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Mechanisms of radiation defect formation in the KI crystal in the deformation field

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Introduction

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At present, it is clearly proved that the cause of the formation of Frankel defects in alkali halide crystals (AHC) under the action of various ionizing radiation is the non-radiative decay of self – trapped anion excitons into primary radiation defects – [*F, H*], [α, *I*] and [υ_c^-, M_i^+] – couples [1-8].

The *F*-center is an electron localized in an anion vacancy ($\upsilon_a^+e^-$), *H*-center (i_a^0) – an interstitial halogen atom occupying a single anionic lattice node – $(X_2^-)_a^0$, α-center – anion vacancy (υ_a^+) and *I*-center (i_a^-) – interstitial halogen ion (X_i^-). For all AHC listed halogen radiation defects (*I, H*-centers) they have a very low stabilization temperature in the region of 20-30 K and 50-55 K, respectively [9-13]. In this regard, for the stabilization of mobile halogen radiation defects, the hypothesis of the creation of cationic Frankel defects: cationic vacancies (υ_c^-) and interstitial alkali metal ions (M_i^+, i_c^+) is proposed. The most urgent problem is to find out the mechanisms of structuring radiation defects, especially in nanoscale materials, for determining the processes of structural materials deterioration in the operational mode under the influence of radiation, temperature and stress of various types of deformation [14-18].

By changing the nearest environment around the *H*-centers, the core of which is a molecule $(X_2^-)_{aa}$ - located in two anionic lattice nodes and is sensitive to the symmetrical arrangement of crystal-forming particles, it is reasonable to expect the effect of increasing their temperature. Indeed, numerous experimental studies [1-2] are devoted to the mechanisms of stabilization of the *I*- and *H*-centers in the AHC by introducing homologous cations of a small radius into the crystal than the main lattice cation, bringing their stabilization temperature almost to room temperature [1]. For example, the temperature of the stabilization H_{AA} (M_i^+) - centers in a KCl crystal is around 250 K. Thus, it was possible to significantly increase the stabilization temperature of the *H*-centers due to the space of impurity cations-homologues of small size, which create an energetically favorable situation for the stabilization of mobile electronic excitations. Similar experimental data are available on the stabilization of interstitial halogen – *I*-center ions [19-22].

Experimental Setup

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The experimental setup allows us to study the absorption spectra of AHC in the conditions of ecreasing lattice symmetry under the constant influence of low-temperature deformation.

The absorption spectra were measured using a "Nicolet Evolution 300" spectrophotometer in the nge from 3 eV to 6 eV. The source of radiation in the device is a xenon lamp. In the ectrophotometer «Evolution – 300», the scale of optical density registration has been expanded ore than three times (up to 5-6 units with a gap width of 1 nm) compared to existing standard ectrophotometers such as SF-4, SF-26, SF-56, SF-256, etc.

To measure the absorption spectra of objects at temperatures below room temperature (300 K), e unit was upgraded by connecting a specially designed glass cryostat, which allows creating a cuum of the order of 10^{-4} Torr inside it. Vacumm was created using a system of two absorption umps connected in parallel in a vacuum system with a cryostat. A cryostat is not a single structure. consists of two parts. The first part of the cryostat is a glass tank. The material of the cryostat-olybdenum glass – is not chosen by chance, it has a low coefficient of expansion, which allows it to e operated in a wide temperature range. Liquid nitrogen is poured into the tank to cool the object nder investigation by contact method. A copper crystal holder is soldered at the bottom of the tank. ne crystal holder has a hole in which the crystal is inserted. To prevent mechanical torsion, correct xation and better contact, presser cheeks are placed on both sides.

The second part of the cryostat has a cylindrical shape. It is also made of molybdenum glass. It s three Windows, two of which are made of LiF - through which the absorption spectra are gistered. The LiF crystal is optically transparent in a wide range of spectrum, which makes it ideal r our research. The lower part of the cryostat is attached to the optical bench of the installation.

The temperature of the crystal in the cryostat was measured by a copper-constantan ermosteam. The absorption spectra of objects were measured at temperatures of 300 K and 80 K.

