Proton and ammonia intercalation into layered iron chalcogenides

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Supplementary Information

Methods

Synthetic conditions

For a typical preparation of ammonia-intercalated FeCh via the *in situ* formation route (from **1** to **2** in Fig. 1), about 10 mmol Fe powder, 12 mmol of chalcogen sources (thiourea, $(NH_4)_2S$, and selenourea), and 25-50 mmol of free guanidine base were mixed with 10 mL de-ionized (DI) water or deuterated water (D₂O) in a Teflon-lined stainless steel autoclave at 125 °C for 3-4 days. In order to assure complete intercalation, additional 3 mL of saturated ammonia water (~30%) can be added to the autoclave, but this is not necessary as pure products can be prepared without additional ammonia water. Afterwards, the content in the autoclave was washed and centrifuged several times until the supernatant was clear. The remaining product was collected, vacuumed dried, and stored in a nitrogen-filled glove box.

To prepare the guanidine base, stoichiometric amount of Na metal and guanidinium hydrochloride (1:1 molar ratio) were separately dissolved in anhydrous ethanol in a nitrogen filled glove box. The two solutions were mixed and filtered to yield a colourless ethanol solution of guanidine. Solid guanidine was obtained by evaporating ethanol under vacuum, and the yield for the product was about

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80%. Since the guanidine precursor is difficult to make, we have tested reactions using KOH to replace guanidine. For the sulfide, replacing guanidine with KOH afforded the same product. However, for the selenide, the product is sensitive to the KOH concentration, as too much KOH afforded $K_{1-x}Fe_{2-y}Se_2$ impurities. This impurity can be suppressed by using D₂O and reducing the KOH concentration. However, reduced KOH concentration often led to incomplete digestion of Fe. Therefore, KOH route is sufficient for the sulfide, whereas the guanidine route is optimal for the selenide.

Characterizations

Powder X-ray diffraction (XRD) data were collected using a Bruker D8 X-ray diffractometer with Cu K α radiation, $\lambda = 1.5418$ Å. Neutron powder diffraction data were collected on the BT-1 high-resolution neutron powder diffraction (NPD) with the Cu(311) monochromator ($\lambda = 1.540$ Å) at the NIST Center for Neutron Research. Electron diffraction patterns were obtained using a JEOL 2100 LaB₆ transmission electron microscope (TEM) at an acceleration voltage of 200 keV. Magnetic susceptibility measurements were performed using a Quantum Design Magnetic Properties Measurement System (MPMS). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using Mettler Toledo TGA/DSC 2 under high-purity Ar. TGA/DSC samples were placed in alumina crucibles covered with alumina lids and heated from room temperature to 600 °C at the rate of 10 °C/min.

Computational methods

All density functional theory (DFT) [1, 2] calculations were performed by using the Vienna Ab-initio Simulation Package (VASP)[3–6] software package with potentials using the projector augmented wave (PAW)[7] method. The exchange and correlation functional were treated by the generalized gradient approximation (PBE-GGA).[8] The cut-off energy, 450 eV, was applied to the valance electronic wave functions expanded in a plane-wave basis set for all chalcogenides.

References

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Figure S1: Powder X-ray diffraction of ammonia-intercalated FeCh.

Table S1: Rietveld refinement of neutron powder diffraction (NPD) data collected at 5 K using a Cu(311) monochromator ($\lambda = 1.540$ Å) for a partially deuterated ammonia-intercalated FeS compound. The atomic displacement of N, H and D atoms was set to equal and the tetrahedral angles α_1 and α_2 represent the S-Fe-S angles in and out of the basal plane, respectively.

Formula = $NH_{1.59(7)}D_{1.93(4)}Fe_{1.94(2)}S_2$, $I4/mmm$, $a = 3.6852(2)$ Å, $c = 15.0467(9)$ Å, $R_{wp} = 4.37\%$						
Atom	Wyckoff	\boldsymbol{x}	y	\boldsymbol{z}	Occ.	U_{iso} (Å ²)
	site					
Fe	4d	0	1/2	1/4	0.97(1)	0.0040(5)
S	4e	0	0	0.3382(5)	1	0.0051(11)
Ν	2a	0	0	0	1	0.0672(15)
D1	2b	0	0	1/2	0.482(16)	$=U_N$
D2/H1	8i	0.271	0	0	0.066(6)/0.111(10)	$=U_N$
$\mathrm{D3/H2}$	16m	0.124	0.124	0.0505	0.149(4)/0.144(7)	$=U_N$
α_1 (°)	α_2 (°)	Fe-Fe (Å)	Fe-S (Å)	D1-S (Å)	D3(H2)-S (Å)	
109.96(14)	108.49(28)	2.6058(2)	2.2271(4)	2.4353(7)	2.5766(5)	



Figure S2: Thermogravimetric analysis /differential scanning calorimetry (TGA/DSC) at a heating rate of 10 $^{\circ}$ C/min under an Ar flow for ammoniaintercalated a) FeS and b) FeSe, respectively. The solid and dotted lines represent TGA and DSC curves, respectively. For both samples, the weight loss above 400 $^{\circ}$ C is negligible, and the changes thereafter are mainly caused to buoyancy.



Figure S3: Curie-Weiss fit of magnetic susceptibility of ammonia-intercalated FeS as a function of temperature. The fit temperature region is 40-300 K. The molar susceptibility is calculated based on per mole iron.



Figure S4: Band structure and density of state (DOS) of ammonia-intercalated (a) FeS and (b) FeSe.

Figure S5: Magnetic susceptibility of FeSe deintercalated using $NH_{3.5}Fe_2Se_2$.

Figure S6: Powder X-ray diffraction of Li/ammonia Co-intercalated FeS.

Figure S7: Magnetic susceptibility of Li/ammonia Co-intercalated FeS.

Figure S8: Rietveld refinement of powder X-ray diffraction data of LiOH intercalated (a) FeS and (b) FeSe prepared by topochemical conversion of $NH_{3.5}Fe_2Ch_2$.