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Evidence for an excited state with a large lattice relaxation in quasi-one-dimensional halogen-bridged Ni complexes

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We investigated the excited states of a one-dimensional charge-transfer Mott insulator $[\mathrm{NiBr(chxn)_2}]\mathrm{Br_2}$ by femtosecond luminescence spectroscopy. In the picosecond region, we observed a luminescence component which is different from that observed under steady-state excitation. This picosecond luminescence has a large Stokes shift and a broad bandwidth, suggesting the existence of an excited state with large lattice relaxation in addition to the excited state with a small relaxation. The dynamical behavior of the luminescence has been qualitatively interpreted in terms of a model assuming two adiabatic potential-energy surfaces.

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The physics of one-dimensional electron lattice systems has been attracting much attention. Halogen-bridged transition-metal complexes are known to have a huge variety of elementary excitations and metastable states. Up to now, the systems having Pt as the transition metal have been subjected to extensive spectroscopic research, and many excited states, e.g., self-trapped excitons, polarons, and solitons have been investigated in detail. In recent years, the systems having Ni as a transition metal are receiving increased attention as a prototype of low-dimensional strong electron correlation systems. In $[\mathrm{NiBr(chxr)_2}]\mathrm{Br_2}$ (chxn: cyclohexanediamine), a strong electron correlation on the 3*d* orbitals of Ni opens a gap, resulting in upper (UHB) and lower Hubbard bands (LHB) and all the Ni ion have unpaired electrons in the LHB. Since the *p* orbital of halogen is located in this gap, this material becomes a charge-transfer-type Mott insulator.[1] This situation is very different from that of a system containing Pt, which forms charge-density waves due to weak electron correlations and strong electron-lattice interactions in the ground state.

Although the existence of a variety of metastable states and elementary excitations is expected in the system having Ni as the transition metal, they are not well understood. Since dynamical measurements of luminescence clearly identify excited states according to energy and lifetime, they provide us with rich information about excited states. Investigation of this material will clarify how the competition between electron-lattice interactions and electron correlations affects physical properties. This competition will also be reflected in the dynamical properties of the excited state.

The main structure of this material is a chain consisting of alternate Ni and Br ions. The Ni ions are surrounded by ligands, which connect with them tightly. Because of large on-site Coulomb energy, Ni ions uniformly take trivalency as $\mathrm{Ni^{3+}}$. Through photoexcitation at 1.35 eV, 4*p*(Br) electrons make the transition to UHB of 3*d*(Ni).[1] As for the relaxation process of the excited states, the photo-induced phase transition has been studied by means of pump-and-probe reflection measurements.[2] The luminescence spectra have been studied under steady-state excitation and a luminescence band with a small Stokes shift and a narrow bandwidth was reported.[3,4] From these results it has been suggested that the electron-lattice interaction is weak in this system, in contrast to PtX.

In this paper, we show evidence for the coexistence of excited states with a large lattice relaxation and a small lattice relaxation in $[\mathrm{NiBr(chxr)_2}]\mathrm{Br_2}$ based on the time-resolved luminescence spectroscopy with 110 fs resolution. Time-resolved luminescence measurement has been done by using the up-conversion technique. Freshly cleaved surfaces of single crystals of $[\mathrm{NiBr(chxn)_2}]\mathrm{Br_2}$ prepared by the electrochemical method were used for these measurements.[5] The sample was excited at a photon energy of 1.55 eV by Ti:sapphire laser pulses, which were amplified by a regenerative amplifier at a repetition rate of 200 kHz. The pulse width was 70 fs and the averaged power was 0.5 mW. The sample was mounted on a sample holder in a vacuum space of a He gas flow cryostat and was maintained at 4 K. The excitation light was polarized parallel to the chain axis of the crystal. The luminescence from the sample was collected by paraboloidal mirrors and was mixed with the amplified fundamental pulses in a nonlinear crystal. We used a $\mathrm{LiIO_3}$ crystal with a thickness of 300 μm, and controlled its position and angle by a computer to realize a good reproducibility in the conversion efficiency and the time origin. Owing to the type I phase-matching condition, only the luminescence component polarized parallel to the chain axis was converted into a sum frequency. The sum frequency light was focused into a double grating monochromator and was detected by a photomultiplier tube combined with a photon counter. Spectral resolution was about 5 nm, which was restricted by the bandwidth of the gating pulses. The overall time resolution of the system was about 110 fs and time intervals of measurements were 66.7 fs. The spectral response of this system was calibrated by using a tungsten standard lamp. The deviation of the timing, which might depend on the wavelength, was estimated to be less than the measurement intervals.

