

## Femtosecond spectroscopic studies of the lattice relaxation initiated by interacting electron-hole pairs under relaxation in alkali halides

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Femtosecond time-resolved spectroscopic studies have been carried out to reveal the relaxation of free electron-hole pairs in KBr. We find that a hole is relaxed to a self-trapped hole with a delay of 10 ps. Two relaxation channels of an electron-hole pair are found: one lasts for 40 ps and leads competitively to a self-trapped exciton (STE) or an  $F$ - $H$  pair; the other terminates within 6 ps, bypasses the STE, and leads to an  $F$ - $H$  pair. The former channel is ascribed to the interplay between an electron and a self-trapped hole, while the latter demonstrates the dynamic interplay of an electron and a hole during their lattice relaxation.

The lattice relaxation induced by fundamental electronic excitation of solids with strong electron-phonon coupling is a topic of basic interest in solid state physics.<sup>1,2</sup> Not only the self-trapping of charge carriers and excitons but also drastic lattice-structure modification is induced by the electronic excitation. The latter includes Frenkel-pair production in metal halides,<sup>1-5</sup> atomic desorption from solid surfaces,<sup>6</sup> structural change in amorphous solids,<sup>7</sup> and phase transformation in low-dimensional solids.<sup>8</sup>

In many systems with strong electron-phonon coupling, in which profound lattice rearrangement by electronic excitation is observed, it is known that these phenomena are the consequence of the relaxation not of individual charge carriers, but of the correlated relaxation of interacting carriers of opposite signs.<sup>1,2</sup> For example, in alkali halides on which the lattice relaxation process after electronic excitation has been studied extensively, the adiabatic potential energy surfaces (APES's) for a hole and for an exciton are known to be substantially different. A self-trapped hole (STH) takes only one stable relaxed configuration in the form of a  $X_2^-$  molecular ion ( $X$  denotes a halogen atom) having a  $D_{2h}$  symmetry, known as the  $V_K$  center,<sup>9</sup> indicating that there is only one minimum in the APES for a hole. In contrast to a hole, the APES for the lowest electronic state of an exciton has a few minima as shown experimentally<sup>10,11</sup> and theoretically.<sup>2,12</sup> Some of these minima are luminescent; these are often called types I, II, and III self-trapped excitons (STE's).<sup>10</sup> They are connected to nonluminescent minima which correspond to Frenkel pairs consisting of

an  $F$  center and an  $H$  center. The difference in the configurations for these minima has been attributed to the location of the  $X_2^-$  molecular ion with respect to the position of the trapped electron;<sup>10,13</sup> the Frenkel pairs are those in which the  $X_2^-$  molecular ion is displaced over at least a few lattice distances.

The difference between the structures of the APES's for a hole and for an exciton is a manifestation of the strong interplay between the electron-phonon and hole-phonon interactions. However, the present understanding of the consequences of the interplay has been limited to that of an electron and the hole which is completely relaxed into the STH configuration.<sup>1,2,14,15</sup> In this paper we show evidence for a dynamical interplay of an electron and a hole "under" relaxation, which leads to lattice relaxation specific to the interaction in alkali halides.

Specimens of a thickness of 3 mm of pure KBr were obtained from a crystal block from Harshaw Chemical Co. Those of  $\text{NO}_2^-$ -doped (0.1 mol %) KBr were grown by the Kyropoulos method in dry argon atmosphere. Use of the doped KBr was for differentiating the relaxation processes of electrons and holes and to reveal their interplay during the relaxation; relaxation of holes dominates in the doped specimen. 100-fs laser pulses, 605 nm in wavelength and 200  $\mu\text{J}$  in fluence, were generated by a laser system comprising a mode-locked  $\text{Ar}^+$ -ion laser, a synchronously pumped, cavity-dumped dye laser with Rhodamine 6G, a pulse compressor, and a four-stage amplifier with a Q-switched yttrium-aluminum-garnet laser. The laser beam, after frequency doubling, was used for generating  $e$ - $h$  pairs by two-photon absorption, and the

fundamental beam was employed for probing optical absorption, after being converted to a white-light beam in a D<sub>2</sub>O cell. The optical absorption spectra were obtained in the range 1.3–3 eV by analyzing the spectra of the source beam and of the light transmitting through the specimen.

