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First principles studies on the electronic structures of $LiM_xFe_{1-x}PO_4$ (M = Co, Ni and Rh)*

Ouyang Xiao-Fang(欧阳小芳)[a], Shi Si-Qi(施思齐)[b,c,†], Ouyang Chu-Ying(欧阳楚英)[a], Jiang Di-You(姜迪友)[a], Liu De-Sheng(刘德生)[a], Ye Zhi-Qing(叶志清)[a,d], and Lei Min-Sheng(雷敏生)[a,d,‡]

[a] *Department of Physics, Jiangxi Normal University, Nanchang* 330022, *China*
[b] *Department of Physics, Zhejiang Sci-Tech University, Hangzhou* 310018, *China*
[c] *Key Laboratory of Advanced Textile Materials and Manufacturing Technology (Zhejiang Sci-Tech University), Ministry of Education, Hangzhou* 310018, *China*
[d] *Key Laboratory for Opt-electronics of Jiangxi Province, Nanchang* 330022 *China*

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The local crystal structures and electronic structures of $LiM_xFe_{1-x}PO_4$ (M = Co, Ni, Rh) are studied through first-principles calculations. The lattice constants and unit cell volumes are smaller for the Co and Ni doped materials than for pure $LiFePO_4$, while larger than for the Rh doped material. The local structures around M atoms in the doped materials are studied in details. The total density of states (DOS) and atomic projected DOS (PDOS) are all calculated and analysed in detail. The results give a reasonable prediction to the improvement of electronic conductivity through Fe-site doping in $LiFePO_4$ material.

Keywords: electronic properties, density of states, first principles, olivine
PACC: 7115A, 7125, 7115H

1. Introduction

It has been known in recent years that phosphate compounds have various potential applications in material sciences.[1] For example, they can be used as cathode materials of rechargeable lithium batteries, and sensors in electronics, in catalysis and so on.[2] $LiFePO_4$ is a member of olivine-type lithium phosphate family, which now has become a very important candidate for cathode materials of lithium ion batteries of power supplies for electric vehicles and hybrid electrical vehicles, due to its advantages such as high stability, high safety, low cost and being friendly to environments. However, the intrinsic low electronic and ionic conductivities restrict their extensive applications in reality. Methods to solve the problems of low conductivity, size minimization[3] and intimate carbon coating[4] have improved the performance of the material to some extent. However, those methods cannot change the intrinsic nature of low electronic conductivity, and one still has a long way to go before they may be widely applied. Later, it is found that Li-site doping[5,6] can improve the electronic conductivity enormously. However, the performance of this material used as cathodes of Li-ion batteries is not so well improved as it is expected through Li-site doping. It is reported that Li-ion diffusion in $LiFePO_4$ is one-dimensional and the dopant at the Li site may block the one-dimensional Li migration pathway.[7–9] Experiments have shown that Fe-site doping is a good option to avoid blocking the migration pathway.[10]

In the present paper, we give our results about the local crystal structure and the electronic structure of the Fe-site doping $LiFePO_4$ materials through density functional theory (DFT) based first-principles calculations which are used in some literatures.[11–15] The mechanism of the improved electronic conductivity is also discussed in detail.

2. Computational details

All the calculations in the present study are performed with the Vienna *ab initio* simulation package (VASP).[16,17] The ground state of the electronic

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†E-mail: siqishi@zstu.edu.cn
‡E-mail: mslei@jxnu.edu.cn

structure is described with DFT and the generalized gradient approximation (GGA).[18] The Vanderbilt pseudo-potentials[19] have been applied to the description of valence and core interactions, and the Perdew–Wang exchange correlation functional (PW91)[20] has been also used for the calculation of the electron exchange correlations energy. In the unit cell, one Fe atom is replaced by one M (M = Co, Ni and Rh) atom for the doped case. Before the calculation of the band structure, both the lattice constants and the ionic positions are fully relaxed. The Monkhorst-Pack[21] scheme with $3 \times 5 \times 7$ k-point sets has been used for the integration in the irreducible Brillouin zone. Energy cut-off for the plane waves is chosen to be 520 eV. The total ground state energy is converged within 3×10^{-6} eV per formula unit. The atomic positions, lattice parameters and cell volumes are fully relaxed, and the final forces on all relaxed atoms are less than 0.05 eV/Å. In all the calculations, spin polarizations are considered because the magnetic atoms may play an important role in the electronic properties.

