

PHASE TRANSITION DRIVEN BY LIGHT: THE KEY ROLE OF X-RAY DIFFRACTION AND TIME-RESOLVED TECHNIQUES

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The optical control of the macroscopic physical properties (magnetic, optical...) of a material by laser irradiation is gaining interest through the emerging field of photoinduced phase transitions. Light-induced changes of the macroscopic state of a material involves subtle coupling between the electronic and structural degrees of freedom, which are essential for stabilizing the photo-excited state, different in nature from the stable state. Therefore the new experimental field of photocrystallography plays a key role. This paper is reviewing different aspects of the use of this technique to investigate the nature, the mechanisms and the dynamics of photoinduced phase transitions. Crystallography coupled to laser excitation allows studying long-lived states, and time-resolved crystallography with 100 ps resolution makes it possible to catch transient states, as well as the mechanisms involved in the dynamical processes over different timescales.

1. INTRODUCTION

A major challenge in physical science is the control of the physical state in a solid material on the atomic motion time-scale (100 femtosecond, $1 \text{ fs} = 10^{-15} \text{ s}$). The femtosecond world of molecular materials represents fascinating possibilities by virtue of photoinduced co-operative and coherent changes in molecular identity, such as charge and/or spin state. Indeed, in co-operative solids the molecules are not independent and the environment of a transformed molecule is not passive but active. The structural relaxation of the electronically excited states following the simultaneous absorption of photons is no more localized on independent molecules but involves many molecules. Light may direct the functionality of a material through spectacular collective and/or cooperative photoinduced phenomena in the solid state. This can trigger the transformation of the material towards another macroscopic state of different electronic and/or structural order, for instance from non magnetic to magnetic[1], from insulator to conductor[2], from paraelectric to ferroelectric [3]. This addresses long-lived instabilities generated by *cw* laser excitation, as well as pulsed light driven transformations.

On the one hand, *cw* light excitation can switch molecular states, through the trapping of the electronic excitation by structural reorganization. For some systems the live-time of the transient photoinduced state easily span over days allowing detailed analysis of the excited structure [4-8]. Light also makes it possible to reach states which can not be observed in normal thermal equilibrium conditions [1].

On the other hand, pulsed laser excitation can generate ultra-fast switching. The increase of sophisticated instrumentation, including ultra-fast time-resolved diffraction [9-18], gives fascinating capabilities not only to observe and understand the elementary dynamical processes in materials but also to watch how matter works and can be directed to a desired outcome. The key point is that in the solid state different degrees of freedom of different nature play their part

on different time scales and the pathway is complex, from the molecular to material lengths and time scales.

2. BROKEN SYMMETRY IN THE PHOTOINDUCED STATE

Among switchable molecular materials, Fe^{II} spin crossover (SC) complexes have been widely studied over the last decades:[1,6-8] the reversible low-spin (LS) \rightleftharpoons high-spin (HS) switching triggered by a change in temperature, pressure, or by light irradiation, has attracted much interest for both basic scientific understanding as well as potential technological applications in information storage or visual displays. Usually, the SC phenomenon is iso-structural. Very recently, it was demonstrated in a new material the new SC material [Fe^{II}H₂L^{2-Me}][PF₆]₂ that light can drive symmetry breaking and that the photoinduced HS state generated at low temperature is different from the HS state existing at room temperature [1]. It is one of the key advantages of X-ray diffraction to be sensitive not only to the molecular structure but also to the order between the constituent molecules of the material.

