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# OPTICAL DETECTION OF SPIN RELAXATION PROCESSES IN THE TRIPLET STATE OF THE SELF TRAPPED EXCITON IN ALKALI HALIDES

Y. Mori†, J.P. von der Weid†† and M. Aegerter

Institut de Physique, Université de Neuchâtel, Rue A.-L. Breguet 1,
CH - 2000 Neuchâtel, Switzerland

The transient response of the triplet self trapped exciton luminescence intensity to a pulsed microwave excitation has been measured for 1.3 K < T < 4.2 K in NaCl, KCl, RbCl, KBr, RbBr and CsBr. The results are quantitatively explained with a theoretical model describing the spin relaxation phenomena as one phonon direct processes. Good agreement is obtained as a function of temperature and magnetic field.

The recombination of self trapped holes ($V_K$ centres) and conduction electrons in pure alkali halides leads among other processes to the observation of self trapped exciton (STE) luminescence emissions. The STE, characterized as relaxed ($V_K + e^-$) centres are aligned along the <110> axis in crystals having the NaCl type structure[1,2] and along the <100> axis in crystals having the CsCl type structure[3]. Time resolved spectroscopy[4,5], optical polarization[4,5,6] and magneto-optical[7,8] data brought much information about the STE emitting states and allowed the identification of the various luminescence bands as arising from the radiative decay of either singlet or triplet relaxed states of the STE, electron spin resonance (ESR) measurements have indeed been performed in triplet states of the STE in several alkali halides[9,10,11]. In this letter, we present for the first time results concerning the spin relaxation processes in the triplet states of the STE in some alkali halide crystals.

The main features which describe the triplet states of the STE in alkali halides are the following. In crystals with the NaCl type structure, the point group which describes the local symmetry is $D_{2h}$ so that at zero magnetic field, the triplet level is splitted into three levels having respectively $A_{1u}$, $B_{2u}$ and $B_{3u}$ symmetries. The radiative transition from the $A_{1u}$ level to the ground state is forbidden, whereas it is allowed from the $B_{2u}$ and $B_{3u}$ levels. In crystals with the CsCl type structure, the symmetry point group is $D_{4h}$. At zero magnetic field, the situation is therefore mostly the same as in the other alkali halides except that the two emitting levels are now degenerated into a $E_u$ doublet.

In the steady state condition under X irradiation, these levels are constantly populated. Since the $A_{1u}$ level has no allowed transition to the ground state, one can understand that if the spin lattice relaxation times are not fast enough, the three triplet levels of the STE will be away from thermal equilibrium, in such a case, the population of the $A_{1u}$ level can be much greater than the population of the other two. Magneto-optical measurements in KI and CsI[12] confirm this fact for T < 10 K. Since for STE having their axis parallel to an external magnetic field, the $A_{1u}$ state does not mix with the other two states ESR transitions can be induced from this level to the two emitting ones, and detected as an increase of circular polarized ($\sigma^+$ or $\sigma^-$) emitted light due to the greater population of the $A_{1u}$ level.

In the present experiments, we measured the transient response of the STE luminescence intensity to a pulsed microwave excitation at temperatures between 1.3 K and 4.2 K. The effect was analysed either in $\sigma^+$ or $\sigma^-$ circular polarization in the following ultra pure crystals NaCl, KCl, RbCl, KBr, RbBr and CsBr. The cleaved or cut samples were annealed at about 450°C in order to eliminate internal strains, then placed in a $TE_{011}$ X band microwave cavity and imerged in a superconductive liquid Helium cryostat (Oxford Instruments Spectro Mag SM4). The samples were placed with a <110> axis parallel to the external magnetic field except for CsBr, which was placed with a <100> axis parallel to the

†On leave from the Department of Applied Physics, Osaka City University, Japan

††On leave from the Physics Department of the Pontificia Universidade Católica, Rio de Janeiro, Brazil

field. The STE emissions were obtained by X irradiation from a 150 kV, 10 mA Tungsten target X ray tube and the emitted light analysed with broad band optical filters, quartz $\lambda/4$ plate and detected by an EMI 9558 QB photomultiplier. Its output was amplified and finally analysed with a HP 5480 A (150 kHz) signal averager (typically with $10^4$ passages).

