LUMINESCENCE OF THE SELF-TRAPPED EXCITON IN KCl

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Recent data on the luminescence of the self-trapped exciton in KCl are analysed, and a theoretical description is given of the temperature-dependence of the intensity, polarisation and lifetime of the emission. We conclude that emission is seen from both the lowest triplet \( \psi_T \) and the corresponding singlet \( \psi_S \), and that recombination from both these states can occur radiatively or non-radiatively. In the processes in which an electron is captured by a \( V_K \) centre and decays to these lowest singlet and triplet states we conclude (i) that when capture is initially into a triplet state the lowest state \( \psi_T \) is reached in almost all cases, (ii) that \( \psi_S \) is only populated via \( \psi_T \), i.e. that when initial capture is into a singlet state recombination is almost certain to occur before \( \psi_S \) is reached, and (iii) during the decay processes following capture, some reorientation of the self-trapped hole can occur.

1. INTRODUCTION

MUCH SPECTROSCOPIC WORK has been done recently on the self-trapped exciton in alkali halides. Luminescence, optical absorption and spin resonance methods have all been used to study the lowest state, a spin triplet with relatively long lifetime. It was long believed that the short-lived, higher energy \( \sigma \)-luminescence (i.e. polarised parallel to the exciton axis) seen in many crystals came from the corresponding spin singlet. Whilst this model explained many features, the energy difference indicated between the two transitions was two orders of magnitude too small. Recent theoretical work has resolved this problem, identifying the higher singlet state from which the observed \( \sigma \)-emission occurs. In the present note we are concerned with the lowest spin singlet, corresponding to the well-studied triplet state. Luminescence from this lowest singlet state is not usually observed, apparently because singlet excitons recombine so rapidly in excited states that the lowest singlet does not get populated. However, the state can be populated by thermal excitation from the long-lived lowest triplet. We shall show that the data of Purdy and Murray demonstrate this, and we shall derive a simple model with reasonable values of the parameters to explain the observed temperature dependence of the lifetime, luminescent intensity and polarisation.

The experimental data for KCl show several striking features. The polarisation, which should be completely \( \pi \)-polarised (dipole moment normal to the exciton axis) if the lowest triplet state were the sole origin of luminescence, is about 20\% \( \pi \)-like at 7\(^\circ\)K, and 5\% at 20\(^\circ\)K. The luminescent intensity has an anomalous plateau around 20\(^\circ\)K, varying rapidly at both higher and lower temperatures. The lifetime behaves conventionally, except that its temperature dependence does not match that of the luminescent intensity. A similar discrepancy between lifetime and intensity changes with temperature has been noted by Pooley and Runciman for KBr, and the lifetimes in other cases have novel features, but the data are less complete and we shall not analyse them here.

2. MODEL AND RATE EQUATIONS

In our model, the lowest two levels of the self-trapped exciton are the triplet \( \psi_T \) and the corresponding singlet \( \psi_S \), which lies higher by an energy \( \Delta \); typically \( \Delta \) is a few hundredths of an eV. Non-radiative transitions between these states occur, with a temperature-dependent transition probability. Recombination of the electron and hole can occur either radiatively or non-radiatively from either \( \psi_S \) or \( \psi_T \); we shall assume this is thermally-activated with the same energy \( E_{NR} \) in each case, but with different frequency factors \( \nu_S \) and \( \nu_T \).

We can write down expressions for the luminescent intensity, lifetime and polarisation by using solutions of the coupled equations for the populations \( x_S \) and \( x_T \) of the singlet and triplet states. Special cases can be
obtained even more readily by assuming thermal equilibrium between $\psi_S$ and $\psi_T$. However, since there is no direct evidence for equilibrium, and since non-equilibrium has been discerned among the magnetic levels of $\psi_T$, we shall emphasise the slightly more complex rate-equation approach.

The coupled equations take the form:

$$\frac{dx_S}{dt} = S_S + W_u x_T - B x_S$$

$$\frac{dx_T}{dt} = S_T + W_d x_S - A x_T.$$  

(1)

Here $S_S$ and $S_T$ are the rates of direct population of the singlet and triplet states. All evidence suggests $S_S$ is negligible, in that a singlet exciton recombines long before it reaches $\psi_S$. Similarly, $S_T$ is nearly temperature-independent: any triplet exciton seems to reach $\psi_T$ before recombination. We shall assume $S_S = 0$ and a constant $S_T$.

A second aspect of the capture process and the non-radiative transitions which follow concerns reorientation: if electrons are captured by aligned $V_K$ centres, do any reorient in the decay to $\psi_T$? We shall assume some reorientation is possible before $\psi_T$ is reached. If $\theta$ is the angle between a $V_K$ axis and the axis of original alignment, we shall define the average degree of misorientation by $\delta = \sin^2 \theta$. The reorientation does not enter in (1) or (2). The transition probabilities $W_u$ (from $\psi_T$ to $\psi_S$) and the reverse transition $W_d$ take the forms:

$$W_u = \tilde{W} \tilde{n}$$

$$W_d = \tilde{W}(1 + \tilde{n})$$  

(3)

(4)

corresponding to one-phonon tunnelling processes; $\tilde{n}$ is the equilibrium occupancy for phonon modes with energy $\Delta$. Finally, $A$ and $B$ involve the recombination terms and $W_u, W_d$:

$$A = \tilde{\tau}_S^{-1} + \nu_T \exp (-E_m/kT) + W_u$$

$$B = \tilde{\tau}_T^{-1} + \nu_S \exp (-E_m/kT) + W_d.$$  

(5)

(6)

Here $\tilde{\tau}_S$ and $\tilde{\tau}_T$ are the radiative lifetimes.

