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Impact of lattice distortion and electron doping on α -MoO₃ electronic structurePeng-Ru Huang¹, Yao He¹, Chao Cao² & Zheng-Hong Lu^{1,3}¹Department of Physics, Yunnan University, Kunming 650091, China, ²Department of Physics, Hangzhou Normal University, Hangzhou 310036, China, ³Department of Materials Science and Engineering, University of Toronto, 184 College Street, Toronto, Ontario M5S 3E4, Canada.

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requests for materials
should be addressed to
Y.H. (yhe@ynu.edu.cn)

Band structure of transition metal oxides plays a critical role in many applications such as photo-catalysis, photovoltaics, and electroluminescent devices. In this work we report findings that the band structure of MoO₃ can be significantly altered by a distortion in the octahedral coordination structure. We discovered that, in addition to epitaxial type of structural strain, chemical force such as hydrogen inclusion can also cause extended lattice distortion. The lattice distortion in hydrogenated MoO₃ led to a significant reduction of the energy gap, overshadowing the Moss-Burstein effect of band filling. Charge doping simulations revealed that filling of conduction band drives the lattice distortion. This suggests that any charge transfer or n-type electron doping could lead to lattice distortion and consequentially a reduction in energy gap.

Room-temperature molybdenum trioxide (α -MoO₃) has a unique orthorhombic structure (space group: *Pbnm*, $a = 3.697$ Å, $b = 13.864$ Å, and $c = 3.963$ Å)^{1,2} which consists of layers of corner sharing and edge sharing MoO₆ octahedra. For its unique crystal and related properties, this oxide has showed potential applications in a variety of fields such as solid catalyst³, electrochromism^{4,5}, battery electrode⁶, charge injection or extraction layer in organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs)^{7,8}. For some applications, MoO₃ is generally in contact with metals or with electron donors, such as hydrogen and alkali atoms. These physical contacts usually create interesting effects that have not been fully understood. For example, Greiner *et al.* reported that the work function and band structure of MoO₃ were significantly altered when it was deposited on metals⁹. According to their UPS valence band spectra, two gap states were observed for the metal deposited MoO₃ films. As they proposed, these states resemble the features of defect states found in oxygen-deficient MoO₃. Another example is a band gap reduction of MoO₃ caused by hydrogen diffusion. Many experiments have been reported that physical appearance of MoO₃ becomes blue when being exposed to H₂^{10–12}. From the optical transmission spectral measurements, Balendhran *et al.* observed a reduction of the optical gap of the MoO₃ flake, from 3.2 eV to 2.6 eV, with increasing H₂ exposure¹¹. Based on Raman shift of the structure, they stated that this optical gap change is related to a structural change of MoO₃ and can be observed in a wide range of processes such as thermal treatment, UV-irradiation and photochemical deposition followed by annealing. To gain a deeper insight into these phenomena, it is of great importance to systematically investigate the relationship between geometric and electronic structures in MoO₃.

Previous theoretical studies on MoO₃ are mainly focused on its structural, electronic and catalytic properties^{13–18}. There is no report on how the lattice distortion and the electron doping affect its band structure. Besides, since the traditional DFT functionals do not accurately describe the van der Waals (vdW) interaction; a repulsive force is found between adjacent layers of MoO₃ despite the interlayer distance. To overcome the problem, previous studies on the bulk phase of this oxide were conducted by assuming the unit cell lattice constant b to an experimental value. This assumption is problematic in the calculation of lattice structure upon inclusion of impurities. Ding *et al.* examined several vdW corrected density functionals on the structural and vibrational properties of MoO₃¹³. According to this report, the optB88 functional method produced the most accurate results on the lattice parameters and bond lengths of MoO₃. This method made it possible to investigate lattice-deformed MoO₃ in a direct and reasonable way.

In this paper, we used the vdW corrected density functional theory calculations to investigate the band structure evolution as a function of lattice distortions and electron doping. By examining the band gaps from various distorted lattice along the a -, b -, and c -axis, we observed an anisotropic behavior. Analysis based on symmetry-resolved density of states (DOS) revealed detailed information about the orbital interaction and the nature of the anisotropic behavior in this oxide. We next considered the effects of electron doping on the crystal, band structure and optical properties of MoO₃ by intercalating H atoms. The results indicate that band gap

reduction is accompanied by structural reconstruction. This is in agreement with experimental observations. To prove that this phenomena is not restricted to H intercalation, simulations of electron doping into the system were presented. Based on our results, a physical picture can be drawn to describe the relationship between geometric and electronic structures in MoO_3 .

