Phase transition in \((\text{EDO-TTF})_2\text{PF}_6\) : domain growth in the thermal hysteresis and ultra-fast photoinduced effects.

L Guérin\(^1\), D Glijer\(^1\), N Moisan\(^1\), M Lorenc\(^2\), M Buron-Le Cointe\(^1\), E Collet\(^4\), H Cailleau\(^1\), A Ota\(^3\), G Saito\(^3\), X Shao\(^4\), H Yamochi\(^4\), M Chollet\(^1\), K Onda\(^5\), T Ishikawa\(^4\), S Koshihara\(^6\)

\(^1\)Groupe Matière Condensée et Matériaux, UMR CNRS 6626, University Rennes 1, Campus Beaulieu, 35042 Rennes Cedex.
\(^2\)European Synchrotron Radiation Facility, Grenoble, France.
\(^3\)Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.
\(^4\)Research Center for Low Temperature and Materials Sciences, Sakyo-ku, Kyoto 606-8502, Japan.
\(^5\)Department of Materials Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551 Japan.
\(^6\)JST, ERATO, KEK

E-mail: laurent.guerin@univ-rennes1.fr

Abstract. The first order phase transition between the metal (M) and insulating (I) phases of the molecular compound \((\text{EDO-TTF})_2\text{PF}_6\) is investigated by single crystal X-ray diffraction. The coexistence of the insulating and metallic phases and the growth of the domains in the thermal hysteresis are clearly observed during the phase transition. We also present ultra-fast optical experiments using a nitrogen gas flow cryostat. A change of the reflectivity in the photoinduced phase was observed just after excitation. We will also discuss the influence of the excitation light polarisation on the efficiency of the photo-induced I-M phase transition.

1. Introduction

The photo-control of the physical properties of materials (optical, magnetic, conduction, ...) represents a fascinating research field. It can occur by virtue of cooperative molecular switching between degenerate or quasi-degenerate ground states, involving changes in the molecular identity, such as charge or spin. The effect of coupling between electronic and lattice degrees of freedom is enhanced in low-dimensional multistable systems and may cause strong and fast photo-induced effects at the macroscopic scale triggered by a rather weak photoexcitation [1]. The generation of coherent processes using excitation by ultra-short laser pulses may generate ultra-fast phase transitions with dynamics on the time-scale of the atomic motion. These collective phenomena are very different in nature from conventional independent photochemical processes.

This is well exemplified in the organic \((\text{EDO-TTF})_2\text{PF}_6\) molecular conductor crystal. This compound undergoes a first order Metal to Insulator (M-I) phase transition at \(T_c = 280\) K. This phase transition implies the cooperative features of a Peierls-like distortion, charge ordering and anion ordering accompanied by a large molecular deformation of the EDO-TTF molecules below \(T_c\). In this system, the donor layer consists of nearly uniform head to tail stacking of the EDO-TTF
(ethylenedioxytetrathiafulvalene) donor molecules (D) and the structural change is associated with a cell doubling [2-3], corresponding to the nesting vector expected from the calculated Fermi surface. The charge-ordering phenomenon coupled with the important structural relaxation of the molecules gives rise to a tetramerization process of the donors and an important bending of the neutral molecules [2,4]. The neutral D molecules are conventionally represented by D$_0$, the fully ionized by D$^+$. In the M phase where the electrons are delocalized, the partially ionization is represented by D$^{+0.5}$. Therefore, the M-I phase transition is schematized as:

M phase : $\cdots$ D$^{+0.5}$D$^{+0.5}$D$^{+0.5}$D$^{+0.5}$ $\cdots$ to I phase : $\cdots$(D$^0$D$^0$D$^+D^+$) $\cdots$

Recently the highly sensitive and ultra-fast photoinduced transition from the I (low temperature) state to the M one was evidenced in (EDO-TTF)$_2$PF$_6$ by ultra-fast time-resolved optical reflectivity up to about room temperature [5-7]. A large reflectivity change induced by the irradiation of femtosecond (fs) pulsed laser was observed using the optical pump-probe technique. The photoinduced I-to-M phase transition in this family of crystals occurs within a few ps as observed by the optical measurements. The I-to-M photo-induced phase transition may occur at relatively high temperature, approaching room temperature, and proceeds sensitively and ultra-fastly with one photon transforming a few hundreds of molecules. The investigation of thermal hysteresis by X-ray diffraction and time resolved pump probe experiments are presented here.