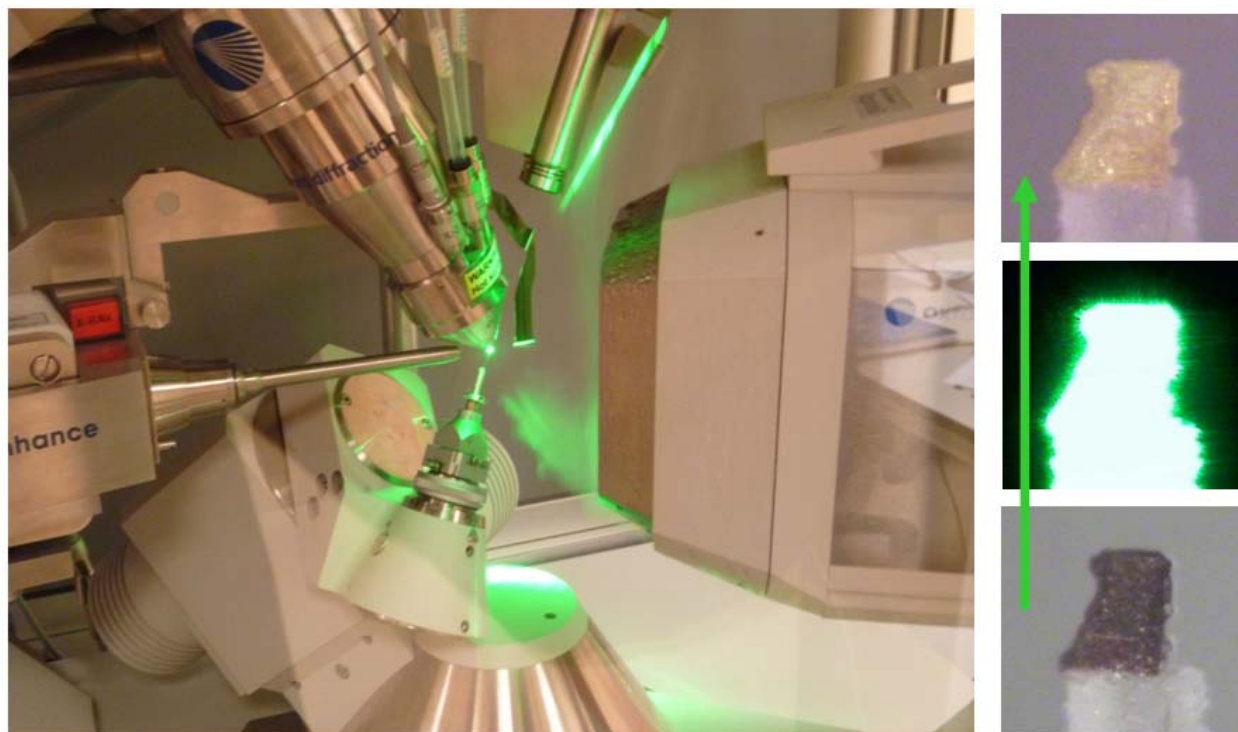


Figure 1: The photo-crystallography experimental set-up (left). The single crystal at 15 K in the He stream is excited by the laser before data collection. The change of crystal color is due to the change of electronic state between LS (violet) and HS (yellow) phases.

The photo-crystallography experiment of the molecular compound [Fe^{II}H₂L^{2-Me}][PF₆]₂ was performed at 15 K, after *cw* photo-excitation at 532 nm (Fig. 1) for generating the metastable photo-induced HS state (PIHS). The structural data were compared to the one at room temperature corresponding to the HS state existing at thermal equilibrium (Fig. 2).

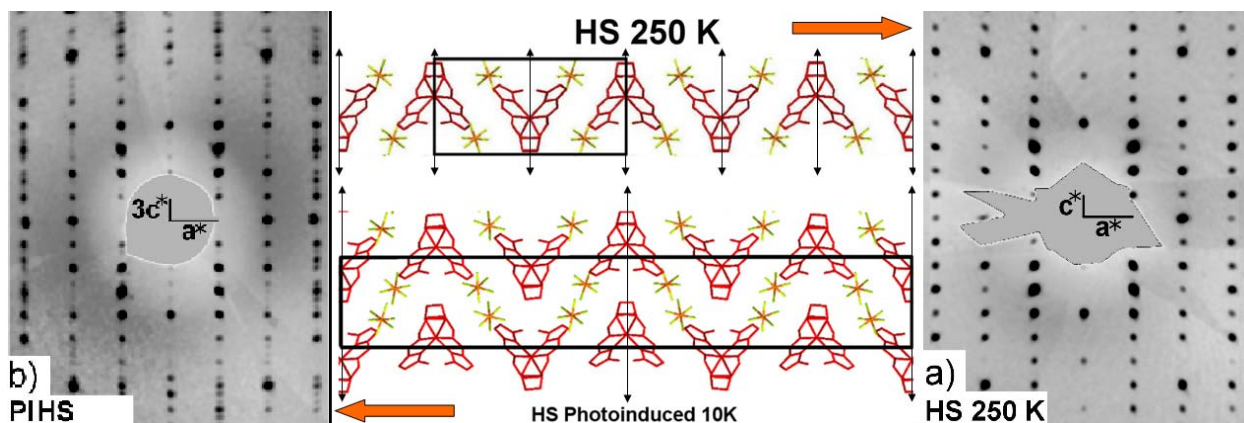


Figure 2: Changes in the diffraction pattern between the HS (a) and PIHS (b) states. The broken symmetry in the PIHS state compared to HS state at high temperature is associated with the deformation of some molecules, associated with the loss of some 2 fold axis.

