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DIELECTRICS

Detection of Defects Binding Free Polarons in Colored Alkali Halide Crystals

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Abstract—The assumption has been made that defects binding free polarons in colored alkali halide crystals are F'-center, i.e., defects that slow down the motion of dislocations (photoplastic effect). This assumption has been confirmed by the experiments performed in this study. Thus, the anion vacancy in alkali halide crystals at a low temperature can capture three electrons: two electrons at a deep level (F'-center) and one electron in a bound polaron state. This electron is retained due to the energy gain in the interaction of a local deformation of the polaron and a local deformation surrounding the F'-center, despite the presence of the Coulomb repulsion.

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1. INTRODUCTION

Earlier [1–4], using two-step photoconductivity at a temperature $T < 78$ K in alkali halide crystals colored under gamma-ray irradiation, we detected and investigated an interesting object, which, by its characteristics, was identified as a polaron, namely:

(1) In a NaCl crystal (it is this crystal that was initially studied), the energy of thermal destruction, the maximum of optical absorption, and the maximum of photoionization (photodestruction) were related as 1 : 2 : 3, which corresponded to the Pekar theory for polarons [5]. It should be noted, however, that for the KCl and KBr crystals studied later, this ratio is satisfied to a lesser extent.

(2) In the theoretical paper [6] devoted to the study of the optical absorption of a small polaron, it was shown that the polaron optical absorption spectrum has the form of a broad peak dissected by narrower equidistant phonon peaks, the energy positions of which on the energy scale corresponds to the formula $E = nE_p$, where E_p is the longitudinal optical phonon energy. This is in good agreement with our experimental results [1, 2]. The only discrepancy is that the half-width of the optical absorption peak is approximately two times less than that obtained in the theory. The theory developed in [6] predicts a decrease in the amplitude of phonon oscillations with an increase in the temperature, which is also confirmed in our experiments.

(3) Sequences of phonon oscillations in the optical absorption and photoionization spectra make it possible to determine, with a high degree of accuracy, the energy of longitudinal optical phonons that manifest themselves in these spectra. It should be noted that, in this case, the size of a phonon from the photoionization spectra is greater than those from the optical absorption spectra of NaCl, KCl, and KBr by 10.8%, 7.4%, and 5.2%, respectively [1, 3, 4]. This confirms the results of the theoretical studies [7, 8], according to which the "softening" of the phonon modes of a polaron as compared to a longitudinal optical phonon of the crystal should be observed.

Thus, undoubtedly, this object is a polaron, but, because at low temperatures it is stable and can be created in high concentrations (the optical absorption of 1/cm was achieved), it is a bound polaron. Possibly, it is this circumstance that distinguishes the polaron under consideration from the polarons of the theory [6] and leads to the fact that the half-width of the optical absorption spectrum of this polaron is approximately two times less than that found in the theory.

In some theories of polaron optical absorption, for example, in [9, 10], it is considered that there is usually a zero-phonon line at an energy E_0 (not always observed in experiments) and a phonon structure (peaks or steps), which are described by the formula $E = E_0 + nE_p$. A distinctive feature of the theory [6] is the energy $E_0 = 0$. This is a very strong distinction, and the fact that it is confirmed in our experiments indicates the correctness of the simplifications used in the theory [6].

Alexandrov and co-authors [7, 8, 11, and others] were much engaged in the theoretical treatment of the optical absorption of a small polaron. The authors of

[11] considered a greater number of parameters of the theory than in [6]. As a result, only for particular values of these parameters, the optical absorption spectrum looks like the spectrum in the experimental work [1]. The energy positions of phonon oscillations in one of these spectra ([11, p. 250, Fig. 1], $\lambda = 2.5$) also agree well will the formula $E = nE_p$, and their repetition period confirms the "softening" of the phonon modes of polarons by 40%, which is indicated in other studies of these authors [7, 8]. An important advantage of the study [11] is the fact that the ratio of the position of the optical absorption maximum to the half-width of the optical absorption spectrum in this theory for particular values of the parameters exceeds the value of 1.5 (in the experiment, it is approximately 2.0), whereas in [6], this ratio is close to 1.0.

Further, it is important to determine crystal defects on which the polaron under consideration becomes bound. This raises an interesting hypothesis that the F'-center can be a trap for the polaron. It is known [12–14] that the F'-center is a stopper for a moving dislocation (photoplastic effect). This effect in colored alkali halide crystals is small. Therefore, the F'-center is not a very strong stopper, and lattice distortions around it are not so great, which can provide a gentle enough capture of the polaron so that the formed bound polaron would not be very different from the free polaron.

