11 Theory

11-1 A Dynamics Study of Ferroelectric Domains in Photo-Excited Three-Dimensional SrTiO$_3$

Photo-induced dielectric enhancement and photo-conductivity has been reported in SrTiO$_3$ [1-3]. The phase transitions were ascribed to photo-induced ferroelectric domains in the crystal and interpreted within a dual electron and phonon coupling model [4]. In the model the odd parity phonon modes were assumed to be of sextic anharmonicity, and to couple with the photo-excited electron in a quadratic manner. In contrast the even parity phonon modes showed harmonicity, coupling linearly with the photo-excited electron. The microscopic origin of the ferroelectric domains was shown to be superparaelectric (SPE) large polarons, shown schematically in Fig. 1, where the vacant circles denote the bare phonons, and the circles within the dashed rectangular denote the phonons which couple with the electron. These phonons are greatly softened due to the electron-phonon coupling, and thus exhibit obvious polarization. However, the previous study [4] simply considered a static picture, whereas the dynamical processes of the formation of the ferroelectric domains in the crystal is very important. The current work addresses this problem.

We employ the molecular dynamics (MD) [5] method to investigate the dynamics of the electron-phonon coupling system, with the initial state being the Frank-Condon state following excitation of a valence band electron to the conduction band.

Within this approach we trace the evolution process of the lattice relaxation. Using a size of $5 \times 5 \times 5$ for the system and $21 \times 21 \times 21$ for the total crystal, we ob-

tain the energy evolution curve shown in Fig. 2 for the electron-phonon coupling system. The curve consists of 8000 1 fs steps. As can be seen in the figure, the total energy is conserved with time while the energy of the system decays gradually. After about 2000 fs, the coupling system evolves into a stable and shallow gap state about 0.003 eV lower than the bottom of the conduction band. In the gap state, the electronic wave function has a quite even distribution within the system in our numerical results [5]. That is, the electron is loosely bound within the lattice region of the system, and is thus a large polaron, and equivalent to a ferroelectric domain. During the relaxation the electron first induces lattice vibrations in the electron-phonon coupling system. However, the energy contained in the crystal lattice is prone to be evenly distributed in order to achieve maximum entropy, and thus the vibrations gradually spread to the whole crystal – an example of crystal damping.

From the above discussion, it is clear the relaxation of the ferroelectric domain in the 3-dimensional SrTiO$_3$ crystal is an ultrafast process, occurring on a picosecond timescale. It should be mentioned that the classification of the relaxation as an "ultrafast process" originates from two approximations. The first approximation claims that the electron-phonon interaction is an ultrafast process. As a result, in each dynamic step the electron exchanges energy with the lattice transiently. The second approximation claims that the energy exchange among the adjacent lattice sites is also an ultrafast process. The two approximations are automatically met in the nonadiabatic evolution process of the electron-phonon coupling system under low temperature conditions. Our calculations show, as expected, that the transition probability between various eigen-states is very small for zero temperature conditions. This small transition probability actually gives rise to the dynamic system evolving almost along the adiabatic energy surface, providing the validity condition for the two above mentioned approximations.
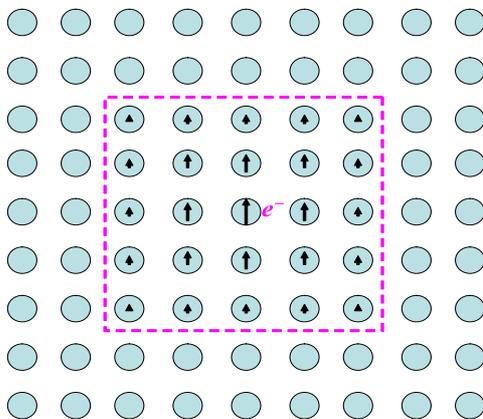

