

Lattice vibrations and their influence on impurity ion energy levels in laser crystals

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Impurity centers formed by 3d-ions in laser crystals are known to exhibit strong electron-vibronic interaction which can be illustrated by broad-band emission and absorption spectra of these hosts. In the present work, an effort is done to analyze an impact of local vibrations on the optical properties of impurity centers by taking into consideration various momentary configurations of crystal lattice ions corresponding to different types of symmetry of normal modes for tetrahedral and octahedral impurity centers. The model calculations were performed for $Y_3Al_5O_{12}:Cr^{4+}$ (for all LS terms of Cr^{4+}), $Al_2O_3:Cr^{3+}$, $LiCaAlF_6:Cr^{3+}$, $CeSc_3(BO_3)_4:Cr^{3+}$ (for lowest LS terms of Cr^{3+}) crystals. Energy levels diagrams as functions of the ligands positions were obtained. It is shown that some displacements of ligands lead to the strong delocalization and crossing of impurity centers energy levels. Such a modulation of "pure electron states" by ligands vibrations can cause the non-radiative transitions (NRT) between two intersecting levels. The model of energy levels crossing for NRT was developed. Analytical expression for the temperature dependence of the NRT probability was derived. Application of the model to the above crystals was made; an agreement with experimental values of the NRT probabilities is discussed.

Key words: 3d-ions, crystal field models, normal vibrations, energy level schemes, non-radiative transitions

1. INTRODUCTION

The models of crystal field treat ligands to be fixed at equilibrium positions (defined, for example, by x-ray diffraction methods), while vibrations of crystal lattice ions constantly change the relative positions of ligands with respect to an impurity ion. Changes of inter-ionic distances and bond angles cause variation of crystal field parameters, which define the energy level structure of an impurity ion. In this way, energy levels of an impurity ion are modulated by ligands thermal vibrations, showing explicit dependence on momentary configuration of an impurity center. In this paper, we present the method which allows to model local vibrations of ligands, analyze their influence on behavior of energy levels, and estimate spectral characteristics of an impurity center. The model described in the paper establishes a direct relationship between ligands vibrations and crystal field theory, on one hand, and ligands vibrations and non-radiative transitions, on the other hand.

2. MODULATION OF LIGANDS LOCAL VIBRATIONS

The main idea of the ligands vibrations modeling is as follows: vibrations of crystal lattice ions are substituted by the set of momentary fixed ligands configurations.

For each configuration, parameters of the crystal field and eigenvalues of an impurity ion Hamiltonian are calculated. These configurations can be chosen in different ways. One way is to keep the matrix of the impurity ion Hamiltonian consisting of as much zero-th elements as possible (sometimes it even allows to get analytical expressions for the Hamiltonian's eigenvalues as functions of ligands coordinates). Another way is just to choose momentary configurations as having the same symmetry as one of normal vibrations which are characteristic for the considered impurity center (for example, A_{1g} or E_g vibrations for O_h group; A_1 , E or T_1 vibrations for T_d group etc). In both ways, the *dynamic* crystal field is simulated by the set of *statical* ("frozen") ligands configurations. This "statical" description of the impurity center dynamics gives a possibility to analyze the impact of the ligands vibrations on the impurity ion energy scheme. This influence can be represented by the following linear equation (for improving accuracy, the quadratic terms also can be taken into account):

$$E = E_0 + \alpha Q, \quad (1)$$

where E_0 is the energy of the impurity ion term when all ligands are located at the positions of equilibrium,

Q is the magnitude of ligands displacement from the positions of equilibrium, α is the coefficient which may be interpreted as an effective diagonal value of the non-linear in general case operator of electron-vibrational interaction calculated on the wave functions of the corresponding state. Electron and vibronic parts of an impurity center are separated explicitly: the former is defined as eigenvalues of the impurity ion Hamiltonian, the latter is introduced by means of momentary ligands configurations. A close relationship between both parts is established through dependence of the energy levels on changing ligands coordinates. This approach has been applied to the impurity centers formed by Cr^{4+} and Cr^{3+} . Tetravalent chromium in $\text{Y}_3\text{Al}_5\text{O}_{12}$ is placed at the center of a tetrahedron formed by four ions of oxygen (the "Cr - O" distance is 1.8 \AA [1]), and (as a good approximation) the local symmetry can be assumed to be T_d . If φ is the

