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P. KASK, V. MIHKELSOO, T. SOOVIK

THE DEPENDENCE OF THE TRIPLET STATE LUMINESCENCE DECAY PARAMETERS ON THE MAGNETIC FIELD. $V_k + e$-CENTRE IN KI

The dependence of the triplet state luminescence decay parameters on the external magnetic field is under theoretical investigation. The corresponding dependence is measured for the emission of the $V_k + e$-centre in KI and described as the result of the change of the radiative and nonradiative transition probabilities in the magnetic field.

Introduction

The long-wavelength intrinsic emission band of undoped alkali halide crystals is due to the radiative transition from the lowest triplet state of the $V_k + e$-centre (or the self-trapped exciton) [1]. The spin-orbital interaction splits the triplet into two sublevels: the metastable A_u and the radiative $B_{2u} + B_{3u}$ (the symmetry of the centre is D_{2h}) [2, 3]. Such a splitting explains the existence of the two exponential components in the luminescence decay curve (in the zero field) [4]. The quality of the triplet state emission of the $V_k + e$-centre is most completely investigated in KI [1–7]. Kabler et al. [2, 3, 5] have detected some magneto-optical effects, including the shortening of the decay times of the slow and fast luminescence components in the magnetic field in the crystal [2, 3]. These effects were explained as being the result of the change in the radiative and nonradiative transition probabilities in the magnetic field [3]. In the change of the radiative transition probabilities, the mixing of the states was taken into account, and in the change of the nonradiative transition probabilities — the change of the resonance phonon frequencies only (as the result of the energy shifts of the states), presuming that the nonradiative transition probabilities are independent from the initial and final wave functions. The agreement with the experiment was not exact.

In the present paper the theoretical description of the dependence of the triplet state luminescence decay parameters on the magnetic field will be discussed. We shall examine the dependence of the nonradiative one-phonon transition probabilities on the magnetic field more exactly. Our experimental results for the luminescence decay of the $V_k + e$-centre in KI will be fitted theoretically.

1. Theory

We shall examine the factors due to which the magnetic field affects the triplet state luminescence.

1A. Rate Equations. After weak excitation, the relaxation of the

luminescence centres can be described with the help of the following coupled equations [3]:

$$\frac{dn_i}{dt}=\sum_{j=1}^{3} a_{ij}n_j, \quad i=1, \ldots, 3, \tag{1}$$

where n_i is the probability, at time t, that level i is occupied. The rate constants a_{ij} can be expressed by the transition probabilities p_{kl} $(k\to l)$: $a_{ii}=-\sum_{j=0}^{3} p_{ij}$; $a_{ij}=p_{ji}$, $i\neq j$ (index 0 marks the ground state). The solution for n_i is of the form

$$n_i=\sum_{j=1}^{3} D_{ij}\exp\left(-\frac{t}{\tau_j}\right). \tag{2}$$

The relaxation times τ_k are the roots of the following algebraic characteristic equation [8]:

$$\det(a_{ij}-\delta_{ij}\tau_k^{-1})=0. \tag{3}$$

As we can see, the luminescence decay times τ_k depend only on the electronic transition probabilities, while the coefficients D_{ij} (hence, the intensities of the luminescence decay components, too) depend also on the initial population of the states.

In the next sections we shall study how the magnetic field influences the transition probabilities.

1B. The Basic Model. We shall assume that we know the arrangement of the energy levels and the electronic transition probabilities in the case of the zero field. The corresponding (energetic) representation will be marked by the upper index 0. The effect of the magnetic field will appear in the change of some energy matrix elements by the quantities of the order of $\mu_B H$. (In not very high fields, only the members linear by H should be taken into account.) In the magnetic field **H** the diagonalization of the energy matrix $\tilde{E}$ occurs by means of the following unitary transformation:

$$\tilde{E}=\tilde{b}^{+}(\tilde{E}^0+\tilde{\beta}H)\tilde{b}, \tag{4}$$

where $\tilde{E}^0$ is the energy matrix on the initial base in the zero field, $\tilde{\beta}H$ — the contribution of the magnetic field to it. (The matrix elements of such a transformation are found after solving the secular equation.) Note that the transformation matrix $\tilde{b}$ determines also the change of the electronic transition probabilities that we are interested in.

