Influence of Intercalated Li on Electronic Structures and Optical Properties of V_2O_5

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Abstract: The density of states and band structures of V_2O_5 and Li-intercalated V_2O_5 ($Li_xV_2O_5$, $x = 0.5$ and 1.0) have been studied using a first-principles calculation based on density function theory with the local density approximation. The results indicate that V_2O_5 is an indirect-gap semiconductor, the intercalation of Li will not change its way of electron transition. While, the intercalation of Li lowers the energy of conduction band, and then narrows the band gap. At the same time, due to the intercalation of Li, the split-off in the conduction band of V_2O_5 disappears because of the split of conduction band. The Fermi level of $Li_xV_2O_5$ increases dramatically due to the electron transfer from Li 2s to the V_2O_5 host, which is probably the main reason why the optical band-gap augments with the Li intercalation.

Key words: first-principles calculation; V_2O_5; Li intercalation; electronic structure; optical properties

1　Introduction

Recently, a lot of studies have been focused on the vanadium pentoxide (V_2O_5), because it is a kind of very important inorganic material. Due to its special crystal and electronic structure, V_2O_5 has been used widely as cathode material for intercalation batteries[11], oxidation catalyst in industry[2], as well as gas sensors and electrode for electrochromic devices[3-5]. As using in electrochromic devices, V_2O_5 can be intercalated and de-intercalated by Li and thus could be defined as both a cathodically and an anodically coloring materials[6-9]. Generally, V_2O_5 is yellow, but the color will change to green and then blue with the intercalation of Li. During the de-intercalation of Li, its color will reversibly change back from blue to green and then yellow. Experimental results have showed that the transmission in the near-ultraviolet region changes strongly and the transmission in the near-infrared region has a slight variation with the increase of the amount of intercalated lithium; while the optical absorption edge moves to the shorter wavelength[6-10]. It was also found that the absorption tail in the low photonic energy region increases with the intercalation of Li. It has been considered that the intercalated Li will donate its 2s electron to the host, and leading to the reduction of partial V^{5+} to V^{4+}[11]. The reaction can be showed as:

$$V_2^{5+}O_5 + xe^- + xLi^+ \rightarrow Li_x^+ V_x^{4+} V_{1-x}^{5+}O_5 \qquad (1)$$

The reduced V^{4+} may play an important role in increasing the absorption tail in the low photonic energy region[12]. So far, the mechanism of change of optical properties of V_2O_5 due to the intercalation/de-intercalation of Li is still not clear. Little work has been done in the study of the influence on the

optical properties of V_2O_5 with Li intercalation/de-intercalation by theoretical calculation. It is well known that the band-to-band transition of electron is the most important part of optical absorption in the semiconductors. There are two transition ways: direct-gap and indirect-gap transition. Close to the absorption edge, the absorption coefficient $(h\nu)$ and the energy of incident photon $(h\nu)$ can be expressed as,

$$(h\nu) = B(h\nu - E_g)^m/h\nu \qquad (2)$$

where B is transition probability, E_g is width of band gap. For the direct-gap transition, $m = 1/2$, and $m = 2$ for the indirect-gap transition. Therefore, the absorption coefficient has close relationship with the band structures of semiconductors. In present work, we use a first-principles calculation based on density function theory (DFT) with the local density approximation (LDA) to calculate the density of states (DOSs) and band structures of $\text{-}V_2O_5$ and Li-intercalated V_2O_5. The purpose of this study is to understand, from theoretical view, the influence of intercalation of Li on the optical properties of V_2O_5.

2   Calculation and Crystal Structure

Vienna *ab-initio* Simulation Package (VASP), which has been well tested in solid-state physics[13 15], is used in our study. VASP is a complex package for performing *ab-initio* quantum-mechanical molecular dynamic simulations with plane wave basis sets and ultra-soft Vanderbilt pseudopotentials.