Methods

Our DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) with the projector augmented wave (PAW) pseudopotentials^{19–23}. Considering the dispersion interaction in the layered structure, the van der Waals functional approach was used, and the exchange-correlation energy of interacting electrons was treated by the optB88 functional developed by Klimeš and coworkers^{24–26}. The energy cut off for the plane-wave basis set was 500 eV. A $(7 \times 3 \times 7)$ Monkhorst-Pack k-point grid was used for geometry optimization and a much denser k-point grid was used for DOS calculations. All considered structures were fully optimized with the force on each atom less than 0.01 eV/Å.

The unit cell we used to calculate the MoO_3 crystal is shown in Figure 1a. It keeps the *Pbnm* space group symmetry with optimized lattice constants $a = 3.944$ Å, $b = 13.982$ Å, and $c = 3.737$ Å. The crystal is based on two nonequivalent bilayers stacked along the *b*-axis. Each bilayer consists of two sublayers of distorted octahedra that are corner-connected along the *a*-axis and edge-shared along the *c*-axis (Figure 1b, c). There are three symmetry distinct oxygen sites: the terminal oxygen O1 is singly coordinated, the bridging oxygen O2 is asymmetrically bonded with the two neighboring Mo atoms, and the symmetric O3 is triply coordinated with two Mo atoms oriented along the *c*-axis and one sublayer Mo atom.

To investigate the effect of lattice distortion on the band structure of MoO_3 , we performed calculations for uni-directional change in the cell constant in order to identify the major contribution from various lattice directions. The percentage of the cell length change was used to quantify the magnitude of distortion, i.e. a positive value means expansion while a negative one contraction. This method can serve as an approximation to the simulation of the strain effect. Furthermore, it enables us to isolate the effect of strain induced lattice distortion into individual directions, which is desired for theoretical analysis of the structural-electronic correlation. The computations of optical properties were carried out through the perturbation theory method that implemented in the VASP code. Herein, the imaginary part of the dielectric function ε_1 was computed by summing over the occupied and unoccupied single-particle Kohn-Sham (KS) states, and the real part of the dielectric tensor was obtained by the usual Kramers-Kronig transformation. The absorption coefficient was derived from the imaginary and real parts of the dielectric function through the formula

$$I(\omega) = 2\omega \left(\frac{[\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)]^{1/2} - \varepsilon_1(\omega)}{2} \right)^{1/2} \quad (1)$$

Results and Discussion

Band structure modification under lattice distortion. The calculated band gaps of MoO_3 as a function of uniaxial lattice distortion along the *a*-, *b*-, and *c*-axis, respectively, are plotted in Figure 2, which shows an anisotropic behavior. The calculated band gap for the equilibrium structure is 1.62 eV and indirect in nature. This value is smaller than the experimental measurement (~ 3 eV) owing to the well known underestimation of the band gap in DFT calculations. However, this does not affect our discussion since we are mainly interested in its relative value. As the lattice was stretched or compressed along the *a*-axis, the band gap decreased or increased remarkably, almost 0.2 eV per 1% distortion around the equilibrium value. However, distortions along the *b*- or *c*-axis changes the band gap moderately and oppositely. Our results agree with a previous report of Li *et al.* who studied the effect of strain on the MoO_3 sheets²⁷. However, in the paper Li *et al.* provided no interpretation for this type of behavior. Here we explore the underlining physics.