3. Results and discussion

3.1. The local structure and structural distortion around the doped atoms

The calculated lattice constants for both $LiFePO_4$ and M-doped $LiFePO_4$ are listed in Table 1. The lattice constants of Co- and Ni-doped materials are a little smaller than those of the undoped $LiFePO_4$, while the lattice constants of Rh-doped materials are a little larger. The lattice constant changes are closely related to the radius of the doping atoms, as the radius of Rh is larger than those of Co, Ni and Fe. This is also confirmed by the enlarged Rh—O bond length and contracted Co—O bond length, which are also listed in Table 1. Furthermore, the dopants do not affect the PO_4 tetrahedrons in the lattice, as the P—O bond lengths for the doped materials are almost the same as those for the undoped materials. This shows that the PO_4 tetrahedrons framework is very stable and results in the structural stability of the material during Li ions insertion and extraction process.

Table 1. The structures and band parameters of pure and doped $LiFePO_4$.

	$LiFePO_4$	$LiCo_xFe_{1-x}PO_4$	$LiNi_xFe_{1-x}PO_4$	$LiRh_xFe_{1-x}PO_4$
a/Å	10.2024	9.9276	10.1479	10.2056
b/Å	5.9555	5.7848	5.9334	5.9743
c/Å	4.6630	4.6307	4.6667	4.6896
Li—O/Å	2.0967	2.0692	2.0967	2.1017
M—O/Å	—	2.1100	2.1333	2.2217
P—O/Å	1.5550	1.5619	1.5550	1.5550
Fe—O/Å	2.1433	2.0439	2.1339	2.1322
$W(\uparrow)$/eV	2.27	2.88	2.45	4.88
$W(\downarrow)$/eV	2.46	2.80	3.64	3.77
Band gap/eV	0.23	—	—	—

Plots in Figs.1 and 2 are the local atomic structures of pure $LiFePO_4$ and Co-doped $LiFePO_4$ respectively. From Figs.1 and 2, the local structural information can be seen clearly. The doping atoms do not change the symmetry of the crystal, and the olivine feature remains in the doped materials. However, the local atomic positions are relaxed significantly, due to the different atomic radii and electronic configurations of the doped atoms, which will be discussed in detail in the following sections. The difference between the FeO_6 octahedral and CoO_6 can also be characterized by the distortion of the angles as shown in Figs.1 and 2.

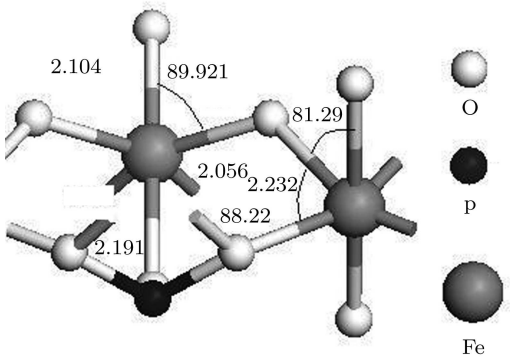


Fig.1. Local atomic structures of $LiFePO_4$.

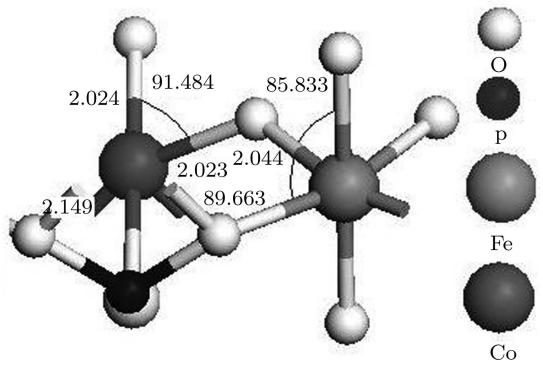


Fig.2. Local atomic structure of $LiCo_xFe_{1-x}PO_4$.

