Stabilizing low symmetry-based functions of [FeII(PM-PEA)2(NCS)2] at room temperature through isosymmetric electronic bistability

Elzbieta TRZOP (Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251,, 35000 Rennes, France)
Francisco Javier VALVERDE-MUñOZ (Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251,, 35000 Rennes, France)
Ricardo Guillermo TORRES RAMíREZ (Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251,, 35000 Rennes, France)
Thierry THIERRY BATAILLE (Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226,, 35000 Rennes, France)
Nathalie DARO (Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR5026, , F-33600 Pessac, France)
Dominique DENUX (Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR5026, , F-33600 Pessac, France)
Philippe GUIONNEAU (Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR5026, , F-33600 Pessac, France)
Hervé CAILLEAU (Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251,, 35000 Rennes, France)
Guillaume CHASTANET (Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR5026, , F-33600 Pessac, France)
Boris LE GUENNIC (Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226,, 35000 Rennes, France)
Eric COLLET (Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251,, 35000 Rennes, France)

Abstract

Symmetry-breaking is crucial for controlling ferroic functions in materials, such as ferroelectricity, ferromagnetism or ferroelasticity, which enables applications in sensors, memories, transducers or actuators. Commonly, ferroic phases emerge from ***descending symmetry-breaking*** (*i.e.* the disordered high-symmetry (***hs***) phase is generally the one stable at high-temperature (***HT***), while the ordered low-symmetry (***ls***) phase is the stable one at low temperature (***LT***)), which limits their practical applications. Only a few rare examples of ***ascending symmetry-breakings*** have been observed, but the driving force remains often unclear.

Here we report on a rare example of ***an ascending high temperature ferroelastic symmetry-breaking*** in a spin-crossover material of $[Fe^{II}(PM\text{-}PEA)_2(NCS)_2]$,[1] studied by magnetic, DSC and X-ray diffraction measurements. This coordination material undergoes an unusual transformation from a low-spin high-symmetry phase ***LShs*** (orthorhombic, ***Pccn***) to a high-spin low-symmetry phase ***HSls*** (monoclinic, $\boldsymbol{P2_1/c}$) upon temperature increase. Information extracted from single-crystal X-Ray diffraction measurements provides detailed insight into the characteristic features associated to the symmetry-breaking and spin-crossover phenomena. DFT calculations and our model, based on Landau's theory,[2] explain well how the cooperative thermal switching of molecular spin state drives a ferroelastic phase transition through a coupled Jahn-Teller distortion. The large entropy gain associated with the electronic bi-stability here overcomes the entropy cost due to symmetry-breaking. This result may pave the way for the potential development of devices with multifunctional low-symmetry ferroic materials operating at room temperature.

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