PHYSICAL REVIEW B **79**, 153103 (2009)

Propagation of a ballistic nuclear wavepacket on an adiabatic potential surface of a one-dimensional Br-bridged Pd complex without a self-trapped exciton state

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(Received 22 February 2009; published 3 April 2009)

The photoexcited state of one-dimensional Br-bridged Pd complex, which is a Peierls insulator, was studied using a femtosecond luminescence spectroscopy from near to mid-infrared region. The ultrafast decay with a time constant of 240 ± 40 fs at all photon energies and delay of the maximum positions up to 160 fs with decreasing the photon energy were observed. These behaviors are ascribed to a slide down motion of the nuclear wavepacket on an adiabatic potential energy surface leading to the Mott-insulator domain without a local potential minimum corresponding to a self-trapped exciton.

DOI: 10.1103/PhysRevB.79.153103 PACS number(s): 78.47.−p, 71.27.+a, 71.35.Aa, 78.55.−m

The dynamical study on the generation of a new phase through the excited electronic states is of a central importance in the photoinduced phase transition (PIPT) phenomena. Generally, the PIPT is expected near the boundary between two stable or metastable phases separated by an energy barrier in the electronic ground state.[1] Investigation of the motion of the nuclear wavepacket (WP) on the adiabatic potential energy surface in the excited electronic state is the most direct way for understanding the mechanism of PIPT. The family of one-dimensional (1D) halogen-bridged transition metal complexes (M-X) provides versatile model systems for this aim, because the physical parameters, i.e., transfer energy t, on-site Coulomb repulsion energy U, nearest-neighbor repulsion energy V, and electron-lattice interaction S in the extended Peierls-Hubbard model, can be controlled by replacement of halogen ions (X:Cl,Br,I), transition metal ions (M:Pt,Pd,Ni), ligand molecules, and counter ions.[2–5] The isolated 1D chain, which consists of alternate halogen X and transition metal M ions, plays a primary role in physical properties through electron transfer and lattice deformation along the chain. When S is large in comparison with U, which corresponds to the case for Pt-X and Pd-X, the ground state has a charge density wave (CDW) phase, i.e., a sequence of (-M^{4+}-X^--M^{2+}-X^--) with alternate displacement of halogen ions. Variety of metastable states, such as self-trapped excitons (STE), solitons, and polarons, are known to be produced via photoexcitation and have been extensively investigated mainly in Pt complexes.[6–10] In contrast, the Ni-X system, in which U is more dominant than S, has a Mott-insulator (MI) type ground state (-Ni^{3+}-X^--Ni^{3+}-X^--), which exhibits homogeneous charge distribution without lattice distortion.[3] The target material in this Brief Report [PdBr(chxn=cyclohexanediamine)$_2$]Br$_2$, which we abbreviate as Pd-Br(chxn) throughout this Brief Report, is located close to the phase boundary of CDW and MI between Ni-X and Pt-X in the phase diagram drawn on the S-U plane. This material has a CDW ground state. Thus the Pd-Br(chxn) potentially becomes a candidate of PIPT material, which has a hidden nearly degenerated ground state accessible via photoexcited state. Indeed Iwano[11,12] calculated the adiabatic potential energy surface, where the excited state produced by one photon excitation can relax to the MI domain without suffering a potential barrier, as contrasted to Pt-X system, where a shallow localized bound state (STE) exists. Matsuzaki *et al.*[13] reported pump-probe reflectance measurements on this material, where they assigned the reflectivity change induced by the photoexcitation to the appearance of the MI domain. Observation of the relaxation path on the adiabatic potential energy surface is a challenging issue for understanding the PIPT process and the competition among the excited states; STE, solitons, polaron and MI domain.

In this Brief Report, we study [PdBr(chxn=cyclohexanediamine)$_2$]Br$_2$, by using femtosecond luminescence spectroscopy, which enables us to trace the motion of the nuclear WP in the excited states. The result indicates the ballistic nuclear WP motion, which reflects the adiabatic potential energy surface without a barrier as predicted near the phase boundary.