angle between vectors drawn from the center of the tetrahedron to the initial (equilibrium) position of the ligand and its current position and if this angle changes at the same rate for all four ligands (the local symmetry in this case is D_{2d}), the dependence of splitting of two lowest terms (${}^3\text{F}$ and ${}^3\text{P}$) of Cr^{4+} ion on φ will be as shown in Fig.1. Value of $\varphi = 0$ corresponds to the undistorted tetrahedron; irreducible representations of the T_d point are shown at the left side of the graph; orbital triplets in the field of D_{2d} symmetry are split into the singlet and doublet levels, these splittings are labeled by the irreducible representations of the D_{2d} point group on the graph. All calculations have been performed in the framework of exchange charge model of crystal field [2]. Similar calculations have also been done for octahedrally coordinated Cr^{3+} in Al_2O_3 , LiCaAlF_6 , $\text{CeSc}_3(\text{BO}_3)_4$.

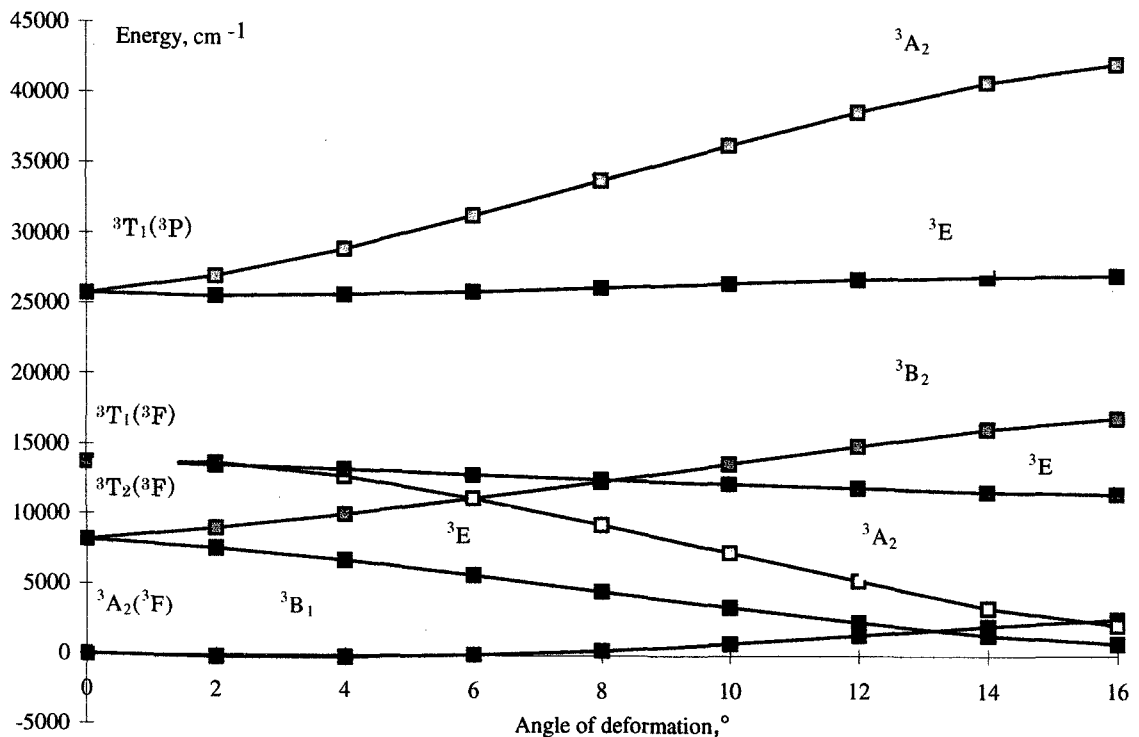


Fig. 1. Dependence of the energy levels splitting on the ligands configuration in the $[\text{CrO}_4]^{4-}$ complex ($\text{Y}_3\text{Al}_5\text{O}_{12}$ doped with Cr^{4+}).

From Fig. 1, one can easily see that even for small values of φ corresponding to small displacements of ligands from the equilibrium positions, the intervals between energy levels of Cr^{4+} are changed significantly (up to 1000 cm^{-1}). This observation is the manifestation of the strong electron-vibronic interaction, which is an essential feature of laser crystals doped with transition metal ions, and allows to explain wide bands in their absorption spectra as the result of the modulation of pure electron levels of an impurity ion by ligands thermal vibrations. Moreover, as it can also be deduced from

Fig.1, there are some configurations of ligands which lead to the crossing of energy levels. These configurations have been supposed to be a reason for the NRT between crossing pair of an impurity ion energy levels [3]; the model developed from this assumption and its applications are described briefly in the next sections.

