Elucidation of Barocaloric Effect in Spin Crossover Compounds with Inelastic Scattering Methods

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Spin Crossover (SCO)

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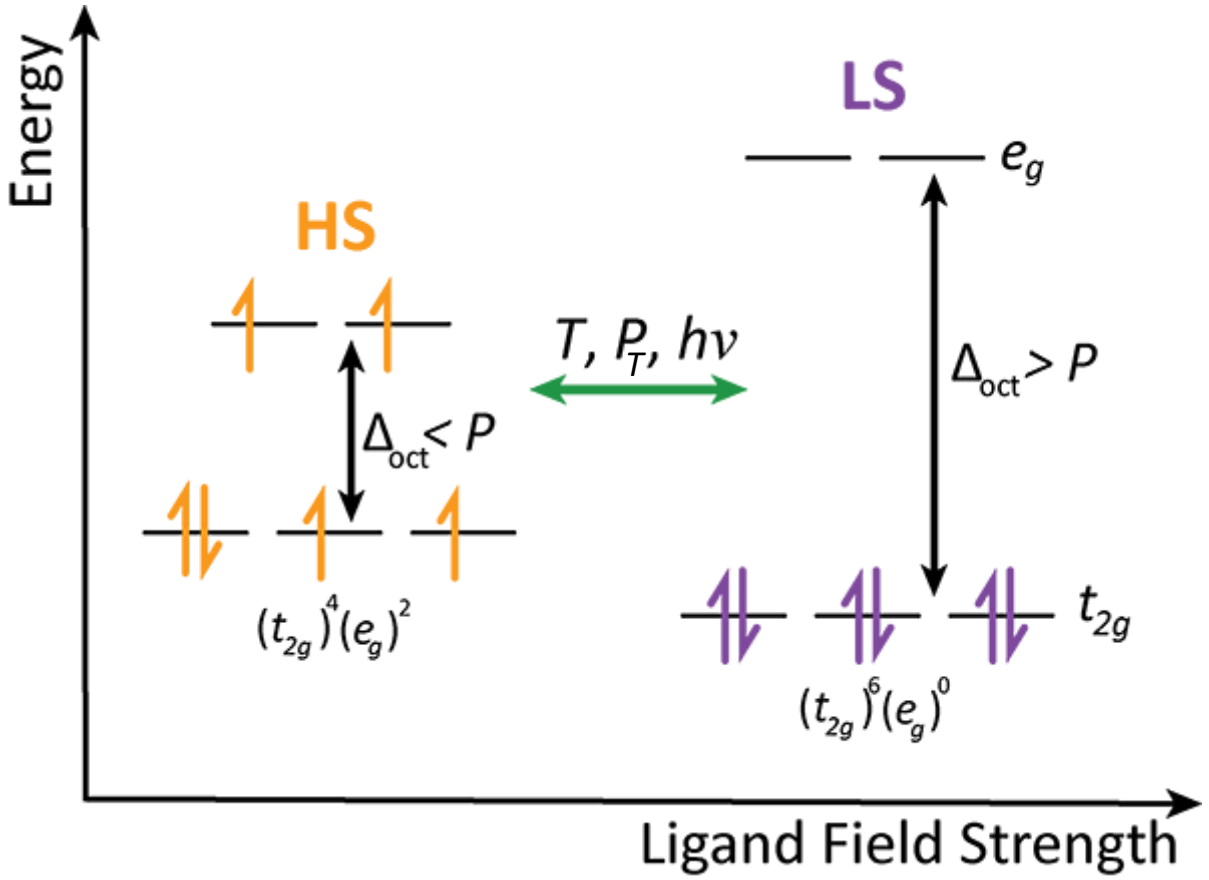
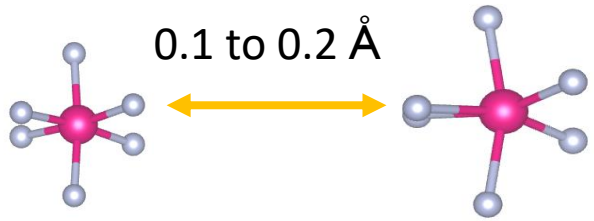
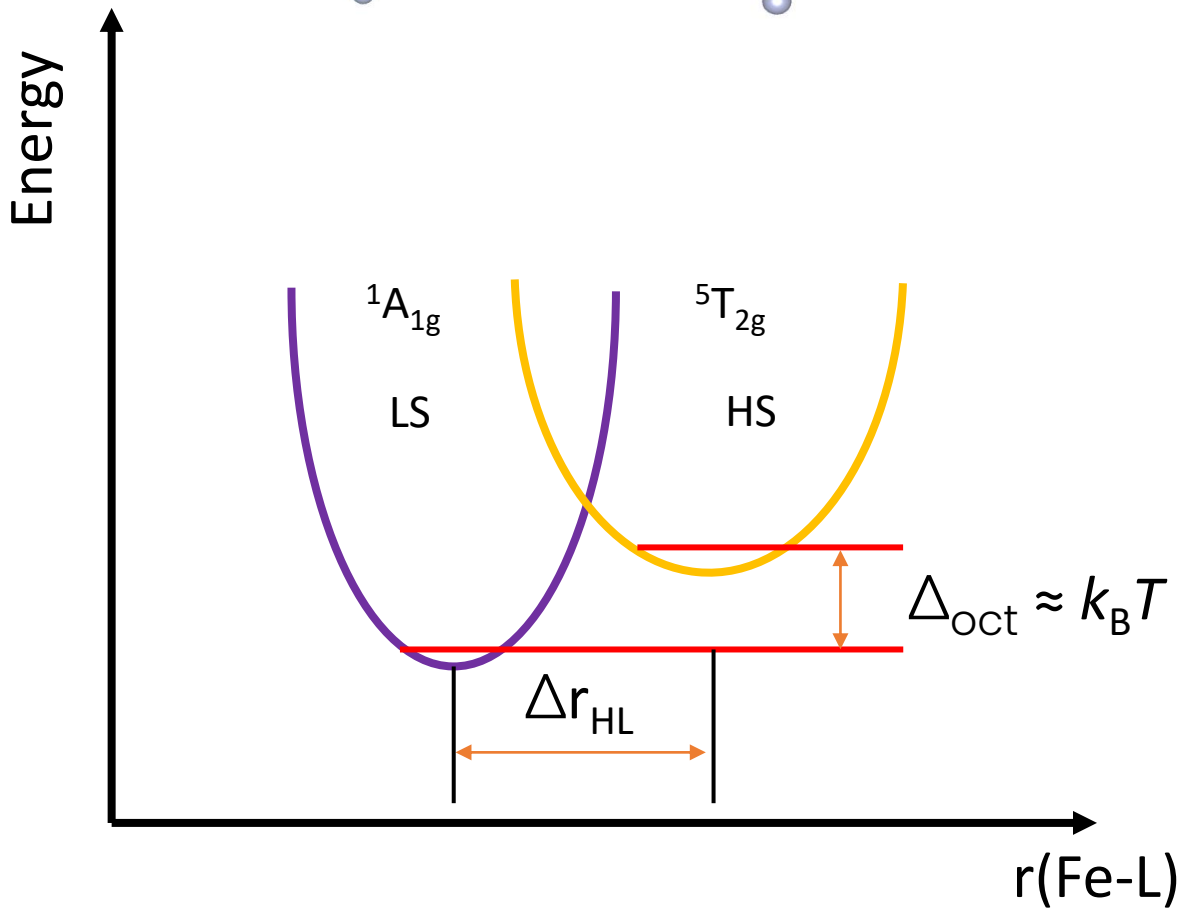
$3d^4$ $3d^5$ $3d^6$ $3d^7$