A typical electron spin resonance spectrum of the triplet STE is shown in figure 1 for RbBr. The microwave modulation frequency used for this recording was 1 kHz. The ESR transitions due to the three inequivalent STE orientations are identified according to the angle between the STE symmetry axis and the external magnetic field. Data for the other crystals have been found similar to those already published[9,10,11].

which characterize the approach to the steady state $\tau_2$ and $\tau_3$. When the microwave field is shut off, the transient response is first characterized by a rapid decrease of the luminescence intensity to a value lower than the initial one, followed by a slow recovery to the steady state, also characterized by two response times. We shall call them respectively $\tau_1'$, $\tau_2'$ and $\tau_3'$ Values of these response times for RbCl, RbBr and CsBr are shown in Table I, together with the radiative lifetime $\tau$ of the $B_{2u}$ or $B_{3u}$ levels in RbCl and RbBr and $E_u$ levels in CsBr. The similarity between $\tau_1'$ and the lifetime $\tau$ for all crystals measured is remarkable, and indeed shows that this particular behaviour is due to the fact that the ESR transitions occur between the forbidden $A_{1u}$ level and the

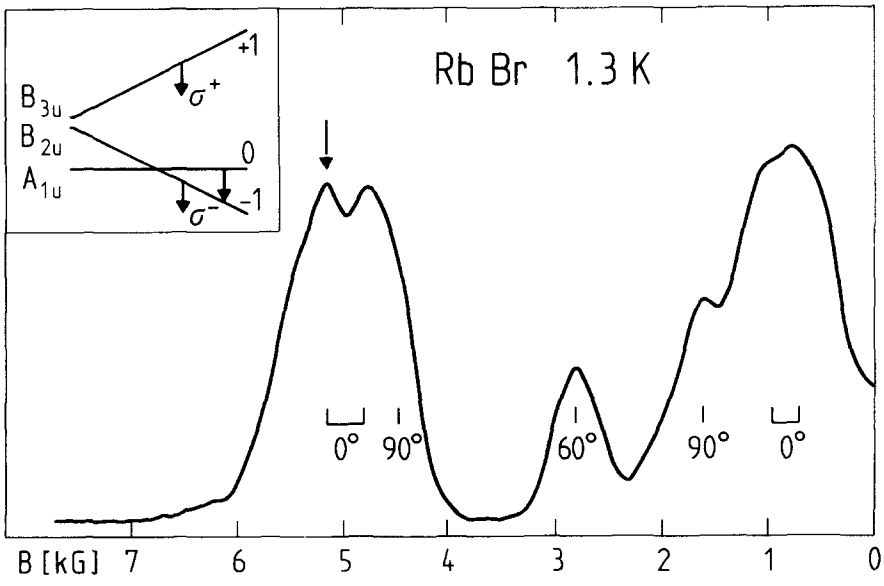


Fig. 1 ESR spectrum of the triplet STE in RbBr at 1 3 K, taken in $\sigma^-$ polarization. The magnetic field is parallel to a <110> direction of the crystal. The arrow indicates the 0° transition shown in the level scheme in the inset which was used for the recording of the transient response shown in figure 2. The microwave frequency was 9.1 GHz and its amplitude modulation frequency 1 KHz. The lines are classified according to the angle between the STE axis and the magnetic field.

The transient response of the STE spin system to the microwave field is quite different from other spin systems as for example close F centre pairs in the same crystals[13]. A typical transient response to pulse microwave excitation is shown in figure 2b, for the 0° ESR line of the STE in RbBr shown in figure 1 When the microwave field is applied, the transient response shows a very steep increase of the luminescence intensity followed by a slow decrease to the steady state. We shall call the rise time $\tau_1$, and the two fall times

allowed levels having the radiative lifetime $\tau$ It should be pointed out that for a given ESR line, the same kind of transient response was observed either in $\sigma^+$ or in $\sigma^-$ polarization

In order to understand the transient response, we assume that the exciton created by the X rays relax in each triplet level with equal probability R, and that one phonon non radiative transitions occur between the triplet STE levels Due to the different spatial wave function of the $A_{1u}$, the $B_{2u}$, $B_{3u}$ (resp

