

# Crystal and electronic structures of lithium fluorosulphate based materials for lithium-ion batteries

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By means of *ab initio* calculations, we study the electronic structure of  $\text{LiFeSO}_4\text{F}$ , which has been shown recently [N. Recham *et al.*, *Nature Mater.* **9**, 68 (2010)] to be an excellent material as a cathode for lithium-ion batteries. We have obtained the crystal structure of  $\text{FeSO}_4\text{F}$ , which was not completely determined experimentally, and compare the one of  $\text{LiFeSO}_4\text{F}$  to available experimental values, resolving the issue about the position of the Li ion. Our calculated intercalation voltage (3.69 V) is found to be in excellent agreement with experiments. Finally, we have studied  $\text{LiCoSO}_4\text{F}$  and  $\text{LiNiSO}_4\text{F}$ , which are found to share a similar crystal structure with  $\text{LiFeSO}_4\text{F}$ .

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## I. INTRODUCTION

It is now widely recognized that fossil-fuel supplies will come to an end,<sup>1,2</sup> and therefore new sources of energy are becoming of increasing interest. In order to store this energy, rechargeable lithium batteries<sup>3</sup> are of particular interest since they have a high degree of portability together with a high conversion efficiency. However, progress in this field are intimately linked with material science and solid-state chemistry, in order to synthesize and study new materials, in particular, those to be used as positive electrodes. While olivine ( $\text{LiFePO}_4$ ) is now a widely studied material,<sup>4-9</sup> it presents its own limitations, such as the one-dimensional Li-ion transport.<sup>10-13</sup> A recent step forward (among many others) was made by Ellis *et al.*,<sup>14</sup> who showed that  $\text{Li}_2\text{FePO}_4\text{F}$  and  $\text{Na}_2\text{FePO}_4\text{F}$  can be used as cathode materials, showing very promising results, which were later on confirmed by *ab initio* calculations.<sup>15-17</sup>

Even more recently, Recham *et al.*<sup>18</sup> have explored an other direction by using  $\text{LiFeSO}_4\text{F}$  as the positive electrode for a lithium-ion battery. They have shown that the corresponding device can deliver a slightly higher voltage (3.6 V) than the one made with  $\text{LiFePO}_4$  while it was not necessary to use carbon coating or nanosizing to obtain an efficient battery. Moreover, they have partly characterized the crystal structures of  $\text{LiFeSO}_4\text{F}$  and  $\text{FeSO}_4\text{F}$  by x-ray powder diffraction, obtained the charge/discharge curves, and studied the transport properties of  $\text{LiFeSO}_4\text{F}$ . However, for a complete understanding of these materials, a theoretical description is very important. In this paper, we present our results obtained by means of *ab initio* calculations concerning the ground-

state properties and the crystal structures of  $\text{LiFeSO}_4\text{F}$  and  $\text{FeSO}_4\text{F}$  in order to obtain the corresponding electronic structure, magnetic order, and the intercalation voltage, as well as a study of the related materials<sup>19,20</sup>  $\text{LiCoSO}_4\text{F}$  and  $\text{LiNiSO}_4\text{F}$ .

## II. COMPUTATIONAL DETAILS

To perform our calculations, we have used the Vienna *ab initio* simulation package (VASP),<sup>21,22</sup> which implement the projector augmented wave method.<sup>23</sup> For the exchange-correlation functional, we have used the Perdew, Burke, and Ernzerhof<sup>24</sup> variant of the generalized gradient approximation (GGA), together with a Hubbard-type correction<sup>25,26</sup> to take into account the strongly correlated nature of the *d* electrons of the iron atoms. We have set  $U=4.95$  eV and  $J=0.95$  eV, which are standard values used in the literature.<sup>27</sup> The experimental crystal structures<sup>18</sup> were used as the starting point of our calculations when available, although in all cases, we have performed a full structure relaxation. A cutoff of 800 eV was used for the plane-wave expansion of the wave function, and a  $8 \times 8 \times 6$  grid was used for the integration over the Brillouin zone, which ensures convergence. This setup has been used for all the materials studied here ( $\text{LiFeSO}_4\text{F}$ ,  $\text{FeSO}_4\text{F}$ ,  $\text{LiCoSO}_4\text{F}$ , and  $\text{LiNiSO}_4\text{F}$ ).

In order to calculate the average intercalation voltage  $V_{avg}$  of the battery, we use the following formalism<sup>28</sup> for the chemical reaction:



then

TABLE I. The magnetic order, lattice parameters, volume of the cell, and magnetic order of Fe ions of LiFeSO<sub>4</sub>F and FeSO<sub>4</sub>F. NM stands for nonmagnetic and AFM for antiferromagnetic order of the iron atoms in the cell. The experimental values are from Ref. 18.

