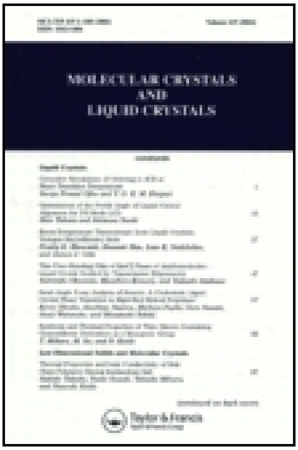

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Patterns During Photoexcitation and High-Spin → Low-Spin Relaxation in $[Fe(ptz)_6](BF_4)_2$ Spin Transition Crystal

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Patterns During Photoexcitation and High-Spin → Low-Spin Relaxation in $[Fe(ptz)_6](BF_4)_2$ Spin Transition Crystal

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The propagation of the high-spin (HS) → low-spin (LS) relaxation at 53 K in a single crystal of the iron (II) spin-crossover compound $[Fe(ptz)_6](BF_4)_2$ was followed by photography, after inducing the local photoexcitation to the metastable HS state at 20 K using the single wavelength (457 nm Ar^+ ion laser) irradiation. The photoinduced formation of the HS – LS patterns with a characteristic diameter of some 0.1 mm was observed to occur inhomogeneously at a macroscopic scale already during photoexcitation. The contrast between the HS (transparent) and the LS (purple) regions was amplified during relaxation. The effect is described in terms of a transient instability, for which a microscopic model in the mean-field approximation is proposed. The mechanism for the development of patterns at the macroscopic scale is discussed.

Keywords: spin transition; photography; laser photoexcitation; instability

INTRODUCTION

Spin transition compounds are a class of inorganic coordination compounds with a central metal ion of d^4 - d^8 electron configuration[1-7] . The ligands are chosen in order to provide a zero-point energy difference between the electronic states of minimum and maximum spin multiplicity on the order of magnitude of thermal energies. The term "spin transition" describes the temperature dependent change of the electronic state in a complex from low-spin (LS) state at low temperatures to high-spin (HS) state at elevated temperatures. One can induce the spin transition by other external perturbations[8], for example light of the appropriate wavelength[9-11] or pressure[12-14].

The question of the distribution of the HS and the LS molecules during the LS → HS photoexcitation (direct LIESST. Light Induced Excited Spin State Trapping[9]) and the HS → LS relaxation[11,15] in the spin-crossover systems raised much of the current discussion[16]. We wondered whether the LS and the HS centers are homogeneously distributed at a macroscopic scale or not, i. e. visible by optical means. This is a question quite similar to that of the existence of spin domains during the thermal transition, for which no direct evidence has been given so far. Different experiments were performed during the HS → LS relaxation[17-21], but none provided a direct answer to the question. The available theories for a long time dealt with the long-range correlations in cooperative systems [22], and were recently expanded to include the short-range correlations [20, 23, 24].

We provide here the first photographed experimental evidence for the formation of transient patterns during photoexcitation and amplifed in the course of the HS → LS relaxation.

EXPERIMENTAL PART

Single crystals of $[Fe(ptz)_6](BF_4)_2$ in the form of hexagonal plates were obtained by slow evaporation from a saturated nitromethane solution [25]. In thick layers the crystals are slightly bluish due to the weak absorption in the near IR region between 750 and 1000 nm. Below 128 K they become dark red. In all experiments the crystals were rapidly cooled from room temperature to 20 K to preserve the R3i crystallographic phase [26] during the thermal HS → LS transition. Irradiations are performed at 20 K with the blue laser light (Ar+ laser, 457 nm, P = 30 mW, irradiation time ~ 40 minutes). The wavelength was chosen in order to ensure a gradient free and slow propagation of the light-induced spin transition [27].

To take the photographs at low temperatures we used a transparent Helium cryostat [28] with a constant Helium flow. A thin, colourless single crystal (0.5 x 5 x 8 mm) was placed on the copper holder of the cryostat. The crystal was cooled down, and only a part of it was irradiated. Then, the temperature was increased to 53 K and the subsequent HS → LS relaxation in the photoexcited part of the crystal was followed by successive photographs. The relaxation rates were measured after the photoexcitation with laser by the absorption spectroscopy, Cary 5E spectrophotometer. To extract the LS fraction we compared the intensities of the typical LS absorption band $^1A_1 \rightarrow {}^1T_1$ at different stages of relaxation by taking the surface under the band. For comparison we also performed magnetic measurements on the SQUID magnetometer by recording relaxations in the temperature region around 50 K after the irradiation with halogen lamp and blue filtre 450 ± 50 nm.

