

Decay of electronic excitations into radiation defects in ionic crystals

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This article reviews the fundamental experimental and theoretical results on the nature of radiation defects and the mechanism of their production in ionic (mainly alkali-halide) crystals. We show that one can produce high concentrations of radiation defects in these crystals by irradiating with photons and particles whose energies do not suffice to displace atoms from lattice sites in elastic collisions with them. On the other hand, excitons and band holes in these crystals have a tendency to autolocalize in the regular lattice. In certain electronic states, excitons prove to be unstable with respect to decay into Frenkel' defects. This is the reason for the low radiation stability of many ionic crystals. We discuss the mechanisms of the above-cited instability and of secondary processes (localization, recombination, charge transfer) in which the products of exciton decay participate, as well as a possible role of such processes in other types of solids.

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1. INTRODUCTION

During the past decade, the problem of the radiation stability of solids has emerged as one of the most important among the many current problems of solid-state physics. On the one hand, this involves the vigorous development of nuclear power, where materials with very high radiation stability are needed. On the other hand, active media are needed for computer technology for optical and electron-beam memories whose sensitivity to irradiation is higher than that of existing materials.

The search for and development of radiation-stable and radiation-sensitive materials must rest on a clear understanding of the mechanisms of production of radiation defects in crystals. Radiation damage in metals and in homopolar semiconductors has been described in the monographs^[1-4].

The aim of this review is to examine the features of production of radiation defects in another important class of solids, the ionic crystal-dielectrics.

Roentgen, Joffe, Pohl, Hilsch, Kurchatov, Tartakovskii, and others^[5-8] took up the study of the changes in properties of the simplest ionic crystals (e.g., NaCl) under irradiation at the very dawn of modern solid-state

physics. The creation of quantum crystal theory set these studies on a firm scientific foundation.^[9-11]

A simple fact was the key to understanding the processes of radiation defect formation in ionic crystals. Powerful irradiation in NaCl crystals by neutrons and γ rays in a vertical channel of a nuclear reactor was shown to yield practically the same results as does irradiation by medium-energy x rays or even ultraviolet irradiation, which selectively creates excitons or separate electrons and holes.^[12] This led to the hypothesis that the radiation instability of ionic crystals is based on the decay of electronic excitations into structural Frenkel' defects. This hypothesis was independently and simultaneously advanced and developed in the USSR,^[13-19] the USA,^[20-22] and England,^[23-25] and it has successfully withstood a decade of testing of its soundness.

In spite of its seeming simplicity, this approach was unexpected and unusual. For a long time, electronic excitations and structural defects had been studied separately in solid-state physics. The discovery of decay of electronic excitations into structural defects required a joint treatment of these phenomena within the scope of a general theory, while theoreticians have approached designing the latter only very recently.^[26, 27] The need

is still felt very keenly of discussing the overall physical pattern of the decay of electronic excitations into structural defects on the basis of the existing experimental data.

2. MECHANISMS OF PRODUCTION OF RADIATION DEFECTS

A. Production of defects in elastic collisions

In most solids, including metals and semiconductors, radiation point defects arise mainly from elastic collisions of the electrons, protons, and other primary particles incident on the crystal (or arising in the crystal) with the nuclei of the atoms of the crystal (see Refs. 1-4). At moderate energies, the primary interaction event is simple: an elastic pair collision that obeys the classical laws of conservation of energy and momentum.

If the primary particle has the kinetic energy E_0 and the mass m , while the mass of the atoms in the crystal is M , then an atom that is displaced from its crystal-lattice site in a pair collision at the angle φ to the direction of incidence of the primary particle acquires the energy

$$E = E_0 \frac{4Mm}{(m+M)^2} \cos^2 \varphi. \quad (2.1)$$

If the transferred energy is larger than some threshold value E_d , then a Frenkel' pair of defects is produced. The atom that is ejected from its site travels away from the created empty site (vacancy) via the interstices (diffusion or channeling), or through a chain of focusing collisions. In the case $E \gg E_d$, the primary displaced atoms can cause a cascade of secondary displacements, whereby several Frenkel' pairs arise. The situation can be analyzed by using model concepts that originate in a study by Kinchin and Pease,^[28] with the use of contemporary computer methods that have been applied by Vineyard^[29] and others (see the detailed review^[30]).

A characteristic feature of the mechanism of elastic pair collisions is the existence of a minimum value E_0 below which defects can't be produced.

At large energies E , the model of elastic pair collisions

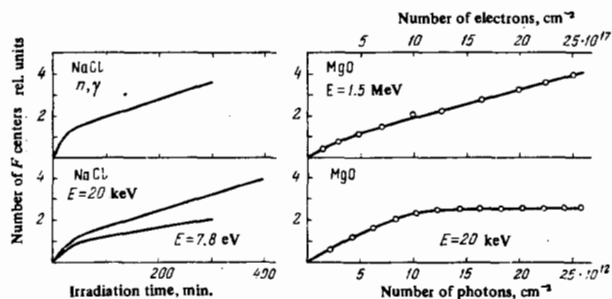


FIG. 1. Relationship of the number of color centers to the time (dose) of irradiation at room temperature for monocrystals of NaCl and MgO. The NaCl crystals were irradiated in a vertical channel of the IRT-2000 reactor^[12] with x-rays of mean energy 20 keV^[12] or with 7.8-eV photons.^[40] The MgO crystals were irradiated with 1.5-MeV electrons^[33] or 20-keV x-rays.^[42]

falls, and we must consider the interaction of the primary particle with a certain region of the crystal, rather than with a single atom. Disordered regions of the crystal (the so-called spikes) arise from this type of interaction. A review of the phenomena that arise here in semiconductor systems is given in the monograph, Ref. 31.

Impact mechanisms for producing radiation defects are universal. They occur even in ionic crystals. A machine calculation of such processes for NaCl and KCl has been performed in Ref. 32. Impact mechanisms of defect formation have been studied experimentally in monocrystals of MgO.^[22, 33, 34] The threshold energy in magnesium oxide for displacement of the oxide ions by electrons is 330 keV, which corresponds to an energy $E_d = 60$ eV.

B. Production of defects in decay of electronic excitations

When particles and quanta interact with solids, they spend most of their energy in exciting the electronic subsystems of the crystals. The varied electronic excitations that arise here can cause the appearance of radiation defects.

Seitz^[11] first studied the possibility of radiationless annihilation of excitons near jogs in dislocations, whereby the dislocation jog can be displaced with simultaneous creation of a vacancy. This hypothesis has been thoroughly tested experimentally in crystals having an elevated concentration of dislocations and in dislocation-free whisker crystals.^[35, 36] It has been convincingly shown that dislocations do not play the decisive role in producing radiation defects in ionic crystals.

Varley^[37] first studied the possible production of Frenkel' defect pairs upon double ionization of the halide ions in alkali-halide crystals. This process gives rise to an unstable group of seven positive ions lying alongside one another. In principle, it can break up by ejecting the positively charged halogen from its crystal-lattice site into an interstice. This hypothesis has also been subjected to detailed experimental tests near the double-ionization thresholds of the halide ions.^[38] They showed (for more details, see Chap. 7) that processes of double (and multiple) ionization of the crystal-forming particles also do not play the decisive role in producing radiation defects in alkali-halide crystals.

Experiments have shown^[12, 14, 39-41] that radiation defects in alkali-halide crystals arise efficiently upon optical generation of excitons or separate electrons and holes. Figure 1 demonstrates this effect in simplest form, where the curves for accumulation of color centers (F centers) are compared for NaCl monocrystals that have been irradiated with neutrons and γ rays in a vertical channel of a nuclear reactor,^[12] with x rays having a mean quantum energy of 20 keV,^[12, 40] and with 7.8 eV photons,^[40, 41] which selectively produce excitons in NaCl. In all three cases, the rapidly growing stage is followed by a less efficient growth in the number of F centers up to high densities of the order of 10^{18} cm⁻³, which considerably exceed the possible content of struc-

tural defects before irradiation.

The process of production of F centers occurs in a completely different way in MgO . Here one observes a linear stage of increase in the number of defects only upon irradiating with fast electrons (1.5 MeV) or in a reactor.^[22, 33, 34] Under the action of x rays, the number of F centers rapidly reaches a saturation level (see Fig. 1) that is determined by the number of oxygen vacancies that had existed in the crystal before irradiation.^[42]

Thus in some but not all ionic crystals, nonradiative decay of excitons and nonradiative recombination of electrons and holes can serve as the cause of formation of radiation defects.

Rabin and Klick^[43] convincingly showed that the processes of production of radiation defects at liquid-helium temperatures are almost independent of the presence in the crystal of impurity or structural defects, and they amount to the production of Frenkel' pairs in regular regions of the crystal structure (for more details, see Ref. 44).

Analysis of the above-cited facts has led Vitol, Lushchik, and Élango,^[13-16] Hersh,^[20, 21] and Foley^[23-25] to the hypothesis that electronic excitations in regular regions of the crystal decay into Frenkel' defects. Vitol^[13] and Hersh^[20] have advanced the hypothesis that excitons decay into neutral F centers and interstitial halogen atoms. Pooley^[23] has proposed the possible radiationless recombination of electrons and holes to yield charged defects: halide vacancies and interstitial halide ions. In order to proceed to discussing these processes, we must first examine in greater detail the nature of the intrinsic electronic excitations and structural defects in ionic crystals.

