I-L Photoinduced Phase Transitions in Molecular Materials

Photoirradiation may create electrons, holes or excitons, which are often accompanied by local structural deformation. Sometimes it causes spatially large structural transformations with the help of cooperativity possessed by interacting electrons and molecules. Thus, a nonequilibrium phase can be generated, which may not be reached by simply changing temperature or pressure because the energy of a photon is much higher than thermal energies. Such photoinduced phase transitions have been studied extensively, both experimentally and theoretically. Thanks to the great progress in laser spectroscopy techniques, charge and lattice dynamics are being clarified in many molecular materials on different time scales including ultrafast and/or coherent dynamics. Now we need to treat relevant itinerant-electron models, whose transfer integrals give transition amplitudes. This is in contrast to stochastic dynamics in classical statistical models, where transition probabilities are determined by the Boltzmann factors at finite temperatures.

I-L-1 Interchain Coupling Effects on Photoinduced Phase Transitions between Neutral and Ionic Phases in an Extended Hubbard Model with Alternating Potentials and an Electron-Lattice Coupling

YONEMITSU, Kenji

[*Phys. Rev. B* **73**, 155120 (7 pages) (2006)]

Dynamics of ionic-to-neutral and neutral-to-ionic phase transitions induced by intrachain charge-transfer photoexcitations are studied in a quasi-one-dimensional extended Hubbard model with alternating potentials and an electron-lattice coupling for mixed-stack charge-transfer complexes. For interchain couplings, we use electron-electron interactions previously estimated for TTF-CA. Photoexcitation is introduced by a pulse of oscillating electric field. The TDHF approximation is used for the electronic part, and the classical approximation for the lattice part. In the ionic-to-neutral transition, the transferred charge density is a strongly nonlinear function of the photoexcitation density, which is characterized by the presence of a threshold. With substantial interchain couplings comparable to those in TTF-CA, the interchain correlation is strong during the transition. Neutral domains in nearby chains simultaneously grow even if their nucleation is delayed by reducing the amplitude of the electric field. With weaker interchain couplings, the growing processes are in phase only when the amplitude of the electric field is large. Thus, the experimentally observed, coherent motion of a macroscopic neutral-ionic domain boundary is allowed to emerge by such substantial interchain couplings. In the neutral-to-ionic transition, by contrast, the transferred charge density is almost a linear function of the photoexcitation density. Interchain electron-electron interactions make the function slightly nonlinear, but the uncooperative situation is unchanged and consistent with the experimental findings.

I-L-2 Inter-Chain Coulomb-Lattice Relaxation and Multicriticality in Charge Transfer Organic Complexes

KISHINE, Jun-ichiro[1]; OHARA, Tomoaki[1]; LUTY, Tadeusz[2]; YONEMITSU, Kenji
([1]Khushu Inst. Tech.; [2]Tech. Univ. Wroclaw)

[*Synth. Met.* **154**, 257–260 (2005)]

We discuss the neutral-to-ionic phase transition and the emergence of multi-criticality in the quasi-one-dimensional charge-transfer salt TTF-CA under pressure. We stress that subtle interplay of Coulomb and lattice processes may be quite sensitive to pressure. Emergence or disappearance of the multi-critical point in a series of charge-transfer salts is understood through this interplay. What's behind is coexistence and coupling of non-symmetry-breaking and symmetry-breaking order parameters.

I-L-3 Quantum Paraelectricity near the Neutral-Ionic Critical Point

YAMASHITA, Yasufumi; YONEMITSU, Kenji

In a series of organic charge-transfer complexes DMTTF-QBr_nCl_{4-n}, the neutral-ionic (NI) phase transition is observed in the chlorine rich complexes for $n < 2.1$. The neutral ground state of DMTTF-QBr_4 is destabilized by applying hydrostatic pressure P, and the NI transition emerges when P exceeds P_c where $T_c = 0$; so-called the quantum critical point (QCP). In the vicinity of the QCP, the dielectric permittivity in the neutral phase follows the Barrett formula characteristic of quantum paraelectricity, which probably originates from charge-transfer fluctuations. In the present study, we have phenomenologically dealt with the NI phase transition by a quantum version of the Blume-Emery-Griffiths (QBEG) model. Applying the mean-field approximation to the QBEG model, the magnitude of ferroelectricity and ionicity as well as the dielectric permittivity are calculated with changing P. The paraelectric ground state with a finite ionicity is realized with the Barrett-type permittivity, which is consistent with the experimental results. In addition, the calculated permittivity agrees well with that of DMTTF-QBr_4 under various pressures including the ionic phase. What we found is that the quantum dipole-flipping term is indispensable to reproduce the experimental results within our model. Therefore, it is highly suggested that charge transfer fluctuations due to the quantum tunneling allow a finite ionicity even in the neutral phase, which realizes the quantum paraelectric ground state near the quantum critical point.

