LUMINESCENCE AND ELECTRONIC STRUCTURE OF THE SELF-TRAPPED EXCITON IN ALKALI FLUORIDES AND CHLORIDES

K.S. SONG
Department of Physics, University of Ottawa, Ottawa, Canada

and

A.M. STONEHAM and A.H. HARKER
Theoretical Physics Division, AERE, Didcot, UK

Luminescence of the self-trapped exciton in alkali halides is analysed on the basis of recent theoretical works. It is shown that the short-lived σ-band originates from an orbital state which is distinct from that of the much studied triplet state. Luminescence from the lowest orbital state consists of two components and this gives rise to the peculiar behaviour of the π-band, as has been reported recently by Purdy and Murray for KCl.

1. Introduction

The self-trapped exciton (STE) in halide crystals has been the subject of much spectroscopic work, both in emission [1] and in absorption [2]. The properties of most interest in this paper concerns the electronic states of the STE which are at the origin of the two luminescence bands. One is the short-lived σ-band (spin-allowed), polarized parallel to the axis of the STE and the other is the long-lived π-band (spin-forbidden) with its polarization vector perpendicular to the axis of exciton. The spin-forbidden transition becomes weakly allowed through the spin-orbit interaction. It has generally been assumed that the two bands derive from the same orbital state. Recent Hartree–Fock calculation [3] on the STE in NaCl has rejected this idea of two states split by exchange effect on the ground of the very small exchange splitting obtained. Instead it was suggested there that the two bands originate from two distinct orbital states. Several recent experimental works [4,5] also pointed to the same conclusion. This problem is now resolved by our pseudo-potential calculation on the electron part of the STE in alkali fluorides and chlorides. For all the systems studied, we find two orbital states of same symmetry (A_{1g} in one electron description), separated by approximately the right amount of energy to explain the two emission bands. We conclude on the basis of these works that the σ-band derive from the spin singlet state of A_{1g}^* (* for higher state), while the long-lived π-band is from the triplet state of A_{1g}, which is also the lowest bound state of the STE in all systems we studied. The

lowest singlet state $^sA_{1g}$ can not be directly populated because of the large recombination probabilities of a singlet exciton. The long-lived triplet exciton is believed to reach the lowest triplet state $^tA_{1g}$ in all systems (explaining thus the observation that π-band is always present, even when σ-band is absent, as in KCl). The possibility then exists that the lowest singlet state be thermally populated from the close triplet state. Recent work of Purdy and Murray [7] on the π-band in KCl strongly indicates that it is indeed the case. They find that the intensity of the π-band varies with temperature quite differently from the lifetime, exhibiting a remarkable plateau at around 20 K. These results suggest the existence of an another exciton state close to the triplet state, connected thermally.

We shall first present a brief account of our pseudo-potential calculation and discuss the results. An analysis of the experimental results of Purdy and Murray will then follow.

2. Pseudo-potential calculation of the STE

We have followed the pseudo-potential approach of Bartram et al. [8] to study the energy levels and the wave functions of the electron bound to the self-trapped hole, which is in its lowest state (B^0_{3u}). Bound states of different symmetries are calculated for the electron part of the STE.

The potential energy consists of the sum of point-ion potential and an "ion-size" correction as introduced by Bartram et al. Upto ten shells of ions were treated in the ion-size correction. The relaxations of the central halogen ions, where the self-trapped hole is localized, as well as those of the two nearest neighbour alkali-ions were taken into account. Linear combinations of large number of Slater-type orbitals with s, p and d character consituted the wave functions. The principal exponents in the Slater-type orbital were determined variationally in a simpler version of the calculation. The entire numerical calculation has been carried out by a computer code named PRISM, developped at Harwell.

Energies obtained for NaCl are shown in table 1 as an example. The results obtained for alkali fluorides and chlorides can be summarized as below.

(1) Bound states of the STE (corresponding to the hole in its lowest state B^0_{3u}) appear as indicated in fig. 1. (States which are connected optically to the lowest state only are shown.)

