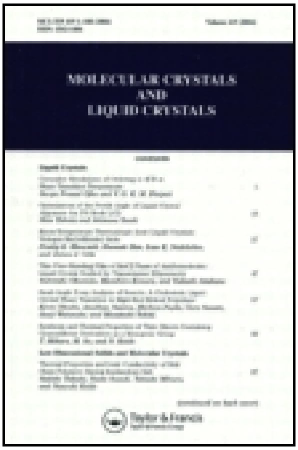

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RELAXATION PROCESSES OF PHOTOEXCITED STATES IN HALOGEN-BRIDGED MIXED-VALENCE METAL COMPLEXES

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Abstract Excitation spectra of the self-trapped exciton luminescence bands and those of photo-induced absorption bands of halogen-bridged mixed-valence metal complexes have been measured. The excitation spectra of luminescence bands begin to decrease from energies smaller than the peak energies of the charge transfer exciton absorption bands. The excitation spectra of photo-induced absorption bands begin to rise from the same energies. These show the competition between the self-trapped excitons and the photo-induced defect states in their generation processes.

INTRODUCTION

The halogen-bridged mixed-valence metal complex (HMMC) can be considered to be one of the prototype materials for the studies of the optical properties of one-dimensional electron system$^{1)}$.

The chain structure of a HMMC is shown in Fig. 1. In Pt, Pd, and some Ni complexes, the one dimensional half-filled conduction bands are divided into valence and conduction bands due to halogen ion distortions and CDWs with periods of twice the metal-metal distance are formed. The electronic excitation across the CDW gap of a HMMC can be observed as an intense charge transfer (CT) exciton absorption band polarized parallel to the chain axis$^{2,3)}$.

In HMMCs, many studies have been made on the self-trapped excitons$^{1,2,4,5-6)}$ (STEs) and the photo-induced defect states (PDSs)$^{7-10)}$. However, the generation processes of them and relation among them have not become clear yet. In order to elucidate the

$$-X^{-}—M^{3+\rho}—X^{-}---M^{3-\rho}---X^{-}—M^{3+\rho}—X^{-}---M^{3-\rho}—$$

FIGURE 1 The chain structure of a HMMC (M=Pt, Pd, or Ni, X=Cl, Br, or I, 0<ρ<1).

generation processes of the STEs and the PDSs from the photo-excited states, the excitation spectra of the STE luminescence bands and the photo-induced absorption (PA) bands of the PDSs have been measured.

EXPERIMENT

The excitation spectra of PA bands, STE luminescence bands, and photo-conductivities have been measured using a 150W Xe arc lamp as a light source. The light from the Xe arc lamp was passed trough a monochromator and a polarizer. The surfaces of the crystals were irradiated by the light. In the excitation spectra measurements of PA bands of $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$, ($Pt\text{-}Cl\text{-}ClO_4$, en=ethylene-diamine), the change of the transmittance was directly measured. In other excitation spectra measurements, the excitation light was chopped, and the AC components of the signals were detected by a lock-in amplifier.

The excitation light power density dependence of the intensities of the PA bands of $[Pt(en)_2][Pt(en)_2Br_2](SO_4)_2 \cdot 6H_2O$, ($Pt\text{-}Br\text{-}SO_4$), were measured using 2.71eV lasing line of an Ar-ion laser as a light source. The light was polarized parallel to the chain axis and chopped (1Hz). The AC components of the transmitted light was detected by the lock-in amplifier.

RESULTS and DISCUSSION

Fig. 2 shows the imaginary part of the dielectric constant (ε_2, broken line), PA spectrum (solid line), and the luminescence spectrum (dotted line) of $Pt\text{-}Br\text{-}SO_4$ for polarization parallel to the .rm38 chain axis. The asymmetric broad absorption band at 2.65eV in ε_2 spectrum is a CT exciton absorption band. The PA bands indicated by A, B, and C are considered to be due to PDSs such as solitons or polarons.[9] The luminescence band is due to a STE.

