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Relaxation processes of the triplet state of self-trapped excitons in alkali-halide crystals

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Résumé. — Les processus de relaxation spin-réseau, de transition radiative et d’excitation microonde ont été étudiés pour l’exciton autopiégé triplet dans les chlorures et bromures d’alcalins en mesurant la réponse transitoire à des impulsions de microonde de la luminescence excitée par rayons X. Le modèle est appliqué aux résultats expérimentaux de la polarisation circulaire. La symétrie du couplage dominant exciton-phonon est discutée.

Abstract. — The spin lattice relaxation, radiative and microwave excitation processes of the triplet state of self-trapped excitons have been studied in alkali chlorides and bromides by measuring the transient response of the X-ray excited luminescence to resonant pulse microwave. The model is applied to magnetic circular polarization data. The symmetry of dominant exciton-phonon coupling are discussed.

1. Introduction. — In alkali halides, the self-trapped exciton (STE) can be regarded as an electron bound to a self-trapped hole (V$_k$ center). Its symmetry axis lies along the $<110>$ direction [1] (NaCl structure) or the $<100>$ direction [2] (CsCl structure). We have studied the magnetic circular polarization (MCP) and the microwave induced transient response of the triplet state luminescence in NaCl, KCl, RbCl, KBr, RbBr and CsBr in order to study the triplet state relaxation processes and the electronic structure.

2. Experimental results. — Single crystals have been placed in an X-band cavity such that the $<110>$ axis ($<100>$ for CsBr) lies parallel to the magnetic field. The luminescence was excited continuously by X-rays and detected by the conventional technique [2, 3].

Typical spectra of MCP are shown in figure 1 for NaCl (or KCl, RbCl) and RbBr (or KBr, CsBr). The peak observed at low field is due to the level

![Image](image-url)

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crossing in the triplet state and its sign depends on the sign of the zero field splitting $D$. When the ESR transition of a STE whose axis is parallel to the magnetic field is excited with square microwave pulses, the $\sigma^-$ polarized luminescence presents the time dependence shown in figure 2 for KBr. Similar behavior is found by detecting the $\sigma^+$ polarized luminescence. All crystals so far studied present similar characteristics.

![Figure 2](image-url)

**Fig. 2.** The transient response of $\sigma^-$ luminescence to the microwave pulse for KBr at 5.8 kG, 1.5 K and microwave power 6 mW. The dotted line is the theoretical response calculated with eq. (11) and parameters in table 1; it is normalized to the experimental one at the first peak.

3. Model and discussion. — When the magnetic field is parallel to the exciton axis, the triplet state can be described by the following spin Hamiltonian

$$H = g_s \beta H_0 S_z + D(S_x^2 - \frac{3}{4}) + E(S_x^2 - S_y^2) + \sum_i I_i \cdot \vec{A}_i \cdot \vec{S}$$

where the radiative process is forbidden for the state $|0\rangle$. In order to simplify the model and calculation, we neglect the energy shift due to the hf interaction and introduce the effective perpendicular field $H_e$ which is a root mean square value of the perpendicular component of the hf field.

We shall adopt the hf interaction constants found for the $V_e$ [4] and F centers [5] to estimate those with the two central halogen ions and the surrounding ions, respectively [6]. The eigenvalues $\epsilon_i$ averaged over the local field $H_e$ and the eigenfunctions

$$\psi_i = a_i |0\rangle + a_{i2} |+\rangle - a_{i1} |-\rangle + a_{i3} |\rangle$$

are obtained by solving the secular equation for equation (1); $\psi_1 = |0\rangle$, $\psi_2 = |-\rangle$, $\psi_3 = |+\rangle$ at high field.