RESULTS

Fig. 1 illustrates the coexistence of the ground, low-spin state and the photoinduced metastable high-spin state at low temperatures (20 K). At ambient temperature both crystals are in the HS state (colourless) Fig. 1a. The rapid cooling of these crystals induces the complete HS → LS thermal spin transition around 128 K [18] without changing the high-temperature crystallographic phase, R3i [26]. At 20 K both crystals are in the LS state which is dark purple, Fig. 1b. Without changing the temperature we covered one crystal and irradiated the other with blue laser light (Ar+, 457 nm, 30 mW). After around 40 minutes complete LIESST[9] took place in the irradiated crystal which turned colourless, while the covered crystal remained in the dark purple low-spin state, Fig. 1c. At this temperature the coexistence

FIGURE 1 Two crystals are mounted to the aluminium plate with rubber cement: a) 295 K, all HS (transparent) b) 20 K, all LS (purple) and c) 20 K after the irradiation of the lower crystal with blue laser light.

See Color Plate I at the back of this issue.

of both states can be preserved for days because of the long lifetime of the metastable HS state[9-11, 29].

Following experiments were performed on another single crystal of $[Fe(ptz)_6](BF_4)_2$ in order to test the homogeneity of the HS fraction (fraction of molecules in the HS state, denoted n_{HS}) during the photoexcitation and relaxation. The crystal was rapidly cooled down to 20 K. The thermal spin-transition did not induce any visible elastic strains, and the surface of the crystal remained almost perfect, as can be seen in Fig. 2 a. As a following step, a black transparency with a small transparent cross was placed in front of the crystal, to partly cover its surface during the irradiation with the blue laser light. The irradiated part of the surface undergoes the light induced LS → HS photoexcitation [9], while the covered part remains in the LS ground state at 20 K, so the two states are present in the same crystal, Fig. 2 b, giving the image of a "Swiss cross". During the irradiation elastic strains due to the large difference in volume between the HS and the LS state (~ 30 $Å^3$/molecule [21, 26]), cause the crystal to crack (black lines). However, the regions between the cracks behave as quasi-independent single crystals.

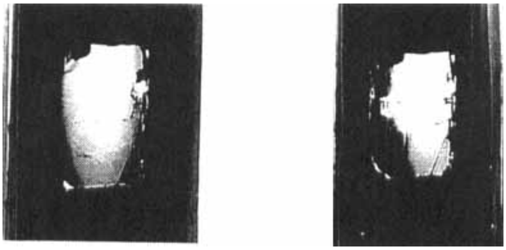

FIGURE 2 a) Single crystal of $[Fe(ptz)_6](BF_4)_2$ at 20 K in the R3i quenched phase, all LS; b) Crystal after selective irradiation at 20 K (blue laser) in the form of "Swiss cross". Formation of the cracks was induced by the blue laser light. See Color Plate II at the back of this issue.

After several irradiations the crystal continues cracking due to repeated HS ↔ LS transitions. In the next experiment the transparency with the black cross has been placed in front of the crystal which was completely in the LS state as seen in Fig. 3 a (purple, 20 K). One induces a weakly pronounced "red cross". Almost all is white because of the light diffusion inducing the LS → HS conversion even in the covered region. Already at the stage of photoexcitation with the blue laser light the formation of the HS - LS macroscopic domains (0.1 mm diameter) takes place, which can be seen immediately after switching off the laser light, in the form of slightly pronounced "honeycomb" patterns.

The question is: how does the HS → LS relaxation evolve, accounting for the initial presence of a homogeneous LS area and the HS - LS inhomogeneites present in the metastable HS crystal?

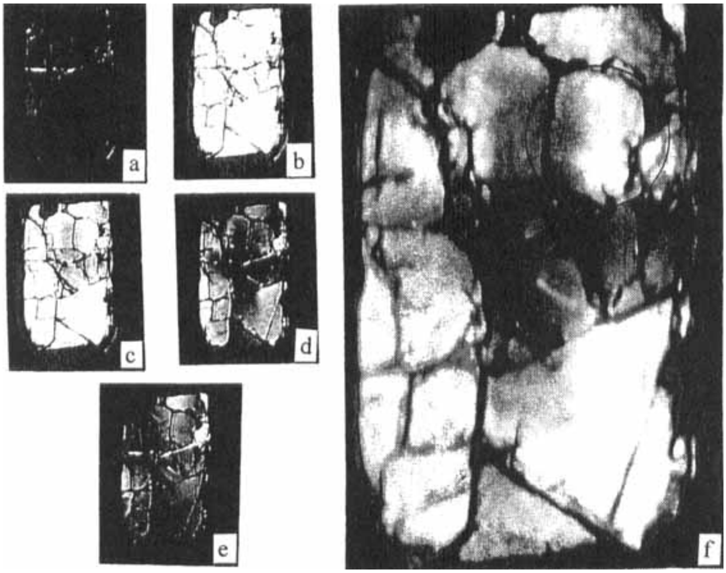

FIGURE 3 a) Crystal in the LS state, the cracks are produced due to repeated irradiations and the formation of elastic strains in the crystal; b) crystal after selective irradiation at 20 K in the form of "red cross", (covered inner part of the crystal); c) T = 53 K, crystal in the course of HS → LS relaxation after 15 min; d) 30 min and e) 60 min; f) Patterns amplified due to transient instability (after 25 min). The circle is around the part which contains both the homogeneous LS region and the region with HS-LS domains (patterns).