$\text{-}V_2O_5$ forms an orthorhombic (P_{mmn}) layer crystal (see Fig 1) with the lattice constants of $a = 1.1510$, $b = 0.3563$ and $c = 0.4369$ nm[16]. The layers with normal direction along [001] are
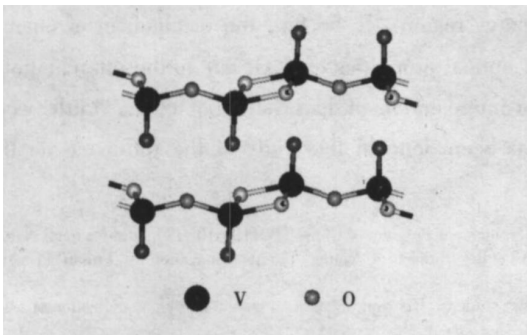
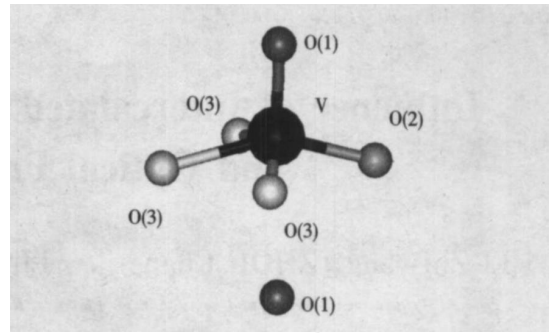

Fig 1   The layered structure of $\text{-}V_2O_5$.

Fig 2   The five-fold co-ordination of V by O in V_2O_5: one double vanadyl bond oxygen O(1), one bridging oxygen O(2), and three triple bonding oxygens O(3).

composed of distorter VO_6 octahedral (see Fig 2) sharing edges or corners. There are three different oxygen atoms in V_2O_5: one vanadyl oxygen O(1), one bridging oxygen O(2), and three triple bonding oxygens O(3). The unit cell in this study contains 14 atoms, four vanadium and ten oxygen atoms.

3   Results and Discussion

3.1   The Electronic Structures of $\text{-}V_2O_5$

The total energy of cell has been calculated with varying lattice constants, and it exhibits a minimum at lattice constants of $a = 1.1497$, $b = 0.3575$ and $c = 0.4355$ nm. It is only about 0.3% relative error comparing with those lattice constants measured from experimental study[16]. The good agreement suggests that this theoretical calculation method is suitable in this study.

The total DOSs, the partial DOSs of V and O, and the energy band structure of V_2O_5 are calculated by using the optimized lattice constants.

The total DOSs (Fig 3) show that the electron states mainly distribute in the two energy regions, one is in -5.12 0 eV corresponding to the valence band (VB) and the other is in 1.61 4.03 eV where the conduction band (CB) appears. A narrow split-off with width of 0.605 eV in CB is found, which has also been reported in experimental study[10]. Fig 4 shows the partial DOSs of V and O. It is obvious that the O 2p state mostly locates in the VB and the CB is almost constructed by V 3d orbital[17]. It is interesting to see that O(3) contributes very little in the CB, and the contribution of
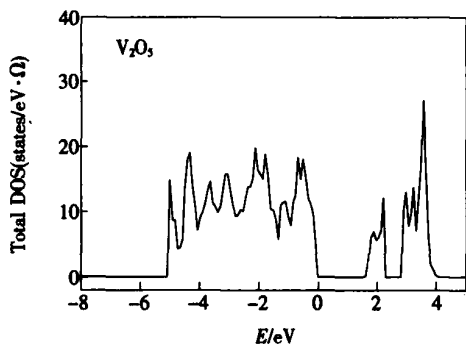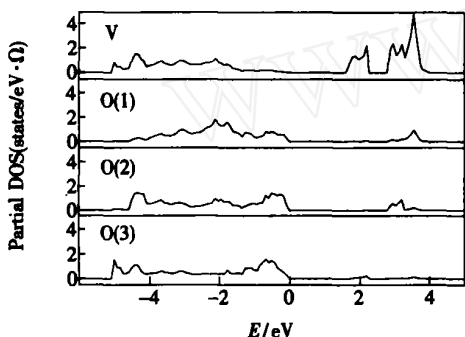
Fig 3   The total DOSs of V_2O_5.

