# Defect formation in solids by decay of electronic excitations

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We consider a new type of nonradiative transitions in nonmetallic solids. The transitions are not accompanied by heat release but by large (compared with interatomic distances) displacements of individual atoms. These instabilities (electrostatic, vibronic, structural), which lead to formation of defects in solid crystals and glasses, are classified. We describe defect-formation processes both in ionic crystals upon decay of self-trapping excitons, and in semiconductors following multiple ionization of atoms near pre-existing charged impurity centers. The mechanisms whereby complex defects are restructured in semiconductors when nonequilibrium current carriers are introduced and when electrons and holes recombine are discussed. The role of current carriers in thermal production of defects is considered. The mechanism of formation of peculiar defects in glassy semiconductors is discussed.

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# **1. INTRODUCTION**

In the many decades of the evolution of the physics of semi-conductors and dielectrics, following the foundation of the quantum theory of solids, it was universally regarded that excitation of the electron subsystem of a crystal leads to a redistribution of the electrons among allowed energy bands, on the one hand, and to a set of local bandgap electron levels due to crystal impurity and intrinsic defects, on the other. It was assumed that the set of defects is itself determined by the prior history of the sample and remains unchanged when the electron subsystem is excited. Two types of transitions between energy levels were considered in quantum theory of semiconductors and dielectrics, viz., radiative, leading to the onset of luminescence, and nonradiative, leading to conversion of the energy absorbed by the crystal into small vibrations of many atoms, i.e., to heat release.

Active collaboration of the present authors has recently led to observation and proof that excitation of the electron systems of a dielectric or a semiconductor not only redistributes the electrons, but frequently also changes the very assortment of point defects. This change is caused either by a rearrangement of the defects already present prior to the excitation of the electron subsystem, or by production in the crystal of [vacancy (v) + interstitial atom (i)]-pair point defects. The concept of such (v, i) pairs was introduced by Ioffe and Frenkel'.<sup>1,2</sup>

The formation and transformation of defects upon excitation of the electron subsystem in a nonmetallic crystal is a new type of nonradiative transition in solids, and among its features are not only heat release but also large displacements of an atom (several atoms) compared with the interatomic distances in the crystal lattice.

The purpose of the present review is to examine the experimental manifestations and mechanisms of the formation and transformation of point defects in solids when their electron subsystem is excited, and to discuss the key problems of a situation that is now evolving in the physics of semiconductors and dielectrics, a situation that calls for a

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unified approach to electron excitations in point defects and solids.

The group of problems considered below is made most timely not only by the theoretical advances of solid state physics itself, but also by the acute need for radiation-enduring, slowly aging, and nondegradable materials for nuclear power, engineering optics, opto- and microelectronics, laser technology, etc., as well as by the need for radiation-sensitive materials for memory devices and other information-display systems.

The emphasis in this review is on a comparison and discussion, from a unified viewpoint as of the 1984 state of the art, of the complicated phenomena that have been previously considered without sufficiently close contact between the specialists engaged in semiconductor physics (see, e.g., the monographs and reviews<sup>4-11</sup>) and those working in the physics of luminescent dielectrics (see, e.g., reviews<sup>12-16</sup>).

## 2. EXPERIMENTAL OBSERVATION OF FORMATION AND TRANSFORMATION OF DEFECTS FOLLOWING EXCITATION OF THE ELECTRON SUBSYSTEM OF A DIELECTRIC OR A SEMICONDUCTOR

Radiative defects are produced in all basic types of solids (metals, semiconductors, dielectrics) by a universal mechanism due to the displacement of the crystal-lattice atoms (ions) from sites into interstices when particles of sufficient energy are elastically scattered by the atoms (elastic-displacement mechanism). At moderate energies the primary interaction between the particle and the crystal is simple, viz., an elastic pair collision that obeys the energy and momentum conservation laws; the sufficient condition for defect formation is the transfer to the crystal-lattice atom (ion) of an energy exceeding a threshold  $E_d$  that depends on the type of crystal and is of the order of 10 eV (see, e.g., Refs. 17 and 18).

It must be recognized that when particles and photons interact with a solid the bulk of their energy is consumed not by elastic displacement of the atoms, but by excitation of the crystal electron subsystem. It was assumed for many years that this fraction of the energy takes no part in the formation of radiative defects, but data accumulated over quite some time indicate that radiative defects are produced in dielectrics and semiconductors not only by elastic displacement but also by excitation of the electron subsystem of the crystal.

This has become particularly pronounced in investigations of wide-gap ionic dielectrics, typical representatives of which are alkali-halide crystals (AHC). It was shown way back by Roentgen and Ioffe<sup>19</sup> that AHC become colored by x rays of moderate hardness (10–100 keV). The main color center is the F center, an anion vacancy that has trapped an electron.<sup>20</sup> The energy of the photo- and Compton electrons produced by x rays is patently insufficient to produce elastic displacement. It was initially proposed that F-center production is due to trivial capture of electrons by anion vacancies present in the crystal prior to irradiation.<sup>20</sup> It became clear later<sup>21</sup> that at room temperatures there are practically

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no solitary anion vacancies in AHC (they become associated with the cation vacancies). This has prompted already in the sixties the study of the conversion of divacancies by capture of electrons and excitons and conversion into F centers accompanied by displacement of cation vacancies. The electron-ion processes of transformation of defects present prior to the irradiation complicate greatly many physical phenomena in AHC.<sup>22</sup>

It was found later<sup>23</sup> that x rays produce F centers at concentrations up to 10<sup>18</sup> cm (much higher than the number of defects prior to irradiation), even in AHC whiskers grown from the solution at 260-300 K, with vanishingly small contents of divacancies and dislocations. Swelling of AHC by xray irradiation was observed,<sup>24</sup> and a parallel investigation of the radiation-induced changes of the crystal density and of the lattice constant has shown that Frenkel (v, i) pairs (FP) are produced in the AHC.<sup>25</sup> Interstitial halide centers (H centers) were observed by an ESR method.<sup>26</sup> It became clear that production of x-ray electron excitations in AHC not only transforms the pre-irradiation defects, but also creates new ones. By way of example, Fig. 1 shows the spectrum of the x-ray-induced absorption at 4.2 K in high-purity KCl.27 The two long-wave absorption bands correspond to the F centers  $(v^+, e^-)$  and interstitial halide atoms [i<sup>o</sup>; (F, H) pair]. The two short-wave absorption bands correspond to anion vacancies ( $v^+$ ,  $\alpha$  centers) and intestitial halide ions  $[(i^-, I) centers].$ 