The objects were previously subjected to X-ray irradiation from the RUP-120 installation (W, 3 A, 100 kV) and elastic deformation in an iron cryostat

RESULTS

The method of directed crystal deformation has long been used in solid state spectroscopy s a method for studying anisotropic centers in cubic crystals. As a result of plastic eformation, structural changes occur in the lattice of a pure AHC, a significant part of which mains in the crystal after the stress is removed [11, 15]. Measurements of thermal and ectrical conductivity, stored energy, and density of deformed AHC indicate that vacancy efects are generated during plastic deformation. In AHC from charge considerations, the acancy defects must be born in pairs, consisting of anion and cation vacancies. Most of these airs are part of larger or smaller clusters. This conclusion was made by the authors on the asis of data obtained by measuring the thermal conductivity of plastically deformed LiF ystals. The possibility of using the results on changes in thermal conductivity during eformation is based on the difference in the efficiency of phonon scattering by single acancies, pairs of vacancies and their clusters: single vacancies are most strongly scattered, hile their complexes do not change the thermal conductivity at all.

In experiments with plastic deformation, special attention was focused on the analysis of e absorption spectra of halogen radiation defects, which are indicators of the concentration f pre-created vacancy deformation defects (divacansions $\upsilon_c^- \upsilon_a^+$).

The experiments were carried out in the following sequence: the crystal was first astically deformed (ε=4-5 %) by uniaxial compression in a cryostat at a high technical acuum (10^{-6} Torr) at room temperature, then the deformed crystal was immersed to 80 K, nd at this temperature it was irradiated with X-ray radiation, after which the absorption pectra were registered at 80 K.

The essence of pulsed crystal annealing was heating the irradiated crystal to a certain mperature, usually in steps of 10-20 K, and at this temperature it was kept for 3-5 minutes, nd then the crystal was cooled again to 80 K by pouring liquid nitrogen into the cryostat servoir [5].

Thus, all measurements of the absorption spectra were performed at 80 K.

Fig. 1 shows the absorption spectra in the range of I3-- centers of an undeformed KI crystal after plastic deformation with a degree of deformation of 3.5 % at 300 K.

