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High-pressure optical studies of doped alkali halides. III. Rates of electron-transfer processes*

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High-pressure studies have been made on the rates of photoinduced electron-transfer processes in NaCl:In. Continuous irradiation in the C band ($^1S_0 \rightarrow {}^1P_1$) of the impurity gives a luminescence which changes (generally decreases) with time, and ultimately reaches a steady state. At the same time absorptions appear which are assigned to In^{++} and to an F center (also, under some conditions a peak assigned to In^0 may appear). The process involves competition between, on the one hand, ionization of the $^1P_1$ electron (initial trap depth ~ 0.1 eV) and trapping at the F center, and, on the other hand, the release of an electron from the F center by absorbing In^+ emission. The processes are characterized by the rate coefficients k_i and k_r. k_i decreases with pressure—probably owing to an increase in the depth of the $^1P_1$ state below the conduction band. k_r exhibits a maximum at $\sim$ 25–30 kbar. This is associated with the overlap of the In^+ emission and F-center absorption which at first increases and then decreases with pressure, as well as with the increased trapping ability of the $^1P_1$ state of the indium ion. Irradiating the sample in the In^{++} absorption band gives a luminescence which decreases rapidly in intensity with time, since this luminescence overlaps the F-band absorption in energy and bleaches it. The rate of bleaching decreases rapidly with increasing pressure since the overlap decreases.

The effect of pressure on the kinetics of photoinduced electron-transfer processes including photostimulated luminescence (PSL) has been measured for NaCl: In. A few observations for NaBr: In are also included. The experimental setup was the same as that previously described[1] except that the luminescent intensities as a function of time were recorded using a Houston Instrument Corp. "OmniScribe" Recorder.

There is a considerable literature concerning photostimulated luminescence.[2–6] Except for the work of Okamoto and Scott,[7] who treat F-center optical bleaching rates, the discussions are largely qualitative.

The processes involved in impurity-doped alkali halides can best be described in terms of Fig. 1. In discussing the processes qualitatively the numbers shown in parentheses indicate the location of the relevant absorption or emission in NaCl: In at or near 1-atm pressure.

NaCl: In exhibits an absorption (313 nm) and emission (415 nm) which correspond to the excitation $^1S_0 \rightarrow {}^3P_1$. This so-called A-peak absorption and emission does not directly involve any electron-transfer processes. There is a higher-energy absorption (250 nm) called the C peak which corresponds to the excitation $^1S_0 \rightarrow {}^1P_1$. This results in the same emission as does excitation in the A peak. There is an intersystem crossing which takes place more rapidly than emission from the $^1P_1$ state.

For the systems of interest here, there is a change with time in the intensity of the emission when the excitation is in the C peak. In general, a decrease is observed, although the intensity may increase (see the section on kinetics). Ultimately a steady state is reached. Both the steady-state intensity and the rate at which it is reached are strong functions of pressure. We describe at this point the process as if it involves a decrease in intensity with time since it is the one most thoroughly studied here. As we show later the process involving an increase is not fundamentally different except for the initial condition. The excited ($^1P_1$) state lies ~0.1 eV below the conduction band at[8] 1 atm (ΔE_{CC} in Fig. 1). The decrease in intensity corresponds to the photothermal ionization of the In^+ electron which is then trapped at another In^+ to form an In^{++} plus an In^0 or at a vacancy to form In^{++} plus an F center. In the study discussed here, where the crystals undergo some plastic deformation under the quasihydrostatic pressure, the major traps are vacancies, so we consider a system consisting of

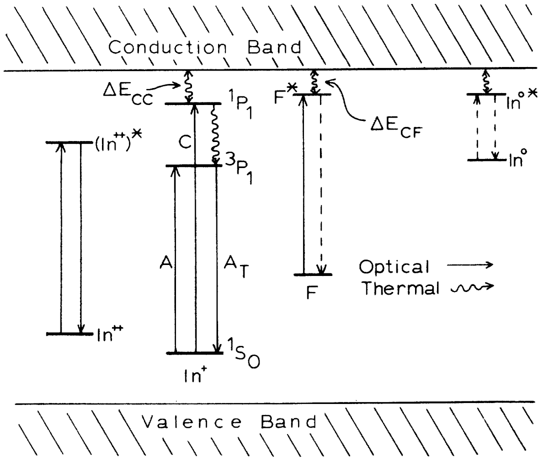

FIG. 1. Schematic diagram for electron-transfer processes in NaCl: In.