Diffraction data reveal different translation symmetry of the PIHS ($a, b, 3c$) compared to the HS (a, b, c) state at room temperature. The structural analysis (Fig. 2) indicates that in the HT phase molecules are located on a 2 fold axis. In the PIHS phase, molecular torsion is associated with the loss of some 2 fold axis and cell triplication, resulting in a sequence of distorted and regular molecules along the c axis [1].

This symmetry breaking which occurs upon generating the photo-induced HS phase (PIHS) demonstrate that different competing false ground states exist and that some of them can only be reached under non equilibrium condition by light irradiation. This is one of the important aspects of the research developed in the emerging field of photo-induced phase transitions.

3. TIME RESOLVED DIFFRACTION: DYNAMICS OF THE SPIN-STATE SWITCHING

Recent reports combining time-resolved optical and X-ray diffraction techniques, demonstrated that the switching of the spin state in a macroscopic crystal constituted of bi-stable molecules involves different mechanisms in time and space. The studies were performed in a Fe(III) solid, triggered by a femtosecond laser flash [10,11]. The ensuing dynamics span from sub-picosecond non-thermal molecular switching to microsecond diffusive heating processes through the lattice. The experiment was performed by using the optical pump / x-ray probe technique developed at the ESRF synchrotron (ID09B beamline).

The existence of different steps, summarized in Fig.3, reflects a sequence of physical processes, hidden in the time domain, leaving different fingerprints for molecular transformation, cell deformation and macroscopic crystal switching:

- Step 1: local LMCT to HS relaxation cascade. It is characterized by an elongation of $\langle \text{Fe-N} \rangle$ bond length, a well-known fingerprint of increased spin multiplicity from electron transfer to less bonding orbitals.
- Step 2: unit cell expansion observed here through the evolution of the lattice parameter a .
- Step 3: thermal switching characterized by an additional increase of the $\langle \text{Fe-N} \rangle$ bond length.

