

I-U Neutral-Ionic, Dimerization and Photoinduced Phase Transitions and Their Dynamics in Mixed-Stack Organic Charge-Transfer Complexes

Mixed-stack organic charge-transfer complexes have columns of alternating donor and acceptor molecules. Neutral-ionic and dimerization phase transitions are observed in them. Since the dimerization was observed in some neutral compounds, importance of the long-range Coulomb interaction has been pointed out. In such compounds, transfer-modulating electron-lattice coupling is known to be strong. Then, the finite-temperature density-matrix renormalization-group method is used to show that such electron-lattice coupling also brings about dimerization in the neutral phase and that the transition becomes continuous then. The tetrathiafulvalene-*p*-chloranil (TTF-CA) complex, on the other hand, shows the discontinuous and simultaneous, neutral-ionic and dimerization phase transitions. It shows the photoinduced phase transition as well. We have solved the time-dependent Schrödinger equation to reproduce peculiarities found in time-resolved spectroscopy, such as a) the threshold intensity above which the transition takes place, b) the macroscopic coherent oscillations of neutral-ionic phase boundaries, and c) the quick loss of the second-harmonic-generation signal.

I-U-1 Finite-Temperature Phase Diagram of Mixed-Stack Charge-Transfer Complexes

YONEMITSU, Kenji

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The mixed-stack organic charge-transfer complex, (BEDO-TTF)(Cl₂TCNQ), has shown a phase transition accompanied with a sharp drop in the magnetic susceptibility and with an increase in the intermolecular overlap, as the temperature is lowered. Here we theoretically consider the possibility for a phase transition from the ionic phase to a neutral phase, which is driven by charge-transfer fluctuations. Using finite-temperature density-matrix renormalization-group calculations for the one-dimensional extended Hubbard model with alternating potentials, we show that, with increasing transfer integral t , a transition from the neutral phase to the ionic phase is induced by spin fluctuations for small t , while another transition from the ionic phase to the neutral phase is induced by charge-transfer fluctuations for large t . Near the phase boundary, the free energy is easily lowered by dimerization of transfer integrals or by staggered magnetic field. Thus, a further transition is also possible to a dimerized nonmagnetic phase or to an antiferromagnetic phase at a lower temperature. In two dimensions, we expect that the effect of charge-transfer fluctuations is larger and that the transition to the dimerized nonmagnetic phase is suppressed.

I-U-2 Lattice and Magnetic Instabilities near the Neutral-Ionic Phase Transition of the One-Dimensional Extended Hubbard Model with Alternating Potentials in the Thermodynamic Limit

YONEMITSU, Kenji

[*Phys. Rev. B* **65**, 205105 (2002)]

The effects of dimerization causing the alternation of transfer integrals on the neutral-ionic phase transition are studied in the one-dimensional extended Hubbard

model with alternating potentials at half filling. The finite-temperature density-matrix renormalization-group method is used to treat the thermodynamic limit. In the ionic phase, the free-energy gain is proportional to $\delta^{4/3}$ with δ being the degree of dimerization even near the phase boundary at low temperatures. In the neutral phase, the free-energy gain is quadratic for small transfer integral far from the phase boundary, but it is nonlinearly enhanced near the boundary. Large transfer integrals make the gain faster than δ^2 , so that they facilitate dimerization. The dimerization in the neutral phase increases the ionicity and lowers the spin excitation energies. These lattice effects are in contrast to the effects of a staggered magnetic field. Relevance is discussed to recently observed dimerization in the neutral phase of ClMePD-DMeDCNQI.

I-U-3 Variation of Excitation Spectra in Mixed-Stack Charge-Transfer Complexes

YONEMITSU, Kenji

[*Phase Transitions* in press]

Local excitation spectra in different spin and charge channels are calculated in the one-dimensional extended Hubbard model with alternating energy levels at half filling for mixed-stack charge-transfer complexes. Near the boundary between the neutral and ionic phases, the electronic system is easily distorted by an additional term that reduces the symmetry and opens a gap. Alternating transfer integrals produce a nonmagnetic spin-Peierls phase; while staggered magnetic fields produce an antiferromagnetic phase. Both of them enhance the ionicity when they are introduced into the neutral phase near the boundary. Accordingly, these additional terms enhance low-energy spin excitations, although these excitations are suppressed when compared with those in the regular ionic phase. The regular ionic phase has a larger spectral weight in the local current channel than the neutral phase. This would imply that, in one dimension and if the lattice effect is negligible, the ionic phase has smaller activation energy in the electric conductivity near the boundary than the

neutral phase.