3. ELECTRONIC EXCITATIONS

Various types of electronic excitations can exist in ionic crystals: conduction electrons (henceforth denoted

as e and e^-), hole (e^+), excitons (e^0), etc.

The intrinsic electronic excitations of ionic crystals have been studied in detail from the spectra of the characteristic energy losses of electrons,^[45] from thin-layer absorption spectra,^[46] and the reflection spectra of monocrystals,^[47] from which one can calculate the spectra of the optical constants $\epsilon = \epsilon_1 + i\epsilon_2$.

Figure 2 shows the absorption spectra for KCl , KBr , and KI crystals.^[48] The narrow bands at long wavelengths correspond to production of excitons at the Γ point of k space. Since the hole component of an exciton (a p -hole) can exist in two states having $j = 3/2$ and $j = 1/2$, two absorption bands correspond to exciton production that have a spin-orbital splitting of about 0.1 eV in KCl , 0.5 eV in KBr , and 0.9 eV in KI .

The intrinsic luminescence spectra are far more complex (see Fig. 2). An intense broad emission band at 3.3 eV was found for KI long ago that has a considerable Stokes shift with respect to the intrinsic absorption.^[48] As subsequent studies have shown,^[49-52] the former corresponds to radiative annihilation of dihalogen autolocalized excitons, the hole component of which is localized on two halide ions (X^-), and which has the quasimolecular structure X_2^- . For KBr and KCl , the corresponding bands lie at 2.4 and 2.3 eV. The stated luminescence bands correspond to triplet-singlet $^3\Sigma_g^- - ^1\Sigma_g$ transitions, and they have π -polarization and lifetimes of 10^{-6} - 10^{-3} sec. For dihalogen excitons in KBr and KI of the type X_2^-e , $^1\Sigma_u^+ - ^1\Sigma_g$ singlet-singlet transitions (4.4 and 4.2 eV) having σ -polarization and lifetimes of 10^{-8} - 10^{-9} sec have also been found.

Recently Kuusmann *et al.* have found (see Ref. 53) a weak luminescence of alkali-halide crystals. They ascribed it (though without strict proof) to emission from autolocalized monohalogen excitons X^0e (6.7 eV in KCl ; 6.2 and 5.7 eV in KBr ; 5.1 eV in KI). Moreover, a weak edge emission from free excitons has been found in the alkali iodides.^[53-55] For KI , the maximum of this emission lies at 5.75 eV, and it immediately adjoins the long-wavelength intrinsic absorption band. Longitudinal-transverse splitting occurs for free excitons in alkali-halide crystals.^[56]

Perhaps excitons exist in three studies in alkali-halide crystals: in the form of free excitons (e^0), in the form of autolocalized monohalogen excitons (X^0e), and in the form of autolocalized dihalogen excitons (X_2^-e).^[53] The X_2^-e excitations are practically immobile at 4° and 77°K. They efficiently undergo saltatory diffusion at temperatures above 110°K in KI , 175°K in KBr , and 210°K in KCl .^[57]

The free-flight paths of free excitons in alkali-halide crystals sharply increase with falling temperature, where the autolocalization processes are highly frozen out because self-trapping of excitons requires an activation energy.^[53-57] Rashba^[58] has treated this problem theoretically.

We can propose a pictorial model of the exciton states in alkali-halide crystals that is based on the existing experimental results. Figure 3 shows the relationship

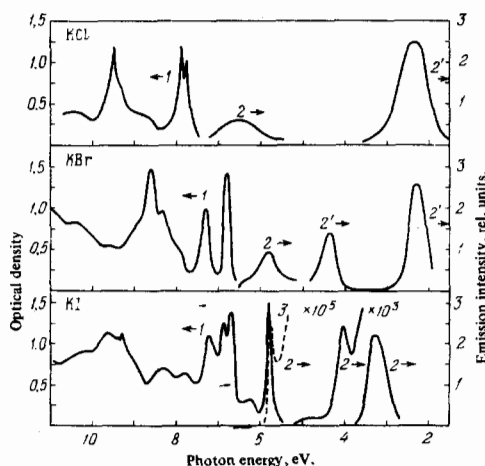


FIG. 2. Intrinsic optical absorption (1) and intrinsic luminescence (2, 2') of KCl , KBr , and KI . The absorption spectra (1) of thin films were measured at 77°K.^[45] The luminescence spectra of monocrystals were measured at 77°K (2) upon excitation with 5-keV electrons^[53, 54] or at 5°K (2') upon excitation with 8-eV photons.^[46]

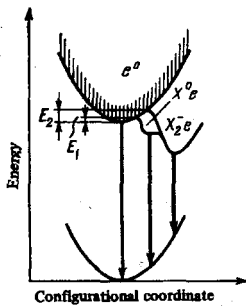


FIG. 3. Schematic relationship of the energy of free excitons e^0 and of autolocalized excitons to the configurational coordinate. The activation barriers E_1 and E_2 are shown for one-center $X_1^0 e$ and two-center $X_2^0 e$ autolocalized excitons. The arrows indicate radiative transitions.

of the energies of free and autolocalized excitons to the generalized configurational coordinate of the heavy particles. In three-dimensional systems autolocalization is possible only at finite deformations that require an activation energy. We can study two activation barriers for alkali-halide crystals: for monohalogen and dihalogen autolocalization (E_1 and E_2). Of course, transitions can also occur between two autolocalized states. For NaI, KI, and RbI, the activation energy for the two-center autolocalization process $E_2 = 15\text{--}20$ meV. For KCl and KBr, the activation energy for one-center autolocalization is less than the energy of the zero-point vibrations, and autolocalization does not freeze out even at 1.8°K .^[56]

Separate electrons and holes arise in the crystals at photon energies exceeding the width of the forbidden band ($E_g = 8.5$; 7.2 ; and 6.4 eV in KCl, KBr, and KI, respectively). Electrons in alkali-halide crystals move through the crystal so quickly that the inertial ionic polarization in the vicinity of a conduction electron is insignificant, and the effective mass of polarons in alkali-halide crystals exceeds the effective mass of band electrons by a factor of less than two.^[59] Holes in alkali-halide crystals move considerably more slowly through the crystal, and the inertial polarization causes a sharp rise in the effective mass of the hole polarons. The phenomenon of autolocalization of holes in alkali-halide crystals is complicated by the possible transformation of relaxed monohalogen holes of the type X^0 into dihalogen molecular states of the type X_2^0 , which Castner and Känzig^[60] have found experimentally by EPR in all alkali-halide crystals, and which have been called V_K centers. Band holes are able to migrate through the crystal structure before autolocalizing only to distances of the order of $10a$ (a is the lattice constant).^[61, 62]

As the existing theories imply,^[63] in ionic crystals activation energy is not needed for autolocalization of charged holes (in contrast to neutral excitons). In alkali-halide crystals, the formation of V_K centers is not frozen out, even at extremely low temperatures.^[64] In KCl and KBr, excitons of the type $X^0 e$ can arise upon recombination of electrons with monohalogen holes, and autolocalized excitons of the type $X_2^0 e$ upon recombination of electrons with V_K centers.

The spectra of the optical constants of the alkali-halide crystals have been studied over a broad range of energies in the last few years by using synchrotron radiation, including the vacuum ultraviolet and the soft x-ray region. The existence of currentless excitations of cations

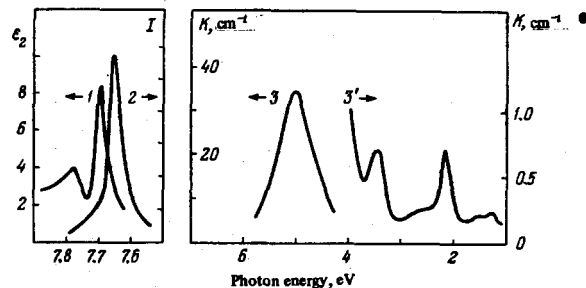


FIG. 4. Optical characteristics of MgO monocrystals. The spectra $\epsilon_2(h\nu)$ ^[66] (1) and the cathodoluminescence spectra^[67] (2) were measured at 77°K , and the absorption spectra (3, 3') were measured at 300°K on MgO crystals that had been irradiated with neutrons.^[22]

(cationic excitons) and of inner electron shells (x-ray excitons) has been established. Energies of 60, 33, and 22 eV, respectively, are needed to produce cationic excitons in the halides of lithium, sodium, and potassium (see, e.g., Ref. 65).

The features of the intrinsic electronic excitations in other binary ionic crystals have been reviewed in Refs. 53 and 56. For MgO monocrystals, which are of greatest interest from the standpoint of this review, the spectrum of $\epsilon_2(h\nu)$ is given^[66] in Fig. 4. The narrow long-wavelength band corresponds to production of F-excitons. An edge luminescence of free excitons has recently been found in MgO that is almost in resonance with the absorption (see Fig. 4).^[67] In MgO, neither excitons nor electrons nor holes enter into the autolocalized state.

