

## Time-resolved photoluminescence study of excitonic relaxation in one-dimensional systems

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Self-trapped exciton luminescence of quasi-one-dimensional (1D) halogen-bridged mixed-valence platinum complexes  $[\text{Pt(II)(EA)}_4][\text{Pt(IV)Cl}_2(\text{EA})_4]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$  (EA = ethylamine) and  $[\text{Pt(II)(en)}_2][\text{Pt(IV)Cl}_2(\text{en})_2](\text{ClO}_4)_4$  (en = 1,2-diaminoethane) are studied by time-resolved photoluminescence experiments. The lifetimes of the luminescence of self-trapped excitons are exceptionally short, of the order of 100 psec. We interpret the short lifetime by a "giant oscillator strength" caused by a strong coupling between the electron and hole of the 1D charge transfer exciton and an extended polaronlike character of the 1D state. The lifetimes of the broad luminescence and of the resonant Raman lines during the barrier-free relaxation process are both faster than 7 psec.

When a free ( $F$ ) exciton is optically excited in a system with strong electron-phonon coupling, it has the possibility to relax to a self-trapped ( $S$ ) exciton.<sup>1</sup> In a three-dimensional (3D) system, the  $F$  state is metastable because of an adiabatic potential barrier between the  $F$  (large polaron) and  $S$  (small polaron) states. In a one-dimensional (1D) system, on the contrary, the  $F$  state cannot exist as a metastable state, but immediately relaxes to the  $S$  state since no potential barrier exists. Recently, this process was demonstrated in a quasi-1D metal complex, Wolfram's red salt<sup>2-4</sup> (WRS), by resonant Raman and luminescence measurement.<sup>5,6</sup>

Wolfram's red salt with the formula  $[\text{Pt(II)(EA)}_4][\text{Pt(IV)Cl}_2(\text{EA})_4]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$  (EA = ethylamine), is the best known of the halogen-bridged mixed-valence metal complexes (HMMC's).<sup>7</sup> The crystal is made of chains of  $-\text{Pt(II)}-\text{Cl}-\text{Pt(IV)}-\text{Cl}-$  surrounded by organic ligands as shown in Fig. 1. The structure of HMMC's can be understood in terms of a 1D commensurate charge-density wave (CDW) of  $-\text{Pa}^{3-\rho}-\text{Cl}^--\text{Pt}^{3+\rho}-\text{Cl}^-$  ( $0 < \rho \leq 1$ ). The lower part of Fig. 1 shows the absorption and the luminescence spectra of WRS. The strongly polarized absorption band was assigned to charge-transfer (CT) absorption from  $d_{z^2}[\text{Pt(II)}]$  to  $d_{z^2}[\text{Pt(IV)}]$ .<sup>8</sup> Raman spectra ( $R$ ) were observed to be a series of stretching  $\text{Cl}-\text{Pt(IV)}-\text{Cl}$  vibrational resonances<sup>9</sup> followed by a strongly Stokes-shifted broad Gaussian-type luminescence band ( $L$ ) from the self-trapped exciton.<sup>5,10</sup> Similar absorption and luminescence bands were observed also in other HMMC's<sup>11-13</sup> such as  $[\text{Pt(II)(en)}_2][\text{Pt(IV)Cl}_2(\text{en})_2](\text{ClO}_4)_4$  (en = 1,2-diaminoethane), which can be abbreviated as  $\text{Pt(en)Cl}$ .<sup>14</sup> Moreover, a broad and continuous luminescence band ( $B$ ) was observed between the excitation energy and the high-energy tail of the  $L$  band.<sup>6</sup> It was assigned to radiative recombination during a barrier-free relaxation process in the 1D system. However, dynamical aspects of the relaxation process have not been investigated so far.

In this Rapid Communication, we report on time-resolved photoluminescence measurements of some HMMC's. We find very short radiative lifetimes of the luminescence ( $L$ ) band of WRS and  $\text{Pt(en)Cl}$ .

Single crystals were prepared following the method described in the literature.<sup>3,15</sup> The sample is excited with a synchronously pumped mode-locked dye laser (wavelength 583 nm) with a repetition rate of 80 MHz and a pulse duration of 4 psec. The excited luminescence is spectrally dispersed by a 0.32-m monochromator and temporally resolved by a 2D Hamamatsu synchroscan streak camera with an S1 or S20 photocathode. Time-integrated

