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Research Article

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A theoretical study of the structure distortion of Li_2FeSiO_4

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ABSTRACT

Li_2FeSiO_4 has potential to be used as the next generation large-scale Li-battery. While its structure is still under controversy: it has been reported an orthorhombic structure by one group, and another group reported a monoclinic structure. In this paper, the first-principle calculation results show that the total energies of the orthorhombic structure and monoclinic structure are so close to each other, which implies the two structures should exist at the same time. The most interesting point is that Li_2FeSiO_4 maybe exists as a more complicated structure in which the orientation of FeO_4-SiO_4 tetrahedron is randomly arranged upwards or downwards.

Key words: Li_2FeSiO_4, First-principle Calculation, Structure, Disorder.

INTRODUCTION

In order to be used in large scale batteries for transportation applications (such as EVs and HEVs), the cathode materials of Li-battery should be low cost, safety and environmentally friendly. $LiFePO_4$, firstly reported by Goodenough et. al. in 1996, is an alternative of the next generation cathode material which have the above listed characteristic [1,2]. Recently, a new silicate-based material, Li_2FeSiO_4, reported by Nytén et. al. in 2005, has a potential to be applied in large Li-battery as $LiFePO_4$ [3]. Li_2FeSiO_4 have large theoretical capacity of about 330mAh g^{-1} with M^{2+}/M^{4+} two-electron reaction, and many researches are focused it [4-16].

For the crystallographic structure of Li_2FeSiO_4, Nytén et al. firstly performed Rietveld refinements for Li_2FeSiO_4 with a powder X-ray profile, and they reported that Li_2FeSiO_4 has an orthorhombic structure with $Pmn2_1$ symmetry[3]. The orthorhombic structure is accepted by some research group in the follow years [4-7]. Nishimura et. al. re-performed Rietveld refinements for Li_2FeSiO_4 with a high resolution powder X-ray profile based on a monoclinic structure with $P2_1$ symmetry [11]. The monoclinic structure also accepted by some group [14- 16].

In fact, the orthorhombic ($Pmn2_1$) and monoclinic ($P2_1$) structures are very close to each other, and it is very difficult to distinguish the two structure with the X-ray diffraction technique, as the detailed discussion in part III of this paper.

In the paper, the results of the first-principle calculation show that the calculated total energies of the orthorhombic structure and the monoclinic structure are very close to each other, which implies the two structures could exist at the same time.

Calculation Method

The calculations reported in this work were performed using the VASP (Vienna Ab-initio Simulation Package) code [17], which is based on density functional theory (DFT) [18-19]. The projected-augmented wave (PAW) approach is used for ion–electron interactions [20-21]. The exchange-correlation energy of electrons is described in the generalized gradient approximation (GGA) with the functional parameterization of PBE [22]. The electron spin polarization is considered. The tetrahedron method with Blochl is used, which could give a good precision of total energy [23]. The criterion of at least 1.0×10^{-5} eV per unit cell is placed on the self-consistent convergence of the total energy. The lattice parameters (cell shape) and atom positions are fully relaxed. In order to increase the precision, the precision controlling parameter "PREC" is set to the highest level, which could guarantees that "the absolute energies are converged to a few meV" [23]. Because that LDA+U or GGA+U could take into account the strong correlation between Fe-3d electrons, in this work, the GGA+U scheme describe by liechtenstein et. al. [24] is implemented and the value of U_{eff} (=U-J) for Fe-3d orbital is 4.3 eV.

RESULTS AND DISCUSSIONS

Relation between Orthorhombic and Monoclinic Structures. The orthorhombic structure and the monoclinic structure are presented in Figure 1a-b, respectively. The relationship between the orthorhombic lattice and the monoclinic lattice is described in Figure 2. The (001) plane of orthorhombic lattice (the original structure) is shown in Figure 2a, and ***a*** and ***b*** are the lattice vectors. When the angle between ***a*** and ***b*** is not equal to 90°, the lattice loses some symmetry operations and changes into monoclinic structure (the transformed structure), whose lattice vector is set up as ***a′*** and ***c′*** as presented in Figure 2b.

