Study of F-Center Formation in KCl on a Picosecond Time Scale

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We have measured the growth of *F*-band absorption at 532 nm in pure KCl following two-quantum band-gap excitation by a 266-nm pulse. The rise time at $T \approx 25$ K is 11 ± 9 psec. Spectral measurements confirm attribution of the early absorption to *F* centers. This absorption reflects the generation of new Frenkel defects with the *F* center created directly in its electronic ground state.

An important nonradiative decay mode available to excitons in alkali halides is the creation of Frenkel defects. The process is analogous to rearrangement reactions found in the photochemistry of molecules. The initial electronic excitation may be imparted by uv radiation, x rays, or energetic charged particles. In the present experiment, two-quantum band-gap excitation is employed. Readily available flux levels suffice, and this method affords an advantage in avoiding the small penetration depth of single-quantum absorption. The coloration is an interesting solid-state photochemical reaction to be studied with techniques of picosecond spectroscopy.

Time-resolved studies using electron pulse excitation have implied that Frenkel defects are formed principally as F and H centers (as opposed to the alternative charge state: halide ion vacancies without trapped electrons, and interstitial halide ions), and that in some alkali halides they are formed, on a transient basis, with much higher probability than had been surmised earlier from the stable defect populations.^{1,2}

An upper limit was found for the *F*-center formation time in KCl and in KBr, comparable to the 3-nsec minimum electron-pulse width available.^{1,3} This limit served to rule out the lowest triplet of the self-trapped exciton (STE) as the principal defect-forming level, and in the case of KBr it provided some evidence against the involvement of the radiative singlet. In view of these results, several recently proposed mechanisms⁴⁻⁶ for Frenkel-defect production in alkali halides have focused attention on higher states of the STE as precursors of the lattice defects. Nonradiative processes passing through such states are expected to take place on a subnanosecond time scale.

In the experimental apparatus (Fig. 1), a modelocked Nd:YAlG (yttrium aluminum garnet) oscillator and single-pulse switch provide a $1.064-\mu$ m pulse in the TEM₀₀ mode. A typical pulse has an

energy of 1 mJ, which has proved to be sufficient for most of our experiments. An amplifier is available for additional gain up to a factor of 10. The second harmonic (532 nm) and the fourth harmonic (266 nm) are generated in deuterated potassium dihydrogen phosphate (KD*P) and ammonium dihydrogen phosphate (ADP) crystals, respectively, with efficiencies of about 40% and 8%relative to the 1.064- μ m fundamental. Following the dispersing prism, the ultraviolet pulse (labeled UV) is sent along a fixed delay path. The green pulse is attenuated by F1 before being directed down a variable optical delay line comprising partial reflectors R1, R2, and R3. Three green-pulse replicas (G1, G2, G3) are generated and subsequently are directed collinearly with the pulse UV. Using the chromatic focus of a fused-silica lens, a small (~30 μm diam) green interrogation spot is centered within a larger area (~ 60 μ m diam) of coloration damage by the uv radiation. Filter F2 intercepts

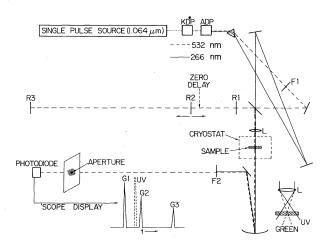


FIG. 1. Apparatus for measurement on a picosecond time scale of absorption at 532 nm following excitation at 266 nm. With the 532-nm beam focused in a benzene cell (replacing F1), stimulated Raman scattering allows measurements at three other wavelengths. any uv radiation which penetrates the crystal. An enlarged (\times 50) image of the first surface of the crystal is formed in the plane of a viewing screen with an aperture stop which passes only green light well within the region of coloration. The sample is translated between successive uv exposures to provide a part of the crystal having no prior damage. Finally, the green interrogation pulses are recorded with a fast vacuum photodiode and a Tektronix 7904 oscilloscope.

In the presentation of our data (Fig. 2), "pulse delay" refers to the time interval Δ from the damaging pulse UV to the interrogation pulse G2, measured between their centers. Pulse G1, arriving at the crystal prior to UV, affords a record of the probe energy incident on the crystal, and G3 records the defect population for a particular pulse UV as assessed at 10-nsec delay. In Fig. 2, D_2/D_3 refers to the ratio of the optical density computed from pulses G2 and G1 to that computed from G3 and G1. Mirror R2 is provided with a translation device to enable variation of the delay of G2. The setting for coincident arrival of UV and G2 at the sample ($\Delta = 0$) is determined by caliper measurements of length and from the calculated group velocities in optical components⁷; the net uncertainty for this position corresponds to about 7 psec.

