

Supplementary materials

Table SI-1: Cation – Anion distances in the Fe and S first-coordination sphere for the *tavorite* and *triplite* corner delithiated phase FeSO₄F.

	Fe – O	Fe – F	S – O
<i>Tavorite</i>	2.01 – 2.02 Å	1.96 Å	1.48 – 1.49 Å
<i>Triplite</i> corner	2.00 – 2.06 Å	1.93 – 1.98 Å	1.48 – 1.49 Å

Table SI-2: Unit cell parameters (in Å) and angles (in °) computed for the LiFeSO₄F *tavorite* and *triplite* corner structures with various U_{eff} values (in eV) and different magnetic orders (AFM = antiferromagnetic and FM = ferromagnetic) and compared to previous works and experiments. All calculations were performed using the same DFT+U formalism and the GGA-PBE functional for exchange and correlation energy.

Phase	U _{eff} (eV)	Magn.	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	
LiFeSO ₄ F Tavorite	This work	3	FM	5.227	5.5314	7.3914	106.30	107.22	98.33
		3	AFM	5.220	5.5397	7.3799	106.29	107.09	98.41
		4	FM	5.218	5.5474	7.3880	106.28	107.10	98.43
		4	AFM	5.218	5.5469	7.3848	106.23	107.11	98.45
		5	FM	5.219	5.5488	7.3910	106.27	107.13	98.43
		5	AFM	5.228	5.5431	7.3927	106.43	107.24	97.99
Ref. 24		4	AFM	5.241	5.579	7.397	107.12	107.21	97.56
Ref. 25		4	AFM	5.13	5.46	7.14	106.43	107.21	98.79
Ref. 26		3	AFM	5.134	5.3087	7.1717	107.824	107.692	98.15
DRX			5.1747(3)	5.4943(3)	7.2224(3)	106.522(3)	107.210(3)	97.791(3)	
300K Neutron			5.18003(7)	5.49165(6)	7.2289(9)	106.4864(9)	107.186(9)	97.9098(9)	
2K Neutron			5.205(1)	5.539(1)	7.274(1)	106.39(1)	107.21(1)	98.46(1)	
LiFeSO ₄ F Triplite corner	This work	3	FM	13.3086	6.3745	10.0603	90.00	120.42	90.00
		3	AFM	13.2236	6.4413	9.7022	90.00	119.20	90.00
		4	FM	13.2211	6.4593	9.9280	90.00	119.91	90.00
		4	AFM	13.2216	6.4437	9.7012	90.00	119.16	90.00
		5	FM	13.2399	6.4599	9.9436	90.00	120.01	90.00
		5	AFM	13.2048	6.4333	9.6914	90.00	119.18	90.00
DRX			13.0225	6.3949	9.8329	90.00	119.6800	90.00	

Figure SI-1 Comparison of the experimental X-Ray diffraction pattern ($\lambda_{K\alpha}(\text{Co}) = 1.79 \text{ \AA}$) of the LiFeSO_4F (bottom) and the delithiated FeSO_4F (top) *tavorite* structures with the simulated X-Ray diffraction patterns deduced from the DFT optimization. DFT+U structural relaxations being known to slightly over-estimate the lattice parameters of condensed phases, the lattice parameters of the DFT-optimized structures have been changed to the experimental ones for an easier comparison.

