

s13.m35.p6 **Generic Phase Diagrams for Spin Crossover Solids Showing Ordering Phenomena.** Dmitry Chernyshov<sup>a,b</sup>, Karl Törnroos<sup>c</sup>, Marc Hostettler<sup>a</sup> and Hans-Beat Bürgi<sup>d</sup>, <sup>a</sup>Laboratorium für Kristallographie, Universität Bern, Freiestr. 3, CH-3012 Bern, Switzerland, <sup>b</sup>Petersburg Nuclear Physics Institute, 188350 Gatchina, Russia, and <sup>c</sup>Department of Chemistry, University of Bergen, 5007 Bergen, Norway. E-mail: chernyshov@krist.unibe.ch

**Keywords:** Spin crossover; Molecular crystals; Landau theory

The collective change of molecular spin states in crystals built from iron(II) complexes may or may not be accompanied by long-range ordering of the different states. In the latter case a one step, in the former a two-step dependence of magnetisation on temperature is observed. In the framework of Landau theory the collective spin change of the second scenario is described as an isostructural transition with a totally symmetric order parameter. The first scenario implies a coupling of two transitions, the spin change and the appearance of long-range ordering. Analysis of the observed symmetry changes and the corresponding form of the Landau free energy leads to a generic phase diagram for crossover from the high spin (HS) to the low spin (LS) phase interrupted by an ordered intermediate phases (IP, figure). The diagram is in good qualitative agreement with experimental data from diffraction, magnetic and optical measurements for a variety of complexes including the tris(2-picolylamine) iron(II) dichloride ethanol and isopropanol solvates. Each of the two compounds has been characterized by ~15 structure determinations in the range 15 to 300 K [1].

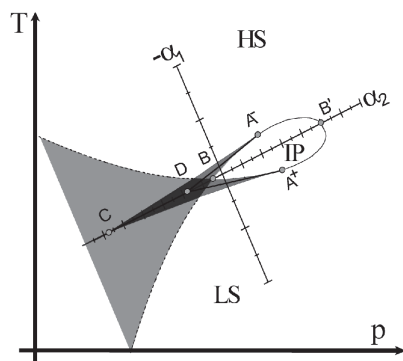


Figure. Generic phase diagram for a two-step spin transition in the "temperature-pressure" plane. HS (LS) indicates the high spin (low spin) phase. IP stands for the intermediate phase with long range ordering of different spin states. In the light grey areas two phases may coexist (HS/LS, HS/IP, or LS/IP), in the dark grey area all three phases may coexist. The letters A-C denote critical points. D is the triple point.

[1] D. Chernyshov, M. Hostettler, K. W. Törnroos and H.-B. Bürgi, *Angew. Chem. Int. Ed.* **42**, 3825 (2003).

s13.m35.p7 **Anisotropy of Structural Compression of Selected Organic Molecular Crystals on Cooling.** T. N. Drebuschak<sup>a,b</sup>, E. V. Boldyreva<sup>a,b</sup> and E. N. Kolesnik<sup>b</sup>, <sup>a</sup>Institute of Solid State Chemistry and Mechanochemistry SD RAS, Russia, and <sup>b</sup>REC-008 "MDEST" Novosibirsk State University, Russia. E-mail: tanya@xray.nsu.ru

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Several selected molecular organic crystals were studied in the temperature range from ambient down to 100 K. Negative thermal expansion was observed along particular crystallographic directions: linear dimensions increased on cooling. For the  $\beta$ -polymorph of glycine this expansion was very weak (within error) [1]. In the orthorhombic polymorph II of paracetamol [2], or in the  $\alpha$ -polymorph of glycylglycine it was rather pronounced. Selected compounds were studied by a single-crystal X-ray diffraction in the temperature range from ambient down to 100 K (STADI4, STOE, Darmstadt). Temperature was controlled using Cryostream Cooler (Oxford Cryosystem). Cell parameters were refined every 25 K. At four temperatures the data collection was carried out and the atomic coordinates were refined. The anisotropy of structural strain was correlated with the changes in the intramolecular geometry and in the intermolecular hydrogen bonds. Negative expansion could be explained by the conformational changes in the molecules, rather than by distortion of intermolecular bonds. For the orthorhombic paracetamol II, the data on the structural distortion on cooling [2] were compared with the data published for the monoclinic paracetamol I (on cooling [3] and under pressure [4]), as well as for the data on the orthorhombic paracetamol II under pressure [4]. For the  $\alpha$ -polymorph of glycylglycine, the anisotropy of structural strain on cooling was compared with that measured for the three polymorphs of glycine [1]. For both compounds studied, the changes in the temperature were shown to affect mainly some of the torsion angles in the molecules. Conformational flexibility of the molecules was shown to be directly related to structural strain on cooling. The effects of cooling and of hydrostatic pressure on the distortions induced in the intramolecular geometry and intermolecular hydrogen bonds, and, as a result, on the anisotropy of lattice strain, were shown to be not identical, and in some cases - noticeably different.

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