I-R Multicritical Behavior of Charge-Transfer Complexes

In the mixed-stack organic charge-transfer complex, TTF-CA, neutral-ionic and dimerization-induced ferroelectric phase transitions are observed. At ambient pressure, they occur simultaneously and discontinuously. Under high pressure, these transitions take place at different temperatures, that is, its phase diagram contains a paraelectric ionic phase in addition to the ferroelectric ionic and neutral phases. To treat both the ionicity (*i.e.*, degree of charge transfer from the donor to acceptor molecules) and the dimerization, which causes a finite polarization, we employ a classical spin-1 model called Blume-Emery-Griffiths model. However, this model itself cannot reproduce the proper solid-liquid-gas phase diagram due to hidden symmetries, so that an additional interaction is necessary.

I-R-1 Ferroelectric Phase Transition, Ionicity Condensation, and Multicriticality in Charge-Transfer Organic Complexes

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To elucidate a novel pressure-temperature phase diagram of the quasi-one-dimensional mixed-stack charge-transfer (CT) complex TTF-CA, we study the quasi-one-dimensional spin-1 Blume-Emery-Griffiths (BEG) model. In addition to the local charge transfer energy and the inter-stack polar (dipole-dipole) interaction, we take account of the inter-stack electrostriction effect. Using the self-consistent chain-mean-field theory, where the intra-stack degrees of freedom are exactly treated by the transfer-matrix method, we reproduce the gas-liquid-solid like phase diagram corresponding to the neutral (N), paraelectric ionic (I_{para}), and ferroelectric ionic (I_{ferro}) phases, respectively. We also give an explanation on the experimentally observed multicritical behavior and concomitant discontinuous inter-stack lattice contraction in TTF-CA.

I-S Photoinduced Phase Transitions in Charge-Transfer, Spin-Crossover, and Binuclear Metal Complexes

Now a variety of materials show photoinduced phase transitions. Their characters depend much on the magnitude of the hysteresis loop. The TTF-CA complex has small hysteresis and the transition is described by a deterministic approach. Especially, macroscopic coherent oscillations of neutral-ionic domain walls need to be described by a model that consists of interacting electrons and lattice displacements. The evolution of the system is described by the time-dependent Schrödinger equation. On the other hand, organometal spin-crossover complexes generally have large hysteresis and the transition is described by a stochastic approach. Ising-like models are sufficient to describe the slow transition between high- and low-spin phases. The evolution of the system is governed by thermal processes and described by the master equation. Even in a case with large hysteresis, a deterministic approach can be useful. In the iodine-bridged binuclear platinum complexes with ligand pop, a photoinduced transition takes place mainly from the charge-density-wave to charge-polarization phases within a large hysteresis loop. Its explanation needs off-diagonal elements of the Hamiltonian, so that a deterministic approach is necessary.

I-S-1 Electronic and Lattice Dynamics in the Photoinduced Ionic-to-Neutral Phase Transition in a One-Dimensional Extended Peierls-Hubbard Model

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Real-time dynamics of charge density and lattice displacements is studied during photoinduced ionic-to-neutral phase transitions by using a one-dimensional extended Peierls-Hubbard model with alternating potentials for the one-dimensional mixed-stack charge-transfer complex, TTF-CA. The time-dependent Schrödinger equation and the classical equation of motion are solved for the electronic and lattice parts, respectively. We show how neutral domains grow in the ionic background. As the photoexcitation becomes intense, more neutral domains are created. Above threshold intensity, the neutral phase is finally achieved. After the photoexcitation, ionic domains with wrong polarization also appear. They quickly reduce the averaged staggered lattice displacement, compared with the averaged ionicity. As the degree of initial lattice disorder increases, more solitons appear between these ionic domains with different polarizations, which obstruct the growth of neutral domains and slow down the transition.

I-S-2 Coherence Recovery and Photoinduced Phase Transitions in One-Dimensional Halogen-Bridged Binuclear Platinum Complexes

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A photoinduced transition from a charge-density-wave (CDW) phase to a charge-polarization (CP) phase has been recently found in a one-dimensional halogen-bridged binuclear platinum complex $R_4[Pt_2(pop)_4I]$-nH_2O (pop = $P_2O_5H_2^{2-}$, R = $(C_2H_5)_2NH_2$). Its mechanism is theoretically studied by solving the time-dependent Hartree-Fock equation for a one-dimensional two-band three-quarter-filled Peierls-Hubbard model. Above a threshold in the photoexcitation intensity, a transition takes place from the CDW to CP phases. The threshold intensity depends on the relative stability of these phases, which can be explained qualitatively by their diabatic potentials. However, the transition from the CP to CDW phases is hardly realized for two reasons: (i) low-energy charge-transfer processes occur only within a binuclear unit in the CP phase; (ii) it is difficult for the CDW order to become long-ranged owing to its weak coherence. The effective transfer integrals required for the coherence are evaluated.

I-S-3 Two-Step Photo-Induced Phase Transitions in a Two-Sublattice Model

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Photo-induced phase transition (PIPT) phenomena in organometal spin-crossover complexes have been widely investigated. As an effective model for a two-step spin transition, we study a two-sublattice spin model that takes into account an intra-site antiferromagnetic coupling and inter-site ferromagnetic couplings. Since each site takes low-spin (L) or high-spin (H) state, the model has four (LL, LH, HL, and HH) possible phases. First, we discuss the temperature dependence of the high spin fraction by using a mean-field approximation. The results indeed show a two-step spin transition due to the competition between the intra- and inter-site couplings. Next, we apply Monte Carlo (MC) simulations including a photoexcitation term. The MC dynamics of the high spin fraction shows non-linear characteristics such as step-like change, threshold-like behavior, and phase separation.

I-S-4 Quasiparticle Structure in the Vicinity of the Heisenberg Model: One and Higher Dimensions

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We study quasiparticle structures in a class of quantum spin and half-filled Hubbard models where the antiferromagnetic correlation is suppressed. First, we focus on the one-dimensional case and study how the solitonic quasiparticles and their bound states appear. Then, we propose its analogue in higher dimensions and compare the results with those of the two-dimensional Hubbard model at half filling on a triangular-type lattice.