

Self-consistent solutions in the continuous model of F centers and the problem of relaxed excited states

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For F centers in an ionic crystal, an excited self-consistent state for the electron and the lattice has been found. The lifetime and the radius of such a state have been calculated. The results are in agreement with experiment.

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INTRODUCTION

Numerous experiments on luminescence in colored crystals have led to the conclusion that above the ground state there is a rather stable (metastable) excited state to which an electron moves in the process of relaxation. From data on spin resonance it follows that this state possesses a large radius, greatly exceeding the distance between the closest neighbors of the lattice. The presence of such a state causes a lag in the luminescence, large Stokes shifting, a specific temperature dependence of photoconductivity and other effects. (An overview of experimental work on this problem can be found in Ref. 1). Despite the large amount of theoretical and experimental work relating to this problem, there still exists considerable uncertainty concerning the nature of this state.

Meanwhile in the authors' work devoted to the study of the structure of polaron states with strong bonds of large radius² it has been shown that besides the ground state the polaron can be located in other excited self-consistent states. An analogous situation occurs for F centers when a plaron is localized in the vicinity of a lattice vacancy in an ionized crystal.

BASIC EQUATIONS

In the continuous model the Hamiltonian that describes the interaction of a point ion and an electron associated with the phonon field of optical vibration is of the form³

$$\kappa = -\frac{\hbar}{2\mu} \Delta - \frac{Ze^2}{\epsilon r} + \sum_f A_f q_f e^{i(\text{fr})} + \sum_f \hbar \omega_f (q_f q_{-f} + p_f p_{-f}) \quad (1)$$

where $p_f = -i\hbar \partial / \partial f q_f$, q_f are the normal coordinates of longitudinal optical oscillations, ω_f is the frequency of the optical oscillations, Ze is the ion charge, $A_f = e / |f| (4\pi \hbar \omega_f / \tilde{\epsilon} V)^{1/2}$, $\tilde{\epsilon}^{-1} = \epsilon_\infty^{-1} - \epsilon^{-1}$, ϵ_∞ and e are the high-frequency and static permittivities.

In the limit of an adiabatically strong bond ($\omega_f \rightarrow 0$), the equation for the electronic portion of the crystal's wave function follows from the Hamiltonian [Eq. (1)]:

$$\left. \begin{aligned} & \left(-\frac{\hbar^2}{2\mu} \Delta - \frac{Ze^2}{\epsilon r} + U(r) - W \right) \varphi(r) = 0 \\ & U(r) = -\sum_f \frac{A_f^2}{2\omega_f} \int e^{if(r-r')} |\varphi(r')|^2 dr' \end{aligned} \right\} \quad (2)$$

Taking into account the equation $1/|r| = 1/2\pi r^2[\exp(if \times r)/f^2]df$ and the fact that for optical phonons one can assume $\omega_f = \omega$, we can rewrite Eq. (2) as a system of two differential equations:

$$\left. \begin{aligned} \frac{\hbar^2}{2\mu} \Delta\varphi(r) + e\Pi(r)\varphi(r) + \frac{Ze^2}{\varepsilon} \frac{\varphi(r)}{r} + W\varphi(r) &= 0 \\ \Delta\Pi(r) + \frac{4\pi e}{\varepsilon} \varphi^2(r) &= 0 \end{aligned} \right\} \quad (3)$$

where the function $-\pi(r)$ in Eq. (3) is understood as the potential created by polarization induced by the localized electron in the vicinity of the defect.

The natural boundary conditions for the system [Eq. (3)] is of the form

$$\left. \begin{aligned} \varphi'(0) + \frac{\mu Ze^2}{\hbar^2 e} \varphi(0) &= 0, & \varphi(\infty) &= 0, \\ \Pi'(0) &= 0, & \Pi(\infty) &= 0 \end{aligned} \right\}$$

RESULTS OF NUMERICAL CALCULATIONS

The system of Eqs. (3) and (3') can be numerically integrated as was done in Ref. 2. In this case the spherically symmetric solutions (modes) of this system represent self-consistent states of the electron and lattice. From the practical point of view, the most interesting cases are the zero and the first modes.

The zero mode [$\varphi(r)$ has no nodes] corresponds to the ground state, which was studied in detail in Ref. 3. It is associated with certain effects such as light absorption by the F center, ionization processes, and a whole series of other important characteristics.

