minimum exists also in the [001]. The energy gained from the displacements is 16.7 and 8.5 meV, respectively.

One important contribution explaining the different behavior arises from the one-electron part of the total energy. In Fig. 2(b) we report the band structure of distorted ReO$_3$, where the Re sublattice is displaced by 3% of the lattice constant $a_0$ along the [001] direction; the same qualitative effects occur for the other two materials. Under displacement of the transition metal, both valence and conduction bands are distorted; in particular, we observe a stabilization in the valence band and a destabilization of the conduction band. Two of the six valence bands ranging from $-2.6$ to $-4.5$ eV are stabilized at a lower energy; on the other hand, the flat conduction band in the $\Gamma$-$X$ direction, that lies in the region of $\approx -2$ eV is destabilized by $\approx 0.9$ eV.

To illustrate the origin of the above splitting in the energy levels, we make reference to Fig. 8. It corresponds to the projected band structure of Fig. 3, after the displacement of the Re ion. In the cubic phase, the two flat bands between $-3$ and $-2$ eV that represent the top of the valence band and the bottom of the conduction band along the $\Gamma$-$X$ direction correspond to pure O 2$p$ and Re $d(t_{2g})$ states (see Fig. 3). The transition-metal displacement causes a hybridization of the two levels, with bonding character in the valence band and antibonding in the conduction band. In Fig. 8, in fact, we clearly see that after the displacement of Re, the levels described above have contributions from both O 2$p$ and Re $d(t_{2g})$. The atomic orbitals involved have $\pi$ symmetry along the Re-O direction; we can therefore ascribe the changes to the onset of a $\pi$ bond between metal and oxygen. In WO$_3$ only the bonding level is filled and the distortion is energetically stable, while in the metallic oxides ReO$_3$ and NaWO$_3$ also the antibonding orbital is populated; this second effect destabilizes the distorted structure of the latter materials and opposes the deformations examined.

A similar hybridization pattern between the transition metal and oxygen states was found to be essential to explain the ferroelectric behavior of ternary perovskites; a more detailed study of the effects of charge distortion and covalence in WO$_3$ is reported in Ref. 21, where the importance of the W-O hybridization for the stability of the tetragonal phase is discussed in detail.

C. Frozen phonon calculation in ReO$_3$

As we have pointed out in Sec. III A, the value calculated from the total-energy minimum for the equilibrium volume of cubic ReO$_3$ is $\approx 0.97\%$ of the experimental cell volume. Such a discrepancy is known to be typical for calculations based on the LDA. Since the curvature of the total-energy hypersurface may be affected by the error in the cell volume and LDA calculations generally agree best with experiment when performed at the experimental lattice parameter, we
performed our phonon calculation for both the theoretical \((a_0=3.71 \text{ Å})\) and the experimental \((a=3.75 \text{ Å})\) values of the lattice constant.

As is known (see, e.g., Ref. 15), \(\Gamma\) phonon vibration modes in the cubic perovskite structure of ReO₃ are split by symmetry into two \(F_{1\mu}\) modes and one \(F_{2\mu}\) mode (all of which are triply degenerate). The \(F_{1\mu}\) modes are active only in the infrared, while the \(F_{2\mu}\) mode is inactive in both the infrared and Raman spectra (silent mode).

In the cubic cell we have a Re atom at \((0,0,0)\), an oxygen atom at \((a/2,0,0)\) \((O_1)\), a second oxygen atom at \((0,a/2,0)\) \((O_2)\), and a third oxygen atom at \((0,0,a/2)\) \((O_3)\). Since the modes at \(\Gamma\) are degenerate with respect to displacements in the \(x, y,\) or \(z\) direction, it is convenient to select a reference one say \(z\), where atoms are displaced by an amount \(u\). Symmetry requires that \(u(O_1)=-u(O_2)\) in the \(F_{1\mu}\) modes and \(u(O_1)=-u(O_2)\) in the \(F_{2\mu}\) mode. To provide a good multi-dimensional fit of the total-energy hypersurface in the evaluation of phonon frequencies, we have performed total-energy calculations for 22 and 4 different displacement patterns (which include individual atoms as well as mixed displacements) for the infrared \(F_{1\mu}\) and silent \(F_{2\mu}\) modes, respectively. Atomic displacements were extended up to 3\% of the lattice constant. A second-order least-squares fit was applied, and the phonon frequencies and eigenvectors were derived.

The frequencies and eigenvectors for both theoretical and experimental cubic structures are shown in Table III. Despite the differences in the calculated frequencies, the corresponding relative displacements of atoms determined for both lattice constants are very close. As can be seen from the eigenvectors, the high-frequency \(F_{1\mu}\) mode is a Re-O stretching mode that involves a displacement of \(O_2\) with respect to the rest of the crystal. The low-frequency \(F_{1\mu}\) mode and the silent mode are O-Re-O bending modes. The difference in the calculated frequencies for these two bending modes can be understood examining their respective eigenvectors: while the silent is a pure oxygen mode, the bending \(F_{1\mu}\) mode includes an important contribution from Re displacement. Due to the large mass of Re, the frequency of the bending \(F_{1\mu}\) mode is smaller.

The calculated frequencies for the two infrared active modes are lower than the ones obtained by IR transmission spectroscopy of ReO₃ film,¹⁵ where two peaks were found at room temperature at 905 and 315 cm⁻¹. It is not possible to ascertain whether such a discrepancy arises from errors due to the LDA or from the fact that the experimental results are obtained for the thin films and therefore are not a valid model for the bulk system. However, the present calculation corroborates a very important fact: the existence of a high-frequency stretching mode \((\omega\approx800 \text{ cm}^{-1})\) in ReO₃.

The existence of high-energy phonons in ReO₃ is particularly interesting. Allen and Schulz²⁸ analyzed the shape and magnitude of the electrical resistivity for four inter-metallic compounds. They concluded that ReO₃ belongs to the normal class of conventional band Fermi liquids, with electron-phonon interactions dominating the resistivity, but showing a sharp departure from the Bloch-Grüneisen formula that could be explained if most of the phonons coupling involves high-frequency vibrations.

### Table III. Frequencies and eigenvectors in ReO₃.

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<th>O₃</th>
<th>Frequency (cm⁻¹)</th>
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### IV. SUMMARY

We have presented \textit{ab initio} calculations of the band structure and Fermi surface of metallic ReO₃. Despite the differences in the calculated bandwidths and band gaps, the general features of the band structure and Fermi surface are not very different from those obtained in an earlier LCAO calculation, where the tight-binding parameters were adjusted to fit the optical and de Haas–van Alphen data.

The differences in structural behavior between WO₃ and the metallic compounds ReO₃ and NaWO₃ have been studied by performing total-energy calculations. The energy changes associated with small deformations from the cubic phase indicate that ReO₃ and the tungsten bronze are stable when cubic, while off-center displacements of the metal ion are stable in WO₃. The different behavior is explained by the strong destabilization of the conduction band that follows the displacement of the transition metal ion. In WO₃ the conduction band is vacant and a stabilization of the valence band due to the \(\text{Wd}–\text{O} p\) hybridization favors the distorted structure, while in ReO₃ and NaWO₃ the destabilizing effect due to the occupation of the conduction band prevails, opposing the deformations. Finally, a frozen phonon calculation of \(\Gamma\) phonons in ReO₃ corroborated the existence of a high-frequency Re-O stretching mode.

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