First, in order to confirm that the electrons generated in KBr:NO<sub>2</sub><sup>-</sup> are trapped by NO<sub>2</sub><sup>-</sup> leaving holes in the crystal, we measured time-resolved optical absorption spectra after irradiation with a 20-ns electron pulse at 80 and 273 K. At both temperatures, the absorption spectra 100 ns after the irradiation showed only the  $V_K$  band in the doped KBr. On the other hand, the optical absorption bands due to the STE's (STE bands), as well as the  $F$  bands, were produced in pure KBr at 6 K and at 80 K, being characteristic in undoped specimens. Therefore, it is clear that the holes are relaxed without interacting with electrons in KBr:NO<sub>2</sub><sup>-</sup> specimens used in the present study.

Figure 1 compares the time-resolved optical absorption spectra for (a) KBr:NO<sub>2</sub><sup>-</sup> at 273 K and for (b) pure KBr at 80 K after irradiation with a femtosecond laser pulse. The delay of the probe pulse with respect to the excitation pulse is indicated at each panel. In the top panels are shown for comparison the STE band and  $F$  band in pure KBr and the  $V_K$  band in KBr:NO<sub>2</sub><sup>-</sup> generated by pulse-electron irradiation. The time-resolved spectra in both specimens before 1.6 ps are similar; only a broad band extending over the whole photon-energy range is observed. Hereafter we call this band the  $B$  band. How-

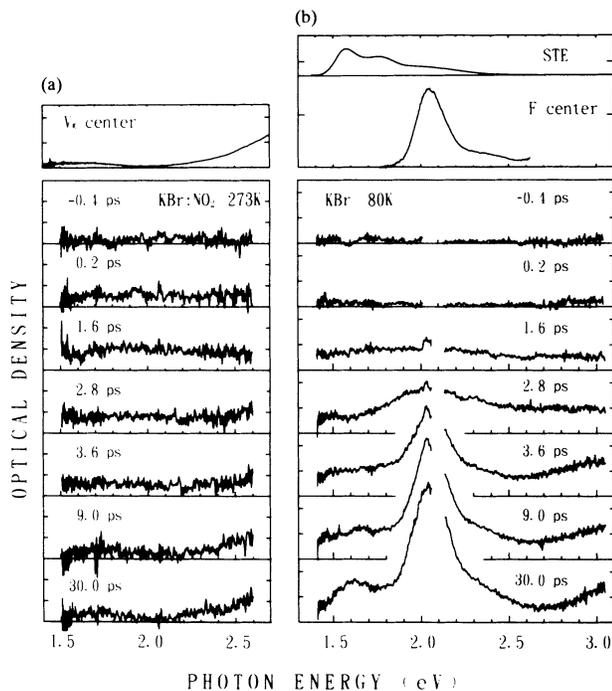


FIG. 1. Time series of optical absorption spectra for (a) KBr:NO<sub>2</sub><sup>-</sup> at 273 K, and for (b) pure KBr at 80 K; the probe pulse delay is given in each frame. The top frames of (a) and (b) show the  $V_K$  band measured at 273 K and the STE and  $F$  bands measured at 6 K, respectively.

ever, significant difference is evident in the spectra after 2.8 ps: The  $F$  band at 2.05 eV and the STE band at 1.6 eV are generated in pure KBr, while in KBr:NO<sub>2</sub><sup>-</sup> the  $B$  band converges, as time proceeds, to the  $V_K$  bands peaked at 1.7 and 3 eV. Only the tail of the 3 eV band is detected in the femtosecond spectroscopy, however,

In Figs. 2(a) and 2(b), we show the time evolution of the optical absorption measured at (a) 2.0 eV and (b) 2.5 eV, for KBr:NO<sub>2</sub><sup>-</sup>; the former monitors purely the  $B$  band and the latter includes the contribution of both the  $B$  band and the  $V_K$  band. It is clear that the  $B$  band reaches a maximum at 1.5 ps after excitation, and decays within 10 ps. The long-lived component in (b) can be ascribed to the  $V_K$  centers, in view of the time-resolved spectra. From these results, it is clear that formation of the  $V_K$  center is delayed by about 10 ps after generation of holes. Evidently the delay of the  $V_K$  center formation is ascribed to the formation of a transient state, the  $B$  state, which exhibits the  $B$  band. Thin solid curves in Figs. 2(a) and 2(b) represent the results of analysis based on the rate equation model. In the analysis, we presume that a hole is first relaxed to the  $B$  state and then to the  $V_K$  center. Gaussian-type distribution for the rate of population into the  $B$  state is included in the model.<sup>16</sup>