I-L-4 Dynamics of Photoexcited States in One-Dimensional Dimerized Mott Insulators

MAESHIMA, Nobuya[1]; YONEMITSU, Kenji
([1]IMS and Tohoku Univ.)

[*Phys. Rev. B* **74**, 155105 (11 pages) (2006)]

Dynamical properties of photoexcited states are theoretically studied in a one-dimensional Mott insulator dimerized by the spin-Peierls instability. Numerical calculations combined with a perturbative analysis have revealed that the lowest photoexcited state without nearest-neighbor interaction corresponds to an inter-dimer charge transfer excitation that belongs to dispersive excitations. This excited state destabilizes the dimerized phase, leading to a photoinduced inverse spin-Peierls transition. We discuss the purely electronic origin of midgap states that are observed in a latest photo-excitation experiment of an organic spin-Peierls compound, K-TCNQ.

I-L-5 Charge Ordering in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$: Cooperative Effects of Electron Correlations and Lattice Distortions

MIYASHITA, Satoshi[1]; YONEMITSU, Kenji
([1]IMS and Tohoku Univ.)

We investigate combined effects of electron correlations and lattice distortions on the charge ordering (CO) in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ theoretically by the two-dimensional extended Hubbard model at 1/4-filling. It is well known that this material undergoes a phase transition from the high-symmetry to the low-symmetry structure by lowering temperature. The ground state is an insulator with the horizontal-stripe CO along t_{p4} (HCO-t_{p4}). The importance of long-range electron-electron interactions is well recognized and the mechanism for stabilizing the HCO-t_{p4} has been argued mainly on the basis of the low-symmetry structure. Because the lattice distortions are coupled with the electron system, giving rise to the first-order transition sensitive to the crystal structure, electron-phonon interactions are also important. Then, by means of the exact diagonalization, we have calculated the ground-state energy and local density of holes by adopting both electron-electron and electron-phonon couplings on the basis of the high-symmetry structure. For electron-phonon couplings, we consider three kinds of distortions: displacements along the *c*-direction (s_c), those along the *a*-direction (s_{p1}) and molecular rotations (s_{p4}), leading to linear modulations in the respective transfer integrals. The s_c-dependence of the local density of holes demonstrates that the coupling s_c induces the HCO-t_{p4}. The coupling s_{p4} also induces this CO, though s_{p1} does not. In this salt, the effects of displacements along the *c*-direction and molecular rotations are stronger than those along the *a*-direction. Thus, electron-phonon interactions are crucial to stabilize both the HCO-t_{p4} and the low-symmetry structure in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$.

I-M Collective Transport through Metal-Insulator Interfaces

Molecular materials are used in many device structures. Charge transport is always through an interface between two materials with different electronic states and work functions. In field-effect transistors fabricated on an insulating material with coherent charge transport under electric fields, the insulator-(source/drain) electrode interface barrier potentials, known as Schottky barriers, play an important role. For band insulators, the Schottky barriers indeed govern the current-voltage characteristics. Quite recently, ambipolar characteristics are found in field-effect transistor device structures based on organic single crystals of a quasi-one-dimensional Mott insulator. Thus, we need to take correlation effects into account in dealing with charge transport through electrostatic potentials that originate from the long-range Coulomb interaction.

I-M-1 Mechanism of Ambipolar Field-Effect Transistors on One-Dimensional Organic Mott Insulators

YONEMITSU, Kenji

[*Proc. Pacifichem* (2005) in press]

The characteristics of a field-effect transistor (FET) fabricated on a crystal of an organic charge-transfer complex depend on the electronic state of the crystal. Ambipolar characteristics are observed for Mott insulators, while unipolar ones for band insulators. We study them in one-dimensional models of electrons. The Hubbard model for a Mott insulator is attached to the tight-binding model for metallic electrodes. We solve the Poisson equation and add its solution for the electrostatic potential to these models in order to reproduce Schottky barriers at the interfaces. We use both the mean-field approximation and the Lanczos exact-diagonalization method in solving the time-dependent Schrödinger equation to obtain essentially the same result. Mott insulators show the ambipolar FET characteristics irrespective of the difference between the work function of the channel and that of the metallic electrodes. In order to exclude the ambiguity introduced in the one-dimensional modeling of the effect of the gate electrode and to allow the direct observation of the correlation between the electronic state in the channel and that at the interfaces, we have removed the gate electrode and employ different metals for the electrodes among which only one interface possesses a large work-function difference. In this case, the current-voltage characteristics are almost anti-symmetric for Mott insulators and very asymmetric for band insulators. These results are also consistent with recent experiments by T. Hasegawa and coworkers. The characteristics for Mott insulators are again caused by the correlation between the electronic state in the channel and that at the interface.