In 1959 Luscik, Liidja, and Jaek<sup>28</sup> developed a procedure for the measurement of the spectra of F-center production by monochromatic ultraviolet radiation and have shown that the F centers are formed when excitons are optically produced and when electrons and holes recombine. Lushchik, Liĭd'ya, and Élango have shown later<sup>29</sup> that irradiation of NaCl crystals in a nuclear reactor produces the same radiation defects as x rays or as vacuum-UV irradiation that generates excitons (e°) or electron-hole (e<sup>-</sup>, e<sup>+</sup>) pairs. Figure 1 shows the data of Vasil'chenko *et al.*<sup>30,27</sup> on the changes, measured by a highly sensitive luminescence method, produced in the absorption of KCl crystals by irradiation at 4.2 K with photons, which selectively produce excitons in the KCl. Large irradiation doses yielded 10<sup>18</sup> cm<sup>-3</sup> FP.



FIG. 1. Optical-absorption spectra of KCl crystals after irradiation by x rays (1, 1') or by exciton-producing 7.77-eV photons (2, 2'). The inset in the upper part of the figure shows models of Frenkel defects [(F, H) and  $(\alpha, I)$  pairs].

The possibility of formation and transformation of defects in semiconductors by electron or photon irradiation at energies noticeably lower than needed to actuate the elasticdisplacement mechanism was noted in experiments.31-48 The first task-oriented research into such processes at "subthreshold" irradiation energies was performed by Starodubtsev et al. (see, e.g., Ref. 34). Ryvkin,49 and Vavilov, Yunusov, et al.<sup>46,47</sup> Lashkarev, Sheinkman, et al.<sup>50</sup> developed highly sensitive photoelectric and luminescence methods of observing radiative defects in semiconductors. The use of these procedures revealed various manifestations of subthreshold and above-threshold production of FP in semiconductors.47-56

The researchers of Vavilov, Kiv, Niyazova, et al.40-47 were devoted to defect formation in silicon by x rays and by electrons of subthreshold energy. By way of example, Fig. 2 shows the data of Ref. 40, interpreted by their authors as confirmation that the decrease in the conductivity of silicon as the energy of the electrons acting on the crystal is varied agrees with the known spectral dependence of the cross section for the silicon-atom K-shell ionization. These data were furthermore regarded as relating the defect formation to ionization of the inner electron shells of these atoms.

A very effective mechanism of defect formation in "subthreshold" irradiation of a narrow-band superconductor (indium antimonide) was observed by Vitovskii, Mashovets, and Ryvkin (Refs. 42, 43, 51; see also Refs. 52-55). Strongly compensated p-type indium antimonide was irradiated at 77 K by x rays having a subthreshold energy of 250 keV. A detailed computer analysis of the temperature dependences of the electric conductivity and of the Hall coefficient has shown that the dominant process in this irradiation is the lowering of the densities of the donors and acceptors, and the corresponding decrease of the densities of the ionized scattering centers (N<sub>D</sub>, N<sub>A</sub>, N<sub>I</sub>). The rates of decrease of N<sub>D</sub> and  $N_A$  are the same and decrease exponentially with increasing irradiation dose (Fig. 3). The hole mobility does not increase in this case. Complete restoration of the initial density and mobility of the holes is obtained by annealing the irradiated crystals from the elementary stage at T < 100 K. This was interpreted as a manifestation of the simple structure of the produced and annealed radiation defects.56-58

It is very important to prove that defect formation in semiconductors can also accompany optical creation of lowenergy electronic excitations-of electrons and holes with



lg[*N<sub>1</sub>, N<sub>2</sub>, N<sub>1</sub>*, cm<sup>2</sup>] 14 0.36 9.72 1.08  $1.44 \, \Phi \cdot 10^{-18} \, \mathrm{cm}^2$ õ 50 100 150 200 t, h

FIG. 3. Donor and acceptor densities  $N_D$  and  $N_A$  (1, 2), as well as densities of ionized scattering centers  $N_I$  (1', 2') as functions of the integral flux of x rays for InSb-Mn (1,1') and InSb-Ge (2, 2').

energies close to the corresponding band edge. An example of a reliably identified process of this type is photothermal decay of donor-acceptor pairs in semiconductors, first investigated by Sheĭnkman and co-workers.<sup>38</sup> The result of this process for CdS-Li is illustrated in Fig. 4. Prior to exposure of the crystal to the light that produces the electron-hole pairs, emission from the donor-acceptor pairs (9.95  $\mu$ m) and a very weak thermostimulated-conductivity peak (60 K) are observed. The irradiation weakens the 0.95- $\mu$ m emission and enhances strongly the 1.01- $\mu$ m emission due to electron recombination at the free acceptors. The peak of the thermostimulated conductivity due to the free donor is simultaneously greatly amplified.

The interplay between formation of defects and capture by them of conduction electrons manifests itself in many semiconductor compounds also under thermodynamicequilibrium conditions. Vinetskiĭ and Kholodar' identified such a situation using as an example the high-temperature conductivity of cuprous oxide. The hole conductivity of Cu<sub>2</sub>O is not intrinsic, as previously assumed, but is due to Frenkel'-pair formation in the copper sublattice and to ionization of the acceptor vacancy  $v_{C\mu}$ .<sup>1)</sup> In pure and well-annealed Cu<sub>2</sub>O crystals, in accordance with thermodynamic calculations, the plot of the hole density n(T) as a function of the temperature at high temperatures shows two sections (Fig. 5). The slope of the plot of  $\ln n (T^{-1})$  corresponding to formation of ionized vacancies  $v_{Cu}$  assumes with rising T a lower value corresponding to weaker ionization of the produced  $v_{Cu}$ . The equilibrium density of  $v_{Cu}$  is determined substantially by the degree of their ionization, i.e., by the equilibrium free-carrier density.59,60



FIG. 2. Defect-formation effectiveness as a function of the energy E of the electrons that irradiate a silicon epitaxial film. The plot is extrapolated to zero thickness  $\sigma_l$ . Circles-experimental data, solid curve-K-shell ionization cross section as a function of the ratio of E to the K-level energy  $E_{\rm K}$ .

