F-Center Formation in NaCl: Picosecond Spectroscopic Evidence for Halogen Diffusion on the Lowest Excitonic Potential Surface

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We have used picosecond white-light spectroscopy to study evolution of absorption in NaCl after pulsed band-gap excitation. Spectra at 80 and 300 K, initially very similar, subsequently develop features of well separated *F*-*H* pairs (300 K) or of self-trapped excitons (80 K). We interpret the spectra in terms of diffusion of the *H* center in the neighborhood of the complementary *F* center, corresponding to reversible interconversion on the lowest potential surface connecting the exciton and the *F*-*H* pair.

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In many simple halide crystals, the lattice itself is not stable upon creation of electron-hole pairs. The generation of permanent defects in alkali halides is a classic problem of radiation damage and of solid-state photochemistry, but the striking interplay between electronic and nuclear degrees of freedom is not completely understood. In the pictures proposed by Pooley and by Hersh, attention was correctly focused upon the self-trapped exciton (STE) as a progenitor of the *F* center.[1] Their considerations were based in part upon the anticorrelation in the temperature dependence of the yields of STE π luminescence and of *F* absorption in a group of crystals which give little *F* production at low temperatures. These include KI, RbI, NaBr, LiBr, NaCl, and LiCl.[2]

Studies[3-5] of the temporal development of absorption in KCl, KBr, and RbBr (crystals having significant *F*-*H* yields at low temperature) have ruled out the thermalized STE ground state ${}^3\Sigma_u^+$ as a precursor in low-temperature defect formation. Thus attention has focused on potential surfaces of the higher STE states.[6,7] Double-excitation experiments[8] have clearly demonstrated a role of such states as intermediates in prompt, low-temperature *F*-*H* pair formation. However, these experiments performed only at low temperature, have not illuminated the above anticorrelation of temperature-dependent yields.

It has been pointed out that the critical barriers and rates for thermally activated defect production must pertain to transport on the lowest STE potential sheet.[9] The occurrence of the backward reaction on this sheet is established by STE luminescence attending *F*-*H* recombination.[10] To explore the kinetics of these processes, we have acquired a series of early-time absorption spectra in NaCl, at temperatures below and above the onset of thermally activated *F*-center formation. Ultraviolet pulses (4.66 eV, 25 ps, 3 ± 1 mJ) were focused to a 2-mm-diam spot on a NaCl crystal. Through two-quantum absorption, electrons and holes were created throughout the 3-mm thickness of the crystal. A visible continuum was generated by focusing (1-m lens) 40% of the amplified 1064-nm beam into a 15-cm cell of D_2O:D_3PO_4 (1:1). Absorption spectra were acquired with a two-beam ratiometry system employing a digital vidicon polychromator. The uncertainty in the condition for coincidence between uv and probe pulses (at a central wavelength) is ±10 ps; relative delays are known accurately. From streak-camera records characterizing group-velocity dispersion, the relative delay between probe wavelengths corresponding to the peaks of STE and of *F*-band absorption was estimated to be 15 ps. We have previously determined that the rise time of absorption in NaCl at 532 nm is ≤ 5 ps at 15 K.[11]

Optical absorption spectra for NaCl at $T = 80$ K are presented in the left column of Fig. 1. Except for the top frame, these are averaged (5–22 shots) spectra for a sequence of delays of the probe pulse. The top left frame has been reproduced from Ref. 4; it displays a spectrum for NaCl at 9 K, recorded approximately 50 μs after excitation by a pulsed electron beam. This absorption, and the corresponding absorption in the current spectra,[12] are identified with the STE in its lowest triplet state, ${}^3\Sigma_u^+$. At 2.75 eV there is a small component identified with *F* centers. Corresponding spectra of transient and of residual absorption for $T = 300$ K are shown in the right column of Fig. 1. The top spectrum was recorded a few minutes after exposure to several uv pulses; it represents stable *F* centers.[12]

The spectra in Fig. 1 reveal, in addition to the mature STE and *F* components observed in the top