Fig 3.(a) shows the polarized component of the ε_2 parallel to the

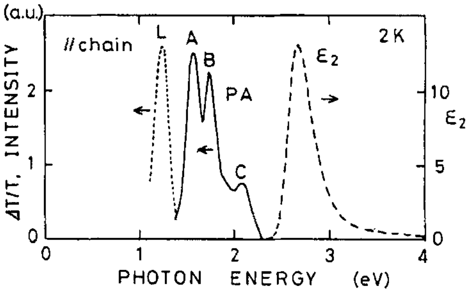

FIGURE 2 The ε_2 (broken line), the PA spectrum (solid line), and the luminescence spectra (dotted line) of $Pt\text{-}Br\text{-}SO_4$ for polarization parallel to the chain axis at 2K.

chain axis. The excitation spectra of the A- (dashed line) and the C- (dotted line) bands are shown in Fig. 3 (b) together with the excitation spectrum of the STE luminescence band (solid line). The excitation spectrum of the B-band is quite similar to that of the A-band and is not shown here. Here, irradiated light is polarized parallel to the chain axis.

It is seen in the figure that the excitation spectrum of the STE luminescence band has a maximum at an energy smaller than the peak energy of the CT exciton absorption band and begins to decrease from the energy. This means that the efficiencies of the nonradiative relaxation processes of photoexcited CT excitons rise from the energy. It is also seen in the figure, that the excitation spectrum of the A-band rises from the same energy. This indicates that the generation of the STEs and that of the PDSs which can be observed as the A- and the B-bands compete with each other. The excitation spectrum of the C-band is apparently different from that of the A-band. This means that the PDS observed as the A and the B- bands and the PDS observed as the C-band are different states.

Quite similar relation between the excitation spectrum of the STE luminescence band and that of the PA band ("A"-band[8]) are

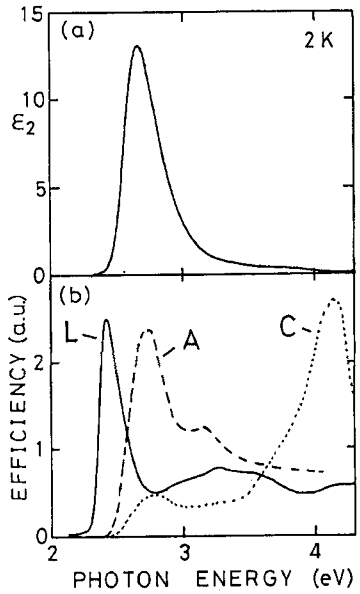

FIGURE 3 (a) The ε_2 (//chain) of Pt-Br-SO_4 at 2K. (b) The excitation spectra of the STE luminescence, the A-, and the C- absorption bands of Pt-Br-SO_4 at 2K.

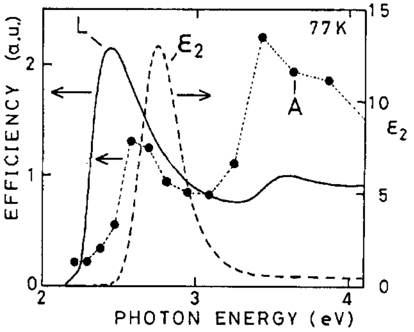

FIGURE 4 The ε_2 (dashed line, //chain), the excitation spectra of the STE luminescence (solid line) and the A-absorption (solid circle) bands of Pt-Cl-ClO_4 at 77K.

also seen in Pt-Cl-ClO_4 as shown in Fig. 4. It is not clear whether the depression around 3.0 eV in the excitation spectrum of the "A"-band is a real structure or an apparent structure due to the saturation effect. Any way, the excitation spectrum of the "A"-band rises from the energy from which the efficiency of the STE luminescence decreases. The excitation spectra of the STE luminescence bands of three other complexes which have efficient STE luminescence bands have been measured. The results are shown in Fig. 5. It is apparently seen that efficiency of the STE luminescences also begin to decrease from the energies smaller than the peak energies of the CT exciton absorption bands which are indicated by arrows. This means that the generation of STEs also compete with nonradiative relaxation processes in these complexes.

