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# Search for the Photo-Induced Hidden Phase in Inorganic and Organic Systems

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We review the dynamical behavior of strongly electron–lattice (orbital) coupled system induced by photo--excitation of fs laser pulse. By virtue of the femtosecond (fs) spectroscopy and picosecond (ps) time-resolved X-ray diffraction measurements, we demonstrate that the photo-irradiation creates new ordered state so called as "hidden phase" which can never be realized under thermo-equilibrium condition. This exotic phase commonly plays the key role for realizing the gigantic photo-induced changes in optical properties of inorganic and organic electron–lattice strongly coupled systems.

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#### 1. Introduction

It is well known that the microscopic lattice structure of solid under thermo-equilibrium condition governs the nature of materials by virtue of the cooperative interactions among constituents. Perovskite manganese oxides such as Pr<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub> (PCMO), Nd<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> (NSMO) and organic charge transfer (CT) salts which show charge ordering at low temperature have been classified as strongly charge-lattice-spin correlated materials. They are typical examples which show the exotic structural phase transitions coupled with changes in magnetic, dielectric and conductive properties. Even if we leave the concept of static structure under thermo--equilibrium condition, dynamical and gigantic changes in various properties may be realized in this class of materials as a result of fluctuation and/or transient change in lattice structure governed by external stimulations via cooperative interaction [1-3]. As expected, strongly lattice-spin-charge correlated materials such as manganites and organic CT salts really show the cooperative phenomena accompanied with gigantic changes in conductivity, optical and magnetic properties induced by weak photo-excitation [4].

The origin of observed exotic photo-response in manganites and CT salts have been commonly assigned as a phase conversion from charge ordered (CO) insulator (I) to metallic (M) phase based on the spectroscopic and conductive studies, strongly suggesting an important role of transient lattice structure [5, 6]. This exotic photo--induced phenomenon is named as a photo-induced phase transition (PIPT) and it is attracting many researchers due to their highly efficient and ultrafast phase conversion process and potential application to photonic switching devices [1–3].

Here, we review the lately obtained experimental re-

sults which demonstrate that gigantic photo-induced changes in optical properties of the organic and inorganic crystals with CO can be commonly attributed to the appearance of a "new phase" [7, 8]. This phase cannot be realized under thermo-equilibrium condition and thus is classified as a hidden phase. Dynamical studies of optical and structural properties of (EDO-TTF)<sub>2</sub>PF<sub>6</sub> bulk crystal and NSMO thin film show unique natures of a hidden phase in charge–lattice–spin strongly coupled systems.

## 2. New CO phase induced by photo-excitation in organic CT crystals

 $(\text{EDO-TTF})_2\text{PF}_6$  is well known for three unique natures as follows (see schematics in Fig. 1) [9–11]: (1) the phase transition temperature from M phase to I one is high ( $T_c = 280$  K). (2) The CO in the low temperature I phase is (1001), which represents the order of  $D^+D^0D^0D^+$  (D = EDO-TTF), though normal CO pattern is (1010), and the EDO-TTF molecule is largely deformed in I phase. (3) In contrast, charge distribution is homogeneous (+0.5, +0.5, +0.5, +0.5) and EDO-TTF molecules are scarcely deformed in high temperature M phase.

The origin of these unique features has been attributed to its strong electron-phonon interaction. About eight years ago, ultrafast gigantic reflectivity change within 250 fs has been observed by photo-excitation in the low temperature phase and this reflectivity change was assigned to the photo-induced I-to-M phase transition [6]. However, it was revealed that the rather narrow photon energy region (1.2–2.0 eV) for optical probing and only the comparison with the spectrum change under thermal equilibrium were not enough to elucidate the photoinduced dynamics in this unique material. The expansion of the photon energy range (0.069 eV (18  $\mu$ m) to 2.1 eV (590 nm)) for probing reflectivity change with fs time resolution by virtue of the development of fs laser technology has made clear that electronic structure in

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Fig. 1. Schematic illustration of charge patterns in  $(\text{EDO-TTF})_2\text{PF}_6$  for low temperature phase (insulator phase with (1001) type charge order) and high temperature one (metallic phase with homogeneous charge distribution) along with the non-equilibrium photo-induced "hidden" state [6, 7, 9–11].

photo-induced state observed just after excitation is quite different from that for thermally induced M phase [7].