Pd-Br(chxn) has the CDW ground state accompanied by a lattice distortion corresponding to the displacement of the Br ions.[4] Furthermore, Takaishi *et al.*[14] reported a direct observation of local valence image of Pd-Br(chxn) by STM, where they found a phase mismatch of the CDW domain, which is in other words a spin soliton, or a Pd^{3+} at the domain wall. Judging from these experimental results, the physical properties of Pd-Br(chxn) would be expected to be similar to that of Pt-X and other wide-gap Pd-X systems. Thus it is expected that the photoexcited states of the Pd-Br(chxn) relax to the STE as observed in Pt-X and other Pd-X systems. However, the narrow band gap (0.72 eV) and the small Peierls distortion in Pd-Br(chxn) suggest that the magnitude of S is relatively small and the CDW state is less stable.[3,4,15] In fact, doping of the Ni ion on Pd-Br(chxn), which increases U, induces the MI phase at a concentration of 15%, indicating that Pd-Br(chxn) is located near the phase boundary between Peierls and Mott insulators on the phase diagram.[4,15] In other words, S and U are competing critically each other in Pd-Br(chxn). As mentioned above, Iwano[11,12] predicts that the photoexcited state relaxes to the MI phase, which exists as a metastable state in Pd-Br(chxn), based on a calculation using the extended Peierls-Hubbard model.

The single crystals of [PdBr(chxn)$_2$]Br$_2$ were prepared by the electrochemical oxidation technique.[15] The sample was

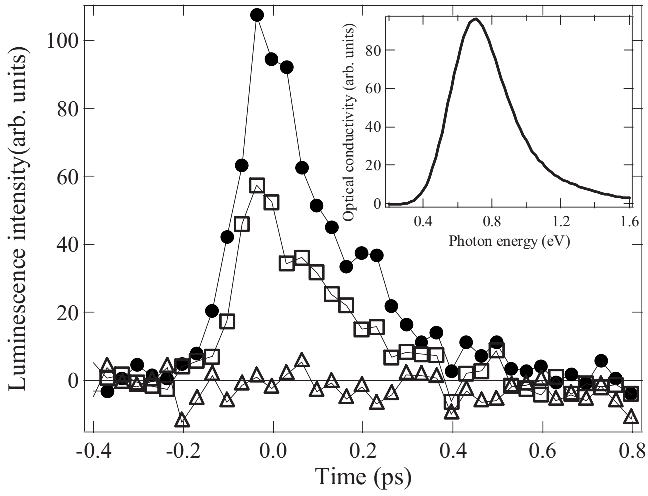

FIG. 1. The closed circles, open squares, and open triangles correspond to the luminescence time evolutions, whose polarization angles are 0°, 45°, and 90° with respect to the 1D chain, respectively. The luminescence photon energy is 0.9 eV and the excitation light is polarized parallel to the 1D chain. The inset is an optical conductivity spectrum of E//1D chain reproduced from Ref. 4.

excited at 1.55 eV using 65 fs pulses from an amplified Ti:sapphire laser pulse (200 kHz repetition rate). The time-resolved luminescence measurements were carried out using a femtosecond up-conversion technique. Paraboloidal mirrors were used to collect and to refocus the luminescence onto a nonlinear-optical crystal (LIO). The luminescence light was frequency mixed in LIO with variably delayed fundamental frequency pulses from the Ti:sapphire amplifier. The up-converted sum-frequency signal was spectrally filtered by a double grating monochromator and detected with a cooled photomultiplier tube (Hamamatsu Photonics R943–02) coupled to a photon counting system. All measurements were conducted at room temperature. The system has sensitivity between 0.23 and 1.3 eV, and the overall time resolution of this system was about 100 fs and the time interval of the measurement was 40 fs. The difference of the sensitivity at each energy was calibrated by using the sum-frequency signal between the light from a tungsten lamp with a sapphire window and the fundamental Ti:sapphire laser light in CW operation. We defined the time origin as a center of the sum-frequency waveform between the gate pulse and the reflection of the pump pulse from the sample surface. The penetration depth of the pump pulse and the escape length of the luminescence introduce an additional delay in the luminescence signal in the backward scattering configuration. This error on the order of 10 fs was also corrected using the optical conductivity data in Ref 4. The excitation density in this work is 10^{-4} per Pd site, which is low enough to allow us to regard the process as a local one photon excitation.

