Kinetics of *F*-center formation in stepwise photoionization of Tl^+ ions in KBr by picosecond laser pulses

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(Submitted 5 March 1990)
Pis'ma Zh. Eksp. Teor. Fiz. **51**, No. 7, 358–360 (10 April 1990)

It has been found that the formation time of *F* centers in the stepwise photoionization of impurity Tl^+ ions in KBr is 30 ± 10 ps. This result is evidence that processes corresponding to the formation of *F-H* pairs in pure crystals may occur during the recombination of an electron with a Tl^{2+} center in an alkali-halide crystal.

The formation of *F* centers in alkali-halide crystals during the application of ultrashort laser pulses was studied in Refs. 1–4. All those studies used pure crystals, which were excited in a two-photon process either in the region of band–band transitions or in the exciton absorption band. The authors attribute the formation of *F-H* pairs to the trapping of a band electron by a V_k center and the decay of a self-trapped exciton into structural defects. The formation time of *F-H* pairs ranges from one to several tens of picoseconds, depending on the particular crystal and the excitation conditions. The stepwise photoionization of impurity mercury-like ions (In^+, Tl^+, etc.) in alkali-halide crystals also leads to the formation of *F* centers,[5] but the data available are not sufficient to explain how these centers form. Our purpose in the present study was to learn about the kinetics of the formation of *F* centers during stepwise photoionization of an impurity center in an alkali-halide crystal at the picosecond time scale.

We selected the KBr crystal with an impurity of Tl^+ ions for these experiments. We used pulsed absorption spectroscopy with an optical delay of the probe pulse with respect to the exciting pulse.[6] A pulse at the fourth harmonic of an Nd:YAG laser with passive mode locking (0.2–0.3 mJ) was focused with a small divergence into a spot 3 mm in diameter on the surface of the crystal. This light sent some of the impurity centers into a low-lying excited state. A pulse at the third harmonic (2–3 mJ), used to photoionize the Tl^+ ions from the excited state, was applied to the crystal 300 ps after the fourth-harmonic pulse. The third-harmonic pulse spanned the area of the excited volume. The probe light was the second harmonic from a parametric generator using a $LiNbO_3$ crystal with thermal tuning. The length of the probe pulse was measured by correlation methods and was found to be 10–12 ps. The probe pulse was focused to a spot 0.5 mm in diameter on the surface of the crystal and passed through the region of maximum coloring of the sample. The intensities of the pulses at the fourth and third harmonics were chosen in such a way that neither would separately lead to a coloring of the crystal or to significant changes ($\Delta D > 10^{-2}$) in the optical density in the *F*-center absorption band in KBr. Since we were interested in the change in the optical density due exclusively to the effect of the third harmonic on a sample excited beforehand by the fourth harmonic, we developed an optical layout for the

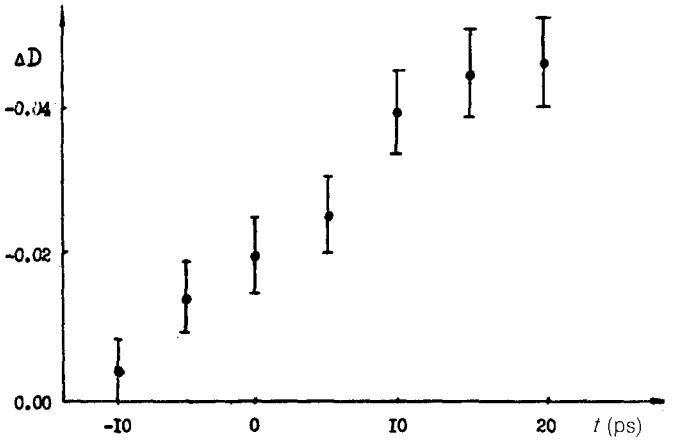

FIG. 1. Kinetics of the bleaching of the absorption from the excited state of Tl^+ ions.

experiment and a program for computer analysis of the results such that the change in the optical density during the application of the fourth-harmonic pulse to the crystal would be subtracted. The physical meaning here is that in the experiments we measured the change in optical density due to the photoionization of the Tl^+ ions from the low-lying excited state caused by the third-harmonic pulse and by subsequent carrier-relaxation processes involving the formation of structural defects. All the experiments were carried out at room temperature.