Figure 2a shows reflectivity spectra for I (black line) and M (dark line) phases and photo-induced state (black dots).



Fig. 2. (a) Static reflectivity spectra in the lowtemperature phase at 180 K and in the hightemperature phase at 290 K along with photo-induced reflectivity spectrum observed at 0.1 ps after photoexcitation under 1.58 eV excitation. The photo-induced spectrum was estimated from sum of doubled reflectivity changes ( $\Delta R/R$ ) and the spectrum in the LT phase. (b) Static and photo-induced optical conductivity spectra derived by the Kramers–Kronig transformation with interpolation, smoothing, and extrapolation [7].

Corresponding absorption spectra obtained by

the Kramers-Kronig transformation are plotted in Fig. 2b [7]. In I phase, three peaks due to CT excitation between EDO-TTF molecules was observed and all of them disappeared in M phase. However, in photo-induced phase observed just (120 fs) after excitation, gigantic optical spectral change occurs and the single band structure appears as shown in Fig. 2b. It clearly shows that the photo-induced state can never be attributed to the one similar to thermally induced M phase and strongly suggest the appearance of a hidden phase. To make clear the electronic origin of this transient state, theoretical study of the transient spectra by solving the time-dependent Schrödinger equation for the one-dimensional quarter-filled Peierls-Holstein--extended-Hubbard model has been developed [12]. As a result of it, we reached the conclusion that the photo-excitation of charge transfer from (1001) to (2000) creates the non-equilibrium (1010) charge order state due to the Coulomb interaction competing with electron-phonon coupling as schematically shown in Fig. 1 [7]. The observed (1010) order has not been realized in the phase diagram under thermo-equilibrium condition. From this point of view, this intermediate state can be classified as a typical example of a hidden phase in organic crystals.

### 3. X-ray identification of thermally inaccessible "photo-induced hidden" phase of manganite

An epitaxial thin film of NSMO (see Fig. 3) with thickness of 80 nm on a (011) surface of perovskite SrTiO<sub>3</sub> (STO) (NSMO/STO(011)) prepared by pulsed laser deposition exhibits the first-order orbital-ordered (OO) insulator (I) to metal (M) transition at  $T_{\rm IM}$  (= 180 K) [13, 14]. X-ray diffraction analysis reveals that this transition is associated with the appearance of uniform ordering of  $d_{x^2-y^2}$  orbital, which then changes into a charge-ordered phase with zigzag-type ordering of  $d_{3x^2-r^2}/d_{3y^2-r^2}$  orbitals (CO–OO) below  $T_{\rm CO-OO} =$ 160 K (see Fig. 4) [15, 16]. The shape of the  $e_{\rm g}$  orbital governs the structural distortions of MnO<sub>6</sub> octahedra, and thus the lattice parameters of NSMO/STO(011) can works as a sensitive probe of the change in  $e_{g}$  orbitals. Indeed, reflecting the structural change at  $T_{\rm IM}$ , a single Bragg diffraction peak of the M phase attributed to (004) $((004)_{\rm H} \text{ peak in Fig. 5a})$  splits into two peaks  $((040)_{\rm L} \text{ and }$  $(004)_{\rm L}$  peaks in Fig. 5b). Therefore, the *b*- and *c*-axis lattice constants and the profile of the (004) and (040)diffractions become a suitable probe for observing photoeffects on structural distortions of MnO<sub>6</sub> octahedra. In the present review, 80 nm NSMO/STO(011) thin film was subjected to time-resolved X-ray diffraction (TR--XRD; see Fig. 6) to observe the photo-induced change in the form of  $e_{\rm g}$  orbital's [8].

To observe the detailed lattice motion, time-resolved X-ray diffraction (TR-XRD) method is powerful tool [17]. Here, we utilized this method as shown in Fig. 6 and Fig. 7 shows different diffraction patterns (DDPs) in



Fig. 3. Schematic illustration of the lattice structure of perovskite manganese oxides  $Nd_{0.5}Sr_{0.5}MnO_3$  (NSMO).