FIG. 4. Luminescence (a) and thermostimulated-conductivity (b) spectra and energy-level scheme (c) of a CdS-Li crystal before (1) and after (2) photoexcitation that dissociates donor-acceptor pairs.



FIG. 5. Temperature dependences of the conductivity and of the number of carriers in  $Cu_2O$  crystals.

# 3. POSSIBLE MECHANISMS OF DEFECT FORMATION

Observation of the formation and transformation of radiative defects in dielectrics and semiconductors by x rays and by electrons at subthreshold energies has raised the question of the possible mechanisms of this phenomenon. It was clear from the characteristic electron-energy loss spectra in solids that electron-crystal interaction gives rise to plasmons, to x-ray and optical excitons, and to separated electrons and holes. Study of the crystal absorption spectra in the ultrasoft x-ray region has revealed the x-ray spectrum structure connected with excitation and ionization of the inner electron shells of the crystal-lattice ions. It is natural to associate subthreshold formation of defects in solids with the production of x-ray electronic excitations (x), of plasmons (p), of optical excitons  $(e^0)$ , or of electron-hole pairs  $(e^-,$ e<sup>+</sup>). Annihilation of these electronic excitations in regular (defect-free) regions of the crystal lattice (R), near point defects and their simple clusters (P), near line defects-dislocations (D), or near surface defects (S) can lead in principle to formation of new defects or to transformation of defects existing in the crystal prior to the irradiation, although the real efficiencies of these processes can differ by many orders of magnitude.

Lushchik, Liĭd'ya, Elango, *et al.* have considered a general classification of various electronic excitations accompanied by defect creation in various crystal-structure elements.<sup>60</sup> It is presented with some modifications in Table I. The letters E and T denote respectively experimentally observed and theoretically considered cases. Low temperature situations, when thermal production of defects is excluded, have been classified. At high temperatures, the number of possible mechanisms of formation and transformation of defects by exciting the electron subsystem is larger. Vinetskiĭ and Kholodar' have shown<sup>5.6</sup> that even introduction of thermalized conduction electrons ( $e^-$ ) or holes ( $e^+$ ) into the crystal can increase the probabilities of thermal production of defects by several orders (see Sec. 6 for details).

The first to be used to explain radiative defect formation in AHC by x rays were historically the x and R mechanisms (see Table I). Varley advanced in 1954 the hypothesis<sup>64</sup> that anion vacancies and interstitials are produced in AHC by multiple ionization of the halide ions, which produces an unstable group of seven positive ions arranged in a row. During its short life this group has time to become so rearranged that the halogen ion is ejected into an interstice and leaves a vacancy.

This viewpoint found wide acceptance,<sup>65</sup> but it is now clear that Varley's mechanism does not explain the main processes that produce defects in AHC. Elango and Saar<sup>66</sup> compared directly the efficiencies of producing F and H pairs in KCl by 195 and 205 eV photons, below and above the threshold of twofold ionization of the  $Cl^{-}$  ions (see Fig. 6a). Although the Varley mechanism could be "switched on" on going from 195 to 205 eV, the difference in the efficiencies of F and H pair production did not exceed 5%. Kiv, Malkin, and Elango examined the causes of the low efficiency of the Varley mechanism in regular sections of a cubic closepacked AHC crystal lattice.<sup>67,68</sup> It was concluded that near the AHC surface the radiative defect formation should be much more effective (x, S mechanism). Recent experiments on the influence of x-ray synchrotron irradiation of NaF crystals, with the products ejected into vacuum analyzed with a time-of-flight mass spectrometer, have shown (Fig. 6b) that the spectrum of surface photodissociation of NaF into fluorine and sodium duplicates the sodium K-shell photoionization spectrum.69

Kiv et al.<sup>70,39,40,45</sup> attempted to apply the Varley model to atomic semiconductors. The role of the anion was played there by the lattice atom proper, and that of the cation by one or more nearest-neighbor holes.

General theoretical investigations by Klinger *et al.*<sup>8,71</sup> and experiments by Mashovets *et al.*<sup>8,9</sup> have shown that the x and P mechanisms considered in Sec. 4 are effective in semi-

TABLE I. Classification of mechanisms of defect formation in ionic crystals (Io) and semiconductors (Sm) in decay of various electronic excitations  $(e^0; e^-, e^+; e^0_M, p, x)$  in regular (R) sections of the crystal and near point (P), line (L), and surface (S) defects.

	e0		e-, e+		e <sup>0</sup> <sub>M</sub>		p		x	
	Io	Sm	Io	Sm	Io	Sm	Io	Sm	Io	Sm
R P D S	E,T E		Е. Т Е	Е, Т	E?	T E?		Т?	Т Е, Т	E, T? E, T

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FIG. 6. Absorption (1) and defect-formation (2) spectra for pair production in KCl (a) and NaF (b) crystals.

conductors, whereas the Varley model and the corresponding x and P mechanism are practically ineffective.

