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STUDIES OF THE TUNNELLING RECOMBINATION BETWEEN V_K - Na^o CENTRE PAIRS IN CsI:Na CRYSTALS

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The tunnelling recombination of trapped holes (V_K) and electrons (Na^o) pairs in CsI:Na crystals is studied by optical detection of ESR in the 420 nm emission. A model is developed and it explains the optically detected ESR spectra. The tunnelling probabilities are determined from the transient ODESR behavior.

It was recently shown that, after X irradiation at low temperatures, sodium doped cesium iodide emits a characteristic blue luminescence (420 nm) which persists for a long time after irradiation[1]. This phenomenon was first observed in alkali halides doped with Ag^+ or Tl^+ ions by Delbecq et al[2,3] and was attributed to the trapped electrons (metal atom) and holes (V_K centres) recombination by a tunnelling process. The intensity I(t) of the afterglow blue luminescence of CsI:Na^+ decays according to a law $I(t) \alpha t^{-1}$ and is strongly quenched by the application of a magnetic field, indicating that the efficiency of the recombination of Na^o - V_K centre pairs is dependent of the total electronic spin of the pair and that the final state after the tunnelling process is mainly reached via a singlet state[1,4]. Nevertheless recent magneto-optical measurements in the 420 nm emissions in CsI:Na^+ showed that a long lived triplet state is also involved in the final state[5].

It was previously shown that optical detection of electron spin resonances (ODESR) can be observed in the 420 nm afterglow luminescence[1] and that the resonance spectrum present some similarity to the I_2^- ESR spectrum[6]. We present here more detailed investigation concerning the V_K - Na^o centre pairs, and a simple model which accounts for the observed ESR spectra and transient response of the ESR signal.

Single crystals of CsI:Na^+ ($\sim$ 200 ppm) grown in our laboratory by the Czochralski technique were mounted in a TE_{011} X band microwave cavity placed in a superconducting split coil cryostat having four optical access (Oxford, Spectromag SM4). The samples were annealed at 450°C in order to prevent internal strains which causes light depolarization. The 420 nm glow emission was obtained with X rays from a 150 kV, 10 mA tungsten target X ray tube (Mueller MG 150) and selected with broad band optical filters. The microwave field was modulated at frequencies between 3 Hz and 3 kHz and the induced change in luminescence detected with a PAR 124 A lock in amplifier. The transient response of the ODESR signal was detected with the same technique described previously[7].

The optical detection of ESR signal can be made either along the axis parallel to the magnetic field or perpendicular to it. The dependence of the spectra on the polarization of the emitted light also gives information about selection rules and symmetry of the emitting centre. The spectrum shown in figure 1 was obtained along a <100> axis parallel to the magnetic field and is independent of the polarization of the emitted light as expected from the symmetry of this configuration. This spectrum was decomposed in two Gaussian-shaped ESR lines which present many features similar to the ESR spectrum of V_K centres in CsI[6], despite the unresolved hyperfine structure. The two lines can be interpreted as arising from spin $\frac{1}{2}$ centres with <100> axial symmetry which can be either parallel or perpendicular to the magnetic field. The fact that the 420 nm emission arises from the recombination of self trapped holes - Na^o centre pairs and that the observed ESR spectrum corresponds to the intensity change in this emission supports the assignment of the ESR spectrum shown in figure 1 to I_2^- molecules aligned in the <100> axis, somewhat perturbed by a Na^o defect. This defect can be described by the following spin $\frac{1}{2}$ Hamiltonian with axial symmetry :

$$\frac{\mathcal{H}}{g_o\beta} = \frac{1}{g_o} \vec{H}\cdot\overleftrightarrow{g}\cdot\vec{S} + \sum_{i=1}^{2} \vec{S}\cdot\overleftrightarrow{A}\cdot\vec{I}_i + \sum_{k=1}^{4} \vec{S}\cdot\overleftrightarrow{A}'\cdot\vec{I}_k + \ldots \quad (1)$$

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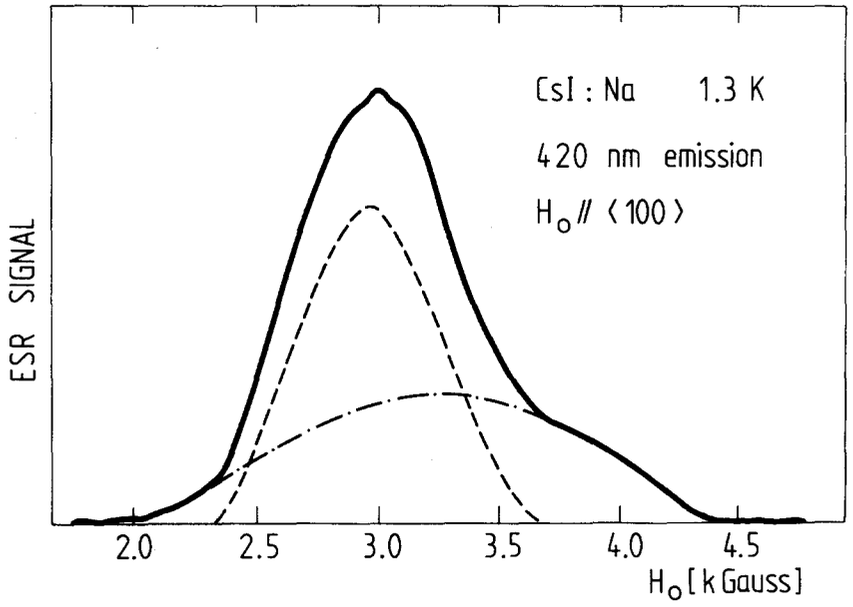