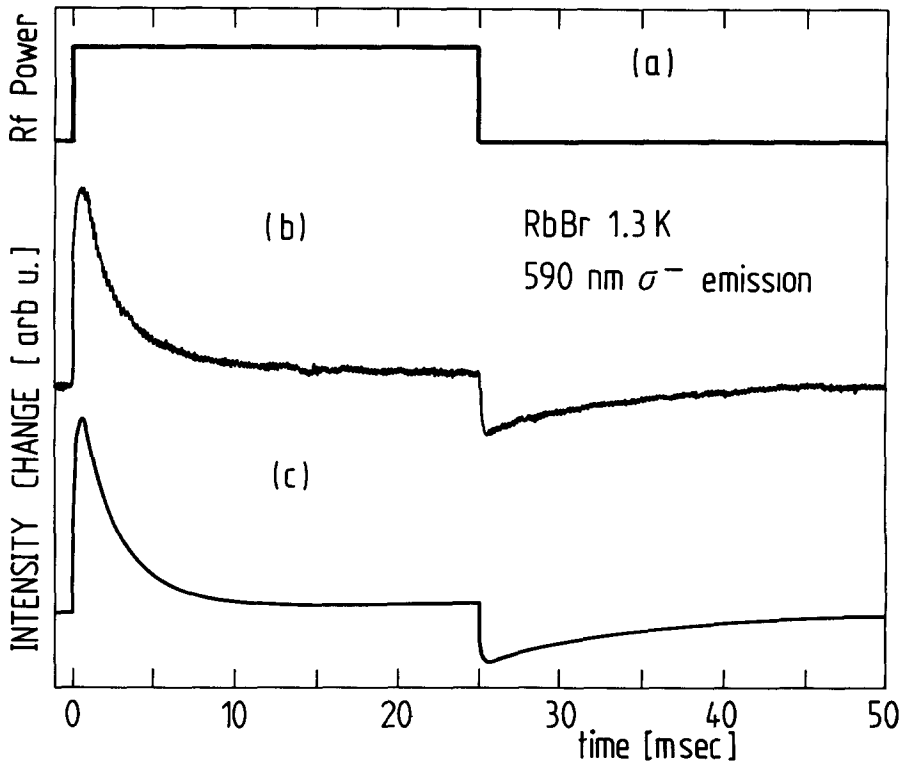


Fig. 2 Transient response of the $\sigma^-$ STE emission intensity (b) to a pulse microwave excitation (a), corresponding to the $M_S$ 0 → -1 ESR line shown in figure 1. The response shown in (b) is the output of the signal averager after $10^4$ passages. Response (c) is a computer simulation of (b) by using equations (1). The recovery times $\tau_3$ and $\tau_3'$ are too long to be observed in the time scale of this figure.

Table I. Values of the response times for the high field 0° line of the triplet STE in RbCl, RbBr and CsBr, measured in $\sigma^-$ polarization at 1.3 K. Emission energies and lifetimes taken from ref. 4 (a) and ref. 14 (b) are also shown.

| | Emission peak (eV) | Lifetime (m sec) | $\tau_1$ (μ sec) | $\tau_2$ (m sec) | $\tau_3$ (m sec) | $\tau_1'$ (m sec) | $\tau_2'$ (m sec) | $\tau_3'$ (m sec) |
|---|---|---|---|---|---|---|---|---|
| RbCl | 2.27 (a) | 5.50 (a) | ≤ 60 | 62 | --- | 5 | 130 | --- |
| RbBr | 2.10 (a) | 0.18 (a) | ≤ 40 | 2.6 | 55 | 0.2 | 5.4 | 93 |
| CsBr | 3.55 (b) | 0.015 (b) | ≤ 10 | 0.36 | > 6 | 0.02 | 0.8 | > 10 |

$E_u$) levels, we shall assume that the frequency factor (F) for the one phonon transition rates between levels which include the $A_{1u}$ level i.e. $A_{1u} \leftrightarrow B_{2u}$ and $A_{1u} \leftrightarrow B_{3u}$ (resp. $A_{1u} \leftrightarrow E_u$) is different of that (F') which describes the one phonon transition rates between $B_{2u} \leftrightarrow B_{3u}$ (resp $E_u \leftrightarrow E_u$) levels. The energy dependence of all these one phonon transition rates will be taken as proportional to the cube of the levels energy difference.

The populations $n_i$ of the three levels will then be connected by the following rate equations,

$$\frac{dn_i}{dt} = R + \sum_{J=1}^{3} C_{iJ}\, n_J \qquad (1)$$

where the rate constants $C_{1J}$ involve the radiative $\tau$ and non radiative decays $\tau_{1J}$, the microwave induced transition rates M etc Indexing the levels $A_{1u}$, $B_{2u}$ and $B_{3u}$ of the STE in RbBr respectively as 1, 2 and 3, typical $C_{1J}$ rate constants used for the analysis of the transient response will be

$$C_{11} = -\frac{1}{\tau_{12}}(\bar{n}_{12}+1) - \frac{1}{\tau_{13}}\bar{n}_{13} - M$$

$$C_{22} = -\frac{1}{\tau} - \frac{1}{\tau_{12}}\bar{n}_{12} - \frac{1}{\tau_{23}}\bar{n}_{23} - M \qquad (2)$$