The π -*zx* orbital determined the band gap of MoO_3 . In the octahedral coordination of transition metal oxides, the *d* orbitals of metal center are split into t_{2g} (*xy*, *yz*, *zx*) and e_g ($x^2 - y^2$, $3z^2 - r^2$) manifolds when coupling with *p* orbitals of oxygen atoms according to symmetry considerations. Generally, t_{2g} states contribute bands near the band gap and e_g states locate further away in energy due to the crystal-field splitting. In this case, the t_{2g} states determine the band structure modification near the band gap when external interactions were applied. In the MoO_6 coordination of MoO_3 crystal, t_{2g} further splits into *xy*, *yz*, and *zx* states due to the octahedral distortion, as shown in Figure 3a. For our presentations, the orbital indexes *x*, *y*, and *z* coincide with the crystallographic axes *a*, *b*, and *c*, respectively. In details, the d_{xy} orbital of Mo center overlaps mainly with the p_y orbital of bridging oxygen O2 and the p_x orbital of terminal oxygen

Figure 1 | The crystal structure of MoO_3 : (a) unit cell, (b) corner-connected and (c) edge-shared octahedra viewed from the *ab* and *bc* planes, respectively. (d) The crystal structure of H intercalated MoO_3 which contain one hydrogen atom (green ball) in a $2 \times 1 \times 2$ supercell.

Figure 2 | Variation of band gaps for MoO₃ with uniaxial lattice distortion along the *a*-, *b*- and *c*-axis, respectively. The magnitude of distortion is defined as the percentage of cell constant change.

O1 to form π type bonding in the *xy* plane (π -*xy*). Similarly, the d_{yz} orbital mainly hybrids with the p_z of O1 and the p_y of O3 to form π -*yz*, and the d_{zx} orbital of Mo hybrids with the p_z of O2 and the p_x of O3 to form π -*zx*. The relative strength of these three pd - π type

hybridizations can be easily distinguished from the widths of their unoccupied bands showed in Figure 3b, and the order is π -*zx* > π -*yz* > π -*xy* for the equilibrium structure. Bear in mind that the π -*zx* hybridization is in the layer plane while the other two are out of it. This order can be understood by the comparison of their MoO₄ tetragonal geometries in the three planes, as shown in Figure 4. Examining the bonding along the three axes, the O3-Mo-O3 chain along the *c*-axis is symmetric having a both bond length of 1.97 Å; the O2-Mo-O2 chain along the *a*-axis is asymmetric having a short bond of 1.78 Å and a long one of 2.19 Å, respectively; the O1-Mo-O3 coordination orientated in the *c*-axis is the most asymmetric since it involves the terminated Mo-O1 bond of 1.71 Å and the inter-sublayer Mo-O3 bond of 2.40 Å (Table 1). Since a regular coordination is more favorable for orbital overlap than a distorted one, the Mo center has the largest orbital overlap with the four neighboring oxygen ions in the *zx* plane in which the symmetric O3-Mo-O3 bonding and the less asymmetric O2-Mo-O2 bonding are involved. The MoO₄ interaction in the *bc* plane is the weakest since the Mo atom is off-centered both along the *a*- and *c*-axes (Figure 4). It is the π -*zx* orbital that contributes the band edges at the VBM and CBM and determines the band gap of the equilibrium structure. As can be seen in Figure 3b, the band width of the π -*zx* orbital increased or decreased significantly as contraction or expansion was applied along the *a*-axis, and the band gap was changed accordingly. The band gap modification upon the *b*- or *c*-axis distortion was also governed by the expansion or shrink of the π -*zx* band, and we do not intend to repeat their DOS evidences here.

Figure 3 | (a) Projected density of states of orbital coupling in the *xy*, *yz* and *zx* plane respectively. (b) Projected density of states of the π -*xy*, π -*yz* and π -*zx* orbitals for pristine MoO₃, 5% *a*-contracted MoO₃ and 5% *a*-expanded MoO₃. The *x*, *y* and *z* axes are identical with the crystallographic axes *a*, *b*, and *c*, respectively.

Figure 4 | The octahedral coordination for pristine MoO₃, 5% *a*-contracted MoO₃ and H_{0.0625}MoO₃ viewed from three planes. Atomic species are color coded as follow: Mo (yellow), terminal O1 (blue), bridging O2 (red), symmetric O3 (purple), and H (green).