In^+, In^{++}, and F centers. The electron trapped in the F center can be excited by the In^+ emission, as discussed below, and can escape from the F^* state to the conduction band ($\Delta E_{CF} \cong 0.07$ eV[8]), from which it can be retrapped by an In^{++} center. It is the balance between this creation and destruction of F centers which gives the steady-state emission mentioned above.

The In^{++} has an absorption near that of the In^+ and an emission at ~500 nm. The In^{++} emission bleaches rapidly with time upon irradiation in the In^{++} absorption band. The In^{++} emission is much more intense than the In^+ emission even though there may be relatively few In^{++} centers because it involves an allowed transition, while the In^+ emission ($^3P_1 \rightarrow {}^1S_0$) is spin forbidden. The bleaching process involves the excitation ($F \rightarrow F^*$) of an electron by the In^{++} emission, its escape from the F^* state to the conduction band, and its retrapping by an In^{++} center. The details are discussed below. The photostimulated luminescence process consists of release of the electron from the F center, its retrapping by In^{++} to form $(In^+)^*$ and the subsequent emission of radiation from $(In^+)^*$ at an energy higher than that of the F-center absorption.

KINETICS

In this section, models are developed which can be used to describe the time dependence of the measured emission intensities. From these models, equations are derived to represent the intensity changes with time, and various rate coefficients can be deduced. The intensity changes of interest here occur on time scales of seconds and minutes, while the individual emission lifetimes are on the order of microseconds.

First, the irradiation process is described. During irradiation in the C-absorption band, In^+ emission occurs, as well as In^+ ionization to In^{++}. The latter process reduces the number of In^+ centers; therefore, the In^+ characteristic emission decreases with time. The intensity of this emission, then, serves as a probe of the number of In^+ centers in the sample at a given time.

The primary simplifying assumptions made at this point are (i) that the predominant electron traps are anion vacancies, forming F centers, and (ii) that the number of vacancies available for F-center formation is independent of and large compared to the number of In^+ centers. These assumptions imply that In^0 centers play only a minor role in the PSL process investigated at high pressure and room temperature. The number of In^+ centers per unit volume at time t is denoted $n_+(t)$, while $n_{++}(t)$ is the concentration of In^{++} centers at time t.

The total concentration of In impurities, n^0, is constant. It is assumed that at $t=0$, all impurities are monovalently charged, so that $n_{++}(0) = 0$.

There are two opposing factors which cause changes in $n_+(t)$. Ionization of In^+ to In^{++} decreases n_+, releasing electrons to be trapped by anion vacancies, forming F centers. This process is described by a first-order rate process, with positive rate coefficient k_i. The coefficient k_i denotes not only the ionization process, but any additional process which, on the time scale of minutes, causes the released electron to remain trapped by the anion vacancy. An increase in $n_+(t)$ is caused by recombination between released electrons and In^{++} centers. Since the number of released electrons is equal to the number of In^{++} centers, the recombination rate is proportional to the square of $n_{++}(t)$, with positive rate coefficient k_r. The differential equation describing both processes is written

$$\frac{dn_+}{dt} = -k_i n_+ + k_r n_{++}^2. \tag{1}$$

Physical considerations require that $n_+(t)$ decrease with time; all In centers are monovalently charged at $t=0$, so that n_+ cannot increase with time initially. The solution to (1) gives

$$n_+(t) = b - \left(\frac{c}{a}\right)^{1/2} \tanh[(ac)^{1/2}(t+d)], \tag{2}$$

where

$$d = \frac{1}{(ac)^{1/2}} \tanh^{-1}\left[\left(\frac{a}{c}\right)^{1/2}(b-n^0)\right], \tag{3}$$

such that $n_+(0)=n^0$, and a, b, and c are appropriate combinations of n^0, k_i, and k_r. The steady-state value of $n_+(t)$ reached at long times is dependent on n^0, k_i, and k_r. Physically, this steady-state value represents an equilibrium between the competing processes denoted by k_i and k_r.

Fitting (2) to experimental data involves a three-parameter fit, using either k_i, k_r, and n^0, or a, b, and c as the parameters. Initial guesses for these parameters can be obtained from the experimental quantities $n_+(0)$, $(dn_+/dt)_0$, and $n_+(\infty)$.

