

The Fundamental Spectral Law For F_2^+ and F_2^+ -Perturbed Centers in LiF Crystals

Yu.M. Titov and N.T. Maksimova

Irkutsk state university, Boulevard Gagarin, 20, Irkutsk, 664003, Russia,
Phone (395-2)242163, Fax (395-2)242194, E-mail: yuri@nm.ru

Abstract – The fundamental law of interrelation between position and half-width of F_2^+ and F_2^+ -like centers absorption bands in LiF crystals is considered in the case of a different degree of a stationary perturbation caused by close located impurity or lattice defects.

1. Introduction

The F_2^+ center is the most simple single-electron charged center. Owing to jump moving and absence of charge compensation concerning crystal lattice, it is unstable at room temperature. Charge compensation by means of impurity or lattice defect results in fastening the center in a lattice, and as a consequence thermostability increases. Last circumstance is a basic reason of wide use of such centers as active laser mediums and passive switches of resonators [1–2]. A fast component of relaxation from the excited states makes it possible to use them in a self-synchronization modes condition [3–4].

On the other hand, stabilizing defect of a crystal lattice creates F_2^+ -perturbed center and leads to displacement of absorption band maximum as well as change of its half-widths. Last circumstance results in change of its interaction with crystal lattice phonons. Interacted with the center phonon modes well revealed in resonance Raman scattering spectrum [4]. Such F_2^+ -perturbed centers also name F_2^+ -like centers owing to similarity of their properties to maternal F_2^+ centers' ones.

2. Approach of Frank-Condone

F_2^+ centers in LiF crystal have strong electron-phonon interaction which is well described by the linear approach. As it was shown by M. Lax in 1952, such case well is described in quasi-classic approach of Frank-Condone. (See, for example, [5]).

Basing on previously-mentioned, consider F_2^+ centers at various degree of perturbation within the framework of strong linear electron-phonon interaction in quasi-classic approach of Frank-Condone. In Fig. 1 the examples of differently perturbed F_2^+ centers are shown.

For simplification we shall neglect influence of perturbation on a position of the ground energy level $1s\sigma_g$ in a relaxation state. In this case the dissociation energy of the center (D_0'' , D_c'') is nearly independent on such perturbation. This circumstance is illustrated

in Fig. 1, as can be seen the appreciable influence of the perturbed factor is revealed at smaller values of configuration coordinate. But in the cause of the first excited state $2p\sigma_u$ situation is different – due to greater spatial localization of that state.

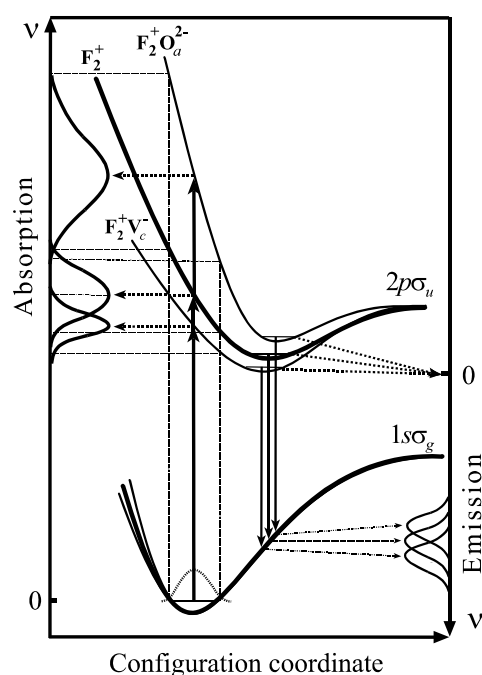


Fig. 1. The dependence of the position of F_2^+ center energy level, absorption and emission bands on the value of perturbation of an impurity or cation vacancy (V_c).

If charging compensation occurs by replacement of fluorine ion, for example, on two-charged ion of little bit greater radius O^{2-} , the perturbed factor will be reduction of volume occupied by $2p\sigma_u$ -orbital. Other case of compensation of a F_2^+ center charge comprises the approach of cation vacancy V_c^- to it. In this case volume occupied by orbit is increased. Both these cases are shown in Fig. 1. Average bold curve corresponds to the state of not perturbed F_2^+ center. From the figure it is also visible, that F_2^+ center absorption bands turn out to be result of "reflection" of the ground state electronic density distribution. As the kind of distribution is close to Gauss, "reflection"

Elementary processes

Table. Properties of non-perturbed and perturbed defects F_2^+ centers in LiF

Centre	Absorption band				λ_{00} , nm	Emission band				Effective phonon, cm^{-1}			Reference
	λ_{max} , nm		Half-width, cm^{-1}			λ_{max} , nm		Half-width, cm^{-1}		Absorb.	Emis.	Raman	
	295 K	77 K	295 K	77 K		295 K	77 K	295 K	77 K				
F_2^+	625,2	645	3470	2474	763,3	908	910	2317	1745, 1734	227	247		[4,6,7]
$F_2^+V_c^-$	~691		~2075										[8]
$F_2^+O^{2-}$	611		3950		737,6	894,6		2320 ± 10	1814 ± 10		260	247	[4]
F_2^+ -like "527"	527,4 ± 15	527 ± 15	6306 ± 100	6000 ± 100	~715?	890 $\pm 0,8$		2333 ± 10	1853 ± 10	632	302	300	[4]

for the straight parts of a branch results to Gauss absorption band. The small curvature of this branch leads to some asymmetry of absorption band, as it was observed in our experiment. The level of asymmetry is more pronounced in the case of F_2^+ centers that are less constricted by defects. The enhance of a sharpness of the branch $2p\sigma_u$ results in increase of absorption band energy, as well as increase its half-width and as the consequence, leads to increase of phonon effective energy, with which the center interacts. For emission bands this circumstance is less significant. In the Table the basic parameters of some LiF crystal F_2^+ -perturbed centers are given.