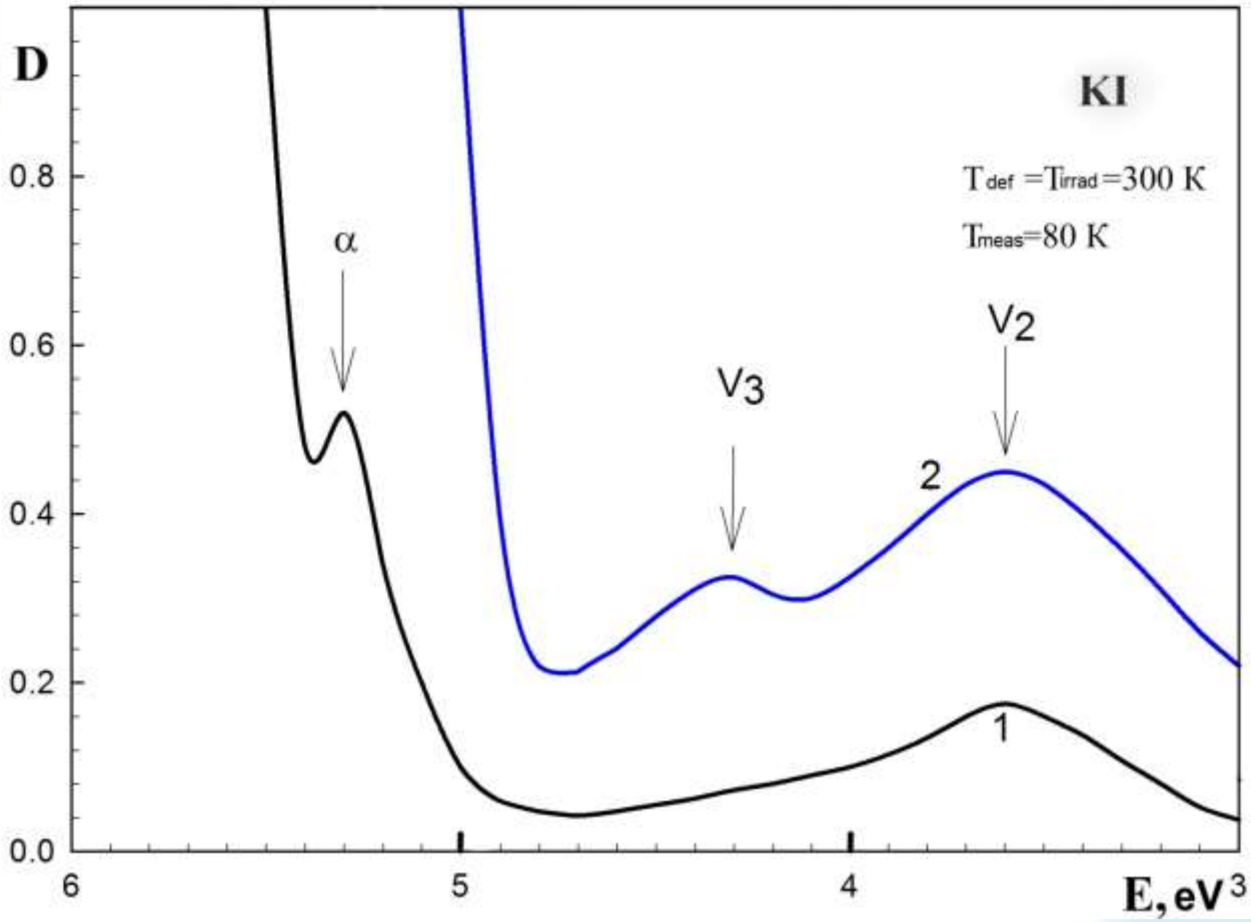


Fig.1. Absorption spectra of X-irradiated KI crystals in the isodose mode (*t*=90 min). 1 - undeformed, 2 - deformed at 300 K up to 4%. Irradiation at 300K, measurement at 80 K.

In the absence of deformation (curve 1, Fig. 1), absorption bands due to α - centers ith a maximum of 5.2 eV and a V_2-center (I_3^-) with a maximum of 3.6 eV were gistered in the absorption spectrum of an X-ray-irradiated KI crystal at 80 K. In the osence of deformation (curve 1, Fig. 1) in the absorption spectrum of an X-ray-radiated KI crystal at 80 K, absorption bands due to-centers with a maximum of 5.2 /, - centers with a maximum of 3.6 eV are registered. The absorption band in the gion of the (I_3^-) - center spectrum with a maximum of 4.3 eV is also registered.

In KI crystals, plastic deformation (curve 2, Fig. 1) significantly increases the oncentration of $V_2 \equiv (I_3^-)^0_{aca}$- centers, as well as the absorption band at 4.3 eV. In the terature [1, 16, 20] concerning the absorption band at 4.3 eV, it is discussed that this and is due to I_3^- - centers. However, the fact that the absorption band at 4.3 eV in the I crystal is similar to the band at 5.3 eV in the KBr crystal, which is effectively created fter plastic deformation, when complex vacancy defects are created, allows us to terpret this band due to $V_3 \equiv ([I_2]_2)_{acac}$-centers. In the crystal lattice, the radiation rmation of a dimer type of $(I_2^-)_2$ is related, which, by its origin, as well as the (I_3^-) - enter, can be formed when two interstitial halogen atoms interact in the field of acancy defects.