The distorted octahedral coordination was the origin of the anisotropic band gap modification upon lattice distortion for MoO₃. Owing to the asymmetric O2-Mo-O2 bonding along the *a*-axis and the O1-Mo-O3 coordination oriented along the *b*-axis, the MoO₆ octahedron is distorted in a manner that the Mo cation is off-centered along both the *a*- and *b*-axis (Figure 4). Lattice distortion had the effect of driving the Mo cation toward or further off the octahedral center depending on the direction. Then, the structural deformation changed the system band gap through the modification of orbital overlap. Consider, firstly, the case that the *a* constant was reduced by 5%, the long Mo-O2 bond was shortened by 0.18 Å while,

interestingly, the short one was slightly elongated by 0.03 Å. This reduced the asymmetry of the O2-Mo-O2 coordination and moved the off-centered octahedral cation along the *a*-axis toward the center of the *ac* plane MoO₄ tetragonon, resulting in a larger orbital overlap of the π -*zx* hybridization. Then the system band gap was reduced because of the expansion of the π -*zx* bands. Contraction along the *b*- or *c*-axis, however, deformed the crystal in an opposite manner compared to that along the *a*-axis. For contraction along the *c*-axis, the O3-Mo-O3 coordination was bended to be of smaller angle, from 143.10° to 134.78°, in the case of 5% distortion. The bending slightly pushed the Mo cation along the *a*-axis away from the tetragonal

Table 1 | Geometric parameters for the pristine MoO₃, distorted MoO₃ and H_{0.0625}MoO₃. The bond parameters for H_{0.0625}MoO₃ measures the octahedron which is most closed to H. The arrows indicate the stretch (↑) or the shrink (↓) of Mo-O2 bonds with respect to that in the pristine structure

	Cell parameters	Mo-O1 (Å)	Mo-O2 (Å)	Mo-O3 (Å)
MoO ₃	<i>a</i> = 3.944 Å <i>b</i> = 13.982 Å <i>c</i> = 3.737 Å	1.709	1.782 2.185	1.968 2.395
Distorted MoO ₃	5% <i>a</i> -contracted	1.706	1.810 ↑ 2.003 ↓	1.951 2.501
	5% <i>a</i> -expanded	1.711	1.761 ↓ 2.391 ↑	1.978 2.347
	5% <i>b</i> -contracted	1.709	1.777 ↓ 2.191 ↑	1.966 2.351
	5% <i>b</i> -expanded	1.709	1.785 ↑ 2.182 ↓	1.969 2.423
	5% <i>c</i> -contracted	1.710	1.776 ↓ 2.195 ↑	1.920 2.471
	5% <i>c</i> -expanded	1.709	1.784 ↑ 2.180 ↓	2.028 2.3345
H _{0.0625} MoO ₃	<i>a</i> = 7.772 Å <i>b</i> = 14.153 Å <i>c</i> = 7.513 Å	1.867	1.789 ↑ 2.027 ↓	1.931 2.182

center in *ac* plane by shortening the short Mo-O2 bond while stretching the long one. The deformation reduced the overlap of Mo $3d_{zx}$ with O2 $2p_z$ and O3 $2p_x$, resulting in the increase of the band gap. Similarly, the *b*-axis contraction further distorted the *ac* plane tetragon by bending the O1-Mo-O3 coordination. The opposite effects of the expansion along these three directions can be expected. Notice that the *a*-axis distortion directly deformed the asymmetric O2-Mo-O2 coordination while distortion along the *b*- or *c*-axis changed it in an indirect way, the band gap modification caused by distortion along the *a*-axis was larger than that along the other two directions at the same percentage of cell length change.

Mechanical strain is possibly the most direct way to introduce lattice distortion which could effectively tune the physical properties of materials by the structure-electronics correlation^{27–29}. In our calculations we isolated the strain induced lattice distortions in individual directions. The results, with appropriate consideration among these directions, are applicable to practical strains²⁷. To understand exact strains in MoO₃, the correlation of distortions in different axes must be addressed. The crystal of the MoO₃ is characterized by the two dimensional covalent bonding network in the *ac* plane and the vdW stacking along the *b* axis. Thus, the *a* and *c* constants are correlated with each other strongly by the in plane covalent bonding. The *b* constants, however, is governed not only by the covalent bonding but also the vdW gap separating the covalent network. According to our study, when MoO₃ is strained along the *a*-axis, it distorts along the *c*- and *b*- axes by some small ratios (as expected from the Poisson's ratios). As shown in Figure 2, distortion of the *b* and *c* lattice constants follows the same trend, but in opposite direction, in modifying the band gap. This is also the situation for *c*-axis strain except for the negative Poisson's ratio between *b*- and *c*- axes. For the *b*-axis strain, compression results in a small expansion of the *a*-axis constant and a small contraction of the *c*-axis constant. However, expansion of the *b*-axis constant hardly affect the cell constants of the other two axes owing to the exist of the vdW gap between layers.