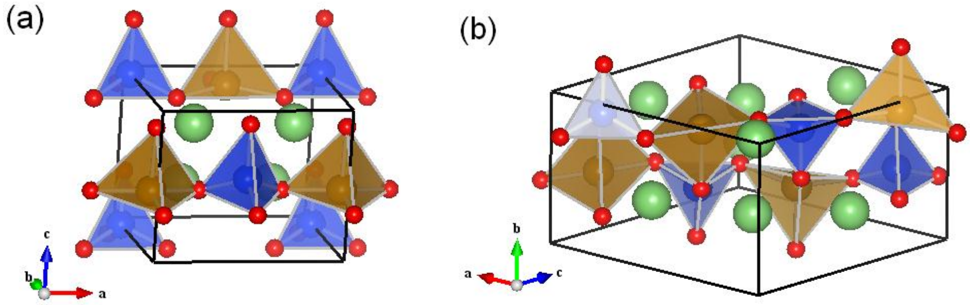


Fig. 1 (a) the orthorhombic structure; (b) the monoclinic structure

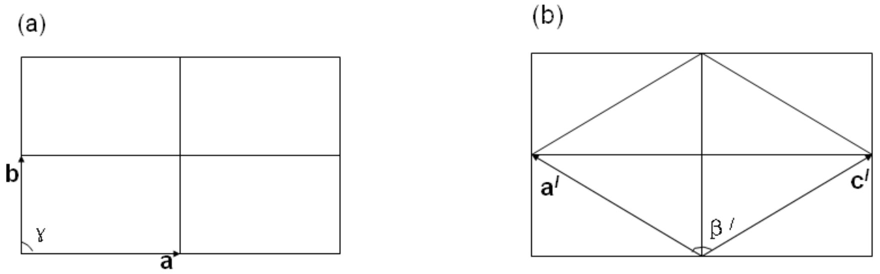


Fig. 2: The relationship between the orthorhombic lattice and the monoclinic lattice is a′=-a+b, b′=c and c′=a+b. (a) The (001) plane of orthorhombic lattice (the original structure), and a and b are the lattice vectors; (b) the monoclinic structure (the transformed structure) is set up in the original structure, and the new lattice vector is a′ and c′

Relative Stability of Orthorhombic and Monoclinic Structure. The calculated lattice constant of the orthorhombic structure under GGA+U scheme are ***a***=6.2859Å, ***b***=5.3674Å, and ***c***=4.9998Å, which is well consist with the experimental values measured by Nytén et al.[3] (***a***=6.266(1)Å, ***b***=5.329(1)Å, and ***c***=5.015(1)Å), and the theoretical values reported by Larsson et al.[5] (***a***=6.313Å, ***b***=5.393Å, and ***c***=4.979Å). For the monoclinic structure, the calculated lattice constant, a′=8.2511Å, b′=5.1075Å, c′=8.2523Å and β′=99.1824°, which well consist with Nishimura et al.' experimental results[11], and it means the present calculation is reliable. Politaev et al.[15] mentioned that the Li-Si distance in the orthorhombic structure was too short. Their analysis was based on the X-ray diffraction results of Nytén et al.[3], in which the lithium position may be is not so exact.

If GGA is applied to calculate the total energy difference between two structures with different symmetry, some error in the order of 10 meV is induced at the same time [25]. Then when the total energy difference between orthorhombic and monoclinic Structure of Li_2FeSiO_4 is very small, it could not be directly calculated under GGA scheme. Fortunately, the orthorhombic structure could be transformed into a corresponding monoclinic structure with the relationship ***a′***=-***a***+***b***, ***b′***=***c*** and ***c′***=***a***+***b***, which is presented in Figure 2 in this paper, and all FeO_4 and SiO_4 tetrahedrons should be keep upwards in the transform. After full relaxation (including the cell shape and atom position), the transformed structure's parameters are ***a′***=8.2657Å, ***b′***=4.9998Å, ***c′***=8.2657Å and *β*= 99.0136°, respectively. The corresponding orthorhombic structure constant calculated with the operation ***a***=(***c′***-***a′***)/2, ***b***=(***c′***+***a′***)/2 and ***c***=***b′***, and the values are ***a***=6.2859Å, ***b***=5.3674Å, ***c***=4.9998Å, and α=β=γ=90°, respectively, which rigidly consists with the directly calculated orthorhombic structure parameters as mentioned above (***a***=6.2859Å, ***b***=5.3674Å, ***c***=4.9998Å).

