12 Theory

12-1 Studies of a Photoinduced Phase Transition from a Charge-density Wave to a Mott Insulator

Recently, photoinduced phase transitions (PIPT) are attracting much interest from a variety of fields such as material sciences, applied physics and chemistry, and pure theory. In particular, as our largest concern, the role of electron correlation seems to be crucial in some material systems. Here, we briefly introduce PIPT phenomena in a quasi-one-dimensional Br-bridged Pd complex (hereafter referred to as a PdBr chain), as an example of such a system.

In Fig. 1, a PdBr chain is schematically illustrated. Fig. 1 (a) shows the state of the chain before photoexcitation – the ground state is a charge-density wave (CDW) that is accompanied by a mixed valency of Pd (Pd^{2+} and Pd^{4+}) and Br-sublattice dimerization. In Fig. 1(b), on the other hand, part of the system has been transformed into another phase by photoexcitation. This newly formed domain is expected to be of a Mott-insulator (MI) phase, since this phase has been found to be metastable in studies of Ni/Pd mixed-metal complexes [1]. As is well known, the MI phase is realized as a result of strong electron-electron repulsion. Since the present situation corresponds to a half-filling case with one d_{z^2} electron at each Pd site, the realized state should be a combination of a mono-valency and an antiferromagnetic alignment of spins at the Pd sites, with suppressed lattice displacements.

Motivated by the above expectation, we explore the possible relaxation paths that yield a MI domain from photoexcited states of a CDW phase [2]. We here assume a form of *pd* model which includes both the d_{z^2} orbital of Pd and the p_z orbital of Br. This model is selected because of the rather strong hybridization between the two orbitals. We then use an adiabatic approximation and calculate adiabatic potential energies as a function of the MI-domain size using a density-matrix renormalization group (DMRG) method. The form of the domain walls (DWs) is of a smooth type, expressed by tanh functions, and the DW width is determined by an optimization.

In Fig. 2, these results are summarized for various electronic states in a 72-site system (36 PdBr pairs). In this calculation, we separate the spin-singlet and triplet states, considering that Pd is a rather heavy element. The photoexcitation from the ground state to the excited states is assumed to occur at zero MI-domain size. The excited states are nothing but exciton states in the CDW phase. As is clearly seen from the figure, all of the excited states lie along monotonously downhill curves, meaning that a substantial size of MI domain, as appearing in Fig. 3, can be formed with no potential energy barrier. This finding is consistent with the very recent experiment by the Okamoto group of Tokyo University [3]. They have actually detected PIPT phenomena in the same material and discovered that the degree of PIPT, defined as the amount of spectral change associated with the transition, is linear with the light intensity. Thus, our interpretation is like this: one MI domain is formed from one absorbed photon, but its growth occurs under the effects of dissipation. Although the process is stochastic and rather complicated, it is expected that statistical averaging will give a certain maximum value to the possible domain size, resulting in a linear process as a whole.

One more important feature of Fig. 2 is the nature of the excitations. For example, the excitation energy for the first excited state looks very small. This energy will be zero in the limit of the infinite system, as is naturally

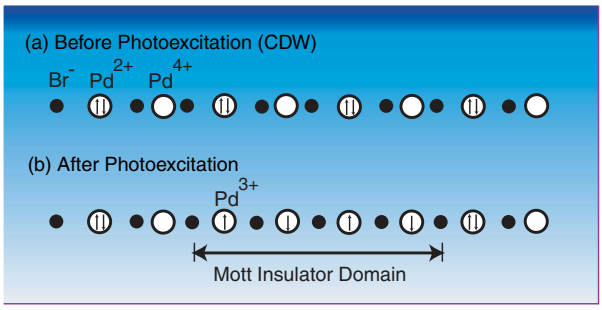

Figure 1
Schematic pictures of a PdBr chain. (a) The CDW (charge-density wave) state in its ground state. A mixed-valency at the metal sites and the halogen sublattice dimarization are realized. (b) A photoinduced state. A metastable Mott-insulator domain (mono-valency of Pd and no halogen displacement) is formed in the central part.

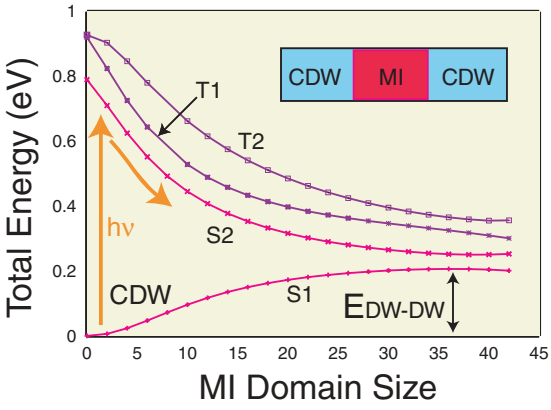

Figure 2
Adiabatic potential energy curves as a function of the MI (Mott insulator) domain size. The symbols "S" and "T" mean the spin singlet and triplet excitations, respectively.

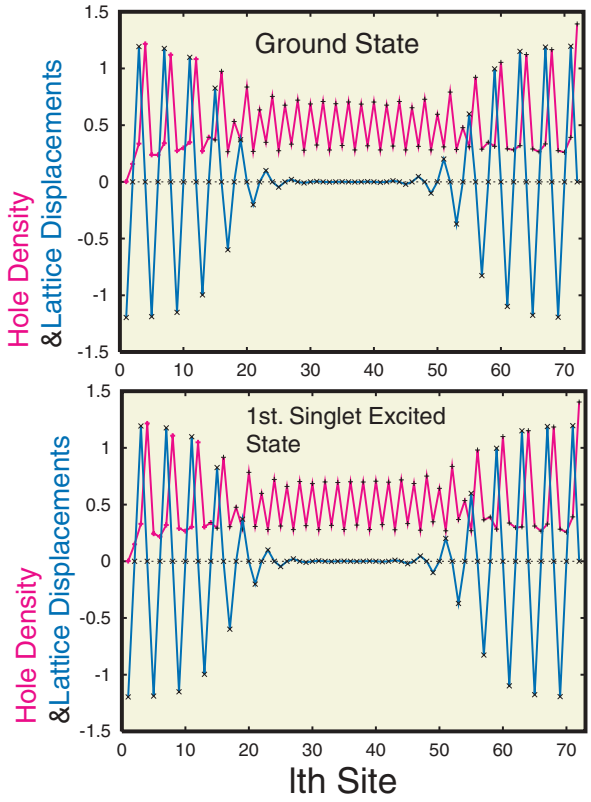

Figure 3
Hole densities in a DW-domain-DW structure of the ground state (upper) and the first singlet (S1) excited state (lower).

expected for gapless spin excitations in this type of system. As another aspect of this excitation, we emphasize the fractional charges of the DWs. It is already known that these DWs have charges of ±1/2|e| [4]. The excitation is regarded also as a bonding to anti-bonding transition of the two fractionally charged DWs. As a whole, the present relaxation has a peculiar nature; the conversion from a pure charge excitation (exciton) to mixed spin and fractional-charge excitations. Further detailed studies, for example, dynamical simulations of the relaxation, are now under way.

K. Iwano (KEK-PF)

References

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