4. STRUCTURAL POINT DEFECTS

Alkali-halide crystals can contain several types of structural point defects: anion and cation vacancies (v_a^- and v_c^+), and interstitial anions and cations (i_a^- and i_c^+). Frenkel^[68] introduced the concept of creation of pairs of defects v_a^- and i_a^- , and v_c^+ and i_c^+ . Schottky showed the possible existence of pairs of defects v_a^- and v_c^+ .^[69] In principle i_a^- and i_c^+ pairs can also exist.

The theoretical calculations of the enthalpy of creation of Frenkel' and Schottky defect pairs (E_F and E_S) under thermodynamic-equilibrium conditions in alkali-halide crystals have been discussed in Ref. 10. They have recently been refined by Schulze and Hardy (Table I).^[70] All of the alkali-halide crystals have $E_S < E_F$.

TABLE I. Enthalpy of Schottky and Frenkel' defects in alkali-halide crystals^[70] (in eV).

Crystal	E_{Sch}	$E_{Fre, anion}$	$E_{Fre, cation}$
NaF	2.49	3.39	3.53
NaCl	2.26	4.60	2.88
NaBr	2.11	4.84	2.56
NaI	1.77	5.45	2.00
KF	1.96	2.67	4.27
KCl	2.20	3.73	3.46
KBr	2.19	4.47	3.16
KI	2.00	4.26	2.73

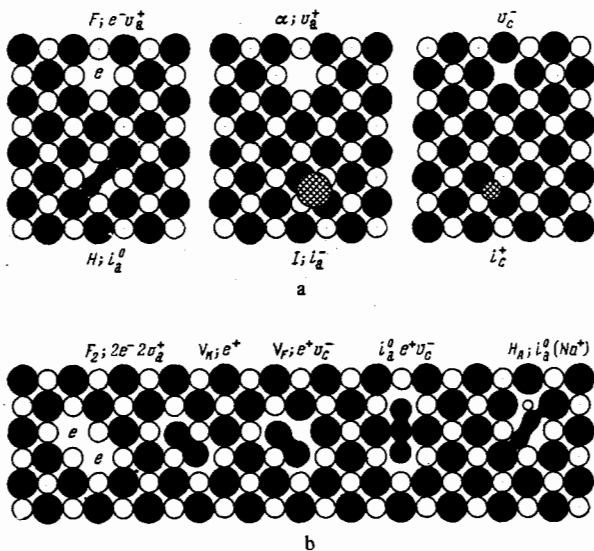


FIG. 5. Models of some defects in alkali-halide crystals. a) Pairs of complementary defects; b) an autolocalized hole and some very simple associations of defects.

In view of this important theoretical conclusion, people generally consider that Schottky defects dominate in alkali-halide crystals. This situation is actually characteristic of thermodynamic-equilibrium conditions,^[11] but an attempt to extend the notion of predominating Schottky defects to the case of irradiated alkali-halide crystals^[11] has met insurmountable difficulties. Under non-equilibrium conditions, alkali-halide crystals contain not only Schottky defects but also Frenkel' defects, both in the anion sublattice (see the reviews^[44,71]) and in the cation sublattice (see the reviews^[72,73]).

Figure 5 shows models of the different point defects in alkali-halide crystals labeled with the historically established symbolic notation for the different centers that we have used and which has been adopted in the literature on the alkali-halide crystals.

Existence of anion vacancies in alkali-halide crystals has been proved by measuring the ionic conductivity.^[10,11] Excitation of halide ions near a v_a^+ corresponds to the characteristic α -bands on the long-wavelength slope of the excitation absorption bands.^[74] F centers ($v_a^- e^-$) arise by trapping of electrons by anion vacancies, and they are justly considered to be the most studied defects in solids.^[44]

Figure 6 shows the absorption spectrum of a KBr crystal that had been irradiated at 5 °K with x rays. The band with the peak at 2.05 eV corresponds to optical excitation of F centers. The band in the region of 6.2 eV corresponds to excitation of halide ions near anion vacancies. In addition to the F and α -centers, the so-called H and I centers (3.3 eV and 5.4 eV) also arise in KBr upon irradiation.

The H centers have been studied in detail by EPR.^[75] They have been established as consisting of X_2^- molecules lying in single anion sites of the crystal. Their absorption is close to that of the V_K^- centers (X_2^- molecules occupying two anion sites). An H center is physi-

cochemically equivalent to an interstitial halogen atom. In KBr, the H centers diffuse through the crystal at temperatures $T > 30$ °K. The existence of interstitial halide ions was first shown in Gebhardt's experiments^[76] on the thermal resistivity of the crystals. The interstitial halide ions distort large regions of the crystal structure, and they scatter phonons efficiently. Annealing of the thermal resistivity induced by irradiation runs parallel with the annealing of the 5.4-eV absorption band in KBr, which has been ascribed to interstitial bromide ions, or the so-called I centers.^[77] Experiments that studied in parallel the changes upon irradiation of the volume of the crystal and of the lattice constant have fully confirmed the existence of interstitial halide ions, and have shown that they correspond to I centers. In irradiated KBr crystals, the I centers anneal in parallel with the α centers in the temperature range 15–30 °K. The properties of H and I centers in the alkali-halide crystals have been reviewed in Ref. 71.

Cation defects in alkali-halide crystals have as yet been insufficiently studied explicitly. Measurements of ionic conductivity have permitted people to get some information on the number and mobility of the cation vacancies.^[10,11] The ionic conductivity of NaBr, KBr, and KCl that involves movement of v_c^- increases under the action of protons and x rays.^[72,76,79] As has been shown by EPR,^[80,81] V_F^- centers ($v_c^- e^+$) arise upon trapping of a hole by a v_c^- , and they are the "antipodes" of F centers. With increasing radiation dose, more complex structures arise in alkali-halide crystals, made of cation vacancies, holes, and interstitial atoms, which have the structure $v_c^- e^+ i_a^0$.^[72,82–84] The spectral characteristics of these centers (an absorption band at 4.6 eV in KBr) are determined by X_3^- molecules that lie in two anion vacancies and one cation vacancy.

There is as yet no strict proof of the existence of interstitial alkali ions in irradiated alkali-halide crystals. There are only mentions of anomalously rapid diffusion of a radioactive isotope of sodium in NaCl crystals at 300–400 °K that couldn't be ascribed to a vacancy diffusion mechanism.^[85] As is proposed in Ref. 84, NO_2^- ions can serve as effective traps for i_c^+ .

Structural defects in $A^{IV}B^{VI}$ ionic crystals have been studied considerably more poorly than in the alkali-halide crystals. Figure 4b shows the changes in the absorption spectra of an MgO monocrystal upon irradiation in a nuclear reactor.^[22] A band is well marked in the spectrum in the region of 5 eV (absorption by F^+ and

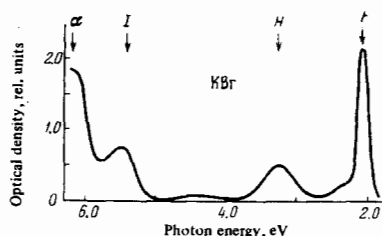


FIG. 6. Absorption spectra of a KBr crystal after irradiation with x rays at 5 °K.

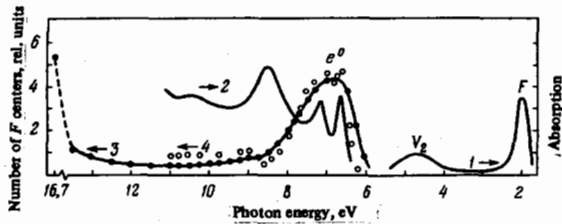


FIG. 7. Production of F centers in KBr crystals by ultraviolet radiation. Absorption spectrum of a thin film (2); the change in the absorption spectrum of the crystal after irradiation with 6.5-eV photons^[90] (1); and the excitation spectrum for luminescence photostimulated from the F centers $I_1(h\nu)$ ^[91] (3); and that for electronic emission $I_e(h\nu)$ ^[88] (4).

F centers, which amount to one or two electrons localized near an anion vacancy), and bands in the region of 2.3 eV (absorption by V^- and V^0 centers, which amount to one or two holes localized near a cation vacancy).^[33,80]

5. PRODUCTION OF DEFECTS IN DECAY OF EXCITONS AND RECOMBINATION OF ELECTRONS AND HOLES

A. Spectra of defect production

In order to study the decay of electronic excitations into structural defects, one must measure the relative and absolute efficiencies of generation of the various structural defects when the various intrinsic electronic excitations are selectively produced by vacuum ultraviolet (VUV) radiation. This problem has been solved by using highly sensitive luminescence and photoelectric methods of detecting small numbers of color centers.^[39, 41, 87-90]

The direct absorption method of determining the number of color centers produced by VUV irradiation has given definite results only for the irradiation of alkali-halide crystals in the region of the long-wavelength slope of the exciton absorption. Figure 7 shows the changes in the absorption spectrum of a KBr monocrystal of high purity after many hours of irradiation at 295 °K by 6.5-eV photons. The irradiation gives rise to F centers (band with a maximum at 2.05 eV) and V_2 centers (band with a maximum at 4.7 eV). One can get up to 10^{18} centers per cm^3 , which considerably exceeds the possible number of anion vacancies in the crystal before irradiation.^[90,11]