As is always the case with a bimolecular process, the rate coefficient k_r is dependent upon the initial value n^0. Dimensional analysis of (1) shows that the true rate coefficient, with units $(\text{time})^{-1}$, is $k_r n^0$. Experimentally, k_r depends on the observed intensity, which depends on amplifier gain and scaling factors, while $k_r n^0$ does not. Further, it must be recalled that photochemical reactions proceed at rates determined by the incident photon flux, since the number of reactants is proportional to the number of available atoms (or molecules) which react and to the number of photons available for absorption. Therefore, the rate coefficients k_x in this study have an intrinsic dependence on incident light intensity; this dependence is simply absorbed in the k_x. To compare magnitudes of the coefficients, one must compare processes with equivalent photon fluxes.

If the initial conditions are changed appropriately, a solution may be found which allows $n_+(t)$ to increase with time. For this to occur, a substantial number of In$^+$ centers must be ionized to In^{++} at "$t=0$", that is, after the irradiation begins but at a time short compared to the experimental measurement time scale of seconds. This initial condition is conveniently described in terms of the parameter $\beta = n_{++}(0)/n_+(0)$. The resulting solution for $n_+(t)$ has a functional form similar to Eq. (2), except that $n_+(t)$ increases with time.

The bleaching process involves the reduction of In^{++} centers by releasing electrons from traps and retrapping at In^{++} sites, forming In$^+$ centers. Since the number of electrons available for recombination is equal to the number of In^{++} centers, the rate of decay of $n_{++}(t)$ depends on the square of $n_{++}(t)$, yielding a bimolecular decay process for $n_{++}(t)$. The solution is

$$n_{++}(t) = 1/k_b(t+\tau), \tag{4}$$

a hyperbolic function. Again, it should be noted that k_b is not a true rate coefficient, as it does not have the correct units, and it does depend on the (experimentally determined) height of some emission signal. The true rate coefficient here is $\tau^{-1} = k_b n_{++}(0)$, which, again, is intrinsically dependent on the bleaching light intensity.

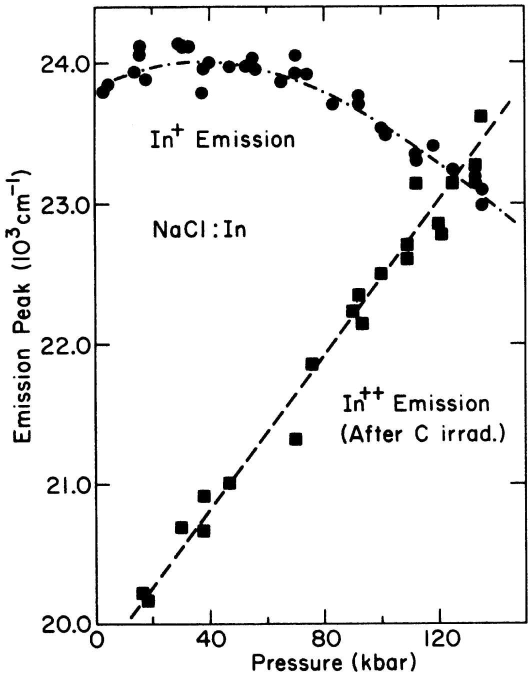

FIG. 2. Shifts of In$^+$ and In^{++} emission peaks with pressure.

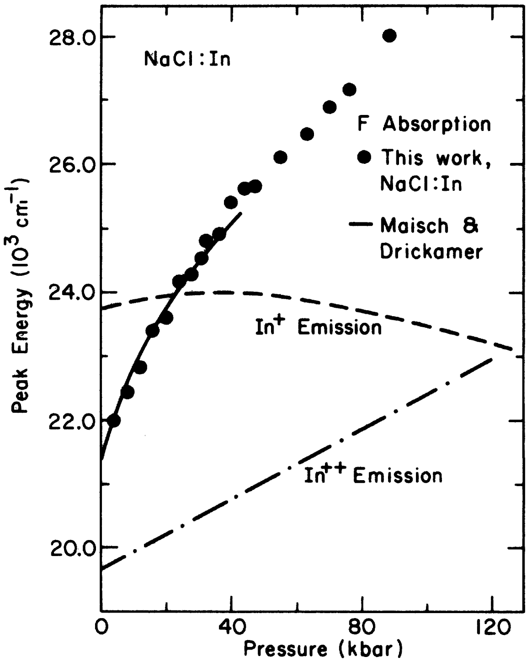

FIG. 3. Shift of F-center absorption peak with pressure, and overlap with In$^+$ and In^{++} emission.