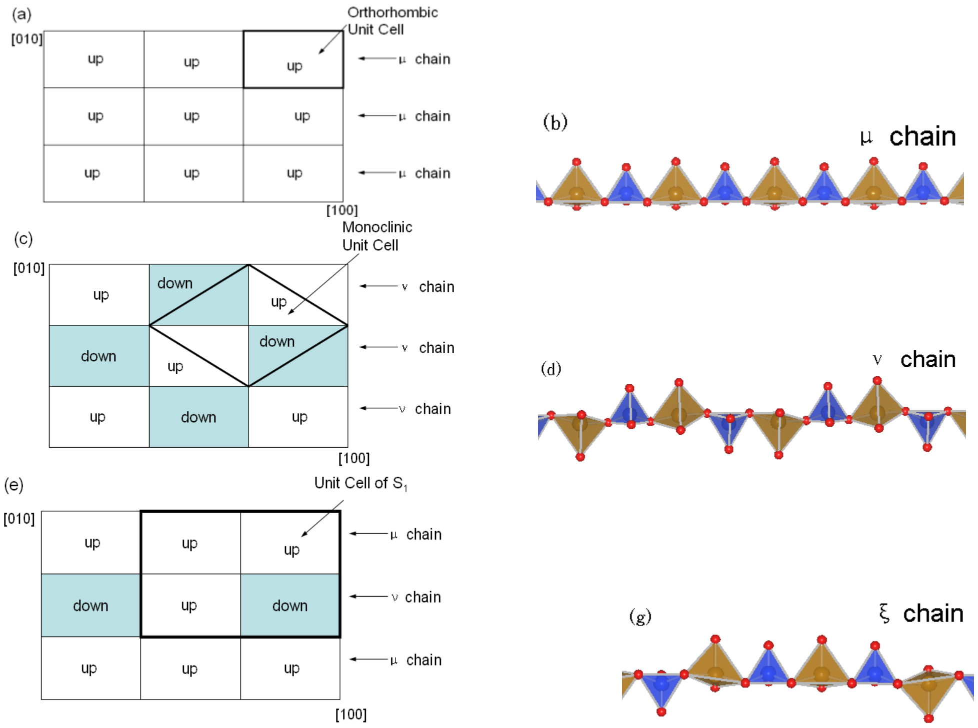
Then to compare the total energies of the orthorhombic ($Pmn2_1$) and monoclinic ($P2_1$) structure cited in the paper could be replaced to compare the two monoclinic structures: one is transformed from the orthorhombic structure; the other is the real monoclinic structure with $P2_1$ symmetry. As shown in table 1, the total energy difference per formula between the two structures is 6meV (GGA) or 4meV (GGA+U). The values are too small for DFT calculation, and it implies that the orthorhombic phase and the monoclinic phase could be exist at the same time.

Table 1 the relative total energy per formula of the structures, (for all the calculation, the electron spin polarization is considered)

	Relative Total Energy per Formula (meV)			
	Orthorhombic	Monoclinic	S_1	S_2
GGA	0	-6	23	23
GGA+U	0	-4	11	22

Orientation disorder of FeO_4-SiO_4 tetrahedrons. As the above discussion, the orthorhombic and monoclinic structures could exist at the same time, and in each of the two structures, FeO_4 and SiO_4 tetrahedrons form one-dimensional corner shared chains along [100] axis. In the orthorhombic structure, all tetrahedrons in the chain are orientated in one direction as shown in Figure 3b, which is specified as μ chain, and the lattice configuration in (001) plane is presented in Figure 3a, in which the FeO_4-SiO_4 tetrahedrons in each unit cell are upward. In the monoclinic structure, the tetrahedrons in the one-dimension chain periodically take opposite orientations as shown in Figure 3d, which is specified as ν chain. Its lattice configuration is presented in Figure 3c, and the FeO_4-SiO_4 tetrahedrons in the unit cell of the original lattice periodically take opposite orientation which looks like black-and-white mosaic picture. The heavy lines are the boundary of the monoclinic structure.

In order to evaluate other configurations, two structures are constructed based on the original lattice. One has a $2\times2\times1$ supercell and denoted as S_1, as the zone surrounded by the heavy lines in Figure 4e; the other has a $3\times2\times1$ supercell and denoted as S_2, as shown in Figure 4f. The relative total energies per formula of the two structures are listed in table 1, which are very close to that of the orthorhombic or monoclinic structure. Then beyond the pure the orthorhombic or monoclinic structure, Li_2FeSiO_4 may exist as some more complex structure, such as S_1 (the above $2\times2\times1$ superlattice) and S_2 (the above $3\times2\times1$ superlattice).