The MCP spectra and the transient response can be calculated assuming the same creation rate $R$ in each level and that the spin relaxation processes at low temperature are governed by one phonon direct process. The populations $n_i(t)$ can be found by solving

$$\dot{n}_i = R + \sum_{j=1}^{3} C_{ij} n_j.$$  \hspace{1cm} (3)

When $\epsilon_3 > \epsilon_1 > \epsilon_2$ and ESR transition is induced between levels 1 and 2, a typical rate coefficient $C_{ij}$ is

$$C_{11} = -1/\tau_1 - (1/\tau_{12}) (\bar{n}_{12} + 1) - (1/\tau_{13}) \bar{n}_{13} - WM.$$  \hspace{1cm} (4)

The phonon number $\bar{n}_{ij}$ is given by the Planck function, and the one-phonon transition rate [7] is

$$1/\tau_{ij} = k |\langle i | b_i | j \rangle|^2 \epsilon_i - \epsilon_j |^3.$$  \hspace{1cm} (5)

The dimensionless operator $b_i$ is part of an exciton-phonon interaction Hamiltonian and its elements should satisfy

$$|\langle - | b_i | 0 \rangle|^2 = |\langle + | b_i | 0 \rangle|^2 = \alpha |\langle + | b_i | - \rangle|^2 = F.$$  \hspace{1cm} (6)

The radiative rate is

$$1/\tau_\alpha = (a_{i2}^2 + a_{i3}^2)/\tau_\alpha$$

and the microwave induced transition rate is

$$WM = (2/\hbar^2) |\langle 1 | g_s \beta H_1 | 2 \rangle|^2 T_2$$

where $H_1$ is the microwave magnetic field and $T_2$ is the transverse relaxation time. The time dependent solution of equation (3) can be written as

$$n_i(t) = n_i(\infty) + \sum \frac{n_i^0}{\pi} \exp(-\omega_\alpha t)$$

where the three decay rates $\omega_\alpha = 1/\tau_\alpha (\alpha = a, b, c)$ are the solutions of the secular equation

$$C_{ij} - \omega_\alpha \delta_{ij} = 0.$$  \hspace{1cm} (9)

The light intensity with polarization $\sigma_{\pm}$ is given by

$$I_{\pm} = \frac{3}{2} \sum_{i=1}^{3} a_{i3}^2 n_i/\tau_i$$

where terms of the order of $\tau_0$ were neglected in the expression for $\tau_{ij}$. Earlier computer simulation [3] of the rate equations showed good agreement with the experimental results with $\alpha < 1$. Attempting to interpret the transient signal, we will seek approximate solutions of the secular equation at zero temperature. When $|\epsilon_2 - \epsilon_1 | \gg g_s \beta H_1$, $\tau_{12}^{-1} \approx \tau_{13}^{-1} \approx \tau_0^{-1}$ and $\tau_{11}^{-1} \approx 0$.

We obtain

$$\tau_a^{-1} = \tau_0^{-1} + \tau_{13}^{-1} + \tau_{23}^{-1}$$

$$\tau_b^{-1} = \tau_0^{-1} + WM$$

$$\tau_c^{-1} = \tau_{12}^{-1} + WM$$

where terms of the order of $\tau_0/\tau_{21}$ and $WM/\tau_0$ were neglected in the expression for $\tau_{21}^{-1}$ and $\tau_{21}^{-1}$ as they
Table I. — Values of the parameters of the model used to draw the curves of figures 1, 2 and 3.

|       | \( \tau_r \) (\( \mu s \)) | \( kF \) (10^{14} \text{ eV}^{-3} \text{ s}^{-1}) | \( \alpha \) | \( |<0|S_z|1>-\gamma|^2T_2 \) | \( \Omega \) (G) | \( D/\beta \) (G) | \( E/\beta \) (G) | \( \theta_2 \) |
|-------|-----------------|-----------------|--------|-----------------|-----------|-----------|-----------|--------|
| KBr   | 120             | 6.4             | 0.06   | 10              | 73        | 5         | 220 [8]   | 800 [8] | 1.983 [8] |
| RbBr  | 150             | 1.0             | 0.04   | 5               | 118       | 16        | 1300 [9]  | 780    | 1.99     |
| NaCl  | 295 [1]         | 1.8             | 0.1    | —               | 34        | 250 [9]  |           |        |          |

are very small [3]. We see from equations (9) and (11) that the transient response after microwave on and off is given by a rapid change characterized by \( \tau^{-1}_r \) and \( \tau_0^{-1} \) followed by a slow recovery to the steady state determined by \( \tau_0^{-1} \). In our experimental conditions, we may neglect the off diagonal elements \( C_{13} \) and \( C_{12} \) and get an approximate solution for the slow component at finite temperature

\[
\tau^{-1}_0 = \tau^{-1}_0(\tilde{n}_{12} + 1) + \tau^{-1}_0 \tilde{n}_{13} + WM. \tag{12}
\]

We see now from both equations (11) and (12) that we should have:

\[
\tau^{-1}_0(\text{microwave on}) - \tau^{-1}_0(\text{off}) = WM. \tag{13}
\]

It can be directly observed in the behavior of \( \tau_0 \) at low microwave power shown on figure 3 (1).