Compound	Method	Mag. order	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å) <sup>3</sup>	$\alpha$ (deg)	$\beta$ (deg)	$\gamma$ (deg)
LiFeSO <sub>4</sub> F	GGA	NM	5.14	5.31	7.17	171.61	107.79	107.91	97.78
	GGA	AFM	5.11	5.42	7.08	173.57	105.99	107.67	98.62
	GGA+ $U$	NM	5.07	5.31	7.06	167.30	106.85	107.84	98.51
	GGA+ $U$	AFM	5.13	5.46	7.14	177.01	106.43	107.71	98.07
	Expt.		5.1747(3)	5.4943(3)	7.2224(5)	182.559(16)	106.522(3)	107.210(3)	97.791(3)
FeSO <sub>4</sub> F	GGA	NM	5.06	5.11	6.99	158.81	107.16	108.36	97.77
	GGA	AFM	5.04	5.04	7.25	160.60	109.52	111.02	90.16
	GGA+ $U$	NM	4.93	4.99	7.02	151.18	109.15	109.66	93.15
	GGA+ $U$	AFM	5.05	5.03	7.26	160.43	109.65	111.13	89.89
	Expt.		5.0735(2)	5.0816(3)	7.3363(4)	163.640(12)	110.975(4)	111.189(4)	88.157(3)

$$V_{avg} \approx -\Delta G/F, \quad (2)$$

where  $\Delta G$  is the Gibbs free energy for the intercalation reaction and  $F$  is the Faraday constant. Neglecting the small changes in volume and entropy,<sup>28</sup>  $\Delta G$  is approximated by the internal energy  $\Delta E$ , calculated as the difference in total energies between LiFeSO<sub>4</sub>F and the sum of FeSO<sub>4</sub>F and metallic lithium in a body-centered-cubic (bcc) crystal structure,

$$\Delta E = E_{tot}[\text{LiFeSO}_4\text{F}] - E_{tot}[\text{FeSO}_4\text{F}] - E_{tot}[\text{Li}] \quad (\text{Li-ion cell}), \quad (3)$$

which gives us access to the value of the theoretical average intercalation voltage.

TABLE II. Fractional coordinates of S, Fe, F, O, and Li of LiFeSO<sub>4</sub>F and FeSO<sub>4</sub>F in the  $P\bar{1}$  structure determined from *ab initio* calculations, with the GGA+ $U$  approximation, for an antiferromagnetic order of the Fe magnetic moments.

Compound	Element	Site	$x$	$y$	$z$
LiFeSO <sub>4</sub> F	S	$2i$	0.324	0.629	0.257
	Fe(1)	$1b$	0.000	0.000	0.500
	Fe(2)	$1a$	0.000	0.000	0.000
	F	$2i$	0.150	0.931	0.767
	O(1)	$2i$	0.598	0.760	0.428
	O(2)	$2i$	0.091	0.635	0.341
	O(3)	$2i$	0.331	0.350	0.159
	O(4)	$2i$	0.273	0.754	0.094
	Li	$2i$	0.273	0.638	0.793
FeSO <sub>4</sub> F	S	$2i$	0.350	0.609	0.256
	Fe(1)	$1b$	0.000	0.000	0.500
	Fe(2)	$1a$	0.000	0.000	0.000
	F	$2i$	0.112	0.929	0.762
	O(1)	$2i$	0.642	0.742	0.403
	O(2)	$2i$	0.158	0.662	0.374
	O(3)	$2i$	0.348	0.297	0.167
	O(4)	$2i$	0.253	0.720	0.080

### III. RESULTS AND DISCUSSION

#### A. Crystal structure

Since the experimental measurements did not allow a complete determination of the crystal structure (lattice parameters and positions of the atoms) of LiFeSO<sub>4</sub>F and FeSO<sub>4</sub>F, we have computed them using the method outlined above. First, there was an indetermination concerning the position of the Li atom in the cell of LiFeSO<sub>4</sub>F: in the experiments, it was reported that the Li<sup>+</sup> ions could occupy two different sites, with different local environments, because from the x-ray data it was not possible to distinguish which position is preferable, and therefore both were tentatively assigned with an occupation of 0.5. Therefore, we computed the total energies of LiFeSO<sub>4</sub>F with lithium being at the position Li1 or Li2 (see Table II of the supplementary material of Ref. 18 for the nomenclature) or even a mix of Li1/Li2 positions. We found that the Li2 site is always more favorable than the Li1 for all the methods (see below) that we have used. Also, in order to check that our result is not dependent on the details of the functional, we have performed the same calculations but using the PW91 functional,<sup>29</sup> and we found a similar result.

