

# An ab initio LAPW study of the $\alpha$ and $\beta$ phases of bulk molybdenum trioxide, $\text{MoO}_3$

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## Abstract

Structure and electronic properties of the  $\alpha$  and  $\beta$ - $\text{MoO}_3$ , have been studied with periodic LAPW calculations. The structure and electronic properties of the  $\alpha$ - $\text{MoO}_3$  are in quite agreement with experimental and previous theoretical results. The oxide is partially ionic and the symmetrically bridging oxygens exhibit more ionic feature while the terminal oxygens are more covalent. The lattice scaling of the  $\beta$ - $\text{MoO}_3$  give results in excellent agreement with the reported experimental pseudo-cubic results. It has been found from density of states (DOS) that  $\beta$ - $\text{MoO}_3$  is not fully ionic system and some covalent contributions are still appreciable. These covalent contributions to the bonding appear derisory compared to the covalent contributions of the  $\alpha$  phase. The  $\beta$ - $\text{MoO}_3 \rightarrow \alpha$ - $\text{MoO}_3$  transformation is explained by metal off-center displacement toward  $\text{O}_1$  (and a little less toward  $\text{O}_2$ ) centers which is stabilized by an increase in covalency between the Mo and oxygen atoms.

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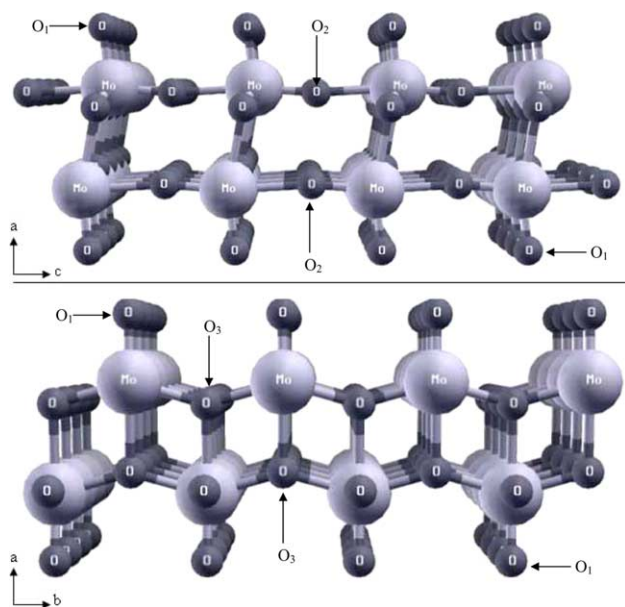
## 1. Introduction

Transition metal oxides are well known for their diverse structural, physical and chemical properties [1–3]. These materials exist in many crystallographic forms with stoichiometries differing only slightly from each other and transition metal ions exhibiting various oxidation states. Among these oxides, molybdenum oxides represent an important class of system which are widely studied and used in many technological applications. In particular, molybdenum trioxide  $\text{MoO}_3$  is an important heterogeneous catalyst [2,4,5], electrochromic component [6] and active material in secondary lithium batteries [7–11].

Molybdenum trioxide can exist in two crystalline polymorphs form, the thermodynamically stable orthorhombic  $\alpha$ - $\text{MoO}_3$  [12], and the metastable monoclinic  $\beta$ - $\text{MoO}_3$  phase [13–16].  $\alpha$ - $\text{MoO}_3$  crystallizes with lattice constants  $a = 13.855 \text{ \AA}$ ,  $b = 3.696 \text{ \AA}$  and  $c = 3.963 \text{ \AA}$ . It has a layer structure in which each layer is built up of  $\text{MoO}_6$  octahedron at two levels, connected along  $y$ -axis by common edges and corners, so as to form zigzag rows and along  $z$ -axis by common corners only (see Fig. 1). Moreover each layer exhibits, in the  $y$ -axis direction, oxygen atoms which are common for three different octahedron. Each octahedra also shares, along  $z$ -axis, two oxygen atoms with two neighboring octahedron. Besides, for each  $\text{MoO}_6$  octahedra there is only one oxygen atom which is doubly bounded to the molybdenum atom ( $\text{Mo}=\text{O}$ ). Therefore, three kinds of structurally different lattice oxygens exist, i.e., terminal oxygen