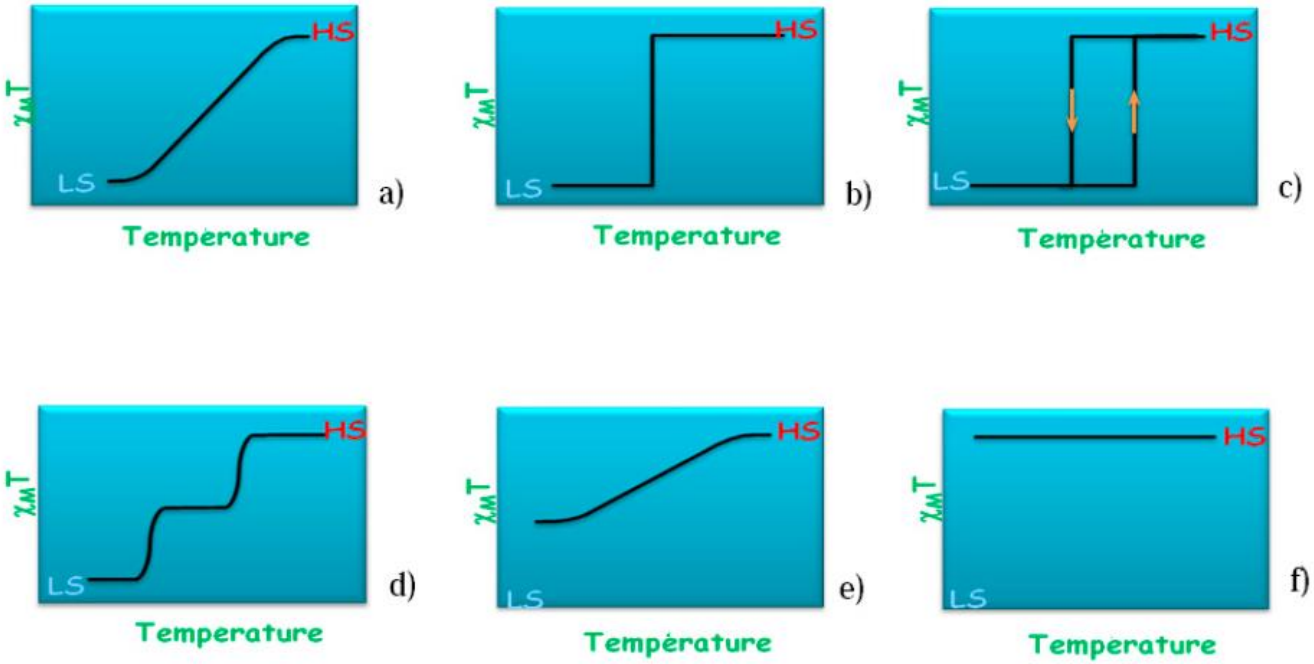
Cr^{2+}, Mn^{3+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{3+}, Co^{2+}, Ni^{3+}



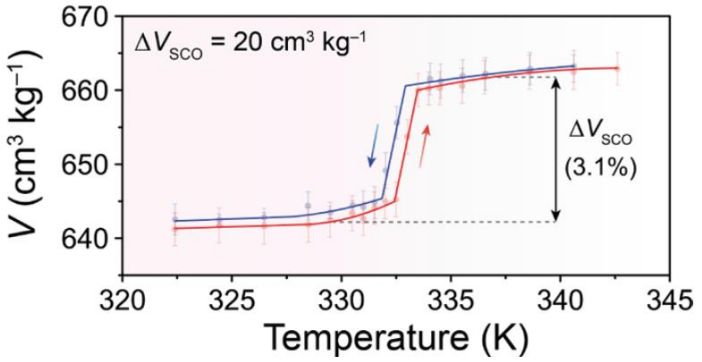


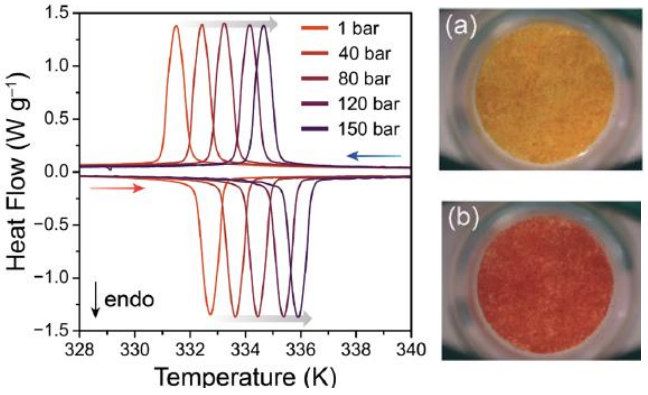


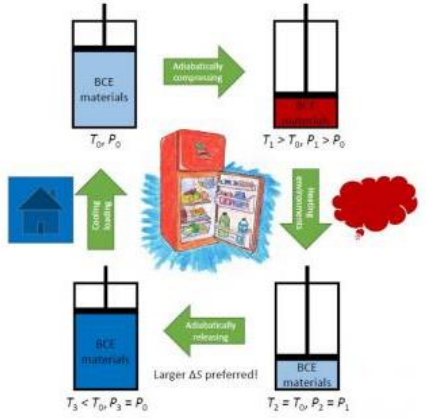
Properties



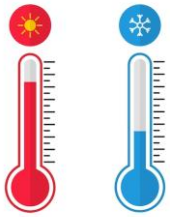
- Large thermal effect
- Color change
- Large Volume Change
- …







Available external stimuli



temperature

light

pressure

Others…

Jinyoung Seo et al. *J. Am. Chem. Soc.* **144**, 6493 (2022).
Samir F. Matar et al. *Int. J. Mol. Sci*. **16**, 4007 (2015).