Figure 1. a) Temperature dependence of the lattice parameters $a$ and $c$ (top), $\beta$ and $\gamma$ (middle) and volume (V, bottom). The first order phase transition is associated with a thermal hysteresis of 4.5 K, and the discontinuous jump of the lattice parameters at 276 K during cooling and 280.5 K during heating.

b) The primitive lattice of the M phase (gray) can be described as a centered one in the lattice of the I phase (white).
2. X-ray diffraction investigation of the thermally induced phase transition

The thermally induced phase transition was investigated using resistivity, magnetic susceptibility [2], X-ray [2-4], calorimetry [8], Raman or reflectivity measurements [9,10]. X-ray diffraction experiments were performed on a single crystal, as a function of temperature, on a four-circle diffractometer Xcalibur3 with a 2D CCD detector. The single crystals were mounted in an Oxford cryosystem nitrogen flow cryostat. Diffraction data were collected in different experimental conditions. The size of the single crystal used was of about 30 × 100 × 400 µm³. Partial data collections were performed, allowing us to get the temperature dependence of the lattice parameters, the intensities of many Bragg reflections, and to observe the coexistence of the two phases in the hysteresis. Figure 1a shows the temperature dependence of the lattice parameters $a$, $c$, $\beta$, $\gamma$, and volume indexed in the low temperature lattice ($b$ and $\alpha$ are not sensitive to the phase transition and are not represented for clarity). With this convention, the space group of the M phase is not the conventional P1 but a centered C1 one. The correspondence between the P1 and C1 is shown schematically on figure 1b. The change from a centered to a primitive cell is characteristic of a symmetry breaking: the Bragg peaks $(hkl) : h+k$ odd are absent in the M phase while they appear in the I phase. The hysteresis associated with the first-order phase transition gives rise to a discontinuous change of the lattice parameters at 276 K on cooling and at 280.5 K on heating the single crystal. The results are very consistent with the ones obtained by magnetic susceptibility [2] and differential scanning calorimetry [8].

3. Phase coexistence and growing of domains in the hysteresis

Looking in detail the system inside the hysteresis may give very important information on the mechanism of the phase transition. Figure 2a presents the reconstructed diffracted intensity in the reciprocal lattice $(h0l)$. For clarity a zoom is made around the $(403)$ Bragg reflection (strong Bragg reflection). The horizontal dotted lines correspond to the $h$ lines in the two reciprocal lattices. The coexistence of the M and I phases gives rise to the coexistence of the corresponding Bragg peaks. The $(401)$ and $(50l)$ peaks are present only in the I phase due to the symmetry breaking. Figure 2b. a) Temperature dependence of the diffraction intensity in the reciprocal lattice $(h0l)$. For clarity a zoom is made around the $(403)$ Bragg reflection (strong Bragg reflection). The horizontal dotted lines correspond to the $h$ lines in the two reciprocal lattices. The coexistence of the M and I phases gives rise to the coexistence of the corresponding Bragg peaks. The $(401)$ and $(50l)$ peaks are present only in the I phase due to the symmetry breaking. b) Temperature dependence of the intensity at maximum of the $(403)$ Bragg reflection in the M and I lattices. It is measured on heating where the phase transition occurs around 280 K.
phases (figure 1a). In figure 2b, the intensity at maximum of the (403) Bragg reflection indexed in the I lattice \((a=9.82, b=11.02, c=11.57, \alpha=102.41, \beta=99.02, \gamma=90.74, \text{ space group } : P1)\) and the intensity of the one indexed in the M one \((a=9.59, b=10.97, c=12.00, \alpha=102.80, \beta=98.57, \gamma=91.07 \text{ space group } : C\gamma)\) are plotted as a function of the temperature. As the temperature increases, the change of the intensity in the M or I lattice corresponds to the growing of the M domains and the disappearance of the I phase between 278 K and 281 K. Because of the change of symmetry, the Bragg peaks indexed \(h+k=2n+1\) are absent in the M phase as shown in figure 2a. The temperature dependence of the integrated intensity of some of these Bragg peaks is plotted on figure 3. The first order phase transition is well characterized by the sudden vanishing of the intensity of these Bragg peaks.