The MCP spectra give further check of the model. In the first attempt to check the position and polarity of the peak, we neglect the contributions to MCP of the excitons other than 0\( ^{\circ} \)STE since there is no level crossing involving the level 1 in these cases. The depopulation of the level 1 around the level crossing occurs by mixing of state via the hf interaction, instead of the population exchange through the no-phonon tunneling introduced by Fowler, Marrone and Kabler [10]. The MCP spectra of RbBr and NaCl calculated from equation (10) with the steady state solution of equation (3) and the parameters of table I are shown by the dotted line in figure 1. Better fitting may be obtained by considering the \( Z \) component of the hf field which produces a distribution of the level crossing field.

If one chooses the space spanned by the zero field eigenfunctions, \( |A_n> \), \( |B_{2u}> \), \( |B_{2g}> \) in \( D_{2h} \) symmetry, the corresponding eigenfunctions to the levels 1 and 2 in equation (2) are given by \( |A_n> \) and linear combinations of \( |B_{2u}> \) and \( |B_{2g}> \), respectively. These properties, together with the fact of \( \alpha < 1 \) suggest that a triplet exciton-phonon interaction with \( B_{1g} \) symmetry is larger than that with \( B_{2g} \) and \( B_{3g} \).

If the spectral diffusion in the inhomogeneous ESR line of STE is much slower than the spin-lattice relaxation, only one spin packet which has been excited by the resonant microwave plays a role on the transient response of luminescence. On the other hand, all spin packets contribute to the transient response in our model, since the \( Z \)-component of the hf interaction is neglected. Therefore, the ratio \( \Delta L_2(\text{theor.})/\Delta L_2(\text{exp.}) \) corresponds to the ratio of the area of the inhomogeneous line and that of the excited spin packet. Using this idea, one can obtain \( T_2 \) to determine the matrix element in equation (8) from \( WM \). The results of \( \langle 0|S_z|1> \) and \( T_2 \) are 0.4, \( 8 \times 10^{-9} \) s and 0.2, \( 2 \times 10^{-9} \) s for KBr and RbBr, respectively.

4. Conclusion. — The spin relaxation and radiative rates as well as the basic features of the magnetic properties of the self-trapped exciton have been obtained by optical detection of pulsed microwave ESR. The symmetry of dominant triplet exciton-phonon interaction is \( B_{1g} \) in the \( D_{2h} \) group.

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(1) Although the model predicts only one time constant longer than \( \tau_0 \), a second recovery was observed in earlier experiments with high microwave power [3]. The origin of this recovery remains unknown, but it is probably due to spectral diffusion process in the inhomogeneously broadened line.

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Fig. 3. — Microwave power dependence of recovery rate \( \tau^{-1}_0(\text{off}) \), \( \tau^{-1}_0(\text{on}) - \tau^{-1}_0(\text{off}) \) and the increase \( \Delta \) of \( \gamma \) luminescence at the peak response for KBr. Solid lines are the corresponding theoretical results.
DISCUSSION

Question. — M. Glasbeek.

Can you give an explanation for the very short $T_2$ values?

Reply. — M. A. Aegertter.

We don't know the reason well. The short $T_2$ suggests the difficulty of ENDOR measurement in KBr and RbBr. Further studies on KCl where ENDOR has been observed are interesting to confirm the way to determine $T_2$ and to understand the mechanism of $T_2$.

Question. — P. Edel.

How can you explain how one can observe a recovery time slower than the lifetime?

Reply. — M. A. Aegertter.

This is because the levels are not in thermal equilibrium at these low temperatures.

References