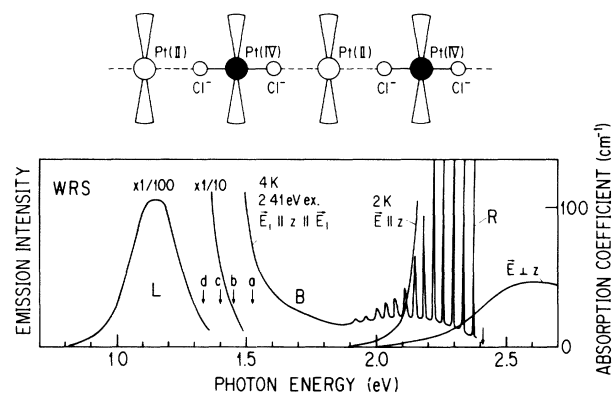


FIG. 1. Schematic structure of a chain of halogen-bridged mixed-valence metal complexes (HMMC), and absorption and luminescence spectra of Wolfram's red salt (WRS),  $[\text{Pt(II)(EA)}_4][\text{Pt(IV)Cl}_2(\text{EA})_4]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$  (EA = ethylamine) (Ref. 6). The charge transfer absorption band is strongly observed for light polarized in the chain direction ( $\vec{E} \parallel z$ ). Luminescence spectrum excited at 2.41 eV is shown for incident and observed light polarized in the chain direction ( $\vec{E}_i \parallel z \parallel \vec{E}_o$ ). A series of Raman lines ( $R$ ), a continuous luminescence ( $B$ ) band, and a strong Gaussian-type luminescence ( $L$ ) band are observed.

spectra of the *L* band were measured using a prism monochromator and a PbS detector (Fig. 1)<sup>6,12,13</sup> or a 0.75-m monochromator and a Ge detector (lower parts of Fig. 2).<sup>16</sup> The quantum efficiency of the *L* band was measured using a Si photodiode optical power meter.

In Fig. 2, the low-temperature (4 K) luminescence lifetimes of the *L* band are shown for (a) WRS and (b) Pt(en)Cl. The luminescence lifetime depends slightly on the sample and on the observed photon energy. We can estimate  $\tau$  as  $100 \pm 10$  psec for WRS and  $90 \pm 30$  psec for Pt(en)Cl. Most of the samples show an increase in the lifetime at higher photon energies of the luminescence. The lifetime is almost constant below 100 K and decreases slightly from 100 K to room temperature. For example, at the peak of the *L* band of WRS sample 2,  $\tau$  is 75, 75, 51, and 39 psec at 4, 87, 200, and 271 K, respectively. Mixed-crystals of  $[\text{Pt}(\text{II})(\text{en})_2][\text{Pt}(\text{IV})(\text{Cl}_{1-x}\text{Br}_x)_2(\text{en})_2](\text{ClO}_4)_4$ , which are abbreviated as Pt(en)Cl<sub>1-x</sub>Br<sub>x</sub>, have similar luminescence spectra as the pure compounds.<sup>17</sup> We measured the lifetimes of the *L* bands of some mixed crystals with  $x=0.1, 0.25, \text{ and } 0.5$ , which were all around 80–180 psec.

Figure 3 shows time-resolved luminescence of the *B* band at various photon energies  $h\nu$  at the high-energy tail of the *L* band of WRS sample 1. The energies of (a)–(d) are indicated by the arrows in Fig. 1. At energies less than 1.33 eV, the lifetime is of the order of 100 psec, i.e., similar as around the peak of the *L* band, shown in Fig. 2(a). However, at higher energies, another component appears which is as fast as the decay of the incident light, in addition to the slow component [Fig. 3(c)]. The radiative intensity of the fast component increases with increasing  $h\nu$ , and for  $h\nu > 1.52$  eV, only the fast component is

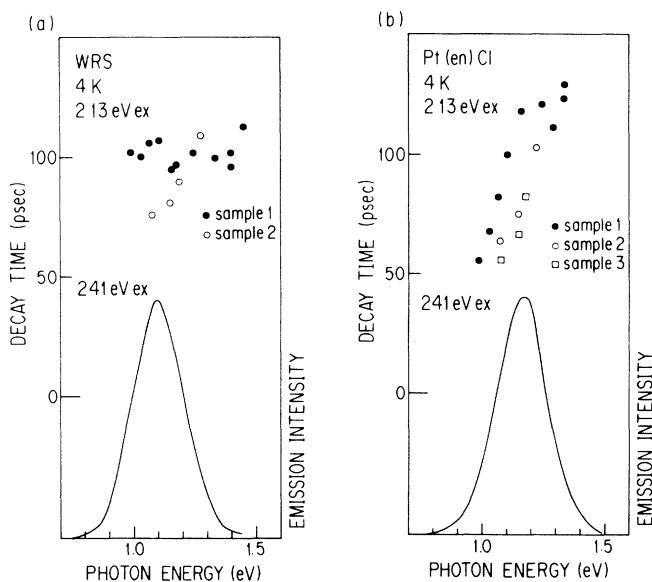


FIG. 2. Lifetimes of the *L* band of (a) WRS, and (b) Pt(en)Cl,  $[\text{Pt}(\text{II})(\text{en})_2][\text{Pt}(\text{IV})\text{Cl}_2(\text{en})_2](\text{ClO}_4)_4$  ( $\text{en}=1,2$ -diaminoethane) excited at 2.41 eV shown in the lower part have been measured with a higher resolution spectrometer than previously, and differ slightly from the spectra in Fig. 1 and Refs. 6, 12, and 13.