1C. Radiative Transition Probabilities in the Magnetic Field. As we know, the radiative transition probability p_{i0} is expressed by means of the dipole matrix element $\langle i|\mathbf{r}|0\rangle$ [9, 10]. If we know these matrix elements in the initial representation, it is easy to calculate them in the final representation, too:

$$\tilde{\mathbf{r}}=\tilde{b}^{+}\tilde{\mathbf{r}}^0\tilde{b}. \tag{5}$$

In this way one accounts for the change of the radiative transition probabilities in the magnetic field.

1D. Nonradiative Transition Probabilities in the Magnetic Field. The one-phonon-stimulated nonradiative transition probability p_{ij} [11–14] can be expressed as

$$p_{ij}\sim|V_{ij}|^2 f(\omega)\bar{n}(\omega). \tag{6}$$

Here $|V_{ij}| = \left|\frac{\partial E_{ij}}{\partial Q_{ij}}\right| \cdot |Q_{ij}|$ is the amplitude of the (one-phonon) time-dependent perturbation matrix element, containing $\frac{\partial E_{ij}}{\partial Q_{ij}} \equiv \alpha_{ij}$ — the linear (by a local vibration Q_{ij}) term of the energy matrix element E_{ij}; $|Q_{ij}|$ — the one-phonon amplitude in coordinate Q_{ij}; $f(\omega)$ — the density of the phonon states, and $\bar{n}(\omega)$ — the average number of the phonons with the energy $\hbar\omega = E_j - E_i$:

$$\bar{n} = \left[\exp\left(\frac{E_j - E_i}{kT}\right) - 1\right]^{-1}. \quad (7)$$

The change of the resonance phonon frequency ω in the magnetic field contributes a factor to the change of the probability p_{ij}. It can be accounted for by the members $|Q_{ij}|^2 f(\omega) \bar{n}(\omega)$, which all depend on the energy difference $E_j - E_i$. As in the case of the long wavelengths ($\omega \ll \bar{\omega}$) $|Q_{ij}| \sim \omega^{1/2}$, $f(\omega) \sim \omega^2$, we get for the probability of the processes with the absorbtion of a phonon

$$p_{ij} \sim (E_j - E_i)^3 \bar{n}, \quad (8)$$

and for the probability of the processes with the emission of a phonon [14]

$$p_{ji} \sim (E_j - E_i)^3 (1 + \bar{n}). \quad (9)$$

Another important factor contributing to the change in the probability p_{ij} (and p_{ji}) in the magnetic field results from the change of α_{ij}. It can be explained in the following way. If we know the dependences $E^0_{ij}(Q^0_{ij})$ in the initial representation, we can calculate them by means of the transformation matrix $\tilde{b}$ in the new representation:

$$\tilde{\alpha}(Q^0_{ij}) = \tilde{b}^+ \tilde{\alpha}^0(Q^0_{ij}) \tilde{b}. \quad (10)$$

If the different vibrations Q^0_{ij} are independent, then

$$p_{ij} \sim \sum_{Q^0_{ij}} |\alpha_{ij}(Q^0_{ij})|^2. \quad (11)$$

By means of the formulae (8)—(11) we can calculate the change of the nonradiative transition probabilities in the magnetic field.

2. V_k + e-centre in KI

We used the above-given theory in calculating the dependences of the luminescence decay times on the external magnetic field for the 3.3eV emission band in KI (V_k+e-centre) at LHeT. We took into account the mixing of the (zero-field splitted) substates of the triplet (A_u, B_{2u}, B_{3u} in the symmetry group D_{2h}) only. The influence of the other states can be neglected due to great energy differences.