3. ENERGY LEVELS CROSSING IN THE THEORY OF NON-RADIATIVE TRANSITIONS

As it was mentioned at the end of the previous section,

the NRT is supposed to occur when the crossing of two electron states of an impurity ion caused by ligands thermal vibrations takes place. The final expression for the temperature dependence of probability w_{ij} of NRT between two states of an impurity ion with energies E_i and E_j derived in [3] is

$$w_{ij} = \frac{2\sqrt{\pi\hbar}\Omega_{ij}^2 \sqrt{\tanh(\hbar\omega/2kT)}}{|\partial E_i / \partial Q - \partial E_j / \partial Q|} \times \exp\left[-\frac{\Delta E^2 \tanh(\hbar\omega/2kT)}{|\partial E_i / \partial Q - \partial E_j / \partial Q|^2} \right] \quad (2)$$

Here Ω_{ij} is the characteristic frequency of the NRT (estimated as $\Omega_{ij} = (m/M)^{1/4} \omega$, where ω is the ligands vibrations frequency, m is the electron mass, M is the total mass of the considered impurity center); $\partial E_i / \partial Q - \partial E_j / \partial Q$ is the difference of derivatives of two energy levels taking part in NRT with respect to the local normal vibrational coordinate Q (this derivative can be taken equal to the α coefficient from Eq. (1)), ΔE is the energy gap between these energy levels when ligands are at the equilibrium configuration, T is absolute temperature, and \hbar and k are Planck and Boltzmann constants, respectively. Results of application of Eq. (2) to the calculations of the NRT probabilities of Cr^{4+} in yttrium-aluminum garnet (YAG) in comparison with experimental data [4] and Cr^{3+} in ruby in comparison with another method of calculation – theory of linear electron-phonon interaction [5,6] – are shown in Tables I and II, respectively.

Table I
Temperature dependence of the ${}^3T_2 \rightarrow {}^3A_2$ NRT probability in YAG: Cr^{4+} ($\omega = 350 \text{ cm}^{-1}$)

T, K	0	100	150	200	250	300
w_{ij} Eq.(2) 10^4 s^{-1}	0	0	0.02	0.86	8.4	39.5
w_{ij} exp.[4] 10^4 s^{-1}	3.0	3.0	4.0	5.0	10.0	12.0

Table II
Temperature dependence of the ${}^4T_{2g} \rightarrow {}^4A_{2g}$ NRT probability in $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ ($\omega = 800 \text{ cm}^{-1}$)

T, K	0	200	300	400	500
w_{ij} , Eq.(2) 10^4 s^{-1}	0	4.8	127	715	2033
w_{ij} [6], 10^4 s^{-1}	3.2	11.0	180	380	3100

The results of calculation are in a rather good agreement with experimental data and another theoretical model at high temperatures, and significantly underestimate the

values of NRT at low temperatures. We explain this discrepancy by different character of interaction of local modes with optical electrons of an impurity ion. At low temperatures *collective* vibrations of the crystal lattice play more important role, and at high temperatures, when collective vibrations become more disordered, the *local* vibrations represent the main channel for non-radiative relaxation of the excitation energy in an impurity center.

4. RELATIONSHIP BETWEEN ENERGY LEVELS CROSSING MODEL AND MOTT MODEL

In one configurational coordinate model the temperature dependence of NRT between two states can be described by a single Arrhenius factor (Mott equation) [7]

$$w_{ij} = S_0 \exp(-\Delta E / kT), \quad (3)$$

where k is the Boltzmann constant and ΔE is the activation energy, that is the energy difference between the ground vibrational state $n=0$ of the excited electron state and the crossover of the potential curves of the ground and excited electron states (Fig. 2).