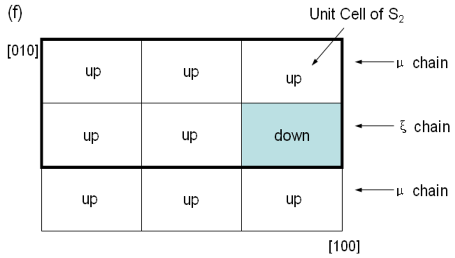


Fig. 4 (a) the lattice configuration of the orthorhombic structure in (001) plane; (b) the chain composed by the FeO4-SiO4 tetrahedrons in the orthorhombic structure (the μ chain); (c) the lattice configuration of the monoclinic structure in (001) plane of the original lattice; (d) the chain in the monoclinic structure (the ν chain); (e) the cell of S1 in (001) plane of the original lattice; (f) the cell of S2 in (001) plane of the original lattice; (g) the structure of ξ chain

S_1 contains two-type chains, μ and ν, which are periodically arranged along [010] direction. Then the structure could be looked as a combination of the orthorhombic and monoclinic structure. In S_2, there are also two-type chains: one is μ, the other is ξ, which is shown in Figure 4g. The ξ chain is different from μ and ν chains, and its periodic unit contains two upward FeO_4-SiO_4 tetrahedrons and one downward FeO_4-SiO_4 tetrahedron. The structures of S_1 and S_2 mention that the orientation arrangement of the FeO_4-SiO_4 tetrahedron does not change the total energy largely, i.e., the order the upward FeO_4-SiO_4 tetrahedron and downward FeO_4-SiO_4 tetrahedrons in Li_2FeSiO_4 could be randomly arranged.

If Li_2FeSiO_4 is synthesized in a system close to equilibrium state and with long-time crystal growth process, it maybe crystallize in the orthorhombic structure or the monoclinic structure. While under the common synthesis condition, the crystallization process is so quick and the orientations of FeO_4-SiO_4 tetrahedrons could not be fully rearranged and relaxed, which only induces slight elastic deformation energy. Then it is difficult to control the synthesis condition and produce the pure orthorhombic (*Pmn2₁*) or monoclinic (*P2₁*) structure, and Li_2FeSiO_4 most likely exists as the FeO_4-SiO_4 tetrahedron orientation disorder structure, in which the orientations of FeO_4-SiO_4 tetrahedrons are randomly arranged upward or downward.

In the orthorhombic structure, all FeO_4-SiO_4 tetrahedrons are upwards, and γ is equal to 90°. If some FeO_4-SiO_4 tetrahedrons turn to downward, γ is slightly different from 90°, such as S_1 (89.9238°), S_2 (89.9968°) and the monoclinic structure (89.9915°). The disorder of FeO_4-SiO_4 tetrahedron orientation also breaks the periodic translation symmetry along [100] and [010] direction of the original lattice. While the lattice scheme is still reserved, as shown in figure 3, and then the structure could diffract X-ray. The $P2_1$ symmetry of the perfect monoclinic structure is broken by the disorder of the tetrahedron orientation, and then there are many weak diffraction peaks beyond the main XRD peaks, which form a uniform noise background.

In Li_2FeSiO_4, the one dimensional chain formed by corner-shared FeO_4-SiO_4 tetrahedrons is the main channel of electron transport. While the orientation disorder of tetrahedron will induce serious electron- and polaron-scattering, i.e., the periodic translation symmetry of Li_2FeSiO_4 is completely destroyed, and it induces large electron- and polaron-scattering. Then the electronic conductivity is largely weakened at the same time. It is not a good news for Li_2FeSiO_4 to be a cathode materials. A way to overcome the problem is to make a complete structure relaxation in the synthesis process, such as with the long-time annealing to produce perfect orthorhombic ($Pmn2_1$) or monoclinic ($P2_1$) structure. Although it is very difficult, it is possible.

CONCLUSION

In the paper, the structure of Li_2FeSiO_4 is studied with the first-principle calculation under the GGA and GGA+U scheme, respectively. The results show that the total energies of the orthorhombic ($Pmn2_1$) and monoclinic ($P2_1$) structure are very close to each other and it is difficult to distinguish them only through power X-ray diffraction. Beyond the two phase, Li_2FeSiO_4 possibly exists as a complicated structure in which the upward and downward the FeO_4-SiO_4 tetrahedrons are not periodically arrangement, which maybe induces large electron-scattering or polaron-scattering, and lower the electronic conductivity.

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