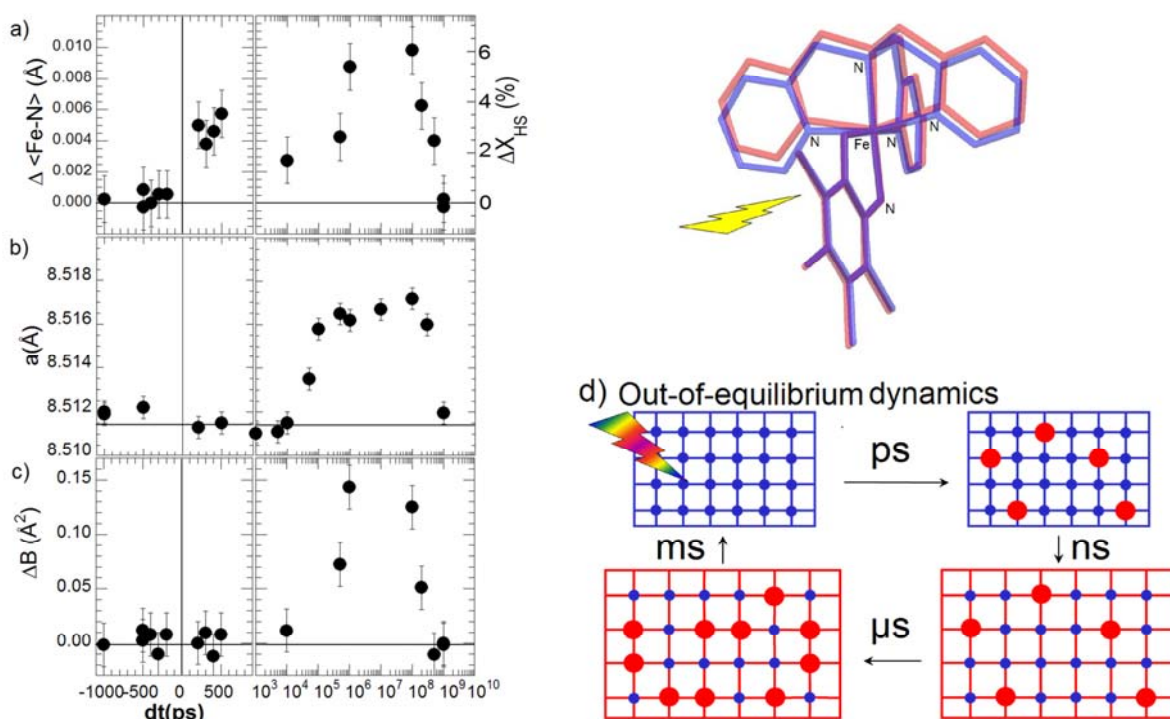


Figure 3: Structural changes after femtosecond laser excitation: a) ΔX_{HS} and $\Delta\langle Fe-N \rangle$, b) lattice parameter a and c) isotropic temperature factor variation ΔB . d) Schematic drawing of the dynamics: HS molecules (red circles) generated within 1 ps by laser pulse in the cold (blue) lattice with mainly LS molecules (blue circles), warm lattice (red) expansion on 10s ns, thermal stabilization of HS population within μs . The HS (red) and LS (blue) structures are also represented (Figure modified from ref 10).

These results shed new light on the complex switching pathway from the molecular to material length and time scales. They pave the way for studying by diffraction techniques the out-of-equilibrium dynamics following laser pulse excitation, what is of fundamental interest in a large variety of materials, since it is important for the design of materials with enhanced functionality.

4. TIME-RESOLVED DIFFUSE SCATTERING TRACKING LOCAL TRANSFORMATIONS

The direct observation of precursor phenomena is an essential key for understanding the mechanism driving the photo-transformation of materials, with challenging issues for both fundamental and applied aspects in material science. Precursor phenomena for photoinduced phase transition may be described in two limit cases: first a collective mechanism (soft mode) and second the generation of localized excitations (precursor clusters). The first one was investigated by 100-femtosecond x-ray diffraction where a coherent phonon triggers the time-dependence of the Bragg reflections [14,17]. Recently we used time-resolved x-ray diffuse scattering to capture the second mechanism. Diffuse scattering, which probes local deviations from the average structure, played a major role for understanding the physics of pre-transitional phenomena around phase transition at thermal equilibrium (Fig 4) [19].

