Structural investigation of the photoinduced spin transition in the three states molecular system \([Fe(2-pic)_3]Cl_2\) EtOH.

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Abstract. We present the detailed results of the investigation by X-ray diffraction of the photoinduced phase transition in the Tris(α-picolyamine)iron(II) Chloride-Ethanol complex. This system undergoes a two-steps spin transition between a high spin state at room temperature and a low spin state at low temperature. The intermediate phase consists of stripes of high spin and low spin molecules. The X-ray diffraction data evidence the structural rearrangement at the molecular scale accompanying the photoinduced change of electronic state between the low-spin phase and the photo-steady high-spin one, which is similar to the stable one in the high temperature phase. The dynamical mechanism of the transformation is discussed with the observation of a domain nucleation process, associated with the coexistence of the stable and photoinduced phases.

1. Introduction

Laser driven solid-solid phase transition [1-4] is a new kind of manipulation of matter by light which offers fascinating possibilities for controlling macroscopic switching of materials at different time-scales from hours down to femtosecond (fs). Indeed, in some photo-active solids, the structural relaxation of the electronic excited states following the absorption of photons is not made of independent processes as conventional excitonic or photochemical ones, but entails a photo-induced phase transformation towards new lattice structure and electronic order at the macroscopic scale. Thus light can trigger the physical properties of a material but also induce symmetry breaking from a stable high temperature phase, and establish a photo-induced self-organized long-range order [4] (structural, magnetic, ferroelectric…) which can be characterized by X-ray diffraction. X-ray diffraction is a basic tool for probing structural phase transitions, and exciting possibilities are developed around photo-induced effects. This technique is sensitive to both the long range (via Bragg peaks) and the short range (via diffuse scattering) orders [5]. Furthermore, by using the appropriate time-resolution, it is possible to follow the nucleation and the growth of a photo-induced phase as it takes place.
2. Photoinduced spin transition
Spin-transition materials of organometal nature are really attractive, since it is possible to trigger the spin state of the complex, from a diamagnetic low spin state (LS, S=0) to a paramagnetic high spin state (HS, S=2) under the effect of external stimuli such as temperature, pressure but also under light irradiation (out of equilibrium photoinduced transition) [6,7]. Depending of the strength of the ligand field of nearly octahedral symmetry surrounding the Iron, the energy splitting of the d orbital is more or less important so that the electronic organization can switch between HS and LS states. An important feature in solid state systems is the possibility to address some information by light irradiation using the LIESST effect (light-induced excited spin state trapping) [7].

The [Fe(2-picolyamine)3],Cl2,EtOH molecular complex investigated here belongs to this class of material and intensive optical and magnetic investigations have been performed at low temperatures under light irradiation [8-11]. The thermal phase transition between the HS and LS phases occurs via two first order transitions [6] at 119 K and 109 K and in this temperature range the intermediate phase (IP) consists of stripes where HS and LS molecular planes alternate [12,13]. The fascinating possibility to photoinduce a new phase has also been discussed in this complex : new signatures in the HS photoinduced phase in comparison with the high temperature HS one, observed by Raman scattering experiments, suggest a structural reorganization and a possible symmetry breaking [11].

In order to understand LIESST effect and more generally light-induced phenomena and phase transition, it is of fundamental interest to investigate photoinduced transformation by x-ray diffraction, to get key information of the mechanisms and the nature of the photoinduced phase transition.