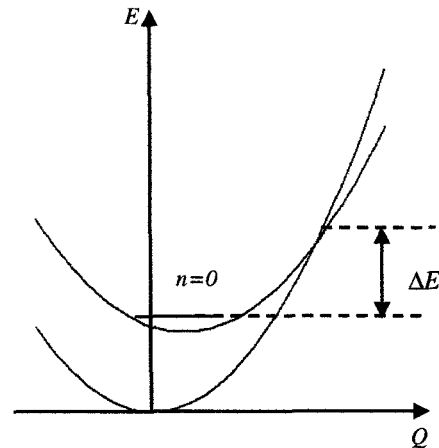


Fig.2. One configurational coordinate model in the theory of NRT

S_0 is called “frequency factor” and is an empirical parameter, which is to be found from experimental dependencies of the lifetime of the excited level. Usually, the value of S_0 is about $10^{12} - 10^{14} \text{ s}^{-1}$, providing the values of NRT probabilities to have the order of magnitude of $10^4 - 10^6 \text{ s}^{-1}$. Chromium-doped crystals of $\text{CeSc}_3(\text{BO}_3)_4$ (CSB) do not follow this general rule, showing very weak temperature dependence of the Cr^{3+} luminescence lifetime: 40 μs at 300 K and 20 μs at 400 K (for comparison, the Cr^{3+} luminescence lifetime in LiSrAlF_6 is 64 μs at 300 K, and only 4 μs at 400 K) [8,9]. This special property of CSB crystals has been explained by an extremely low value of the frequency factor – about $5 \times 10^7 \text{ s}^{-1}$ from experimental data [8]. In this section we evaluate the value of frequency factor for CSB: Cr^{3+} crystal using Eq. (2).

It is easy to see that the exponential pre-factor in Eq. (2) is analogous to the frequency factor S_0 in Eq. (3), and the non-dimensional argument of the exponential function in Eq. (2) can be represented as the ratio of some "effective" energy of the transition ε to the product of kT . (Here we would like to stress out the difference between ΔE in Eq. (2) and (3): in the former it is the difference between minima of potential curves of the ground and excited state, meanwhile in the latter it is defined within the potential curve of the excited state, as it is shown in Fig. 2)

Again, exchange charge model has been used to calculate energy level scheme of Cr^{3+} in CSB crystal. Information on crystal structure has been taken from [10]. There is only one type of the scandium octahedral position, which is occupied by chromium ions. Due to the local distortions, the point symmetry of the $[\text{CrO}_6]^{9-}$ is reduced to the C_2 group, which has one-dimensional representations only. Therefore, degeneracy of all orbital triplets of Cr^{3+} is taken off completely. The energy scheme obtained after the Hamiltonian diagonalization is as follows (in cm^{-1} ; the levels are labeled by irreducible representations of the C_2 point group (before arrows); "parents" representations of the O_h point group and LS terms are given after arrows): 0 ($B \rightarrow A_{2g}$ from 4F); 14580, 15118, 15989 ($A + A + B \rightarrow T_{2g}$ from 4F); 19817, 21704, 21891 ($A + B + B \rightarrow T_{1g}$ from 4F); 32602, 33694, 33789 ($A + B + B \rightarrow T_{1g}$ from 4P).

Application of Eq. (2) results in small values of the Cr^{3+} NRT probabilities (from 0 to 300 s^{-1} if phonon frequency varies from 1000 to 100 cm^{-1} , correspondingly), and values of S_0 ranging from $9.0 \times 10^{10} \text{ s}^{-1}$ to $9.7 \times 10^7 \text{ s}^{-1}$, if the limits of the phonon frequency variation are the same, as above. In case of low phonon frequency, the value of S_0 is close to that one obtained from experimental measurements of the luminescence lifetime. From this, one can suppose that low-frequency phonons interact more efficiently with optical electrons of Cr^{3+} than high-frequency phonons.

A physical explanation to the small value of S_0 may be as follows: due to the essentially heterodesmic structure of CSB crystals there is no promoting vibration, which can bring an impurity center to the point of crossing of parabolae of the ground and excited states (Fig. 2), from which the further non-radiative relaxation to the ground vibrational level of the ground electronic state can take place.

5. CONCLUSIONS

The method of modeling ligands vibrations is outlined in this paper. It allows to represent an influence of a dynamical crystal field on the optical properties of an impurity center by using a set of different momentary ligands configurations, for each of them energy level scheme is calculated by means of crystal field models. It is shown that the intervals between energy levels of an impurity ion depend significantly on the local configuration. The energy crossing model in the theory of NRT has been developed; its applications to the calculations of NRT probabilities in two different crystals and estimation of the frequency factor in the Mott model are given.

6. ACKNOWLEDGMENTS

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