Figure 1
Schematic diagram of the SPE large polaron. The circles within the rectangular area represent polarons which couple with the excited electron.
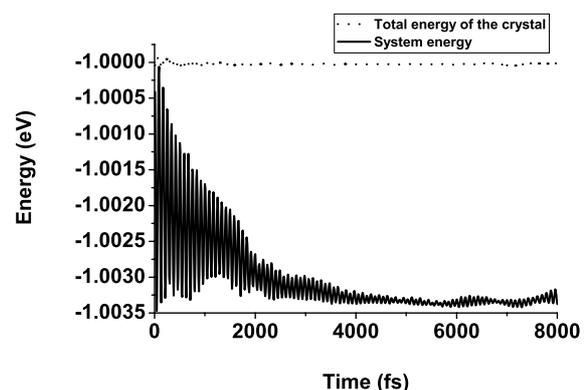

Figure 2
Energy evolution curve of the electron-phonon coupling system.

In conclusion, we have shown within the MD method that the relaxation of ferroelectric domains excited in SrTiO$_3$ with ultraviolet light is an ultra-fast process of picosecond order.

Y. Qiu[1,2] and K. Nasu[2,3,4] ([1]Zhejiang Normal Univ., [2]The Grad. Univ. for Adv. Stud., [3]KEK-PF, [4]JST-CREST)

References
[1] T. Hasegawa, S. Mouri, Y. Yamada and K. Tanaka, *J. Phys. Soc. Jpn.*, **72** (2003) 41.
[2] H. Katsu, H. Tanaka and T. Kawai, *Jpn. J. Appl. Phys.*, **39** (2000) 2657.
[3] M. Takesada, T. Yagi, M. Itoh and S. Koshihara, *J. Phys. Soc. Jpn.*, **72** (2003) 37.
[4] Y. Qiu, C.Q. Wu and K. Nasu, *Phys. Rev. B*, **72** (2005) 224105.
[5] Y. Qiu, K. Nasu and C.Q. Wu, *Phys. Rev. B*, **75** (2007) 064103.

11-2 The Quantum Domain Structure of Electronic Excitations Found in Ionic-Neutral Transition Materials –An Ultra-Fast Photo-Induced Phase Transition

Studies of photo-induced phase transitions – macroscopic changes in the properties of materials induced by the absorption of radiation – have entered into a new stage, focussing intensively on the fundamental aspects of excited-state dynamics. There are two important conceptual aspects – the lattice dynamics (the movement of the constituent atoms), and the pure electronic dynamics that accompanies the phase transitions. As can be expected, these different dynamics occur on different timescales. Lattice motion takes place on timescales longer than the periods of the relevant phonon modes (0.1 ps to 1 ps), whereas the electronic dynamics occurs on much faster timescales.

Modern techniques in optical physics have made it possible to study lattice dynamics in detail, and observations have been established of so-called coherent phonons. The technique is still under development, and there is great hope for the direct detection of electronic dynamics using the lasers and synchrotron radiation light sources of the future.

Motivated by these developments, in this study we discuss the pure electronic transitions which are expected for the quasi-one-dimensional organic solid TTF-CA. This system exhibits a neutral (N) -ionic (I) phase transition [2]. The N ground state is illustrated in Fig. 3(a). Upon photo-excitation of the N ground state a sequential progress of electronic excitations toward the I phase is expected, as depicted in Fig. 3(b)-(d). These one-by-one movements of electrons are considered to
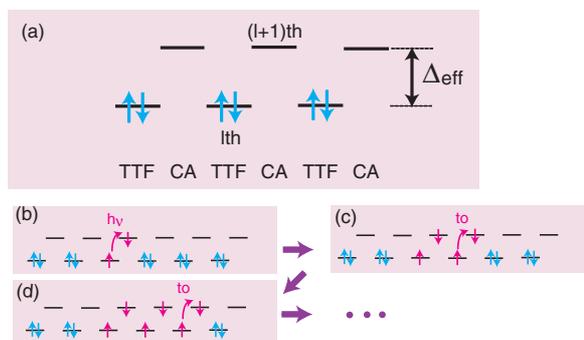

