

# **Crystal field distribution in disordered materials doped with chromium**

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An analysis of the crystal field distribution and distribution of the electron lattice coupling of disordered materials doped with  $\text{Cr}^{3+}$  ions is presented. The theoretical background contains the extended crystal field model based calculations of the emission line-shape and kinetics. The multi-site effect in the gallogermanate and lithium tantalate crystals and aluminosilicate glasses is analysed in detail.

## **1. Introduction**

Dielectric crystals doped with transition metal and rare earth ions are well known as active media for high power lasers operating in the UV, visible and IR regions [1], phosphors, scintillators [2], chemical sensors, optical memory cell and many other devices. The advantages of these materials are related to very broad energy gap, which makes them transparent for the light from UV to far IR. Also the broad gap is suitable for creation of the localized states related to the optically active centers (natural defects or dopands).

The energetic structure of the localized states is determined by local bonding environment, crystal or ligand field strength and symmetry, interaction of the defect with lattice vibrations and ability of creation of the local vibration modes. As far as perfect crystals are considered one expects to deal with discrete sites which although may differ from each other yield the discrete energies, like rare earth ions, or homogeneously broadened bands like transition metal ions.

The lattice disorder related to the uncontrolled dopands, imperfections or intrinsic defects influences the energy of localized states. Also some crystals like gallogermanates contain the disorder-related interstitials or statistical distribution of sites occupied by two or more different ion species. In glasses, since they have not the long-range order each center is characterized by different second and next coordination spheres.

The influence of the host on the energetic structure of localized system is described by parameters defined by the crystal field theory. In perfect crystals one has the multi-site effect producing a few crystallographically inequivalent well defined sites, which can be identified by the EPR spectroscopy. In the case of disordered crystals, ceramics and glasses we deal with continuous distribution of the

crystal field rather than with the discrete sets of the sites. Specifically in glasses, since the material is macroscopically homogeneous, the EPR technique is useless for identification of sites.

It is suggested that chromium be used, specifically the  $\text{Cr}^{3+}$  ion, as the indicator of the lattice disorder. The analysis of optical spectra (emission/absorption, luminescence excitation and luminescence kinetics) is said to give the information on the distribution of environmental disorder in the lattice.

## 2. Energetic structure of the $\text{Cr}^{3+}$

The most important arguments for using chromium ion result from the fact that the octahedrally coordinated  $\text{Cr}^{3+}$  ( $3d^3$ ) can be relatively easily incorporated to the lattice and that the energetic structure of this ion is exceptionally well described by standard crystal field theory. In the simplest case of pure cubic field the system is described by the crystal field strength parameters  $10Dq$ , the Racach parameters  $B$  and  $C$ , and the spin orbit coupling  $\zeta$  [3]. The ground state is always the  ${}^4A_2$ , whereas depending on the crystal field strength the excited state is  ${}^4T_2$  (for  $Dq/B < 2.2$ ) or  ${}^2E$  (for  $Dq/B > 2.2$ ). The former is called the weak crystal field, whereas the latter the strong crystal field site. From the spectroscopic point of view two effects are important. The first is the electron-phonon coupling that is negligible in the case of the  ${}^2E$  state and significant in the case of the  ${}^4T_2$  state. Thus the  ${}^2E \rightarrow {}^4A_2$  transition results in the narrow emission lines whereas the  ${}^4T_2 \rightarrow {}^4A_2$  yields the homogeneously broadened band. The second effect is the spin-orbit interaction that produces the  ${}^4T_2$  state splitting and allows the  ${}^2E \rightarrow {}^4A_2$  transition. The lower symmetry field splits additionally the  ${}^4T_2$  state, which effect although being of the first order is not usually seen due to the wide homogeneous broadening of the  ${}^4T_2 \rightarrow {}^4A_2$  band. However, lower symmetry field can be easily seen in the case of the strong field  ${}^2E \rightarrow {}^4A_2$ . The  ${}^2E$  state splitting (proportional to the product of the spin-orbit coupling and trigonal field strength) results in the  $R_1, R_2$  emission. Changes in the sequence of the excited states were experimentally detected in series of crystals characterized by various crystal field strength [4], and by application of high hydrostatic pressure to the weak field materials to increase the crystal field [5]–[8].

To get the information on the distribution of crystal field from the spectra of the  $\text{Cr}^{3+}$  ion one needs a model that relates the effects of environment and the electron-lattice coupling to the structure of the vibronic states and radiative and non-radiative deexcitation rates of the excited system.