$Fe(PM\text{-}BiA)_2(NCS)_2$

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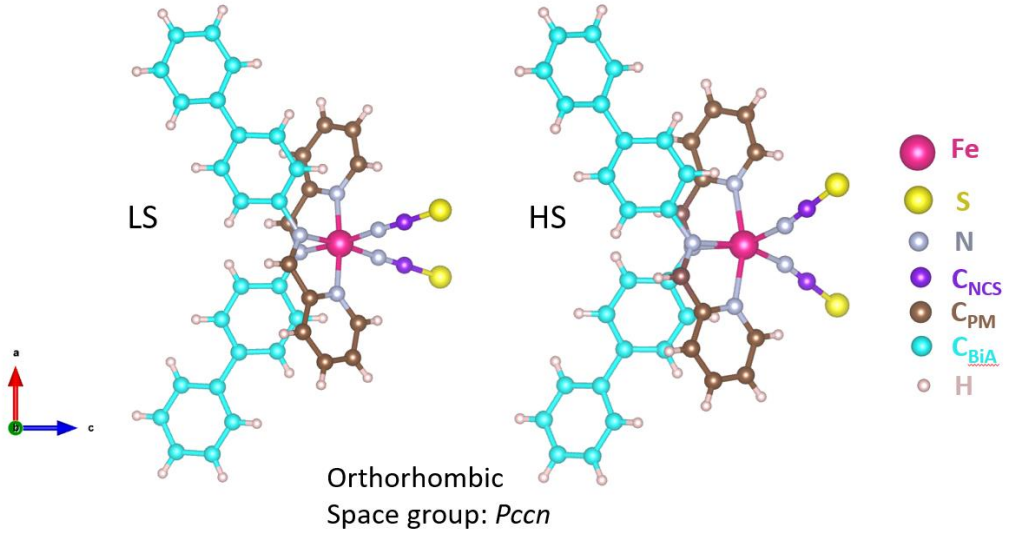
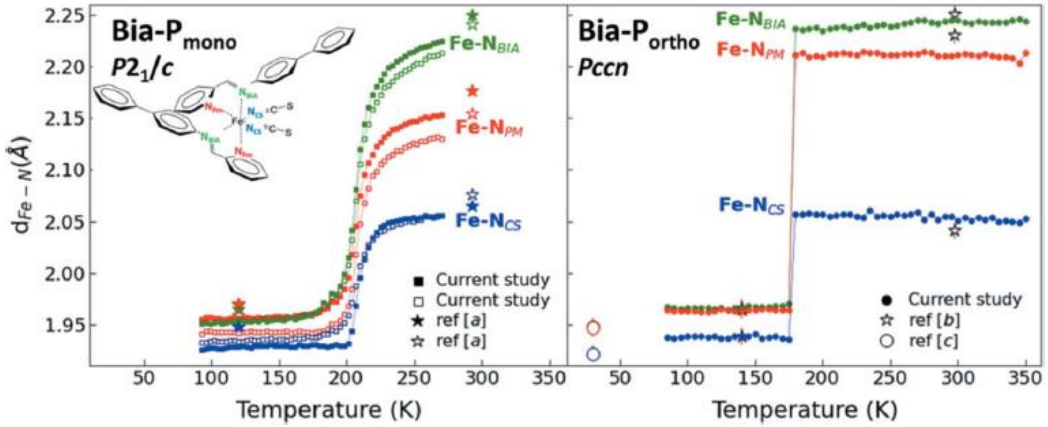
Compound	T_{SCO} (K)	$\lvert\Delta S\rvert$ (J/K mol)	$\lvert\Delta S\rvert$ (J/K kg)	$\partial T_{SCO}/\partial p$ (K/GPa)	Maximum ΔT_{ad}	Pressure required (GPa)
$[Fe(PM\text{-}BiA)_2(NCS)_2]$	170	58	84	66	8.4	0.12
$[Fe(phen)_2(NCS)_2]$	180	49	92	220	8.3	0.04
$\{Fe[H_2B(pz)_2]_2(bipy)\}$	160	48	95	188	7.6	0.04
$\{Fe(pmd)_2[Cu(CN)_2]_2\}$	140	36	80.5	380 (avg.)	5.6	0.013
$[Fe(pmea)(NCS)_2]$	184	60 (calc.)	44	146	4	0.03

Monoclinic
$P2_1/c$
$T_{1/2}$ = 208 K
T_{hys} =1 K

Orthorhombic
Pccn
$T_{1/2}$ = 177 K
T_{hys} = 5 K



Orthorhombic
Space group: *Pccn*



H. Shahed et al. *Acta Crystallogr. Sec. B*. **B79**, 1-14 (2023).
Karl G. Sandeman. *APL Mater.* **4**, 111102 (2016).

Entropy

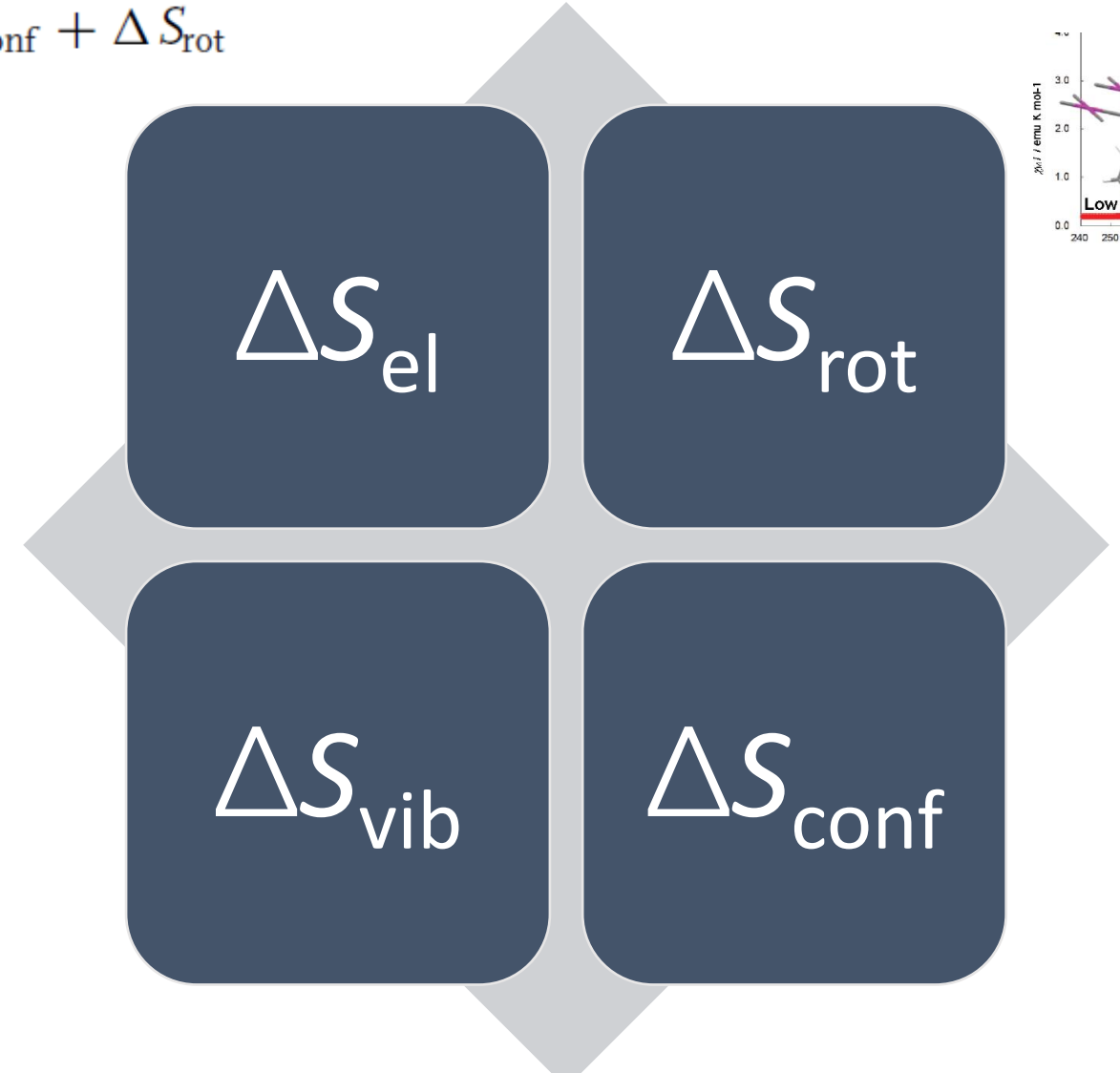
$$\Delta S = \Delta S_{el} + \Delta S_{vib} + \Delta S_{conf} + \Delta S_{rot}$$

$$\Delta S_{el} = R ln\left(\frac{2S_{HS}+1}{2S_{LS}+1}\right)$$

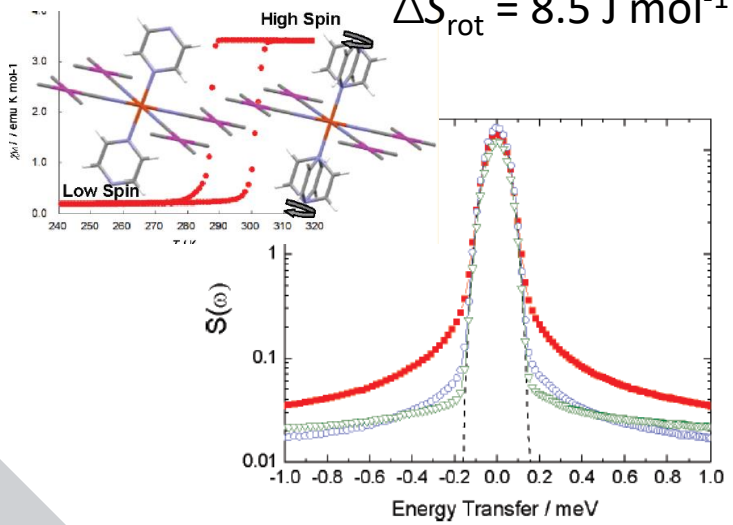
= 13.5 J mol^{-1} K^{-1}

$$\Delta S_{vib} = R\sum_{\lambda} ln\left[\frac{v_{\lambda}^{LS}}{v_{\lambda}^{HS}}\right] =$$