In order to measure the spectrum for production of F centers by fluxes of equal numbers of VUV quanta at different frequencies, Lushchik, Lid'ya, Yaek, and Kyaembre first applied methods based on detecting F centers from the intensity I_1 of recombination luminescence^[39, 40, 87] or that of electronic emission I_e .^[88, 89] These arise in the irradiated crystal upon illuminating it with photons in the region of the F absorption band. Figure 7 shows the $I_1(h\nu)$ and $I_e(h\nu)$ spectra for KBr

¹⁾Smakula^[91] observed in 1930 the appearance of F centers in KBr in an analogous irradiation. He used crystals that had been grown in air. They had a high content of OH^- ions, which are efficiently converted into F centers.

crystals. F centers are produced with maximum efficiency in KBr at 295 °K by 6.4–8.0-eV photons, which selectively generate excitons.^[88-91] F centers are also produced by optical generation of separate electrons and holes by photons having $h\nu > 8$ eV, and they give rise to excitons by recombination. A sharp increase in the number of F centers produced is observed in the region of 16.7 eV, where the photons generate photoelectrons so hot that they have enough energy to give rise to "secondary" excitons by electron impact.^[92, 93]

Analogous spectra for production of F centers at 295 °K have been measured for NaCl,^[12, 89, 94] KCl^[88, 91, 95] and KI.^[39, 88, 93] Spectra for production of F centers have been obtained for KI^[50, 87] and KCl^[95] at 80 °K, and for KI and KBr also at 5 °K.^[96] The absolute quantum efficiency for production of long-lived F centers in optical generation of monohalogen excitons in KBr at 295 °K is no lower than 0.1.^[97, 98]

Variants of thermoactivation spectroscopy have also been used to detect the products of decay of electronic excitations into structural defects. After KBr had been irradiated at 5 °K or 80 °K, the crystal was heated at a constant rate. During the heating process, the intensity of the luminescence that arose from recombination of various complementary defects was recorded (Fig. 8). The thermoluminescence (TL) peaks characterize the temperature ranges where the various defects become mobile. A thermoluminescence peak at 26 °K arises after irradiation of KBr with 7.8-eV photons at 5 °K, and it corresponds to the high-temperature stage of the thermal annealing of the I centers.^[96] After irradiation of KBr with 7.8-eV photons at 80 °K, thermoluminescence peaks arise at 110°, 145°, 175°, 235°, 330°, and 390 °K.^[99] The 175 °K peak corresponds to annealing of the EPR signal of the V_K centers, the 110 °K peak to annealing of the absorption of the H_A centers ($\frac{1}{2}e^-$ near an Na^+), the 235 °K peak to annealing of the V_F centers, and the 390 °K peak to annealing of the $v_c^+ \frac{1}{2}e^-$ centers.

Study of the spectra for production of the above-cited thermoluminescence peaks by VUV radiation has permitted showing that centers are produced upon optical generation of excitons and separate electrons and holes in KBr and KCl that undoubtedly contain interstitial halogen atoms.^[95, 99]

Thus another product of decay of excitons in KBr and KCl besides the F centers is the H centers. This is a

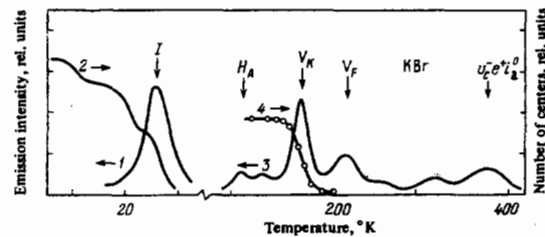


FIG. 8. Thermoluminescence of KBr crystals after irradiation with 7.8-eV photons at 5 °K^[96] (1) and at 80 °K^[99] (3), as well as the change in optical absorption by I centers (2) and in the EPR signal of the V_K centers (4). The rate of warming of the crystals is about 0.15°/sec.

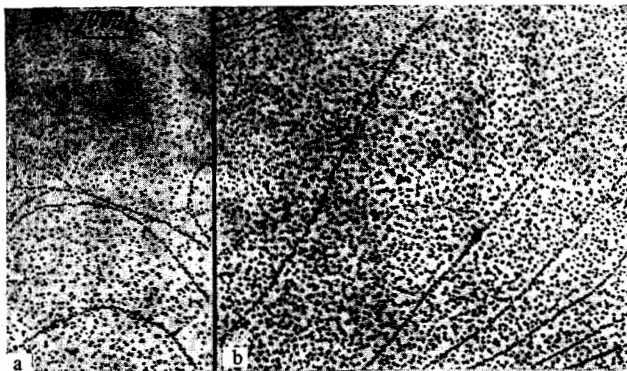


FIG. 9. Electron-microscopic observations of the decay products of excitons decorated with gold on the [100] surface of KBr crystals.^[101] Unirradiated surface (a), surface irradiated with 6.7-eV photons (b).

direct experimental confirmation of the hypothesis of Refs. 13 and 20. A thermoluminescence I peak^[98] could be detected after action of 6.9-eV and 7.7-eV photons on KBr at 5 °K, which give rise to excitons and separate electrons and holes. Production of cation vacancies has been found in KBr and NaBr upon optical generation of excitons and electron-hole pairs.^[72, 73, 82]

Excitons in KCl and KBr migrate for small distances until they autolocalize ($5a$ and $15a$, respectively).^[57] This creates favorable conditions for decay of excitons without participation of pre-irradiation defects, the number of which had been reduced in KCl and KBr purified by zone-melting to the level of 10^{16} cm^{-3} .^[72, 100]

In Ref. 101, the products of decay of excitons in KBr crystals were detected by electron microscopy. They used the method of Betge and Distler with preliminary decoration of the defects with metallic gold. Figure 9 shows electron micrographs of two cleavage faces of KBr. One of them was irradiated before decoration with 6.7-eV photons, which produce excitons, while the other was not irradiated. Generation of excitons leads to a manifold increase in the number of defects. Analogous effects that increase with dose were obtained for KCl and NaBr.

B. Defect production in recombinations of electrons and holes

Patten and Keller^[102] have performed an elegant EPR experiment that indicates the possible appearance of F and H centers upon recombination of electrons with V_K centers. A KCl-Tl crystal was irradiated with x rays at 77 °K. Thallium atoms Tl^0 arose upon capture of e^- by thallium ions Tl^+ . An equivalent number of e^+ became localized in the form of V_K centers. Optical destruction of the Tl^0 centers at 26 °K led to recombination of the electrons with the V_K centers and the appearance of H centers. Here the EPR signal of the V_K centers declined and an EPR signal of the H centers appeared. Estimates showed that 2–3 stable H centers are created per 100 recombinations in KCl-Tl.

Hall, Hughes, and Pooley^[103] have studied the production of H centers in KCl-Pb crystals upon recombina-

tion of electrons with V_K centers that had been oriented optically with linearly polarized light. Disoriented H centers arose upon recombination.

Zazubovich and Osminin^[104] have observed production of F and H centers in irradiated KCl-Tl crystals upon optical release of holes from Tl^{2+} centers and their recombination with the electrons of Tl^0 centers by tunneling. They determined the number of F centers by the absorption method, and the appearance of the H centers from the H thermoluminescence peak (43 °K).

C. Kinetics of pulsed defect production

An important contribution to the understanding of processes of radiation-defect production in alkali-halide crystals has come from a study by Ueta, Hirai *et al.* on the kinetics of production and disappearance of short-lived color centers using high-flux electron accelerators that gave nanosecond pulses of an electron beam of energy of the order of 1 MeV.^[105–108] By using a pulsed absorption technique over a broad temperature range (1.8–300 °K), they measured short-lived excited absorption spectra of crystals of KCl,^[105] KBr,^[106] KI,^[107] and NaCl.^[107] The spectra manifested both absorption by triplet dihalogen excitons (see also Ref. 109) and F -center absorption.

They measured the temperature-dependences of the efficiency of production of F centers (η_F). For KCl and KBr, η_F rises by a factor of five upon heating from 1.8 to 4 °K, with activation energies respectively of about 1 and 2 meV, whereas it varies little upon further heating.^[64] For KI, η_F is very small in the range 4–100 °K, and it rises sharply in the range 100–120 °K (activation energy 130 meV).^[107] For KI and RbI, the production of stable F centers upon irradiating in the region of the exciton absorption band has also been observed to freeze out.^[20, 39, 87]

References 105–108 have shown that the number of F centers in all the studied crystals increases to its maximum value in a time of less than 10 ns. Only in crystals having a large content of pre-irradiation anion vacancies is the growth time of the number of F centers measured in microseconds, while it coincides with the lifetime of F centers in the excited $2p$ state. In the latter case, the F centers arise by trapping of electrons by anion vacancies. Yet in crystals having a small number of pre-irradiation anion vacancies, the F centers arise in the ground $1s$ state.

Production of H and α centers has also been detected upon pulsed irradiation in KBr. At 5 °K, the number of F - H pairs produced was 50-fold greater than the number of α - I pairs. The number of F - H pairs rapidly declines after irradiation is stopped, while the number of α - I pairs varies little. Hence the number of F - H and α - I pairs becomes approximately equal. They interpreted this effect as resulting from annihilation of close-lying F - H pairs. In particular, the latter were revealed by the fact that the absorption bands of the F and H centers immediately after the irradiation had been stopped were somewhat broadened as compared with those of centers more remote from each other.^[106]

The time for production of F and H centers proved to be shorter in all crystals than the lifetime of triplet dihalogen excitons, or in KCl, that of singlet ones. Hence they drew the important conclusion that the decay into F and H centers does not arise from the radiation relaxed state of the dihalogen excitons.