The first mode [$\varphi(r)$ has one node] represents the first (excited) self-consistent state, to which an electron may move in the process of relaxation following photoexcitation. It is associated with luminescence, photoconductivity, and other effects.

In Table I values are given for a series of ionized crystals, which correspond to the first self-consistent state: the effective radius $\langle r \rangle$ of the electronic state; the electronic ($W_1 = W_1^{2s^*}$) and the total (J_l) energies; electron levels (nonself-consistent) in the $2p^*$ ($W_1^{2p^*}$) and $1s^*$ ($W_1^{1s^*}$) states; the oscillator strengths for the transition between $2p^*$ and $1s^*$ states ($f_{2p^*-1s^*}$).

PHOTOEXCITATION AND THE LIFETIME OF EXCITED STATES

We will now study the process of electron photoexcitation from the ground state to the first allowed state.

TABLE 1. Summary of results for the first mode (experimental values of m/m , obtained by the cyclotron resonance method⁷).

Cristal	ε	$Z\tilde{\varepsilon}/\varepsilon$	μ/m	$\frac{W_1}{e^2 \mu / \hbar^2 \tilde{\varepsilon}^2}$	$\frac{J_1}{e^4 \mu / \hbar^2 \tilde{\varepsilon}^2}$	$\frac{\langle r \rangle_1}{\hbar^2 \tilde{\varepsilon} / e^2 \mu}$	$W_1^{1s^*} / W_1$	$W_1^{2p^*} / W_1$	$f_{2p^* \rightarrow 1s^*}$
KCl	4.68	0.84	0.922	- 0.244	- 0.161	31.2	2.38	1.06	0.43
KBr	4.78	0.95	0.700	- 0.285	- 0.194	26.2	2.46	1.05	0.58
KJ	4.94	1.2	0.536	- 0.393	- 0.283	18.5	2.63	1.05	0.50
RbCl	5.0	0.78	1.03	- 0.223	- 0.145	34.5	2.33	1.06	0.57
RbJ	5.0	1.12	0.72	- 0.355	- 0.251	20.6	2.58	1.05	0.52
AgCl	12.3	0.48	0.431	- 0.130	- 0.075	63	2.04	1.08	0.65
AgBr	13.1	0.49	0.287	- 0.133	- 0.077	62	2.05	1.07	0.67
TlCl	13.9	0.19	0.651	- 0.063	- 0.029	147	1.69	1.10	0.78
TlBr	29.9	0.22	0.525	- 0.069	- 0.033	133	1.73	1.10	0.76

Following Ref. 1, we will relate the $1s, 2s, 2p, \dots$ states to the lattice configuration corresponding to the ground electronic state, and the $1s^*, 2s^*, 2p^*, \dots$ states to the configuration corresponding to the lowest excited itate. Then the following cycle is studied for optical transition from the ground state to the first excited state. Upon light absorption the electron moves from the $1a$ state to the $2p$ state [this transition corresponds to the maximum oscillator strength $f_{sp} \approx 0.7-0.8$ (Ref. 3)] with the same lattice configuration (the Franck-Conlion principle). As a result of nonradiating processes i. e., with emission of phonons) the electron relaxes to the $2p^*$ state. Light emission occurs upon transition from the $2p^*$ state to the $1s^*$ state with an unchanging lattice configuration already corresponding to the $2p^*$ state. Finally, as a result of nonradiative process the electron returns to the initial $1s$ state.

Cur proof lies in the fact that at the stage when the electron relaxes from the excited $2p$ state, it moves to the first self-consistent $2s^*$ state. This state lies somewhat higher in energy than the $2p^*$ state, although close to it (Fig. 1). Therefore, as a result of nonradiative processes the electron can easily transfer to the $2p^*$ state, from which a transition occurs to the $1s^*$ state with emission of light.

