Photo-induced phase transition probed by time-resolved X-ray diffraction.

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Introduction

A new frontier in the field of structural science is the emergence of the fast and ultra-fast X-ray science. Recent developments in time-resolved X-ray diffraction promise direct access to the dynamics of electronic, atomic and molecular motions in condensed matter triggered by a pulsed laser irradiation, i.e. to record "molecular movies" during the transformation of matter [1]. These laser pump and X-ray probe techniques provide now an outstanding opportunity for the direct observation of a photoinduced structural phase transition as it takes place. On the one hand, the X-ray short-pulses of about 100 ps around third-generation synchrotron sources have been used for structural investigations of sub-nanosecond photoinduced processes in molecular solid systems with a large number of atoms per unit cell [2-6]. On the other hand, new X-ray sources, such as laser-produced plasma ones, generating ultra-short pulses down to 100 fs have been used to study sub-picosecond processes in more simple materials [7-10]. This opens the way to femtosecond X-ray crystallography, with rather low X-ray intensities and limited experimental possibilities at present but this new ultra-fast science rapidly progresses. In new projects, the different properties (flux, divergence, stability …) of the X-ray beam, in addition to the time resolution, have to be considered on equal footing. It is the aim of this contribution to discuss the state of art and the perspectives of fast and ultra-fast X-ray scattering techniques to study photoinduced phase transitions and to present the contribution of crystallographic methods. In addition, ultra-fast X-ray scattering will play a central role within the fascinating field of manipulating coherence, for instance to directly observe coherent atomic motions induced by a light pulse, such as optical phonons.

Photoinduced phase transition

The manipulation of matter and it physical properties by light represents a fascinating goal both for the application of materials and for a more fundamental research around the interaction between electronic and structural degrees of freedom and the physics of out of equilibrium phenomena [11]. Most of the processes in the transformation of matter are governed by atomic motions - including most of biology and chemistry, and a good part of physics – at different time-scales. The time-scales corresponding to the vibrational period duration of the atomic motion, typically around 100 femtoseconds or 1 picosecond, are therefore of fundamental interest. An important physical feature is to take into account the difference in nature between a photoinduced phase transition and conventional homogeneous photoinduced chemical or biochemical processes where molecules transform in an independent way with respect to each other. In some materials, the relaxation of the photo-excited state is not localized on one or few molecules but a macroscopic switching of material occurs. Such photoinduced phase transition effects look similar to the phase transition undergone by materials at thermal equilibrium. However, it generates an out of equilibrium state with a finite life time, so that a recovery to thermal equilibrium occurs. The dynamical aspect is therefore an important point since transformation can occur on the picosecond time-scale. By combining optical and X-ray diffraction methods, fundamental keys can be obtained in order to understand such phenomena. Function of materials and mechanisms of transformation can then be understood opening the way to applications. Time-resolved techniques make it possible to catch photoinduced transient states with a time resolution which can reach 100 femtosecond. This means that the dynamics of the electronic and structural degrees of freedom can now be probed so that we can really see with an atomic resolution how matter rearrange.

Optically controlled phase transition represents a new kind of manipulation of matter by light which is associated with cooperative phenomena between the constituent molecules of solids.. Such transformations of molecular materials are triggered by a laser excitation and two types of mechanisms exist: the transformation may be generated under a continuous laser irradiation or it may be generated by a laser pulse containing a number of photon of the same order as the one of the molecules in the solid. Thus, strong photoinduced cooperative phenomena take place in some photo-active materials where the structural relaxation of the electronic excited states following the absorption of photons are not independent processes, as in conventional excitonic or photo-chemical ones, but entail a photoinduced phase transformation towards a new lattice structure and electronic order (important coupling between the electronic and lattice degrees of freedom). This opens a way for light to trigger the physical properties of a material and the molecular state but also to induce symmetry breaking from a stable insulating high temperature phase, and so to establish a self-organized long-range order (structural, magnetic, ferroelectric,…). The change of the electronic state of the molecules is then well characterized by optical techniques whereas X-ray diffraction makes it possible to observe the structural relaxation at the atomic scale. In addition to the investigation of the photo-steady or long live-time photoinduced states possible with conventional experiments, the investigation of ultra-fast processes is now possible using pump-probe time-resolved techniques.