The calculations were performed at the following values of the parameters corresponding to the qualities of the V_k+e-centre in KI in the zero field [7]:

$$E(B_{2u}, B_{3u}) - E(A_u) \equiv E^0_{ab} = 7.9 \text{ K} = 0.68 \text{ meV},$$
$$p(B_{2u} \to A_g) = p(B_{3u} \to A_g) = 0.98 \times 10^6 \text{ sec}^{-1},$$
$$p(A_u \to B_{2u}) = |V^0(B_{2g})|^2 \bar{n}_{ab},$$
$$p(A_u \to B_{3u}) = |V^0(B_{3g})|^2 \bar{n}_{ab},$$

$$|V^0(B_{2g})|^2=|V^0(B_{3g})|^2=0.88\times10^6\ \text{sec}^{-1},$$
$$V^0_{B_{2u}\to B_{3u}}(B_{1g})=0,$$
$$g=2.$$

On the basis of $|B_{3u}\rangle$, $|B_{2u}\rangle$, $|A_u\rangle$ in the energy units of E^0_{ab} we take

$$\tilde{E}^0=\begin{pmatrix}\frac{1}{3} & 0 & 0\\ 0 & \frac{1}{3} & 0\\ 0 & 0 & -\frac{2}{3}\end{pmatrix}.$$

If we take $E^0_{ba}/\mu_B g$ as the unit of the magnetizing force H, we get for $\mathbf{H}\|[001]$, $V_k\|[011]$

$$\tilde{\beta}=\begin{vmatrix}0 & \frac{1}{\sqrt{2}} & 0\\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}}\\ 0 & \frac{1}{\sqrt{2}} & 0\end{vmatrix}.$$

For example, for $H=0.5$ ($\equiv$30 kGs) the energy matrix $\tilde{E}^0+\tilde{\beta}H$ is diagonalized with the help of the matrix

$$\tilde{b}=\begin{pmatrix}0.6498 & -0.7530 & 0.1032\\ 0.7370 & 0.5910 & 0.3280\\ 0.1860 & 0.2892 & 0.9390\end{pmatrix}.$$

Only the values of the parameters V^0_{kk}, corresponding to the dependence of the diagonal energy matrix elements on the vibration coordinates, were unknown. (In the potential minimum of the state k $\alpha_{kk}=0$, but different states may have their minima at different points.) For the calculation of the dependences of nonradiative transition probabilities on the magnetic field one must know only the differences in the values of the parameters $V^0_{kk}-V^0_{k'k'}$. (The remaining part in the $\tilde{V}^0$-matrix is multiple to the unit matrix; it does not change in the unitary transformation, and, therefore, does not make any contribution to it.) We assumed that

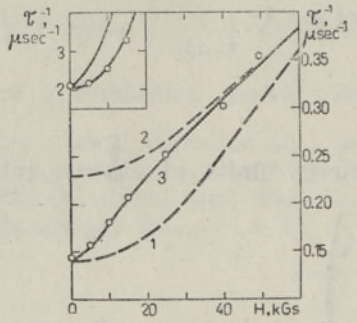
$$V^0_{B_{2u},B_{2u}}-V^0_{A_u,A_u}=V^0_{B_{3u},B_{3u}}-V^0_{A_u,A_u}\equiv d,$$

and therefore

$$\tilde{V}^0=\begin{pmatrix}c(A_g) & 0(B_{1g}) & V^0(B_{3g})\\ 0(B_{1g}) & c(A_g) & V^0(B_{2g})\\ V^0(B_{3g}) & V^0(B_{2g}) & c-d(A_g)\end{pmatrix},$$

where $c(A_g)$ is a nonsubstantial constant. The value of d was estimated from the experimental data.

The measurements were carried out in the following way. The KI crystal, X-rayed previously at LNT, was placed into the superconductive



The dependence of the luminescence decay times of the V_k+e-centre in KI on the magnetic field. Dots — experimental results for $\mathbf{H} \parallel [001]$, curves — calculated dependences for $V_k \parallel [011]$. Curve *1* has been calculated at $d = 0$, curve *2* — for the case when the excited states are in thermal equilibrium, curve *3* and the two continuous curves for the slower components in the left upper corner, at $d^2 = 10^8$ sec^{-1}. The parameter d accounts for the shift of the potential minima in the different states of the spin triplet.

solenoid lying in liquid helium. Three orientations of the crystal were used, with the direction of the magnetic field parallel to the crystallographic axes [001], [011] and [111], respectively. Luminescence was stimulated by the light pulses of the spark discharge (with the pulse duration of about 0.1 μsec) through the red filter KC-13 (in this way the recombination of the V_k-centres with electrons is stimulated), and detected by the cooled PM of type ФЭУ-64 by the single photon counting method [15] on the multichannel time analyser NTA-512B (EMG, Hungary), through the blue filter combination ФС-6 + СЗС-21 in the direction of the magnetic field.

