F center deexcitation induced by local vibration tunneling

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A new concept of electronic deexcitation of defects has been developed for systems where the electron couples very strongly with a local lattice mode. The model is based on a classical-quantum description of the configuration curve diagram and proposes that an electronic transition may be induced when the wave packets of the lattice oscillators in the upper and lower states involved overlap. It was successfully applied to the *F*-center system, at low temperature, in almost all the alkali halides. The luminescence efficiency derived from the model explains very well the observations, even the fact that the F^* electron always reaches the relaxed excited state.

Until now the current model for the electronic deexcitation of *F* centers in ionic crystals states that the experimental temperature-independent quenching of luminescence is produced by a crossover between the excited- and ground-state curves for the following hosts: LiI, NaI, NaBr, LiCl, LiBr, and LiF. The first model of that type is known as the Dexter–Klick–Russel (DKL) criterion for the occurrence of luminescence[1] that was later improved by Bartram and Stoneham.[2]

This model predicted no *F*-center luminescence in NaI and NaBr crystals. Indeed, a study with zone-refined NaI and NaBr found the *F*-center luminescence to be extremely weak.[3] The same study showed that dilute *F* centers in both NaI and NaBr can reversibly be converted by optical excitation into F' centers via a thermal activated process which leads, at high enough temperature, to a full conversion efficiency.[3] The measured activation energies (30 and 60 meV for NaI and NaBr) fit very well in the trend for the energy gap ΔE between the relaxed excited state ($\tilde{F}^*$) and the conduction band, established with the effective-mass model for other alkali halides.[4] Electron ionization therefore occurs in the relaxed excited $\tilde{F}^*$ state in NaBr and NaI, as it does in normal *F* centers. As apparently all optically excited electrons can reach this state from which ionization occurs, it must be deduced that the observed strong nonradiative deexcitation in NaI and NaBr must take place in the same state as well. The main conclusion from Baldacchini *et al.*[3,5] is, therefore, that the nonradiative decay occurs not during relaxation by a crossover process (as it is currently accepted), but rather after a relaxation from the relaxed $\tilde{F}^*$ state by a rate determining process which competes with a very weak radiative process and with a thermally activated ionization process. Considering the actual disagreement between the current theoretical model and the observation, we propose a new model based on the tunneling of the local-mode lattice oscillator which effectively couples with the *F* electron in the optical cycle.

In that case, a nonradiative electronic transition from the relaxed excited state of the *F* center is *induced* by a tunneling of the local-mode oscillator which couples with the excited electronic state (upper oscillator) to the one which couples with the ground electronic state (fundamental oscillator).

Let us consider an effective local mode of frequency W as an harmonic oscillator described by a wave packet Ψ with a position probability density

$$|\Psi(x,t)|^2 = (\alpha/\sqrt{\pi})\exp[-\alpha^2(x - a\cos wt)^2],$$

where $\alpha^4 = mK/\hbar^2$ (m is the reduced mass of the oscillator), K is the force constant, $\hbar$ is the Planck constant divided by 2π, and x is the direction of tunneling corresponding to the closest approximation between both parabolic curves (in the configuration coordinate diagram) for the total energy of the system. The wave packet of the upper oscillator oscillates without changing shape with frequency W and classical amplitude a about $x = x_0$ (x_0 is the separation between the two minima of the potential curves, seen in Fig. 1). Figure 1 shows the configuration coordinate diagram for the two lowest electronic states of the *F* center in the tunneling direction (x). The probability of tunneling from any energy level placed above the minimum of the relaxed excited state (point *C* in Fig. 1) can be calculated by solving the overlap integral of the two wave packets centered at x_1 for the upper oscillator and at x_2 for the fundamental oscillator with $t = 0$, $2\pi/W$, and $4\pi/W$. The tunneling must occur between the two closest turning points of both oscillators, considering that the fundamental oscillator is in a high vibrational level and consequently, has a higher probability to be found at the turning points. The overlap integral is given by

$$I = \int_{-\infty}^{+\infty} \frac{\alpha_0\alpha_e}{\pi} \exp[-\alpha_e^2(x - x_1)^2] \times \exp[-\alpha_0^2(x - x_2)^2]\,dx,$$

where x_1 and x_2 are defined in Fig. 1.