RESULTS

In Fig. 2 we show the shifts of the In$^+$ emission and In^{++} emission with pressure. Figure 3 exhibits the shift of the F-center absorption peak. The solid line represents the data of Maisch and Drickamer[9] with the pressure reduced by 12% to correspond to modern calibration. Using these peak locations and the measured half-widths one can calculate overlap of the In$^+$ and In^{++} emissions with the F-center absorption. These results are of use in our discussion below.

Figures 4-6 exhibit the relative values of the rate coefficients for ionization (k_i), recombination (k_r), and bleaching (k_b or τ^{-1}) normalized to the value at 8 kbars. The scatter reflects (i) the difficulty in fitting the intensity-vs-time curves, especially for k_i and k_r where three parameters must be evaluated; (ii) the possibility that in various samples more or fewer electrons were trapped at In$^+$ sites; and (iii) the difficulty in maintaining a fixed light flux at the sample in these, our first experiments on electron-transfer rates at high pressure. The trends are, however, quite clear. (Note that the relative rate coefficients are plotted on a logarithmic scale).

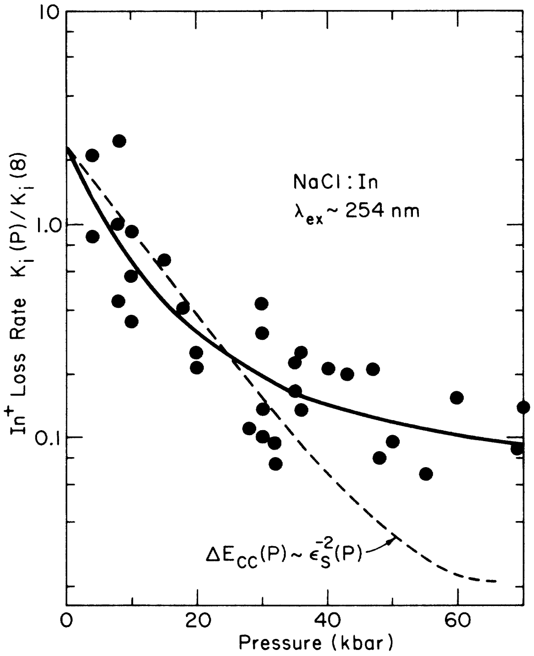

FIG. 4. $k_i/k_i(8)$ vs pressure (k_i is the In$^+$ loss rate coefficient).

Thermal effects were observed to affect negligibly the irradiation and bleaching data. That is, blocking the incident radiation in either process for long times caused no observable change in the emission signal upon restarting the radiation.

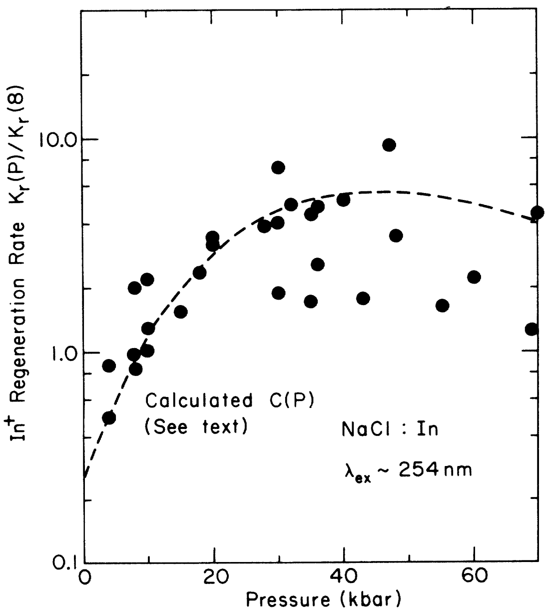

FIG. 5. $k_r/k_r(8)$ vs pressure (k_r is the In$^+$ regeneration rate coefficient).