$30\% \sim 70\% \Delta S_{tot}$



ΔS_{rot} = 8.5 J mol^{-1} K^{-1}



Fe(pz)[Pt(CN)$_4$]

J. Alberto Rodríguez-Velamazán et al. *J.Am.Chem.Soc.* **134**, 5083 (2012).

Methodologies

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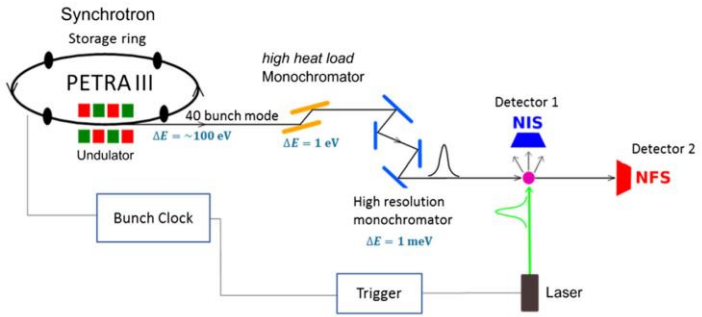
Required sample

Partial Density of States (P01@Petra III)

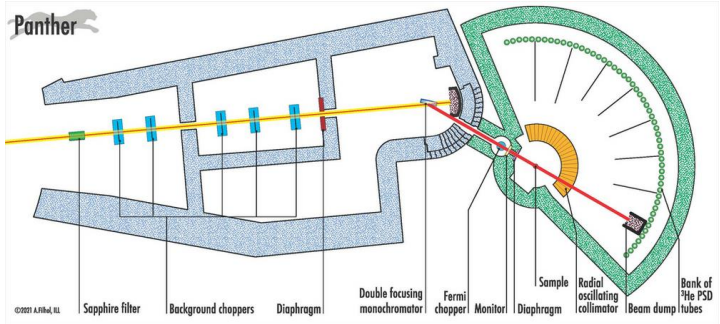


- Determine the partial density of states of Fe^{2+} by using NIS.
- Study the pressure effect on the partial DOS of Fe^{2+}.

^{57}Fe SCO sample

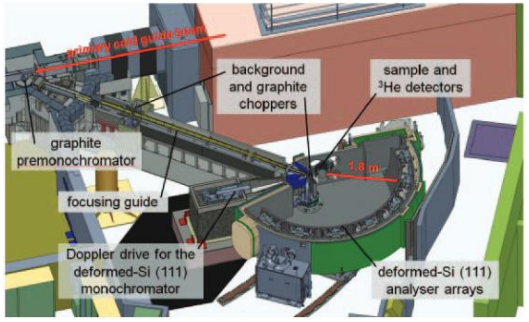
Density of states (Panther@ ILL) (scheduled)

- Explore the lattice dynamics beyond the entire Brillouin zone.
- Deuterated sample will be used to avoid the incoherent contribution from H.



Protonated and deuterated complexes

Local Dynamics (EMU and Pelican@ANSTO)



- Study the local dynamics at different timescale;
- Determine the geometry of the local motions;
- Extract the entropy contribution from local motions.

Protonated complexes

Synthesis

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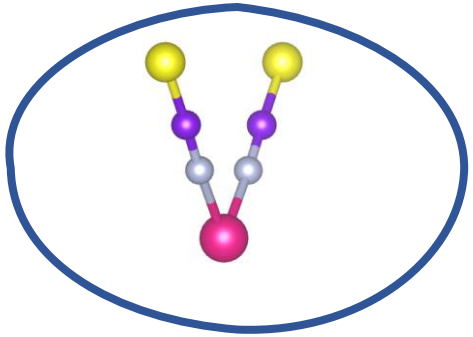
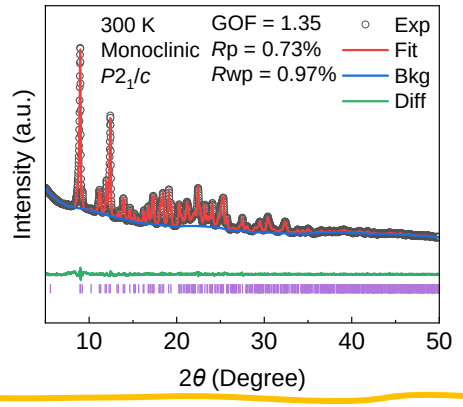
$Fe(NCS)_2$

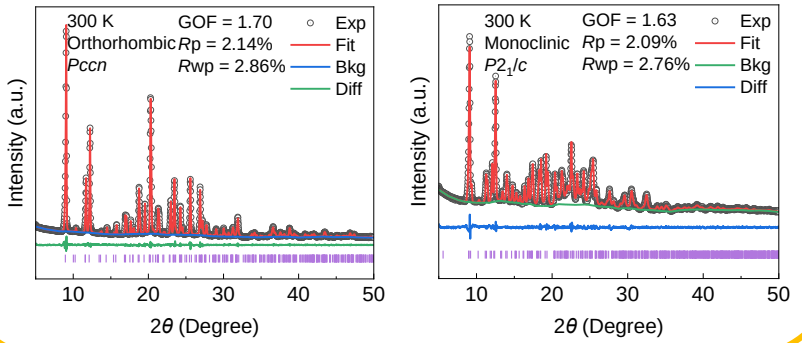


$FeSO_4 + 2KNCS = Fe(NCS)_2 + K_2SO_4$

Substitute the $FeSO_4$ by $^{57}FeSO_4$

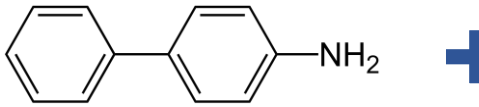


Protonated sample

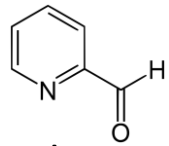


Deuterated Sample

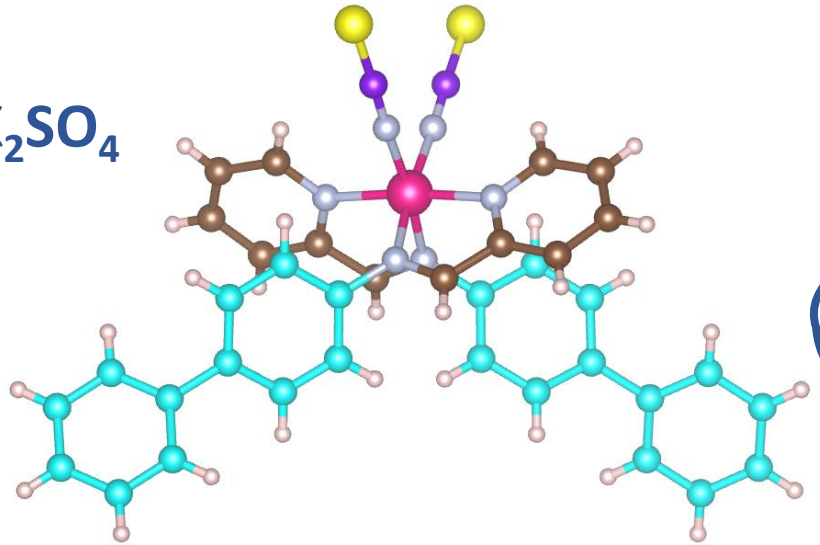
- ❑ More than 95% deuteration level has been achieved on 4-Aminobiphenyl.
- ❑ The deuteration for Pyridin-2-aldehyde is still ongoing