In measurements of the steady-state luminescence spectra, the excitation photon energy was 1.55 eV (Ti:sapphire laser) or 2.4 eV (Ar ion laser). The luminescence light was monochromatized by a triple grating monochromator (SPEX Triplemate) and was detected by a cooled charge-coupled device (CCD).

Figure 1 shows the time dependence of the luminescence intensity measured at various photon energies between 0.8

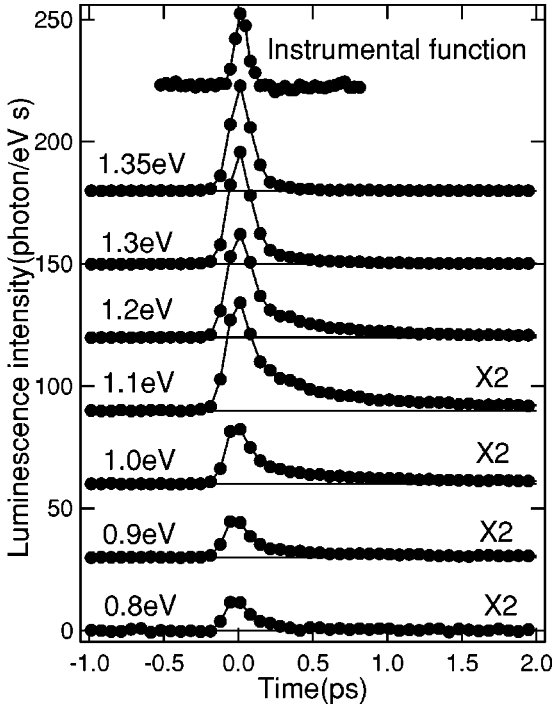

FIG. 1. The curve denoted "instrumental function" shows the time response of this measurement setup. The lower curves show the time evolution of the luminescence intensity at energies denoted the left side.

and 1.35 eV. The ordinate scale is proportional to the number of photons per unit energy interval per second. The background level was determined from the average of the signal in an interval of 5 ps before the time origin and subtracted from the data. The second harmonic of fundamental frequency obstructed the luminescence measurements around 1.55 eV. However, below 1.35 eV, this effect was negligible. The instrumental response function shown in Fig. 1 was measured as a cross correlation between the scattering from the sample surface and the gating pulse. Luminescence decay profiles were not affected by this instrumental response function. But it is hard to estimate the buildup time of luminescence, because the observed rise in the signal was close to the instrumental function. As can be seen in Fig. 1, the decay profiles depend on the photon energy. At high energy regions, the decay curves can be fitted by single exponential functions with a short lifetime. In contrast, the decay profiles in the low-energy region under 1.2 eV contain long lifetime components. In fact, the decay curve for 1.1 eV can be well fitted by a double exponential function as shown in Fig. 2. The decay constants obtained from the fitting were 150 and 1470 fs.