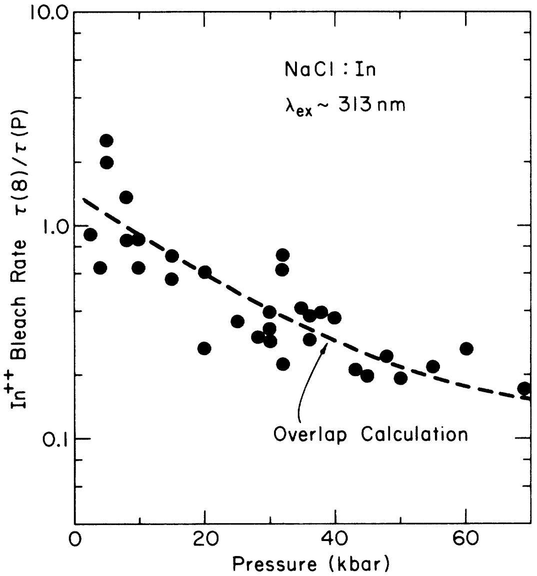

FIG. 6. $k_b/k_b(8)$ or $\tau(8)/\tau$ vs pressure (k_b is the bleaching rate coefficient for In^{++}).

Application of purely hydrostatic pressure to 5 kbars in the liquid cell on samples pressed into pellets, and therefore somewhat plastically deformed, gave very similar relative changes for the rate coefficients to those shown in Figs. 4–6.

Unstressed NaCl: In crystals, as zero pressure to 5 kbars (hydrostatic), showed no change in In$^+$ emission during the irradiation process, but gave a measureable In^{++} peak, which bleached away during excitation in the A band. The electron traps in an unstressed crystal are probably due to small amounts of vacancies and In^0 centers. Since most In^0 traps are thermally quenched at room temperature, the number of In$^+$ ions actually remaining ionized (on the time scale of the measurement) is quite small; hence, no In$^+$ emission intensity reduction with time is observed. Owing to the strength of the In^{++} transitions, however, their emission (and subsequent bleaching) may be observed for even small amounts of In^{++} present.

DISCUSSION

NaCl : In

There are four parameters which establish the coefficients k_i, k_r, and k_b. These include the escape probabilities for an electron from the excited ($^1P_1$) state of In$^+$ and from the excited state of the F center, as well as overlaps of the In$^+$ emission with F-center absorption and of In^{++} emission with F-center absorption. If one assumes hydrogenic wave functions the trap depths will depend either on ϵ_s^{-2} or n^{-4}, where ϵ_s is the static dielectric constant and n the refractive index,[10-13] depending on whether or not the lattice polarization follows the motion of the excited electron.

A fit of Samara's data (to 12 kbar)[14,15] to a quadratic polynomial in the pressure allows one to extrapolate ϵ_s to higher pressures. Using the value for $\partial(\ln n^2)/\partial p = 1.56 \times 10^{-4}$ kbars^{-1} given by Wexler and Weir,[16] one can extrapolate to find n, the refractive index, vs pressure for NaCl. These results are given in Table I. From the data shown in Fig. 3, the overlap $D(F\text{-In}^+)$ between the F absorption and the In^+ emission can be found as a function of pressure; the In^{++} emission and F-absorption overlap $D(F\text{-In}^{++})$ can also be computed. These results are given in Table II. Values for the half-widths are 3700 cm^{-1} for the In^+ emission, 3800 cm^{-1} for the F band, and 4100 cm^{-1} for the In^{++} emission. These are essentially constant with pressure.

Let us consider first the bleaching process illustrated in Fig. 6. The process involves overlap of In^{++} with F absorption to excite the F electron, and the escaping tendency of the excited F electron. The dashed curve in Fig. 6 is calculated using the overlap data of Table II, and clearly fits the data within experimental error. This implies that the escaping tendency of the excited F electron varies little with pressure; i.e., that ΔE_{CF} varies as n^{-4} rather than ϵ_s^{-2} (see Table I).

The decrease in the coefficient k_i with increasing pressure (Fig. 4) could be caused by an increase in ΔE_{CC} or a decrease in ΔE_{CF}. The dashed curve in Fig. 4 is calculated from the assumption that $\Delta E_{CC} \sim \epsilon_s^{-2}$. Considering the gross extrapolation involved in getting high-pressure values of ϵ_s, the agreement is reasonable. A variation of ΔE_{CF} with ϵ_s^{-2} would give entirely the wrong trend, so again, it would appear that ΔE_{CF} depends on n^{-4}.