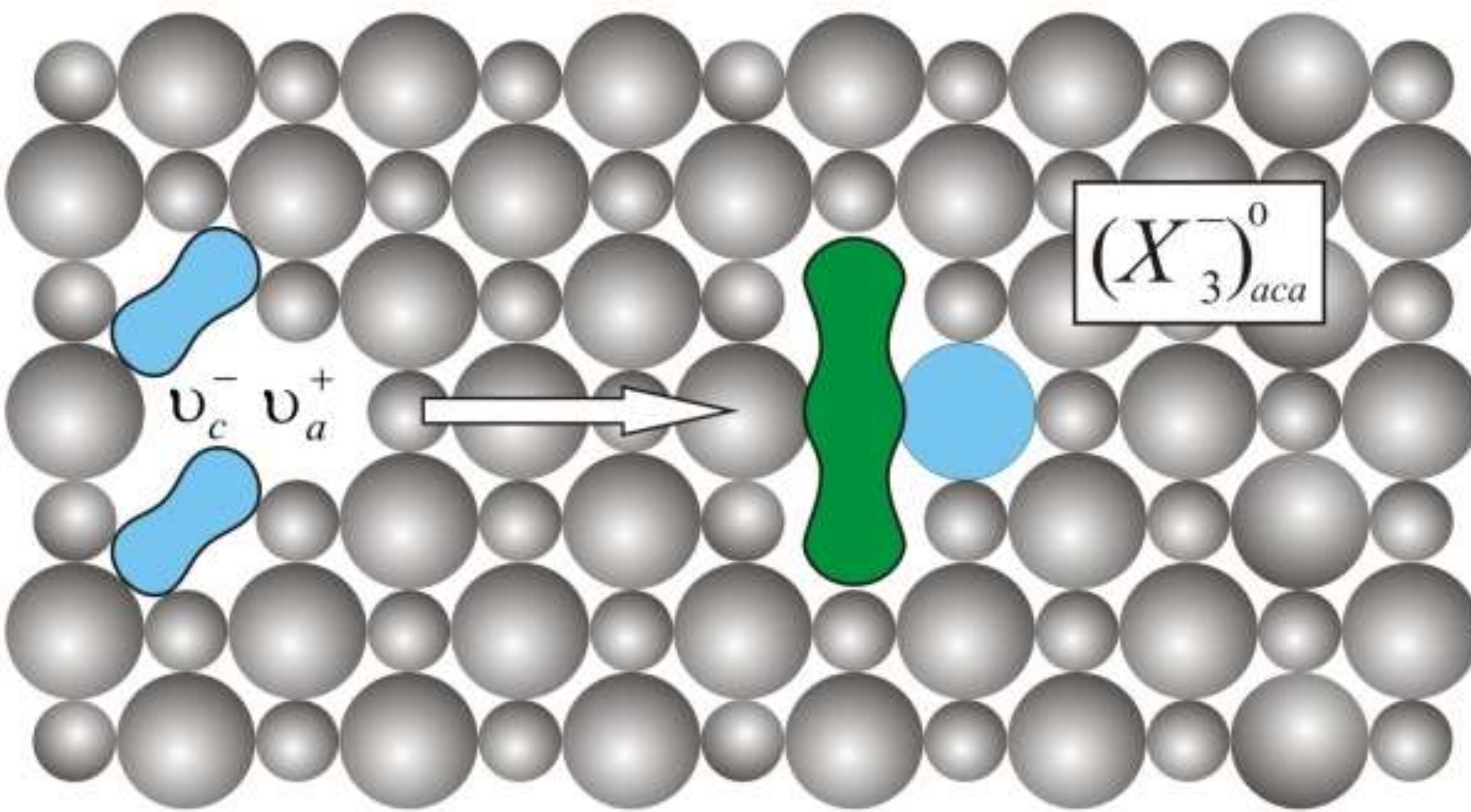
When X-ray irradiation at 300 K of a pre-plastically deformed KCl crystal (the osorption spectra were measured at 80 K), in addition to the elementary $(Cl_3^-)^0_{aca}$ enter, similarly to the KBr crystal, absorption spectra of $([Cl_2]_2)_{acac}$ centers with a aximum at 5.8 eV appear. When X-ray irradiation at 300 K, pre-plastic deformed KI ystal, in addition to the elementary $(I_3^-)^0_{aca}$ center (maximum absorption spectrum at 8 eV), similarly to KBr and KCl crystals, absorption spectra of $([I_2]_2)_{acac}$ centers with a aximum at 4.5 eV appear.