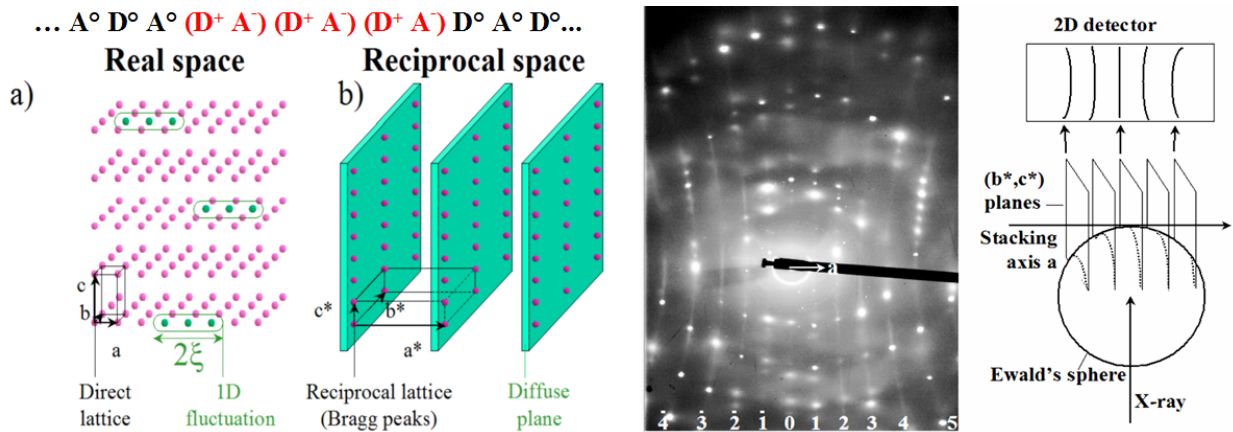


Figure 4: Diffuse scattering: The diffusion of the x-ray by a 3D periodic lattice (pink spheres, a) results in diffraction at the node of the reciprocal lattice (sphere, b), which is the Fourier-transformed of the 3D periodic arrangement of molecules in the crystal. As atoms in a crystal possess some degrees of freedom, local deviations ($\Delta F_n = F - F_n$, green spheres, a) may appear within a unit cell n . It gives rise to diffuse scattering, which is located on the Fourier-transformed of the spatial correlations function between the fluctuations. Fluctuations extending along one direction over a correlation length ξ , give rise to diffuse planes (green, b) passing through some nodes of the reciprocal lattice. Such diffuse planes perpendicular to the stacking axis a , are observed for TTF-CA and projected as lines on the 2D detector. These planes are associated with the 1D exciton-strings (right).

The charge-transfer molecular compound TTF-CA (tetrathiafulvalene -*p*- chloranil, $C_6H_4S_4 - C_6Cl_4O_2$), is made of mixed-stack sequence of alternating TTF donor (D) and CA acceptor (A) molecules, which stimulates the cooperative electron transfer along the stack. It undergoes a photoinduced phase transition at solid state [3] between a neutral and an ionic ferroelectric phase (dimerized). Neutral (N) state, ... $D^0 A^0 D^0 A^0$..., (I) states, ... $(D^+ A^-)(D^+ A^-)$...

The photo-induced phase transitions are discussed in the literature as resulting from a new class of collective excitations, the so-called 1D lattice-relaxed charge-transfer exciton-strings. These nano-scale objects, represented by ... $D^0 A^0 (D^+ A^-)(D^+ A^-)(D^+ A^-) D^0 A^0$... are made of train of dimerized I molecules extending along the crystalline stacking axis a . The direct experimental evidence of the thermally-induced 1D exciton-strings has been possible [19] for TTF-CA (Fig. 4).

Time-resolved x-ray diffuse scattering experiments [18] were performed at the Photon-Factory Advanced Ring synchrotron on the beamline NW-14A [13]. Fig. 5 shows the time dependence of the diffuse plane, increasing just after the laser excitation. This is a direct signature of the photo-generation of the local precursor clusters with short-range structural order, appearing in the first steps of the photoinduced transformation. In other words, the laser excitation drives a cooperative 1D transformation along the stacking axis a , as schematically indicated in Fig. 5. The observed rising time [18] of the diffuse scattering between -50 -ps and 50 -ps is limited by the convolution of the signal with the 50-ps time resolution used, and so takes place on an ultrafast time-scale.

The present results directly evidence the photo-generation of short-range precursor clusters of the photoinduced phase transition. Regarding the dynamics, two fascinating questions have to be discussed for future investigations. First, what is the size of the photoinduced exciton-string (ξ') and what is their dynamic of formation? This should strongly depend on the pumping photon energy. Second, on which time scale the interstack ordering between the exciton-strings appears and how does it proceed?

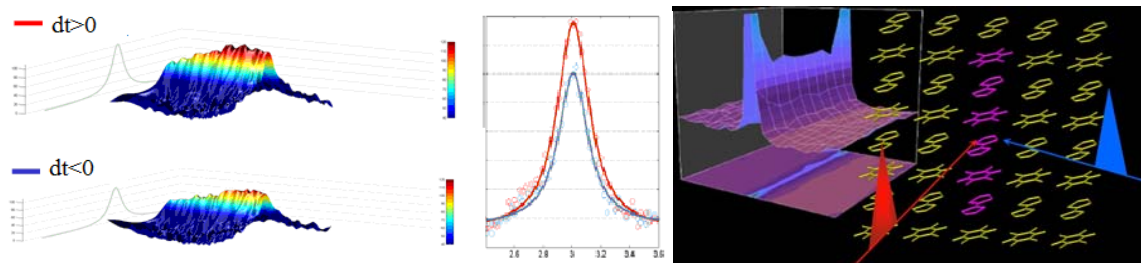


Figure 5: Evolution of the diffuse scattering before (-100 ps) and just after (50 ps) laser excitation. The increase of the diffuse plane is directly related to the photo-excitation of 1D cluster along the stack, as schematically indicated on the right.

The next generation of pulsed x-ray sources such as X-FEL, promising larger x-ray flux than the one available nowadays and a shorter time resolution (100-fs), will revolutionize such experiments of structural dynamics on ultra-short time scales.

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