I-T Charge-Transfer Excitations and Fluctuations in Quasi-One-Dimensional Organic Conductors

i) 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. We have already studied how the crossover of the normal-phase properties above the phase transition temperatures to three-dimensional ones is achieved by increasing intermolecular overlaps between the neighboring chains and/or reducing electron correlation. The umklapp process has been essential to the confinement of fermions and to the antiferromagnetic long-range order. However, it was difficult to treat excitation spectra by the previous analytic approaches. Now a numerical approach is employed to deal with the dimensional crossover experimentally observed in excitation spectra. ii) In quasi-one-dimensional mixed-stack organic charge-transfer complexes with a half-filled band, neutral-ionic phase transitions with decreasing temperature, with increasing pressure, or with irradiation of light have been extensively investigated. Recently, complexes with inter-columnar networks have been synthesized and examined. Among them, the (BEDO-TTF)(Cl_2TCNQ) complex shows an unusual phase transition accompanied with a sharp drop in the magnetic susceptibility. A completely new mechanism for the transition from the ionic to neutral phases is proposed and numerically investigated. Even in the conventional, quasi-one-dimensional complex, TTF-CA, time-resolved spectroscopic data just after the irradiation of light are accumulated during the photo-induced phase transition. We also study the dynamics of neutral and ionic domains in such a non-equilibrium condition.

I-T-1 Intra- and Inter-Chain Excitations near a Quantum Phase Transition in Quasi-One-Dimensional Conductors

YONEMITSU, Kenji

[*Mol. Cryst. Liq. Cryst.* in press]

We study intra- and inter-chain excitation spectra near a quantum phase transition in a spinless fermion model on a two-leg ladder at half filling by the finite-temperature density-matrix renormalization-group method. Above a critical strength of intrachain nearest-neighbor repulsion, a gap appears, accompanied with a long-range order of density modulation in the checkerboard pattern at zero temperature. The intrachain excitation spectra do not change so much in the gapless phase below the critical strength, while the interchain excitation spectra are considerably altered by the intrachain repulsion even in the gapless phase. Relevance to the optical conductivity in quasi-one-dimensional electron systems is suggested.

I-T-2 Collective Excitations and Confinement in the Excitation Spectra of the Spinless-Fermion Model on a Ladder

YONEMITSU, Kenji

[*Phys. Rev. B* submitted]

Intra- and inter-chain, local charge-transfer excitation spectra and the single-particle density of states are calculated by the finite-temperature density-matrix renormalization-group method in the spinless-fermion model on a ladder with varying intra-chain nearest-neighbor repulsion and with small inter-chain transfer integral at and near half filling. Collective excitations govern the low-energy intra-chain spectra, while only individual local excitations are present in the inter-chain spectra. As a consequence, at half filling, the intra-chain repulsion affects the inter-chain spectra more sensitively than the intra-chain spectra. Meanwhile, the inter-chain transfer integral affects the intra-chain spectra more sensitively through modifying the density-density correlation strength. The difference between the intra- and inter-chain spectra in the insulating phase can be interpreted from the viewpoint of confinement. It is found that the doping dependence of the local charge-transfer excitation spectra is similar to the dependence on the inter-chain transfer integral. It is because the inter-chain motion of fermions is not band-like but incoherent. Similarities between these findings and the experimentally observed, optical conductivity spectra in the quasi-one-dimensional organic conductors, $(TMTSF)_2X$, are pointed out.

I-T-3 Quantum and Thermal Charge-Transfer Fluctuations for Neutral-Ionic Phase Transitions in the One-Dimensional Extended Hubbard Model with Alternating Potentials

YONEMITSU, Kenji

[*Phys. Rev. B* submitted]

Effects of quantum and thermal fluctuations on transitions between the ionic phase and the neutral phase are studied by applying the finite-temperature density-matrix renormalization-group method to the one-dimensional extended Hubbard model with alternating potentials at half filling. Charge-transfer fluctuations lower the energy of the neutral phase more than that of the ionic phase, which is in contrast to the spin fluctuations favoring the ionic phase. As a consequence, with increasing intermolecular overlap between the neighboring donor and acceptor sites, we expect a spin-fluctuation-induced transition from the neutral phase to the ionic phase, and a charge-transfer-fluctuation-induced transition from the ionic phase to the neutral phase, near the phase boundary. Relevance to a recently observed phase transition in a new class of

mixed-stack charge-transfer complexes is discussed.