For simplicity, we further restrict the two-state model by the assumption that both the ground- and excited-state energies depend harmonically on the configuration coordinate with the same effective frequency. The assumption of equal frequencies is by no means essential, but available data do not seem sufficiently reliable to justify allowance for unequal frequencies. For example Dawson and Pooley[6] found $\omega_e^2/\omega_0^2 = -0.2$ for KCl, while Klick, Patterson, and Knox[7] found $\omega_e^2/\omega_0^2 = +1.4$ for the same crystal; both groups used optical absorption data.

With the assumption of equal frequencies, the integral is given by

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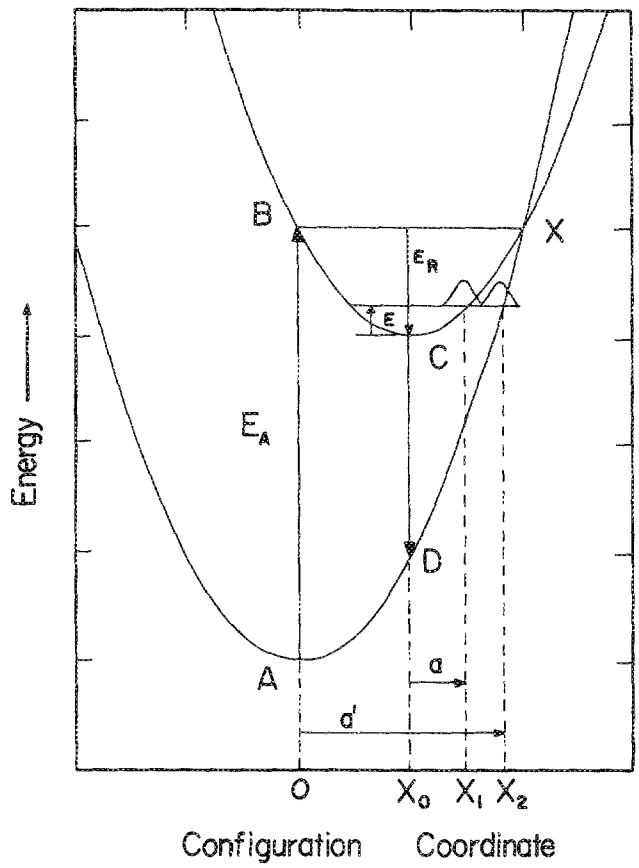

FIG. 1. Energy diagram for the ground and excited state of an F center as a function of the configuration coordinate X. The tunneling from level E placed above the minimum of the excited state, may occur if the two wave packets (centered at the respective turning points X_1 and X_2) of both oscillators are overlapping.

$$I = (\alpha/\sqrt{2\pi})\exp[-(\alpha^2/2)(x_2 - x_1)^2], \tag{1}$$

so the tunneling probability rate is given by

$$p = \nu I_n, \tag{2}$$

where I_n is the normalized overlap integral given by I/C [I is given by Eq. (1)]. C is a normalization constant calculated from the requirement that I_n must be equal to unity when $x_1 = x_2$ (the case of full wave packets overlap). The deduced value of C was $\alpha/\sqrt{2\pi}$. ν which appears in Eq. (2) is the attempt frequency for tunneling and is equal to the frequency of the effective local mode which couples with the F center.