The optical conductivity, which is reproduced from Ref 4, is shown in the inset of Fig. 1. This broad absorption band at 0.72 eV with a bandwidth of 0.4 eV has been assigned to the lowest charge transfer (CT) exciton, in which an electron transfers from Pd^{2+} to Pd^{4+}. According to the theory on Pt-X,[16] the broad bandwidth at a finite temperature is ascribed to a thermal fluctuation of the lattice strongly coupled to the electronic state. The excitation energy in our experiment (1.55 eV) corresponds to the upper tail of the CT exciton band. The excitation pulse generates high energy excitons or free electron-hole pairs in the conduction band. In our previous work, the WP oscillation on the adiabatic potential surface was observed under excitation at the high energy tail, 1.2 eV higher than the CT absorption peak in Pt-Br,[17] which is very similar to the situation in Pd-Br(chxn). This means the excess energy of the photogenerated exciton is lost within a very short time compared to the oscillation period, before starting the propagation on the adiabatic potential surface. Otherwise the oscillating feature would be smeared out and no oscillation signal should be observed. Thus in Pd-Br(chxn), too, we can expect that the excited state produced by the 1.55 eV photon will immediately relax to the exciton and start the motion of the WP.

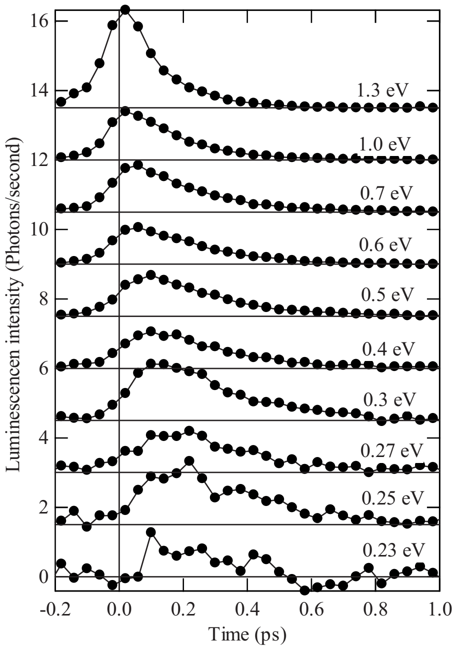

FIG. 2. The time evolutions of the luminescence observed in Pd-Br(chxn) at room temperature. The photon energies are indicated on right side. The luminescence intensity is shown in a unit proportional to photons/second/eV. The multiplication factors are indicated near the curves.

Figure 1 shows the polarization characteristics of the luminescence at a photon energy of 0.9 eV under the excitation light polarized parallel to the 1D chain. There is no luminescence signal at an angle of 90° with respect to the 1D chain, i.e., the luminescence is polarized parallel to the 1D chain. In the case of the excitation light polarized perpendicular to the 1D chain, no luminescence was observed in any polarization. These results suggest that this luminescence originates from the CT transition along the 1D chain.

Figure 2 shows time evolutions of the luminescence intensity. The spectrum of the transient luminescence is shown in Fig. 3(a) (closed circles), which is derived from the data in Fig. 2 by integrating the signal from −0.7 to 1.3 ps.

The circles in Fig. 3(b) show the peak position of the time evolution curves in Fig. 2 at each energy as a function of the