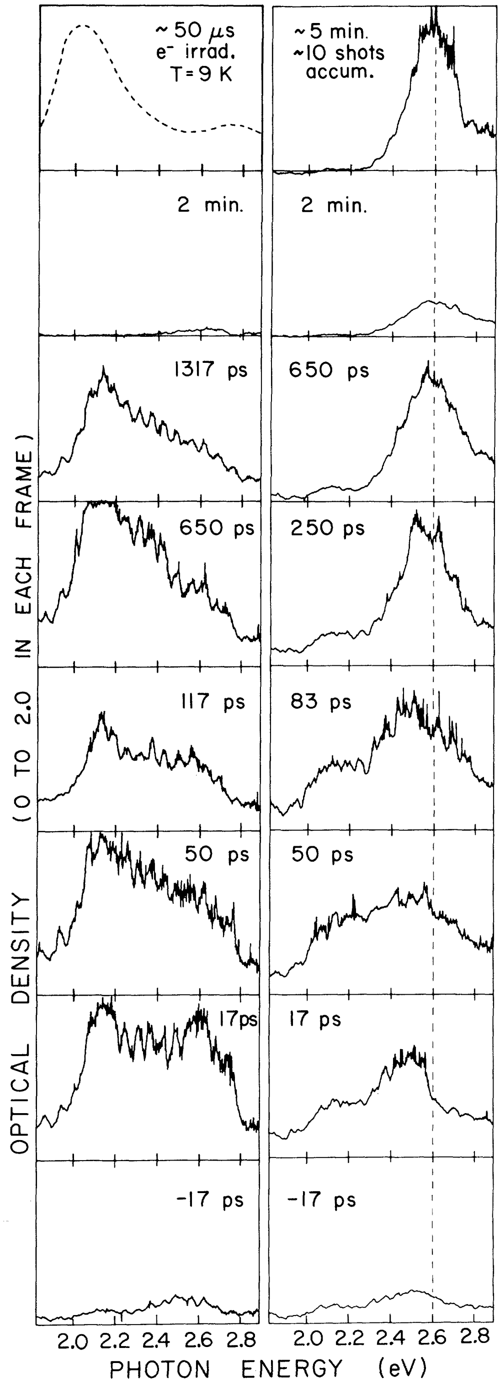

FIG. 1. Time series of absorption spectra for NaCl at 80 K (left) and 300 K (right); the probe pulse delay is given in each frame. The top left frame is taken from Ref. 4.

frames, early absorption at intermediate energy. Even at 80 K, well below the onset of efficient formation of stable F centers in NaCl, F-like absorption is very prominent in the early frames. The

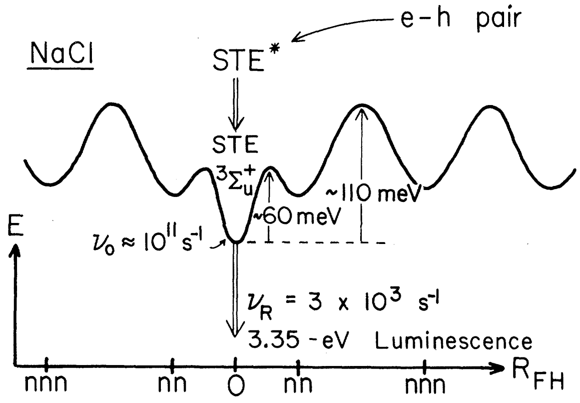

FIG. 2. Hypothetical section of the adiabatic potential surface connecting the configurations for the STE $^3\Sigma_u^+$ and for the F-H pair, along the generalized reaction coordinate R_{FH} describing separation of the defects. Creation of STE's at the origin results from band-gap excitation or from recombination of F and H defects. There is a lower potential curve (not shown) connecting F^+-H^- pairs with the crystal ground-state configuration reached in STE luminescence.

−17-ps frames (not acausal, in virtue of pulse overlap) are almost identical at the two temperatures. The spectra develop progressively into the STE for 80 K and into the F band for 300 K. The early F-like peak lies ~0.1 eV to the red of the ultimate F band.

To account qualitatively for these observations, we introduce a hypothesis developed in Ref. 9; see the model potential curve in Fig. 2. The relaxation coordinates are discussed in Kabler and Williams.[13] The curve represents a portion of the adiabatic potential surface connecting the $^3\Sigma_u^+$ STE with the nearest-neighbor (nn) and next-nearest-neighbor (nnn) F-H pair configurations. The central minimum, at $R_{FH}=0$, locates the STE. The hole associated with this STE resides on a bonded halogen-halide dimer Cl_2^-, there being no vacancy. The successive minima correspond to a vacancy and a displaced halogen atom forming F-H pairs in positions nn, nnn, etc. The coordinate R_{FH} represents migration of an H center relative to the F site as origin. This representation may be applied either to a linear [110] replacement sequence or to thermal diffusion as developed below.[14]