$$C_{33} = -\frac{1}{\tau} - \frac{1}{\tau_{13}}(\bar{n}_{13}+1) - \frac{1}{\tau_{23}}(\bar{n}_{23}+1)$$

$$C_{12} = \frac{1}{\tau_{12}}\bar{n}_{12} + M$$

where the $\bar{n}_{1J}$ is given by the Planck function

$$\bar{n}_{1J} = \left[\exp\left(\frac{|\varepsilon_1 - \varepsilon_J|}{KT}\right) - 1\right]^{-1} \qquad (3)$$

and the one phonon transition rates $\tau_{1J}$ are given by

$$\frac{1}{\tau_{1J}} = F|\varepsilon_1 - \varepsilon_J|^3 \qquad J = 2,3$$

$$\frac{1}{\tau_{23}} = F'|\varepsilon_2 - \varepsilon_3|^3 \qquad (4)$$

The computer simulation of the transient response of the triplet STE corresponding to the ESR line indicated in figure 1 is shown in figure 2c As observed experimentally, the model predicts the same kind of behaviour for both $\sigma^+$ or $\sigma^-$ polarization A model in which the frequency factors F and F' are identical cannot explain this last observation. For the case shown in figure 2c, the best fit for the transition rates are $\tau_{12} \simeq 160$ msec, $\tau_{13} \simeq 14$ msec, $\tau_{23} = 0.12$ msec The temperature dependence due to the change of the Planck function $\bar{n}_{1J}$ and the magnetic field dependence predicted by the model are also in good agreement with the experimental observation The latter process can be easily tested in CsBr crystal, where the zero field splitting D is large (D = 6240 Gauss) Marked change in the transient response times are observed between the low field and high field 0° resonance lines due to the difference in the phonon transition rates $\tau_{1J}^{-1} \alpha |\varepsilon_J - \varepsilon_1|^3$ (eq 4)

The transient response to pulse microwave excitation was also measured in the ESR lines of STE having their axis at 60° or 90° with respect to the external magnetic field The situation is somewhat different and more complicated because under magnetic field the levels are mixed and the radiative transition to the $A_g$ ground state become partially allowed from all states. Nevertheless in all measured transitions there are six characteristic response times, which depend on the particular ESR line considered. The model prediction of the shape of the transient response at a given ESR line actually depends mainly on the field mixing between the $A_{1u}$, $B_{2u}$ and $B_{3u}$ (respectively $A_{1u}$ and $E_u$) states through the one phonon transition frequency factors F and F'

In conclusion, we should point out that although quite simple, the model presented in this report gives reasonable qualitative and quantitative description of the unusual experimental spin relaxation processes in the STE relaxed triplet state of alkali halide crystals. We therefore confirm that these processes occur mainly via one phonon direct transitions between the triplet levels, the $A_{1u}$ level being weakly coupled to the other two levels. Further experiments are under way and the complete results will be published in a forthcoming paper.

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REFERENCES

1. KABLER M N., Physical Review 136, 5A, 1296 (1964)

2 MURRAY R.B and KELLER F J , Physical Review 137, A942 (1965)

3 SIDLER T., PELLAUX J P , NOUAILHAT A and AEGERTER M., Solid State Communications 13, 479 (1973)

4 KABLER M N and PATTERSON D A , Physical Review Letters 19, 652 (1967)

5 PURDY A.E , MURRAY R B., SONG K S and STONEHAM A M , Physical Review B15, 2170 (1977)

6 PELLAUX J P , IIDA T. and AEGERTER M., Proceedings of the International Conference on Defects in Insulating Crystals, Gatlinburg, Tennessee, U S A , 336 (1977)

7 MARRONE M J and KABLER M N., Physical Review Letters 27, 1283 (1971)

8 FALCO L , von der WEID J P and AEGERTER M , Proceedings of the International Conference on Defects in Insulating Crystals, Gatlinburg, Tennessee, U S A , 126 (1977)

9 MARRONE M J , PATTEN F W and KABLER M N., Physical Review Letters 31, 467 (1973)

10. WASIELA A., ASCARELLI E. and MERLE D'AUBIGNE Y., Journal de Physique 34, C9-123 (1973).
11. CALL P.J., HAYES W., HUZIMURA R. and KABLER M.N., Journal of Physics C, 3, 1815 (1970).
12. FOWLER W.B., MARRONE M.J. and KABLER M.N., Physical Review B8, 5909 (1973).
13. SCHNEGG P.A., JACCARD D. and AEGERTER M., Physica Status Solidi (b) 63, 587 (1974).
14. POOLEY D. and RUNCIMAN W.A., Journal of Physics C 3, 1815 (1970).