The intrinsic absorption in dielectrics and semiconductors has a complicated structure, part of which is due to the formation of metastable excitons  $(e_M^0)$  whose energies are superimposed on the continuum of the interband transitions. Notwithstanding the possibility of partial autoionization of the metastable excitons, some fraction of  $e_M^0$  produces in crystals the so-called "above-edge radiation"<sup>72</sup> and can in principle undergo decay with defect production.<sup>73</sup> As applied to semiconductors, processes of this type (the  $e_M^0$  and **R** mechanisms) were investigated theoretically by Tolpygo, Telezhkin, *et al.*<sup>75</sup> Plasmon mechanisms of defect formation in semiconductors and dielectrics have so far not been observed in experiment. Their theoretical analysis was attempted by Oksengendler.<sup>74</sup>

As already noted, it has been reliably established that Frenkel' defects can be formed in AHC via exciton annihilation or electron and hole recombination, both in regular sections of the crystal and near defects ( $e^0$ , R;  $e^0$ , P;  $e^-$ ,  $e^+$ , R;  $e^-$ ,  $e^+$ , P)<sup>12,14,76</sup>. The reason can be assumed to be the strong local electron-phonon interaction and the low energy (compared with that of the excitons) of FP formation in AHC (see Sec. 5). In semiconductors (CdS, InSb, Si, Ge, and others) the exciton energy is considerably lower than that of defect formation, and the low-temperature  $e^0$ , R and  $e^-$ ,  $e^+$ , **R**-mechanisms have apparently not yet been observed; on the other hand, numerous manifestations of the  $e^-$ ,  $e^+$ , P;  $e^-$ ,  $e^+$ , D and other mechanisms were found.<sup>11</sup>

Two types of mechanism for defect formation in solids must be distinguished: impact (fast) and non-impact (slow). Natural examples of the former are (v, i) pair production processes with atom-displacement times  $\tau_{dis} \ll \tau_D$  $\equiv \omega_D^{-1}(\omega_D)$  is the Debye frequency), whereas  $\tau_{dis} \gtrsim \tau_D$  for the non-impact mechanisms. Typical impact and non-impact mechanisms are respectively those with classical elastic-displacements type and the  $(e^0, R)$  mechanism in AHC. It will be shown subsequently that defect formation in decay of electronic excitations proceeds via non-impact mechanisms with atom-displacement energy  $E_{dis} < E_d$ .

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## 4. ELECTROSTATIC MECHANISMS OF DEFECT FORMATION

#### a) Basic theoretical concepts

Electrostatic defect-formation mechanisms come into play when the energy of the electrostatic interactions between the charged electronic excitations and the other charges, dipoles, etc., exceeds noticeably the energies of the other interactions in the crystal. A theoretical analysis of such mechanisms by Klinger<sup>71,72,78</sup> has shown that the produced electrostatic instability of the atomic configuration can cause athermal (temperature-independent) defect formation upon decay of a low-symmetry excitation, whereas high-symmetry excitations (particularly in the well-known Varley model) are associated more readily with low-efficiency thermally activated processes.

The most effective low-symmetry mechanism<sup>71,77,78</sup> is due to repulsion of positive ions in nonmetallic solids, especially in semiconductors, which contain initially centers with positive charge  $q_1|e|(\geq |e|)$  and with sufficiently high relative density  $c_+$  ( < 1). The gist of this mechanism, both in crystals (particularly semiconductors such as Ge and III-V compounds) and in amorphous, glasslike (a-As<sub>2</sub>Se<sub>3</sub>, a-Se and others) semiconductors is the following. Ionization of the inner *i*th shell of the atom in a radiation field of high energy ( $\gtrsim 10^2 \text{ eV}$ ) generates, via the Auger process, a positive charge  $q_2^{(i)}|e|(\ge 2|e|)$  with a finite lifetime  $\tau_l^{(i)}$ . If this charge is produced near a positively charged center, lowsymmetry excitation of the local atomic configuration is produced, viz., a pair of positive ions separated by a distance R > a (a is the interatomic distance). A distinguishing feature of this pair is that the characteristic repulsion energy of  $E_0^{(i)}(R)$  of the configuration exceeds considerably the energy of the other interactions. The electric instability that displaces one of the ions from a site to a (non-nearest) interstice and produces a long-lived Frenkel' pair takes place when the Coulomb repulsion energy  $E_0^{(i)}(R) = q_1 q_2^{(i)} e^2 / \kappa(R) R$  is high enough,

$$E_0^{(1)}(R) - E_{\rm dis}^{\rm i} \equiv \Delta_1 > 0 \tag{4.1}$$

 $(\varkappa(R))$  is the effective dielectric permittivity of the medium for the ion pair). At any rate, if condition (4.1) is met, creation of a Frenkel' pair does not require a finite activation energy. The characteristic (lowest) displacement energy  $E_{\rm dis}^{(i)}$  needed to produce a long-lived Frenkel' pair is of the order of the energy  $E_{\rm T}$  for its thermal formation,  $E_{\rm T} \leq E_{\rm dis}^{(i)}$  $\ll E_{\rm d}$ , and the typical ion-displacement time is comparable with  $\tau_{\rm D} \equiv \omega_{\rm D}^{-1}$ ,  $\tau_{\rm dis}^{(i)} \approx (1-3) \cdot 10^{-14} \, {\rm s} \gtrsim \tau_{\rm D}$ .

The total probability of the elementary act of creation of a long-lived Frenkel' pair, calculated in the quasiclassical approximation (for atoms) within the framework of the sudden-perturbations theory, is of the form<sup>71,77</sup>

$$W^{(i)} \equiv W^{(i)}(R) \approx \exp\left(-\frac{\tau_{dis}^{(i)}(R)}{\tau_{l}^{(i)}}\right).$$
 (4.2)