The standard crystal field theory was developed to include the electron-lattice interaction. Thus the Hamiltonian of the system was given by

$$H(\bar{q}, \bar{Q}) = H_{\text{cf}}(\bar{q}, \bar{Q}^0) + \sum_i H_{\text{cr}}(Q_i) + \sum \left. \frac{dH_c(\bar{q}, \bar{Q})}{dQ_i} \right|_{\bar{q} = \bar{q}^0} [Q_i - Q_i^0]. \quad (1)$$

The first term is the electronic part of the Hamiltonian that is given by the standard field crystal model, the second term is the vibronic Hamiltonian and the third is electron-lattice interaction Hamiltonian. In form (1),  $q$  and  $Q$  correspond to

electronic and ionic coordinates, respectively.  $\bar{Q} = \{Q_1, \dots, Q_n\}$  is the vector in the configurational space,  $Q_1, \dots, Q_n$  are the normal vibration modes defined by the irreducible representations of the respective point group.

To solve the problem formulated by expression (1) we use the basis of the Born–Oppenheimer wave functions

$$\Phi_\nu(\bar{q}, \bar{Q}) = \varphi_\nu(\bar{q}, \bar{Q}^0) \prod_i \chi_{\nu_i}^{n_i}(Q_i)$$

where  $\nu$  represent the crystal field spinorbitals defined by the irreducible representations of the double group defining the symmetry of the center,  $n_i$  is the vibronic quantum number. The above assumption allows us to parameterize the electron–lattice coupling by the quantities

$$V_{\nu\nu'}^i = \int d\bar{q} \varphi_\nu^*(\bar{q}, \bar{Q}^0) \left. \frac{dH_{cf}(q, \bar{Q})}{dQ_i} \right|_{\bar{Q} = \bar{Q}^0} \varphi_{\nu'}(\bar{q}, \bar{Q}^0).$$

One can solve the problem using the adiabatic or diabatic approximation. In the adiabatic limit one diagonalizes the Hamiltonian (1) using the electronic part of the wave function  $\varphi_\nu$ , separately for each point of the configurational space. As a result one obtains the electronic energies  $E_\alpha(\bar{Q})$  presented in the form of configurational coordinate diagrams. The vibronic states can be calculated numerically separately for each electronic manifold  $\alpha$ . Finally, one obtains the energies of the vibronic states  $E_\alpha^{\bar{m}}$  and respective wave functions given as follows:

$$\Psi_\alpha^{\bar{m}}(\bar{q}, \bar{Q}) = \sum_\nu \alpha_{\nu\alpha}(\bar{Q}) \varphi_\nu(\bar{q}, \bar{Q}^0) \prod_i \chi_{\alpha i}^{k_i^{\bar{m}}}(Q_i) \tag{2}$$

where  $\bar{m} = (k_1^{\bar{m}}, \dots, k_i^{\bar{m}}, \dots, k_N^{\bar{m}})$  represents the set of quantum numbers of the collective vibronic state. The advantage of this method is that the vibronic and electronic parts of wave function are still well separated. One defines the radiative transition probabilities as the respective matrix elements

$$P_{\beta\alpha}^{\bar{m}} = \int d\bar{Q} \int d\bar{q} \Psi_\alpha^{\bar{m}*}(\bar{q}, \bar{Q}) M(\bar{q}) \Psi_\beta^{\bar{m}}(\bar{q}, \bar{Q}).$$

Considering the electronic transition moments

$$T_{\nu\nu'} = \int d\bar{q} \varphi_\nu^*(\bar{q}, \bar{Q}^0) M(\bar{q}) \varphi_{\nu'}(\bar{q}, \bar{Q}^0)$$

as the parameters one obtains

$$P_{\beta\alpha}^{\bar{m}} = \left| \sum_\nu \sum_{\nu'} T_{\nu\nu'} \prod_i \int dQ_i \alpha_{\alpha\nu}(\bar{Q}) \alpha_{\beta\nu'}(\bar{Q}) \chi_{\nu_i}^{k_i^{\bar{m}}}(Q_i) \chi_{\nu'_i}^{k_i^{\bar{m}}}(Q_i) \right|^2. \tag{3}$$

Using the adiabatic approximation one omits the non-adiabatic part of the Hamiltonian that additionally mixes the states. Therefore this approximation cannot be used in an arbitrary case.