3.2. The electronic properties

The distortion of the local atomic structure plays an important role in changing the electronic structure of the material. As is known, the d-orbit is always split into t_{2g} and e_g orbits under an octahedral crystal field, and the gap between t_{2g} and e_g orbits is affected by the local crystal field, which can be slightly changed by the local atomic structure distortion in the doped material.

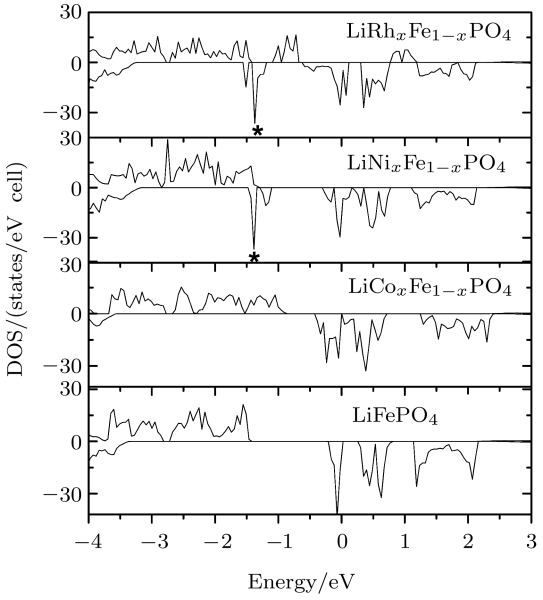


Fig.3. The total DOSs around the Fermi levels of $LiFePO_4$ and M-doped $LiFePO_4$. The tetrahedron method with Blöchl correction smearing is used and the broadening width is 0.1 eV. The Fermi energy is set to be 0 eV.

In order to obtain the quantitative results on the electronic structure of the $LiFePO_4$ and Fe-site doping materials, the total density of states (DOS) and atomic projected DOS are both calculated and analysed in the present study. The results give reasonable prediction to the improvement of electronic conductivity through Fe-site doping. Figure 3 compares the DOS around the Fermi level before and after doping, and it shows clearly that there exist much more states that are located near the Fermi level in the doped materials. Atomic projected DOS analysis shows that those states are mainly contributed from the doped d-electron states. The valence bands shift upward due to the d-electron states of the doped atoms, while the conduction bands shift downward. This will result in a narrower band gap of the doped materials as shown in Fig.3.

More interestingly, there exists a large difference in DOS between the Ni-, Rh-, and Co-doped materials. In the minority-spin channel of the Co-doped material, the states are quite continuous to some extent. However, in the Ni- and Rh-doped materials, those states are separated from each other by a large gap, and the lower part of the minority-spin channels are completely occupied, as marked by stars in Fig.3. As there are more electrons occupying the minority-spin channels, the magnetic moments of the Ni- and Rh-doped materials should be much smaller than those of the Co-doped material. In this sense, the electronic structure is influenced by the magnetic atoms.

Figure 4 shows the atomic projected DOSs on one Fe atom in pure $LiFePO_4$ and on one M atom in the M-doped $LiFePO_4$. In each plot, the upper panel is