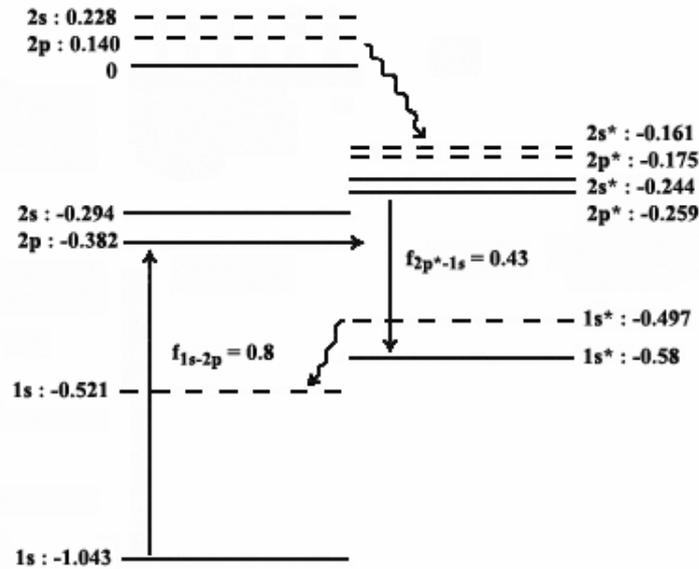


FIG. 1. Distribution of F -center energy levels in KCl crystals for the zero and first mode (energy in units $e^4 \mu / \hbar^2 \tilde{\varepsilon}^2$). Electron energies are indicated by the solid lines; dashed lines indicate the total energy. The arrows show the absorbing and emitting electronic transitions. The wavy lines are the nonradiative relaxations of the electron and the lattice.

The transition time from the $2p^*$ state to the $1s^*$ state can be found (the transition energies and oscillator strengths are given in Table I) using the usual formulas for transition probabilities¹:

$$\tau_{2p^* \rightarrow 1s^*}^{-1} = \frac{2e^2 \omega_{2p^*, 2s^*}^2 n(\omega)}{\mu c^2} f_{2p^* \rightarrow 1s^*}; \quad \omega_{2p^*, 1s^*} = \frac{W_1^{2p^*} - W_1^{2s^*}}{\hbar}, \quad (4)$$

where $f_{2p^* \rightarrow 1s^*}$ is the oscillator transition strength $2p^* \rightarrow 1s^*$, $n(\omega)$ is the index of refraction.

Calculation of the transition time according to Eq. (4) (without accounting for the frequency dependence of the index of refraction) leads to agreement with the experimental results⁴ (Table II).

EFFECTIVE RADIUS

The effective radius of the state, $\langle r \rangle_1 = \int \varphi_1^* r \varphi d\tau$, is an important characteristic of the model. Its value provides a criterion for applying the continuous approximation. In experiments on spin resonance the effective size of the wave function for the relaxed excited state was measured, which, in accordance with the previous point, corresponds to the $2p^*$ state. Its value turned out to be $\langle r/a \rangle \approx 4.9$ for KBr and $\langle r/a \rangle \approx 5.2$ for KI.¹ Numerical calculations of the radii for the $2p^*$ state give values close to the experimental results: ≈ 5.6 for KBr and ≈ 7.1 for KI. We will now turn our attention to the fact that the size of the strictly self-consistent state, corresponding to the first mode, for these crystals is ≈ 6.5 for KBr and ≈ 8.5 for KI. The large sizes for the effective radius in the first self-consistent state guarantee high accuracy when using the continuous approximation for calculating levels that correspond to the potential well of this state.

CONCLUSION

The results obtained in this work explain the nature of relaxed excited states. Numerical calculation of such states provides values close to the experimental results for the effective radii and luminescence lag

TABLE 2.

	KCl	KBr	KI	
$10^6 \tau \mu \text{ sec}$	0.59	1.1	2.1	Experiment
$10^6 \tau \mu \text{ sec}$	0.8	1.2	2.0	Theory

times, one should stress that the system of Eqs. (3)-(3') studied in this work are asymptotically accurate only in the limit of an infinitely strong, adiabatic bond of the electrons with the phonons, i. e., in the limit as $\omega \rightarrow 0$. Despite the fact that for the majority of F centers such an approximation is fairly well fulfilled (the motion frequency of the electron in the potential well greatly exceeds the oscillator frequency of the lattice ions), the results can be considered only as extrapolations in relation to real crystals.