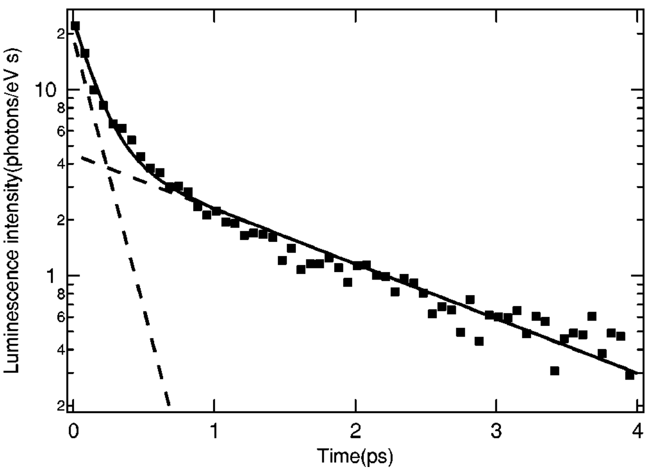

FIG. 2. The marks show the time evolution of the luminescence intensity at 1.1 eV, and the solid curve is a fitting function: $I(t) = 4.5\exp(-t/1.47) + 19\exp(-t/0.15)$. The dashed curves are the exponential components of the fitting function.

Figure 3 shows the time dependence of the luminescence spectra constructed from the data in Fig. 1. In order to avoid large fluctuations due to the low signal level after 1 ps, the signals were averaged within an appropriate period to obtain the data points. The data at 2 and 4 ps were the values averaged over 200 and 300 fs, respectively. For ease of viewing, the curves have been multiplied by the appropriate factors indicated in the figure. From Fig. 3, we can see two characteristic features in the time evolution of the spectra. The first is the change in the spectral bandwidth with time. Just after the buildup of the luminescence, the spectral bandwidth is larger than 0.3 eV, and it reduces to about 0.2 eV at 4 ps. In particular, the intensities at 1.3 eV and 1.35 eV decreased more rapidly than those of other energy regions within 0.5 ps. The second feature is the movement of the peak position of the luminescence spectrum to lower energy. Just

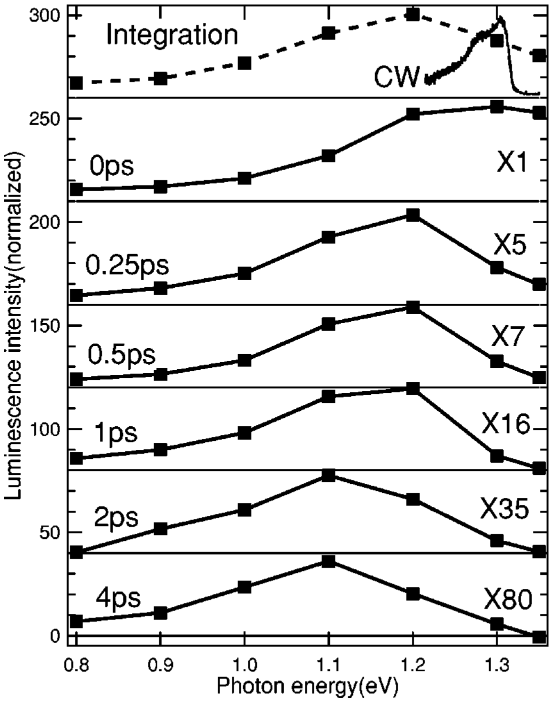

FIG. 3. The uppermost dashed curve denoted as "integration" shows a spectrum integrated from 0 to 10 ps. The solid curve denoted cw shows steady-state luminescence spectrum under 1.55 eV cw laser excitation. The lower curves show the time evolution of the luminescence spectra at indicated delay times. Their peak intensities are normalized by multiplying factors indicated at the right side.