In KI crystals, plastic deformation (curve 2, Fig. 1) significantly increases the oncentration of $V_2 \equiv (I_3^-)^0_{aca}$ - centers, as well as the absorption band at 4.3 eV. In the terature [13] concerning the absorption band at 4.3 eV, it is discussed that this band is ue to I_3^-- centers. However, the fact that the absorption band at 4.3 eV in the KI crystal similar to the band at 5.3 eV in the KBr crystal, which is effectively created after astic deformation, when complex vacancy defects are created, allows us to interpret is band due to $V_3 \equiv ([I_2]_2)_{acac}$-centers. In the crystal lattice, the radiation formation of dimer type of $(I_2^-)_2$ is related, which, by its origin, as well as the (I_3^-)-center, can be rmed when two interstitial halogen atoms interact in the field of vacancy defects.

When X-ray irradiation at 300 K, pre-plastic deformed KI crystal, in addition to the ementary center - $(I_3^-)^0_{aca}$ (maximum absorption spectrum at 3.8 eV), similarly to KBr nd KCl crystals, absorption spectra of centers $([I_2]_2)_{acac}$ with a maximum at 4.5 eV opear.

Thus, in KBr, KCl and KI crystals, previously created by plastic deformation of di (u_c^- $_a^+$), - and a quartet of 2 [$u_c^- u_a^+$] vacancies, contribute to the formation of halogen diation defects of mainly $(X_3^-)^0_{aca}$ - centers when two interstitial halogen atoms teract, schematically presented in Fig. 2, according to the following reaction:

$$u_c^- u_a^+ + (X_2^-)^0_a + (X_2^-)^0_a \rightarrow (X_3^-)^0_{aca} + X_a^-$$



ig. 2. Diagram of interaction of two *H*-centers in the divacansion field ($\upsilon_c^-\upsilon_a^+$) with the formation $\upsilon_c^-\upsilon_a^+ + H + H \rightarrow (X_3^-)^0_{aca} + X_a^-$ - centers in AHC

The above experimental results suggest that pre-plastic deformation affects ndiation defect formation in KBr and KI mainly through numerous point defects that ccur during deformation.

In KBr, KCl and KI crystals, vacancy defects created by plastic deformation play the ole of a probe for stabilizing mobile interstitial halogen atoms, which effectively creates r_3^-, Cl_3^- and $(I_3^-)^0_{aca}$ centers, respectively.

The essence of further experiments on absorption spectroscopy is to investigate the echanisms of formation of $(X_3^-)^0_{aca}$ centers in KBr, KCl and KI crystals under a constant astic deformation that should change the migration of the interstitial halogen atom self. At low-temperature elastic deformation, vacancy defects are not created in the ttice as in the case of plastic deformation.

It should be noted that in contrast to plastic deformation with low-temperature astic deformation, experiments are carried out under the influence of stress at 80 K in e compressed state of crystals.

The main method was to compare the absorption characteristics of radiation defects nd the efficiency of their creation when irradiated in the isodose mode with X-rays in vo samples at 80 K: undeformed and uniosompressed. To eliminate the homogeneities of the crystals for comparative experiments, the samples were mirror alves that appeared during the split. Experiments on elastic deformation of crystals ere carried out as follows: the crystal was cooled to the temperature of liquid nitrogen high vacuum in the cryostat (the real temperature of the crystal is 90-100 K), and en at this temperature the deformation was carried out to the degree of 1-1.5 %, hich corresponded to the elastic part of the deformation.

Figure 3 shows the optical
osorption spectra of KBr, KCl,
nd KI crystals irradiated with
-rays at 80 K. As can be seen
om the comparison of the
osorption spectra of
ndeformed (curve 1) and
niaxially deformed crystals at
w temperatures (curve 2), the
ature of radiation defects
ccurring in both cases does not
nange when the load is
oplied.