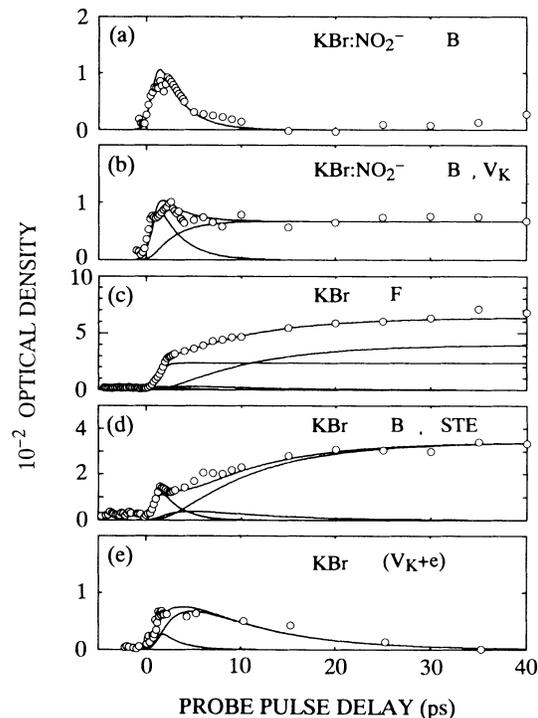


FIG. 2. Optical density changes at (a) 2.0 eV and (b) 2.5 eV in KBr:NO<sub>2</sub><sup>-</sup> at 273 K and (c) 1.92 eV, (d) 1.60 eV, and (e) 1.33 eV in pure KBr at 80 K as a function of delay after two-photon band-to-band excitation. Thin solid curves are the results of analysis by using a modified rate-equation model. Each figure includes the component due to the  $B$  band, although it is not clearly seen in (e), in which the scale of the ordinate is expanded. Centers responsible for the optical absorption changes at respective photon energies are given in each figure.

As seen in Fig. 2(b), the time evolution of the optical absorption at 2.5 eV can be described satisfactorily as a superposition of the two components: one due to the  $B$  band and the other due to the  $V_K$  band. The decay time of the  $B$  state into the  $V_K$  center is found to be 3.0 ps. Thus we conclude that the  $B$  state is a precursor of the  $V_K$  centers, or a hole under relaxation.

The time evolutions of the optical absorption at 1.92 eV, 1.60 eV, and 1.33 eV in pure KBr are shown in Figs. 2(c), 2(d), and 2(e), respectively, where solid curves are the results of analysis similar to those in Figs. 2(a) and 2(b). The optical absorption measured at 1.92 eV is almost exclusively due to the  $F$  band as seen in Fig. 1(b). Clearly two modes in the growth of the  $F$  band are observed: the rapid growth that occurs within 6 ps and the slow one that continues over 40 ps at 80 K. Both modes of growth of the  $F$  band are evidently not due to electron trapping by preexisting anion vacancies,<sup>17</sup> but are indicative of formation of the Frenkel pairs from  $e$ - $h$  pairs. Since about 10 ps is required for the relaxation of a hole as described above, the rapid growth of the  $F$  centers can be ascribed to the interplay between an electron and the hole under relaxation. On the other hand, the slow growth of the  $F$  band occurs in the time regime after the hole relaxation is completed. The slowly growing component of the  $F$  band is described in terms of  $1 - \exp(-t/\tau)$ , with  $\tau = 9$  ps.

In contrast to the growth of the  $F$  band, the growth of the STE band exhibits only the slow component; the apparent fast growth at 1.60 eV is not due to the STE band but is primarily due to the  $B$  band as evidenced by the time-resolved spectra shown in Fig. 1(b). The growth of the STE band is found to be parallel to the slow growth of the  $F$  band. On the other hand, the optical absorption change at 1.33 eV shows a rapid growth within 5 ps and slow decay lasting for 40 ps. Comparing the time-resolved spectra, it can be divided into two components: one behaves similarly to the  $B$  band and the other grows more slowly and is not annihilated completely for 40 ps. The latter component is absent in  $\text{KBr:NO}_2^-$ , but is seen only in pure KBr. The time constant of the decay of this component is found to be 9 ps, identical to those of the slow growth of the  $F$  band and of the STE band. It follows that the slow growth of the  $F$  and STE bands is due to the conversion from the intermediate state which exhibits optical absorption particularly at 1.33 eV into  $F$ - $H$  pairs and STE's. This intermediate state is formed within 10 ps after excitation, probably in parallel to the fast  $F$ -center-formation process.