From these expressions one can derive the quantities observed. The steady-state luminescence $I$ is the sum of triplet and singlet contributions:

$$I = I_T + I_S$$  

(7)

and the associated polarisation $P$, chosen to conform with reference 6 is

$$P = \left[\frac{(I_S - I_T)/(I_S + I_T)}{(I_S + I_T)/(I_S - I_T)}\right](1 - 2\delta)$$  

(8)

since the singlet part is $\sigma$-polarised and the triplet part $\pi$-polarised. Expressions for $I_S$ and $I_T$ are:

$$I_S = (I_0 W_u/\tilde{\tau}_S)/(AB - W_u W_d)$$

$$I_T = (I_0 B/\tilde{\tau}_T)/(AB - W_u W_d).$$  

(9)

(10)

The lifetime $\tau$ can also be predicted (again chosen to agree with reference 6):

$$\tau^{-1} = \frac{1}{2} \left\{(A + B) \pm \sqrt{(A - B)^2 + 4W_u W_d}\right\}.$$  

(11)

These expressions involve eight parameters. Some can be estimated fairly directly, for example from $\tau(T)$ and $P(T)$ at the lowest temperatures. The temperature of the observed plateau in $I(T)$ is also useful. We find a reasonable fit with the parameters in equation (12). No serious attempt at optimisation has been carried out but the agreement (shown in Fig. 1) is quite good. The results are shown for $\delta = 0$, the main effect of increasing $\delta$ being to improve the absolute magnitude of the polarisation results: $\delta$ is probably around 0.3.

$$\begin{align*}
\tau_S &= 4 \times 10^{-8} \text{ sec}, & \tau_T &= 4 \times 10^{-3} \text{ sec}, \\
\Delta &= 180^\circ \text{K}, & E_m &= 190^\circ \text{K}, \\
\nu_T &= \nu_S = 5 \times 10^8 \text{ sec}^{-1}, & W &= 10^7 \text{ sec}^{-1}.
\end{align*}$$  

(12)

3. DISCUSSION

The general character of the intensity $I(T)$ can be understood qualitatively, including the plateau in the range $15-25^\circ \text{K}$. Even at the lowest temperatures, the reorientation term $\delta$ ensures that $P$ is not wholly $\pi$-like. As the temperature rises, the population of $\psi_S$ rises, increasing $I(T)$ and decreasing $P(T)$. The lifetime $\tau(T)$ also decreases as non-radiative processes overwhelm the triplet emission. At the plateau, the non-radiative transitions from both $\psi_S$ and $\psi_T$ are negligible.
build-up of luminescence temporarily, although the population of $\psi_s$ gives an increasing contribution at higher temperatures. To give more precise details, the radiative and non-radiative recombination rates of the triplet state become equal around $13^\circ$K; in the absence of other processes, the singlet luminescence would exceed that from the triplet at around $17^\circ$K; and the singlet radiative recombination exceeds the non-radiative part at all the temperatures of interest.

The splitting $\Delta$ of $180^\circ$K for the self-trapped exciton is in line with the values around $615^\circ$K cited for the unrelaxed exciton for NaCl. It is harder to estimate $E_{nr}$, but it seems widely agreed that this is small, and our fit of $190^\circ$K is plausible. There is no simple way to estimate the factors $\nu_s, \nu_T$ for the non-radiative transitions, and we have taken them equal for simplicity alone. But the values of $5 \times 10^8$ sec$^{-1}$ are in a reasonable range.

4. CONCLUSION

Our analysis of Purdy and Murray's data indicates that luminescence from the lowest singlet state of the self-trapped exciton (as opposed to the usual $\sigma$ luminescence from a higher singlet) can be detected when the state is populated thermally. The analysis is in good agreement with currently-accepted values of parameters and with other theoretical predictions. We further conclude that virtually all excitons reaching this singlet state do so via the corresponding triplet state, that non-radiative recombination from both singlet and triplet is significant, and that there is probably some reorientation of aligned $V_K$ centres during electron capture and subsequent transitions to the lowest states.

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REFERENCES

9. Presumably the non-radiative transitions occur via the crossover point where the configuration-coordinate curves of the relaxed exciton and the recombined exciton meet. If so, the activation energy for the singlet case should be marginally larger than that for the triplet. To lowest order, if the slopes of the upper and lower configuration coordinate curves are in the ratio $r$ at the crossover, then the singlet energy should be higher by about $\Delta r/(1 - r)$. For any realistic model (cf. reference 2) $r$ is very small, and since $\Delta$ and $E_{nr}$ are comparable, we neglect this sophistication.