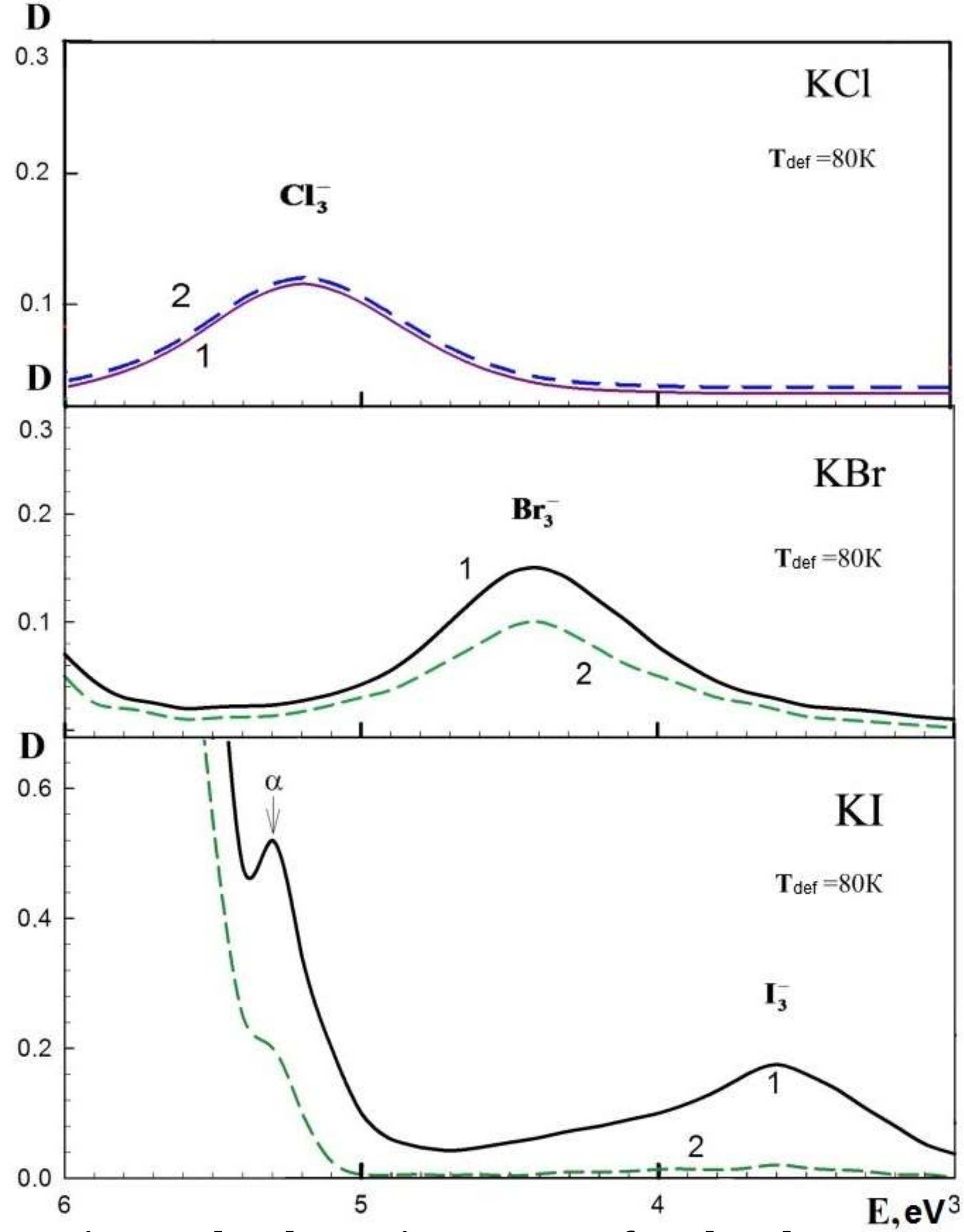


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Fig. 3. Effect of low-temperature elastic deformation on the absorption spectra of KCl and KBr crystals after X-ray irradiation for 3 hours at 80 K. 1 – in the absence of deformation; 2 – at low temperature (at 80 K) deformation (ε =1.5%).

In all crystals, the main radiation defects are *F*-, $(X_3^-)^0_{aca}$ -centers (here *X*-halides): in Cl crystals, the *F*- and Cl_3^--centers have absorption bands with maxima at 2.3 and 5.2 V, respectively; in KBr crystals, the *F* - and Br_3^- - centers at 2.06 and 4.6 eV, espectively; in KI crystals, the *F* - and I_3^-- centers at 1.87 and 3.6 eV. The creation of α-enters (excitation of a halogen in the anion vacancy field) is also seen in KI crystals.