In Table I, we present our calculated lattice parameters, angles, and volumes, for LiFeSO<sub>4</sub>F and FeSO<sub>4</sub>F crystal cells. Our results are compared with the available experimental data.<sup>18</sup> We have investigated the effect of the magnetic ordering of the iron atoms on the structure by performing calculations for nonmagnetic (NM) as well as spin-polarized electron density. In this last case, the antiferromagnetic (AFM) arrangement of the magnetic moments is found to be lower in energy than the ferromagnetic one, so only the results for an AFM order will be presented. We have also investigated the effect of different exchange-correlation potentials by comparing the results obtained with plain GGA to the results obtained with the GGA+ $U$ . From our results, it appears that the GGA+ $U$  together with an AFM ordering gives results which are the closest to the experimental values. In this case, the values of the lattice parameters and the volume of the cell are slightly underestimated. Our calculated angles are reasonably close to the experimental values

(always less than  $0.5^\circ$  for the GGA+ $U$ /AFM calculation), which means that we reproduce correctly the shape of the triclinic cell, for both  $\text{LiFeSO}_4\text{F}$  and  $\text{FeSO}_4\text{F}$ .

In Table II, we present our calculated positions of all elements within the unit cell of  $\text{LiFeSO}_4\text{F}$  and  $\text{FeSO}_4\text{F}$ , computed with the GGA+ $U$  approximation, and with an AFM ordering of the magnetic moments. In the case of  $\text{LiFeSO}_4\text{F}$ , they were also obtained experimentally<sup>18</sup> (apart for lithium, as mentioned above). On the overall, the agreement is quite good but more can be learned by inspecting the interatomic distances: the Fe-O, Fe-F, and S-O distances are all in good agreement with experiments. For instance, the largest discrepancy is for the Fe1-O1 bond length which is obtained from our calculation to be equal to 2.10 Å while it is 2.19 Å from the x-ray experiment. The other distances are reproduced with a difference of less than 0.06 Å. However, the situation is different for the bonds involving the lithium specie: for example, the Li-O1 bond length is obtained to be 2.60 Å while the same distance is only 2.45 Å from the experiments. On the contrary, the Li-O3 distance is calculated to be 1.94 Å, a value smaller than 2.33 Å. These differences between theory and experiments concerning the precise position of the Li atom certainly means that the Li atom is located in a region with a very shallow potential, and some small difference in the total energies are reflected by some significant difference in the bond lengths, although one should keep in mind that on the overall, we reproduce quite nicely the structure of  $\text{LiFeSO}_4\text{F}$ .

Concerning  $\text{FeSO}_4\text{F}$ , we have obtained the internal position by removing the Li atoms from the structure of  $\text{LiFeSO}_4\text{F}$  and then performed a full relaxation. Since the final lattice parameters obtained in this way come very close to experiments (see Table I), we believe that our procedure has succeeded and we provide in the Table II the internal coordinates of  $\text{FeSO}_4\text{F}$ , which could be compared to some future experiments. In  $\text{FeSO}_4\text{F}$ , the main features of the crystal structure of  $\text{LiFeSO}_4\text{F}$  are preserved: in particular, the  $\text{SO}_4$  tetrahedras are almost unchanged, but the other bonds have accommodated the missing lithium atoms, with Fe(1)-F being now equal to 1.94 Å and Fe(2)-F is now equal to 1.92 Å instead of 2.00 Å in  $\text{LiFeSO}_4\text{F}$ .

## B. Electronic structure and intercalation voltage

Beside the computation of the crystal geometry, we performed the study of the corresponding electronic structure. In Fig. 1, we present our calculated partial density of states (PDOS) of  $\text{LiFeSO}_4\text{F}$  (left column) and  $\text{FeSO}_4\text{F}$  (right column) for all the nonequivalent atoms in the cell. These PDOS are obtained for the fully relaxed geometry, as described above, and using the GGA+ $U$  with an AFM ordering of the Fe magnetic moments. Comparing the PDOS of the Fe atom, it appears that the loss of the Li atom had some important consequences: in particular, the unoccupied states for Fe have been shifted down in energy. Also, the states below the Fermi level are radically changed. This corresponds, as expected, to the change from  $\text{Fe}^{\text{II}}$  (in  $\text{LiFeSO}_4\text{F}$ ) to  $\text{Fe}^{\text{III}}$  (in  $\text{FeSO}_4\text{F}$ ). One particular feature is that the peaks in the PDOS of Fe(1) and Fe(2) in  $\text{LiFeSO}_4\text{F}$ , which are at roughly