Bradford, Williams, and Faust^[110] have studied production of F centers in KCl crystals acted on by picosecond laser pulses that produced electrons and holes in a two-photon process. The time for production of F centers in KCl at 10°K proved to be about 10^{-11} sec. That is, it was about two orders of magnitude longer than the optical-vibration period.

6. MECHANISMS OF DECAY OF ELECTRONIC EXCITATIONS TO PRODUCE DEFECTS

A. Models of decay processes

Hersh^[20] and Pooley^[23] have studied the decay of auto-localized dihalogen excitons into structural defects as resulting from predissociation of excited X_2^-e molecules. Similar processes have been studied long ago for free diatomic and polyatomic molecules.^[111,112] Figure 10 shows the adiabatic potentials of a diatomic molecule as a function of the distance between the nuclei. In line with the Franck-Condon principle, a state arises upon photoexcitation (the transition 1-2) that has a considerable excess of vibrational energy. If the molecule possesses the state 3 that has a repulsive potential, then radiationless 2-3 transitions can arise as it passes through the region α during vibrational relaxation, and the molecule dissociates into atoms.

Of course, the situation is more complex for diatomic molecules within a crystalline lattice. Yet even in this case, one can treat photodissociation of X_2^-e molecules that had initially occupied two anion sites into an X^- ion in a lattice site and an X^- ion in an interstice, with release of one anion site (according to Pooley,^[23] this amounts to creation of I and α centers).

According to Hersh,^[20] (Fig. 11a), photodissociation of X_2^-e molecules can transfer a halogen atom X^0 into an interstice with release of a single anion site that retains an electron (an F center is formed). Then the interstitial halogen atom can assume the energetically more favorable configuration of an H center.

Vitol, Lushchik, and Élango (see, e.g., Ref. 113) have treated another model of the decay of dihalogen excitons X_2^-e . Its meaning is explained by Fig. 11b, which is taken from Ref. 113. An X_2^-e molecule that had ini-

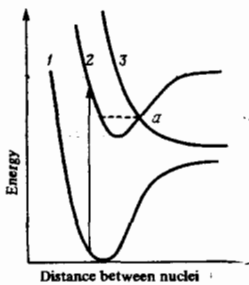


FIG. 10. Adiabatic potentials of diatomic molecules (schematic).

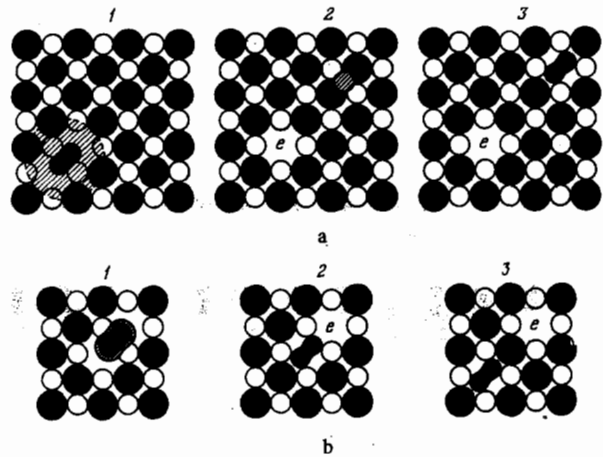


FIG. 11. Stages in the processes of dissociation (a) (according to Ref. 20) and of displacement (b) of X_2^-e molecules leading to the production of F and H centers in alkali-halide crystals.

tially occupied two anion sites (1) can be displaced into one anion site upon transition from one electronic excitation state into another (which is accompanied by release of vibrational energy), while leaving the electron in another anion site (2). If the excess vibrational energy of X_2^- suffices to allow strong interaction with an X^- ion adjoining it in the $\langle 110 \rangle$ direction, then a relay displacement of the X_2^- state can proceed further into the next crystal-lattice site (3). Consequently the dihalogen exciton decays into F and H centers. Itoh and Saidoh^[114] have proposed that the H center moves away from its site of origin in the excited state.

Lushchik^[115,116] has proposed another model of the decay of excitons into Frenkel' defects. If a monohalogen auto-localized X^0e exciton is produced in the crystal, and it is then converted into a dihalogen auto-localized X_2^-e exciton, then intense vibrations must arise at the instant of transition between these states, which strongly differ in the equilibrium positions of the heavy particles. For a dihalogen exciton of the molecular type, these vibrations must be local in nature (and they actually are, as analysis of the hot luminescence spectra of dihalogen excitons shows^[55,56]). This allows the vibrational energy to be concentrated at the X_2^-e center, and it hinders its rapid dissipation into the thermostat crystal. One assumes that F and H centers can consequently be produced, or that the energy can be transferred to the nearest cations of the crystal to produce cation Frenkel' defects.

B. Energetics and dynamics of defect-production processes

Smoluchowski *et al.*^[28] have theoretically calculated for KCl crystals the different variants of production of Frenkel' defects upon recombination of electrons with auto-localized holes. They estimated the energies of creation of charged and neutral anion Frenkel' pairs v_a^+ and i_a^- , and $v_a^+e^-$ and i_a^0 . The calculations showed that 12-15 eV must be spent for predissociation of X_2^-e molecules to yield v_a^+ and i_a^- . If F centers and unrelaxed

interstitial halogen atoms arise from the predissociation, then 8.2 eV must be spent. The minimal energy expenditures (5–7 eV) are those needed for producing a relaxed H center together with an F center. They concluded from these theoretical calculations that the fundamental mechanism of primary decay of electronic excitations into defects amounts to creation of F and H centers, while the α and I centers that have been detected in irradiated crystals do not arise directly in the decay of electronic excitations, but from secondary reactions. Élango has continued to study the energetics of production of anion Frenkel' defects. By using energy cycles, he has determined the energy for production of F and H centers for certain alkali-halide crystals. He obtained the value of 7 eV for KCl.^[117]

Table II gives the energies of free and autolocalized monohalogen excitons in KCl, the energy of an autolocalized dihalogen exciton, and the theoretically calculated thermodynamic-equilibrium energies for producing various Frenkel' defects: $v_a^+e^-$ and i_a^0 , v_a^+ and i_a^- , and v_c^- and i_c^+ , as well as the calculated minimum energies for decay of excitons into certain Frenkel' defects. Although $v_a^+e^-$ and i_a^0 pairs are less favorable energetically under equilibrium conditions than v_a^+ and i_a^- pairs, the energies for producing pairs of charged defects in the decay of an exciton are considerably greater than for pairs of neutral defects. The situation can change radically if the excitons do not decay at regular lattice sites, but in the vicinity of pre-irradiation defects. For example, the decay of an exciton near a cation vacancy to yield v_a^+ and i_a^- no longer requires surmounting such a high barrier. Nobody has estimated rigorously the minimum decay energy for producing the cation defects v_c^- and i_c^+ .

Vitol and Grabovskis,^[119] Itoh and Saidoh,^[114] and Toyozawa^[27] have analyzed dynamic instabilities in a dihalogen autolocalized X_2e exciton. Their fundamental idea is that the simultaneous existence of the intramolecular vibrations of the halogen particles along the axis of the X_2 molecule (Q_1 instability) and of displacements of the X_2 molecule as a whole with respect to crystal-lattice sites (Q_2 instability) considerably facilitates the displacement of X_2^- molecules from two anion sites into one. Toyozawa^[27] views the reason for such a displacement to be the mixing of even and odd electronic states.

Another form of vibrational instability in a crystal containing dihalogen excitons has been treated in Ref. 119. It causes a considerable part of the vibrational energy to be converted after excitation of a local Q_1 -vibration into displacements of the cations closest to the X_2^- that lie perpendicular to the axis of the molecule (Q_3 instability). This process can in principle give rise to the cation Frenkel' defects v_c^- and i_c^+ from the decay of dihalogen excitons. This situation can arise in NaBr and NaI crystals, and also in exciton decay in KCl-Li or KBr-Na crystals near impurity ions that are light and small in size.^[118]

As experiments have shown,^[102,120] decay of excitons into anion Frenkel' defects is facilitated in KCl-Br and KBr-I crystals. This fact has been interpreted as resulting from an asymmetric partition of the energy between the impurity and the majority halide ions that favors defect formation.

Study of the final stage of decay of electronic excitations into defects is complicated. This stage is the separation of the components of the Frenkel' pair to distances of several lattice constants at low temperatures at which the trivial diffusion of relaxed H centers is frozen.

Pooley has proposed that the separation of the generated F and H centers results from a sequence of focusing collisions along anion chains in the $\langle 110 \rangle$ directions.^[23] This model seems attractive, yet we must bear in mind that excitons decay efficiently into F and H centers even in MgF_2 crystals in which focusing collisions are ruled out by the low crystal-lattice symmetry (see, e.g., Ref. 121). Moreover, oriented V_K centers in KCl are converted into disoriented H centers.^[103]

It seems promising to apply the method proposed in Ref. 122 for calculating the initial distribution function of the Frenkel' pairs with respect to the distances between their components. Here one determines the kinetics of tunneling luminescence as a way of studying the complicated process of separation of the components of a created Frenkel' pair.