I-U-4 Dynamic Spin Correlations near Neutral-Ionic Phase Transitions

YONEMITSU, Kenji

[*Physica B* submitted]

Near the neutral-ionic phase transition in the one-dimensional extended Hubbard model with alternating potentials at half filling, the effects of alternating transfer integrals and a staggered magnetic field on the local spin excitation spectrum are studied by using the finite-temperature density-matrix renormalization-group method. In the neutral phase, the alternation increases the ionicity and lowers the spin excitation energies toward the ionic phase, while the staggered magnetic field does not modify the spectrum up to a critical field above which the system becomes ionic.

I-U-5 Thermodynamics of Neutral-Ionic and Ferroelectric Phase Transitions in the Two-Chain System

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It remains an open issue to clarify the microscopic mechanism of the neutral-ionic phase transition and the photo-induced ferroelectric phase transition in the mixed-stack organic charge-transfer complex, TTF-CA. Of particular importance is to grasp the microscopic origin that distinguishes the neutral-ionic phase transition from the ferroelectric phase transition. The order parameter of the former transition is the charge concentration on the electron donor and acceptor sites, while that of the latter transition is the electric dipole moment that may be related to the microscopic electric current accompanied with the time-reversal symmetry breaking. Starting with a phenomenological argument, we first study thermodynamics of these phase transitions and consider how the interplay of electron correlation, lattice degrees of freedom and dimensionality effects enter the problem. We apply the transfer integral method to a two-chain system with a thermodynamic potential with triple minima. Mapping the problem onto a tunneling Hamiltonian and diagonalizing it, we study the phase transitions upon changing temperature and other controllable parameters. Finally, we discuss the neutral-ionic and ferroelectric phase transitions.

I-U-6 Domain-Wall Dynamics after Photoexcitations near Neutral-Ionic Phase Transitions

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[*Phase Transitions* in press]

Real-time dynamics of domain walls between the

neutral and ionic phases just after photoexcitations is studied by fully solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model, not by relying on the adiabatic approximation. The unrestricted Hartree-Fock approximation is used for electrons, and the lattice displacements are treated classically. Three characteristic time scales are observed: rapid oscillation of ionicity owing to the local charge transfer; slow oscillation of lattice displacements; and even slower and collective motion of domain walls. Steady growth of a metastable domains is achieved after complicated competition of micro domains. The relevance to recently measured, time-resolved photorefectance spectra in TTF-CA is discussed.

I-U-7 Variation Mechanisms of Ground-State and Optical-Excitation Properties in Quasi-One-Dimensional Two-Band Electron Systems

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[*Mol. Cryst. Liq. Cryst.* **379**, 467 (2002)]

We study i) the ground-state and optical-excitation properties of halogen-bridged binuclear metal complexes, which are known as MMX chain compounds, by the strong-coupling expansion for a one-dimensional two-orbital extended Peierls-Hubbard model, and ii) the dynamics of domain walls between the neutral and ionic phases in mixed-stack charge-transfer complexes, by solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model with alternating energy levels. We find in i) that competition between electron-electron and electron-lattice interactions and competition between short- and long-range interactions are both important for the electronic phase variation, and in ii) that charge and lattice dynamics immediately after photoexcitations is complex and not explained simply within the domino picture.

I-U-8 Photoinduced Dynamics of Ionicity near the Neutral-Ionic Phase Boundary in a One-Dimensional Extended Peierls-Hubbard Model

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[*Synth. Met.* submitted]

Dynamics of the ionicity after photoexcitations in mixed-stack charge-transfer complexes is numerically studied by using a one-dimensional extended Peierls-Hubbard model with alternating potentials at half filling. The time-dependent Schrödinger equation and the Newton equation are solved for the electronic and lattice parts, respectively. Fourier analysis is performed for the ionicity. During the photoinduced phase transition, slow components are dominant and very broad reflecting complex motion of domain walls and lattice displacements. After the transition, fast and slow oscillations are

clearly seen, which correspond to the electronic and lattice motion, respectively.

I-V Self-Doping, Nonlinear Excitations and Photoinduced Transitions between Charge and Lattice Ordered Phases of Metal Complexes

Halogen-bridged binuclear platinum complexes show a variety of electronic phases owing to competing kinetic energy, Coulomb repulsion, and electron-lattice coupling. When the ligand is pop, electrons are so localized that the perturbation theory from the strong-coupling limit works very well for the ground and optically excited states. When the halogen is iodine in addition, as the distance between the neighboring MM units increases by changing counter ions or by reducing pressure, a discontinuous transition takes place from the charge-density-wave phase to the charge-polarization phase. This has been explained theoretically. In those materials which show the pressure-induced transition, a photo-induced transition is observed in the hysteresis loop. The transition is, however, only from the charge-density-wave to charge-polarization phases. We have clarified its mechanism. a) The lowest-energy photoexcitation brings about inter-unit charge transfer only in the former phase. b) The high-energy photoexcitation in the latter phase transfers charge so locally that the former phase never proliferates.

