Light-induced phase separation (LIPS) in [Fe(ptz)₆](BF₄)₂ spin-crossover single crystals: experimental data revisited through optical microscope investigation

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Abstract. We discuss the available experimental data for light-induced phase separation (LIPS) in the spin-crossover crystal [Fe(ptz)₆](BF₄)₂. They are found in qualitative agreement with a spinodal instability process described by a macroscopic mean-field master equation. Sizable discrepancies with the model are discussed in terms of diffusion of light due to structural transformations of the crystal.

1. Introduction and theoretical background

Light-Induced Instability [1] is a non-linear effect observed in spin-crossover cooperative systems. It leads to the so-called Light-Induced Thermal Hysteresis (LITH) [2] and Light-Induced Optical Hysteresis (LIOH) [1, 3]. Phase separation was reported long ago at the thermal spin transition [4], and photo-induced phase separation was only recently reported [5-7]. We investigate the phase separation properties of the well-know spin-crossover compound [Fe(ptz)₆](BF₄)₂ in the quenched R₃ phase, by using photo-magnetic [6], neutron diffraction [7] and optical microscope investigations [8], with the theoretical background of light-induced spinodal instability defined in [3]. On the other hand we recently showed that the colorimetric analysis of images enabled to separate the diffusion effects from the absorption data for monitoring the behavior of the photo-chromic system [9].

Noticeably, [Fe(ptz)₆](BF₄)₂ does not undergo phase separation when the photo-induced phase transition is performed at low temperature [10]. On the contrary, Morimoto et al. [11] observed phase separation upon (intense) laser irradiation single pulse above 90 K. The relaxation properties of [Fe(ptz)₆](BF₄)₂ remarkably follow the mean-field model description [12] and support the use of the Macroscopic Mean-Field Master Equation (see [13] for complete presentation), written as:

\[ \frac{dn}{dt} = (1-n(t)) k_{opt} - n(t) \times k_{HL}(T, n) \]

where: \( n \) is the population of the metastable (HS) state, \( k_{opt} \) accounts for the absorption cross section, quantum yield and intensity of the irradiation light, \( k_{HL}(T, n) \) is the cooperative relaxation rate constant given by \( k_{opt} \exp(-E_g/k_B T) \exp(-\alpha n) \) with \( \alpha = 2zJ/k_B T \) [12]. It is worth noting that the mean-field approximation is based on the random character of the mixture of HS and LS states [12].

Instability occurs for \( \alpha > 4 \) [1] and gives rise LITH loop shown in Figure 1a. The hatched area denotes the spinodal instability domain, where the system is instable with respect to spatial fluctuations of \( n \) and undergoes "spinodal" phase separation. The isothermal evolution under light is shown in Figure 1b for different initial states, and phase separation is expected in the hatched interval.
Results and discussion
We report on the LIPS effect in the quenched phase (R3) of [Fe(ptz)₆](BF₄)₂ single crystals provided by Profs. J. Jeftic and Y. Garcia. Photo-magnetic, neutron diffraction and microscope optical investigations were performed at Versailles, Rennes (GMCM, Prof. E. Collet) and Grenoble (ILL, Dr G.J. McIntyre) respectively.

2.1. Photo-magnetic measurements (after [6, 8])

The isothermal variations of the HS fraction under light are shown in Figure 2a, for various initial states of the sample. In the spinodal instability range, the sample behaves as expected, with \( n \sim \) constant as in a phase-separated system. However, for non-excited initial state (bottom curves), the system trespasses the expected photo-stationary state, with spurious (chaotic?) behaviour reported in [6] as a Barkhausen-like effect. The properties of the aged state are revealed by the subsequent relaxation curves in the dark, see Figure 2b: the “reference” behaviour (black symbols) is the relaxation curve of the system initially saturated at low temperature which closely follows the mean-field model predictions. The other curves provide evidence for the phase separated state of the initial
state of relaxation, that is, of the system aged under light. Precisely, most of the inner curves could be conveniently overlapped by linear combinations of the outer ones, which are roughly representative of the two photo-stationary states of the system [8]. An additional “exotic” feature (to be discussed) was an irreversible change of the crystal after complete LIESST and partial reverse LIESST effect at low temperature, which drastically changed the photo-excitation and relaxation properties of the crystal.

2.2. Neutron diffraction data (after [7])

The crucial experiment is reported in Figure 3: after specific photo-thermal preparation of the sample which builds up a random mixture of HS LS states (~ 50 : 50), the sample is aged under light-induced conditions. The splitting of the Laue spot gives evidence for phase separation at the spatial resolution of the technique (some 10-100 nm). The kinetics of the phase separation was followed using the second central moment of the peak profile, and shows a crossover between a rapid initial regime and a subsequent slower mean-field regime, in line with the underlying nucleation and growth process. It is worth noting that none of the other experiments (photo-excitation, relaxation LITH loop) reported in [7] did show similar splittings. The “exotic” feature reported in [7] was the “powder-like” Laue pattern obtained at the end of the cooling branch of the LITH loop, which even disappeared when the crystal was returned to its LS state by thermal annealing at 65K.

![Figure 3](image)

**Figure 3.** (a) Laue neutron data on the light-induced phase separation of [Fe(ptz)_6](BF_4)_2 at 53.1 K; (b) temporal evolution of the second central moment of the line shape of the Laue spot (after [7]).
2.3. Optical microscope investigation (after [8])

We recently undertook an optical microscope investigation of the optical densities for imaging the like spin domain (LSD) structures or at least monitoring diffusion effects of light similar to those recently reported in [14]. So far, we showed that the colorimetric analysis could provide separate information on optical and diffusion processes [9], but we failed to observe any effect clearly related to the onset of the LSD structures. We however observed that images with crossed polarisers provided precious information on the ordered/ disordered structural transformation which occurs at the thermal spin transition of \([\text{Fe(ptz)}_6]\)(BF₄)₂ [15]. Diffusion effects are visible in Figure 4 as white areas which are specific of the disordered R₃ structure. We report in Figure 4 (bottom) similar images obtained after repeated photo-thermal treatments, which gives evidence for the contamination of the aged crystal by the disordered R₃ structure. This key feature was also observed on the cooling branch of the LITH loop (sec. 2.2).

2.4. Discussion and conclusion

The previous works [6,7] showed that LIPS effectively occurs under spinodal instability conditions. We now propose a further mechanism based on diffusion of light which increases the light path through the sample, and consequently may enhance the effective photo-excitation rate. The dependence of the enhancement effect upon the local state of the sample creates the local feedback which might explain the “exotic” features quoted here as well as the threshold effect reported in [11]. The diffusion observed here seems related to the onset of disordered R₃ structure. The interplay between structural changes and diffusion of light may be an important issue in the field of PIPT.

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