The rise time of D_2/D_3 in Fig. 2 includes a substantial contribution from the nonzero pulse widths. We have developed integral expressions for D_2/D_3 as a function of the interrogation pulse delay Δ , the density D_3 at 10 nsec, the maximal density ηD_3 (η a parameter ≥ 1), pulse-width parameters, and a measure τ of the intrinsic rise time on some model for the coloration process itself. We write

$$D_2/D_3 = a^{-1} \ln \int_{-\infty}^{\infty} dt G(t) \exp[-\eta a F(t)]$$

Here $a = 2.303D_3$, G(t) represents the green pulse, and F(t) describes the fraction of the peak density ηD_3 which has developed by time t. F(t) is given by

$$F(t) = \int_{-\infty}^{t} dt' \,\mathfrak{F}(t-t')C(t'+\Delta),$$

where $\mathfrak{F}(t-t')$ describes the intrinsic coloration process and $C(t'+\Delta)$ represents the generation of carriers. For the present analysis G and C are taken to be normalized Gaussians.⁷ For $\mathfrak{F}(t-t')$ we have considered the exponential form $1 - \exp[-(t-t')/\tau_e]$, and also a step function. In either case an analytic approximation for the error function is useful.

The curve in Fig. 2 is a two-parameter variational best fit with the exponential form for \mathcal{F} ,

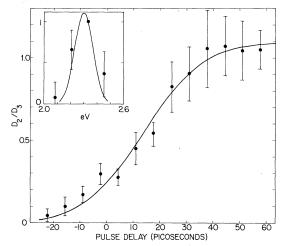


FIG. 2. For KCl at $T \approx 25$ K, we plot fractional optical density (D_2/D_3) at 532 nm versus delay after the 266nm pulse. The density D_3 is measured at 10 nsec. The curve is a best-fit convolution of pulse shapes with an exponential form for defect production, yielding $\tau \approx 11$ psec. Error bars denote ± 1 standard deviation about the mean. Inset: A four-point absorption spectrum measured about 85 psec after uv excitation; the curve is the normal F band at 25 K.

yielding $\tau_e = 11$ psec and $\eta = 1.10$; the standard error is $\sigma = 0.05$. The pulse widths (full width at half-maximum, FWHM) employed were $W_{c} = 32$ ± 7 psec, from measurements with an Electro-Photonics streak camera, and $W_{\rm c} = 18.5 \text{ psec.}^7$ In the part of the growth curve in which the defect population changes significantly within a pulse width, the shape retains some dependence upon the maximal density and so upon D_3 . The plotted curve employs $D_3 = 0.74$, the average from our useful data. Within the useful range 0.05 $\leq D_3 \leq 1.5$, the curves obtained do not depart from this curve by more than 0.1, or 2σ . Variation of W_{c} produces little improvement of fit. Similar results are found for the step-function choice of F. Considering the uncertainty in the curve fitting in addition to that in determination of the position of R2 for $\Delta = 0$, we attach an overall uncertainty of 9 psec to the rise time τ .

In our experiment, a fraction 5×10^{-5} of the 532nm energy reaches the sample. In the absence of the $\times 10^{-2}$ attenuator (F1 in Fig. 1), definite effects of saturation are evident. There may be residual effects of this kind even with F1 in place. The value $\eta - 1 = 0.10$ is believed to be an indication of depletion of the ground-state *F*-center population by the pulse G2, but in principle it encompasses annealing effects as well.

The decay of absorption is not monitored be-

yond 10 nsec. Low-temperature decay characteristics at later times are probably similar to those observed after electron-pulse excitation.^{2,8} In that work there was found nonexponential decay with principal components having $\tau \leq 20 \ \mu$ sec, leaving a stable *F* band $\approx 10\%$ of the peak.² Less detailed measurements performed with the sample at room temperature yield a growth curve very similar to that observed at low temperature, but the absorption decays to about 50% of its peak value within 8 nsec. The decay is attributed to pairwise annealing of *F* and *H* centers.

We have made a comparison of the spectral profile of early absorption with the normal Fband, using, in addition to the 532-nm second harmonic, three other wavelengths derived by stimulated Raman scattering in benzene (inset. Fig. 2). Interrogation at 532 nm was performed 70 psec after the uv pulse. The Raman-shifted pulses may be delayed an additional 30 psec, but the absorption has little time dependence for Δ >40 psec. We have plotted the absorption at each Raman wavelength relative to that at 532 nm. The solid curve is a Gaussian with FWHM and peak appropriate to the KC1 F band at 25 K, the estimated local temperature (see below). The fit is sufficiently close to identify the absorption with F centers. Laser pulse heating cannot account for the evident broadening, since a temperature of about 110 K would be required. The broadening may well be due to perturbing effects of H centers very near some of the F centers, in the population of transient pairs. In the electronpulse experiments, there was found a background absorption due to self-trapped excitons.²

Coloration-depth profiles produced in a thick crystal by pulses of varying power are consistent with absorption of uv energy by a two-quantum process. Transmission measurements show that about 30% of the incident uv pulse energy is deposited in our 0.8-mm-thick sample. In the first 0.4 mm of the sample, where the coloration is most dense, an energy density of approximately 1 J/cm^3 is deposited in a typical shot. For an equilibrium sample temperature of 10 K, we estimate that the local temperature rises only to about 25 K. Because of divergence of the focused beam as well as pulse depletion, the profile of coloration versus depth is nonuniform. The average *F*-center density produced in the first 0.4 mm of the sample in our low-temperature work is estimated⁹ to be 10^{17} cm⁻³, and a similar optical density at room temperature required about 2×10^{17} cm⁻³.