This process is independent of the temperature T (is athermal),  $dW^{(i)}/dT = 0 = d\sigma_1/dT$ , if

$$\frac{\mathrm{d}\boldsymbol{c}_{\star}}{\mathrm{d}T} = 0, \quad \frac{\mathrm{d}\boldsymbol{\sigma}_{\mathrm{ion}}^{(i)}}{\mathrm{d}T} = 0 = \frac{\mathrm{d}}{\mathrm{d}T} \frac{\boldsymbol{\tau}_{\mathrm{dis}}^{(i)}}{\boldsymbol{\tau}_{\star}^{(i)}}, \quad (4.2')$$

whereas for the usual  $c_+ Z_i < 1$  the cross section of the process is

$$\sigma_{\mathbf{I}} = c_{+} \sum_{\mathbf{i}} \sigma_{\text{ion}}^{(\mathbf{i})} Z_{\mathbf{i}} \equiv \sum_{\mathbf{i}} \sigma_{\mathbf{I}}^{(\mathbf{i})}, \quad Z_{\mathbf{I}} = \sum_{R \geqslant a} W^{(\mathbf{i})}(R), \quad (4.3)$$

where  $\sigma_{ion}^{(i)}$  is the total cross section for the ionization of the *i*th shell. The process considered is most effective when the duration  $\tau_l^{(i)}$  of the ion repulsion is long enough,

$$\tau_{l}^{(i)} \geq \tau_{dis}^{(i)}(R) \geq \tau_{dis}^{(i)}(a) \quad \text{at} \quad R \geq a.$$
(4.4)

Theory permits a calculation or an estimate of the parameter  $Z_i$  of the mechanism efficiency, with  $Z_i \gtrsim z$  for (4.1) and (4.4) (z is the coordination number of the proper atom). The region, characterized by the radius R, where the process is most effective is determined by conditions (4.1) and (4.4). Under situations usually realized in semiconductors, the temperature-independence condition (4.2') and the high-efficiency condition (4.4) can be met in practice:  $Z_i$  $\sim (R_i/a)^3$  at  $R_i \ge a$  for typical  $q_2^{(i)}$ ,  $2 \le q_2^{(i)} < 10$ , and  $\tau_l^{(i)}$  $\approx 10^{-13} - 10^{-14}$  s  $\gtrsim \tau_{dis}^{(i)}(a) \approx (1-3) \cdot 10^{-14}$  s. The last estimate corresponds to realization of an effect observed in Ref. 1, the "slowing down" of the surfacing of an Auger hole from the *i*th inner shell of an atom into a broad valence band having a width  $D_v \gtrsim 3 \text{ eV}$  typical of semiconductors such as Ge and of III-V and II-VI type (compared with the "surfacing" into the valence band of an individual atom.

The efficiency of the mechanism considered is thus limited only by the smallness of  $c_+$  (usually  $c_+ \leq 10^{-1}$ . Its cross section  $\sigma_{\rm I}$  can noticeably exceed the cross section  $\sigma_{\rm d} \sim 10^{-24}$  cm<sup>2</sup> for the production of FP via the elastic-displacements mechanism (at irradiation energies close to the threshold value), viz.,  $\sigma_{\rm I} \gtrsim \sigma_{\rm d}$  at  $c_+ \gtrsim 10^{-3} - 10^{-4}$  and  $Z_{\rm i} \approx 1 - 10$  and at typical values  $\sigma_{\rm ion}^{(i)} \sim 10^{-20}$  cm<sup>2</sup>. This conclusion is at variance with the case of (photo)ionization of the valence shell (i=v) of an atom in a crystal, since  $\tau_l^{(\nu)} \approx \tau_v \approx \hbar/D_v < 10^{-15}$  s for the usual  $D_v \gtrsim 3$  eV, but can again become valid for amorphous semiconductors at low T and described by jumps  $\tau_l^{(v)} \rightarrow \infty$  as  $T \rightarrow 0$  (see Ref. 77 and Sec. 8).

If the condition (4.1) is not met, the process can still be realized via thermal activation.

As shown by Klinger, decaying low-symmetry electronic excitations that are due to pairs of ions of opposite sign (ionized atoms near existing negatively charged centers—acceptors of density  $c_{-} < 1$  etc), can also enhance the defect formation (compared with the thermal mechanism) via interband attraction and lowering the FP production energy. The process is then thermally activated,  $W_{-}^{(i)}(R) \leq \exp(-\tau_{dis}^{(i)}(R)/\tau_{l}^{(i)})\exp(-\varepsilon_{a}^{(i)}(R)/T) \leq \exp(-\tau_{dis}^{(i)}(R)/\tau_{l}^{(i)})$  with an activation energy  $\varepsilon_{a}^{(i)}(R) > T$  for  $E_{dis}^{(i)} > |E_{0}^{(i)}(a)|$  (or is possibly athermal at  $\varepsilon_{a}^{(i)} = 0$  if  $\varepsilon_{dis}^{(i)} < |E_{0}^{(i)}(a)|$ ) and can be effective at sufficiently large  $c_{-}$  (<1).

The role of the initially charged center can be assumed, in particular, by the core of a donor (+) or acceptor (-)center of large radius (the procedure is therefore frequently referred to as the "impurity-ionization" mechanism), or by a deep center on which a carrier is self-trapped, such as a hole (+) or electron (-) in a semiconductor, a cation (+) in an ionic crystal, and an intrinsic hole (+) or electron (-) pair in a glassy semiconductor (see Refs. 79a, 8, and 200 and Sec. 8).

Another type of defect formation, brought about by electrostatic interactions, can be realized when the decaying electronic excitation and the local configuration are highly symmetric, having the point symmetry of the considered three-dimensional crystal (e.g., when the Varley model<sup>64</sup> is applicable). Although apparently there are no quantitative relations for the probabilities  $W_{\rm S}^{\rm (i)}$  and cross sections  $\sigma_{\rm I}^{\rm (S)}$  of the defect-formation process for such a multiparticle system (see Refs. 71 and 78b), a qualitative analysis suggests that the elementary act of the process is the following. Repulsion of the intrinsic positive ions (having a charge  $e_0$ ) from the charge  $q_2^{(i)}|e|$  formed by the ionization produces a slow shift  $u_i (\leq a/2)$  of these ions, accompanied by dipole formation (j = 1, 2, ..., z). The interaction between the charge and the dipoles, with energy  $E_{ep}^{(i)} < 0$ , together with the thermal fluctuations, lowers the symmetry of the local configuration and the energy of the thermal FP production, and therefore increases the defect-formation probability  $W_T \rightarrow W_S^{(i)}$  $\leq \exp(-t_{\rm dis}^{(i)}(\tau_{\rm dis}^{(i)})^{-1})\exp(-E_{\rm s}^{(i)}/T)$ , with  $E_{\rm s}^{(i)} = 0$  at  $Q_{\rm i}$  $\equiv E_{\text{dis}}^{(i)} - (E_0^{(i)} - c_1 | E_{\text{ep}}^{(i)} |) < 0, \text{ but } E_{\text{S}}^{(i)} = Q_i \text{ at } Q_i > 0$  $(c_1 \sim 1)$  is also possible. One can expect that the real time of ion displacement (from the site) is  $t_{dis}^{(i)} \gg \tau_{dis}^{(i)}$  and that the charge-dipole interaction can weaken the Coulomb repulsion noticeably. The mechanism discussed should then have an exponentially small cross section, and accordingly no such process was observed experimentally in a three-dimensional crystal, see Refs. 8, 12, and 71 (the situation may be different for a similar process on the surface of a crystal with lower symmetry than that of the lattice; see Sec. 3 and Refs. 67-69).