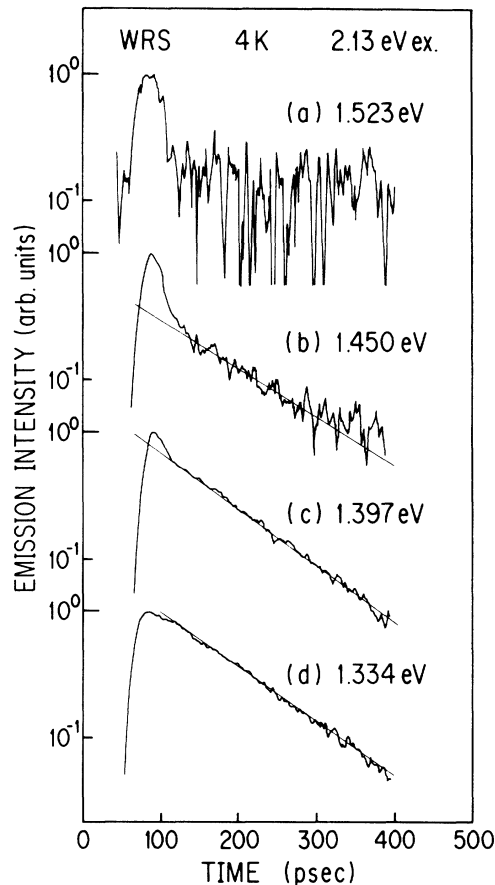


FIG. 3. Lifetimes of the luminescence of WRS sample 1 at the energies where the fast and slow components coexist. The observed photon energies of the luminescence shown in (a)–(d) are indicated by arrows in Fig. 1.

observed [Fig. 3(a)]. The lifetime of the fast component and the series of Raman lines *R* are measured to be less than 7 psec.

The luminescence from the *S* state is observed in various materials<sup>1</sup> such as alkali-halides,<sup>18</sup> solid rare gases,<sup>19</sup> and organic molecular crystals.<sup>20</sup> However, the lifetimes of these *S* states are always longer, around 1 nsec to 10  $\mu\text{sec}$ . The lifetime of the *S* state of the HMMC's determined here is exceptionally short. The overall lifetime  $\tau$  is determined by

$$1/\tau = 1/\tau_r + 1/\tau_{nr}, \quad (1)$$

where  $\tau_r$  is the radiative lifetime and  $\tau_{nr}$  is the nonradiative lifetime. The quantum efficiency of the luminescence from the self-trapped state  $\eta_{r,\text{STE}}$  is given by

$$\eta_{r,\text{STE}} = \tau_{nr}/(\tau_{nr} + \tau_r). \quad (2)$$

To get more information about the origin of the short lifetime, we measured the external quantum efficiency of the *L* band  $\eta_r^{\text{ext}}$ . The relationship between  $\eta_r^{\text{ext}}$  and  $\eta_{r,\text{STE}}$  is given by

$$\eta_r^{\text{ext}} \leq \eta_r = \eta_{\text{STE}}\eta_{r,\text{STE}}, \quad (3)$$

where  $\eta_r$  is the internal quantum efficiency of the *L* band,

and  $\eta_{\text{STE}}$  is the creation efficiency of the self-trapped state by the laser excitation. We get  $\eta_r^{\text{ext}} = 0.025 \pm 0.01$  excited at 2.41 eV both for WRS and Pt(en)Cl. In any compounds, the measured value of  $\eta_r^{\text{ext}}$  is much, often more than 10 times, smaller than the value of  $\eta_r$ . Thus, typical values of  $\eta_r = 0.20$  and  $0.025$  (= the minimum value) are used in the following discussion.