The luminescence decay measurements in the magnetic field with the orientation $\mathbf{H} \parallel [011]$ gave more than one slow decay component. Unfortunately we were not able to separate them on the background of statistical noise. In the other two orientations we separated one main slow decay component and approximated the fast components as one exponential function (we had their signal in the first two measuring channels of the analyser only). The experimental results for the orientation $\mathbf{H} \parallel [001]$ are denoted in the figure by dots. Here are also given three different theoretical curves for the slow component decay time, which have all been calculated according to the direction $V_k \parallel [011]$. Curve *1* has been calculated for $d = 0$. This corresponds to the extreme case in which the change of the $\hat{V}$-matrix is not noticeable and the shortening of the slow component decay time is mainly due to the change of the radiative transition probabilities. However, this is not the case. Curve *2* shows the calculated decay time for the other imaginable extreme case, when the excited states are populated at any moment according to the Boltzman distribution. That corresponds to the case where nonradiative transition probabilities (between the excited states) considerably exceed radiative transition probabilities. The substantial increase of the nonradiative transition probabilities in the increasing magnetic field leads to the transition of the observed decay time from curve *1* to curve *2*. Curve *3* corresponds to the value of the parameter $d^2 = 10^8$ sec^{-1} and is in good agreement with experimental data. In the left upper corner of the figure the measured decay time of the fast component and the calculated decay times for $V_k \parallel [011]$ are given. The calculated decay time of the "slower fast" component and the measured decay time of the fast component are in good agreement. (Note that the measured fast decay component actually consists of four exponential components — another nonequivalent orientation $V_k \parallel [110]$ gives two more fast components — but the above-mentioned "slower fast" component of the equivalent orientations to $V_k \parallel [011]$ must be the most intensive.) The increase of the nonradiative transition probabilities leads to the shortening of the fast components' decay times.

Let us mention that in the case of the crystal orientation **H** || [111] we got a good theoretical fit for the experimental curve at the same value of d, too.

The data reduction and the calculation of the theoretical curves were carried out on the computer "Nairi-2".

Summary

1. The theory about the influence of the magnetic field on the triplet state luminescence from local centres in solids is given, at which the change of the one-phonon nonradiative transition probabilities in the magnetic field is carefully taken into account.

2. With the help of the single photon counting method the precise dependences of the V_k+e triplet-singlet luminescence decay times on the magnetic field in KI at LHeT have been measured.

3. A good agreement between these experimental and corresponding calculated (on the basis of the above-mentioned theory) dependences has been obtained.

4. Fitting the calculated curves into the experimental data, some new information about the potential minimum shift of the triplet states of the V_k+e-centre in KI has been obtained ($d^2 = 10^8$ sec^{-1}).

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Academy of Sciences of the Estonian SSR,
Institute of Physics

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P. KASK, V. MIHKELSOO, T. SOOVIK

TRIPLETSE SEISUNDI LUMINESTSENTSI KUSTUMISPARAMEETRITE SÕLTUVUS MAGNETVÄLJAST. V_k + e-TSENTER KI-s

Teoreetiliselt uuriti tripletse seisundi luminestsentsi kustumisparameetrite sõltuvust välisest magnetväljast. See sõltuvus KI V_k+e-tsentri kohta mõõdeti eksperimentaalselt ning seletatakse kiirgus- ja mittekiirgusüleminekute tõenäosuste muutumisega magnetväljas.

П. КАСК, В. МИХКЕЛЬСОО, Т. СООВИК

ЗАВИСИМОСТЬ ПАРАМЕТРОВ ЗАТУХАНИЯ ЛЮМИНЕСЦЕНЦИИ ТРИПЛЕТНОГО СОСТОЯНИЯ ОТ МАГНИТНОГО ПОЛЯ. $V_k + e$-ЦЕНТР В KI

Рассматривается зависимость времени затухания люминесценции триплетного возбужденного состояния от внешнего магнитного поля. Подобная зависимость для свечения $V_k + e$-центра в KI получена экспериментально и описывается как результат изменения вероятностей излучательных и безызлучательных переходов в магнитном поле.