According to the definitions in Fig. 1 and using the assumption that both oscillators have the same force constant, $K_e = K_0 = K$, we calculated the two maximum amplitudes for tunneling (for an energy level placed an amount of energy E above the relaxed excited state) given as follows:

$$a' = [(2E_A - 2E_R + 2E - \hbar W)/K]^{1/2},$$

$$a = [(2E - \hbar W)/K]^{1/2},$$

$$X_0 = [(2E_R - \hbar W)/K]^{1/2},$$

where

$$E_A = (A + \tfrac{1}{2})\hbar W \approx A\hbar W \quad (A \gg 1),$$

$$E_R = (S + \tfrac{1}{2})\hbar W \approx S\hbar W \quad (S \gg 1),$$

$$E = (n + \tfrac{1}{2})\hbar W,$$

and E_A is the maximum of the F absorption band for the main transition $1s \rightarrow 2p$, E_R is the energy of relaxation to the relaxed excited state ($B \rightarrow C$) and also equal to the energy of relaxation in the ground state ($D \rightarrow A$, Fig. 1), S is the Huang–Rhys factor and is equal to the number of local phonons involved in the relaxation process, and n is the vibrational quantum number of the level of the upper oscillator from where the tunneling must occur.

By using the expressions for a, a', and X_0 in Eqs. (1) and (2) we have the tunneling probability (rate) for a particular vibration level n:

$$p = \nu e^{-\gamma},$$

where

$$\gamma = [(A - S + n + \tfrac{1}{2})^{1/2} - S^{1/2} - n^{1/2}]^2.$$

We must consider now that the system is at some temperature T, consequently the contribution from all tunneling transitions of different vibrational levels must be taken into account. The final result is obtained by the summation over all the vibrational levels with the occupation probability $e^{-n\hbar W/KT}$. So, the effective tunneling probability (rate) of the system at temperature T is given by

$$P = \sum_{n=0}^{\infty} \nu e^{-\gamma} e^{-n\hbar W/KT}. \tag{3}$$

In the present work we wish to calculate the tunneling rate for the relaxed excited state ($n = 0$) for several alkali halides in order to test the model and compare it to the crossover. We also know from previous results that the electron reaches the relaxed excited state after optical excitation of the F center (at temperature below 77 K) in NaI and NaBr so, if tunneling exists in these cases it must be from a state with $n = 0$. Before presenting the results, we show the relevant experimental parameters (in Table I) used in the present

TABLE I. Values of the relevant experimental parameters for the F center in several alkali halides.

Host	E_A (eV)	W (10^{13} s^{-1})	S	$\Lambda = S/A$
NaI	2.1	2.73	44	0.384
NaBr	2.3	2.37	55	0.373
LiCl	3.3	2.61	71	0.370
LiBr	2.767	2.73	55	0.358
LiF	5.102	5.86	43	0.325
NaCl	2.77	2.77	40	0.260
KI	1.875	1.21	54	0.230
KBr	2.064	1.37	51	0.222
RbI	1.708	1.37	40	0.210
KF	2.847	2.78	30	0.193
KCl	2.313	1.86	36	0.190
RbCl	2.036	1.22	37	0.182
NaF	3.702	5.77	17	0.175
RbF	2.409	2.43	26	0.173
RbBr	1.851	1.82	25	0.162
CsI	1.718	1.67	12	0.077
CsBr	1.951	1.52	3.7	0.019
CsCl	2.169	1.22	4.8	0.018
CsF	1.876	3.647	0.7	0.009

TABLE II. Probabilities of tunneling and radiative deexcitation of F centers at low temperatures.