One can perform calculation in the diabatic limit. Using the same Born–Oppenheimer wave functions one diagonalizes the Hamiltonian (1) in the full vibration space  $\varphi_\nu \prod_i \chi_{\nu_i}^{n_i}$ . This procedure includes automatically the non-adiabatic

interaction but the additional errors are related to limited number of vibronic states that can be taken into account. Also the results cannot be presented in the form of the configurational coordinate diagrams. After diagonalization one obtains the wave vectors corresponding the energies  $E^m$

$$\begin{aligned} \Psi_m(\bar{q}, \bar{Q}) &= \\ &= \sum_{n'_1} \dots \sum_{n_i} \dots \sum_{n'_N} \sum_v a_v^m(n'_1 \dots n_i \dots n'_N) \phi_v(\bar{q}, \bar{Q}^0) \chi_{v_1}^{n'_1}(Q_1) \dots \chi_{v_i}^{n'_i}(Q_i) \dots \chi_{v_N}^{n'_N}(Q_N). \end{aligned} \quad (4)$$

The probability of radiative transition is then given by

$$\begin{aligned} P^{mp} &= \left| \sum_{n'_1} \dots \sum_{n_i} \dots \sum_{n'_N} \sum_{m'_1} \dots \sum_{m_i} \dots \sum_{m'_N} \sum_v \sum_{v'} T_{vv'} a_v^m(n'_1, \dots, n_i, \dots, n'_N) a_{v'}^p(m'_1, \dots, m_i, \dots, m'_N) \right. \\ &\quad \int \chi_{v_1}^{n'_1}(Q_1) \chi_{v_1}^{m'_1}(Q_1) dQ_1 \dots \\ &\quad \left. \int \chi_{v_i}^{n'_i}(Q_i) \chi_{v_i}^{m'_i}(Q_i) dQ_i \dots \int \chi_{v_N}^{n'_N}(Q_N) \chi_{v_N}^{m'_N}(Q_N) dQ_N \right|^2. \end{aligned} \quad (5)$$

Note that in the case of  $\text{Cr}^{3+}$  it is enough to consider the ground  ${}^4A_2$  and the excited  ${}^4T_2$ ,  ${}^2E$  and  ${}^2T_1$  electronic manifolds. Also the vibronic structure can be described in a proper way by considering the effective one-dimensional vibration mode [9]. One simulates the emission and absorption line-shapes  $L(\hbar\Omega)$  considering the specific distribution of the sites  $\Theta_X$ , where  $X$  is variable that unambiguously describes the sites

$$L(\hbar\Omega) = \sum_n \sum_m S(E^m, kT) \int \Theta_X P^{nm}(X) dX \delta[(E^m - E^n) - \hbar\Omega]. \quad (6)$$

One takes into account the distribution of the cubic crystal field strength,  $10Dq$ ,  $\Theta_{10Dq}$ , distribution of the electron-lattice coupling  $S\hbar\omega$ ,  $\Theta_{S\hbar\omega}$  and distribution of the trigonal field that is related to the  ${}^2E$  state splitting  $\Delta$ ,  $\Theta_\Delta$ .

### 3. Examples

The adiabatic approximation has been used for analysis of the inhomogeneous broadening of the  $R_1$  line emission in (Ca, Zr)-substituted  $\text{Cd}^3\text{Ga}_5\text{O}_{12}:\text{Cr}^{3+}$  [10], [11]. The  $\text{Cr}^{3+}$  that occupies the medium field sites is characterized here by relatively small electron-lattice coupling  $S\hbar\omega = 1200 \text{ cm}^{-1}$ . Since the crystal field is medium position of the  $R_1$  line emission is determined by the spin-orbit coupling of the  $\Gamma_8$  components of  ${}^4T_2$  and  ${}^2E$  states. Assuming the initial distribution of the  ${}^4T_2$  electronic manifold energy that has been related to the number of the Ca, Zr-Gd, Ga substitutions in unit volume one obtains the distribution of the energy of the emitting state. Using Poisson distribution of the energy of  ${}^4T_2$ , as related to the statistical distribution of the number of the interstitials in the unit volume of the garnet, [10], one has also calculated the radiative transition rates and simulated