Fig 4   The DOSs of V 3d and O 2p in V_2O_5 O (1) vanadyl oxygen, O (2) bridging oxygen, and O (3) triple bonding oxygen
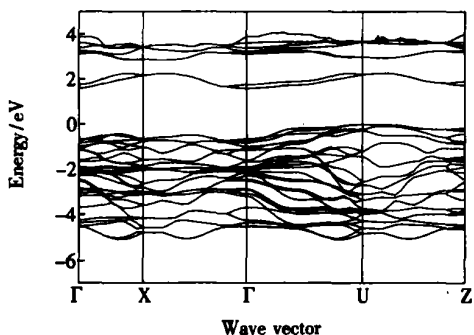

Fig 5   The band structure of V_2O_5.

O (1) in the CB locates in higher energy band than that of O (2). These results suggest that different O have different bonding properties with V.

The band structures (Fig 5) show that there is a band gap of 1. 61 eV between the bottom of the CB at （0, 0, 0）point and the top of the VB at U (0, ,) point, which indicates that the V_2O_5 is an indirect-gap semiconductor. The band gap is smaller than the experimental results, which are usually between 1. 90 and 2. 46 eV. This is reasonable for using LDA[13].

3. 2   The Electronic Structures of $Li_{0.5}V_2O_5$

We introduce one L i atom on the line of vanadyl oxygen and vanadium without changing the lattice constants of V_2O_5[18] as shown in Fig 6 The chemical formulation thus can be written as $Li_{0.5}V_2O_5$.
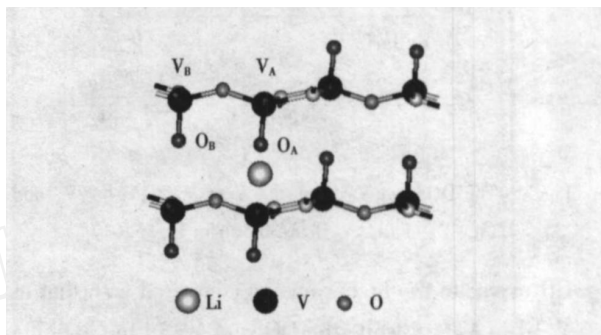

Fig 6   The location of L i in the cell of V_2O_5.

During the calculation L i is relaxed along *c* axis When the total energy of the system reaches a minimum, the location of L i shifts a little bit to vanadyl O ion. Then, the DOSs and the band struc- tures of $Li_{0.5}V_2O_5$ have been calculated Fig 7 shows the comparison of the total DOSs of $Li_{0.5}V_2O_5$ and V_2O_5. It is obvious to notice that the narrow split-off in the CB of V_2O_5 disappears in that of $Li_{0.5}V_2O_5$. The width of VB region of $Li_{0.5}V_2O_5$ is - 6. 17   0 eV, which is about 1. 02 eV wider than that of V_2O_5. CB moves to the higher energy compared with that of V 3d in V_2O_5; while the DOSs of V_B 3d in CB.
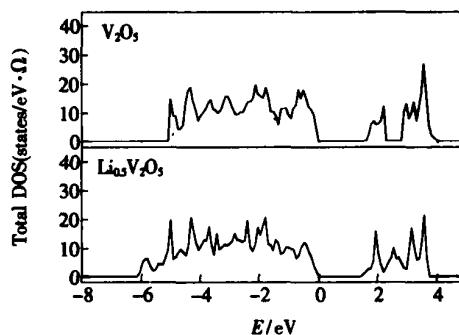

Fig 7   The comparison of the total DOSs of V_2O_5 and $Li_{0.5}V_2O_5$.

