PARAMAGNETIC FRENKEL DEFECTS IN IRRADIATED ALKALI-HALOID CRYSTALS

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In the EPR spectra of γ-irradiated NaF, 6LiF, and LiF crystals with natural content of isotopes (independent of the impurity composition), the hyperfine structure (HFS) is observed against the background of a broad band. Absorption saturation in the system of defects responsible for the HFS and the broad band occurs at widely different power levels of microwave radiation, and broad band suppression takes place at registration in quadrature. The experimentally measured intensity distribution and the number of EPR lines in the 6LiF crystal correlate with the calculated data when the spin interaction of an unpaired electron with 14 equivalent fluorine nuclei is taken into account. A model of major radiation-induced paramagnetic defects in the form of Frenkel pairs, in which one component (the negatively charged quasi-molecule consisting of two halogen atoms) can be responsible for the HFS and the other component (F-center) for the broad band in the EPR spectrum, is proposed.

Keywords: hyperfine structure, alkali-haloid crystal, irradiation defect, two-component nature, EPR spectrum.

Introduction. The hyperfine structure (HFS), revealed by Lord in the EPR spectra of x-radiation-colored LiF and NaF crystals [1], has been the subject of many investigations that followed [2-7]. In all these works, the HFS was attributed to the unpaired electron localized in the region of the halogen vacancy, i.e., to the F-center. In a number of works devoted to the investigation of the changes in the parameters of crystals exposed to x-radiation [8-16], it is substantiated that the radiation coloration of these crystals is due to the formation of two-component defects, and in the case of coloration upon annealing under stoichiometry-breaking conditions, only one-component defects are formed. The existence of two-component defects in radiation-colored crystals is supported by the fact that these crystals are completely decolorized upon annealing, which is due to the annihilation of the components of Frenkel defects. At the same time, analogous annealing of crystals colored as a result of stoichiometry breaking does not affect the absorption intensity due to the fact that the components necessary for annihilation with F-centers are absent from these crystals. However, the spectra of the second component (the first component is an F-center) were recorded only for crystals irradiated at ~80 K [17, 18]. The lack of clear knowledge of the structure and properties of the main radiation defects predetermined the objective of the present work: to develop a model of radiation defects in alkali-haloid crystals that will describe their optical and paramagnetic properties.

Model of Major Paramagnetic Defects. Figure 1 shows variants of the proposed model of a two-component defect differing in the distance between the components. The first component is a halogen vacancy with

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Fig. 1. Variants of the model of a paramagnetic two-component defect in alkali-haloid crystals: $F$-centers (1) positioned in the 2nd (a), 3d (b), and 5th (c) coordinate spheres of a negatively charged quasi-molecule (2) consisting of two halogen atoms.

an electron localized in its region ($F$-center), the second component is formed on the basis of a displaced halogen atom in the form of a negatively charged quasi-molecule consisting of two halogen atoms (($FF_1^-$, $(ClCl)_2^-$, etc.). Both components of such a Frenkel defect are similar in charge to halogen ions of a defect-free lattice, and their stabilization is provided by the unpaired electron. At the same time, the components of a potentially possible two-component defect in the sublattice of alkali ions cannot be stable because of the absence of the necessary stabilizing element.

The negatively charged quasi-molecules consisting of two halogen atoms are known as $V_\alpha$-centers [19]. $V_\alpha$-centers are formed at low-temperature ($T < 80$ K) irradiation and are stable in certain crystals at temperatures up to $130$ K. According to the model proposed, a $V_\alpha$-center is the second component of a thermally unstable Frenkel defect (Fig. 1a). The comparatively high localization of the unpaired electron within the quasi-molecule predetermines the weak spin-lattice interaction and the large paramagnetic relaxation time. The above-indicated molecules are similar in their structure and paramagnetic properties to the thermostable ($HH_2^-$)-type quasi-molecules [20, 21], which are also characterized by a high degree of localization of the unpaired electron.

Calculations [22] show that the internuclear distance in a quasi-molecule ($FF_1^-$) is very sensitive to the parameters of the crystalline surrounding. The cases presented in Figs. 1b and 1c are similar to each other, but they differ from the variant presented in Fig. 1a not only in the distance between the components, but in the crystalline surroundings of the quasi-molecules as well. In this case, the EPR spectra of such quasi-molecules and $V_\alpha$-centers should naturally have both similar features and distinctions.

The electron density in the first component of the Frenkel defect is delocalized practically over all six alkali ions of the first coordination sphere. Such delocalization can provide a strong spin-lattice interaction of the unpaired electron with six metal ions and 24 halogen ions located in the second and third coordination spheres. The strong spin-lattice interaction predetermines the short paramagnetic relaxation time (accordingly, the absence of paramagnetic absorption saturation) and the large width of the absorption line. An additional contribution to the line broadening is made by the HFS unresolved because of the delocalization of the electron density.

The distance between the components predetermines the thermostability of the Frenkel defect. In the case where the first coordination spheres of the second component (quasi-molecule) and the first component ($F$-center) are in contact, the thermodissociation of the quasi-molecule is sufficient for the components to be annihilated (Fig. 1a). Figures 1b and 1c show variants of a thermostable two-component defect in which the components separate three and five coordination spheres (the model also admits variants with a larger distance between the components). In these variants, as compared with the variant presented in Fig. 1a, the thermo-