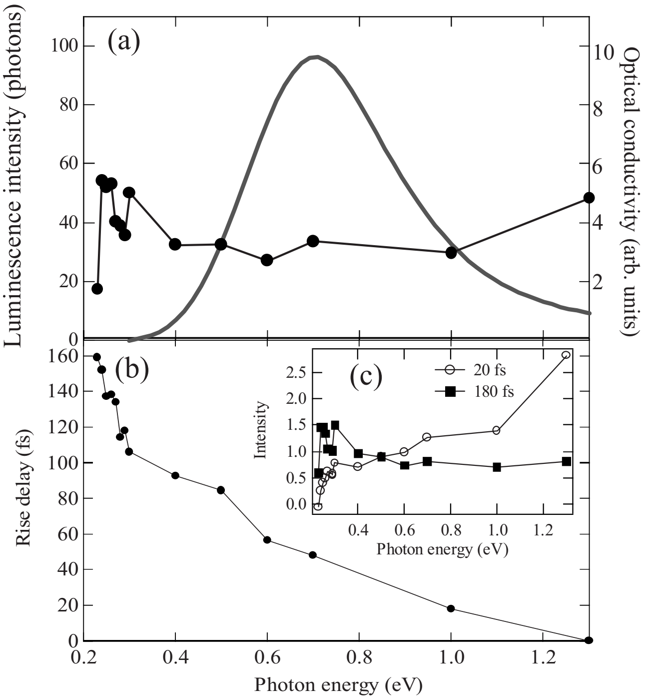

FIG. 3. (a) The gray line indicates optical conductivity spectrum, which is reproduced from Ref. 4. The closed circles indicate the integrated transient luminescence spectrum obtained from the data in Fig. 2. (b) The peak position of the luminescence waveform as a function of the luminescence photon energy. (c) The time-resolved spectrum of the luminescence constructed from the data in Fig. 2.

luminescence photon energy. The peak positions are obtained from the curve fitting assuming a function

$$I(t) = A\left\{1 - \exp\left(-\frac{t - t_0}{\tau_1}\right)\right\}\exp\left(-\frac{t - t_0}{\tau_2}\right).$$

The fitting coefficients, τ_1 and τ_2, are rise and decay time constants, respectively. We observed the luminescence at 0.3 eV, at which the optical conductivity reaches zero. The luminescence maintains comparable intensity even at 0.23 eV. This result strongly suggests that the large lattice relaxation proceeds in Pd-Br(chxn) just as in the case of Pt-*X* Although an intense luminescence peak due to STE is observed in Pt-*X*, the integrated luminescence spectrum shows no peak structure in the Stokes side as shown in Fig. 3(a). Wada *et al.*[2] investigated the relation between the CT absorption and the luminescence energy systematically on several kinds of the Pt-*X* and some other Pd-*X*. They found an empirical rule, that is, the luminescence energy is proportional to the CT absorption energy and the ratio of the former to the latter is (1/2.3). Therefore, if the STE state had existed in Pd-Br(chxn), the peak energy of the luminescence band would be about 0.31 eV, which is well within our measurement region, according to this rule. Normally, the STE luminescence intensity is orders of magnitude larger than the hot luminescence. From the absence of any indication of an isolated luminescence band down to 0.23 eV, we can conclude that Pd-Br(chxn) has no STE state.

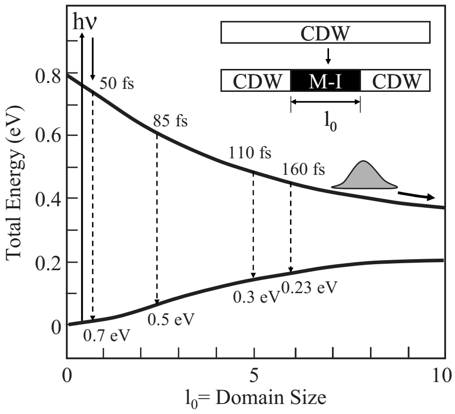

FIG. 4. The solid lines indicate the potential energy surfaces, which are reproduced from Refs. 11 and 12 in Pd-Br(chxn). The horizontal axis, 1_0=domain size, indicates the size of the MI domain. The luminescence energies and the peak delay times are indicated at the bottom and the top of the dashed arrows, respectively.

We discuss our results comparing with the WP dynamics in Pt-*X*. The time evolution curves of the luminescence in Pd-Br(chxn) are very different from those of Pt-*X*. In Pt-*X*, the STE luminescence shows a slow rising at the center of the luminescence band and corresponding decay profiles on both sides, reflecting a cooling process.[18] In addition, a waveform reflecting the nuclear WP oscillation with dephasing is observed.[19–21] In contrast, the luminescence time evolution of Pd-Br(chxn) shows none of these features as shown in Fig. 2.