2. DESCRIPTION OF THE EXPERIMENTS, RESULTS, AND DISCUSSION

For the verification of the above hypothesis, we carried out the following experiments. The experiments were performed on an automated setup intended for the measurement of two-step (photoinduced) photoconductivity. Single-crystal nominally pure (the content of impurities was less than 10^{-3}%) NaCl samples $4 \times 4 \times 10$ mm in size were irradiated with gamma irradiation to a dose of 5×10^6 rad. Such a sample was placed in an optical helium cryostat in an upright position between two electrodes and cooled to $T = 20$ K. The light source was an SI-8 incandescent lamp with a vertically positioned ribbon radiator, the image of which was projected onto the sample with a lens 80 mm in diameter. The light spectrum was changed using glass filters 80×80 mm in size.

Experimentally, three different states of the crystal in terms of the concentration of F'-centers can be realized.

(a) After cooling in the dark, there are no F'-centers in the crystal.

(b) The exposure of the sample to light in the F-band (F-light, filters SS8 and S3S14) for a sufficiently long time (in our experiments, 300–600 s) creates, because of the large overlap of the F- and F'-bands, a dynamically equilibrium state with a sufficiently high concentration of F'-centers.

(c) The exposure of the sample to the orange light (filter OS14, wavelength 580–2700 nm) for 300 s and more leads to the transformation of the sample into another dynamically equilibrium state with a significantly lower concentration of F'-centers.

Thus, by alternating these exposures, the sample can be repeatedly transformed from state (b) to state (c), and vice versa. However, the sample can be transformed from these states into state (a) only by its heating with the subsequent cooling in the dark.

Each measurement consisted of three successive steps:

Step 1—the "setting of the instrument to zero." The exposure to the infrared light (filters IKS3 + IKS1) for 10 s destroyed all the infrared traps (bound polarons) in the sample, if they existed there.

Step 2—the "coloring or labeling of available traps for bound polarons in the sample." A small dose of F-light (the intensity accounted for 0.1 of the maximum value, exposure 2 s) was used to release a portion of electrons from F-centers. They occupied all the traps available in the sample, thus forming bound polarons in the concentration proportional to the concentration of these traps.

Step 3—the measurement of infrared photoconductivity caused by the presence of bound polarons in the sample. The signal was proportional to the concentration of polarons and, hence, to the concentration of polaron traps in the sample.

Thus, if the hypothesis is correct, state (b) should correspond to a strong photoconductivity signal as compared to that in state (c). The result is presented in Fig. 1. The x axis represents the time of F-light exposure. Point a corresponds to the photoconductivity signal in the absence of the initial light treatment (state (a) of the sample). The presence of a photoconductivity signal means that, in this state, the sample contains a small amount of electron traps (not necessarily polaron traps) depleted by the infrared light. Further, after the 5 min exposure to the F-light (the up-right arrow), which transforms the sample into state (b), we obtain a strong photoconductivity signal indicating a sharp increase in the concentration of polaron traps. Then, the exposure to the orange light for 300 s transforms the sample into state (c) (the down arrow), which leads to a sharp decrease in the photoconductivity signal (decrease in the concentration of polaron traps). Further, these experiments can be repeated several times, which is demonstrated by the figure. Thus, the higher concentration of F'-centers corresponds to a higher concentration of polaron traps, which confirms the hypothesis that the F'-center is an effective trap for polarons.

It is known that, in addition to the F-centers, colored alkali halide crystals contain more complex electron color centers: M-, R-centers, and so on toward their complexity. The region of sensitivity of the complex centers to light is shifted, with their complication,

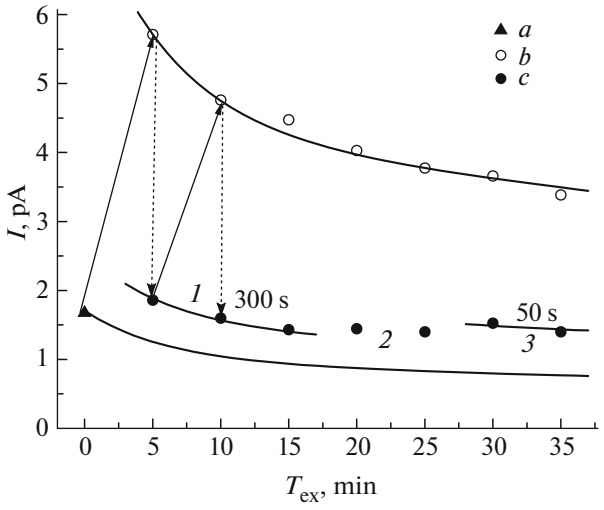

Fig. 1. Influence of different light treatments on the concentration of polaron traps: (*a*) signal without light treatment; (*b*) F-light, 300 s; and (*c*) orange light (OC14). Exposure time: (*1*) 300 s, (*2*) 200 and 150 s, and (*3*) 50 s. The up-right arrows illustrate the F-light treatment for 300 s. The down arrows indicate the orange light treatment for 300 s.