Photoinduced ferroelectric order evidenced by 100 ps X-ray diffraction.

In some molecular materials, the absorption of a photon by a molecule gives rise to an electronic excited state localized around one or several molecules. Such an excitation may be trapped by a lattice relaxation associated with a change of a bond length, of a torsion angle… Therefore isolated excited molecules are generated in the material, with a finite life-time. If a large number of such excited species can be simultaneously generated with regard to the relaxation time scale, they can couple to each other and the system can switch to another state at the macroscopic scale with a new electronic state and another structural rearrangement (for instance light can induce order). This differs from well-known light-induced disordering phenomena, such as surface melting or demagnetization. This new type of photo-induced effects is exemplified by molecular charge-transfer materials that are readily tuned between competing neutral (N) and ionic (I) ground states [12]. The photo-induced phase transformation in these materials, taking place on a ps time-scale, are highly co-operative and highly non-linear. The present birth of time-resolved photo-crystallography at synchrotron source gives a golden opportunity to directly observe the photo-induced structural change at the atomic level and the symmetry breaking by recording “complete” diffraction pattern with a 100 ps time resolution associated with the pulsed structure of the synchrotron source at the ESRF. We will present the direct evidence of the N-to-I photo-induced structural phase transformation, i.e. after photo-irradiation of the high-symmetry N phase, stable at high temperature. The monochromatic X-ray diffraction data establish unambiguously the 100 ps time-evolution of the intensity of some Bragg peaks and the appearance of new Bragg peaks characterizing the ferroelectric order in the photo-induced I state [5].. The delay dependence of Bragg reflections intensities shows that the macroscopic transformation is completed in about 500-ps [5-6]. The most important feature is the evidence of a long-range ferroelectric ordering in the established photoinduced phase. This type of self-organized ordering process driven by light from a high symmetry phase takes advantage of intrinsic cooperativity which may also be present in other types of materials. Interesting precursor phenomena, including the seeding process and coherent phonons, have recently been observed by femtosecond reflection spectroscopy under a resonant charge-transfer excitation [13]. To complement the picosecond investigations, femtosecond x-ray sources will be of fundamental use to study these ultrafast phenomena. Such structural investigations will be essential not only for basic science but also for realizing highly efficient photo-switching devices.

Ultra-fast processes studied by 100 fs X-ray diffraction.

The investigations of experimental results with a sub-ps time resolution, down to 100 fs, have been obtained by using laser produced plasma X-ray sources. These results concern some more conventional and more simple hard solids, i.e. inorganic solids with only a few number of atoms by unit cell. In these compounds, the electronic excitations are delocalized. Thus, when a very large fraction of valence electrons is photo-excited in the conduction band, this leads to an electronic-lattice destabilization which can generate a new periodic lattice structure or even melting, often related to an insulating-to-metal instability. In other words, intense light pulses may trigger long range lattice instabilities which can be ultra-fast, since only small coherent atomic motions are involved.

The first example is given by the non thermal photoinduced surface melting in semi-conductors [7]. The term “non thermal” means that this surface melting takes place on the sub-ps time scale before the typical electron-phonon thermalization one. This is observed in different materials and it is characterized by the disappearance of the Bragg reflections associated with the loss of the periodic lattice. Such processes are really ultra-fast since the highly excitation of electronic degrees of freedom triggers impulsive coherent atomic motions on a time scale which can reach few hundred fs only. The material transforms in an disordered quasi-liquid state before the thermal relaxation occurs, as for InSb semi-conductor [7]. The generation of a dense electron-plasma was confirmed by optical measurements, which can not allow to evidence melting since the optical signal associated with the liquid state is very difficult to separate from other contributions. Therefore, in order to investigate such an ultra-fast melting the 100 fs diffraction technique is appropriate. The excitation pulse causes disorder in the sample, eliminating diffraction peaks so that the X-ray signal drops to zero. Similar results have also been obtained by other groups on other semi-conductor materials and by utilizing thin films. It will be interesting in future, when higher X-ray intensity will be available, to investigate in which way the quasi-instantaneous disordered state obtained just after the disappearance of Bragg peaks is similar or different of the liquid one at thermal equilibrium.

