Exploring the Role of Dynamics in the Barocaloric Nature of Spin-Crossover Compounds

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A current alternative to vapor compression technology is given by the solid-state refrigeration based on the barocaloric effect (BCE) [1], i.e., a change in temperature when hydrostatic pressure is applied. The materials belonging to this category attract the attention of the worldwide scientific community due to their environmental friendliness, cost-effectiveness, and high efficiency. Spin crossover compounds (SCO) form a distinctive class of transition metal complexes which have the ability to switch between the two spin states of the 3d electrons using an external perturbation such as temperature, pressure, light irradiation and (de)solvation [2].

The driving force that governs the SCO phenomenon is directly associated with the entropy increase upon low spin (LS)→ high spin (HS) transition and is primarily dominated by the vibrational entropy change [3]. Thus, in order to tune the BCE, a thorough understanding of the phonon modes involved in the SCO process is essential. In this study, we explore the role of lattice dynamics in the barocaloric nature of the spin-crossover compound [Fe(Pm-BiA)$_2$(NCS)$_2$], where Pm-BiA = (N-(2'-pyridylmethylene)-4-amino-bi-pheynyl). In this material, the central metal ion Fe(II), embedded in an octahedral environment, exhibits a SCO from the diamagnetic low spin (t_{2g}^6, singlet) state, present at low T-high P, to the high spin state ($t_{2g}^4\ e_g^2$, quintet), present at high T-low P. The compound exhibits two polymorphs with distinct mechanisms of spin transition: monoclinic ($P2_1/c$) with a gradual transition and orthorhombic (*Pccn*) with an abrupt transition [4]. In this work, we address the underlying dynamical features that govern the different nature of transitions in the two polymorphs. Further, as SCO is an entropy driven process, we elucidate the pressure dependence of vibrational entropy and its correlation with the SCO transition temperatures and their hysteresis. The results of this study are complemented from first principles calculations, utilizing VASP and other post-processing tools.

References

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