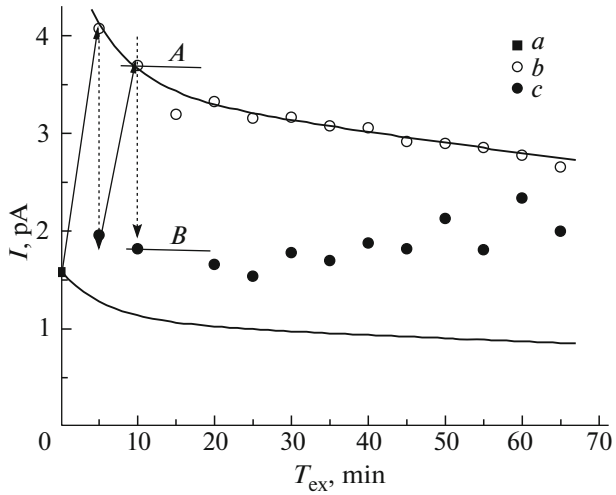

Fig. 2. Influence of different light spectra on the destruction of polaron traps: (*a*) signal without light treatment; (*b*) F-light, 300 s; and (*c*) light through different filters in the sequence JS14, OS14, KS10, KS13, KS14, KS15, KS17, KS18, KS17, OS14, and KS19.

toward the red region and further toward the near-infrared range. In the normal state, these centers, like the F-centers, have a neutral charge state and do not produce around themselves a local deformation of the crystal. But having captured an electron, they, like the F'-centers, deform around themselves the crystal lattice and can thus become traps for polarons. Naturally, the question arises as to whether or not they are traps for polarons. The point is that the transmission band of the OS14 filter lies in the range from 580 to 2700 nm. Consequently, these centers are collected and destroyed synchronously with F'-centers. Therefore, in order to clarify the role of these traps, we performed the following experiment:

First, the appropriate time of light exposure (filter OS14, in what follows, from KS10 to KS19) was chosen so as to go beyond the state of dynamic equilibrium and, thus, to make the signal more sensitive to a change in the exposure or the spectrum of light destroying traps. This is demonstrated in Fig. 1. Points *1* correspond to the exposure of the sample to the orange light for 300 s, points *2*—for 200 and 150 s, and points *3*—for 50 s. It can be seen that, only after the exposure for 50 s, the signal reliably differs from the dynamic equilibrium signal (points *1*).

It can be seen from Fig. 1 (and also from Fig. 2) that points *b* do not fall on a straight line. The reason is that the concentration of F-centers in the sample decreases under the action of the F-light. This circumstance leads to the fact that the portion of electrons injected into the sample under the action of the F-light (the second step of the measurement procedure) also does not remain constant, but decreases, which leads to a decrease in the sensitivity of measurements in accordance with a certain law. The curve passing through points *b* and demonstrating this law represents the sum of two exponential functions. The slow exponential function (t = 250–300 min) corresponds to the conventional gradual bleaching of the crystal under the exposure to light, which is typical of gamma-irradiated alkali halide crystals. The fast exponential function corresponds to a decrease in the concentration of F-centers due to the redistribution of electrons from these centers under the action of the F-light on the electron centers, which cannot retain additional electrons at room temperature, but fairly well retain them at low temperatures. Upon heating of the sample, this part of electrons is partially returned to the F-centers. The photoconductivity signal from some already existing traps in the sample (point *a*) also varies according to this law, which is demonstrated by the curve emanating from point *a*. The fact that points *c* are located above this curve means the impossibility to completely destroy all F'-centers under the action of the orange light, as was mentioned above. Similarly, the curves are drawn through points *1* and points *3*.