Two effects give rise to the observed pressure behavior of the relative rate coefficient k_r. First, as pressure increases, $\Delta E_{CC}(P)$ increases, and the C state more efficiently retains electrons which have recombined with In^{++}, thereby regenerating In^+. Second, the relevant optical transitions have changing overlaps, shown in Fig. 3 and Table II.

TABLE I. Pressure dependence of static dielectric constant ϵ_s and refractive index n.

P(kbars)	ϵ_s [a]	n^2 [b]
0	5.90	2.25
10	5.37	2.254
20	4.92	2.257
30	4.56	2.261
40	4.30	2.264
50	4.12	2.268
60	4.03	2.271
70	4.03	2.275

[a] Extrapolation from quadratic fit to Samara's data (Ref. 15).

[b] Extrapolation of Waxler and Weir's results (Ref. 16).

TABLE II. Pressure dependence of overlaps.

P (kbars)	$D(F\text{-In}^+)$	$D(F\text{-In}^{++})$
0	0.620	0.726
10	0.868	0.524
20	0.996	0.327
30	0.965	0.225
40	0.830	0.147
50	0.700	0.124
60	0.567	0.104
70	0.412	0.083

In^+–F-center overlap increases with pressure at low pressure, maximizes near 25 kbars and then decreases (see Table II). To obtain the most probable values of ΔE_{CC} as a function of pressure we assumed a 1-atm value of 0.1 eV and calculated the changes from the solid curve of Fig. 4, which is a least-squares fit to the $k_i(P)/k_i(8)$ data. The product of these two factors, appropriately scaled,

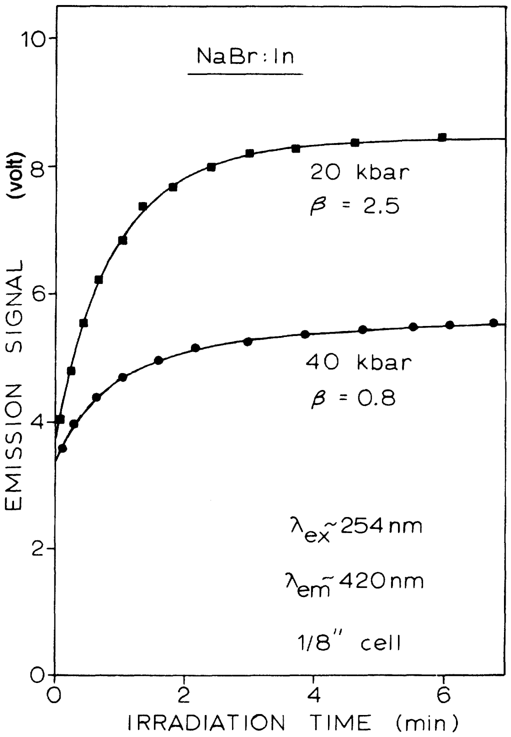

FIG. 7. Rate data for intensity of In^+ emission with time while irradiating in the C band for NaBr: In at 20 and 40 kbars. Solid curves are least-squares fit to data (see text).

is shown as the dotted curve in Fig. 5. It fits the data remarkably well.

NaBr : In

PSL was briefly investigated in NaBr : In. The overlap of the In^+ emission, In^{++} emission, and F-absorption bands was found to be qualitatively similar to that found using NaCl : In. During irradiation in the C band, however, the In^+ increased with time, as shown in Fig. 7. As discussed in a previous section, such a result is possible, given an "initial" concentration of In^{++} centers. The data in Fig. 7 were fit to an equation analogous to (2), but for n^+ increasing with time; the fits to the data are the curves of Fig. 7, along with the fit values of β.

The pressure dependence of k_i and $k_r n^0$ is qualitatively similar to the NaCl : In data: k_i decreases with increasing pressure, while k_r increases (to 40 kbars). With increasing pressure, β decreases as well, by roughly one order of magnitude in 40 kbars. This is entirely consistent with the results for k_i and k_r. As pressure increases, fewer centers remain ionized. Since $\beta = n_{++}(0)/n_+(0)$, the relative number of In^{++} centers ionized at "$t=0$" decreases with pressure as well.

For NaBr : In, it is evident that $\beta \neq 0$ at $t=0$. Visual observations indicated that, after very short C-band excitation of NaBr : In, the density of F centers may have been quite high, implying $\beta \neq 0$; absolute comparisons of the F concentrations in NaCl : In and NaBr : In were experimentally not possible.

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