The second example concerns a fs photoinduced solid-solid phase transition in the oxyde of vanadium VO_2 [8]. It is known to undergo an insulator-to-metal transition at 340 K and changes in the electronic band structure are associated with structural changes between a low-T monoclinic and a high-T rutile phase. The formation in two steps of the metallic rutile phase consecutive to the laser excitation was evidenced. The first step, occurring at the very surface corresponds to a macroscopic transition within less than 500 fs. Such a time scale, shorter than the typical internal thermalization time of a non equilibrium phonon distribution, means that this excitation regime can not correspond to the conventional pathway for a first-order phase transition (nucleation and then growth of the new phase). Therefore the excitation of a dense carrier population across the band gap may significantly perturb the potential energy surface of the electronic ground state and depress the barrier separating the two phases. Further experiments are necessary to answer the fundamental questions : which comes first in the sample, the structural change or the electronic one, which microscopic process is responsible for initiating the structural distortion and what causes the disappearance of the gap after optical excitation.

The third example corresponds to the observation of coherent optical phonons in a material by ultra-fast X-ray diffraction [9]. Bismuth is one of the prototype materials in which coherent optical phonons are generated upon femtosecond laser excitation. The optical phonons at the center of the Brillouin zone should affect the X-ray diffraction intensity because of the changes in the structure factor through the oscillatory atomic motion which occurs coherently. Following the effect from a short laser pulse, K. Sokolowski-Titen *et al.* directly observed from the changes in the Bragg peaks intensity the large-amplitude coherent atomic vibrations. From the measurements, it is possible to extract the phonon frequency, and , as the variation of the intensity occurs with a different sign for different Bragg reflections, it is possible to separate such coherent atomic motion inside the unit cell from the signal associated with incoherent dynamics, for example melting as discussed above.

Toward 100 fs X-ray crystallography.

It is of fundamental interest to get new X-ray sources with 100 fs time-resolution for the investigation of the first step of the different processes associated with the transformation of matter by light irradiation, that is to reach the time scale corresponding to the lattice relaxation of the electronic excited state [14]. In order to study more interesting materials which can be functional, the properties of the X-ray beam have to be defined. In addition to the time resolution, the X-ray brightness is also important as well as the stability. In fact, the photoinduced processes are not always associated with the disappearance or the appearance of Bragg reflection. Sometimes only weak modifications correspond to the structural reorganization [15]. It is also necessary to measure a large number of Bragg reflections and this requires to have an X-ray beam with low divergence. This is also important for the investigation of the change of the lattice parameters and coexistence of phases. The spatial resolution is therefore also an important aspect of the properties of the beam. Finally, as processes do not always occur in a coherent way, local transformation of matter may occur. In such a case some diffuse scattering appears, more or less spread out within the reciprocal space. In the case of molecular systems presenting N-I transition, such one-dimensional local order was observed at thermal equilibrium [16]. The mechanism of the photoinduced transformation is associated with the formation of 1D strings in the 1 ps time-scale which couple to each other on the 100 ps time–scale where the system switch to the 3D photoinduced phase. The evolution of this diffuse scattering as the transformation takes place will give key information for understanding the transformation of matter over different scales, from the isolated molecule to the macroscopic domain. Here again, as diffuse scattering is typically 5 order of magnitude lower than the Bragg reflections, the brightness of the source is of fundamental interest. The divergence of the X-ray beam is here again an important aspect since a good spatial resolution makes it possible to get information about the correlation as matter transforms.

Femtosecond X-ray pulses will have tremendous applications in a broad area of science, including condensed matter physics, chemistry, biology, and engineering because the ability to time-resolve at the femtosecond level will open up entirely new fields of scientific research. Therefore all the different experimental set-up making it possible to reach such time-scales, such as slicing technique developed around synchrotron sources [17], have to be considered because of complementary aspects, in order to design the more interesting sources for future.

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