In order to get more insight into the slow growth, we examined the spectra for pure KBr at 6 ps, when the rapid growth of the  $F$  band is terminated, and at 40 ps. We found three prominent features: the decay of the absorption around 1.33 eV, the growth of the STE and  $F$  bands, and the significant sharpening of the absorption band between 2.5 and 3 eV. It is known that the  $V_K$  band shows a much broader low-energy tail than the  $H$  band, although their peak energies are similar.<sup>18</sup> The progressive sharpening of the band above 2.6 eV is interpreted as the conversion from the  $V_K$  band to the  $H$  band; an analysis of the time-resolved spectra between 2.5 and 3.0 eV

indicates the conversion from the  $V_K$  band to the  $H$  band is characterized by a time constant of about 9 ps, which is identical to that of the decay of the absorption at 1.33 eV. Thus the intermediate state in pure KBr is characterized spectroscopically by the  $V_K$ -like absorption band in the ultraviolet region and the optical absorption in the infrared region below 1.5 eV. This feature is essentially the same as that obtained for the type-I STE in alkali halides,<sup>19</sup> which has been considered to be an electron trapped by a  $V_K$  center, having a  $D_{2h}$  symmetry.<sup>10,13</sup> Thus we assign the intermediate state which governs the slow growth of the STE and  $F$  centers to be the type-I STE.

From the arguments above, the slow growth of the STE and Frenkel pairs can be interpreted as the off-center relaxation; the  $X_2^-$  molecular ion is displaced from the  $D_{2h}$  symmetry to  $C_{2v}$  symmetry along a  $\langle 110 \rangle$  direction. Measurements of similar time-resolved spectra of pure KBr carried out at the temperature region from 4.2 to 200 K have shown that the time constant of the slow growth of the  $F$  band decreases as the temperature increases from 9 to 5 ps. The result indicates that the off-center relaxation on the lowest APES is assisted by phonons.

One of the striking features of the present results is that the  $F$  center is generated not only through slow process described above but also through the fast process within 6 ps, during which relaxation of holes is under way. Therefore, it is evident that the fast growth of the  $F$  center occurs due to the interaction of an electron with the hole under relaxation. The hole under relaxation can be described as electronically and vibrationally excited states of the  $V_K$  centers; the internuclear distance of the two halogens is not the equilibrium distance and furthermore the hole may not be shared equally by the two halogens. The optical transition energy of such an unrelaxed hole is presumed to vary from close to zero to the peak energy 3.22 eV of the  $V_K$  band depending on the degree of relaxation. Since the relaxation at various sites may not be in phase, the holes under relaxation are considered to give rise to a broad band. In  $\text{KBr:NO}_2^-$  in which electrons are prohibited to interact with the holes,  $V_K$  centers are eventually formed through the vibrational relaxation. The result that the annihilation of the  $B$  band leads to the  $V_K$  band in  $\text{KBr:NO}_2^-$  is totally consistent with this interpretation.

In pure KBr, the hole under relaxation will start to interact with an electron at some stages of the relaxation. The present results revealed two pathways of the complex consisting of an electron and the hole under relaxation: one to the type-I STE and the other to the Frenkel pairs bypassing the STE's. The former channel is analogous to the well-known process of the trapping of an electron by a  $V_K$  center. It occurs following the relaxation of the unrelaxed hole to the  $V_K$  center; an electron maybe added at any stage of the relaxation of the hole. On the other hand, the latter channel is a new channel; we presume that it starts by interaction of an electron with the hole under relaxation. The off-center instability is naturally different from that for the former channel. The existence of this channel has provided evidence for the dynamical

interplay of the electron-lattice and hole-lattice interaction to induce local lattice rearrangement.

Most models<sup>4,20-25</sup> of Frenkel-pair formation from an exciton or an  $e$ - $h$  pair proposed so far have been based on the assumption that the hole relaxation into the  $V_K$  center is the primary step; any further relaxation occurs after the hole self-trapping is completed. The present investigation has revealed a new channel that is initiated from an unrelaxed hole interacting with an electron and leads directly to a Frenkel pair. Obviously the relaxation pathway of an  $e$ - $h$  pair is dependent on the degree of relaxation at the onset of electron-hole interaction; the

branching into two different channels is governed by dynamical factors dependent on the configuration of the  $e$ - $h$  pair during relaxation. This finding will shed new light on understanding the physical basis of the presence of a variety of channels of exciton relaxation in several non-metallic solids.<sup>1,2</sup>

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