Figure 1 ESR signal detected optically in the 420 nm emission of CsI:Na at 1.3 K. The magnetic field is parallel to a <100> direction of the crystal. The microwave frequency was 9.1 GHz.

where $\overleftrightarrow{A}$ describes the hyperfine interaction of the electron with the nuclear spin I_i (5/2) of each iodine nucleus and $\overleftrightarrow{A'}$ describes the superhyperfine interaction with the magnetic moments of the Cesium nuclei I_k (7/2) of the first shell. The nuclear Zeeman and quadrupole interactions were not included. The principal values of g and the estimated values of A and A' are shown in the Table I and compared with the same parameters of the V_K centers in CsI[6]. The estimation of A and A' was made from the observed linewidths and using the fact that the hyperfine structure cannot be resolved[8].

TABLE I

	$g_{//}$	$g_{\perp}$	$A_{//}$ [G]	$A_{\perp}$ [G]	A' [G]
V_K-Na^o	2.04	2.22	248	110	∿ 20
V_K	1.89	2.27	360.6	136	≲ 3

Results of a measurement with magnetic field parallel to a <111> crystalline axis are shown in figure 2. As expected for defects aligned in a <100> axis a single ESR line is observed, with g value and linewidth in agreement with the predictions of the spin Hamiltonian of eq. 1.

The most important difference between unperturbed V_K centres and the V_K-Na^o pair lies in the hyperfine interaction between the electronic spin and the cesium nuclei of the first shell. The axial symmetry is kept in both cases but the electronic wave function of the I_2^- molecule in the V_K-Na^o pair is different of the V_K center one. A possible explanation for this is the lack of inversion symmetry in the V_K-Na^o pair. The Coulomb interaction with the electronic charge of the Na^o impurity may be responsible for a contribution of 6 S wave function of the four cesium ions of the first shell to the wave function of the I_2^- molecule, the cesium ions being not anymore in a nodal plane of the unpaired electron of the I_2^- molecule as it is the case or an unperturbed V_K centre. This hypothesis assumes that the Na^o is a substitutional and therefore negatively charged defect. However there is no experimental evidence that Na^+ impurity in CsI lies in a substitutional position as it does in KCl crystals[9]. We cannot exclude the possibility that Na^o centres are neutral interstitial defects and that lattice relaxations are responsible for the perturbation of the I_2^- molecule wave function.

The origin of the ESR signal detected in the 420 nm luminescence of CsI:Na can now be understood with the simple physical[1] model described in fig. 3. The V_K-Na^o pairs are not stable; after a tunnelling process a new emitting state is formed with a complex radiative decay to the ground state. This emitting state contains a long lived triplet state (τ_T = 6.7 s) and a singlet state ($\tau_S \approx 10^{-9}$ s), the characteristics of this system being very similar to a perturbed self-trapped exciton[5].

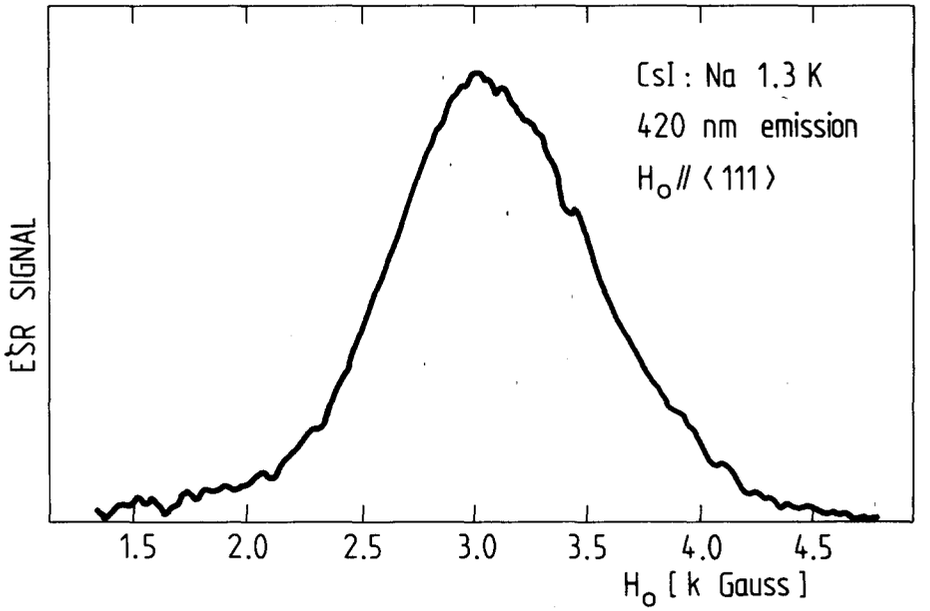

Figure 2 ESR signal detected optically in the 420 nm emission of CsI:Na at 1.3 K. The magnetic field is parallel to a <111> direction of the crystal. The microwave frequency was 9.1 GHz.

