Early history and theoretical problems of photo-induced structural phase transitions

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Abstract. Early history and theoretical problems of photo-induced structural phase transitions are reviewed, in connection with various materials involved in this phenomenon. We also review new measurement methods that exceed the conventional visible photon by photon spectroscopy.

1. Introduction

Large varieties of materials are now around us. These materials are such ones, that few kinds of macroscopic numbers of atoms or molecules are condensed with a definite composition ratio. While, without changing this chemical composition, a material can take various phases from gaseous and liquid phases to crystalline ones, as temperature decreases from high to low. Even at low temperatures, a material can take various crystalline phases, whose lattice structure and electronic state change as temperature decreases. However, all these states are so-called equilibrium phases, in the sense that the free energy of each state takes its global minimum at each temperature.

Let us now proceed to non-equilibrium phases generated from an equilibrium one by some external excitations or stimulations. Usually, these states are transient ones having higher energies than the equilibrium one, but, depending on the way of stimulations or excitations, we can get much more varieties of states, even if the starting equilibrium phase is same. They also surely relax down to the starting equilibrium one after a period of time. However, if they are locally stable state, in the sense that their free energy takes local minima separated from the global one by substantial energy barriers, the time required for the relaxation will be long. In that case, we can complete necessary observations to determine their characteristics within this period of time. Hence, such a long-lived locally stable non-equilibrium phase is effectively same as the equilibrium ones.

Very recently, there discovered a new class of solids, which, being shone by only a few visible photons, become pregnant with a macroscopic excited domain that has new structural, electronic and even magnetic orders, quite different from the starting ground state. This phenomenon is called “photo-induced phase transition” (PIPT) and we can generate new long-lived locally stable macroscopic non-equilibrium phases, through the excitations or stimulations by a few visible photons. The purpose of this paper is to review its early history, new measurement methods and theoretical problems of photo-induced structural phase transitions [1, 2, 3].
2. Early history and present

The photo-induced phase transition study has firstly started by using an organic charge transfer crystal, Tetrathiafluvalene-p-Chloranil. Both Tetrathiafluvalene (TTF) and p-Chloranil (CA) are planar organic molecules, and their crystal has a quasi 1-d chain like structure, in which these two molecules are alternately stacked along this 1-d chain axis.

In the true ground state of this crystal at absolute zero of temperature, both TTF and CA become a cation and an anion, respectively, and make a dimer with each other. This is called the ionic (I- ) phase. On the other hand, we also have the neutral (N- ) phase, in which neutral TTF and CA are stacked alternately without dimerization. This is the accidentally pseudo-degenerate false ground state, and at absolute zero of temperature, it is just above the ionic true ground state.

Keeping this material in the low enough temperature, but shining a strong laser light of about 0.6eV~2.3eV on to it, we can generate the N-domain even in the ionic true ground state. This change was experimentally confirmed by the change of the optical reflectivity. In the spectral shape of original optical reflectivity of the TTF-CA crystal at the I-phase, we can see a characteristic peak structure at around 3eV, and this peak corresponds to an intra-molecular electronic excitation of $^+$ TTF. Hence its intensity can be used as a macroscopic indicator for the presence of the cationic TTF molecules in this crystal.

When this crystal is shone by a light with an energy of 2.3eV, we can get a relative change of this reflectivity as shown by Koshihara [4]. The intensity of the aforementioned peak is clearly seen to decrease. It means that a macroscopic number of neutral TTF molecules (N-domains) have been generated in the I-phase. This is nothing else but the PIPT. From this decrease of the peak intensity, we can determine that the domain is composed of about 200 ~ 1000 neutral pairs, and it can last for about $10^{-7}$ second [4].

At present, however, this type PIPT study has been extended to many kinds of materials, not only to other organic charge transfer crystals, but also to various metal complex crystals, Prussian blue analogues, and even to Perovskite type metal oxides [1, 2, 3].

3. New measurement methods

The standard technique to observe or to measure these PIPT phenomena has been the so-called modulation spectroscopy, in which another visible photon is shone to detect a spectroscopic change between before and after the transition. Very recently, however, we have succeeded to observe the photo-induced structural phase transition more directly by using the time-resolved x-ray diffraction. Using the TTF-CA crystal mentioned before, Collect has succeeded to detect the PIPT from the N-phase to the I-phase at 93K, by the time-resolved x-ray diffraction method [5].

More over, the STM is also devised, in connection with the photo-induced structural phase transition from the graphite to the diamond [6], as well as the electron diffraction method [7].

4. Theories for PIPT

Theoretical study for the PIPT was undertaken by Toyozawa, as multi-phonon instabilities of an electron-hole pair across the band gap of insulating solids [8]. While, taking the 1-d localized electron-phonon coupled system, Hanamura has clarified the occurrence condition for the diacetylene photo-polymerization [9]. This localized model was afterwards extended more systematically, within the classical and adiabatic approximations [10], and also by including the quantum and diabatic effects [11] of the electron–phonon coupling.

Theories for the PIPT in itinerant many-electron systems are now divergent, and reviewed by Yonemitsu [3] in detail. They involve, the Hubbard-Peierls models, the DMFT, the exact
diagonalization and the classical time-dependent methods. These theoretical problems will be
discussed earnestly in the third international conference of the PIPT (November 11-15, 2008, Osaka
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