One possibility to explain the short lifetime of the  $S$  state of the HMMC's is that  $\tau_{nr} \ll \tau_r$ , in which case  $\eta_{r,\text{STE}}$  is small and  $\tau$  is determined mainly by  $\tau_{nr}$ , and another is that  $\tau_{nr} \gg \tau_r$ , in which case the radiative lifetime  $\tau_r$  determines the overall lifetime  $\tau$ . If  $\tau_{nr} \ll \tau_r$ ,  $\tau_r$  must be less than  $(1/\eta_r - 1)\tau_{nr}$  from Eqs. (2) and (3). Thus, the maximum value of  $\tau_r$  is 400 psec ( $\eta_r = 0.20$ ) or 4 nsec ( $\eta_r = 0.025$ ). If  $\tau_{nr} \gg \tau_r$ , we get  $\tau_r = 100$  psec. The transition probability of the radiative process is given by<sup>21</sup>

$$1/\tau_r = 14.5f\sqrt{\epsilon}E(\text{eV})^2(\mu\text{sec}^{-1}), \quad (4)$$

where  $f$  is the oscillator strength of the luminescence,  $\epsilon$  is the unknown dielectric constant (we assume a reasonable value of  $\epsilon \sim 10$ ), and  $E$  is the observed photon energy. Our experimental result yields  $f \sim 40$  ( $\eta_r = 0.20$ ) or  $f \sim 4$  ( $\eta_r = 0.025$ ) if  $\tau_{nr} \ll \tau_r$  and  $f \sim 170$  if  $\tau_{nr} \gg \tau_r$ , which, in any case, is a much larger value than obtained for other materials. This giant oscillator strength can be explained by a combination of two effects in a strongly coupled 1D electron-phonon system: (1) a large overlap between electron and hole of the exciton and (2) an extended motion of the center of mass of the exciton.

A CT absorption band with a very large oscillator strength is commonly observed in HMMC's. For example, the oscillator strength per unit cell,  $f_{\text{abs}}$ , is 3–4 in Pt(en)Cl.<sup>12,22</sup> The oscillator strength of the luminescence per unit cell,  $f_0$ , is also expected to be large. Since only one excited electronic state can produce the luminescence,  $f_0$  must be less than 1. Thus, we estimate  $f_0$  as  $\sim 1$ . This value is already much larger than that of the 3D excitons in other materials. However, it only partly explains the short lifetime of the  $S$  state. Let us discuss the second effect.<sup>23,24</sup> The  $S$  state in a 1D system may have an extended polaronlike character, when the short-range interaction has a moderate coupling constant as in HMMC's.<sup>25</sup> Hence, the size of the  $S$  state, i.e., the range where the center of mass of the exciton moves around, might be larger than that of the ordinary small polaron which is localized in one unit cell of  $\text{Pt}^{3-\rho} - \text{Cl}^- - \text{Pt}^{3+\rho}$ . The number of unit cells occupied by the  $S$  state,  $N$ , is given by  $f/f_0$ , if we attribute the enhancement of the ob-

served oscillator strength to this effect. We get  $N \sim 40$  ( $\eta_r = 0.20$ ) or  $N \sim 4$  ( $\eta_r = 0.025$ ) if  $\tau_{nr} \ll \tau_r$ , and  $N \sim 170$  if  $\tau_{nr} \gg \tau_r$ .

We suggest the existence of a variety of microscopic origins of the  $S$  state in HMMC's in order to explain the fact that the lifetime becomes longer with increasing  $h\nu$ . A 1D motion of the  $S$  state as a solitonic exciton (Davydov's soliton)<sup>26</sup> has been already suggested,<sup>6</sup> and large value of  $N$  makes such a motion possible. In the case of  $\tau_{nr} \ll \tau_r$ , possible nonradiative channels are the escape of electrons by tunneling through or surmounting the potential barrier.<sup>27</sup> From the shortening of the lifetime around room temperature we estimate the barrier height as 20 meV, and only the tunneling process will be observed at less than 100 K. Several escape models to various metastable states are possible.<sup>25,28–31</sup>

We finally comment on the dynamical aspect of the relaxation process. The lifetime of Raman lines  $R$  and the broad band  $B$ , which were assigned to radiative recombination during the relaxation process, must be shorter than 10 psec. We checked this experimentally: the  $R$  and  $B$  band follow directly the shape of the exciting laser pulse and are faster than 7 psec. At the higher energy tail of  $L$ , as shown in Figs. 3(b) and 3(c), both fast and slow components coexist. The lifetime of the slow component is approximately the same as that of the peak of the  $L$  band. Thus, we assign the fast component as luminescence  $B$  emitted during the relaxation, and the slow component as luminescence  $L$  emitted from the equilibrium state.

In summary, we have studied the lifetimes of the luminescence of the self-trapped exciton in quasi-1D HMMC's by time-resolved photoluminescence measurements. The lifetime of the decay of the  $L$  band is exceptionally short, of the order of 100 psec. The quantum efficiency of the  $L$  band is more than 0.025. We interpret the short lifetime by a "giant oscillator strength" caused by a strong coupling between the electron and hole of the 1D charge-transfer exciton and an extended polaronlike character of the 1D state. The  $B$  band and the Raman lines  $R$  are faster than 7 psec. Our time-resolved data further support the existing model of the barrier-free relaxation and recombination processes in 1D systems.

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