Further, in order to elucidate the role of "red" centers, we carried out the experiment, the results of which are presented in Fig. 2. Points *b* (open circles, quantity *A*) demonstrate the result of the photoconductivity measurement after the 300 s exposure to the F-light. Points *c* (closed circles, quantity *B*) indicate the photoconductivity signal after the subsequent 50 s exposure to the light of different spectral composition (different filters, from OS14 to KS10 and, further, to KS19, that shift the spectral band consistently toward

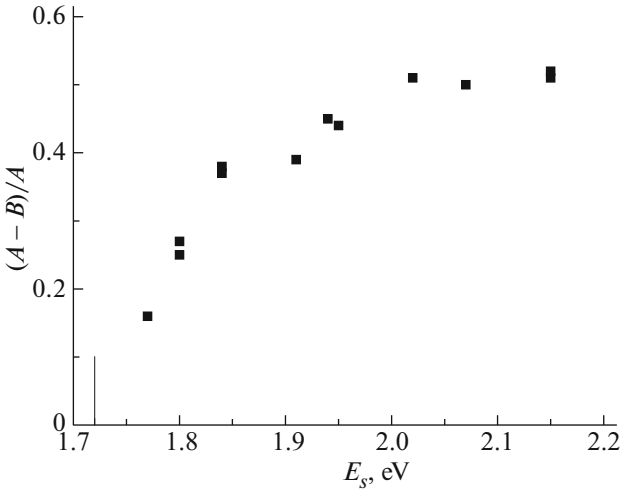

Fig. 3. Spectral dependence of the photodestruction of polaron traps. E_s is the position of the short-wavelength edge of the filter transmission band at a level of 0.5. The vertical line at E_s = 1.72 eV shows the long-wavelength edge of the spectrum of F'-centers [15].

the long-wavelength range), which destroys polaron traps. The transmission band of these filter starts at the energy E_s (at a level of 0.5) and continues toward lower energies to L = 2700 nm. The energy E_s was varied from 2.2 eV for the OS14 filter and to 1.8 eV for the KS19 filter.

The relative depth of the destruction $(A - B)/A$ is plotted in Fig. 3 as a function of the energy E_s. We can see a sharp decrease in this quantity with a shift toward the long-wavelength range. This indicates that, among the F-light induced polaron traps, there are predominantly traps destroyed by the light in the region $L <$ 680 nm; i.e., the role of "red" centers is very small or absent altogether.

Thus, the F'-center can retain one more electron in the form of a bound polaron, despite the presence of the Coulomb repulsion. This electron is retained due to the energy gain in the interaction of a local deformation of the polaron and a local deformation, surrounding the F'-center, at some distance from the F'-center. As a result, a spherical region (possibly, a spherical cavity) is formed around the F'-center, in which the polaron can move like a free polaron in the crystal, thus exhibiting properties similar to those of the free polaron. This leads to far-reaching consequences. For example, the properties of a free polaron, which are difficult to experimentally measure because of the short lifetime of this polaron, should not be very different from the properties of the bound polaron. This gives for the depth of the polaron level (band) in NaCl the value of 0.162 eV, which is deeper than the level of an excited F-center (0.08–0.15 eV). As a result, the electron can escape from the excited F-center into the crystal in the form of a free polaron at arbitrarily low temperature (in [14], at T = 1.6 K). The decay of the photoconductivity with a decrease in the temperature in the vicinity of 70 K is explained not only by the thermally activated electron emission from the excited F-center into the conduction band, but also by the fact that the F'-centers at $T <$ 70 K are, for polarons (in the semiconductor terminology), the effective traps, whereas at $T >$ 70 K, they are trapping centers.

3. CONCLUSIONS

(1) The hypothesis that the traps binding polarons are the same color centers which are created under the illumination of the sample by the F-light and lead to the photoplastic effect, i.e., F'-centers, has been confirmed.

(2) In addition to F'-centers generated upon exposure of the sample to the F-light, in the crystal there is a small concentration of electron traps capturing electrons and losing them under the influence of infrared light. The question as to whether the bound polaron states in this case are created on them remains open.

(3) The role of electron color centers losing electrons under the influence of red light ($L >$ 700 nm) in the binding of free polarons is very small or absent altogether.

(4) The conclusions drawn in the theoretical study [6], and also in [11] for some values of the parameters under consideration, are in good agreement with the experimental data [1–4], namely, in matters of the position and half-width of the optical absorption peak, the presence of a system of equidistant phonon oscillations, the position of this system with respect to the origin of the energy axis, the dependence of the energy on the temperature, and the presence of "softening" of phonon modes of a polaron formation in relation to the size of a conventional longitudinal optical phonon.

(5) The qualitative explanations have been given for the reasons of this agreement, the effective escape of electrons from excited F-centers into the crystal (the photoplastic effect is observed at a temperature of 1.6 K [14], as well as for the participation of F'-centers in the formation of the observed decay of the photoconductivity during cooling in the temperature range from 70 to 80 K.

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