Figure 3
Schematic figure explaining the pure electronic photo-induced phase transitions expected for TTF-CA. (a) Electron distribution in the neutral ground state. (b)-(d) The process of domain formation. A photoexcitation represented by hν is followed by successive electron transfers of which the matrix element is to.

be coherent in the sense that they are free from lattice movements. We therefore expect a very rapid process. This feature directs us to another viewpoint; the observation of such domain formations through energy spectroscopy, since the states of the I domain are now well defined as excited states. The red lines of Fig. 4 show optical conductivity spectra in the visible-light region calculated using an extended Hubbard model with a site-alternate potential. The panels are arranged in such a way that the quantum transition point (QTP) between the N and I phases is approached going from bottom-right to top-left. The spectrum drastically changes as the QTP is approached. Far from the QTP (bottom-right), the spectrum consists of a single peak due to an ordinary exciton. The spectrum is strongly deformed as the QTP is approached, becoming dominated by domain excitations (top-left). The blue lines of Fig. 4 show $n_{ex}(\omega)$, the number of excited electrons. The fact that $n_{ex}(\omega)$ becomes large near the QTP backs up the interpretations made above.

In the rest of this article, we claim that the domain excitation feature can also be observed using synchrotron radiation. By using high-energy radiation, it is possible to analyze momentum dependence. We thus propose to study the dispersion relation of the domain. In Fig. 5(a), calculated results for inelastic X-ray scattering are shown. We have assumed the same model Hamiltonian as that used for the results shown in Fig. 4, and evaluated the density-density correlation function. The features