Figure 3. Temperature dependence of the integrated diffraction intensity of the (hkl) Bragg peaks with \(h+k=2n+1\), characterizing the symmetry breaking between the primitive (I phase) to centered (M phase) unit cells.

4. Time-resolved optical experiments
The photoinduced phase transition in \((\text{EDOTTF})_2\text{PF}_6\) was investigated using a time-resolved pump-probe reflectivity measurement. The femtosecond pulses were generated in a mode-locked Ti:Sapphire laser (Coherent, MIRA) and amplified in a 1kHz CPA amplifier (SpectraPhysics, HURRICANE). The output pulses are centred at 800 nm and their duration is bandwidth limited (around 100 fs). The output power was split in 9:1 proportions, where 90% of the total pulse intensity seeds the optical parametric generator (Light Conversion, TOPAS), and the remaining 10% of the intensity was used directly for optical pumping of the crystal. The 800 nm pump light was used to excite the crystal and the excitation photon energy (1.55 eV) was nearly resonant with the charge transfer band [9]. The delay between pump and probe pulses was controlled with a stepper motor translation stage with a minimum step of 66 fs. In order to obtain a maximal reflectivity signal, the parametric generator was set to 720 nm for probing since at this wavelength, the probe photon energy (1.72 eV) is centered on a band which seems characteristic of the M phase [9]. Its polarization was parallel to the stacking axis of EDO-TTF molecules. The reference and reflected signals were picked up by 1ns photodiodes and then fed to time gated integrators (LeCory, Wavesurfer 424, 200 MHz oscilloscope). The single crystal \((3\times1\times0.5 \text{ mm})\) was mounted in an adapted Oxford cryosystem nitrogen flow cryostat to reach a temperature down to 100 K.

In figure 4a, a time profile of the reflectivity change \((\Delta R/R)\) at 100 K was observed at 1.72 eV with an excitation intensity of \(2.4\times10^{19} \text{ photons cm}^{-3}\) and a polarization parallel to the EDO-TTF molecules stacking axis. For \(\delta t > 1.5\text{ps}, \) the \(\Delta R/R\) value remains constant; thus the phase conversion process is completed in 1.5ps. Such an ultrafast phenomena cannot be explained simply by a laser heating effect. At \(\delta t=3\text{ps}, \) the reflectivity change reaches about 20% with an excitation density of \(2.4\times10^{19} \text{ photons cm}^{-3}\).
Such photoinduced conversion indicates a strong cooperative effect in this crystal since one photon will excite about 50 EDO-TTF molecules. The dependence of reflectivity change with the excitation intensity was reported in a previous paper [5]. At this excitation energy, the reflectivity change may reach more than 50% whereas in this experiment, only 20% change is observed. This discrepancy may come from the different cryogenic system used in this experiment. With the cryosystem nitrogen flow cryostat, ice was forming on the surface of the sample which reflected a large part of the pumping 800 nm light. Thus, the ice limits the excitation density on the crystal.