I-T-4 Photoexcitations and Domain-Wall Dynamics near Neutral-Ionic Transitions

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Recently, time-resolved photoreflectance spectra of TTF-CA have been measured just after photoexcitations by several groups. They are useful for the understanding of dynamical processes in the photoinduced phase transition, *e.g.*, creation and propagation of domain walls between the neutral and ionic phases. Real-time dynamics of such domain walls is studied by numerically solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model within the unrestricted Hartree-Fock approximation. Since thermal lattice fluctuations would be regarded as random initial conditions for lattice displacements, we add static impurities to the chain as a first step. Domain walls are generated at these impurity sites by photoexcitations. It is found that motion of domain walls depend at the early stage on the strengths of impurities and the intensity of photoexcitations.

I-T-5 New Photoinduced Phenomenon in Polymers

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[*Phys. Rev. A* in press]

Numerical simulation has shown that a polymeric molecule can possess a new photoinduced phenomenon, photoinduced polarization reversion, in which the electric dipole of the polymeric molecule is reversed by absorbing one photon. This paper provides an analytic theory by means of a response function to prove that a polymer with a bipolaron has a negative static polarizability and explains the physical origin of this new photoinduced phenomenon in detail. This paper also presents a dynamical calculation for the photoinduced polarization reversion, from which the relaxation time for the dipole reversion can be determined.

I-U Cooperation or Competition between Electron Correlation and Lattice Effects in One-Dimensional π-*d* Electron Systems

i) Quasi-one-dimensional π-*d* hybrid electron systems, $(DCNQI)_2M$, are known to show a metal-insulator transition originating from the collaboration of the Peierls (*i.e.*, electron-lattice) and Mott (*i.e.*, electron-electron) mechanisms, which is contrary to the MMX chains. Although stability of the insulator phase with lattice modulation of period three is known in a wide pressure range, *i.e.*, in a wide range of the π-*d* level difference, its theoretical treatment was very difficult because of strong correlation and highly nonlinear lattice effects. Strong commensurability effects on the stability are investigated by extensive numerical calculations. Another phase found nearby is consistent with the tendency observed by recent experiments. ii) Various charge-ordered phases are found accompanied with different lattice modulation patterns in quasi-one-dimensional halogen-bridged binuclear metal complexes, which are often called MMX chains. The dependence of the charge ordering, the lattice distortion and the optical conductivity spectra on the ligand, the counter ion and the halogen ion has been explained by competition between electron-lattice and electron-electron interactions, that between site-diagonal and site-off-diagonal interactions, and that between short-range and long-range interactions.

I-U-1 Strong Commensurability Effect on Metal-Insulator Transition in $(DCNQI)_2Cu$

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[*Mol. Cryst. Liq. Cryst.* in press]

$(DCNQI)_2Cu$ salts, which are one-dimensional π-*d* electron systems, show unique physical properties associated with hybridization between π bands of DCNQI molecules and *d* orbitals of Cu. The metal-insulator transition is regarded as a cooperative phenomenon due to the Peierls instability in the 1/3-filled π band and the Mott instability in the *d* orbitals, 5/6 of which are occupied. We study stability of three-fold lattice distortion in the insulating state of $(DCNQI)_2Cu$ by exactly diagonalizing a two-band Peierls-Hubbard model on the 6×2 lattice. Self-doping is essentially important and caused by strong commensurability pinning, which is a consequence of moderate coupling of DCNQI π electrons with lattice and strong correlation of Cu *d* electrons.