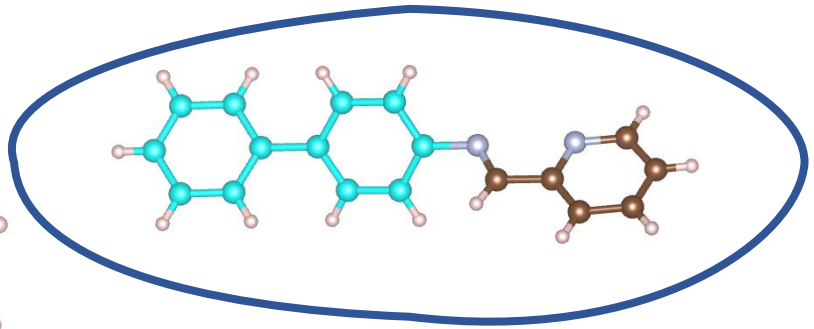
4-Aminobiphenyl



Pyridin-2-aldehyde



$Fe(PM\text{-}BiA)_2(NCS)_2$



PM-BiA ligand

Lattice dynamics

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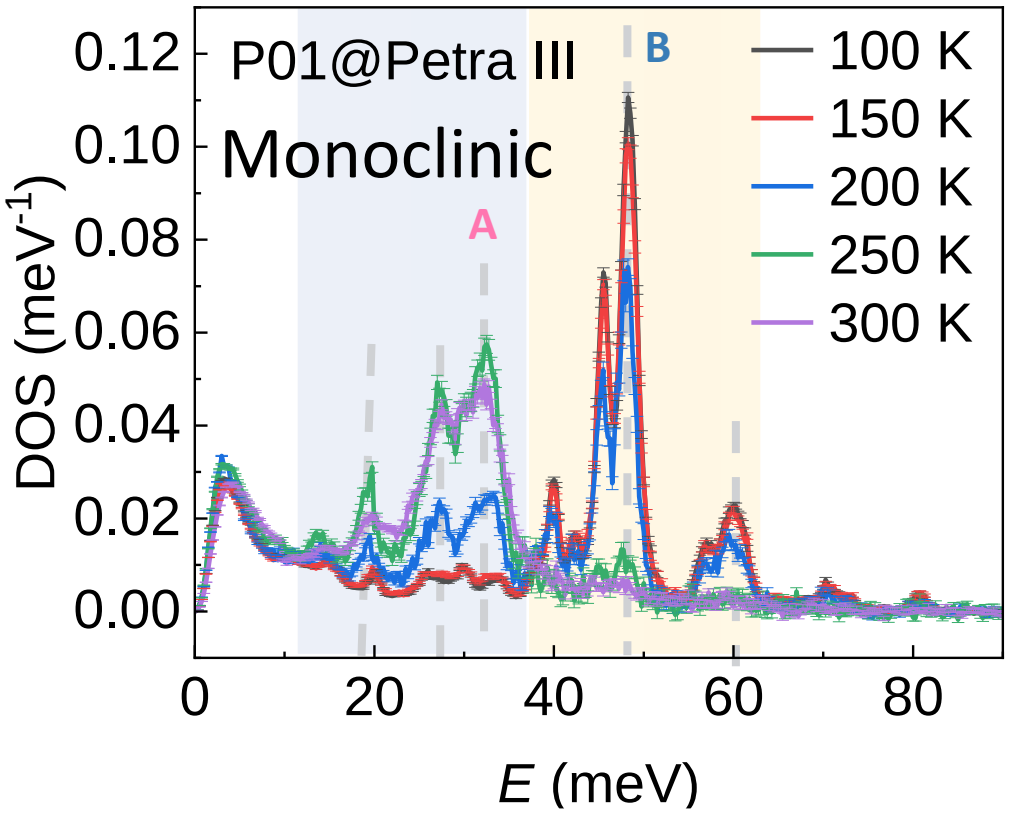
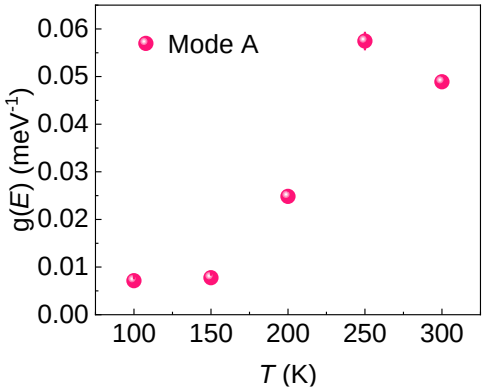
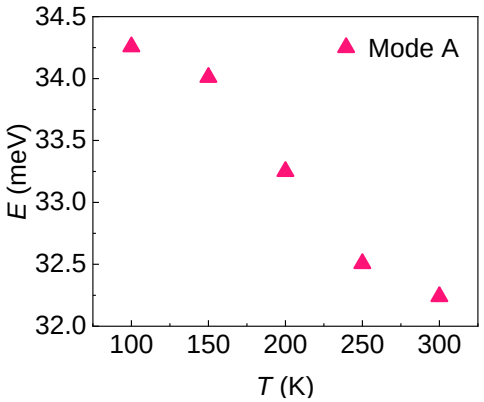
- Temperature induced Fe-contributed phonon modes correspond to the gradual SCO transition of the monoclinic sample.

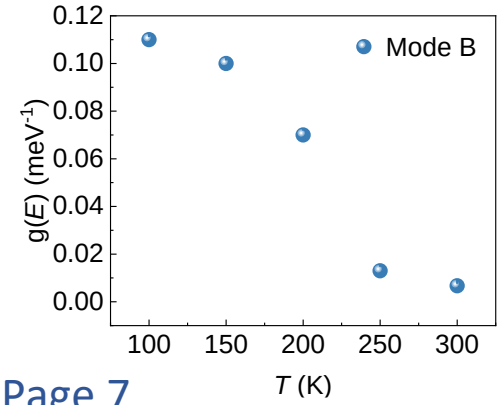
$$S_1 - S_2 = 3N_A k_B \int_0^\infty \left(g_1(E) - g_2(E)\right) \ln(E)\, dE.$$

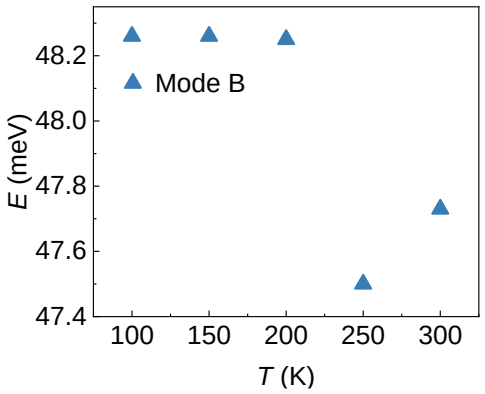
$\Delta S_{T_0 \to T}$ = 12.72 J mol^{-1} K^{-1} **30.2% of ΔS_{tot}**