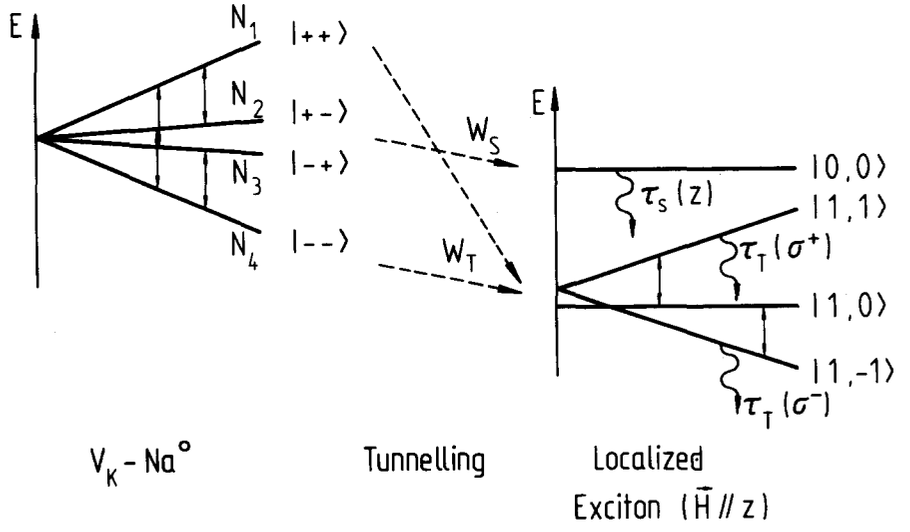

Figure 3 Schematic diagram of the electronic processes occuring with V_K - Na^0 pairs in CsI:Na crystal. The left side shows the energy levels of the spin ½ pairs in a magnetic field before the tunnelling process. After the transfer process with transition probabilities W_S and W_T shown in the middle, the system behaves as a localized exciton whose singlet and triplet level scheme is drawn on the right side for a magnetic field $\vec{H}$ parallel to the exciton axis.

The vertical arrows show the different possible ESR transitions which can be optically detected in the 420 nm emission represented by the wavy lines.

Let W_S and W_T the tunnelling probabilities to singlet and triplet states, g and g' respectively the g-factors of the I_2^- molecule and Na^o defect and N_i the population of the four energy levels of the pair in the steady state. Neglecting the spin-spin interaction the energy levels of the $V_K - Na^o$ pair for a given magnetic field orientation can be written as :

$$E_{1,4} = \pm \tfrac{1}{2} (g+g')\beta H$$
$$E_{2,3} = \pm \tfrac{1}{2} (g-g')\beta H \qquad (2)$$

The total intensity emitted will be given by

$$I = (N_1 + N_4) W_T + (N_2 + N_3) W_S \qquad (3)$$

Note that the tunnelling probabilities W_S and W_T are actually a function of the distance between the I_2^- molecule and the Na^o defect. Since we are dealing with steady state populations under continuous X irradiation our values of W_S and W_T correspond to the mean value over a distribution $W_{S,T}(r)$, the defects being far away contributing with a very small amount of light. In this approximation the microwave field induces spin flips in the two components of the pair changing therefore the populations N_i^o of the levels. The intensity of the total emitted light will be changed and its measurement as a function of the field should eventually give the ESR spectra of the I_2^- and Na^o nearby defects. Only ESR lines associated with I_2^- molecules are actually observed in our measurements. The fact that ESR lines due to Na^o defects could not be seen is still unexplained and requires further investigation.

The transient response of the ODESR signal presents the same behaviour observed previously in the ODESR of triplet self-trapped excitons in alkali halides except that only four response times instead of six are observed[7]. This is also consistent with a resonance in a two level system (spin $\frac{1}{2}$) in which the cross relaxation involving the Na^o levels can be neglected. The lifetime of the $V_K - Na^o$ pair ($W_S + W_T$) can be estimated from the transient response signal[7]. Using the ratio $W_T/W_S \cong 0.17$ obtained from the phosphorence measurements[1] the mean value of the tunnelling transition probabilities are approximately $W_S^{-1} \simeq 1.2$ msec and $W_T^{-1} \simeq 7.0$ msec.

Under particular experimental conditions we also observe another ODESR signal which can be associated with resonances in the triplet state of the localized excitons created after the tunnelling process in agreement with the schematic diagram of figure 3. Detailed results will be published elsewhere[5].

Although quite simple, the model presented here gives a good qualitative explanation for the observed data and, for the first time, an estimation of the tunnelling probabilities between I_2^- and Na^o centres. So far we are not able to decide if the Na^o defects are substitutional negatively charged defects or interstitial neutral ones although the first hypothesis seem to be more likely. Further experiments on cesium halides doped with monovalent cation impurities are under way in order to give a more complete description of the phenomenon.

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