Experimental report

11/05/2025

Proposal: 7-02-220 **Council:** 4/2023

Title: lattice dynamics study of Fe2+ coordination octahedron in spin crossover complex Fe(PM-BiA)2(NCS)2

Research area: Materials

This proposal is a new proposal

Main proposer: Ji QI

Experimental team: Ji QI
Joerg VOIGT

Local contacts: Stephane ROLS

Samples: FeC38N6S2H28

Instrument	Requested days	Allocated days	From	To
PANTHER	5	2	17/06/2024	19/06/2024

Abstract:

Barocaloric effect is characterized as a thermal response (adiabatic temperature and isothermal entropy changes) in a material resulting from compression. The orthorhombic Fe(PM-BiA)2(NCS)2 is an typical spin crossover (SCO) compound that exhibits giant entropy change (¿S = 58 J mol-1 K-1) accompanied by an abrupt SCO transition around 170 K with 5 K hysteresis, which is an ideal candidate to serve as barocaloric materials. Further, the vibrational entropy change dominated by phonon excitations of Fe-N coordination octahedrons is estimated as the largest contribution to the overall entropy change. In order to investigate the dynamic features across the SCO transition and explore its barocaloric nature, we propose to perform inelastic neutron scattering (INS) experiments on the orthorhombic Fe(PM-BiA)2(NCS)2 at Panther in ILL to obtain the neutron weighted phonon density of states (PDOS) mainly below 80 meV (around 640 cm-1) in a temperature window from 100 K to 300 K. The underlying mechanism of barocaloric effect in the SCO compounds is expected to be elucidated through our work.

Experimental report of the proposal 89391

The inelastic neutron scattering experiment was performed to study lattice and local dynamics on spin crossover (SCO) compounds $Fe(PM\text{-}BiA)_2(NCS)_2$ through the thermal neutron time-of-flight spectrometer Panther at ILL. The (002) and (004) reflections of the highly oriented pyrolytic graphite (PG) monochromator were configured to set the incident E_i at 15 meV and 90 meV for accessing different dynamic ranges, respectively. Around 0.15 g of monoclinic and orthorhombic polymorphs of $Fe(PM\text{-}BiA)_2(NCS)_2$ were used for the experiment. To reduce the multiple scattering, the powder samples were filled in an aluminium holder with a thickness of 0.1 mm. A cryostat was used to achieve a low temperature environment from 100 to 300 K. The resulting $S(Q, E)$ data were reduced and analyzed in the software Mantid.

The generalized phonon density of states of both polymorphs were directly accessed from 100 to 300 K with an interval of 50 K, as shown in Fig.1 (a) and (b). According to the DFT calculation, the change of phonon excitations above 60 meV is correlated with the change of the vibration of Aminobiphenyl. Meanwhile, as displayed in Fig.1 (c), an apparent diffuse scattering at low energy was realized in both polymorphs, indicating the existence of dynamic disorder. Fig. 1(d) and (e) depict the fitting of a constant-Q cut of $S(Q, E)$ and the elastic incoherent structure factor (EISF) analysis, the outer phenyl ring of the Aminobiphenyl was found to show a dynamic reorientation with a two-site model (Fig. 1(f)), which also contributes around 10% of the total entropy change.

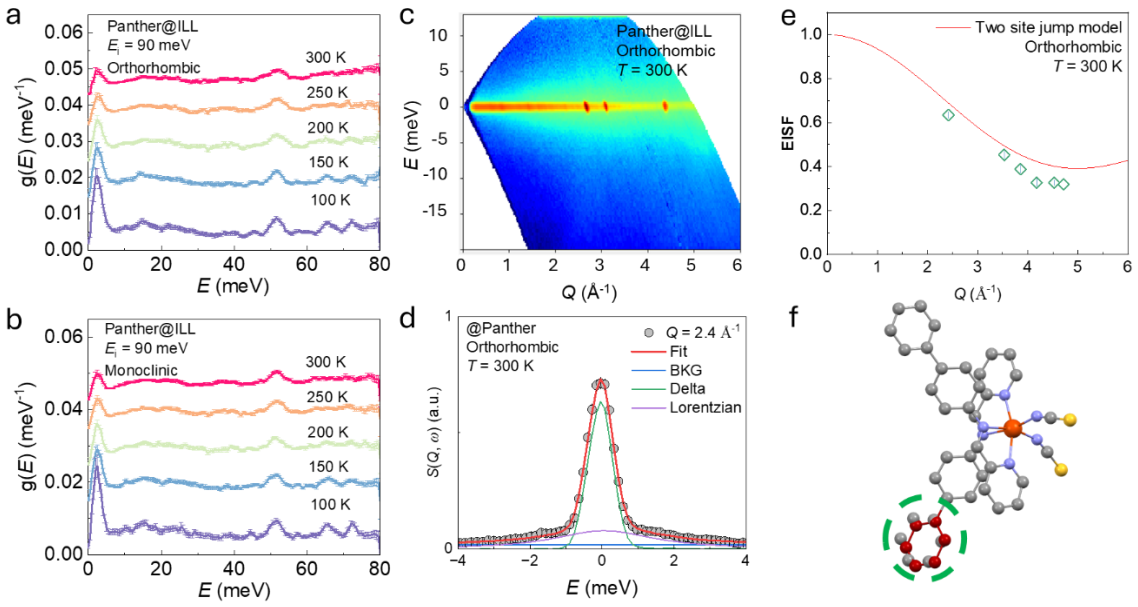


Figure 1 (a) and (b) Phonon density of states of orthorhombic and monoclinic $Fe(PM\text{-}BiA)_2(NCS)_2$ across the spin transition. (c) The $S(Q, E)$ of orthorhombic polymorph with E_i = 15 meV at 300 K. (d) The fitting of constant-Q cut of the $S(Q, E)$ in (c) at Q = 2.4 Å^{-1}. (e) The EISF analysis of orthorhombic polymorph at room temperature. (f) The schematic diagram of the dynamic disorder of the phenyl group.