(2) M-like absorptions ($A_{1g} \rightarrow B_{1u}$, B_{2u}, B^*_{3u}) as observed by Williams and Kabler

Table 1
Pseudo-potential results of energy levels of the STE in NaCl (with the hole in B^0_{3u} state).

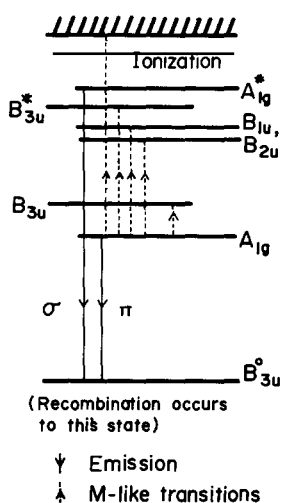| State	A_{1g}	B_{3u}	B_{2u}	B_{1u}	B^*_{3u}	A^*_{1g}	B_{3g}	B_{2g}
Energy (eV)	−2.77	−2.44	−0.88	−0.82	−0.77	−0.21	−1.03	−0.11

Fig. 1. Energy levels of an electron trapped by a V_k-centre. The emission bands, as well as the M-like absorption bands, of the STE are indicated. (Hole is in B^0_{3u} state.)
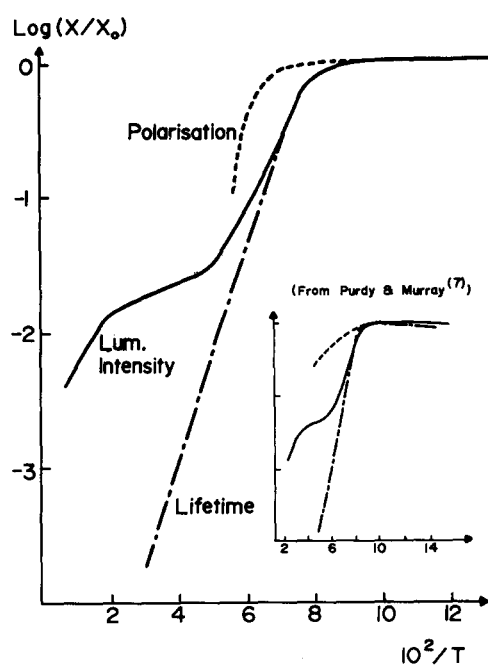

Fig. 2. Theoretical variation of the intensity, lifetime and polarization of the emission from the lowest orbital state of the STE in KCl as a function of temperature (Box shows the experimental results of ref. [7]).

[2] appear at the right ranges of energy. First two are π-polarized, the last being of σ. One more σ-polarized absorption ($A_{1g} \to B_{3u}$) is predicted at a lower energy (around 0.5 eV in NaCl).

(3) One more state of A_{1g} symmetry (same as the lowest) is found for all the systems we studied, at about 2 eV above the first one. We believe that the spin singlet state of this orbital state is responsible for the σ-emission band.

The calculated dipole matrix-element for this recombination ($A_{1g}^* \to B_{3u}^0$) agrees well with the experimental value [4] for NaCl.

3. Luminescence of the self-trapped exciton

The results of our calculation strongly indicates that the well-known σ and π luminescence bands from the STE originate from two distinct orbital states: from A_{1g}^* and A_{1g} respectively. In all systems we studied, these two states are found separated by about 2 eV, agreeing with the energy difference of the two emission bands. We propose that the spin triplet state of the STE associated with many of the recent experiments is $^tA_{1g}$ and the short-lived σ-emission band originates from the singlet state of the other level, $^sA_{1g}^*$. The question then arises as to the possible emission from $^sA_{1g}$ (of the lowest orbital state), which has not been detected as such. Recent work of Pudry and Murray [7] on the temperature dependence of the π-band in KCl strongly suggests that this emission from $^sA_{1g}$ state is indeed present. They have measured lifetime, intensity and the degree of polarization of the π-emission from 7 K to about 30 K (their results are reproduced in fig. 2 (box)). Lifetime τ shows the conventional rapid decay with temperature. The intensity I, however, shows a remarkable plateau at around 20 K, while decaying rapidly at higher and lower temperatures. Similar behaviour has also been reported by other workers [4,9]. The polarization P of the luminescence decreases from a maximum of about 20% π at the lowest temperature to about 5% π within the measured temperature range.