C. Proposed mechanisms of decay of autolocalized excitons

C. Proposed mechanisms of decay of autolocalized excitons

The existing experimental data and theoretical considerations imply that F and H centers are produced with great efficiency in KCl, KBr, and KI crystals by conversion of a monohalogen autolocalized exciton into a dihalogen one.

When a crystal is irradiated with ionizing radiations, autolocalized X^0e excitons can arise both by recombination of electrons with autolocalized monohalogen holes and by excitation of the crystal structure by electron impact. The effect has been found^[123-125] that the initial efficiency of creation of F centers is considerably diminished by introducing Ag^+ , Tl^+ , and Pb^{2+} ions into KCl

TABLE II. Energies of various states of excitons and defects in KCl crystals.

State	Energy, eV	Reference
Exciton:		
free	7.8	56
autolocalized monohalogen	~7.5	56
autolocalized dihalogen	~6	109
Pairs of defects:		
$v_a^+e^- + i_a^0$	5-7	26
	~7	117
$v_a^+ + i_a^-$	3.7	70
$v_c^- + i_c^+$	3.4	70
Minimum energy of decay:		
$e^0 \rightarrow v_a^+e^- + i_a^0$	5-7	26
$e^0 \rightarrow v_a^+ + i_a^-$	12-15	26

and KBr crystals. These ions easily capture electrons and thus hinder the production of excitons by recombination. This shows that the production of excitons by recombination is important in defect formation by radiation. The recently described^[126] diminution at 6 °K of the efficiency of creation of F centers in KBr caused by introduction of Na^+ ions, whereas the luminescence of the dihalogen excitons generated by recombination remained independent of the sodium content, can be explained by the idea that generation of autolocalized X_2^0e excitons by recombination is required for efficient production of F and H centers.

After the appearance of a monohalogen autolocalized exciton, the possibility exists at the instant of the conversion



that the X_2^-e molecule will be displaced into a single crystal-structure site to form a relaxed H center and an F center. Perhaps this process requires the activation energy $E_3 \approx 1-2$ meV that was found experimentally for KCl and KBr.^[64]

According to Ref. 108, the efficiency of the production of F centers in KBr crystals declines at $T > 30$ °K, and the number of triplet dihalogen excitons determined by absorption simultaneously increases. One can explain this situation by assuming that the activation energy E_1 in KBr for one-center autolocalization is smaller than E_2 for two-center autolocalization (see Fig. 3). According to Refs. 20, 39, 87, and 107, the production of F centers in KI and RbI crystals is frozen at $T < 100$ °K. We can understand this if $E_1 > E_2$ in these crystals and dihalogen autolocalized excitons are preferentially produced at low temperatures.

This treatment is based on the idea that the decay of an exciton into defects is most efficient when it passes through the state of a monohalogen autolocalized exciton. To judge from the quantum yield of luminescence of monohalogen excitons (10^{-3}), their lifetime amounts to about 10^{-11} sec, which is close to the experimentally determined time for creation of F centers in KCl and KBr by picosecond laser pulses.^[110] Intense local vibrations arise in the X_2^-e molecule at the instant of creation of a dihalogen exciton by the reaction (6.1), and they can displace the X_2^-e by one lattice site to form a relaxed H center and an F center.

Of course, we cannot consider the studied concrete mechanism of decay of excitons into Frenkel' defects to be unique. Experiments show that $F-H$ pairs undoubtedly arise when electrons recombine with relaxed V_X centers^[102,103] according to the reaction



The appearance of local vibrations in recombination of electrons with V_X centers can occur in transitions from the upper excited (e.g., $2p_x$ ^[27]) to the lowest state of the X_2^-e center. We can understand from this standpoint the recent results of Williams,^[118] who found an

increased efficiency of creation of F centers in crystals when a large number of relaxed autolocalized X_2^-e excitons were generated and they were then excited by laser radiation (694 nm) from the lowest to higher states.

We must note that the efficiency of defect production in transitions starting from the lowest electronic state of X_2^-e is small.^[105-108]

D. Conditions for decay of electronic excitations into defects

Regardless of the details of the mechanisms of decay of electronic excitations into structural defects that have been treated in this section, they are evidently based on electron-vibrational interaction that makes possible the conversion of the potential energy of electronic excitations into displacements of the ions of about a lattice constant.

We can discuss on the basis of the laws of conservation of energy and momentum the conditions for possible decay of electronic excitations into Frenkel' defects. If the energy of the intrinsic electronic excitations (E_e) is larger than the energy for production of radiation defects (E_d), while the lifetime of the electronic excitations in the unit cell (τ_i) is longer than the vibration period of the particles that form the crystal (τ_v), then the electron-vibrational interaction can lead to decay of the electronic excitation into Frenkel' defects. We can treat the inequalities $E_e > E_d$ and $\tau_i > \tau_v$ as being the approximate conditions for possible decay of electronic excitations to produce defects via electron-vibrational interactions.

High-energy electronic excitations having $E_e > E_d$ can always be created in crystals, but the overwhelming majority of them have a very short lifetime (such as many of the x-ray excitations and optical resonance excitations), or else too short a lifetime in a fixed unit cell of the crystal (such as free excitons in many crystals). In these cases, decay of electronic excitations into defects is improbable. Only in certain crystals are the inequalities $E_e > E_d$ and $\tau_i > \tau_v$ compatible.

The situation is especially favorable for decay of those electronic excitations that have converted to the autolocalized state. Then the inequality $\tau_i > \tau_v$ is evidently satisfied. The analysis performed in Refs. 53 and 56 of the possibilities of autolocalized excitons in different ionic crystals showed that one-center and two-center self-trapped excitons exist in the alkali and alkaline-earth halides, in lithium hydride, and in certain halides of lead and silver. All these systems have low radiation stability. Ionic crystals that lack autolocalized excitons (MgO , Al_2O_3) have an extremely high radiation stability.

We note that the inequality $\tau_i > \tau_v$ can also be satisfied in principle for certain electronic excitations: resonances whose energy is larger than the minimum energy of interband transitions. As has been recently shown,^[53,127] a fraction of them can decay radiatively ("super-edge luminescence"), in spite of the partial autoionization of these excitations. Radiationless decay into defects is also possible in principle for certain ex-

citations of this type. Facts have been amassed for a long time on the existence of above-threshold mechanisms of radiation-defect formation in homopolar semiconductors, for which $E_e < E_d$ for stable excitons (see the review^[128]). It is not ruled out that this phenomenon is based on decay of excitons of low mobility (resonances at structural defects).

7. X-RAY EXCITATIONS AND DEFECT PRODUCTION

As we have noted, Varley^[137] advanced the idea that the main cause of production of Frenkel' defects in ionic crystals under the action of low-energy radiation is the multiple ionization of anions, whereby their placement at lattice sites becomes unstable owing to electrostatic repulsion exerted by the surrounding cations. Starodubtsev and Kiv^[129] have shown that an analogous situation can arise also in covalent semiconductors because a multiply ionized atom in the homopolar system polarizes its environment and decreases the effective number of covalent bonds.

Varley's mechanism has been widely cited in discussing experimental results on radiation-defect production in ionic crystals (see the reviews^[130,131]). However, the theoretical estimates^[132] that have been performed have shown that the lifetime of multiply ionized states of anions is determined by the time for capture of the electrons of adjoining anions, and it amounts to 10^{-14} – 10^{-15} sec. This is smaller than the lattice vibration period, and it is probably too small for accumulating the momentum needed to displace the anion into an interstice. This conclusion has also been confirmed during a computer simulation of the process.^[133]

Élango^[134] has noted that multiply charged states of atoms in crystals can be created with some selectivity by ionization of certain inner electron shells of these ions by ultrasoft x-ray photons. For example, in alkali chlorides the threshold energy for production of Cl^+ ions coincides with the $L_{2,3}$ absorption edge of Cl^- (quantum energy of 202 eV). Saar and Élango^[138] have studied the production of Frenkel' defects in KCl – Na crystals irradiated with photons of energies 195 ± 4 and 215 ± 5 eV. They showed that the efficiency of production of H_A and F centers by quanta of the cited energies is the same within 5%. This fact implies that the probability of decay of a Cl^+ state into two holes considerably exceeds the probability of shifting the halogen into an interstice. Cruz-Vidal *et al.*^[135] have performed a thorough study of the effect of ionization of the K shells of Cl^- , Br^- , K^+ , and Rb^+ leading to a four- or fivefold ionization of the corresponding ions on the efficiency of production of F centers in KBr , RbBr , and KCl , and they also got a negative result.

The results discussed above are an experimental proof of the extremely low efficiency of the Varley mechanism in alkali-halide crystals. These crystals consist of close-packed atoms of alternate charges, and they have a high degree of lattice symmetry. These facts hinder the rapid accumulation of the momentum needed for ejecting an anion into an interstice.

Apparently a collective analog of the Varley process

occurs in ionic crystals: Coulombic breakdown of a region of the crystal, from which a large number of electrons are ejected by the ionizing action of charged particles.^[136] This has been shown by the pictorial experiments of Geguzin *et al.*^[137]

Experimental data amassed in recent years show that multiple ionization of atoms leads to production of point defects in semiconductors (see Refs. 128 and 138).