See Color Plate III at the back of this issue.

The temperature of the crystal was elevated to 53 K and kept constant, to reach a convenient value of the HS → LS relaxation rate, so that the complete relaxation requires ~ 70 minutes. The temperature is homogeneous because the crystal is surrounded with the He(g). Photographs are taken every 5 min and in Figs. 3 c, d, e we see the situation after 15, 30 and 60 minutes. It is concluded that there is no visible diffusion of the LS centers from the initial LS region at the expense of the HS region, -at the resolution of the photographs-. Rather, an amplification of the contrast is observed: (i) between the HS and the LS regions in the form of the LS "net" (purple) around HS "droplets" (transparent), (ii) the formation of patterns on the previously irradiated areas with laser. This can be clearly seen in Fig. 3 d, f where the crystal is shown at the advanced stages of relaxation (30, 25 minutes). In the enlargement (Fig. f) one "single crystal" domain is encircled, in which the homogeneously purple part was covered prior to photoexcitation (mostly LS) and the left part is the relaxing area previously photoexcited by laser light. In the covered area the relaxation advances homogeneously: this part of the crystal becomes darker and darker as the fraction of LS becomes more important. In this case the distribution of HS and LS units is homogeneous at the macroscopic scale, as well as at the scale of 20 μm as observed under the microscope[30].

To find the clue to our observations we performed relaxation measurements after a laser photoexcitation and a broad band excitation. It is interesting to note that the preparation of the HS metastable crystal by the laser light (457 nm) at 20 K induces different state of the material each time the experiment is repeated, although the HS fraction is always close to 100 % as checked by measuring the absorption spectra (complete absence of the $^1A_1 \rightarrow {}^1T_1$ absorption band characteristic for LS). The result that follows is the random distribution of the relaxation rates relaxation at 53 K (t = 50 ± 15 min), Fig. 4 a.

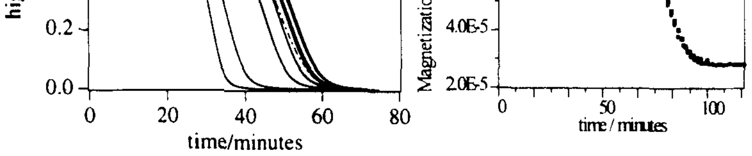

FIGURE 4 a) Absorption spectroscopy measurements: HS → LS relaxations at 53 K in $[Fe(ptz)_6](BF_4)_2$ crystals, random distribution of the relaxation rates after photoexcitation with laser light of 457 nm; b) Magnetic measurements: reproducible relaxations at 53 K after photoexcitation with halogen lamp equipped with 450 ± 50 nm filter.

We also performed the broad band photoexcitation with the halogen lamp equipped with a blue filter (450 ± 50 nm). The resulting relaxation curves, deduced from magnetic measurements, were reproducible, Fig. 4b, in accordance with microscopic observations of the absence of patterns[30].

DISCUSSION

An important point is that patterns formed when photoexcitation is performed with a laser light are probably formed due to interferences in the crystal. Such inhomogeneities are amplified in the course of relaxation.

Interferences in the crystal may be related to reflections on the edges, diffusion on defects or stresses. Diffusion may arise because of possible kinetically induced change of crystallographic phase in the course of LS ↔ HS transitions, which may affect the optical properties. The crystallographic phase R3i relaxes cooperatively with the cooperativity constant $\alpha = 5$, while in P1i phase $\alpha = 1$, and the relaxation is almost single exponential. The coexistence of two phases in the crystal might explain the distribution of the relaxation rates. The question remains whether we induce the crystallographic phase transition in some parts of the crystal at different repetitions of photoexcitation, and should be elucidated by crystallographic measurements. We also observed the wavelength dependence of the form of the patterns which will be published elsewhere[30].

