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SPIN-ORBIT COUPLING IN Cr^{3+} ION IN SOLID STATE MATERIALS *

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In this paper we introduce a new model describing the coupling of 2E and 4T_2 states of octahedrally coordinated Cr^{3+} ion, which includes spin-orbit and electron-lattice interactions and takes into account the electronic structure of both states. The model is used to calculate doublet lifetime. We have applied this model to the series of Cr^{3+} doped garnets characterized by the varying crystal field parameter $10 Dq$ and O_h symmetry of the Cr site and to the kyanite ($\text{Al}_2\text{O}_3:\text{SiO}_2$), which is the case of different Cr^{3+} sites in one material, characterized by the relatively large component of the low symmetry crystal field. The agreement with experiment is reasonable.

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Luminescence in any octahedrally coordinated Cr^{3+} system is determined by the relative energies and sequence of the two lowest excited states, 2E and 4T_2 . For the, so called, low field materials quartet is lower and luminescence of the system is dominated by the broad band, spin allowed transition ${}^4T_2 \rightarrow {}^4A_2$ decaying with time constant of the order of a few μs . High field materials, e.g. ruby, emit sharp line, spin forbidden luminescence with decay times in the ms range [1]. The low and intermediate field Cr^{3+} systems continue to attract attention of the researchers in the field of the solid state tunable lasers [2]. Although the search for new materials has considerably slowed down due to the large number of materials discovered by now, the field remains active since there are many aspects which are not fully understood but are important for successful laser operation. One we would like to focus on in this paper is concerned with the radiative lifetime of the doublet 2E

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state. In intermediate field materials, e.g. alexandrite, the emitting state is quartet 4T_2 but, because of thermal equilibrium between quartet and doublet based on very fast non-radiative transitions [3], the actual decay time of emission is determined by the radiative lifetimes of both quartet and doublet states [4, 5]. It was suggested earlier that spin-orbit interaction coupling 2E and 4T_2 states was responsible for breaking of selection rule forbidding the ${}^2E \rightarrow {}^4A_2$ transition [6]. Therefore, in that approach, the admixture of the 4T_2 wavefunction into the 2E wavefunction, which depends on the doublet-quartet energy separation ΔE , determines the radiative lifetime of doublet. The simple model reproduces reasonably well doublet radiative lifetimes but fails to explain the energies of perturbed states for the series of Cr^{3+} : garnets (GSGG, YSGG, GGG, YGG and YAG) [7]. In this paper we wish to present a new and comprehensive approach which will take into account both spin-orbit interaction and lattice relaxation.

There are two important features of our model. The first is the consequence of the fact that the distribution of energies between electronic and lattice relaxation terms in the total Hamiltonian of the Cr^{3+} -lattice system depends on the choice of a frozen lattice position Q_0 . The usual choice of Q_0 at equilibrium position of the ground state 4A_2 , although very convenient and widely used, is somewhat arbitrary and implies that the 2E state is the one which does not relax. We therefore choose $Q_0 = \frac{1}{2}(Q_1 + Q_2)$ where Q_1 and Q_2 are equilibrium positions for 2E and 4T_2 states respectively. The second feature follows from the observation that the order in which those two perturbing terms are included in the zero-order Hamiltonian may be of importance. For the two electronic states we are concerned with (2E and 4T_2) the electron-lattice term H_{e-p} is diagonal only for the full symmetry lattice distortion whereas the spin-orbit term H_{s-o} contains non-zero off-diagonal matrix elements. Therefore H_{e-p} term may contribute to the mixing of the 2E and 4T_2 states through the large full symmetry lattice distortion only after some initial mixing is introduced through the H_{s-o} term (see also [8]). It is important to note that because the only nonvanishing matrix elements of H_{s-o} are between U' spinor components there is no interaction of doublet with the E' and E'' spinor components of the quartet.