properly the changes in the  $R_1$  line-shape in time [11]. The same approximation has been used for analysing the luminescence line-shape of the  $\text{Cr}^{3+}$  in gallogermanate crystals [12]–[14] and aluminosilicate glasses [15]. In these materials,  $\text{Cr}^{3+}$  occupies the weak field sites, thus the dominant feature in the emission is the broad band related to the  ${}^4T_2 \rightarrow {}^4A_2$  transition. The  $R$  line emission, which appears in some of the gallogermanates is the minor effect. Analysing the dependence of the broad band maximum on the excitation energy allowed relating the energy of the minimum of the  ${}^4T_2$  electronic manifold to the electron–lattice coupling. Actually it has been found that the sites in the gallogermanate crystals differ mainly in the electron–lattice coupling energy. In the case of  $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  (CGGO) and  $\text{Sr}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  (SGGO) the distribution of the quantity  $Sh\omega$  was Gaussian, given by mean value of about  $3800 \text{ cm}^{-1}$  and standard dispersion equal to about  $750 \text{ cm}^{-1}$  [14]. The large mean value of  $10Dq$  and  $Sh\omega$  as well as standard dispersions of these quantities were related directly to disorder in gallogermanates caused by the  $\text{Ga}^{3+} \text{ Ga}^{4+}$  interstitials. It has been found that CGGO and SGGO, where the interstitials appear in the next shell neighbouring the  $\text{Cr}^{3+}$  ion, they produce the broader distribution of the  ${}^4T_2$  energy than in the case of  $\text{La}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  (LGGO), where the disorder is in outer shells [13]. Detailed investigations of the fluorescence line narrowing of the  $R_1, R_2$  lines emission allowed estimating the distribution of trigonal field. A strong correlation between the distribution of the  $\text{Ga}^{3+} \text{ Ge}^{4+}$  interstitials and the trigonal field has been detected. In the case of CGGO and SGGO (the interstitials are close to  $\text{Cr}^{3+}$  site) the trigonal field and the  $R_1, R_2$  splitting differ very much from site to site [13], whereas for LGGO and  $\text{La}_3\text{Ga}_5\text{SiO}_{14}$  (LGS) where interstitials are far from the  $\text{Cr}^{3+}$  site, the  $R_1, R_2$  splitting almost does not change [14].

An interesting result is the weak correlation between electron–lattice coupling and minimum energy of the  ${}^4T_2$  electronic manifold in aluminosilicate glasses [15]. This effect can be explained by larger lattice disorder in glasses.

#### 4. Summary

The diabatic approximation has been used for analysis of the  $\text{Cr}^{3+}$  sites in the case of the congruent  $\text{LiTaO}_3$  crystals. This material is characterized by the existence of  $\text{Li}^+$  vacancies. It is expected that the broad band luminescence related to the weak field  $\text{Cr}^{3+}$  ions is additionally inhomogeneously broadened. The high hydrostatic pressure has been used to make the weak-field–strong-field transition of the  $\text{Cr}^{3+}$  [16]. As a result one obtained the triple  $R$  line structure, related to three dominant sites  $\alpha, \beta$  and  $\gamma$ . The analysis of the  $R$  line shape dependence on pressure allowed determination of the distribution of the  $10Dq$  parameter for each of the sites considered [16]. The particular sites have been related to the distribution of the  $\text{Li}^+$  vacancies. The important conclusion of this investigation concerns the correlation between the energy of the  ${}^4T_2$  and  ${}^2E$  states. It has been found that the sites characterized by lower energy of the  ${}^4T_2$  state have higher energy of the  ${}^2E$  state. The parameters of the sites distribution are listed in the Table.

T a b l e. Parameters of the  $\text{Cr}^{3+}$  sites.  $E$  and  $\sigma_E$  are the mean value and the standard dispersion of the energy distribution.

Site	$E^0(^4T_2)$ [ $\text{cm}^{-1}$ ]	$\sigma_T$ [ $\text{cm}^{-1}$ ]	$dE(^4T_2)/dp$ [ $\text{cm}^{-1}/\text{kbar}$ ]	$E^0(^2E)-R_1$ line [ $\text{cm}^{-1}$ ]	$\sigma_E$ [ $\text{cm}^{-1}$ ]	$dE(^2E)/dp$ [ $\text{cm}^{-1}/\text{kbar}$ ]
$\alpha$ (two $\text{Li}^+$ vacancies in the vicinity of $\text{Cr}^{3+}$ )	>14017	?	?	13900	10	-2.9
$\beta$ (one $\text{Li}^+$ vacancy in the vicinity of $\text{Cr}^{3+}$ )	13453	100	13.5	3919	10	-2.7
$\gamma$ (no $\text{Li}^+$ vacancies in the vicinity of $\text{Cr}^{3+}$ )	13283	150	13.5	4023	16.7	-2.9

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