The cracks in the crystal induced by photoexcitation are also leading to independent relaxation histories in each cracked part, see Figs. 3 a-f. Such structural damages due to repeated thermal and optical cycles may induce inhomogeneous optical properties, finally resulting in an inhomogeneous photoexcited state of the crystal before the relaxation is observed. Indeed, the reflected intensity on single crystals or powders of various Fe(II) spin-transition compounds has been observed to increase irreversibly upon cycling temperature or direct/reverse LIESST[31]. In addition, such an aging effect is shown to sizeably change the photoexcitation apparent yield and - to a lesser extent - the relaxation rates for the studied system[33].

The peculiarity of the relaxation in cooperative systems is that the rate depends on the average state of the system. The relaxation rate increases while the population of the metastable state decreases. Such a self-accelerated relaxation is evidenced by the sigmoidal shape of the $n_{HS}(t)$ curves[10, 15]. A simple explanation for this dependence was given in terms of a progressive modification of the configurational energy diagram, with an increase in the energy difference between the two potential wells, that is a decrease in the height of the energy barrier of the metastable state. Then, assuming an energy barrier linearly depending on the HS fraction, the HS → LS relaxation rate was written, in the thermal activation regime :

$$k_{HL}(T,n_{HS}) = k_{\infty}\exp\left(-\frac{E_a(n_{HS})}{kT}\right) = k_{\infty}\exp\left(-\frac{E_a(0)+an_{HS}}{kT}\right)$$
$$= k_{\infty}\exp\left(-\frac{E_a(0)}{kT}\right)\exp(-\alpha(T)n_{HS}) = -\frac{dn_{HS}}{dt} \qquad (1)$$

where $E_a(0)$ is the activation energy at the end of the relaxation ($n_{HS} = 0$). The term $\alpha(T)$ is the self-acceleration coefficient, proportional to the inverse temperature for the temperature region above 50 K[10, 15]. α is associated with the cooperativity of the system. The LS → HS relaxation process has been neglected since $k_{LS}/k_{HS} = (n_{HS}/n_{LS})_{equil} \rightarrow 0$ at the experimental temperatures.

We have plotted in Fig.5 the function $\Phi_{down}(n_{HS}) = -\,dn_{HS}/dt$. For $\alpha > 1$, the curve presents an extremum in the range $0 < n_{HS} < 1$. This extremum, analogous of a spinodal point (a limit of instability domain), is denoted here $\tilde{n}_{HS}$. In the interval $\tilde{n}_{HS} < n_{HS} < 1$, the system is unstable with respect to n_{HS} inhomogeneities: the lower n_{HS}, the larger Φ_{HL}, i.e. the faster the evolution of the system. This results in a transient tendency of the material to develop inhomogeneities of the n_{HS} value. While relaxation takes place, any initial n_{HS} fluctuation is amplified, till the spinodal point is reached; beyond, the system becomes stable with respect to the n_{HS} fluctuations, which progressively damp out. The origin of initial fluctuations may be: at the microscopic scale, thermal fluctuations and defects; at the macroscopic scale, internal stresses and inhomogeneous thermo-optical conditions during the past history of the material, namely interferences induced by laser in the present case.

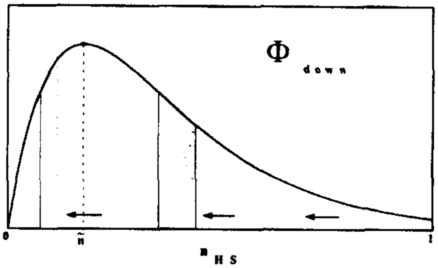

FIGURE 5 The driving force for transient instability, illustrated by a $\Phi_{HL}(n_{HS})$ plot. An initial n_{HS} -distribution broadens till $\tilde{n}_{HS}$, then damps out.

In the temperature region where the speed of relaxation is competitive with the photoexcitation we observed similar effects leading to instability and demixtion under permanent illumination in the spin-crossover series (Fe, Co)$(btr)_2(NCS)_2.H_2O$. They were correlated to the cooperativity of the system, using the same non-linear relaxation term in the macroscopic master equation[32, 34]. The modelling of the spatio-temporal instabilities will remain to be done. We are setting a new equipment for observing the patterns under permanent light, as expected from the instabilities we reported in[32, 34].

CONCLUSIONS

For the first time the HS → LS relaxation was followed by photography in the spin-crossover crystal. Patterns have been observed, associated with inhomogeneous mechanism induced by photoexcitation with laser light. They were related to structural modifications in the crystal followed by random distribution of relaxation rates. It would be interesting to investigate systems that would not involve such structural modifications upon HS ↔ LS transitions. The contrast between HS and LS region was amplified during the relaxation. These effects have been explained as due to a non-linear relaxation term of cooperative origin. The actual mechanism which enables the instability to develop at the macroscopic scale remains, however, to be elucidated, including the internal stresses concomittent to the change of the spin state for the present system.

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