Fig 8 displays the DOSs of V 3d states The locations of V_A and V_B are indicated in Fig 6. There are strong differences between the DOSs of V_A 3d and V_B 3d states due to the different influences from intercalated L i The DOSs minimum of V_A 3d in the
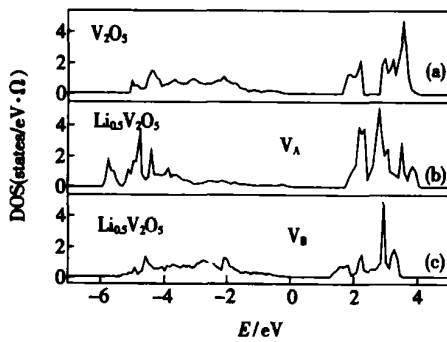
Fig 8　The DOSs of V: （a）the V of V_2O_5; （b）V_A and
（c）V_B of $Li_{0.5}V_2O_5$ as shown in Fig 6.

CB moves to the higher energy compared with that of
V 3d in V_2O_5; while the DOSs of V_B 3d in CB shifts
to lower energy. The DOSs of V_A 3d in the VB be-
comes broader and moves to lower energy, at the
same time, it decreases in the higher energy region
of VB. The CB of V_B 3d does not show obvious
change, except for a little bit broadening Fig 9
shows that, compared with these of O in V_2O_5, the
DOSs of the nearest vanadyl oxygen O_A 2p also shifts
to lower energy and increases in higher energy region
in the V_B due to the effect of intercalated Li Corre-
spondingly, little influence is found for O_B 2p state,
which is farer away from the intercalated Li atom.
Experimental data have reported that the intercalated
Li will transfer its 2s electron to V ion and then
leads to the reduction of V^{5+} to V^{4+} [11]. The strong
effects on the DOSs of V_A 3d and O_A 2p found in our
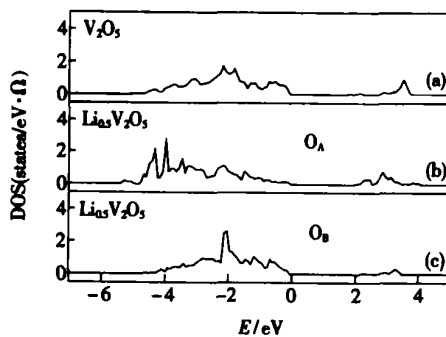calculation results somewhat support the experi-
mental data

Fig 9　The DOSs of O（1）2p: （a）the O（1）of V_2O_5,
（b）O_A and （c）O_B of $Li_{0.5}V_2O_5$ as shown in Fig 6.

Fig 10 shows the band structures and Fermi
levels （E_F）of V_2O_5 and $Li_{0.5}V_2O_5$. The band-gap

of $Li_{0.5}V_2O_5$ is about 1. 33 eV, which is about
0. 231 eV smaller than that of V_2O_5. Since the
bottom of CB and the top of VB still locate on （0,
0, 0） and U（0, , ） respectively, the properties
of electron transition of $Li_{0.5}V_2O_5$ do not change.
The band structures also suggest that there is not any
impurity level caused by intercalated Li, but the
symmetrical characteristic of system is reduced. The
energy bands that are degenerated split off move to
the low energy region. The intercalation of Li lowers
the energy of conduction band and narrows the band
gap. But why dose the optical absorption edge move
to the shorter wave with Li intercalation as reported
by experimental measurements[10]? During the cal-
culation, we found that the Fermi level of $Li_{0.5}V_2O_5$
increases to 1. 85 eV owing to the electron transfer
from Li 2s to the V_2O_5 host, which already locates in
the CB region and is about 0. 52 eV higher than the
bottom of CB. As it is known that the energy bands
below the Fermi level would be filled up by elec-
trons, so the electron from VB only can transfer to
CB above the Fermi level, which practically increases
the optical band-gap because of the intercalation of
Li This might be the main reason why the absorp-
tion edge moves to shorter wave after the intercala-
tion of Li proved by the experimental measurements