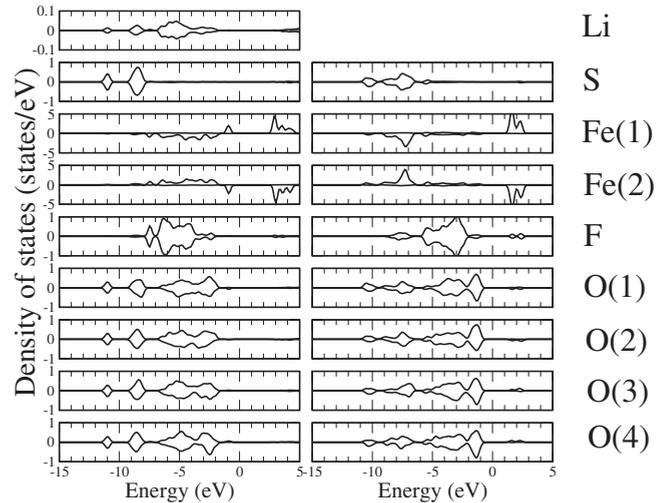


FIG. 1. Partial density of states for all the nonequivalent atoms computed with the GGA+ $U$  approximation for an antiferromagnetic ordering of the Fe atoms. Left:  $\text{LiFeSO}_4\text{F}$ . Right:  $\text{FeSO}_4\text{F}$ . The Fermi level is put at 0 eV.

1 eV below the Fermi level, have totally disappeared in the corresponding PDOS of  $\text{FeSO}_4\text{F}$ . However, the PDOS of all the other elements are also affected by this electron redistribution: the PDOS of S, F, O(1), O(2), O(3), and O(4) are shifted toward higher energies and get closer to the Fermi level in  $\text{FeSO}_4\text{F}$  in comparison with  $\text{LiFeSO}_4\text{F}$ . These modifications of the PDOS are the direct consequence of the charge reorganization of the Fe atom, as well as the shortening of the bonds, which are both coming from the removal of the lithium atoms.

Next, we have calculated the intercalation voltages following the procedure presented above, the results are summarized in Table III. We have tested the effect of spin polarization [SP versus nonspin polarization (NSP)] as well as the effect of the Hubbard (+ $U$ ) correction on the calculated voltage. With the GGA+ $U$  approximation, and for a spin-polarized calculation (with antiferromagnetic order), the experimental value of 3.6 V is reproduced almost perfectly (3.69 V). On the contrary, other methods of calculations either underestimate (GGA-NSP and GGA-SP) or overestimate (GGA+ $U$ -NSP) the calculated intercalation voltage in comparison with experiments. It is quite satisfactory that the

TABLE III. Calculated intercalation voltages of  $\text{LiFeSO}_4\text{F}$  battery. NSP stands for nonspin-polarized and SP for spin-polarized calculations. The experimental value is from Ref. 18.

Composition	Method	Voltage (V)
$\text{LiFeSO}_4\text{F}$	GGA (NSP)	2.74
	GGA (SP)	3.08
	GGA+ $U$ (NSP)	4.27
	GGA+ $U$ (SP)	3.69
	Expt.	3.6

TABLE IV. Calculated lattice parameters, angles, and volume of the cell of LiCoSO<sub>4</sub>F and LiNiSO<sub>4</sub>F. The experimental values are from Ref. 20.

Compound	Method	Mag. order	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å) <sup>3</sup>	$\alpha$ (deg)	$\beta$ (deg)	$\gamma$ (deg)
LiCoSO <sub>4</sub> F	GGA+ $U$	AFM	5.22	5.50	7.32	184.7	107.1	108.4	97.6
	Expt.		5.1721(7)	5.4219(7)	7.1842(8)	177.80(4)	106.859(6)	107.788(6)	97.986(5)
LiNiSO <sub>4</sub> F	GGA+ $U$	AFM	5.17	5.42	7.26	179.2	107.1	108.2	97.8
	Expt.		5.1430(6)	5.3232(7)	7.1404(7)	172.56(4)	106.802(9)	107.512(8)	98.395(6)

method which is taking into account correctly the effect of the strong correlation on the Fe site, is indeed the one which is able to obtain the most precisely the value of the intercalation voltage.