Figure 4. a) Time profile of the $\Delta R/R$ observed at 100K. The probe photon energy was 1.72 eV. The pump photon was 1.55 eV and the excitation intensity was $2.4 \times 10^{19}$ photons cm$^{-3}$. With a pump polarization parallel to the stacking axis, a large change of the reflectivity is observed and corresponds to a transition from an insulator to a metallic phase, while no change is observed with perpendicular polarization.

b) Excitation polarization dependence on the reflectivity change. The angle is defined as the angle between the pump light polarization and the stacking axis. The reflectivity change dramatically decreases as the angle increases. Phase conversion is strongly correlated to the pump polarization (inset).

This experiment was performed under the same conditions but changing the pump polarization from parallel to perpendicular to the EDO-TTF stacking axis. No reflectivity change was observed with regards to the incertitude of the measure (figure 4a). Using a different setup, the evolution of the reflectivity change was studied as a function of the angle between the pump light polarization and the stacking axis (figure 4b). The maximum efficiency is reached when the pump polarization is parallel to the stacking axis of the molecules while only 10% efficiency is obtained for a perpendicular to stacking axis polarization (inset, figure 4b and also [11]). Thus to achieve a strong phase conversion, it is fundamental to excite with a laser polarization parallel to the stacking axis.

5. Conclusion

These X-ray diffraction results present the first order M-I phase transition around 280K associated with a thermal hysteresis of 4.5K in (EDO-TTF)$_2$PF$_6$. The coexistence of insulating and metallic domains was evidenced by the appearance of bragg peaks of both phases in the hysteresis. The metallic phase was photoinduced with a rather low excitation at 100 K and with a polarization parallel to the stacking axis. At the present stage, this photoinduced phase transition is a wonderful example of the fastest switching of macroscopic properties of a molecular material (insulator to metal). This phase switching on these time scales is impossible to achieve using conventional techniques playing on external fields like temperature, pressure, electric field. This opens a new area for organic conductors...
where a rather weak light excitation can control, with 1ps response time, a molecular phase switching. In the framework of photo-induced phase transitions, this family of crystals becomes an attractive candidate for applications in molecular devices.

References
[1] Nasu K 2004 *Photoinduced phase transitions* (Singapore: World Scientific)
[2] Ota A, Yamochi H and G. Saito 2002 *J. Mater. Chem.* **12** 2600
[3] Ota A, Yamochi H and Saito G 2003 *Synth Met* **135-136** 643-644
[4] Aoyagi S 2004 *Angew. Chem. Int. Ed.* **43** 3670-3673
[5] Chollet M, Guérin L, Uchida N, Fukaya S, Shimoda H, Ishikawa T, Matsuda K, Hasegawa T, Ota A, Yamochi H, Saito G, Tazaki R, Adachi S, Koshihara S 2005 *Science* **307** 86-89
[6] Chollet M, Guérin L, Uchida N, Fukaya S, Ishikawa T, Koshihara S, Matsuda K, Yamochi H, Ota A and Saito G 2005 *Journal of Luminescence* **112** 275-278
[7] Ushida N, Koshihara S, Ishikawa T, Ota A, Fukaya S, Chollet M, Yamochi H and Saito G 2004 *J. Phys. IV France* **114** 143-145.
[8] Saito K, Ikeuchi S, Ota A, Yamochi H and Saito G 2005 *Chem. Phys. Lett.* **401** 76-79
[9] Drozdova O, Yakushi K, Ota A, Yamochi H and Saito G 2003 *Synth Met* **133-134** 277-279
[10] Drozdova O, Yakushi K, Yamamoto K, Ota A, Yamochi H, Saito G, Tashiro H and Tanner D B 2004 *Phys. Rev. B* **70** 075107
[11] Chollet M, Guérin L, Uchida N, Fukaya S, Ishikawa T, Koshihara S, Matsuda K, Yamochi H, Ota A and Saito G 2005 “Ultrafast Phenomena XIV” in *Springer Series of Chemical Physics* **79** 771