Host	γ	P (s^{-1})	R (s^{-1})	Luminescence η[a]	
NaI	3.6	9.5×10^{10}	$\sim10^{6}$	1×10^{-5}	No[b]
NaBr	4.83	3×10^{10}	$\sim10^{6}$	3.3×10^{-5}	No
LiCl	6.59	5.7×10^{9}	$\sim10^{6}$	1.8×10^{-4}	No
LiBr	6.34	7.7×10^{9}	$\sim10^{6}$	1.3×10^{-4}	No
LiF	8.42	2×10^{9}	$\sim10^{6}$	5×10^{-4}	No
NaCl	18.21	5.4×10^{4}	8×10^{7}	0.93	Yes
NaF	23.47	5.9×10^{2}	$\sim10^{6}$	1	Yes
KF	32.83	2.4×10^{-2}	4.8×10^{6}	1	Yes
RbI	34.93	1.5×10^{-3}	$\sim10^{5}$	1	Yes
RbF	36.74	4.3×10^{-4}	2.4×10^{6}	1	Yes
KI	36.98	1.7×10^{-4}	4.5×10^{5}	1	Yes
KBr	38.58	3.8×10^{-5}	9×10^{5}	1	Yes
RbBr	40.56	7×10^{-6}	1.2×10^{6}	1	Yes
KCl	40.62	6.7×10^{-6}	1.8×10^{6}	1	Yes
RbCl	46.57	1.1×10^{-8}	1.7×10^{6}	1	Yes
CsF	63.43	$<10^{-8}$	2×10^{7}	1	Yes
CsI	72.98	$<10^{-8}$		1	Yes
CsBr	141.88	$<10^{-14}$	6.5×10^{5}	1	Yes
CsCl	199.61	$<10^{-14}$		1	Yes

[a] $\eta\rightarrow$ predicted efficiency.
[b] No and yes refer to the observation of luminescence.

As one can see, for five alkali halides, NaI, NaBr, LiCl, LiBr, and LiF, the tunneling rates (P) are bigger than the radiative rates for luminescence (R), making the deexcitation extremely nonradiactive. For the remaining alkali halides (Table II), the tunneling rates are smaller than the radiative rates making the deexcitation via luminescence with full efficiency in most of the cases. The efficiency of luminescence, η, was calculated by the relation $\eta = R/(P+R)$.

With this model we could explain all the experimental observations regarding the F-center luminescence. The tunneling rates derived from this model, for NaBr and NaI, are in the same order of magnitude as the ones obtained by Baldacchini *et al.* in Ref. 3, for the F center in the same host materials. Also, the predictions of η below unity for NaCl derived from this model, is in agreement with the experimental observations.[8] The F excited electron always reaches the minimum of the potential curve (relaxed excited state) from where the system can either be relaxed to the ground state or ionized to the conduction band producing an F' center depending on the temperature of the system.

model for several alkali halides. The values shown in Table I were extracted from Ref. 6 where the authors studied mainly the temperature dependence of the linewidth in absorption of F centers. These values are the same used by Bartram and Stoneham in the crossover model.[2] The parameter Λ given by the relation S/A is exactly the one used in Ref. 2.

By using these values in Eq. (3) and setting $n=0$, we have the effective tunneling probability from the minimum of the potential curve of the excited state. The results of this calculation are presented in Table II.

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Near-band gap optical behavior of sputter deposited α- and α+β-ZrO_2 films

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The functional dependence of the optical absorption coefficient on photon energy in the 4.9–6.5 eV range was determined for α- and $\alpha+\beta$-ZrO_2 films grown by reactive sputter deposition on fused silica. Two allowed direct interband transitions in α-ZrO_2 were identified, with energies equal to 5.20 and 5.79 eV. Modification of these transitions in $\alpha+\beta$-ZrO_2 is reported.

Monoclinic α-ZrO_2 is the only stable form for an infinite-size ZrO_2 crystal at standard temperature and pressure. However, it is well known[2–5] that when the crystallite size is small, α-ZrO_2 and one of its high-temperature polymorphs, tetragonal β-ZrO_2, coexist. β-ZrO_2 in the composite is not a metastable phase nor the result of stabilization by impurities. It is a consequence of the dominance of the surface energy contribution to the Gibbs free energy of formation when the crystallite surface area-to-volume ratio exceeds a critical value.[4]

We previously reported[6] that phase transition from α-Zr$\rightarrow\alpha$-ZrO_2 in the sputter-deposited Zr-O system involves the formation of $\alpha+\beta$-ZrO_2 structures. The shape of the fundamental optical absorption edge was found to be different for films that contain a β-ZrO_2 component compared to films that are single-phase α-ZrO_2. The functional depen-

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