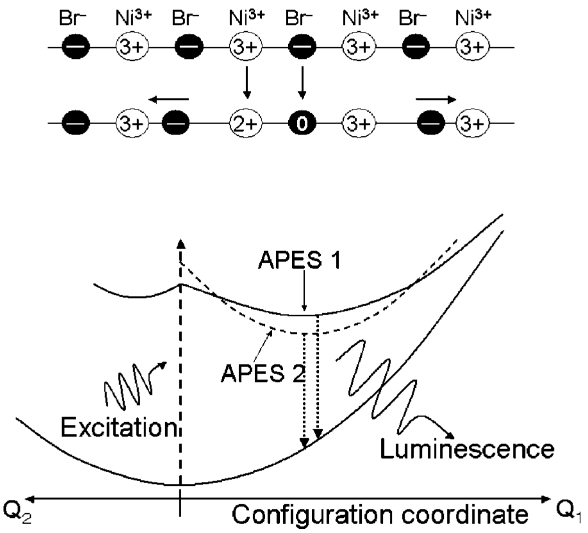

FIG. 4. The upper image is a schematic of the one-dimensional structure of the sample. The configurations before excitation and after lattice relaxation are illustrated. The lower image is the APES assumed in the model.

after the buildup of the luminescence, the spectral peak lies around 1.3 eV and it moves gradually toward lower energy to a final position around 1.1 eV. The integration of the luminescence from 0 to 10 ps is also plotted in Fig. 3. The peak of the picosecond luminescence spectra is located around 1.2 eV, and bandwidth is as large as 0.3 eV. For comparison, the steady state luminescence spectra under 1.55 eV cw laser excitation are plotted in Fig. 3.

The optical properties of this material have been investigated by several groups. In the absorption spectra, an intense peak was observed at 1.35 eV and assigned to a charge-transfer excitation corresponding to an electron transfer from a Br^- to an Ni^{3+} ion.[1] The luminescence spectra under steady-state excitation have been reported recently by Takaishi *et al.*[3] and Iwano *et al.*[4] In both investigations, the luminescence peak was located around 1.3 eV, giving a very small Stokes shift of approximately 0.02 eV. The bandwidth of the spectrum was below 0.05 eV.

We can compare these values with those in halogen-bridged platinum complexes (abbreviated as Pt-X:X=Cl, Br I), which are known to show luminescence bands due to self-trapped excitons. This family of materials has a linear chain similar to that of Ni-Br, but the ground state is the charge density wave (CDW) state. In Pt-Br, for example, the Stokes shift amounts 0.8 eV, and the bandwidth is about 0.3 eV, indicating the existence of a very strong electron lattice interaction.

The reported small Stokes shift and small bandwidth in Ni-Br suggest that the electron lattice interactions are weak.[3,4] In contrast to these reports, the peak of the integrated picosecond component of the luminescence spectra in our experiment lies around 1.2 eV and gives a Stokes shift about 0.15 eV, which is considerably larger than the value obtained from the steady-state measurements. The possible lattice relaxation is shown in . 4. In the ground state, the Br ions are located at the midpoints of neighboring Ni ions. The Ni ions are tightly bound to the ligand molecules, and the positions of the halogen ions are determined by the balance of the Coulomb forces from the surrounding ions. Even after the charge-transfer excitation, the neutral Br between Ni^{2+} and Ni^{3+} will keep the same position, because it does not experience the Coulomb force. On the other hand, the neighboring Br^- ions will make displacement due to the change of the Coulomb force as pointed by arrows. This lattice deformation could be the cause of the Stokes shift, though quantitative estimation is difficult. Another important difference is their bandwidths. The bandwidth larger than 0.3 eV for the picosecond component is consistent with the existence of large electron-lattice interactions.