3. Experiment
X-ray diffraction experiments were performed as a function of temperature in order to compare both the already known structures of the LS (low temperature), the HS states (high temperature) and intermediate phase (IP) with the photoinduced one at 10 K. It was performed on a four-circle diffractometer with a 2D CCD detector with a NONIUS Kappa CCD (MoKα radiation). The single crystals were mounted either in an adapted Oxford Diffraction Helijet Helium flow cryostat allowing to reach temperature down to 10 K, or in an Oxford cryosystem nitrogen flow cryostat for temperature above 80 K. Diffraction data were collected in different experimental conditions and structure were solved at 170 K (HS state), 80 K and 10 K without (LS state) and with (HS state) laser irradiation [12] : the single crystal, of about 150 µm thick, was continuously irradiated in order to convert it from the LS to the photoinduced HS state. The irradiation were performed with a 1mW/mm² laser power at 632.8 nm (1.9 eV). At this wavelength, the penetration depth is about 60 µm in the LS state, and it increases as the sample transforms to HS state to reach about 260 µm after complete transformation [14]. Compared to the thickness of our samples, the irradiation can be considered as relatively homogeneous. At this temperature the relaxation time is quite long so that the photo-stationary state can be easily reached. A data collection was then performed under continuous laser irradiation. The data reduction leads to 4703 independent reflections from which 4640 with I>2.0σ(I). The whole structure was refined with SHELXL97 [15] by the full-matrix least-square techniques; 292 variables and 4640 observations with I>2.0σ(I). The results gave R = 0.033, Rw = 0.090 for the LS state at 10 K and R = 0.044, Rw = 0.107 for the photoinduced HS state.

4. Structural investigation of thermal and photoinduced phase transition
Slow dynamics phenomena or photo-steady states can be studied on conventional X-ray sources. That is the case of the photoinduced spin transition in different materials investigated up to now [16-18] and it is also possible for the molecular crystal [Fe(2-picolyamine)3],Cl2,EtOH. The X-ray diffraction experiments presented here discuss the three stable phases observed at thermal equilibrium and the nature of the photo-induced phase in a more detailed way than presented in previous work [12]. It as been recently reported that a symmetry breaking occurs in the intermediate phase (IP) with a long
range order of alternating HS (S=2) and LS (S=0) molecules [12,13], whereas the HS and LS phases have the same symmetry. The temperature dependence of the lattice parameters presented on figure 1 clearly shows the two phase transitions. Bragg reflections characterizing the symmetry breaking discontinuously appear in the IP [12] and two first order transitions between HS and IP phases at 119 K and between IP and LS ones at 109 K are also characterized by a discontinuous change of the lattice parameters $a$, $b$, $c$ and $\beta$.

An important signature, characteristic of the phase transition between the spin states, is the change in the intra-molecular structure. The electronic redistribution, modifies the bonding strength between the Iron and the surrounding Nitrogen atoms and is then strongly coupled with the structural degrees of freedom. The average Iron-Nitrogen distance changes from $<\text{Fe-N}> = 2.200 (2)$ Å in the HS to 2.015 (2) Å in the LS, as shown on figure 2. In the IP phase, the bond lengths of the alternating HS and LS molecules are slightly lower and higher respectively than the one of the stable HS and LS phases, in good agreement with previous work [13]. Such a difference may be due to the local elastic stress due to HS/LS striping, influencing the amplitude of the ligand field around the Fe atoms.

The structural signatures of the photoinduced state concern both intra- and inter-molecular reorganization. In addition to the change of the lattice parameters (figure 1), an increase of the $<\text{Fe-N}>$ bond length (2.197 (2) Å), similar to the one between 80 K and 170 K, is observed in the photoinduced phase. The ligand structure of the photoinduced phase is in detail similar to the one of the high temperature HS phase and, as the space group is conserved, no symmetry lowering is observed. We could not find the structural signatures of the IP, neither in the photo-steady nor in the dynamical
Figure 2. Dependence of the average $<\text{Fe-N}>$ bond length with temperature and laser irradiation. The error bar is within the symbols. The shaded area corresponds to the range where the IP phase is stable. In this phase, a long range ordering of layers made of HS and layers made of LS molecules takes place.

ranges. Therefore we can conclude from all the crystallographic data (see also reference 12) that the photoinduced HS phase is very similar to the HS one at thermal equilibrium both for the inter and intra molecular structures. To conclude, the photoinduced HS phase looks like what should be the high temperature HS phase at 10K, if no phase transition occurs.