In KCl and KBr crystals, the concentration of *F*-centers remains unchanged when the oltage is applied (look at curves 1 and 2, Fig. 3). This indicates that there are no gnificant changes in the efficiency of creating stable radiation defects. Remain that uring plastic deformation of crystals, the effect of increasing the efficiency of creating $X_3^-)^0_{aca}$ - centers were registered.

Thus, for KCl and KBr crystals, elastic low-temperature deformation leads to a ecrease in the efficiency of creating $(X_3^-)^0_{aca}$-centers, in contrast to plastic deformation, here di-and a quartet of vacancies are pre-create.

The absorption spectrum of KCl and KBr crystals shows that both in the absence and t low-temperature elastic deformation, there are no additional absorption bands haracteristic of local radiation defects.

Note that in the KBr crystal, compared to the KCl crystal, the efficiency of creating $X_3^-)^0_{aca}$-centers is noticeably reduced.

Low-temperature elastic deformation has a completely contrasting effect on the fficiency of radiation defect formation in the KI crystal. The number of radiation efects in a stressed crystal is more than an order of magnitude lower compared to what formed in an unstressed crystal. Moreover, the number of both complementary *F*- and - centers and α-centers decreases (i.e., the efficiency of creating the latter follows the fficiency of creating *F*- and I_3^--centers).

Fig. 3 clearly shows a decrease in the rate of radiation defect formation when pplying mechanical stress and a decrease of about 5 times the concentration of *F*-enters. The arrow indicates the direction of decreasing the concentration of I_3^--centers.

Various reasons can lead to a decrease in the efficiency of creating stable radiation efects in the AHCs when the lattice symmetry decreases: either the exciton decay hannel into *F, H* - pairs becomes unprofitable, or reverse recombinations increase due difficulties in separating primary *F, H* defects, or the efficiency of the association of terstitial *H*-centers decreases.

The first two reasons for reducing the efficiency of radiation creation X_3^--centers ads to the closure of the channel of non-radiative decay of electronic excitations, and ne third reason depends on the interaction distance of the mobile halogen atom etween each other in a stressed lattice. Thus, based on the results obtained, it can be oncluded that at 80 K, the application of uniaxial compression and X-irradiation cause a rong decrease in the efficiency of creating stable radiation defects in the KI crystal, hile a similar effect does not change the efficiency of radiation defect formation in ure KCl and KBr crystals. Experimentally, using the example of a KI crystal, we also ound that the effect of reducing defect formation is due to the elastic part of the niaxial deformation of the crystal and that it is not associated with a change in the ssociation of primary interstitial defects in a stressed sample.

Thus, the only explanation for the reason for the decrease in defect formation in ressed KI crystals remains a decrease in the efficiency of the non-radiative channel for ne decay of excitons to radiation defects in the elastic deformation field of the lattice

CONCLUSION

The mechanisms of effective creation of X_3^--centers in a local ecrease in symmetry by the light cation field, plastic and elastic eformation have been studied by the experimental method of bsorption (absorption spectra) and thermal activation (ionic onductivity and thermostimulated depolarization currents) pectroscopy in a wide temperature range (80-300 K) :

– In pre-plastically deformed KCl, KBr and KI crystals, $V_2 \equiv (X_3^-)^0{}_{aca}$-enters are effectively created when two interstitial halogen atoms nteract in the divacancy field ($\upsilon_c^- \upsilon_a^+$).

– In pre-plastically deformed KCl, KBr and KI crystals, absorption ands of $V_3 \equiv ([X_2]_2)_{acac}$-centers are registered, which are formed when wo interstitial halogen atoms interact in the vacancy – 2 ($\upsilon_c^- \upsilon_a^+$) uartet field.

– The absorption spectrum of crystals of KCl, KBr and KI has stablished the following regularities: in KCl crystals elastic tension oes not affect the radiation efficiency of the creation $(Cl_3^-)^0{}_{aca}$-centers n the crystal KBr is a redistribution of halogen radiation defects in the rystal KI elastic deformation leads to a decrease in the efficiency of reation of radiation defect $(I_3^-)^0{}_{aca}$-centers.

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