APPENDIX

Algorithm for solving the boundary-value problem [Eqs. (3)-(3')]

The system of Eq. (3) with a simple substitution of variables, leads to⁵

$$\xi'' + \xi[(\eta/x) - 1] = 0, \quad \eta'' + (\xi^2/x) = 0 \quad (5)$$

The boundary conditions (3') in these variables take on the form

$$\left. \begin{array}{l} \text{at } x \rightarrow 0: \xi(x) \rightarrow 0 \quad \eta(x) \rightarrow N, \\ \text{at } x \rightarrow \infty: \xi(x) \rightarrow 0 \quad \eta'(x) \rightarrow 0. \end{array} \right\} \quad (5')$$

The parameter H in Eq. (5') in every solution of the system of Eqs. (5)-(5') is clearly associated with the physical parameter $\nu = Z\tilde{\varepsilon}/\varepsilon$:

$$\nu = N \int_0^{\infty} \xi^2(x) dx$$

The system of Eqs. (5)-(5') is analogous to the system of equations for the polaron of a strong bond (and coincides with it for $N = 0$).² We will present the solution for the system (5) in the vicinity of the point $x=0$ in the form of the following series:

$$\left. \begin{array}{l} \xi(x) = a_1x + a_2x^2 + \dots, \\ \eta(x) = N + b_1x + b_2x^2 + \dots \end{array} \right\} \quad (6)$$

Thus the first of the boundary conditions (5') is fulfilled automatically. Substituting Eq. (6) into Eq. (5), we obtain relations for the coefficients a_i and b_i . These coefficients are clearly determined by the values of the two parameters $a_1 = a$ and $b_1 = b$:

$$\left. \begin{array}{l} \xi(x) = a_1x - \frac{aN}{2} + \frac{a}{6} \left(1 + \frac{N^2}{2} - b \right) x^2 + \dots, \\ \eta(x) = N + bx - \frac{a^2x^2}{6} + \frac{a^2N}{12}x^4 + \dots \end{array} \right\} \quad (7)$$

So there exists a dual parametric family of solutions for the system (5) which satisfies the first of the boundary conditions (5').

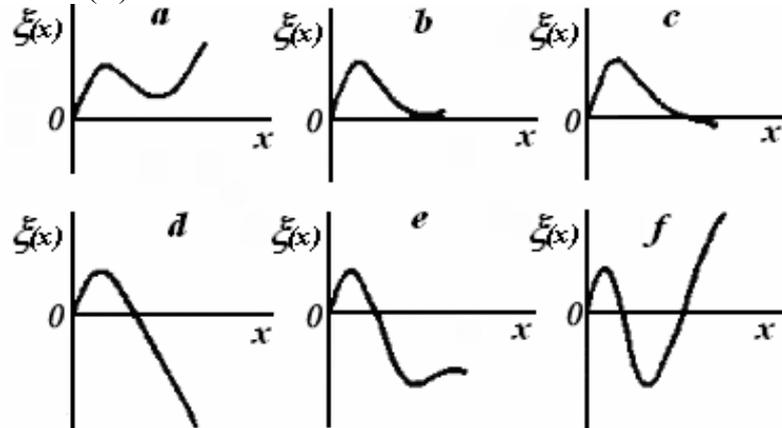


FIG. 2. Functions $\xi(x; a, b)$ for various values of the parameters a and b . Cases (a) - (f) correspond to successive point taken from the curve $f(a, b) = \eta' \equiv (x_k; a, b) = 0$.

For the system of differential equations (5) we define the Cauchy problem over the range $[x_0, x_k]$. For this, with sufficiently small $x = x_0$, we assign the values $\xi(x_0)$, $\xi'(x_0)$, $\eta(x_0)$, $\eta'(x_0)$, which correspond to certain values of the parameters a and b in the expansions (7). Taking x_k sufficiently large, we find (numerically) a connection between the parameters a and b , which assures fulfillment of the condition $\eta'(x_k) = 0$. If we now look; the solution $\xi(x)$ for various values of the parameters a and b , taken along the curve $f(a, b) = \eta'(x_k; a, b) = 0$, an explicit law appears in their behavior (Fig. 2) indicating the existence of various solutions to the system of Eqs. (5)-(5') having no zeros, one zero, two zeros etc.

Automation of the search for solutions to Eqs. (5) was carried out by the authors using a series of programs⁶ developed at the Scientific Research Computer Center, Academy of Sciences U. S. S. R.

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