For the considered electrostatic mechanisms, the atomic-displacement time is comparable with  $\tau_D$ , so that they can be legitimately regarded as "slow" and non-impact.

It has already been noted that in earlier attempts to apply the Varley model to semiconductors such as Ge and III–V compounds (Refs. 40, 45, 47) it was assumed that the Frenkel' pair is produced by repulsion between the two holes produced by ionization of a deep shell of the atom and displaced to neighboring convalent bonds in a regular crystal. At the typical  $D_v \gtrsim 3$  eV, however, in the case  $D_v \gtrsim U_c$  ( $U_c$  is the energy of the repulsion between the holes) the lifetime of such holes is very short ( $\tau_l^{(v)} \approx \tau_v \leq 3.10^{-16}$  s), so that in practice the non-impact production of FP is exponentially suppressed to the extent that  $\exp(-\tau_{dis}^{(v)}/\tau_l^{(v)})$  is small for  $\tau_{dis}^{(v)} \approx 10^{-14}$ – $10^{-13}$  s and the scale of  $\tau_{dis}^{(v)}/\tau_l^{(v)}$  is 50–100.<sup>2)</sup>

Thus, effective non-impact electrostatic mechanisms of formation of primary defects (and of transformation of existing ones) in semiconductors are in accord with the lowsymmetry models considered by Klinger (and not with Varley-type models): they are decisively governed by the charged centers present prior to the irradiation.

# b) Experimental manifestations of low-symmetry electrostatic mechanisms in semiconductors

We consider now the experimental manifestations of the highly effective low-symmetry electrostatic mechanism,



FIG. 7. Possible cases of Frenkel'-defect formation in doped atomic semiconductors and in InSb crystals.

named the "impurity-ionization" mechanism.<sup>8,51–56</sup> In this case we can compare quantitatively the experimental results with Klinger's theoretical predictions considered in the preceding subsection.

Figure 7 shows schematically, with indium antimonide as the example, possible cases of production of pairs and groups of positive ions in III-V compounds. Positive-ion pair production is possible in the presence of donors: when an atom of group V (antimony) is replaced by one of group VI (tellurium) and one of the nearest host atoms is ionized, a pair of positive ions is produced (case 1). The same occurs when a group-III atom (indium) is replaced by one of group IV (germanium)---ionization of one of the nearest host atoms leads again to production of a pair of positive ions (case 2). When a deep shell of the germanium impurity ion that replaces antimony is ionized (case 3), a charge can be produced via the Auger effect and a group of five positive ions is obtained. This situation is similar to, but not identical with, the case considered by Varley,<sup>64</sup> but does not, however, lead to effective production of defects (see above). In case 3, the decisive role is played by the fact that the germanium impurity ion has an acceptor state near the edge of the valence band, and this lengthens considerably the duration of the localization of the positive charge on the impurity ion, and increases thereby the defect-production probability. In all the cases considered, the defects produced have a relatively simple structure. If a host atom leaves a site, a vacancy appears alongside the host interstice, and a vacancy + donor complex can be produced. If an impurity leaves a site, an impurity interstitial atom and a vacancy are produced.

Experimental results of various workers were quantitatively analyzed<sup>77,78</sup> to assess the possibility of interpreting them in terms of the impurity-ionization mechanism. To this end, the calculated and experimental cross sections for defect formation were compared for each observed case of defect formation in the case of "subthreshold" irradiation. The cross sections were compared by calculating the ratio  $\sigma_{\exp} (c + \Sigma_i \sigma_{ion}^i)^{-1}$ , which is equal to  $Z_{\exp}$ , in the case when the impurity-ionization mechanism operates. If this ratio lies in the reasonable range indicated above for  $Z_{exp}$ , it can be quite reliably assumed that action of the impurity-ionization mechanism is observed, and the "acting" electron shells are those whose ionization yields the more resonable value of  $Z_{exp}$ . This method was used to analyze practically all the published cases when "subthreshold" defect formation in semiconductors was observed. It turned out that almost all the results (except those for silicon) can be interpreted in the framework of the impurity-ionization mechanism.

Silicon doped with arsenic to a density  $5 \cdot 10^{19}$  cm<sup>-3</sup> was irradiated with 9-keV electrons and was then investigated by

the method of backscattering of the H<sup>+</sup> ions. This determined directly the density of the As atoms displaced from the sites (including those contained in the vacancy + donor complexes), i.e., the density of those effects that can be produced when the impurity-ionization mechanism is in operation. The value of  $Z_{\text{eff}}$  (even if it is assumed that the defects are produced only when K<sup>+</sup> shells are ionized) is low ( $\leq 0.002$ ), i.e., the mechanism is not effective in silicon.

The results for germanium can be well interpreted in terms of the impurity-electrostatic mechanism if it is assumed that the defects appear when the K and L shells are ionized at room temperature. In this case  $Z_{exp}$  is close to 4, i.e., atoms from the first coordination sphere of the impurity atom can take part in the defect formation.