The first step, as usual, is to solve the electronic problem for the lattice fixed at Q_0 . Having new mixed electronic wave functions [9] we calculate electron-phonon interaction matrix elements $V_{\lambda\lambda'} = \langle \phi_{\lambda} | \frac{\delta V}{\delta Q} | \phi_{\lambda'} \rangle$ with $V(q, Q)$ being the total instantaneous potential seen by electron. The off-diagonal terms are taken into account as a perturbation contributing to the mixing of 4T_2 and 2E states whereas diagonal terms are used to calculate the relative relaxation in those states in respect to Q_0 .

Since the transition moment matrix element between the unperturbed states 2E and 4A_2 is zero, the matrix element (and radiative lifetime) connecting the perturbed excited state 2E with the ground state 4A_2 is determined by the mixing coefficients c and d . Using harmonic approximation we obtain the following relation

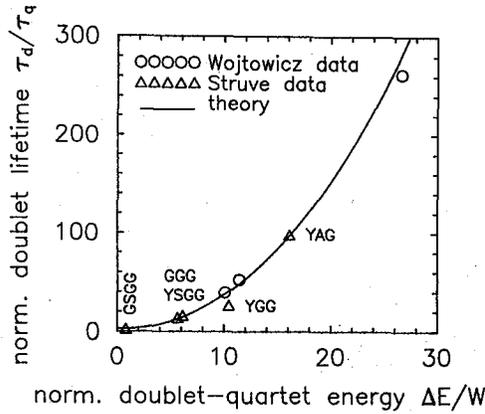


Fig. 1. Normalized doublet radiative lifetime vs. normalized quartet-doublet energy separation, experiment and theory. τ_q for garnets was 90 μs , for kyanite — 12.2 μs , W for garnets was 62 cm^{-1} and for kyanite 52.6 and 103 cm^{-1} for two split doublet components.

for the ratio of radiative lifetimes

$$\frac{\tau_d}{\tau_q} = \frac{M_{E''}^2}{M_{U'}^2} \left[1 + 2 \frac{c^2 d^2}{(c^2 - d^2)^2} \sum_n \frac{(-n\hbar\omega + S\frac{\sqrt{2}-1}{\sqrt{2}})^2 S^n}{n! (\Delta E_1 + n\hbar\omega)^2} \right] \times$$

$$\left[d^2 + 2 \frac{c^4 d^2}{(c^2 - d^2)^2} \sum_n \frac{(-n\hbar\omega + S\frac{\sqrt{2}-1}{\sqrt{2}})^2 S^n}{n! (\Delta E_1 + n\hbar\omega)^2} - \frac{2\sqrt{2}c^2 d^2}{(c^2 - d^2)} \sum_n \frac{(-n\hbar\omega + S\frac{\sqrt{2}-1}{\sqrt{2}}) S^n}{n! (\Delta E_1 + n\hbar\omega)} \right]^{-1}$$

where S is the Huang-Rhys parameter of $U'(^4T_2)$ and $U'(^2E)$ states, ΔE_1 is the energy difference between doublet and quartet at Q_0 , $M_{E''}$ and $M_{U'}$ are the transition moment matrix elements between E'' and U' spinor components of the quartet 4T_2 and of the ground state 4A_2 , respectively.

The model, as presented above, was tested for two different cases. In the first case we took data published previously by Struve and Huber for the series of garnets [7]. In this case the symmetry of the Cr site is relatively high, and splitting of the 2E state is negligible (comparing to ΔE_1). The reasonable agreement between experiment and calculations was achieved in the case of all garnets, as shown in Fig. 1, for spin-orbit matrix element $W = 62 \text{ cm}^{-1}$ and $M_{U'}/M_{E''} = 1.29$. The second case, of kyanite [10], is a more complicated one since, because of the significant low symmetry crystal field component, the 2E splitting is comparable to

ΔE_1 . Good agreement between experiment and model calculations in this case was achieved for the same value of $M_{U'}/M_{E''}$ (1.29!) and $W = 52.6 \text{ cm}^{-1}$ for one doublet component and 103 cm^{-1} for the second confirming the apparent difference between two doublet components (E' and E'' spinor components). All results are presented in Fig. 1.

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