

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 ψ_T and the corresponding singlet ψ_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 ψ_T is reached in almost all cases, (ii) that ψ_S is only populated via ψ_T , i.e. that when initial capture is into a singlet state recombination is almost certain to occur before ψ_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,¹ optical absorption² and spin resonance³ 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 σ -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 it indicated between the two transitions was two orders of magnitude too small. Recent theoretical work^{4,5} has resolved this problem, identifying the higher singlet state from which the observed σ -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 Murray⁶ 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 KCl⁶ show several striking features. The polarisation, which should be completely π -polarised (dipole moment normal to the

exciton axis) if the lowest triplet state were the sole origin of luminescence, is about 20% π -like at 7°K, and 5% at 20°K. The luminescent intensity has an anomalous plateau around 20°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 Runciman⁷ for KBr, and the lifetimes in other cases⁸ 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 ψ_T and the corresponding singlet ψ_S , which lies higher by an energy Δ ; typically Δ 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 ψ_S or ψ_T ; we shall assume this is thermally-activated with the same⁹ energy E_{NR} in each case, but with different frequency factors ν_S and ν_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 ψ_S and ψ_T . However, since there is no direct evidence for equilibrium, and since non-equilibrium has been discerned among the magnetic levels of ψ_T ,³ we shall emphasise the slightly more complex rate-equation approach.

The coupled equations take the form:

$$\frac{dx_S}{dt} = S_S + W_u x_T - B x_S \quad (1)$$

$$\frac{dx_T}{dt} = S_T + W_d x_S - A x_T \quad (2)$$

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 ψ_S . Similarly, S_T is nearly temperature-independent: any triplet exciton seems to reach ψ_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 ψ_T ? We shall assume some reorientation is possible before ψ_T is reached. If θ is the angle between a V_K axis and the axis or original alignment, we shall define the average degree of misorientation by $\delta \equiv \sin^2 \theta$. The reorientation does not enter in (1) or (2). The transition probabilities W_u (from ψ_T to ψ_S) and the reverse transition W_d take the forms:

$$W_u = W\bar{n} \quad (3)$$

$$W_d = W(1 + \bar{n}) \quad (4)$$

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

$$A = \tau_S^{-1} + \nu_T \exp(-E_{nr}/kT) + W_u \quad (5)$$

$$B = \tau_S^{-1} + \nu_S \exp(-E_{nr}/kT) + W_d \quad (6)$$

Here τ_S and τ_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:

$$I = I_T + I_S \quad (7)$$

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

$$P = [(I_S - I_T)/(I_S + I_T)](1 - 2\delta) \quad (8)$$

since the singlet part is σ -polarised and the triplet part π -polarised. Expressions for I_S and I_T a.e:

$$I_S = (I_0 W_u / \tau_S) / (AB - W_u W_d) \quad (9)$$

$$I_T = (I_0 B / \tau_T) / (AB - W_u W_d) \quad (10)$$

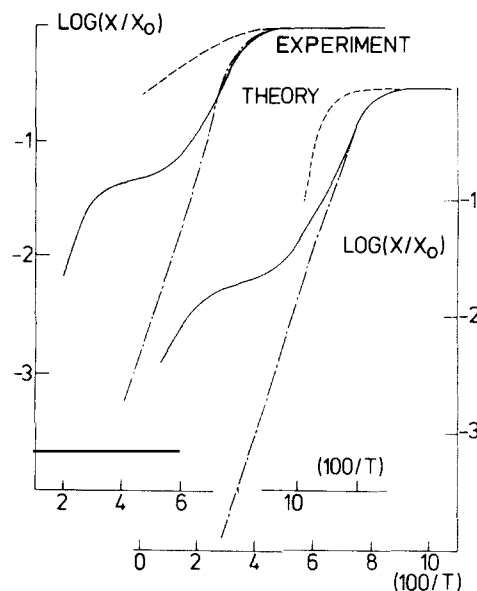


Fig. 1. Experimental data of Purdy and Murray (upper left) and predictions of present paper (lower right) are compared. The parameters are those of equation (12). — Luminescence; - - - Lifetime; - · - Polarisation.

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

$$\tau^{-1} = \frac{1}{2} \{ (A + B) \pm \sqrt{(A - B)^2 + 4W_u W_d} \}. \quad (11)$$

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 δ being to improve the absolute magnitude of the polarisation results: δ is probably around 0.3.

$$\left. \begin{aligned} \tau_S &= 4 \times 10^{-8} \text{ sec.} & \tau_T &= 4 \times 10^{-3} \text{ sec.} \\ \Delta &= 180^\circ \text{ K} & E_{nr} &= 190^\circ \text{ K} \\ \nu_T = \nu_S &= 5 \times 10^8 \text{ sec}^{-1} & W &= 10^7 \text{ sec}^{-1}. \end{aligned} \right\} \quad (12)$$

3. DISCUSSION

The general character of the intensity $I(T)$ can be understood qualitatively, including the plateau in the range 15–25°K. Even at the lowest temperatures, the reorientation term δ ensures that P is not wholly π -like. As the temperature rises, the population of ψ_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 ψ_S and ψ_T are

build-up of luminescence temporarily, although the population of ψ_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°K; in the absence of other processes, the singlet luminescence would exceed that from the triplet at around 17°K; and the singlet radiative recombination exceeds the non-radiative part at all the temperatures of interest.

The splitting Δ of 180°K for the self-trapped exciton is in line with the values around 615°K cited for the *unrelaxed* exciton² and predictions⁴ of a few hundred °K for NaCl. It is harder to estimate E_{nr} , but it seems widely agreed that this is small,^{2,10} and our fit of 190°K is plausible. There is no simple way to estimate the factors ν_S, ν_T for the non-radiative transitions, and we have taken them equal for simplicity alone. But the values of $5 \times 10^8 \text{ sec}^{-1}$ are in a reasonable range.

We have tried a small number of other sets of parameters. Roughly speaking, only modest variations in Δ, E_{nr}, ν_T and the two lifetimes appear possible, whereas

ν_S and the temperature dependence (if any) of δ are much less definite.

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 σ -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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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 Δ and E_{nr} are comparable, we neglect this sophistication.
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