All the features of the impurity-ionization mechanism of defect formation are observed for *p*-InSb (Refs. 5, 52, 54). X-irradiation (60 keV) at a temperature below 100 K (region of defect stability) decreases exponentially the density of the electrically active impurity ions (donors and acceptors) in strongly compensated crystals when the irradiation dose is increased (see Fig. 3). This means that the cross section for the "deactivation" of the impurity atoms (i.e., the cross section for the formation of defects that contain impurity atoms) is linear in the density of the electrically active impurity atoms, as follows indeed from the theory. The density of the charged scattering centers, determined independently from the carrier mobilities, also decreases with increasing dose (see Fig. 3). The defects become annealed (Fig. 8) in one clearly defined stage, thus giving evi-



FIG. 8. Isochronous thermal annealing of effects induced by x-irradiation in InSb-Mg (1) and InSb-Ge (2) crystals. The annealing changes the densities of the donors  $N_D$  and acceptors  $N_A$  (1, 2), the densities of the hole-scattering centers  $N_x$  (1', 2'), and the mobilities of the holes at 20 K (1", 2").



FIG. 9. Schematic illustration of the features of the separation of the vacancies (v) and of the interstitial atoms (i) for the impurity-ionization mechanism of defect formation in antimony-doped germanium at various distances between the ionized atom and the charged impurity.

dence that their spatial structure is simple.

The value of  $Z_{exp}$  of a binary compound can be estimated by two methods. It can be assumed either that a regular atom (indium or antimony) located near an impurity donor is ionized, or that an impurity atom (acceptor-germanium in the antimony sublattice) is ionized. Under either assumption the value of  $Z_{exp}$  turns out to be reasonable if it is assumed that the defects are produced by ionization of any of the deep shells of indium or antimony, including the subvalent N shell, or of any of the deep shells of the Ge impurity atom:  $Z_{exp} \approx 20$  for irradiation at 4.2 K and  $Z_{exp} \approx 2$  for  $T_{irr}$ = 77 K. Experiments have shown that the efficiency of the electrostatic mechanism increases with decreasing temperature. Since neither the Coulomb interaction nor the Auger process depends on temperature, it remains to assume that the defects with small  $Z_{exp}$  (i.e., defects produced with participation of nearer impurity-atom neighbors) turn out to be more stable. This can have two causes: 1) The smaller the distance between the positive ions the larger their Coulomb interaction and the larger the distances between the produced vacancy and the interstitial atoms, so that the (v, i) pair recombination probability is lower. 2) At a short distance between the positive ions, the probability of formation of a stable "vacancy + impurity atom" complex is higher. This situation is illustrated in Fig. 9.

Vailov and co-workers<sup>57,58</sup> observed "subthreshold"



FIG. 10. Intensity of cathodoluminescence of various centers as a function of the energy of the irradiating electrons in diamond of type Ia.<sup>57,58</sup> The arrows denote the K-shell ionization energies of certain impurity elements in the diamond.

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defect formation in diamond, which they interpreted in terms of the "impurity-ionization" mechanism. They were able to observe the energy threshold for the onset of cathodoluminescence due to the appearance of the vacancies. This threshold coincides with the K-shell ionization energy of the Mn, Co, and Fe impurity atoms (Fig. 10). They suggest that the pre-existing positive ions can be those of nitrogen (donors).

In the case of above-threshold irradiation, the action of the impurity-electrostatic mechanism is most frequently masked by the action of the elastic-displacement mechanism. Mashovets et al. 53,55 have shown that conditions exist that ensure the possibility of observing the impurity-ionization mechanism even for above-threshold irradiation. One such condition is a high density of the corresponding impurity. Thus, the cross section for formation of defects, including a group-V impurity atom, was obtained for n-Ge as a function of the density of this impurity (Fig. 11).<sup>53,55</sup> The value of the cross section at densities  $3 \cdot 10^{17}$  cm<sup>-3</sup> agrees well with the cross section for the elastic-displacement mechanism.<sup>3)</sup> This is followed by a rapid increase of the cross section for defect formation, and the cross section becomes proportional to the donor density, as it should in the considered lowsymmetry electrostatic mechanism; the value obtained is  $Z_{exp} = 3.5$ . Conditions favorable for the observation of the action of the impurity-ionization mechanism in "abovethreshold" irradiation are produced also if the irradiation is at low temperature, when the intrinsic defects produced by



FIG. 11. Plot of the effective cross section for defect formation in Ge crystals with different densities  $N_{\rm D}$  of the donors (P, As, Sb, Bi).

the elastic-displacement mechanism are immobile and cannot interact with the impurity atoms. A process of this type, which is manifested by a lowering of the density of shallow donors, was observed<sup>56</sup> for indium antimonide exposed to  $\gamma$ rays at 4.2 K.

# 5. DEFECT FORMATION IN EXCITON DECAY AND ELECTRON-HOLE RECOMBINATION IN IONIC CRYSTALS a) Experimental manifestations of the exciton mechanism of defect formation

The numbers of F centers, as functions of the energy of the photons incident on a crystal (5–21 eV) (known as the defect-formation spectra), were measured for AHC in 1959– 1965 and it was shown that the  $(v^+e^-)$  F centers are most effectively produced by selective formation of excitons by photons, and also by recombination of electrons and holes.<sup>28,29,62,81–83</sup>

On the basis of this fact, Vitol, Lushchik, and Élango<sup>84–87</sup> advanced the hypothesis that creation of radiative defects in AHC is due to nonradiative annihilation of self-trapping excitons or to recombination of electrons with self-trapped holes. A similar conclusion was arrived at simultaneously by Herch<sup>88</sup> and Pooley.<sup>89</sup> This hypothesis was confirmed by direct experiments. Creation not only of F centers, but also of interstitial halogen atoms was observed in Refs. 90–92 for KCl and KBr by luminescence methods and by the method of exoelectronic emission with optical production of excitons. Creation of H centers by photostimulated recombination of electrons with self-trapped holes in KCl–Tl and KCl–Ag was recorded in Refs. 93 and 94 by ESR and optical methods.