I-V-1 Self-Doping Effect on the Mott Transition Accompanied with Three-Fold Charge Ordering in (DCNQI)₂Cu

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[Synth. Met. in press]

The commensurate state with three-fold lattice distortion in the insulating phase of (DCNQI)₂Cu is studied based on a two-band Peierls-Hubbard model by using the density-matrix renormalization-group method. With strong electron correlation among the *d* electrons, self-consistent lattice modulation strongly blocks the charge transfer between the π and *d* orbitals in order to keep the commensurability condition even when the π -*d* level difference is widely varied. A transition to an incommensurate phase requires a large deviation of the π -*d* level difference from the optimal case.

I-V-2 Spin Solitons in the Alternate Charge Polarization Background of MMX Chains

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[APES'01 proc. in press]

We study spin solitons in the alternate charge polarization background of the MMX chains, using the unrestricted Hartree-Fock approximation to a one-dimensional Peierls-Hubbard model. The effects of the electron-lattice coupling and the electron-electron interaction on the shape of the soliton are discussed.

I-V-3 Photoexcited States and Photoinduced Dynamics in Electronic Phases of MMX-Chain Systems

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[Synth. Met. submitted]

In the one-dimensional two-band three-quarter-filled Peierls-Hubbard model for halogen-bridged binuclear metal complexes $R_4[\text{Pt}_2(\text{pop})_4\text{I}]_n\text{H}_2\text{O}$ with counter ion *R* and pop = P₂O₅H₂²⁻, a transition from the charge-density-wave phase to the charge-polarization phase is photoinduced, but the opposite process is not. Its origin is explained by considering differences in low-energy photoexcitations in the two phases and coherence of respective order parameters. The different dynamics is demonstrated by solving the time-dependent Schrödinger equation.

I-V-4 Electromodulation Spectra of Optical Absorption in One-Dimensional Strongly Correlated Systems

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[Synth. Met. submitted]

Electromodulation spectra of optical absorption in one-dimensional strongly correlated electron systems are theoretically investigated by numerically solving the time-dependent Hartree-Fock equation for the extended-Hubbard model coupled to a classical external vector potential. The calculated spectra are qualitatively in good agreement with experimental results for one-dimensional Mott insulators.

I-W Dimensional Crossovers in Electronic Phases and Their Excitation Spectra of Quasi-One-Dimensional Organic Conductors

In quasi-one-dimensional segregated-stack organic charge-transfer complexes with a quarter-filled band, (TMTTF)₂X and (TMTSF)₂X, variation of physical properties under physical or chemical pressure can be viewed as a dimensional crossover. At this particular band filling, the umklapp process is essential to the confinement of fermions and to the antiferromagnetic long-range order. The dimensional crossover is demonstrated also in charge-transfer excitation spectra by the finite-temperature density-matrix renormalization-group method. Electron correlation is so strong in the most conducting direction that electron motion is confined in this direction at low energies. The perpendicular motion takes place only incoherently. This explains the observed behavior that is reminiscent of the doped Mott insulators.

I-W-1 Dimensional Crossovers and Phase Transitions in Strongly Correlated Low-Dimensional Electron Systems: Renormalization-Group Study

KISHINE, Jun-ichiro; YONEMITSU, Kenji

[*Int. J. Mod. Phys. B* **16**, 711 (2002)]

In this review article, we have described our recent achievement on dimensional crossovers and phase transitions from incoherent metallic phases, based on the two-loop level perturbative renormalization-group approach. As a canonical example, we first take up spin-density-wave phase transitions in the quasi-one-dimensional organic conductors (TMTTF)₂X and (TMTSF)₂X, and elucidate the nature of the transitions in terms of the dimerized quarter-filled Hubbard chains. Secondly, we discuss the novel superconductivity in the doped ladder system Sr_{14-x}Ca_xCu₂₄O₄₁ under high pressure, and analyze the superconducting transition from the incoherent metallic phase (spin gap metal phase) in terms of the weakly-coupled Hubbard ladders. Thirdly, motivated by the experimental findings of the crossover from an antiferromagnetic phase, Anderson localization phase, and a normal Fermi liquid phase upon Cu doping in a organic compound (DI-DCNQI)₂Ag_{1-x}Cu_x, we discuss interplay of randomness, electron correlation, and dimensionality effects in weakly-coupled half-filled Hubbard chains

with weak quenched random potentials. Finally we discuss some two-dimensional electron systems where the two-loop renormalization-group procedure is well defined and works.