The disappearance of the STE state is supported also from the observed short lifetime of the luminescence (240 ± 40 fs). In Pt-Br, the oscillation period of the STE is 290 fs (Refs. 20–22) and a similar oscillation period of STE is expected in Pd-Br(chxn), because this oscillation originates from the vibration of the bridging halogen ions. Thus the observed lifetime is shorter than one period of STE oscillation, if it ever exists. In other words, STE state cannot be defined within this short lifetime.

From these discussions, we are forced to the relaxation process accompanying a large lattice distortion without the STE state. Since the CDW ground state of Pd-Br(chxn) is located near the boundary between the Peierls and the Mott-insulator phases in the phase diagram,[4,15] the MI domain can exist as a metastable state. It is predicted that a photoexcited state relaxes to the MI without a potential barrier, i.e., the MI phase domain appears in the CDW ground state in Refs. 11 and 12. Figure 4 shows the adiabatic potential energy surface of Pd-Br(chxn), which is reproduced from Refs. 11 and 12. In this diagram, the abscissa is not an ordinary configuration coordinate axis, but the size of the MI domain. This curve represents the energy along the valley on the potential energy surface in the multidimensional configuration coordinate space. In the MI domain, all the Pd ions take trivalent state and the Peierls displacements of the Br ions are released. The STE state is viewed as a minimal MI domain consisting of two trivalent ions. The potential surface has a local minimum, i.e., STE in Pt-*X* and other Pd-*X* complex. In contrast in Pd-Br(chxn), the potential surface is opened toward the direction of expansion of the domain size at that point. Thus the STE state does not exist and the photoexcited state relaxes to the new state, i.e., the MI domain.

Under the condition mentioned above, the dynamical relaxation process will be as follows. The luminescence time-evolution curves, which show delays of the peak position with decreasing photon energies, reflect the WP propagation on the potential surface. The domain of the MI phase would spread broader accompanying a release of the deformation energy, because there is no potential barrier as shown in Fig. 4 and this dynamics corresponds to the slide down motion of the WP. The time evolution (see Fig. 2) of the luminescence below band edge (0.3 eV) reflects the propagation of the WP into the gap where there is no electronic states before excitation. In other words, the release of the Peierls distortion means decrease in the dimerization order parameter, which in turn decreases the gap energy in a band picture, but due to the strong electron correlation energy on the metal site, the system becomes again MI. The move of the luminescence energy toward low energy corresponds to the decrease in the gap (2Δ) energy.[23,24]

The delay of the peak position reaches 160 fs at 0.23 eV as shown in Fig. 3(b). Figure 3(c) also shows the shift of the WP position to the low energy side at 180 fs. Based on the energy diagram in Fig. 4, the transition energies of 0.5, 0.3, and 0.23 eV correspond to the domain sizes of 2.5, 5, and 7 metal sites, respectively. We have to note that this diagram gives only a rough estimation, because a slight energy difference yields a large error in the domain size at lower energies. It is meaningful to compare this domain size with the size of the spin soliton, which is also constructed from Pd^{3+} sites. The direct observation of the spin soliton spreading 10 Pd^{3+} site has been reported in Ref. 14, which is comparable to the size of the photogenerated MI domain.

Comparison of the Pd-Br(chxn) system with the trans-polyacetylene, which is a famous Peierls system possessing soliton states, may be useful.[24] The soliton pair is immediately generated from an *e-h* pair within the time scale of 100 fs *in trans*-(CH)x.[25,26] These solitons make recombination after random walk. The large lattice relaxation energy resulting from the STE-like lattice deformation can readily assist the growth of the Pd^{3+} domain, instead of stabilizing the STE state. Our experimental result indicates that the time scale to stabilize the MI domain is larger than 160 fs, which is the peak position on the time-evolution curve at our lowest observable energy, 0.23 eV (see Fig. 2).

To conclude, we performed femtosecond luminescence spectroscopy in $[PdBr(chxn)_2]Br_2$ and observed a transient luminescence from near to mid-infrared region. The large Stokes shifts and the ultrafast decay of the luminescence indicate existence of a large lattice relaxation and the nonexistence of a local potential minimum corresponding to STE on the relaxation path, respectively. We attributed the ballistic nuclear WP dynamics to the relaxation process from the Peierls insulator toward the MI domain.

This work was supported in part by the Grant-in-Aid for Scientific Researches (B) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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