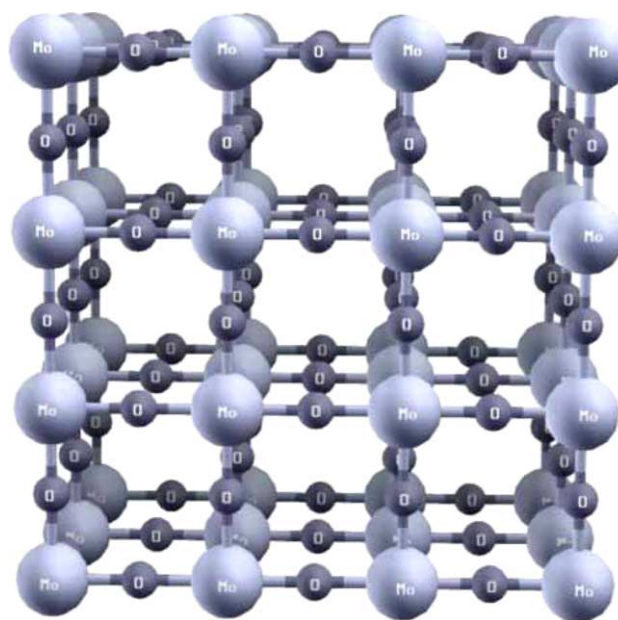
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Fig. 1. Crystal structure of  $\alpha$ -MoO<sub>3</sub>.

(singly coordinated, O<sub>1</sub>), asymmetric bridging oxygen (doubly coordinated, O<sub>2</sub>, O<sub>2</sub>'), and symmetric bridging oxygen (triply coordinated, O<sub>3</sub>, O<sub>3</sub>'). The MoO<sub>3</sub> layers are parallel to the (1 0 0) crystal plane, such as, the inter layer interaction is weak, and hence the (1 0 0) plane is the most exposed and thermodynamically most stable, where only O atoms are exposed on the surface.  $\beta$ -MoO<sub>3</sub> is similar to WO<sub>3</sub> and is related to the three-dimensional ReO<sub>3</sub> structure [13], which consists in corner-connected octahedra network, as shown in Fig. 2. It crystallizes with lattice constants  $a = 7.122 \text{ \AA}$ ,  $b = 5.366 \text{ \AA}$ ,  $c = 5.566 \text{ \AA}$ , and  $\beta = 92.01$ . The  $\beta \rightarrow \alpha$  transformation is both exothermic and photochromic, with yellow  $\beta$ -MoO<sub>3</sub> converting to the white  $\alpha$  phase above 400 °C at moderate heating rates [13]. The relatively high-transformation temperature implies that  $\beta$ -MoO<sub>3</sub> ought to have a fair measure of kinetic stability at or near room temperature. Nevertheless, X-ray diffraction measurements have shown that  $\alpha$ -MoO<sub>3</sub> can be stabilized in the ReO<sub>3</sub> structure ( $\beta$ -MoO<sub>3</sub>) by partially substituting molybdenum by tungsten [14].

Many applications of the molybdenum trioxide are prepared in thin film form [17]. A micro-Raman spectroscopy characterization [18] has shown that the films are almost composed by the  $\beta$  phase or (and) splashed species which consist of a mixture of the  $\alpha$  and  $\beta$  phases. In addition,  $\beta$  phase has been a subject of deeper spectroscopic study [19]. In this study, the authors have shown that this photochromic material is promising in the areas of color displays and camouflage applications. Despite these applications and the more general importance of the  $\beta$ -MoO<sub>3</sub>, both experimental and theoretical studies are still lacking. In contrast,  $\alpha$ -MoO<sub>3</sub> has been the subject of many experimental [2–12] and theoretical

Fig. 2. Crystal structure of  $\beta$ -MoO<sub>3</sub>.

[20,21] studies with respect to their structural and electronic properties (Note that the amount of theoretical work still few compare to the experimental one). In order to fill this gap, we initiated the present study. In doing so, we aim in particular to investigate the forces involved in the bonding between metal and oxygen and to understand why the  $\beta$  structure is metastable.

In this paper, both MoO<sub>3</sub> phases are studied using a periodical boundary condition ab initio LAPW method. In Section 2, we describe briefly computational details and Section 3 presents results and discussion. Finally, we summarize our conclusions in Section 4.

## 2. Computational details

The detailed geometries of both MoO<sub>3</sub> phase are obtained, in the present calculations, from total energy optimization, where the experimental structure for the orthorhombic structure is used as a starting point for the  $\alpha$  phase [12]. The monoclinic phase has much more degrees of freedom than the  $\alpha$  phase, and hence requires much more computing power for the structural optimization. We have therefore, chosen as a model system, the pseudo cubic structure (defect perovskite or ReO<sub>3</sub> like structure) suggested by McCaron in his initial description of this MoO<sub>3</sub> form [13]. This kind of approximation has been already used for the monoclinic WO<sub>3</sub> structure, which has been well described with the cubic ReO<sub>3</sub> like type structure [22,24]. To check this approach, we have compared the calculated band gap of the optimized cubic structure with the calculated band gap of the experimental monoclinic structure. It was found that the calculated band gap for the pseudo-cubic structure is

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