The interpretation of these results are fairly straightforward with our model. An exciton formed in the singlet state is very unlikely to reach the lowest singlet state $^sA_{1g}$, because of the large recombination probabilities. Exciton formed in the triplet state, with its much larger lifetime, is expected to reach the lowest state $^tA_{1g}$ and populate it directly. It may then be possible that the singlet level $^sA_{1g}$ is thermally populated from the triplet $^tA_{1g}$ state. These two levels are separated by the exchange splitting Δ, which is believed to be a few hundredths of an eV [1,3]. The observed plateau in I, as well as the decrease of P, are simply due to the contribution of the radiative decay of the singlet state $^sA_{1g}$ (σ-polarized emission).

For a detailed analysis we have solved a pair of rate equations for the population of the two levels. Following points were assumed in setting up the eq. [10]:

(1) Two levels are connected to each other through one-phonon tunnelling process.

(2) The singlet state is not directly populated and the triplet state is directly populated at a constant rate.

(3) Both levels have radiative and non-radiative recombination channels, characterized by a radiative lifetime τ_i and the usual non-radiative decay frequency $\nu_i e^{-E_i/kT}$.

On solving the rate equations, simple expressions for the steady state luminescence I, the polarization P and the long lifetime τ are obtained in terms of the parameters of the model. The following set of parameters is found to give a good fit (not necessarily optima) to the data of Purdy and Murray [7]:

$$\tau_s = 4 \times 10^{-8} \text{ s}, \qquad \tau_t = 4 \times 10^{-3} \text{ sec}, \qquad \Delta = 180 \text{ K}, \qquad E_s = E_t = 190 \text{ K},$$

$$\nu_s = \nu_t = 5 \times 10^8 \text{ s}^{-1} \quad \text{and} \quad W = 10^7 \text{ s}^{-1}$$

(W is tunneling probability in the one-phonon process).

These values are well within the accepted ranges of the respective parameters [10].

The lifetime τ and the intensity I are both well accounted for by our model as can be seen in fig. 2. The experimental data [7] shows a more gradual decrease up to the highest temperatures measured, $\simeq 30$ K. The fact that the polarization is only about 20% π even at the lowest temperature (7 K) can be explained by assuming that the V_k-centre undergoes some reorientation during the decay of the electron from a higher state to the lowest triplet state [10]. It is also possible that a temperature-independent tunnelling mechanism connects the lowest triplet and singlet states, thereby contributing to a reduction of π-character even at very low temperatures.

4. Conclusion

We have studied the electronic structure of the self-trapped excitons in alkali-halides by calculating the states of the electron bound to the V_k-centre. A series of bound states of different symmetries are found. We have obtained good agreement with such experimental data as the transient M-like absorption, σ and π luminescence and the ESR measurements on the lowest triplet state. We conclude that the two luminescence bands originate from two distinct orbital states of same symmetry. Furthermore we found that luminescence from the lowest singlet state can be detected when the state is populated thermally from the triplet state.

Acknowledgement

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Discussion

Y. Nakai: Could you give us your anticipation about the nature of the luminescence for heavier halide crystals?

K.S. Song: It is more difficult to perform a similar calculation for alkali bromides or iodides. For one thing we do not have informations about the equilibrium distance of the V_k center in these materials. It is possible, however, to speculate about the state of the bound electron of the self-trapped exciton in these systems. It can be seen [6] that the energy level of the lowest bound state A_{1g} moves upward as we go from MF to MI, resulting in the decrease of the M-like absorption energy. This is in agreement with the tendency observed by Williams and Kabler [2].