I-U-2 Optical Excitations in XMMX Monomers and MMX Chains

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[*Mol. Cryst. Liq. Cryst.* in press]

We study optical excitations in $K_4[Pt_2(pop)_4X_2]$ monomers (X = Cl, Br, I), using an extended Hubbard model. We show that long-range transfer integrals and long-range Coulomb interactions are substantially large to reproduce the experimental results. Due to the strong long-range Coulomb interactions, it is expected that the optical conductivity spectra of the MMX chains have two peaks in the charge polarization phase.

I-U-3 Ground State Phases and Optical Properties in Extended Peierls-Hubbard Models for Halogen-Bridged Binuclear Metal Complexes

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[*J. Mater. Chem.* **11**, 2163 (2001)]

Mechanisms of a variety of charge and lattice ordered phases observed in halogen-bridged binuclear metal complexes are theoretically studied by applying the exact diagonalization and strong-coupling expansion methods to one- and two-band extended Peierls-Hubbard models. In $R_4[Pt_2(pop)_4I]_nH_2O$ [R = Na, K, NH_4, $(CH_3(CH_2)_7)_2NH_2$, *etc.*, pop = $P_2O_5H_2^{2-}$] containing charged MMX chains, three electronic phases are suggested by experiments. We find that the variation of the electronic phases originates not only from competition between site-diagonal electron-lattice and electron-electron interactions but also from competition between short-range and long-range electron-electron interactions. On the other hand, in $Pt_2(RCS_2)_4I$ (R = CH_3, *n*-C_4H_9) containing neutral MMX chains, a site-off-diagonal electron-lattice interaction and the absence of counter ions are found to be crucial to produce the recently found, ordered phase. The optical conductivity spectra are also studied, which directly reflect the electronic phases. Their dependence on the electronic phase and on model parameters is clarified from the strong-coupling viewpoint.

I-V Charge Order, Lattice Distortion and Magnetism in Two-Dimensional Organic Conductors and Metal-Complexes

i) Quasi-two-dimensional metal complexes, $Et_nMe_{4-n}Z[Pd(dmit)_2]_2$, have strong dimerization and two bands consisting of the HOMO and the LUMO, which have different degrees of anisotropy. The cation controls the relative magnitudes of inter-molecular overlaps between neighboring dimers. They were known from our previous calculations to effectively control the degree of magnetic frustration and consequently whether the ground state is antiferromagnetic or paramagnetic. In the previous analysis, the interaction strengths had to be assumed. Now close comparisons between the experimental and theoretical optical conductivity spectra enable us to quantitatively estimate the magnitudes of different interaction strengths. ii) Among quasi-two-dimensional organic conductors, the θ-phase compounds are known to show metal-insulator transitions accompanied with charge ordering. Although long-range Coulomb repulsion is generally believed to be essential to the paramagnetic charge-ordered phase, the optical conductivity spectra do not show an excitonic band expected from our previous calculations. Then additional interaction terms might be important for the charge-ordering transitions. In fact, $(BEDT\text{-}TTF)_2RbZn(SCN)_4$ that has a lattice-distorted ground state has a rather high transition temperature. Both numerical and analytic calculations indeed suggest that weak electron-lattice coupling plays an important role.

I-V-1 Optical Conductivity for Possible Ground States of Dimerized Two-Band $Pd(dmit)_2$ Salts

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[*Mol. Cryst. Liq. Cryst.* in press]

We have studied the optical conductivity for possible ground states of $Pd(dmit)_2$ salts, by exactly diagonalizing a two-band Hubbard model for a dimer. The one-dimer model is useful to reproduce the overall structure of the optical spectra, since the intra-dimer transfer integrals, *A*h and *A*l, are an order of magnitude larger than the inter-dimer transfer integrals. Our results reproduce dominant peaks of the optical spectra measured by Tajima *et al.* and confirm their argument from the strong-coupling viewpoint. The peak position and the intensity are generally affected by electron-electron interactions. The interaction strengths are estimated and used in the estimation of effective exchange interaction strengths between dimers. The cation dependence of the magnetic properties is reconsidered.