5. Photo-switching of macroscopic domains

In a photoinduced phase transition, a long range 3D ordering occurs so that the crystal structure is modified at the macroscopic scale: a very large number of adjacent unit cells are transformed in the same way forming macroscopic 3D domains. Therefore, each domain, photoinduced or stable one, diffracts X-rays, with an associate intensity, $I_{\text{photo}}(hkl)$ and $I_{\text{stable}}(hkl)$ for a given $(hkl)$ Bragg peak [5]. Since the lattice parameters are different, the diffraction process is incoherent between domains. If the cell parameters are sufficiently different, the two different Bragg peaks, respectively associated with one of the two coexisting phases, are spatially separated in the diffraction pattern. At the opposite if the difference of the lattice parameters is not large enough, the measured intensity $I_{\text{measured}}(hkl)$ integrated during the data reduction is the weighted independent contribution of photoinduced and stable domains, with respective fraction $x$ and $(1-x)$:

$$I_{\text{measured}}(hkl) = x \times I_{\text{photo}}(hkl) + (1-x) \times I_{\text{stable}}(hkl)$$

Starting from the measured intensity, the refinement of both the structure of the photoinduced phase and its fraction $x$ can be difficult since they are highly correlated. However, if some hypothesis are used the refinement of the photoinduced structure can be simplified.

We have plotted on figure 3 the dependence of the variation of the intensity of more than 2600 $(hkl)$ Bragg reflections between the HS at 170 K and LS states at 10 K ($I_{\text{HS}}-I_{\text{LS}}$) and the photoinduced HS and LS states at 10 K ($I_{\text{photo}}-I_{\text{LS}}$). The linear dependence is a good indication of the similarity between the HS and photoinduced HS states, as indicated by the structural parameters discussed before. The average slope we obtain is really close to unity, meaning that the variation associated with the thermal transition $I_{\text{HS}}-I_{\text{LS}}$ is similar to the one observed with the photo-induced effect $I_{\text{photo}}-I_{\text{LS}}$. The temperature effect giving rise to an important change of the Debye-Waller factor between 170 K and the LS and photoinduced states at 10 K was taken into account (see Wilson plots in [12]). In addition, since only single peaks exist in the photo-stationary HS and stable LS states, $x$ is respectively taken equal to 1 and 0 in order to refine both structures. That is another indication that at the macroscopic state the crystal is in one of those two phases. Notice that this photoinduced phase transition phenomena is not associated with a laser heating effect, since there is no significant change of the Debye-Waller factor between the LS and photoinduced HS states at 10 K [12].

The mechanisms of the photoinduced transformation and relaxation processes, driving the recovery of thermal equilibrium state once the laser irradiation is switched off, are of fundamental interest. As shown on figure 4 there is an evolution of the diffraction pattern between the photo-stationary excited HS state and the LS one. A splitting of the Bragg reflections occurs during the relaxation, indicating the coexistence of macroscopic excited HS domains and relaxed LS ones. Because of the significant difference in the lattice parameters, the position of the Bragg reflections are modified in the diffraction
Figure 3. Relation between the variation of the Intensities of more than 2600 \((hkl)\) Bragg reflections between the HS at 170 K and LS states \((I_{HS} - I_{LS})\) and the photoinduced HS and LS states \((I_{photo} - I_{LS})\). The linear dependence is a good indication of the similarity between the HS and photoinduced HS states. The slope we obtain is really close to unity (line), indicating that 100% of the crystal is transformed.

pattern between HS and LS states. The coexistence of the two phases is associated with the coexistence of the peaks as schematically shown on figure 4. This is the direct signature of a nucleation mechanism and coexistence of the two phases at mesoscopic scale. This result is of fundamental interest since models describing the relaxation process are usually based on the mean field approach and then describe the system as homogeneous. We have observed a similar effect during the excitation process with the growth of photoinduced mesoscopic domains, as it has already been observed by optical microscopy [9]. All those results are the direct signature of the importance of the cooperative effects in such systems. The formation and nucleation of domains is an important feature to take into account in the future theoretical models, to describe the photo-switching and relaxation at the macroscopic scale.

6. Conclusion
X-ray diffraction is a powerful tool to investigate molecular switching, by getting information at the atomic scale. The results presented here show that the nature of the photoinduced phase in the \([\text{Fe}(2\text{-pic})_3]\text{Cl}_2\text{EtOH}\) complex is similar to the HS one stable at high temperature. However, with regard to the possibility to photoinduce symmetry breaking [11] and to switch between different states using different laser excitation wavelengths [19], it may be interesting to try in a near future to generate the IP from the other phases or to excite it in order to generate one of the other phases.

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