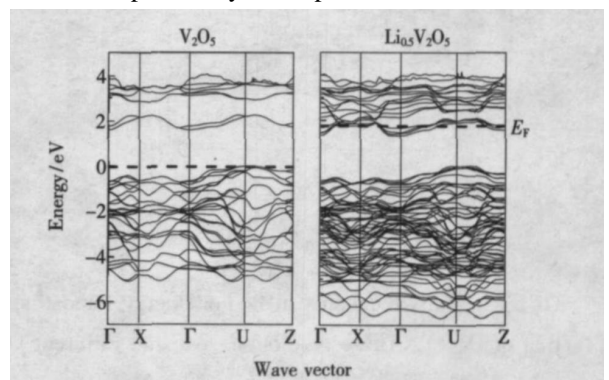Fig 10　The band structures of V_2O_5 and $Li_{0.5}V_2O_5$.

3. 3　The Electronic Structures of LiV_2O_5

Using the same model, we continue to intro-
duce another Li into the $Li_{0.5}V_2O_5$ cell The location
of Li is close to O_B atom in Fig 6. The chemical for-
mulation is thus LiV_2O_5, its band structure com-
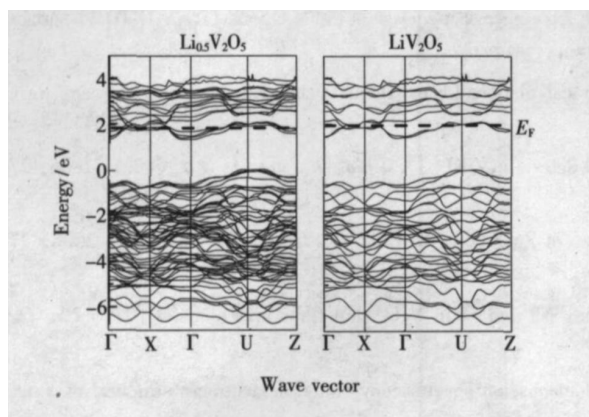pared with V_2O_5 and $Li_{0.5}V_2O_5$, and the E_F is shown
in Fig 11.

Fig 11   The band structures of L i$_{0.5}$V$_2$O$_5$ and L iV$_2$O$_5$.

The band-gap of L iV$_2$O$_5$ is about 0. 24 eV narrower than that of V$_2$O$_5$. The broadening of VB is more evident, but the bands on the bottom of CB degenerate again, and make the band-gap of L iV$_2$O$_5$ a little larger than that of L i$_{0.5}$V$_2$O$_5$. More amount of L i intercalation still does not change the positions of the bottom of CB and the top of VB. In addition, the Fermi level increases to 1. 91 eV, which is about 0. 06 eV higher than that of L i$_{0.5}$V$_2$O$_5$ and 0. 52 eV higher than the bottom of CB. Therefore, it makes the optical band-gap ever bigger This result agrees well with that the optical absorption edge move to the shorter wave with the more amount of L i intercalation.

4   Conclusion

By using DFT calculation with LDA，the equilibrium lattice constants, DOSs and energy band structures of V$_2$O$_5$, L i$_{0.5}$V$_2$O$_5$ and L iV$_2$O$_5$ have been investigated. We found that the electron transfer property of V$_2$O$_5$, which is indirect band gap, does not change with the increase intercalation amount of L i, but the Fermi level of host increases with the increase amount of intercalated L i That might be the main reason for the optical absorption edge of L i$_{0.5}$V$_2$O$_5$ and L iV$_2$O$_5$ moving to the shorter wave region, as the electron can only transfer from VB to CB above the Fermi level

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