The effect of electron doping. Hydrogen intercalation in MoO₃ were computed to investigate the effect of electron doping on the structural and electronic properties of MoO₃. The material system studied in this paper was constructed by bonding one hydrogen atom to a terminated oxygen in a $2 \times 1 \times 2$ supercell (Figure 1d), which can be represented as H_{0.0625}MoO₃. Our calculations shown that the Mo-O1 bond was elongated by 0.16 Å as the terminated oxygen binded with the H atom. In addition, the longer Mo-O2 bonds were shortened by 0.05–0.17 Å while the short ones were elongated by 0.01–0.04 Å. As a result, the lattice constant along the *a*-axis was reduced by 1.5% (Table 1). These results suggest that the impurity-lattice interaction for hydrogenated MoO₃ is extensive along the *a*-axis owing to the asymmetric O2-Mo-O2 chain. Consequently, the resulting band structure is metallic as shown in Figure 5a. According to Bader atomic charge analysis³⁰, each hydrogen atom donated 0.6 electron to the host oxide, slightly changing the atomic charge of the neighboring Mo atoms from their stoichiometric value. The doping electrons occupied the electronic states at the bottom of the conduction band. Most importantly, the separation between the CBM and VBM was substantially reduced by ~ 0.5 eV. According to discussion in the previous section, the reduction of band gap is attributed to the deformation of the octahedral coordination. As could be seen from the octahedral structure shown in Figure 4, the bonding of H remarkably reduced the distortion of the MoO₆ octahedron. The bands near the gap, especially the π -*zx* band, were expanded owing to the enhanced orbital overlap (Figure 5b).

The narrowing of the fundamental band gap has a direct effect on the optical properties of the system. Figure 6a shows the real (ϵ_1) and imaginary (ϵ_2) parts of the polarized dielectric function for MoO₃.

Figure 5 | (a) Total density of states of H_{0.0625}MoO₃ compared to that of MoO₃. (b) Projected density of states of the π -xy, π -yz, and π -zx orbitals near the H impurity for H_{0.0625}MoO₃.

The dielectric functions show anisotropic responses to polarized light with the electric vector parallel to the *a*-axis ($E \parallel a$) and the *c*-axis ($E \parallel c$) owing to the distinct coordination along these two directions, in agreement with experimental measurements on MoO₃ single crystals³¹. The low energy peaks of the imaginary dielectric function arose principally from the O 2p to Mo 4d transitions. The absorption spectra derived from the dielectric functions also show distinct features for polarized light parallel to the *a*- and *c*-axis (Figure 6b). From the spectra, the optical band gap for the pristine MoO₃ was ~ 2 eV, which is about 1 eV under estimated as compared with experimental value but is in agreement with previous DFT calculations³². For the H intercalated MoO₃, the absorption spectra were significantly modified. Firstly, new absorption bands emerged in the original gap due to the intraband transition in the partially filled conduction bands. Most interestingly, instead of having a blue-shift caused by the Moss-Burstein effect of band filling, the absorption band arose from the interband transition expanded and moved the absorption onset toward lower energy. The red-shift must result from the reducing band gap caused by the structural deformation. The narrowing of the fundamental band gap, suppressing the filling of the conduction band, reduced the optical band gap.

Our calculated results of the band gap narrowing are supported by experimental observations. Balendhran *et al.* recently studied the reduction process for MoO₃ flakes through controlled H₂ exposure¹¹. Their measured $(\alpha h\nu)^2$ - $h\nu$ curves showed that the optical gap of MoO₃ reduced gradually with increasing H₂ exposure. Meanwhile, in their Raman spectra, the sharp peak at 820 cm⁻¹ gradually disappeared and a broad peak at 780 cm⁻¹ emerged. Since the peak at 820 cm⁻¹ is assigned to the stretching mode of the Mo-O2 bonding, the Raman shift was obviously attributed to the deformation of the O2-Mo-O2 coordination. According to our calculations, the short Mo-O2 bonds were stretched by the hydrogen inclusion. Consequently, the force constant between Mo and O2 and hence the vibration frequency of the Mo-O2 bonding was reduced by the intercalation of H atoms.