In the first stage of the experiments, the probe wavelength was fixed at $\lambda = 476$ nm. According to our estimates, this wavelength corresponds to absorption from a

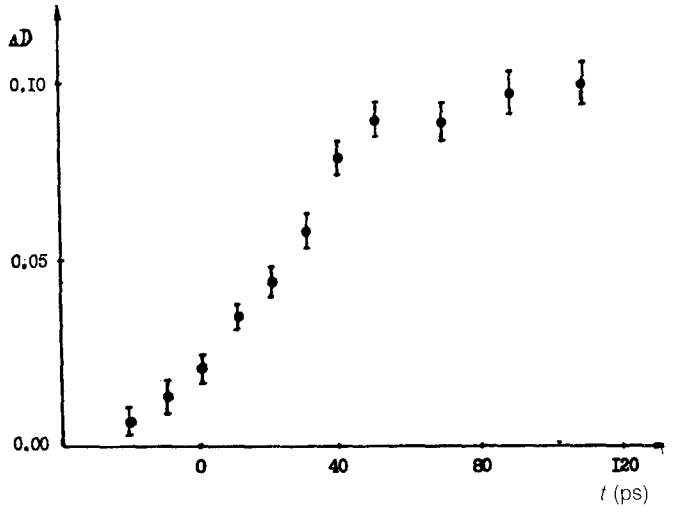

FIG. 2. Kinetics of the increase in the absorption in the F band.

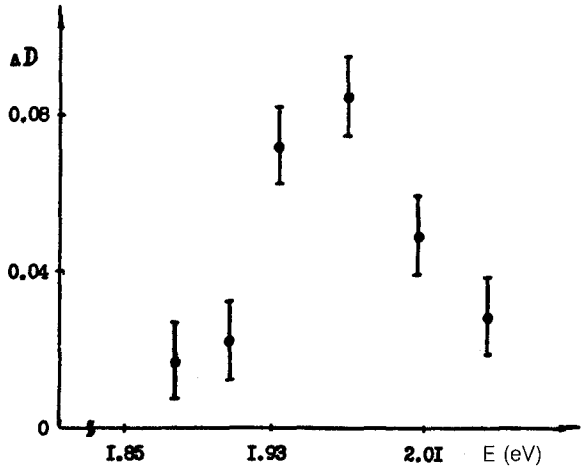

FIG. 3. Absorption spectrum of the color centers that form.

relaxed excited state into the conduction band. Figure 1 shows the bleaching curve ($\Delta D < 0$), where the independent variable is the delay of the probe pulse with respect to the third-harmonic pulse. In this case the bleaching occurs because electrons are sent from the excited state of the impurity center into the conduction band by the third-harmonic pulse. The kinetics in Fig. 1 is determined by the instantaneous response of the medium and characterizes the time resolution of the apparatus.

In the second stage of the experiments, the probe wavelength was near the maximum of the F-center absorption in KBr ($\lambda = 620$ nm). The absorption-increase curve found as a result is shown by Fig. 2. We easily see that the changes in the optical density here are slower than in the preceding case of an instantaneous response of the medium. A numerical calculation carried out under the assumption that the response of the medium is exponential and that the exciting and probe pulses are Gaussian shows that the formation time of the color centers is $\tau = 30 \pm 10$ ps.

Figure 3 shows the absorption spectrum of the color centers which have formed. These measurements were carried out at a fixed delay ($\Delta t = 100$ ps) of the probe pulse with respect to the third-harmonic pulse. This spectrum agrees satisfactorily with the known absorption spectrum of F centers in KBr.

In summary, this study has shown that the stepwise photoionization of Tl^+ centers in KBr leads to the formation of F centers in a time $\tau = 30 \pm 10$ ps, i.e., in a time characteristic of the formation of F-H pairs in pure alkali halide crystals during the recombination of an electron with a V_k center. The data available at this point are not a sufficient basis for exactly identifying the type of F centers that form; in particular, we do not know whether the F center has a Tl^+ ion in its nearest neighborhood. We regard the following circumstance as important: Since the hole localizes at the activator during the photoionization of the Tl^+ ion, the formation of the F centers [or F_A(Tl) centers] is probably due to the recombination of the electron with a Tl^{2+} center. The results of this study thus support our earlier suggestion that processes

corresponding to the formation of *F-H* pairs in pure crystals may occur during the recombination of an electron with a hole localized at an impurity center in an alkali-halide crystal.[7]

We wish to thank P. G. Baranov and L. E. Nagli for a discussion of the results and also M. V. Anosov for assistance in writing the program.

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Translated by Dave Parsons