The above facts show that the competition between the generation of the STEs and that of the PDSs which can be observed as "A"- and "B"-bandsin Pt-Br-SO_4 and Pt-Cl-ClO_4 commonly occurs in the relaxation processes of CT excitons in the complexes with efficient STE luminescence bands. According to the results of the electro-refrectance measurements, the CT exciton absorption bands are made of single component exciton transition$^{11)}$. It is quite strange that the efficiencies of the generation of STEs and PDSs change so steeply in the energy region of the CT exciton absorption band. There may be two possible mechanisms of the competition between the generation of the STEs and that of the PDSs in the relaxation processes of the photoexcited CT excitons as follows. 1) The CT excitons begin to relax on different passes immediately after their generation. The relaxation rates of CT excitons on these passes have large energy dependence by some reason. 2) The CT excitons first relax on the pass to the STEs. Some of them dynamically convert into PDSs trough the crossing point of the potential surfaces of the STEs and the PDSs before

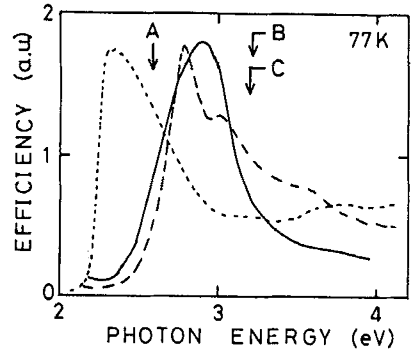

FIGURE 5 The excitation spectra of the STE luminescence bands and the peak energies CT exciton absorption bands of $[Pd(en)_2]$-$[Pt(en)_2Br_2](ClO_4)_4$, (dotted line, A), $[Pd(en)_2][Pt(en)_2Cl_2]$-$(ClO_4)_4$, (broken line, B), and $[Pt(chxn)_2][Pt(chxn)_2Cl_2](ClO_4)_4$, (solid line, C) at 77K.

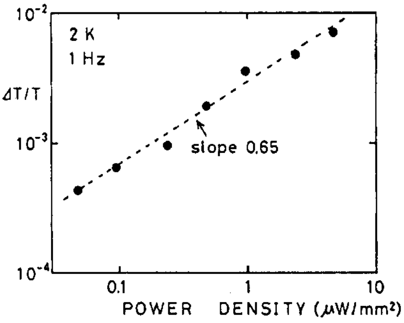

FIGURE 6 The excitation light power density dependence of the intensity of the A-band of Pt-Br-SO_4 at 2K.

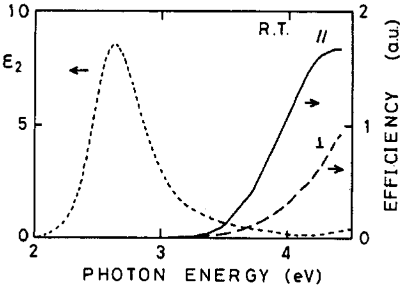

FIGURE 7 The excitation spectra of the photo-conductivity of Pt-Br-SO_4 for excitation light polarized parallel (solid line) and perpendicular (broken line) to the chain axis and ε_2 (dotted line, //chain) of Pt-Br-SO_4 at room temperature.

they reach thermal equilibrium. Anyway, more studies are needed to reach a clear conclusion.

In order to get more information about the PDSs of Pt-Br-SO_4, the excitation light power density dependence of the PA bands and the excitation spectra of the photo-conductivity have been measured.

The excitation light power density dependence of the A-band are shown in Fig 6. The points lie on a line of slope 0.65. The B- and the C- bands also have sub-linear power density dependences. These seem to shows that the annihilation processes of the PDSs are not geminate recombination processes and that the PDSs are mobile even at 2K.

Fig. 7 shows the excitation spectra of photo-conductivity at room temperature for the excitation light parallel and perpendicular to the chain axis. The polarized component of ε_2 parallel to the chain axis are also shown in the figure. It is seen that excitation spectrum of the photo-conductivity for the excitation parallel to the chain axis is quite similar to that of the excitation spectrum of the C-band in Fig. 3 (b). This indicates that the PDS which is observed as the C-band is a charged state.

CONCLUSION

We have found that the generation of the STEs and that of the PDSs which are observed as "A"- and "B"-bands compete with each other in the relaxation processes of the CT excitons of the complexes with efficient STE luminescence bands. There are two kinds of PDSs. One of them is efficiently generated from the CT excitons. Another kinds of PDS is not efficiently generated from the CT exciton and has charge.

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