Given sufficient thermal energy, the system may transform reversibly and repeatedly among these configurations without leaving the single electronic potential sheet represented in the figure. We suggest that the STE nonradiative decay rates[15,16] are associated with the barriers between minima. Note that this hypothesis is distinct from the usual interpretation,[2,16] that thermal quenching of STE luminescence is due entirely to nonradiative transitions to the ground state of the crystal; we suggest that the latter channel is of secondary importance in NaCl. We hypothesize that the nonradiative rate which governs removal of STE and $FH_{\rm nn}$, and corresponding generation of F-H pairs, results from escape of the halogen atom over the nnn barrier. Further migration is favored over return to $R_{FH}=0$, by the rapidly increasing number of available interstitial sites with increasing R_{FH}. In Fig. 2, the radiative decay rate of the STE is $\nu_R = 3\times 10^3$ s^{-1}.[17] The nonradiative rate is given approximately by $\nu_{\rm NR} = \nu_0 \exp(-E_2/kT)$, where $\nu_0 \cong 1\times 10^{11}$ s^{-1} and $E_2 \cong 110$ meV. These values for ν_0 and E_2 are averages of determinations[15,16] from thermal quenching of STE luminescence. The barrier E_1 was not determined.

We suggest that the short-lived absorption intermediate between the STE and F bands, $\cong 2.3$ to 2.5 eV, is in some manner associated with nn minima. For sufficiently low lattice temperature and little local vibrational excitation, the system could actually be confined for a significant period to such minima.[18,19] With substantial vibrational excitation, however, the motion (possibly aperiodic) may include the central and some nn minima together. To estimate a statistical weight for the $FH_{\rm nn}$ band, we consider the full set of $FH_{\rm nn}$ configurations in which the F vacancy is fixed on one of the two "primary" (STE) halide sites. These must be equivalent in regard to energy minimum (but not activation energy) and spectrum (but not polarization). We find 24: two configurations in which the H defect is centered on the other primary site; eight in which the H is centered on one of four halide sites near each primary site (related by a rotation); and fourteen more remote configurations.

It is striking that even the 80-K spectra suggest a transiently "hot" system. As the STE relaxes from higher states at $R_{FH}=0$, the last nonradiative transition within the triplet manifold traverses 2.1 eV. Thus the nascent $^3\Sigma_u^+$ STE may carry some energy $E_{\rm ex}$ well in excess of its value for equilibrium with the lattice; it may remain hot briefly. If $E_{\rm ex} > E_1$, the occupation probability may be essentially equal for the central minimum and for any one of the $n_a = 2$, 10, or 24 accessible nn minima. The oscillator strengths are similar ($\cong 1$) for the STE band, the F band, and probably the F-like band. Thus in the initial spectra, prior to any relaxation, F-like absorption could be favored over the STE by a factor as large as n_a. In fact in the earliest spectra (-17 ps) at both temperatures, F-like absorption is favored over STE absorption by a factor of 2 or 3. For each of the 50-ps frames, we may presume that the STE has equilibrated with the lattice. For 300 K the F-like and the STE bands have roughly equal strengths at 50 ps. If we assume $n_a = 10$, then the data are accommodated by $E_1 \cong 60$ meV.

In late-term development at 80 K, the population accumulates at $R_{FH}=0$, subject to radiative decay as an STE. At 300 K the $R_{FH}=0$ and nn populations are together depleted by escape over the barrier E_2, and we observe the normal F band growing in at the expense of the more localized components. The room-temperature STE lifetime apparent in Fig. 1 corresponds satisfactorily to

$$\nu_{\rm NR}^{-1} = \nu_0^{-1}\exp(E_2/kT) = 815\ \text{ps},$$

with the parameters taken from the literature as described above. While the STE-FH potential curve is only schematic, the model provides a reasonable account for the temporal development of the several spectra features.

In summary, these data reaffirm the role of the lowest excitonic potential surface in primary defect production in NaCl and, by generalization, in other crystals lacking an efficient low-temperature channel. Defect production follows promotion to a potential sheet on which the barriers to halogen diffusion are small. Clearly, the thermally activated process may occur in parallel with production directly from higher STE states, in crystals such as KCl and KBr.[9]

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