In Fig. 2 some data from the table are shown. The direct line is drawn as average weighted of experimental points, and is described by the equation (for LiF: F_2^+ -like centers at 295 K)

$$\Delta\tilde{\nu}_i = 0,94 \cdot \tilde{\nu}_i - 11530 \text{ [cm}^{-1}\text{]}.$$

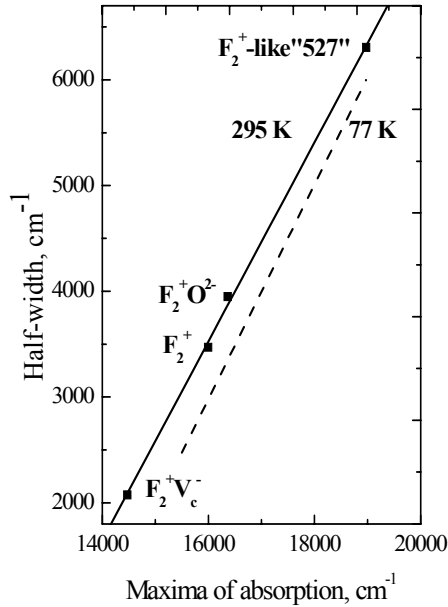


Fig. 2. The linear dependence between energy levels of absorption band maximum and their width on half height for F_2^+ -perturbed centers in LiF crystals.

Below for comparison the dependence for the same crystal at temperature 77 K is shown.

Let's consider it now from positions of a principle of Frank-Condone: we shall put down the equations of converging straight lines for section repulsion branches of $2p\sigma_u$ -states, as

$$\tilde{\nu}_i = K_i(Q_1 - Q) + \tilde{\nu}_1, \quad (1)$$

where $K_i = d\tilde{\nu}/dQ$ – factor describing slope of a curve for i -center (i – a variety of F_2^+ -perturbed center), $\tilde{\nu}_1$ – energy position of a descending point of straight lines, and Q_1 – its configuration coordinate. On the base of (1) we can write the equations for definition of a maximum absorption position ν_{mi} ; and they half-width $\Delta\tilde{\nu}_i$ depending on factor of slope of a curve K_i :

$$\tilde{\nu}_{m_i} = K_i(Q_1 - Q_0) + \tilde{\nu}_1, \quad (2)$$

$$\Delta\tilde{\nu}_i = K_i\Delta Q_0$$

here Q_0 – configuration coordinate of an equilibrium position of the center in the basic state, ΔQ_0 – double effective amplitude of its fluctuations near Q_0 (Fig. 2) on half from a maximum of electronic distribution in the basic state. Joint decision of two equality (2) with exception K_i , will result to

$$\Delta\nu_i = \frac{\Delta Q_0}{Q_1 - Q_0} \cdot \tilde{\nu}_{m_i} - \frac{\Delta Q_0}{Q_1 - Q_0} \cdot \tilde{\nu}_1. \quad (3)$$

Comparing (3) with (1), we make the conclusion, that these equations describe the same dependence. Hence, we can identify factors in these equations and their physical sense became clear.

$$\tilde{\nu}_1 \approx 12270 \text{ cm}^{-1} \quad \frac{\Delta Q_0}{Q_1 - Q_0} \approx 0,94$$

Value $(Q_1 - Q_0)/0,5\Delta Q_0$ describes the relation of the F_2^+ center spatial relaxation level to the effective amplitude of equilibrium fluctuations ($0,5\Delta Q_0$), $\tilde{\nu}_1$ describes energy of a descended point in the case of linear approximation of the excited state repulsion branches, its en-

ergy level is a little bit lower than a potential minimum $2p\sigma_u$ state of a non-perturbed F_2^+ center.

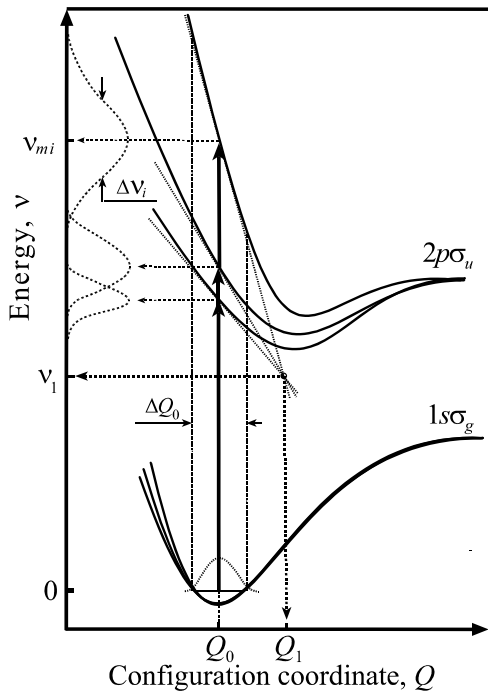


Fig. 3. Quasi-classic approach for F_2^+ center with different level of the defect perturbation.

Conclusion

Making a final conclusion we can say that similar dependences can be received for other crystal matrixes

contained color centers with strong electron-phonon interaction.

The given functional relation can be useful as one of identification criteria of the belonging an investigated absorption band to family of defect perturbed F_2^+ centers (F_2^+ -like centers).

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