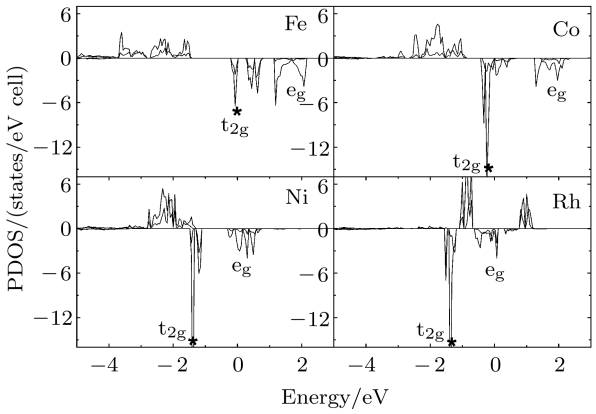


Fig.4. Atomic projected DOS of d-states of one Fe(M) atom in $LiFePO_4$($LiM_xFe_{1-x}PO_4$). The tetrahedron method with Blöchl correction smearing is used and the broadening width is 0.1 eV. The Fermi energy is set to be 0 eV.

for the majority-spin channel and the lower panel is for the minority-spin channel. Both the majority spin and the minority spin are separated into t_{2g} and e_g bands. To facilitate the discussion later, let $W\uparrow(W\downarrow)$ denote the bandwidth of the majority- (minority-) spin d band. The calculated band parameters are

listed in Table.1. The spin-up bands and spin-down bands are overlapped for the Ni- and Rh-doped materials and the minority-spin bands shift down a little. These results show that the electronic structure of pure $LiFePO_4$ is insulating with a band gap of about 0.23 eV, while the doped materials are all metallic. The metallic characteristic electronic structure of the doped materials indicates that the electronic conductivity should be largely improved. For the cases of Ni- and Co-doped materials, the impurity energy bands are located in the conduction band. But the impurity bands of the Rh-doped material lie in the valence band.

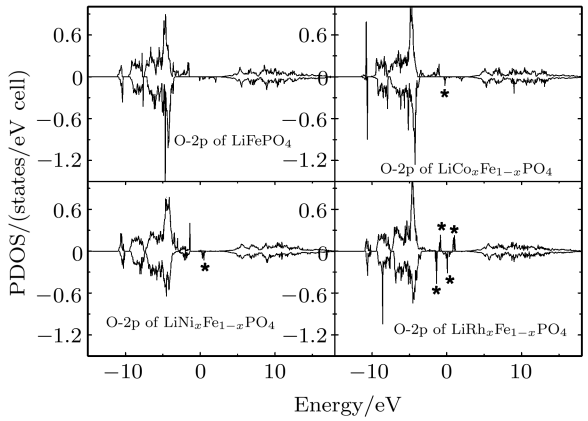


Fig.5. The O -2p atomic projected DOS of the O atom bonded with one Fe (M) atom in $LiFePO_4$($LiM_xFe_{1-x}PO_4$). The tetrahedron method with Blöchl correction smearing is used and the broadening width is 0.1 eV. The Fermi energy is set to be 0eV.

Figure 5 shows the atomic projected DOS on one oxygen atom bonded with one Fe (M) atom in $LiFePO_4$($LiM_xFe_{1-x}PO_4$). Those oxygen states are quite similar to each other in general, but the states around the Fermi energy exhibit some differences between the pure $LiFePO_4$ and M-doped $LiFePO_4$. Those differences mainly originate from the different interactions between Fe—O and M—O bonds. In the doped materials, some additional states are observed near the Fermi level as shown in Fig.5. As the doped M atoms have more electrons than the host Fe atoms, some charges are transferred to the neighbouring O atoms as marked by stars in Fig.5.

4. Summary

In summary, we have performed a detailed investigation on the electronic properties and the local structures of the pure and M-doped materials ($LiFePO_4$ and $LiM_xFe_{1-x}PO_4$), and provided a first-principles prediction that $LiFePO_4$ materials, with the Fe site doped by M (M = Co, Ni, and Rh) possess better electronic conductivity than pure material. The mechanism for the improvement of the electronic conductivity is proposed, and the relationship between the local atomic structure and the electronic structure is also discussed. The obtained results show that both the local structural distortion around M atoms and the spin polarization states of M atoms are important to the electronic properties of the doped materials. We have also observed that some charges are transferred from M atoms to adjacent O atoms in the M-doped $LiFePO_4$ materials.

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