Theory of Photoinduced Phase Transitions

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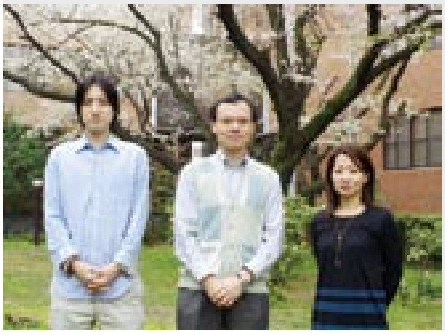

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Photoirradiation of materials usually creates electrons and holes, which are often accompanied by local structural deformation. With the help of cooperativity, the electronic and/or structural deformation can proliferate to change the physical property such as conductivity, permittivity, and magnetic susceptibility. The resultant nonequilibrium phase may not be reached by changing temperature or pressure because the energy of a photon is much higher than thermal energies. Our theoretical researches are focused on the mechanisms and dynamics of photoinduced phase transitions, how they are controlled, and how the photoinduced electron-lattice states are different from those which are realized in thermal equilibrium.[1]

1. Growth Dynamics of Photoinduced Domains in Charge-Ordered Conductors[2,3]

We focus on quasi-two-dimensional quarter-filled-band charge-ordered insulators, θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ and α-(BEDT-TTF)$_2$I$_3$, where quite different photoinduced melting dynamics are observed. To elucidate such dynamics of initially quite similar, “horizontal-stripe” charge orders, we theoretically study photoinduced evolution of the wave functions in extended Peierls-Hubbard models on anisotropic triangular lattices. The exact many-electron wave function coupled with classical phonons is used for 12-site systems, and the unrestricted Hartree-Fock approximation is used for 144-site systems. These charge orders are stabilized by both Coulomb repulsion and electron-lattice interactions. Their relative importance is different between the two materials.

In θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, the high-temperature metallic phase has a crystal structure with a high symmetry so that different charge-order patterns are nearly degenerate. At low temperatures, a relatively large lattice distortion emerges as molecular rotations (Figure 1, left panel), lifting the degeneracy among these patterns. The lattice stabilization energy is consequently large, so that a high photoexcitation density is required for the melting. Because each hole-rich stripe is stabilized by uniform molecular rotation, a photoinduced metallic domain created by local photo- excitation grows in a quite anisotropic manner (Figure 2, left panel). The photoinduced charge dynamics shows a complex behavior owing to a large number of nearly degenerate eigenstates.

In α-(BEDT-TTF)$_2$I$_3$, the high-temperature metallic phase has a crystal structure with a low symmetry so that charge disproportionation already takes place from kinetic origin. At low temperatures, a small lattice distortion (Figure 1, right panel) is sufficient to stabilize the charge order. The lattice stabilization energy is small, and a low photoexcitation density is sufficient to melt the charge order, producing a metallic phase. Because each hole-rich bond is locally stabilized, a photoinduced metallic domain created by local photoexcitation grows isotropically (Figure 2, right panel), *i.e.*, in any direction of the conducting layer. Thus, a very large metallic domain is finally photogenerated. The photoinduced charge dynamics shows a coherent oscillation when resonantly excited.

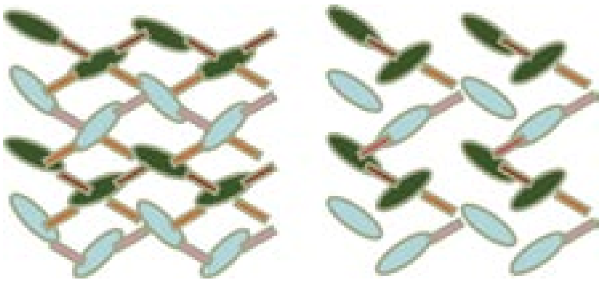

Figure 1. Schematic molecular arrangements in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ (left) and α-(BEDT-TTF)$_2$I$_3$ (right). The ellipses with dark and bright colors represent hole-rich and hole-poor molecules, respectively. Note the angles of ellipses. The rectangles with dark, intermediate, and bright colors correspond to large, intermediate, and small transfer integrals, respectively.