I-V-2 Charge Ordering Patterns and Their Excitation Spectra in Two-Dimensional Charge-Transfer Compounds

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[*Mol. Cryst. Liq. Cryst.* in press]

Charge ordering (CO) states are found in the insulating phase of θ-$(BEDT\text{-}TTF)_2MM'(SCN)_4$ (M =

Rb, Cs, M' = Zn, Co) by various experimental studies. In the CO states, the charge density is disproportionate and the spin degrees of freedom survive. We calculated the optical conductivity spectra of some CO states in the quarter-filled extended Hubbard model by use of the random phase approximation (RPA) on the basis of the Hartree-Fock (HF) states. If the intersite interactions are essential, an excitonic effect should be significant to affect the peak positions and the spectral shape. Such excitonic effect is included in the RPA. We chose the values of intersite interaction strengths as to reproduce the experimentally observed degree of charge transfer about 0.4 in the HF calculation for each CO pattern. The conclusion from the RPA calculation is consistent with the Tajima *et al.*'s result as regards the number of peaks depending on the CO patterns. The RPA calculation shows a strongly excitonic character in the spectral shapes. However, the experimental data have no excitonic peak but rather broad bands probably ascribed to the inter-band transitions. This fact indicates that the above nearest-neighbor interaction strengths are too strong to explain the spectral shapes. To resolve this contradiction, not only the intersite interactions but also other interactions, *e.g.*, electron-lattice interactions, would be needed.

I-V-3 Paramagnetic Charge-Ordered States by Cooperation of Coulomb Repulsion with Electron-Lattice Coupling

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Charge ordering is clearly seen below around 190 K in the slowly cooled θ-$(BEDT\text{-}TTF)_2RbZn(SCN)_4$ sample, where the crystal structure slightly changes at the transition temperature. If the same sample is rapidly cooled, the charge ordering becomes obscure from the room temperature down to about 20 K. It had been theoretically suggested that the charge ordering originates from the intersite repulsion in this quarter-filled system. Then, we previously calculated the optical conductivity spectra in the random phase approximation and showed that an excitonic effect should be significant if the intersite interaction is really essential. However, the experimental data show no excitonic peak but rather broad bands, which indicate that the intersite interaction is insufficient for the charge ordering. An additional interaction would resolve the contradiction by cooperatively stabilizing the charge ordering. We exactly diagonalize the Hamiltonian with an electron-lattice interaction suggested by X-ray diffraction experiments and compare the results with the second-order perturbation theory from the strong-coupling limit. Weak electron-lattice coupling indeed enhances the effect of long-range Coulomb repulsion on the charge ordering, but keeps the paramagnetism.

I-W Vortices in the Mixed State of High-Temperature Cuprate Superconductors

To elucidate anomalous metallic properties around the high-temperature superconductivity in copper oxides has been one of the major challenges in condensed matter physics. The key issue is competing low-energy instabilities near the superconducting ground state, including antiferromagnetic, stripe, or flux instabilities. Theoretical controversy between the spin-liquid and the Fermi-liquid approaches to the issue is far from resolution. Among the spin-liquid approach, the SU(2) gauge theory recently attracts attention because the flux state predicted by it may be related with another theory or with some numerical calculations. A criterion of whether such approach is valid or not is given by whether its consequence can be experimentally detected or not. Now, atomic resolution scanning tunneling microscope (STM) techniques are well developed. Here, we propose a promising STM experiment to detect signature of the flux state around the superconducting vortex and discuss consequences of the hidden SU(2) gauge structure in underdoped cuprates.

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

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[*Phys. Rev. Lett.* **86**, 5365 (2001)]

Based on the SU(2) lattice gauge field 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 (χ_{ij}) and pairing (Δ_{ij}) order parameters of physical electrons. We find that whereas the center in the vortex core is a SF state, as one moves away from the core center, a correlated staggered modulation of χ_{ij} and Δ_{ij} 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 structure inside the V-shaped profile when measured on the bonds. The staggered peak-dip 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.