

Vibronic coupling constants for V^{3+} doped in $Li(Al,Ga)O_2$ crystals

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In this paper, we present the results of the theoretical evaluation of the vibronic linear coupling constants for the V^{3+} doped in $Li(Al,Ga)O_2$ crystal. In the case of a tetrahedral complex V^{3+} : $Li(Al,Ga)O_2$ the interaction with full symmetric A_1 , tetragonal E and two trigonal vibrations $T_2^{(1)}$ and $T_2^{(2)}$ are considered. The linear vibronic coupling constants are numerically calculated for each case of the Jahn-Teller interactions and all considered types such interaction are expected to give information on the new peculiarities of the absorption and emission bands, as well as of non-radiative transitions between the electronic states of impurity ions.

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1. Introduction

The transitional metal ions doped in different host matrix are of particular interest from spectroscopic point of view because they have been reported as promising candidates as active media for broadband optical amplifiers and tunable laser systems in the visible and near infrared regions [1-4]. This is because the initial and final of its electronic transitions are strongly coupled to the lattice phonon modes and, thus, the associated emission bandwidths become much broader than that of other ions. Among this ions the V^{3+} is of particular interest from spectroscopic point of view [2].

In previous paper we have been modeled the crystal field parameters and simulated the lowering energy levels scheme for V^{3+} ions doped in $Li(Al,Ga)O_2$ [5], in the case of static crystal field.

In this article we report on the evaluation of the vibronic Jahn-Teller coupling parameters between ${}^3A_2(e_2)$, $3T_2(t_2e)$, ${}^3T_1(t_2e)$ and ${}^3T_1(t_2^2)$ energy state of V^{3+} and a_1 , e and t_2 vibrations of the host lattices. The parameters are estimated with the aid of the exchange charge model of the crystal field accounting for the exchange and covalence effects [6,7].

The linear vibronic coupling constants are numerically calculated for each case of the Jahn-Teller interactions and all considered types such interaction are expected to give information on the new peculiarities of the absorption and emission bands, as well as of non-radiative transitions between the electronic states of impurity ions.

2. Linear Jahn-Teller vibronic coupling parameters

The general formula of Jahn-Teller vibronic coupling parameters have been established, in the point charge model of crystal field theory, in papers [8,9], for both octahedral and tetrahedral complexes. In papers [10,11] the expression for these parameters have been established for tetrahedral complex, in the exchange charge model of crystal field.

The general formula of Jahn-Teller vibronic coupling parameters for tetrahedral complex, in the exchange charge model of crystal field, are [10,11]:

$$\begin{aligned}
 v_{A_1}(E) &= \frac{2e^2 I_{A_1}}{27R^6} \left(-25Z \langle r^4 \rangle - 18R^4 G(S_4(R) - RS'_4(R)) \right) \\
 v_E(E) &= -\frac{8e^2 I_E}{63R^6} \left(5Z \langle r^4 \rangle - 9Z \langle r^2 \rangle R^2 - 18R^4 G S_2(R) + \right. \\
 &\quad \left. + 18R^4 G S_4(R) \right) \\
 v_E(T_2) &= \frac{4\sqrt{2}e^2 I_E}{189R^6} \left(20Z \langle r^4 \rangle + 27Z \langle r^2 \rangle R^2 + 54R^4 G S_2(R) + \right. \\
 &\quad \left. + 72R^4 G S_4(R) \right) \\
 v_{T_2}^{(1)}(T_2) &= \frac{e^2 I_{T_2}^{(1)}}{378R^6 \sqrt{2}} \left(8 \langle r^2 \rangle (100 \langle r^2 \rangle + 81R^2) Z + \right. \\
 &\quad \left. + 9R^4 G [24(3S_2(R) - 2RS'_2(R)) + (79S_4(R) - 64RS'_4(R))] \right) \\
 v_{T_2}^{(2)}(T_2) &= \frac{4e^2 I_{T_2}^{(2)}}{189R^6} \left(\langle r^2 \rangle (-50 \langle r^2 \rangle + 27R^2) Z + 18R^4 G (3S_2(R) - 10S_4(R)) \right)
 \end{aligned} \tag{1}$$

