

MS13-1-18 Elucidation of Barocaloric Effect in Spin Crossover Compounds
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Abstract

The search for new efficient materials and refrigeration mechanisms is a key challenge to replace the conventional vapour 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 temperature dependent single crystal diffraction performed at the BM01 station (SNBL, ESRF) on SCO complexes consisting of Fe²⁺ as a central ion bound to six nitrogen atoms. Our focus is Fe(PM-Bia)₂(NCS)₂, (FeN₆S₂C₃₈H₂₈), which crystallizes in two polymorphs depending on the synthesis route. Polymorph A crystallizes orthorhombic (*Pccn*) and undergoes an abrupt spin transition around 175 K. Polymorph B crystallizes monoclinic (*P2₁/c*) and undergoes a gradual spin transition around 210 K [3].

From the structural data, we extracted the temperature dependence of the Fe-N distances (Figure 1). The width of the transition region differs strongly between the two polymorphs. This indicates the importance of intermolecular interactions (e.g. S—C contacts) for the spin transitions in both polymorphs. From the structural data based on the Fe-N distances, the entropy change at the HS-LS transition can be extracted. Our temperature dependent studies provide a good basis for the high pressure experiments on these compounds which are currently being performed by us.

References

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Fe-N bond lengths as function of temperature.

