Supporting Information for:

## $A(NH_3)_xFePS_3$ (A = Li, K): intercalated Fe thiophosphate via the liquid ammonia method

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## Details about the mechanism of de-intercalation process

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The de-intercalation process in this work was derived from a method reported in literatures for de-intercalating the  $LiMoS_2/KMoS_2$  to obtain the metastable phase 1T  $MoS_2$ .<sup>1,2</sup> Based on the literatures, the corresponding reactions in this work could be deduced as below :

$$Li(NH_3)_x FePS_3 + y H_2O \rightarrow Li_{1-y}(H_2O)_z FePS_3 + x NH_3 + y LiOH + y/2 H_2(g)$$
(1)

$$Li_{1-y}(H_2O)_z FePS_3 + (1-y)/2 I_2 \rightarrow FePS_3 + (1-y) LiI + z H_2O$$
 (2)

In first reaction, a hydration process is supposed to occur, which may further increase the interlayer distance and reduce the interaction between sulfur and intercalated guests. This can promote the removal of lithium into the acetonitrile solution in the second reaction.

In second reaction, the intercalated sample likely undergoes a redox process where the lithium in between the [FePS<sub>3</sub>] layers reacted with iodine to form LiI in acetonitrile solution.

Initially we carried out the second step at room temperature (~20  $^{\circ}$  C) but found that the products showed the low-quality data of PXRD. Then the temperature was increased to 60  $^{\circ}$  C and the PXRD pattern was improved.

The PXRD pattern in Fig. S9 indicates the successful de-intercalation for  $Li(NH_3)_xFePS_3$ . But related experiments are still required in future, to confirm the mechanism speculated here.

S2

Crystal system				Monoclinic		
Space group				<i>C2/m</i> (No. 12)		
Radiation type				Cu Kα		
Wavelength (Å)				1.5406		
2θ range (°)				5 - 80		
a (Å)				5.9455(1)		
<i>b</i> (Å)				10.2900(2)		
c (Å)				6.7199(1)		
$\beta$ (°)				107.1682(4)		
$V(Å^3)$				392.80(2)		
Z			4			
Atom	Sita			_	Occur	$II (\hat{\lambda}^2)$
Atom	Sile	X	У	Z	Occu.	$U_{\rm iso}({\rm A}^2)$
Fe	4g	0	1/3	0	1	0.013(2)
Р	4i	0.0394(7)	0	0.1690(7)	1	0.023(2)
<b>S</b> 1	4i	0.7417(3)	0	0.3647	1	0.016(2)
S2	8j	0.2404(3)	0.1517(3)	0.2401(3)	1	0.016(2)

Table S1. The structural parameters of FePS<sub>3</sub> from Rietveld refinement at 298(2) K.

**Table S2.** Comparison of layer distances d (Å) for the alkali metal intercalated samples for FePS<sub>3</sub> (from this work) and FeSe (from literatures<sup>3-6</sup>) systems from the liquid ammonia method.

Atom	Layer distance d (Å)			
1 tom	FePS <sub>3</sub> system	FeSe system <sup>1-4</sup>		
Matrix	~6.42	~5.52		
Li-poor	~9.58			
Li-rich	~9.54	~8.3		
Na-poor				
Na-rich		~8.7		
K-poor	~9.52	~7.8		
K-rich	~9.40	~7.4		

Atom	Occu.	U <sub>iso</sub> (Å <sup>2</sup> )
Fe	1	0.018(2)
Р	1	0.017(2)
<b>S</b> 1	1	0.015(1)
S2	1	0.015(1)
N1	0.326(3)	0.027(1)
N2	0.295(3)	0.027(1)

**Table S3.** The refined occupation and equivalent isotropic displacement parameters for Li(NH<sub>3</sub>)<sub>x</sub>FePS<sub>3</sub> sample.

**Table S4.** Magnetic parameters for FePS<sub>3</sub>, K(NH<sub>3</sub>)<sub>x</sub>FePS<sub>3</sub>, Li(NH<sub>3</sub>)<sub>x</sub>FePS<sub>3</sub> and the deintercalated FePS<sub>3</sub> from Curie-Weiss fitting.