The operators $v_{T_2}^{(1)}(T_2)$ and $v_{T_2}^{(2)}(T_2)$ are related to two types of T_2 vibrations. The value R is the distance between the impurity ion and ligands in which the adiabatic potential has minimum,

$S_i(R)$ is the overlap integrals [5], $S'_i(R) = \frac{dS_i(R)}{dR}$, Ze is the effective ligand charge (equal 3) and $\langle r^l \rangle$ is taken from [5]. The mean value of f was taken approximately 200N/m for all vibrations. The frequency $\omega_{\bar{\mu}}$ is taken the same for all vibrations (100 cm⁻¹). The parameters Dq and G are that from [5]. $l_{\mu\bar{\Gamma}} = (\hbar\omega_{\mu\bar{\Gamma}} / f_{\mu\bar{\Gamma}})^{1/2}$ with $\omega_{\mu\bar{\Gamma}}$ the frequency of the vibration $\mu\bar{\Gamma}$ and $f_{\mu\bar{\Gamma}}$ is the force constant, symbol $\bar{\mu}$ enumerates the repeating vibration representations.

3. Results and discussions

In order to calculate the vibronic coupling constants for the V³⁺: Li(Al,Ga)O₂ system using the equations (1), we first need the parameters involved in these equations. We taken the parameters Dq , G and R from paper [5], the overlap integrals and its derivative were calculated also, from [5] and for vibration energy we taken the common value 100 cm⁻¹ for all type of vibrations of host lattices. They are given in Table 1.

Table 1. Parameters of the exchange-charge model for Li(Al,Ga)O₂ crystals, doped with V³⁺ ions. (a_0 - Bohr radius).

Crystal	Dq (cm ⁻¹)	G	R (Å)	$S_2(R)$	$S_4(R)$	$S'_2(R)$ (a ₀ ⁻¹)	$S'_4(R)$ (a ₀ ⁻¹)	$\hbar\omega$ (cm ⁻¹)
LiAlO ₂	762	1.6	1.76	0.0470	0.0138	0.0247	0.043	100
LiGaO ₂	750	2.5	1.84	0.0379	0.0116	0.0196	0.0371	100

With these parameters and equations (1) we obtained the results from Table 2.

Table 2. Vibronic coupling constants (in cm⁻¹) for Li(Al,Ga)O₂ crystals, doped with V³⁺ ions.

Crystal	$\nu_E(T_2)$	$\nu_{T_2}^{(1)}(T_2)$	$\nu_{T_2}^{(2)}(T_2)$	$\nu_{A_1}(E)$	$\nu_E(E)$
LiAlO ₂	531 (196)	502 (-296)	189 (-35)	-146 (16)	-282 (-126)
LiGaO ₂	277 (260)	415 (-60)	71 (-54)	16 (108)	-381 (-130)

In the parenthesis are the values of coupling constants due to the covalence effect. It can see that these contributions are important. In both cases of the crystals doped with V³⁺, the strong vibronic coupling

is that between the trigonal deformations of the host lattice and the triple degenerate state of the vanadium ions.

4. Conclusions

In this paper the linear vibronic coupling constants for Li(Al,Ga)O₂ crystals, doped with V³⁺ ions, have been simulated in the exchange charge model of crystal field, using the results of one our earlier paper. In that paper we modeled crystal field parameters and simulate the low-lying energy levels schem in the frame of the exchange charge model. In our calculations in this paper we used the parameters obtained in that paper. The Jahn-Teller energies have been calculated taking into account the effect of both point charges of the ligands, and the overlap of the wave functions of the vanadium ions and that of the ligands, on the impurity ions. We underline the contribution from covalence to the calculated constants (in parenthesis in Table 2). The calculations gave the information about the magnitude of the vibronic linear coupling constants and also, on the relative strength of interaction with vibration modes of different symmetry. The method may be applied for another 3d ions doped in optical materials.

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