We have characterized the ambient vacancy concentration in our pure KCl¹⁰ by studying the first coloration stage under room-temperature x irradiation, following Mitchell, Wiegand, and Smoluchowski.¹¹ The first stage saturates at about 1.8 $\times 10^{16}$ cm⁻³. Furthermore, at low temperature it has been demonstrated that *F* centers formed by charge transfer to vacancies must pass through the first excited state, delaying the 532-nm ground-state absorption by the 0.6- μ sec excitedstate lifetime.¹² Thus the absorption observed in the present experiment reflects the creation of new lattice defects rather than the transfer of electrons onto preexisting vacancies.

Our results make possible determination of the efficiency for production of Frenkel defects by recombination of electrons and holes in KC1. For two-quantum absorption, approximately 60 eV of energy deposition is required per F center formed (at either temperature); i.e., about 15% of electron-hole recombinations lead to creation of a Frenkel defect. This agrees with a value 17% (± 8% uncertainty on each efficiency) based on electron-pulse studies of coloration,^{2,5} using an estimate of 25 eV required per carrier pair created by energetic electrons.¹³ Still higher efficiency can be inferred for KBr.^{1,2,5}

In conclusion, within about 11 psec after excitation the system relaxes by carrier thermalization through ~ 0.8 eV, and by exciton formation and nonradiative transitions through ~1 eV, culminating with ejection of Cl^0 to form an *F* center in its ground state. There is little time for relaxation across large electronic gaps. Since the first four levels of the self-trapped exciton are separated typically by more than five phonons, this suggests that halide motion leading to defect formation starts from fairly high-lying electronic levels of the STE. On the other hand, a certain compactness of the electron orbital is required in the most recently proposed mechanisms.⁴⁻⁶ The electron is viewed as settling into the developing vacancy, providing stabilization as the Cl₂⁻ molecular ion translates as a unit along a [110] direction. More than one STE state may have the requisite symmetry and compactness to initiate this odd-parity relaxation. It is likely that the intermediate states of the system are not well described in the adiabatic approximation.

We wish to thank M. N. Kabler for useful conversations.

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from caliper measurements. Also it contributes to the pulse widths for UV and for carrier generation. In our analysis with Gaussian line shapes, we have taken $W_{UV} = (\frac{1}{2}W_G^2 + 13^2)^{1/2}$, and $W_C = 2^{-1/2}W_{UV}$. ⁸Y. Kondo, M. Hirai, T. Yoshinari, and M. Ueta, J.

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Effect of Transverse Magnetic Fields on dc Josephson Current*

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We have observed diffraction patterns in critical dc Josephson tunnel current versus magnetic field applied perpendicular to the junction plane. The patterns can be explained by assuming that the perpendicular field penetrates the edge of each film and channels through the junction parallel to the films. An "edge penetration depth," λ_{\perp} , gives a quantitative description of the patterns and their dependence on the angle of field direction. We have found $\lambda_{\perp}(T) \propto (1 - T/T_c)^{-1/2}$.

If a magnetic field is applied parallel to the plane of a Josephson tunnel junction, the zerovoltage critical current (I_c) as a function of magnetic field (H) will exhibit a diffractionlike pattern.^{1,2} Existing theory²⁻⁴ shows that I_c is given by

$$I_{c} = I_{J} \left| \frac{\sin(\pi H L d / \Phi_{0})}{\pi H L d / \Phi_{0}} \right| , \qquad (1)$$

where I_{I} is the Josephson zero-voltage critical current in zero magnetic field, L is the dimension of the junction perpendicular to H, $d = 2\lambda_{\parallel}$ $+ l \approx 2\lambda_{\parallel}$ with λ_{\parallel} the surface penetration depth and l the oxide thickness, and Φ_0 is the magnetic flux quantum equal to 2×10^{-7} G cm². The critical current goes to zero whenever the junction contains an integral number of flux quanta, i.e., for the *n*th zero the magnetic field satisfies

$$H_n = n\Phi_0/Ld$$
, $n = 1, 2, ...$ (2)

According to this theory, if the magnetic field is applied at an angle θ with respect to the plane of

the junction (see inset of Fig. 1) the magnetic field necessary to produce the nth minimum of

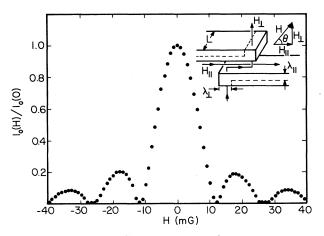


FIG. 1. Typical diffraction pattern for $\theta = 90^{\circ}$ at T =2.50 K. Junction dimensions are 0.74 mm \times 0.35 mm. The inset shows the magnetic-field orientation relative to the junction.