It is also of fundamental interest to determine the possibility of decay into structural defects of excitations involving the inner electron shells of the cations and anions. The energy of these excitations amounts to tens and hundreds of electron volts, while their lifetimes can exceed the lattice vibration period. Studies^[139–142] have shown that ultrasoft x radiation creates F centers in all studied alkali-halide crystals. The energy losses near the surface, which are caused by diffusion to the surface of current carriers from depths of 100–10,000 Å, play an important role in defect production. It has been possible to detect a fine structure in the energy-storage spectra of x rays near the K edge of Li^+ in LiF ^[139] and the $L_{2,3}$ edge of Cl^- in NaCl ^[141] that involves the features of decay of x-ray excitons. Experiments performed with synchrotron radiation^[142] have shown that more than 10^{18} cm^{-3} of F centers can be produced upon irradiating KCl and KBr crystals with quanta of energies 45–130 eV. However, opportunities did not arise in interpreting the obtained results of adducing special mechanisms of defect production that do not boil down to decay of low-energy excitons. Search for such mechanisms is more promising in crystals in which the low-energy electronic excitations can't give rise to defects (e. g., in metal oxides).

8. RECOMBINATION, CHARGE TRANSFER, AND STABILIZATION OF DEFECTS

In principle, one can describe the processes of decay of excitons into structural defects in the form of the following reactions (see, e. g., Ref. 15):



As we have shown above, the efficient operation of reaction (8.1) for KCl and KBr should be considered to be rigorously proved. There are serious arguments in favor of the existence in KBr and especially in NaBr of reaction (8.4).^[72,73] Some possible manifestations of reaction (8.2) have been described.^[96]

Not all of the defects that arise in the decay of excitons can exist for a long time. This is provided by recombination of complementary Frenkel' defects (v_a^+ and i_a^- , v_c^- and i_c^+ , $v_a^+ e^-$ and i_a^0 , $v_c^- e^+$ and i_c^0) to restore the regular lattice (R). For example, defects are annealed by the reaction



or even by the reaction that has been studied in Ref. 143:



The only Frenkel' pairs that can last long are those that have both components stably localized in spatially separate regions of the crystal structure. At liquid-helium temperatures, practically all defects in alkali-halide crystals (v_a^+ , i_a^0 , v_c^+ , v_c^- , i_c^+ , and $v_c^-e^+$) are immobile after vibrational relaxation. The defects i_a^0 and i_c^0 become mobile in the temperature range 20–50 °K, and v_c^- and $v_c^-e^+$ enter into saltatory diffusion in the temperature range 150–250 °K, and perhaps $v_a^+e^-$ migrates at temperatures above room temperature.

Hopping diffusion of defects leads to recombinational annihilation of complementary defects only if the defects haven't become stabilized by association of noncomplementary defects. Highly stable associations have been found in alkali-halide crystals of certain identical noncomplementary defects; F_2 centers ($2v_a^+2e^-$), F_3 centers ($3v_a^+3e^-$), and perhaps H_2 centers ($2i_a^0$). The possibility is being studied of pair and triplet associations of non-identical noncomplementary defects $i_a^+i_c^+$, $v_a^+v_c^-$, $v_c^-i_a^0$, $v_a^+i_c^0$, $v_c^-i_a^0i_a^0$, $v_c^-i_a^0e^+$, etc. Defects can also be stabilized in real crystals at various impurities. For example, impurity ions of metals having a smaller size serve as effective traps for H centers.

As was noted in Ref. 15, one of the ways of stabilizing defects is for some of them to emerge onto the surface of the crystal. Surface crystallites can grow by migration of i_a^- and i_c^+ to the surface, as have been found by electron microscopy,^[144] while migration of i_a^0 and i_c^0 to the surface leads to release from the crystal of the halogen and the alkali metal, as has been detected by mass spectroscopy.^[145,146]

If the defects are separated from each other by only several lattice constants, then tunneling electronic transitions between the defects become effective. The following reaction would be especially interesting:



It leads to charge transfer among defects and conversion of $F-H$ pairs into $\alpha-I$ pairs.^[26] This reaction, which is yet to be studied, can be accompanied by tunneling luminescence. The following reaction, which has been well studied in terms of its characteristic tunneling luminescence,^[147] can also occur:



9. EFFICIENCY AND KINETICS OF ACCUMULATION OF F AND H CENTERS

A. Experimental data for KCl and KBr

The efficiency and kinetics of accumulation of radiation defects in ionic crystals is determined by the efficiency of the complicated processes of defect production, recombination, charge transfer, and stabilization that have been treated in the previous sections.

It has been shown experimentally (see the reviews^[22,41,44]) that the dominant stable defects in KCl

and KBr crystals over a broad range of absorbed doses D and temperatures of irradiation are pairs of F and H centers localized at regular lattice sites or near other defects. Here the concentration N_F of F centers increases linearly with D up to values of 10^{17} – 10^{18} cm⁻³, while it saturates at the level of 10^{19} – 10^{20} cm⁻³ for larger D . The energy $E_F = D/N_F$ that is spent in creating a single stable F center by the high-energy radiation at the onset of irradiation depends on the specific crystal in terms of the ratio of dimensions of the halogen and of the interstitial cavity (Rabin-Klick diagram): the higher this ratio is, the larger E_F is.^[43] At 4 °K, E_F for KCl and KBr lies near 2000 eV.^[148]

Figure 12 shows the temperature-dependence of the efficiency N_F/D of accumulation of F centers. N_F/D sharply declines above the temperature of delocalization of H centers (about 30 °K), and it becomes dependent on the traps for H centers that exist in the crystal. At temperatures of 100–200 °K, N_F/D increases again with an apparent activation energy of 0.03–0.10 eV.^[16,149] A strong dependence of N_F/D on the concentration and type of the various pre-irradiation defects and on the intensity of irradiation also arises. That is, the reciprocity law breaks down: N_F is not a single-valued function of D . At 200–250 °K, N_F/D reaches its maximum, and declines with further temperature increase with an activation energy 0.4–0.6 eV.

General considerations imply that N_F must be proportional to the concentration N_e of excitons produced, to the yield η_F of the decay of excitons into F and H centers, and to the probability ρ_F of survival of the created centers until the instant of observation:

$$N_F = N_e \eta_F \rho_F. \quad (9.1)$$

The excitons in ionic crystals in irradiation with high-energy radiation mainly arise from recombination of electrons and holes. The number of electron-hole pairs produced upon irradiation in semiconductors and insulators can be expressed as D/q , where q is the mean energy needed to produce one electron-hole pair ($q = (1.7-2.0)E_e$ for alkali-halide crystals^[19,150]). Hence, whenever we can neglect trapping of electrons and holes by trapping centers, we have $N_e = D/q$.

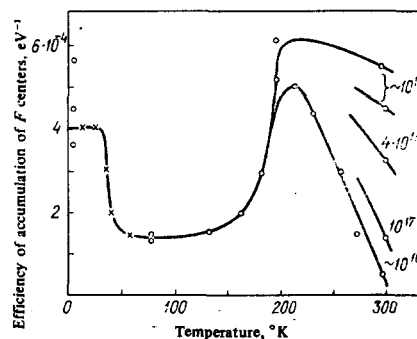


FIG. 12. Temperature-dependence of the 4 °K and 80–300 °K regions from Ref. 22. The absorbed dose rates are indicated at the right in eV · cm⁻³ · s⁻¹.

One can measure the value of η_F under conditions in which the defects are produced by picosecond laser pulses. The only experiment of this type that has yet been performed gave the value $\eta_F = 0.15$ for KCl at 10°K .^[110] The dependence of N_F on the time and the temperature of irradiation in KCl and KBr is mainly determined by the factor ρ_F .

B. Isolated pairs

The experimental data imply that the mean displacement of an H center from the genetically-related F center amounts to several lattice constants. Hence we can expect that for low N_F we can consider the genetic pairs of F and H centers to be noninteracting (isolated). We can consider a sign of the isolation of the defect pairs to be a linear dependence of N_F on D , which is often observed up to 10^{17} – 10^{18} cm^{-3} .

For isolated pairs, ρ depends on the time t in terms of n , the spatial distribution of the defect pairs pairs^[121, 122, 151, 152]

$$\rho(t) = \int_0^\infty n(r, t) dr, \quad (9.2)$$

which has been normalized at $t=0$ (Fig. 13). The physical interpretation of Eq. (9.2) is simple: all the pairs are assumed to have survived at the instant $t=0$ when the defects are produced.

Let us assume the variation of $n(r, t)$ to be caused only by tunneling charge transfer, whose probability is approximately described by

$$w = w_0 \exp\left(-\frac{r}{r_0}\right), \quad (9.3)$$

Here w_0 and r_0 are parameters that respectively have values near 10^6 sec^{-1} and $0.8a$ for F centers.^[153] Then, according to Ref. 122,

$$\rho_T(t) = \int_0^\infty n(r, 0) \exp\left[-w_0 t \exp\left(-\frac{r}{r_0}\right)\right] dr. \quad (9.4)$$

A simple analysis of (9.4) shows that the mean radius r_T of the sphere within which tunneling transitions can occur expands with time according to the law

$$r_T(t) = r_0 \ln(w_0 t), \quad (9.5)$$

while $\rho_T(t)$ is approximately equal to the fraction of the pairs having $r > r_T(t)$, i. e.,

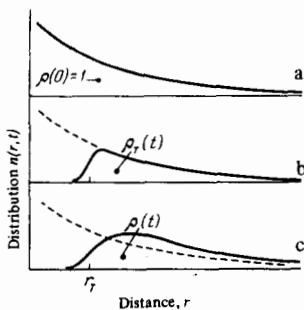


FIG. 13. Distribution of the number of F - H pairs with respect to the distance between partners: a) at the instant of formation; b) after the time t , with account taken of tunneling charge transfer; c) after the time t , with account taken of tunneling charge transfer and diffusion of H centers.

