On the influence of intensive parameters in a thermodynamic model for spin transition complexes

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I. INTRODUCTION

One of the most important characteristic of the spin crossover complexes [1] is represented by the bistable character at molecular level making these materials appealing candidate in switching devices, signal amplification and information storage but also as efficient contrast agents. Recently, spin crossover particles organized in a nanostructure have been produced [2] to allow systematic studies of particle size effects. These nanostructures are of considerable technological interest as full optical memories.

At the fundamental level, the six d-electrons, for a typically solid iron based compound could be found perfectly paired and this is refer as the low spin state (LS) or distributed according to the Pauli principal obtaining a net magnetization and identified as high spin state (HS). The macromolecules can switch between LS and HS states under external perturbations like temperature, pressure, electromagnetic radiation or magnetic field. This transition may be found to be perfectly reversible or with hysteresis depending on the interactions. The standard characterization is based on magnetic measurements, optical absorption or transmission, X-ray diffraction or Raman spectroscopy.

II. MODEL AND RESULTS

In this paper we are proposing a new approach for modeling simultaneously the pressure and temperature effects (see Fig1 – left side) by combining the Ising and thermodynamic model. The system is described by its Gibbs free energy supposing that LS and HS states coexist as two components in a solid solution, similar to the Guggenheim regular solution theory [3]. The total Gibbs energy is a linear combination between the site fraction and the Gibbs energy of the unconverted material and totally converted material respectively plus an interaction term that depends simultaneously on the HS and LS fractions. Also, we have added an entropy term that reduces the total energy because there are many ways to distribute LS and HS molecules within the assembly. The converted fraction is evaluated using the procedure from Ref [4] based on the master equation. The concentration variation with time is proportional to transition rates from LS to HS and HS to LS respectively, which depends on the energy barriers, temperature and intrinsic fluctuation time. The barriers are numerically determined from the total Gibbs free energy.

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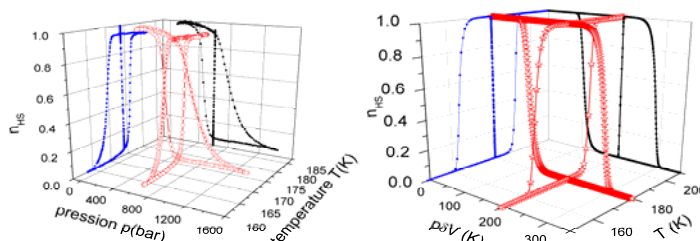

Fig.1. Thermal and piezo hysteresis loops (left – experiment, right – simulation).

Finally, we can express the fraction of the HS molecules as function of degeneracy, interaction parameter, pressure, temperature and the gap energy between the two species.

The limits of the model presented above were studied extensively, focusing especially on the influence of different parameters of the hysteretic properties. The model reproduces the nonlinear dependency of the thermal hysteresis on the interaction parameter and on the pressure, as experimentally observed. Increasing the interactions, the width of the hysteresis loop increases and the center of the hysteresis moves to lower temperatures. The pressure rises the transition temperatures almost linear reducing the hysteresis until it disappears completely. We have combined these parameters reproducing the experimental data (see Fig. 1).

In the full paper we present a systematic study of the parameters that influence the hysteresis loop, the kinetic effects and we shall address the problems related with higher order magnetization processes, as well. We shall present an extension of the model to include the effect of light, known to be very important at low temperatures.

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