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MS12: Young Crystallographers Lightning Talks

Elucidation of Barocaloric Effect in Spin Crossover Compounds

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The search for new efficient materials and refrigeration mechanisms is a key challenge to replace the conventional vapor compression technology. An attractive alternative technology uses the caloric refrigeration cycle, which is based on the adiabatic temperature and isothermal entropy change upon tuning an external parameter such as pressure, electric field or magnetic field. Recently, spin crossover (SCO) compounds have been recognized as promising candidates, which exhibit large barocaloric effects: Large isothermal entropy changes have been reported for some of these SCO compounds at fairly low hydrostatic pressures (< 1.2 GPa) [1]. In SCO complexes the central metal ion switches between a low spin (LS) state at low temperature / high pressure and a high spin (HS) state at high temperature / low pressure. The LS to HS transition involves an increase of the spin entropy, but a larger part of the entropy change originates from changes in the intramolecular vibrations [2].

In this work, we report on magnetization measurements and single crystal synchrotron radiation diffraction on SCO complexes consisting of Fe^{+2} as a central ion bound to six nitrogen atoms. Our focus is $Fe(PM\text{-}Bia)_2(NCS)_2$, PM-Bia = (*N*-(2′-pyridylmethylene)-4-amino-biphenyl), which crystallizes in two polymorphs depending on the synthesis route. Polymorph P1 crystallizes orthorhombic (*Pccn*) and undergoes an abrupt spin transition around 170 K. Polymorph P2 crystallizes monoclinic ($P2_1/c$) and undergoes a gradual spin transition around 200 K [3].

From the structural data, we extracted the temperature dependence of the Fe-N distances (Figure 1), which can then be used to determine the high spin fraction. From the fitting of the temperature dependence of the high spin fraction, we obtained the change in entropy (ΔS), the change in enthalpy (ΔH), and the cooperativity (Γ). The values obtained for ΔS and ΔH on the basis of the structural data are substantially different from the values of the entropy as deduced from heat capacity measurements [4]. The width of the transition region, differs strongly between the two polymorphs. This indicates the importance of intermolecular interactions for the spin transitions in both polymorphs.

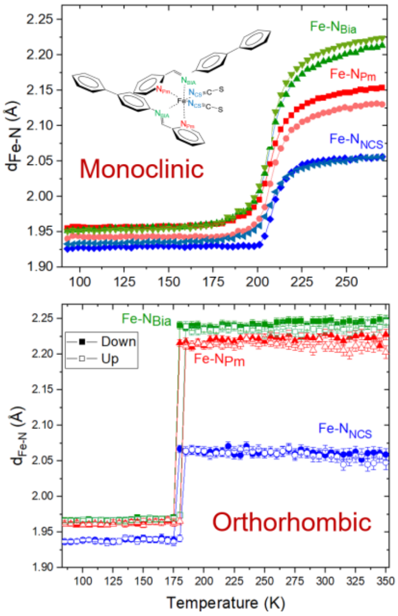

Figure 1: Fe-N bond length as function of temperature for monoclinic polymorph (above) and orthorhombic polymorph (below): the closed symbol is for cooling down and the open symbol for warming up. The inset is a schematic representation of $Fe(PM\text{-}BiA)_2(NCS)_2$ = cis-bis(thiocyanato)bis(*N*-(2′-pyridylmethylene)aminobiphenyl)iron(II).

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