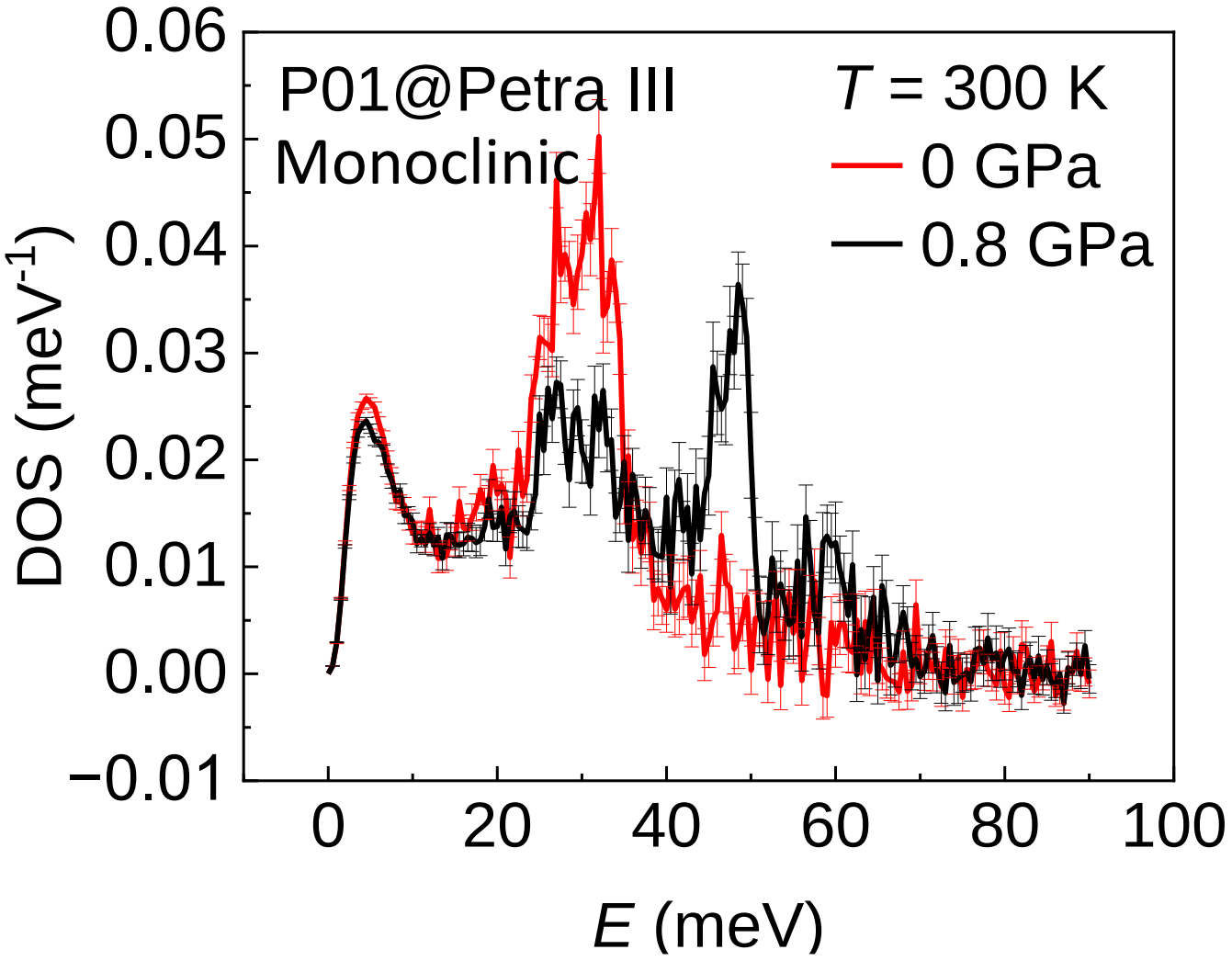








PDOS vs P

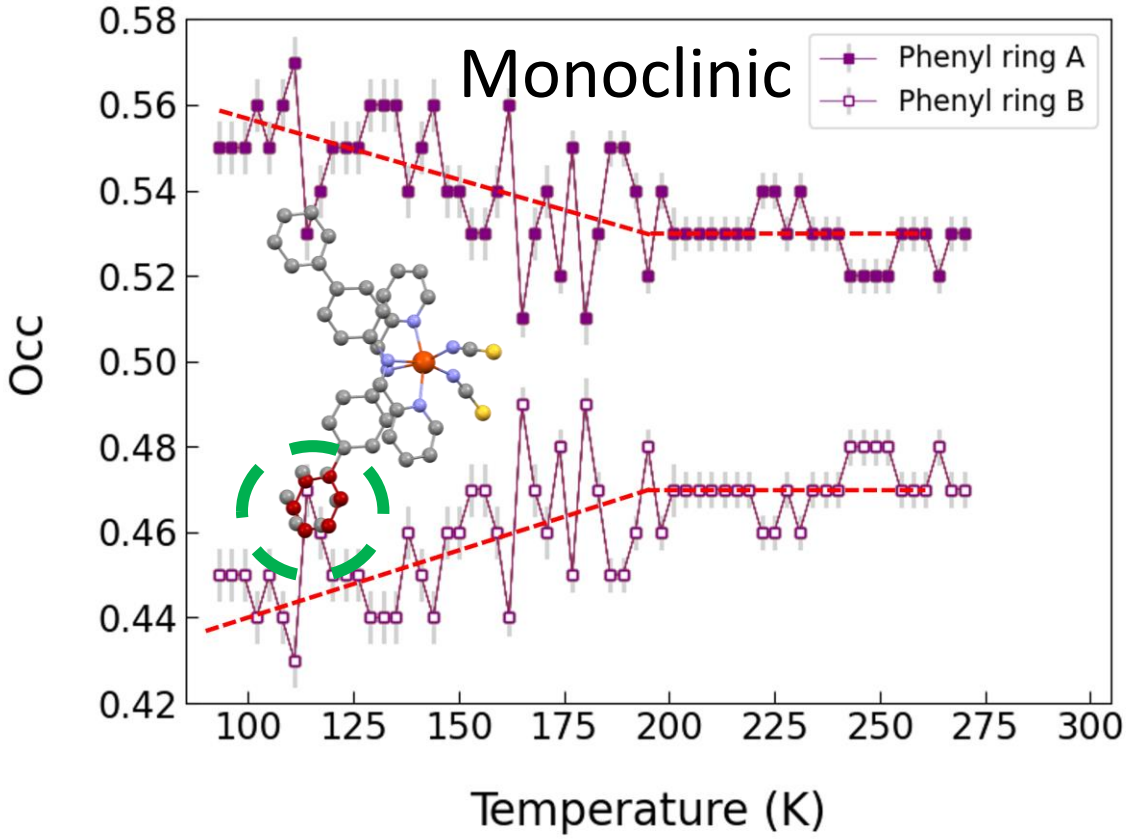


- The pressure triggered SCO transition can be observed under 0.8 GPa at 300 K.
- 0.8 GPa is not sufficient to completely suppress the HS at 300 K

$\Delta S_{P_0 \rightarrow P}$ = 8.48 J mol^{-1} K^{-1}

Local dynamics

- The temperature dependent occupation of the phenyl ring indicates the dynamical disorder in the system.