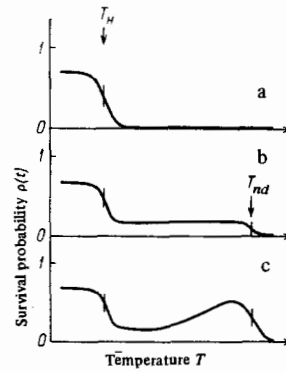


FIG. 14. Schematic temperature-dependence of the survival probability of F centers. a) Crystal having no traps for H centers; b, c) crystal having traps for H centers of one type, with account for tunneling charge transfer (b), and of tunneling charge transfer and diffusion of H centers (c).

$$\rho_T(t) = \int_{r_T}^\infty n(r, t) dr. \quad (9.6)$$

If the variation of $n(r, t)$ is caused by a diffusion-controlled process, it is hard to find the analytic form of $n(r, t)$ and of the corresponding $\rho_T(T)$.^[153, 154] Yet the overall character of this function remains as before; the probability of survival increases with increasing r . Moreover, we can expect an increasing diffuseness of $n(r, t)$ with respect to r with increasing temperature, owing to relocalization of H centers into ever deeper and more distant trapping centers (Fig. 13).

In most actual situations, tunneling and diffusional processes act simultaneously. For example, in individual cases in which the diffusion-controlled recombination process runs much faster than tunneling charge transfer (the high-temperature region), we can write approximately

$$\rho(t) = \rho_T(t) \rho_R(t). \quad (9.7)$$

The quantity ρ_F can be limited only approximately as applied to F - H pairs. Analysis of the results of Refs. 102, 106, and 148 shows that $\rho_F \approx 0.1$ at 4°K for survival times greater than a minute. According to Ref. 155, the mean distance between F centers stable at 300°K and trapped H centers is $7a$. This implies that $r_T < 7a$.

Figure 14 shows schematically the temperature dependence that is implied by the abovesaid. Curve a corresponds to the case of an ideal crystal lacking trapping centers for H centers. In the temperature range from 4°K to $T_H = 30$ – 60°K , the H centers are localized in the regular lattice. Owing to recombination and charge transfer of close pairs, ρ_F has some steady-state value less than unity. Total recombination occurs at $T > T_H$, and $\rho_F = 0$. In crystals that have trapping centers for H centers, a certain fraction of the H centers persists in them at $T > T_H$ up to the temperature T_{nd} (curve b). Diffusion of H centers out of the zone of tunneling transitions leads to an additional temperature-dependence increase in ρ_F (curve c) with an apparent activation energy somewhat smaller^[16, 154] than that of the thermal diffusion of H centers.

The experimental temperature dependences of N_F/D (Fig. 12) have a shape resembling curve c in Fig. 14. The complexity of the detailed interpretation of the ac-

tual curves is explained by the existence of several types of trapping centers for H centers and also by some other temperature-dependent processes (mobility of vacancies and V_F centers). The even greater complexity of the kinetics of accumulation of radiation defects and its temperature-dependence are caused by various pre-irradiation defects. The latter lead (besides the above-studied trapping of H centers) to trapping of electrons and holes, as is expressed in a decrease in the effective value of N_F .^[125] This also decreases the mean distance between the F and H centers.^[152]

C. Random distribution of pairs

We must take account of the cross-interaction of the components of different pairs at large irradiation doses. This is manifested in the deviation of the kinetics of accumulation of defects from linear and in the onset of bimolecular stages of annealing of defects.^[22, 25, 44] The defect distribution in the crystal approaches randomness with increasing dose. Here the probability p of finding the closest F center at the distance R from an arbitrarily chosen H center is

$$p(R) = 4\pi N_F R^2 \exp\left(-\frac{4}{3}\pi R^3 N_F\right). \quad (9.8)$$

We can calculate from (9.8) the fraction of the H centers that lie by chance in spheres of instability of given radius about the F centers. Equation (9.8) implies some major deviations from random distribution: decline in efficiency of accumulation with increasing N_F , non-monomolecular kinetics of recombination of defects, dependence of the accumulation on the irradiation power for a fixed dose (breakdown of the reciprocity law), etc. A computer simulation of the accumulation process with account taken for tunneling charge transfer has been performed by Tale, Millers, and Kotomin.^[153] They got a kinetics of accumulation of F and H centers that qualitatively agreed with experiment and they showed that defects of like sign could aggregate.

In most actual cases of irradiation, the defect distribution has a complicated pairwise-random nature.

Further increase in the irradiation power and dose leads to a number of interesting effects in alkali-halide crystals^[44]: production of a metal colloid and pre-colloid color centers^[156] (see also the review by Shvarts *et al.*^[157]), appearance of dislocations (Andronikashvili *et al.*^[158]) and dislocation loops,^[159] brittle fracture of the crystals (Vaisburd *et al.*^[160]), and other phenomena whose detailed treatment would fall outside the scope of this paper.

10. CONCLUDING REMARKS

The great amount of experimental material shows that radiation defects arise in solids not only from the already well studied elastic collisions of the high-energy particles with the nuclei of the crystal structure, but also from decay of certain long-lived electronic excitations. In many ionic crystals, the latter mechanism of production of radiation defects dominates. It remains to find out to what degree the decay of electronic excitations to produce defects affects the stability of semi-

conductors and metals.

Ionic crystals show a correlation between the phenomena of autolocalization of electronic excitations (in particular, excitons) and that of decay of electronic excitations to produce Frenkel' defects. Ionic crystals that lack autolocalized electronic excitations (MgO , Al_2O_3), etc. have high radiation stability. In the most fully studied alkali-halide crystals, Frenkel' defects are especially efficiently produced by decay of autolocalized excitons.

Although the types of defects and ways of forming some of them in the alkali-halide crystals have been studied in great detail, there are a number of weakly studied areas and even blind spots in our current views of radiation-defect formation in ionic crystals. Study of the short-lived electronic excitations that arise in the vibrational relaxation of excitons remains to be continued, and a quantitative theory is lacking for the decay of electronic excitations into structural defects. No analysis has been made of the possible decays of high-energy electronic resonance excitations into structural defects in ionic crystals, semiconductors, and metals. The specifics of the electronic excitations and structural defects in radiation-stable crystals like MgO and Al_2O_3 has been insufficiently studied.

Analysis of the kinetics of accumulation and annealing of radiation defects in ionic crystals shows that spatial correlations between the complementary defects that are produced play an important role in these phenomena. The possible appearance of at least three types of Frenkel' pairs and their interaction (in particular, by tunneling) with one another and with other defects complicates the radiation effects in ionic crystals.

It might open up interesting prospectives for the radiation physics of condensed systems (in particular, biological) to find *selective* mechanisms of producing radiation defects upon selective excitation of the inner electron shells.

We wish to express the hope that our view will prove to stimulate action in the development of experimental studies, and especially the appearance of theoretical studies of radiation-defect formation.

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Synthesis and physical properties of single-crystal films of rare-earth iron garnets

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The synthesis conditions, certain problems of epitaxial growth, and methods of controlling the quality of single-crystal iron-garnet films are discussed. The main physical properties of garnet films are considered, such as optical absorption, Faraday rotation, the characteristic length, the saturation magnetization, the coercive force, the magnetic anisotropy, the mobility, and the dynamic transformation of domain walls. Measurement methods and some results of the investigation of these properties are described. The reproducibility and the temperature dependence of the principal parameters of the films are discussed.

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1. INTRODUCTION

Interest in the investigation of thin magnetic films is due both to the singularities of their structure and physical properties, which promise to cast light on many fundamental problems of solid state physics, and to the prospects of the practical utilization of these films in electronic technology. Among the trends that lead to advanced devices for automation and computer technology is development of memory and logic devices based on the motion of domains in magnetically uniaxial materials.^[1-6] Research is also being carried out on magneto-optical devices for the reduction and storage of information in ferrites.^[4]

Principal attention is being paid to ferrites with garnet structure $R_3Fe_5O_{12}$ (where R is an yttrium or rare-earth ion),^[7,8] a distinctive magnetic structure—cylindrical magnetic domains (CMD) bubble (Fig. 1)—is produced in films of this material, with the easy magne-

tization axis normal to the plane of the film, when a constant magnetic field is applied in the same direction.

Among the advantages of domain devices for computer logic and memory over their semiconductor analogs we can single out the following:

- a) the small (micron and submicron) dimensions of the bubble make it possible to obtain a binary information recording density 10^8 – 10^9 bit/cm²;
- b) low power consumption (0.04 W to perform 10^{12} binary operations per second);
- c) possibility of storing the information without consuming energy;
- d) ability of circuits using domain interactions in a homogeneous magnetic medium to perform multiple functions;
- e) the possibility of producing these circuits by the