Poster

Correlation between structure and dynamic properties in SCO complex Fe(PM-BiA)$_2$(NCS)$_2$

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The barocaloric effect (BCE) is characterized as a thermal response (variation of temperature or entropy) in solid-state materials induced by external hydrostatic pressure and cooling technologies based on the BCE have emerged as a promising alternative to conventional vapor-compression cooling [1]. Recently, spin crossover (SCO) transitions, where the low spin (LS) and high spin (HS) states can be switched by hydrostatic pressure, were proposed as a potential mechanism to generate outstanding BCE [2]. The considerable overall entropy change across the SCO transition is primarily attributed to the significant change in lattice vibration, which is directly linked to the dynamic features [3].

In this study, we correlate the structural changes of a classic SCO complex in the vicinity of a spin transition as functions of temperature and pressure with the dynamic properties and aim at a better understanding of the role of cooperativity on the transition. The two polymorphs of Fe(PM-BiA)$_2$(NCS)$_2$ (with PM = N-2'- pyridylmethylene and BiA = 4-aminobiphenyl) are ideal in this respect, as the orthorhombic polymorph (*Pccn*) features a high cooperativity indicated by an abrupt transition, while the gradual transition in the monoclinic polymorph ($P2_1/c$) hints towards a low cooperativity [4]. From the structural studies, we determined which intermolecular interactions (hydrogen bridges, π-π interactions, van der Waals interactions) play a key role at the spin transition in both polymorphs.

We investigate the changes in dynamic features at the temperature- and pressure-induced spin transition using different spectroscopic methods on a wide range of energy and time scales in combination with ongoing ab-initio modelling. Raman and IR spectroscopy give access to the energy difference of vibrational energy levels in the molecules. The Fe-related phonon density of states in the monoclinic polymorph is obtained through nuclear inelastic scattering (NIS) to extract the Fe-related vibrational entropy change in the energy range well below 100 meV. The result from quasi-elastic neutron scattering (QENS) confirms the existence of dynamic disorder in the order of picoseconds corresponding to sub-meV energy. Our combined approach allows us to unravel the different entropy contributions (electronic, vibrational, configurational) to the overall entropy change at the spin transition.

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