Quasi-elastic neutron scattering is the solution.

$$S(Q,\omega) = S_{coh}(Q,\omega) + S_{inc}(Q,\omega)$$

- Geometry of motion
- Time scale of diffusion

$S(Q,\omega)=S_{inc}(Q,\omega)\otimes R(Q,\omega)$ ➡ Longest time scale

Elastic incoherent scattering factor ➡ $EISF = \frac{I_{elastic}}{I_{elastic}+I_{inelastic}}$

Location	Instrument	Energy resolution (μeV)	Energy range (meV)	Q-range (Å^{-1})
ANSTO	EMU	1.1	−0.028 to 0.02	0.4–1.8
ISIS	IRIS	17.5	-0.55 to 0.57	0.6-1.6
ANSTO	Pelican	65	-19.99 to 2.59	0.2-1.8

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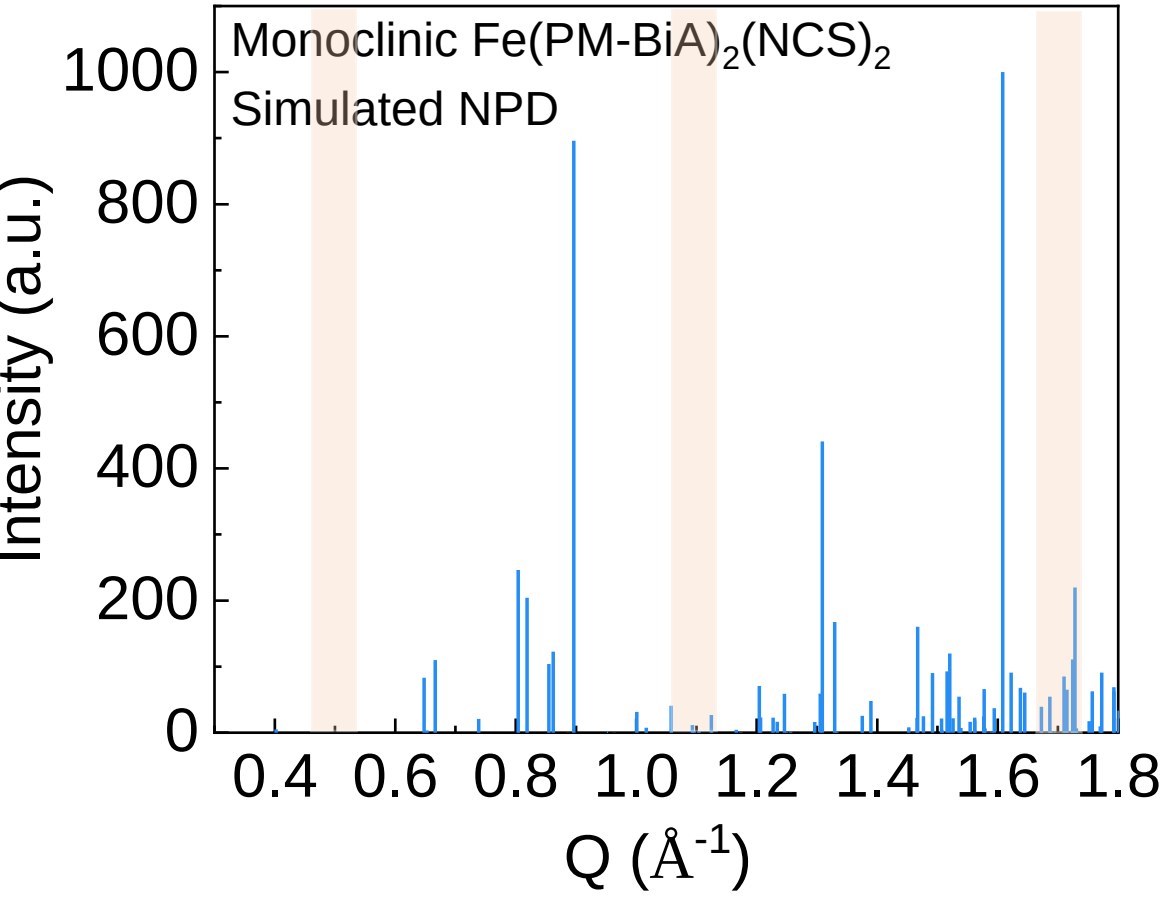
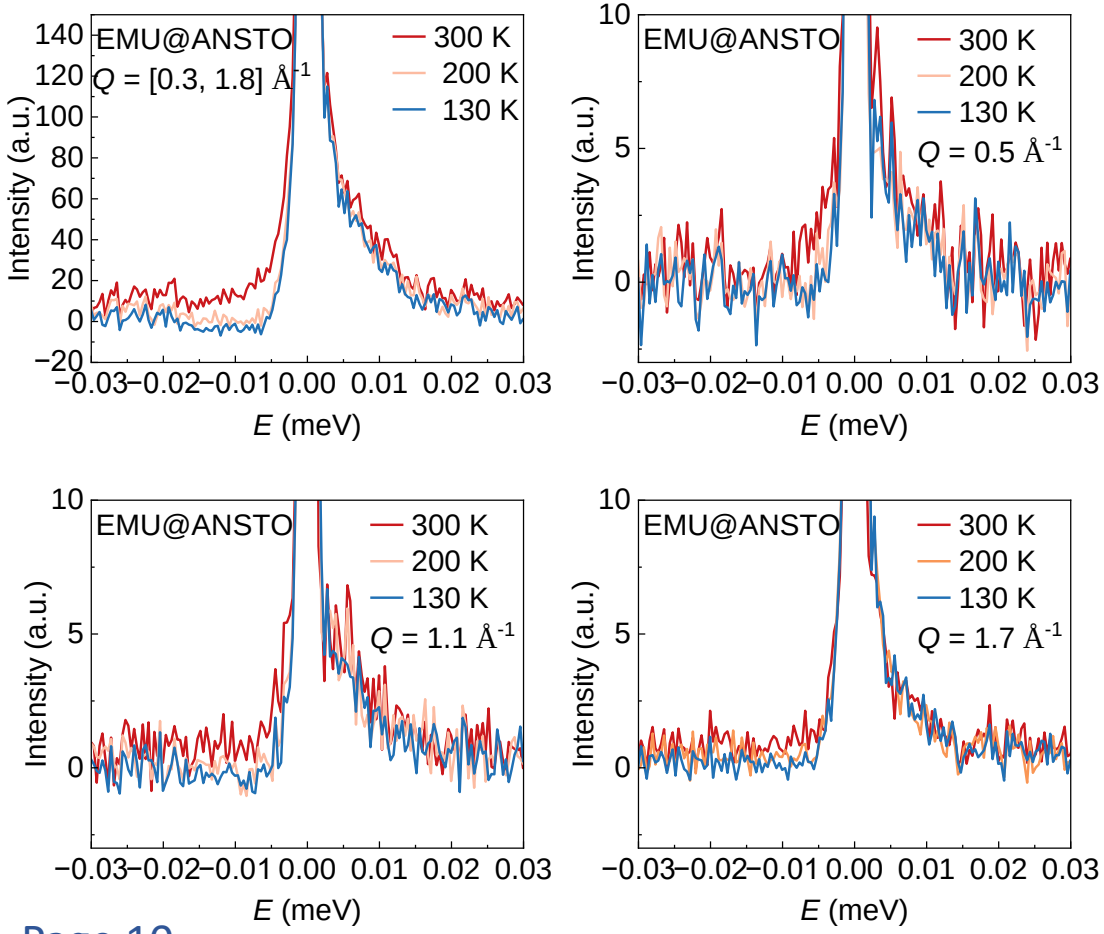
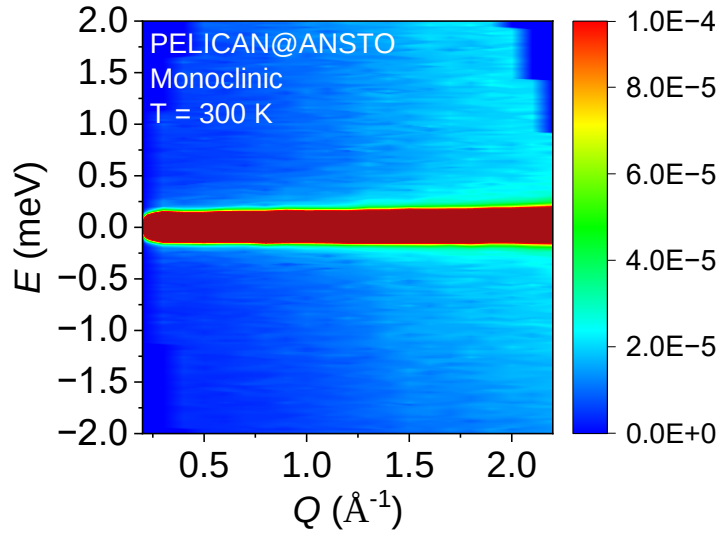
Local dynamics