	C (emu mol <sup>-1</sup> Oe <sup>-1</sup> K)	$\mu_{\rm eff}(\mu_{\rm B}/{\rm Fe})$	$\theta(\mathbf{K})$	$T_{N}(K)$
FePS <sub>3</sub>	3.189	5.05	-19.9	127
K(NH <sub>3</sub> ) <sub>x</sub> FePS <sub>3</sub>	1.236	3.14	-129.8	-
Li(NH <sub>3</sub> ) <sub>x</sub> FePS <sub>3</sub>	0.856	2.62	-37.4	-
FePS <sub>3</sub> from de-intercalation	2.657	4.61	-50.7	129



Figure S1. PXRD pattern for polycrystalline FePS<sub>3</sub> with the structural refinement.



**Figure S2.** PXRD patterns for four intercalates with highly preferred orientation. The pattern for FePS<sub>3</sub> matrix is also plotted for comparison. Inset shows the enlarged (001) diffraction peaks for intercalates and FePS<sub>3</sub>. It is clearly seen that there was residual FePS<sub>3</sub> in  $K_{0.5}(NH_3)_x$ FePS<sub>3</sub> and  $Li_{0.5}(NH_3)_x$ FePS<sub>3</sub>, while in  $K(NH_3)_x$ FePS<sub>3</sub> and  $Li(NH_3)_x$ FePS<sub>3</sub> the FePS<sub>3</sub> matrix totally disappeared.



Figure S3. The SEM photograph for (a) FePS<sub>3</sub> matrix and (b) Li(NH<sub>3</sub>)<sub>x</sub>FePS<sub>3</sub> sample.



Figure S4. The EDS results for Li(NH<sub>3</sub>)<sub>x</sub>FePS<sub>3</sub>sample.



Figure S5. The EDS results for K(NH<sub>3</sub>)<sub>x</sub>FePS<sub>3</sub> sample.



Figure S6. XPS of Fe 2p electrons for FePS<sub>3</sub> matrix (left side) and Li(NH<sub>3</sub>)<sub>x</sub>FePS<sub>3</sub> (right side).



Figure S7. PXRD patterns for  $K(NH_3)_xMnPS_3$ ,  $K(NH_3)_xCoPS_3$ ,  $K(NH_3)_xNiPS_3$  and the three MPS<sub>3</sub> hosts.



Figure S8. Diffuse reflectance spectrum for FePS<sub>3</sub> (up) and Li(NH<sub>3</sub>)<sub>x</sub>FePS<sub>3</sub> (down)



**Figure S9.** Temperature dependence of the inverse susceptibility  $1/\chi$  for (a) FePS<sub>3</sub>, (b)  $K(NH_3)_xFePS_3$  and (c)  $Li(NH_3)_xFePS_3$  with the Curie-Weiss fitting (red lines). The isothermal magnetization curves at 10 K for (d)  $K(NH_3)_xFePS_3$  and (e)  $Li(NH_3)_xFePS_3$ . Deviation from linearity is clearly observed with the obvious hysteresis and there is no sign of saturation up to 5

T, consistently point to the spin-glass behavior at low temperature. The enlarged part near zero point is shown in (f), highlighting the magnetic hysteresis.



Figure S10. The PXRD pattern for FePS<sub>3</sub> obtained by de-intercalating Li(NH<sub>3</sub>)<sub>x</sub>FePS<sub>3</sub> sample.



**Figure S11.** (a) Temperature dependence of the magnetic susceptibility and (b) the inverse susceptibility for FePS<sub>3</sub> obtained by de-intercalating  $Li(NH_3)_x$ FePS<sub>3</sub>sample.



**Figure S12.** Temperature dependence of the magnetic susceptibility for (a)  $K(NH_3)_xFePS_3$  and (b)  $Li(NH_3)_xFePS_3$  under 20 Oe.

## Reference

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