To further the investigation, we simulated the electron doping by adding extra electrons into the unit cell of MoO₃ and neutralizing the system via a homogenous positively charged background. As shown in Figure 7, the system band gap reduced monotonically with

Figure 6 | (a) Real (upper) and imaginary (lower) parts of the dielectric function for MoO_3 . (b) Absorption spectra for MoO_3 (upper) and $\text{H}_{0.0625}\text{MoO}_3$ (lower). The red and black lines correspond to light polarization parallel to c and a , respectively, and the dash line is a guide for the eye to compare the absorption onset.

increasing extra charge and finally converged as the electron concentration reached one electron per Mo atom. Accompanied by the reduction of the band gap was the decrease of the asymmetry of the O2-Mo-O2 coordination. In the pristine MoO_3 , the bond length difference between the two Mo-O2 bonds was 0.5 Å. The difference was gradually reduced and finally eliminated as the doping concentration reached one electron per Mo. From this observation, the band gap narrowing was connected to the deformation of the O2-Mo-O2 coordination. Most importantly, since our simulations rule out the influence of the atomic size and other chemical parameters, the driving force was obviously the filling of the conduction band by

the extra electrons. Thus, the band structure modification and the octahedral deformation in MoO_3 is correlated and could be triggered by any process involving the electron doping. Indeed, in a previous report, a lithium insertion was also found to modify the crystal and band structure of MoO_3 significantly³².

A physical picture can be established for the structure-electronics correlation in MoO_3 . (i) For the asymmetric O2-Mo-O2 chain in MoO_3 is easily deformed, the distorted octahedral coordination can be significantly reconstructed to be close to that of a regular octahedron. (ii) The octahedral deformation increases the pd - π type hybridization of Mo $3d$ and O $2p$, resulting in the

Figure 7 | Bond asymmetry (length difference) of the O2-Mo-O2 coordination (left, black circle) and the band gap reduction (right, red circle) for electron doped MoO_3 as a function of electron concentration.

extension of the band edges and the narrowing of the fundamental band gap. (iii) The driving force for the structural reconstruction could be an epitaxial type structural strain or any n-type electron doping.

The above theoretical results also provide insights into the observed gap states for MoO₃ deposited on metals⁹. Either the epitaxial-type of lattice strain effect or the electron doping by charge transfer at the metal/oxide interface could lead to the distortion of MoO₃ lattice, resulting in additional peaks near the band gap. These electronic states are essentially the extension of the π - π orbitals.

Conclusion

In summary, a systematic study on the effect of lattice distortion and electron doping in MoO₃ was carried out. We found that the VBM and CBM of MoO₃ were determined by the pd orbital interaction of the Mo with the bridging O2 and the symmetric O3. For the asymmetric bridging coordination, the O2-Mo-O2 chain was easily deformed by external interaction, and its deformation was closely connected to the band gap modification in MoO₃. Distortion along this chain effectively modified the system band gap, while distortion along the b - or c -axis modified the system band gap less effectively. The intercalation of hydrogen atoms was also found to significantly deform the O2-Mo-O2 chain, resulting in the emergence of band tail states and band gap narrowing. Simulations confirmed that the driving force of the lattice distortion was the filling of the conduction band. The results observed in hydrogenated MoO₃ could be anticipated in any process involving electron doping. Our results explain the optical gap reduction and the Raman shift in H₂ exposed MoO₃, and the gap states emerged in the MoO₃ deposited on metals. This work shows that understanding the relationship between geometric and electronic structures is essential to understand the physical properties of metal oxides.

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Author contributions

P.R.H. performed the calculations, prepared the figures and wrote the manuscript. Y.H., Z.H.L. and C.C. discussed and commented on the calculations and results. Z.H.L. and Y.H. revised the manuscript. All authors reviewed the manuscript.

Additional information

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