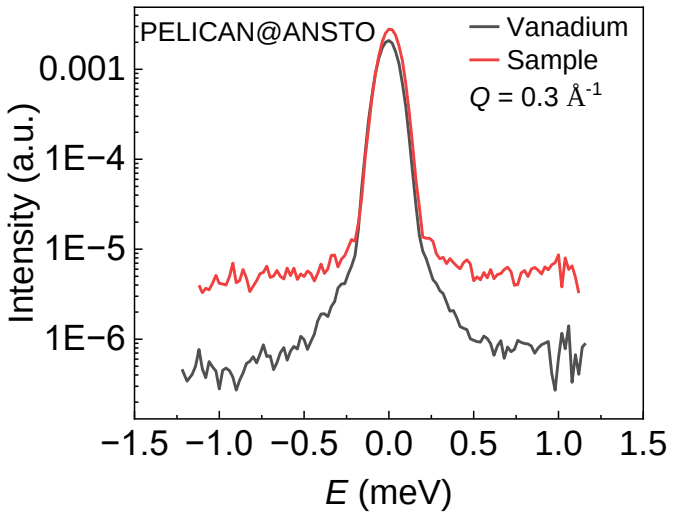
- The neutron backscattering indicates that there is no local mode at nanosecond scale.

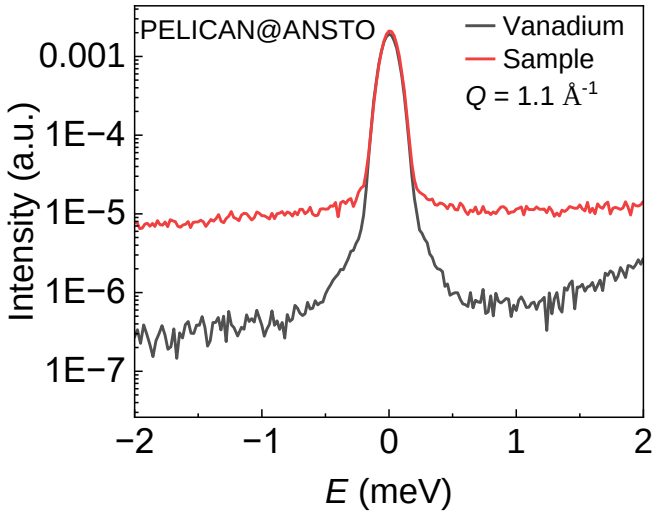


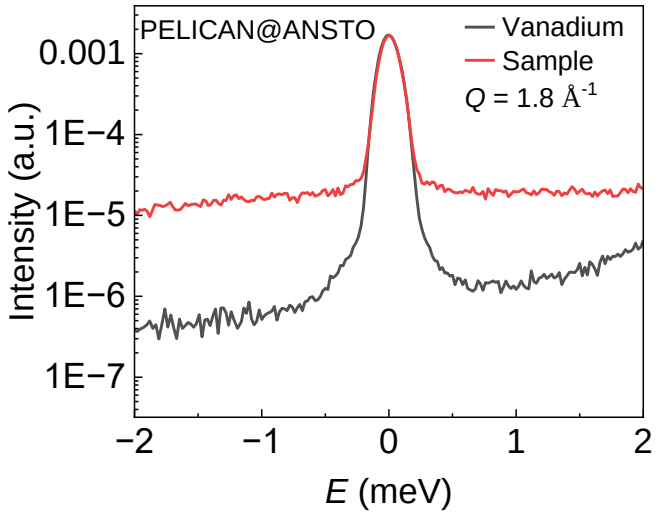


Local dynamics









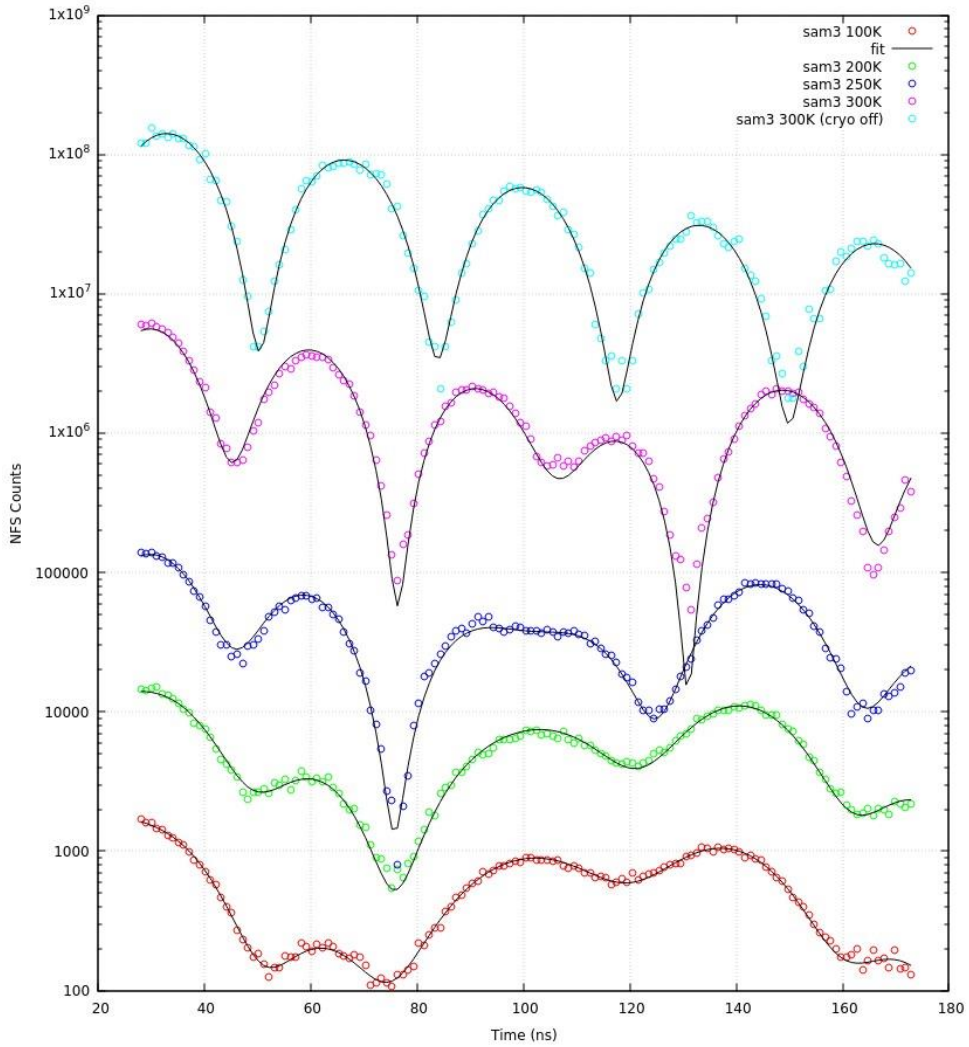
- An apparent Q dependence feature of the $S(Q, E)$ indicates the localized modes in this system.
- The wide QENS signal indicates an extremely fast local mode at picosecond scale.

Summary

1. Protonated sample and ^{57}Fe SCO compounds are ready for further experiments.
2. The Fe-contributed entropy change (12.72 J mol^{-1} K^{-1}) is extracted from the DOS, which is 30.2% of the total entropy change (42 J mol^{-1} K^{-1}).
3. The INS experiment at Pelican confirmed the existence of fast localized modes in the monoclinic compound.

Outlook

- Deuteration.
- INS at Panther.
- Detailed local motion.
- Polarized neutron.



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KIT
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Thanks for your attention!