In general, we expect that the time-integrated luminescence spectrum is equal to the steady-state luminescence spectrum. However, there was a considerable difference between the picosecond component and the steady-state luminescence. In the measurements of the steady-state luminescence spectra, we examined the effect of the excitation condition on the spectral shape. The luminescence spectra under excitation at 2.4 and 1.55 eV did not show any appreciable difference in the energy range covered by the CCD detector. We measured the spectra with mode-locked pulses with a pulse width of 1.5 ps and a repetition rate of 80 MHz at a fluence of $8.3\ \mathrm{nJ/cm^2}$ on the sample surface. In this case also, the spectrum was the same as that under cw excitation. Moreover, in the time-resolved luminescence measurements, the luminescence intensity maintained linearity in the excitation density range from $10-40\ \mu\mathrm{J/cm^2}$. From these results, we concluded that the difference of the spectral shape cannot be ascribed to the difference of excitation conditions. The only sensible way to understand this situation is to assume the lifetime of the steady-state luminescence to be very long. In this case, the long lifetime component cannot be detected in up-conversion measurement. One possible interpretation is to assign the band with a small Stokes shift to the free exciton and the other to the self-trapped exciton. However, it is hard to expect a long lifetime of the free exciton, because there should be no energy barrier between the free and the self-trapped exciton states in the one-dimensional system, according to the general theory of self-trapping.[6] Another interpretation is to assume two different lattice configurations in the relaxed state. Actually, the coexistence of two types of lattice relaxation (on-center and off-center halogen dimer configurations) associated with excitons has been reported for alkali halides.[7,8]

Next, we proceed on to the dynamical behavior of the luminescence. As we have already presented, the peak shifts to lower energy and the bandwidth decreases during relaxation. First we consider the possibility of wave-packet motion. In systems with a strong electron-phonon interactions, we can expect to observe a wave-packet motion on an adiabatic potential energy surface (APES) in the configuration coordinate space.[9,10] This model can explain the shift of the luminescence peak to lower energy. If the damping is very large, returning motion is not necessarily observed. But in this measurement, the peak shift requires 2 ps, which is far larger than the oscillation period of 300 fs found in a similar material, Pt-Br. Thus, this model seems unlikely.

The second possibility is the cooling of the excited species on an APES. In this model, just after excitation, the excited species is assumed to be distributed on an APES following a Boltzmann distribution with a high temperature corresponding to the excess energy in the photoexcitation. They will be cooled down as time elapses, then the spectral bandwidth decreases. This is similar to the situation found in Pt-Cl, in which the narrowing of the luminescence spectra is well understood in terms of a cooling model.[11] If we assume an anharmonic APES, it is possible to reproduce the movement of the center of gravity of the luminescence spectrum. However, even in this case, we can easily see that the spectral peak does not move.

In the third model, we suppose two energy levels, as illustrated in Fig. 4, in which the luminescence photon energy of APES 2 is smaller than that of APES 1. We assume that the lifetime of APES 2 is longer than that of APES 1. In this model, just after excitation, the excited species will be distributed on the APES 1, and the cooling on this APES causes decreasing of the luminescence bandwidth. The population on APES 1 will be then transferred to APES 2 across the crossing points and will decay slowly, reflecting the longer lifetime of APES 2. In terms of this model, we can understand the double exponential decay behavior in Fig. 2, the decreasing of the spectral bandwidth, and the peak shift simultaneously.

The existence of two closely located energy levels has been reported by Okamoto *et al.*[12] based on nonlinear optical susceptibility measurements. These levels are found for the configuration without lattice deformation and we have no information about the energy lineup after lattice relaxation.

In the near-infrared region, the lifetime of spontaneous emission is estimated to be around several nanoseconds, if it is a fully allowed transition. However, the observed lifetime of the luminescence is only several picoseconds, suggesting that the lifetime is dominated by a nonradiative relaxation process. It is possible to expect a large nonradiative path to open after large lattice relaxation, because the APES s of the excited state and ground state come closer as shown in Fig. 4.

In conclusion, we observed the luminescence spectra of $[\mathrm{NiBr(chxn)_2}]\mathrm{Br_2}$ in the picosecond region and have found that they are not identical with those observed in steady-state luminescence. The large Stokes shift (0.15 eV) and the broad spectral width (0.3 eV) of the picosecond component showed the existence of an excited state with a large lattice relaxation, in addition to that with a small relaxation. This indicates that the electron-lattice interaction in this system is not weak. The dynamical Stokes shift and the narrowing of the spectra are well understood in terms of a model assuming two energy levels in the excited state. Theoretical studies will be required to understand the multiple lattice relaxation and the decay dynamics in strongly correlated systems with a strong electron-lattice interaction.

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