I-W-2 Correlation-Induced Dimensional Crossovers of Charge-Transfer Excitations in Quasi-One-Dimensional Organic Conductors

YONEMITSU, Kenji

[*Synth. Met.* in press]

Applying the finite-temperature density-matrix renormalization-group method to the spinless fermion model on a two-leg ladder, we have calculated the dynamical structure factors for the local charge transfer processes along the chains and across the chains. The intra-chain excitation spectra are sensitive to the inter-chain transfer integral and the chemical potential, while the inter-chain excitation spectra are sensitive to the intra-chain electron correlation. These dynamical properties are due to the collective motions of fermions along the chains and the energy-dependent confinement of fermions in the chains. At low but finite energies, the effects of the increasing inter-chain transfer integral on the local charge-transfer spectra are similar to those of the chemical potential deviating from zero.

I-X Underlying Gauge Structure and Competing Orders in Underdoped Cuprate Superconductors

The key issue in theoretical understanding of the high-temperature cuprate superconductors is how to describe the low-density carriers coupled with competing infrared collective degrees of freedom originating from strong correlation inherent in the doped Mott insulators. Although realization of the *d*-wave superconducting ground state upon doping has been established both experimentally and theoretically, it still remains as a highly challenging problem to describe the low-energy contenders such as the flux phase, the antiferromagnetic phase, the stripe phase, and so on. Here, we take account of the contenders as much as possible. First, based on an SU(2) formulation of the *t*-*J* model, we consider a superconducting vortex, where the flux state is stabilized in its core, and propose its physical consequences. Then, as a next step, both flux and antiferromagnetic degrees of freedom are included.

I-X-1 Signature of the Staggered Flux State around a Superconducting Vortex in Underdoped Cuprates

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[*Phys. Rev. B* **65**, 064526 (2002)]

Based on the SU(2) lattice gauge theory formulation of the t - J model, we discuss possible signature of the unit cell doubling associated with the staggered flux (SF) state in the lightly doped spin liquid. Although the SF state appears only dynamically in a uniform d -wave superconducting state, a topological defect [SU(2) vortex] freezes the SF state inside the vortex core. Consequently, the unit cell doubling shows up in the hopping and pairing order parameters of physical electrons. We find that whereas the center of the vortex core is a SF state, as one moves away from the core center, a correlated staggered modulation of the hopping and pairing becomes predominant. We predict that over the region outside the core and inside the internal gauge field penetration depth around a vortex center, the local density of states exhibits staggered peak-dip (SPD) structure inside the V-shaped profile when measured on the bonds. The SPD structure has its direct origin in the unit cell doubling associated with the SF core and the robust topological texture, which has little to do with the symmetry of the d -wave order parameter. Therefore the structure may survive the tunneling matrix element effects and easily be detected by STM experiment.

I-X-2 Underlying SU(2) Gauge Structure and Hidden Staggered Flux State in the Lightly Doped Spin Liquid

KISHINE, Jun-ichiro

[*J. Phys. Chem. Solids* **63**, 1559 (2002)]

The staggered flux state, that enters the low-energy spectrum of the d -wave superconducting state in the lightly doped spin liquid systems is discussed, based on an SU(2) lattice gauge theory formulation of the t - J model. An appropriate gauge transformation to describe physical quantities such as staggered orbital currents is proposed. Using this gauge (physical gauge), the staggered orbital current correlation is computed and consistency with a Gutzwiller-projected Monte Carlo analysis is argued.

I-X-3 Coexistence of Staggered Flux and Antiferromagnetic States in Superconducting Vortices in the Lightly Doped Mott Insulator

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Based on an SU(2) lattice gauge theory formulation of the t - J model, we numerically studied electronic states inside superconducting vortices in the lightly

doped Mott insulator. Applying the Bogoliubov-de Gennes type formulation to the vortices in the system, we found that an antiferromagnetic state coexists with the staggered flux state for doping smaller than some critical concentration. This is the first finding of the coexistence of the resonating-valence-bond type on-bond singlets and the on-site spin degrees of freedom. Relevance of this finding to the recent NMR experiments on the vortex core states is argued.