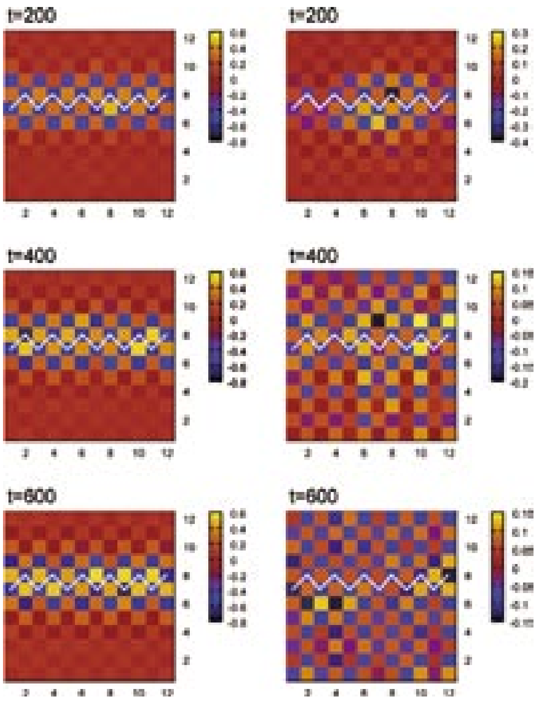

Figure 2. Charge densities at different times, from which those before photoexcitation are subtracted.[2] The left and right panels show θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ and α-(BEDT-TTF)$_2$I$_3$, respectively. The squares indicate molecules, and the white lines hole-rich stripes.

2. Quantum Electron–Vibration Interference in Photoinduced Insulator–Metal Transition

As described above, a photoinduced insulator-to-metal transition is realized in α-(BEDT-TTF)$_2$I$_3$. In reality, the transition is achieved in two stages: An ultrafast one consisting of mainly electronic processes and a slow one consisting of domain processes responsible for the critical slowing down. Although the latter stage can be described in principle by statistical mechanics, the former stage directly reflects interactions among electrons and interactions between electrons and phonons. The latest experimental technique allows us to observe such early-stage dynamics.

Here, it is important to consider electron–molecular-vibration (EMV) couplings. Charge transfers between neighboring molecules are governed by intermolecular transfer integrals. Their magnitudes are about 0.1 or 0.2 eV. The energy range of C=C stretching vibrations inside a molecule is also 0.1 to 0.2 eV. Thus, they can interfere with each other (Figure 3). Then, we theoretically study photoinduced evolution of the wave function in an extended Holstein-Peierls-Hubbard model. The exact many-electron–phonon (molecular vibration) wave function coupled with classical lattice phonons is used for 8-site systems.

Photoexcitation directly oscillates an electron back and forth between neighboring molecules. It excites a molecular vibration through the EMV coupling. They are initially in phase. Soon, their motions become out of phase, causing destructive quantum interference (Figure 4, 50 to 100 fs).

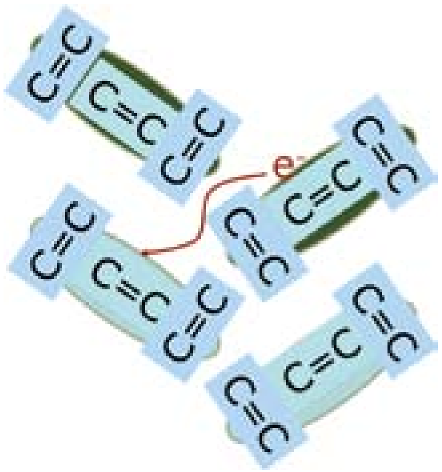

Figure 3. Schematic illustration of electron–molecular-vibration coupling.

After that, the electronic motion is synchronized with the slower motion of molecular vibrations (Figure 4, after 100 fs) and finally dephased. In reality, there are several modes of molecular vibrations with different energies and coupling strengths. However, the quantum interference obtained above qualitatively simulates the experimentally observed, early-stage dynamics.

From this analysis, the EMV coupling turns out to stabilize the charge order as well as the intersite Coulomb repulsion. The relative importance of molecular vibrations and lattice phonons depends on the timescale of observation. The former is important at the early stage, while the latter is important at the later stage.

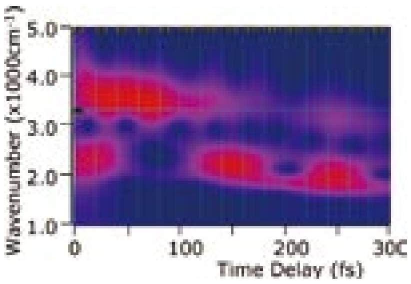

Figure 4. Wavelet transform of photoinduced charge-density modulation.

References

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2) Y. Tanaka and K. Yonemitsu, *J. Phys. Soc. Jpn.* **79**, 024712 (8 pages) (2010).
3) S. Miyashita, Y. Tanaka, S. Iwai and K. Yonemitsu, *J. Phys. Soc. Jpn.* **79**, 034708 (9 pages) (2010).