### C. LiCoSO<sub>4</sub>F and LiNiSO<sub>4</sub>F

Following the initial discovery of LiFeSO<sub>4</sub>F as being an excellent material to be used as a cathode, further studies<sup>19,20</sup> were conducted on the compounds LiM<sub>2</sub>SO<sub>4</sub>F and Li(Fe<sub>1-x</sub>M<sub>x</sub>)SO<sub>4</sub>F ( $M$ =Mn, Co, or Ni). It was found that LiCoSO<sub>4</sub>F and LiNiSO<sub>4</sub>F belong the space group  $P\bar{1}$  (such as LiFeSO<sub>4</sub>F) while the structure of LiMnSO<sub>4</sub>F seems to be widely different, with a monoclinic lattice containing 8 f.u./cell. While the structure was determined fully for LiCoSO<sub>4</sub>F, it was difficult to obtain by means of x-ray diffraction the atomic coordinates of LiNiSO<sub>4</sub>F. Therefore, starting from the geometry of LiFeSO<sub>4</sub>F, we have fully optimized the structure of LiCoSO<sub>4</sub>F and LiNiSO<sub>4</sub>F. However, we did not attempt to perform calculations on Li(Fe<sub>1-x</sub>M<sub>x</sub>)SO<sub>4</sub>F since this would require the use of a supercell to model the alloying, leading to very time demanding calculations. Our calculated lattice parameters for LiCoSO<sub>4</sub>F and LiNiSO<sub>4</sub>F are reported in Table IV. Like for LiFeSO<sub>4</sub>F, the agreement is quite good, and this confirms the experimental results that LiFeSO<sub>4</sub>F, LiCoSO<sub>4</sub>F, and LiNiSO<sub>4</sub>F have very similar crystal structures. However, contrary to LiFeSO<sub>4</sub>F, for which our calculations produced lattice parameters that are slightly underestimating the experimental values, the calculated lat-

tice parameters and volumes are slightly overestimated for LiCoSO<sub>4</sub>F and LiNiSO<sub>4</sub>F. This is due mainly to the overestimation of the  $c$  lattice parameters [7.32 Å versus 7.1842(8) Å for LiCoSO<sub>4</sub>F and 7.26 Å versus 7.1404(7) Å for LiNiSO<sub>4</sub>F]. In Table V, we report the atomic coordinates of the atoms in LiNiSO<sub>4</sub>F, to be compared with some future experiments. The bond lengths involving lithium are found to be 2.01 Å for Li-O<sub>3</sub> and 2.55 Å for Li-O<sub>1</sub>, which compares well with the values obtained for LiFeSO<sub>4</sub>F (1.94 Å and 2.60 Å), although slightly different. While some bonds are preserved, for instance, Ni1-F and Ni2-F are still equal to 1.99 Å, some others are modified, such as Ni1-O<sub>2</sub>, which is now equal to 2.10 Å. All these changes are reflected in the dimensions of the cell, and therefore the replacement of Fe by an other transition metal (Co or Ni) has some nontrivial consequences, although, as mentioned above, the overall geometry is preserved.

## IV. CONCLUSION

We have studied the crystal and electronic structures of LiFeSO<sub>4</sub>F and FeSO<sub>4</sub>F by means of *ab initio* calculations. In particular, we have obtained a complete structure determination of FeSO<sub>4</sub>F, which was not provided so far by experiments. We have calculated the corresponding average intercalation voltage, and obtained a good agreement with the experimental value, provided that the correct methodology is used. Finally, we have studied the compounds LiCoSO<sub>4</sub>F and LiNiSO<sub>4</sub>F, and discussed their similarities and differences with LiFeSO<sub>4</sub>F. We expect that our work will initiate further experiments on the LiM<sub>2</sub>SO<sub>4</sub>F family of compounds, in particular, for fully resolving their structures, and ultimately will help with the design of improved cathodes for Li-ion batteries.

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TABLE V. Fractional coordinates of S, Ni, F, O, and Li of LiNiSO<sub>4</sub>F in the  $P\bar{1}$  structure determined from *ab initio* calculations, with the GGA+ $U$  approximation, for an antiferromagnetic order of the Ni magnetic moments.

Compound	Element	Site	$x$	$y$	$z$
LiNiSO <sub>4</sub> F	S	$2i$	0.327	0.642	0.255
	Ni(1)	$1b$	0.000	0.000	0.500
	Ni(2)	$1a$	0.000	0.000	0.000
	F	$2i$	0.123	0.921	0.760
	O(1)	$2i$	0.607	0.762	0.420
	O(2)	$2i$	0.101	0.654	0.344
	O(3)	$2i$	0.320	0.357	0.150
	O(4)	$2i$	0.278	0.776	0.099
	Li	$2i$	0.272	0.642	0.788

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