Fig. 4. Schematic views of the orbital structure of NSMO/STO in high temperature (M) and low temperature (CO–OO) phases [15, 16].

which the diffraction peaks obtained under the respective conditions are plotted after subtracting the diffraction patterns at 100 K. Sample temperature was kept at 100 K and thus the NSMO is in CO–OO (I) phase before photo-excitation. The top curve in Fig. 7 is a hypothetical DDP obtained by converting 5% of the CO–OO phase at 100 K into the M phase at 180 K. It should be noted that the photo-induced DDPs in Fig. 7 (lower part) differ significantly from thermally induced one (upper part). The salient features are the complete absence of the diffuse peak profile located around Q = 6.58 Å  $^{-1}$  that signifies the growth of the metallic (M) clusters and also the lack of thermal broadening of the CO-OO peaks. The excitation photon density  $(0.8 \text{ mJ/cm}^2)$  was one photon per every 60 Mn ions, the enhanced metallic fraction reflects the cooperative nature of this photo-induced effect [8].

The experimental evidence shows that after the initial photo-excited state, the system falls into a new insulating state with a homogeneous and well ordered structure. Thermal effects in this phase are found to be minimal. No photo-induced conversion of the CO–OO (I) phase into the M phase occurs. Instead, photo-excitation of the CO–OO (I) phase induces the new phase, which is not accessible by thermal control of physical parameters, and thus can justifiably be termed a hidden state. It should be noted that while this hidden state is realized by slight,



Fig. 5. (a) X-ray diffraction intensity profile (solid circles) near the (004) reflection of NSMO in high-temperature phase (labeled  $(004)_{\rm H}$ ) observed at 180 K. (b) The  $(004)_{\rm H}$  peak splits into two peaks in the low-temperature phase as indicated by the peaks labeled  $(040)_{\rm L}$  and  $(004)_{\rm L}$  measured at 100 K. *Q* denotes the magnitude of the scattering vector. The solid lines in (a) and (b) are Lorentzian fits to the data after subtracting the contribution (broken gray line) from the (004) peak of the STO substrate [8].



Fig. 6. (a) Experimental setup for TR-XRD with a time resolution of 100 ps and (b) timing chart for the measurement. A circularly polarized laser beam with a wavelength of 800 nm (1.55 eV), a pulse width of 130 fs, and a repetition rate of 945 Hz was used to pump the sample. The X-ray energy was 15 keV ( $\lambda = 0.826$  Å). Details of the system for the TR-XRD measurement are presented in Ref. [17].



Fig. 7. DDPs for temperature (a) and photo (b) effects. For thermal effect, the diffraction pattern at 100 K is subtracted from those obtained at 180 K in a heating run without laser irradiation. photo-induced DDP was obtained by subtracting the diffraction pattern observed just before the laser pulse at  $\Delta t = -5$  ps from the one at  $\Delta t = 150$  ps after laser irradiation. The sample temperature was kept at 100 K during photo-excitation. Bars indicate statistical error [8].

homogeneous, and cooperative changes in the lattice on a subpicometer scale, it induces a large change in optical properties and hence in the electronic structure [8]. This result also demonstrates that a hidden state in chargeorbital coupled systems is a key concept for designing photo-switching materials free from thermal effects and damage due to structural change after photo-excitation.



Fig. 8. Illustration contrasting the orbital character of a photo-induced CO–OO phase ("hidden" state) with that of a thermally induced M phase converted from the initial CO–OO phase (ground state). The degree of photo-induced change in the orbital polarization is exaggerated for clarity [8].

A model calculation for a ground state shows a 0.3% increase in the ratio of  $d_{3z^2-r^2}/(d_{3x^2-r^2}$  or  $d_{3y^2-r^2})$  under 0.8 mJ/cm<sup>2</sup> excitation based on the observed structural changes [18, 19]. Combining all the observations, Fig. 8 shows an illustration of the different orbital characteristics of a photo-induced hidden state and a thermally induced phase.

## 4. Conclusions

We have demonstrated that the new photo-induced state which can be named as a hidden state in (EDO--TTF)<sub>2</sub>PF<sub>6</sub> crystals and NSMO/STO(011) emerges via the relaxation process from photo-excited initial state. Hidden phase has been discussed mainly from the theoretical view point until today [2]. However, by virtue of the progress in quantum beam technology, various types of charge and orbital patterns are waiting to be discovered for various applications through collaboration of TR-XRD and time-resolved spectroscopic studies, especially on fs time scales.

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