THE ANNIHILATION PROBABILITY FOR THE COMPONENTS
OF A PRIMARY F–H PAIR IN THERMALLY
ACTIVATED MOTION

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Annihilation probabilities $P_a$ have been calculated for the components of a primary $F–H$ pair for various interaction functions $E(r)$. It is shown that $P_a$ is small for $E(r) = 0$ but increases for $E(r) < 0$, being also a function of temperature, with a negative temperature coefficient for $E(r) < 0$.

The spatial separation of the components of a primary $F–H$ pair resulting from a decay of an electronic excitation [1] is one of the main factors that determine the result of color-center accumulation. There is a high probability of decay of such an excitation into spatially separated defects. Alkali halides and alkaline-earth fluorides require 60-100 eV to produce one such pair [2–5], which means that the energy yield ($\varepsilon$) in the production of $F–H$ defects exceeds 0.3, since the production of a single electronic excitation requires about 2–3 $E_g$ ($E_g$ is the forbidden-band width) [6]. Consequently, spatial separation should occur with a very high probability. It is therefore assumed [7] that the separation occurs via a chain of successive substitutional collisions, which can provide a high probability of separation over a certain distance, with the process terminating in activated motion of an $H$ center with a reduced activation energy [8, 9]. However, such collisions cannot explain the spatial separation of the components in a Frenkel pair by more than 2–3 times the interatomic distance in $MgF_2$ [10]. Consequently, this cannot be the dominant separation mechanism.

We have examined spatial separation via thermally activated $H$-center movement; we examined the probability of annihilation of an $F–H$ pair when the $H$ center wanders randomly over the anion nodes, the controlling parameter being the number of jumps from node to node. The process is described by a Markov chain [11]. The annihilation probability $P_a$ for a wandering $H$ center and an $F$ center at the origin is calculated as the product of the vector for the probability of the initial distribution and the transition-probability matrix raised to the power $n$, where $n$ is the number of jumps.

States differing only by permutation of the moduli of the node coordinates are combined into grouped states, since they do not differ in the set of transition probabilities. States corresponding to the conditions

$$|x| \geq \frac{n + |x_0| + 1}{2}, \quad |y| \geq \frac{n + |y_0| + 1}{2}, \quad |z| \geq \frac{n + |z_0| + 1}{2},$$

$$|x| + |y| + |z| \geq n + 1 + \frac{|x_0| + |y_0| + |z_0|}{2},$$

are taken as absorbing states, since the particle starting from a node with coordinates $(x_0, y_0, z_0)$ cannot reach the origin via node $(x, y, z)$ in $n$ steps. The probability $P_{ij}$ of transition from some state $i$ to any of

the adjacent $l$ states is clearly a function of the interaction energy $E(r)$ for the components of a primary pair. Then the probability of transition to some state $k$ is defined for thermally activated motion by

$$P_{ik} = \frac{\exp \{ [E(r_i) - E(r_k)] / 2kT \}}{\sum_{j=1}^{l} \exp \{ [E(r_j) - E(r_i)] / 2kT \}}$$

(3)

If $E(r) = 0$, the transitions to all $l$ states are equally probable ($l = 12$ for alkali halides). Also, $P_{ij}$ is the function of temperature if $E(r) \neq 0$.

A pair of F and H centers is produced in the primary decomposition of an electronic excitation [12,13]; $E(r)$ is dependent on the orientation of the H center with respect to the axis passing through the centers and the value may be positive or negative [14,15]. As the reorientation activation energy $E_r$ for an H center is less than the activation energy $E_a$ for motion of such a center [16,17], the mean value of the 12 possible $E_i(r)$ affects the probability of an H center passing from node $i$ to node $j$. It would appear that $E_i(r)_{av}$ is close to zero, and it seems certain that the $E(r)$ for F and H centers may differ substantially from the result of [14,15], since F and H centers produced in the hot state have reduced $E_a$ [8,18], evidently because the centers are in excited states. Therefore, the behavior of $E(r)_{av}$ is not as yet known, so we used functions of the form

$$E(r) = \alpha / r^m$$

(4)

where $\alpha$ and m are constants.

Figure 1 shows results for F–H pairs; $P_{ij} = 1/12$ if $E(r)$ is zero, and $P_a$ does not exceed 0.18 in 10 jumps even if the centers initially lie at adjacent nodes. Further, $P_a$ falls rapidly as the initial distance between the components increases. If the H center starts from nodes having coordinates (002) or (112), then $P_a$ after nine steps takes the values 0.084 and 0.055 respectively. The interaction between components has a marked effect on the separation; $P_a$ increases considerably if there is an attractive force between centers. The probability also increases for short distances as $m$ in (4) increases, i.e., the interaction becomes more rigid, but $P_a$ generally is larger if $m$ is small provided that the H center starts from a (220) node or a more distant one.

The temperature during the irradiation affects the probability of transition from state $i$ to adjacent states $j$ given by (3) if $E(r) \neq 0$; Fig. 2 shows $P_a$ as a function of temperature for various forms of interaction for $\alpha = -0.046$ [14] and $m$ of 1, 2, and 3. In all cases the annihilation probability shows a large negative temperature coefficient. The temperature dependence shifts to lower temperatures as the rigidity of the interaction increases. Figure 2 also shows the temperature dependence of the probability $P_b$ that the H center will pass outside a sphere of radius five times the interatomic distance around an F center in 10 steps.

![Fig. 1](image1.png)

**Fig. 1.** Annihilation probability $P_a$ as a function of number of jumps $n$ by an H center for $E(r)$ (eV) of: ●) 0; ✗) 0.046/r; ○) 0.046/r²; □) 0.046/r³. The initial coordinates of the H center with respect to the F center are shown in the figure, $T = 100\text{K}$.

![Fig. 2](image2.png)

**Fig. 2.** a) $P_a$ as a function of temperature for $n = 10$; b) separation probability $P_b$. The symbols are analogous to those of Fig. 1.