at $k = 0$ are almost the same as those seen in Fig. 4, while the features at $k = \pi/2$ are qualitatively different, with the structure of the domain excitations missing. This peculiar property is explained within the framework of an effective model - the "domain model" [1]. In Fig. 5(b), we show the domain dispersions derived using this model. All of the dispersions are those of a single domain, with different quantized sizes. Although this model is much simplified, the obtained intensities and dispersion features are consistent with the overall features seen in Fig. 5(a). In particular, the vanishing domain contributions at $k = \pi/2$ are based on the suppression of domain-domain conversion by a phase can-
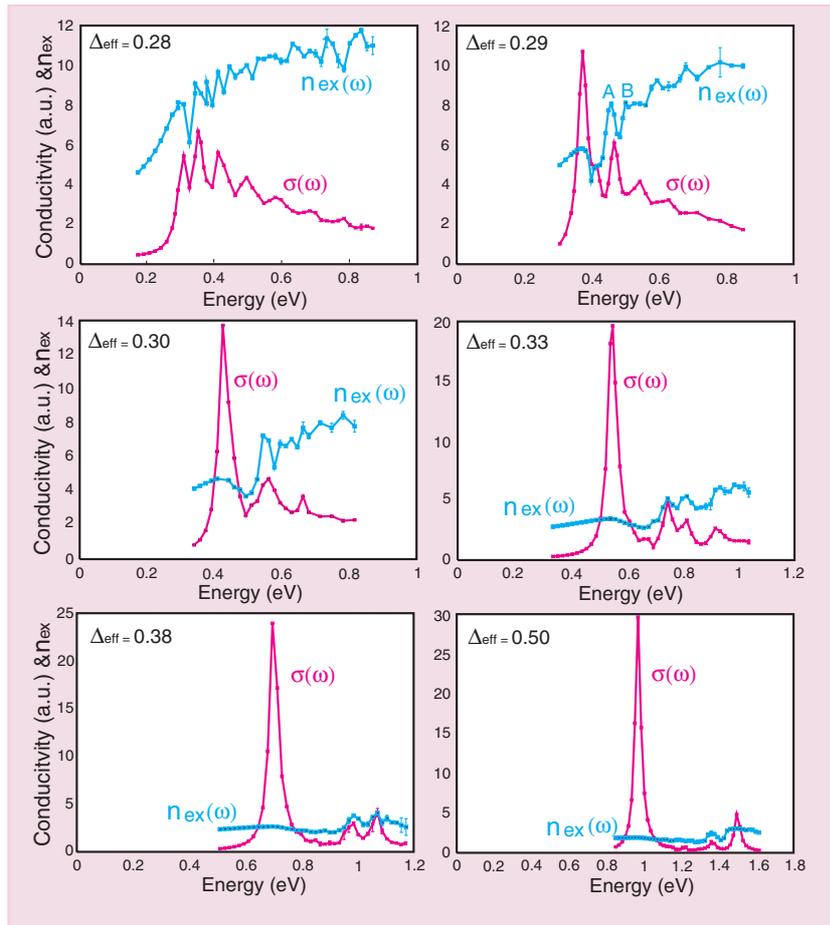
Figure 4
Optical conductivities $\sigma(\omega)$ and the number of electron excitations $n_{ex}(\omega)$, within the neutral phase. Δ_{eff} is the control parameter, and the quantum transition point is located around $\Delta_{eff} = 0.27$ eV.
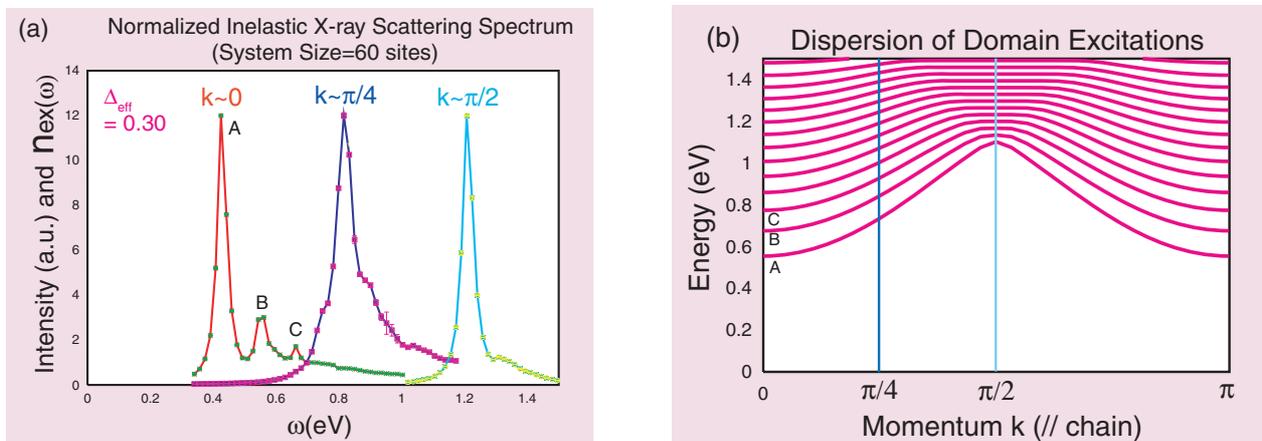

Figure 5
(a)Inelastic X-ray scattering spectra at three *k* points. (b) Possible dispersions of domain excitations derived from a domain model. The labels A-C indicate the domain excitations that appear explicitly in both figures.

cellation at this point. We also remark that similar features can also be observed using momentum-resolved photoemission. Our preliminary results confirm this idea but suggest that the involved processes are more complicated, possibly by coupling with spin degrees of freedom. Further studies are currently in progress towards the complete understanding of this novel topic – domain formations coupled with spin rearrangements.

K. Iwano (KEK-PF)

References
[1] K. Iwano, *Phys. Rev. Lett.*, **97** (2006) 226404.
[2] For a general review, see S. Iwai and H. Okamoto, *J. Phys. Soc. Jpn.*, **75** (2006) 011007.