Optical formation of excitons  $(e^0)$  and of electron-hole pairs  $(e^-, e^+)$  in AHC is accompanied by the reaction

$$e^{0} \rightarrow v^{+}e^{-} + i^{0},$$
 (5.1)

$$e^{-} + e^{+} \rightarrow e^{0} \rightarrow v^{+}e^{-} + i^{0}.$$
 (5.2)

Lushchik, Vitol, Vasil'chenko, *et al.* have observed<sup>95</sup> that at 4.2 K optical formation of excitons leads in KCl, KBr, RbBr, and CsBr not only to production of (F, H) pairs but also to creation of pairs of charged defects, viz., anion vacancies and interstitial ions of the halogen [( $\alpha$ , I) pairs], via the reactions

$$e^{0} \rightarrow v^{+} + i^{-}, \qquad (5.3)$$

$$e^{-} + e^{+} \rightarrow e^{0} \rightarrow v^{+} + i^{-}.$$
 (5.4)

Tunneling charge exchange of (F, H) pairs produces  $i^-$  in the crowdion configuration, which can be displaced at 4.2 K by several lattice constants, thus preventing their recombination with v<sup>+</sup> (Refs. 27 and 97).

The possibility of radiative formation of Frenkel' defects in the cation sublattice of an AHC was considered in Refs. 86 and 62. Since these defects are not optically active in the transparency region of an ideal crystal, cation defects have so far been little investigated, although the fact that they are produced by x rays and by exciton-generating UV radiation is beyond doubt.<sup>97-99</sup>

Ueta, Williams, Ito *et al.*<sup>100–102</sup> observed and investigated in KCl and KBr the short-lived (v, i) pairs predicted by Frenkel'.<sup>3</sup> Typical of short-lived (F, H) pairs are formation

times  $10^{-11}$  s (Ref. 102) and recombination times  $10^{-9}$ - $10^{-3}$  s (Ref. 101). The number of (F, H) pairs in KBr at 5 K, at the first instant after defect formation by nanosecond electron-beam pulses, is tens of times larger than the number of ( $\alpha$ , I) pairs. After several seconds, however, the number of long-lived (F, H) pairs becomes already several times smaller than the number of ( $\alpha$ , I) pairs.<sup>101</sup>

The experimental results considered show unequivocally that the radiative formation of defects in AHC is based on FP production in nonradiative annihilation of self-trapped excitons  $e_s^0$  and on recombination of electrons with self-trapped holes  $e_s^+$  in regular regions of the crystal lattice.

Self-trapping hinders the transfer of electronic excitations to the pre-existing defects. In AHC, however, defects can be produced also by exciton-impurity mechanisms. The e<sup>0</sup> and e<sup>+</sup> migrate at 4.2 K prior to self-trapping over distances of the order of  $10^2 a$ , so that a fraction of the electronic excitations is transferred to intrinsic and to impurity defects. At temperatures 100–300 K, the  $e_s^0$  and  $e_s^+$  that take part in the hopping diffusion can also interact with the defects. Interaction of excitons with clusters of anion and cation vacancies can lead, e.g., to F centers and to  $V_F(v^-e^+)$  centers that are separated from them in space.<sup>22,78</sup> Such reactions are quite common for AHC with defect density  $10^{-5}-10^{-3}$ (Ref. 76). In AHC with pre-existing defects, electronic excitations can also be directly produced alongside with the defect by using light in the region of the long-wave tail of the intrinsic absorption of the crystal. It was thus possible to produce in KCl-Na and KCl-Br, selectively, F centers that were located alongside Na<sup>+</sup> or Rb<sup>+</sup> ions.<sup>27,76,103</sup>

Significant information on the mechanism of (F, H) and ( $\alpha$ , I) pair production in AHC is obtained by investigating the spectra of FP production by vacuum UV radiation at 4.2 K.<sup>14,27,94,95,103-106</sup> By way of example, Fig. 12 shows spectra, measured by highly sensitive luminescence methods, of the formation of (F, H) and ( $\alpha$ , I) pairs in KCl crystals.<sup>27</sup> The long-lived (F, H) pairs are effectively produced both in the region of the exciton absorption bands (e<sup>0</sup> with n = 1, 2) and when e<sup>-</sup> and e<sup>+</sup> are produced by photons whose energies exceed the band gap ( $E_g$ ). Long-lived ( $\alpha$ , I) pairs are produced in KBr at 4.2 K mainly via  $e_S^0$  decay. The efficiency of ( $\alpha$ , I) pair production in KCl and KBr via re-



FIG. 12. Absorption spectra (1) and (F, H)-pair and  $(\alpha, I)$ -pair production spectra (2 and 3) in KCl crystals. The spectra were measured at 4.2 K by luminescence methods.



FIG. 13. a) Differential thermal annealing of the stored energy (1) and of the linear dimensions of the crystal (2) for x-irradiated KCl crystals; b) thermal annealing of x-ray induced ESR signal of H centers (3), and also of F-stimulated 3 eV tunnel luminescence (4) and of optical absorption of  $\alpha$  centers (5) for KCl-Rb irradiated by 7.6-eV photons.

combination of  $e^-$  and  $e_s^+$  is lower by at least an order than via  $e_s^0$  decay.<sup>76</sup>

Important information on the mechanism of production and recombination of (F, H) and ( $\alpha$ , I) pairs in AHC was obtained by thermoactivated spectroscopy methods. The crystal irradiated at 4.2 K is heated at a constant rate and the annealing of the different defects, which manifests itself in weakening of the optical absorption<sup>107</sup> or in release of stored energy (Fig. 13), is investigated.<sup>108</sup> When pulsed annealing is used, much information is provided by investigating the **ESR** of defects such as paramagnetic interstitial halogen atoms (H centers) (see Fig. 13).<sup>93,109</sup>

The use of highly sensitive luminescence methods enabled Lushchik, Vasil'chenko, et al. to study the annealing of  $(\alpha, I)$  and (F, H) pairs in KCl and KCl-Rb irradiated by photons in the exciton absorption band, 31,95,104,103 and also when electronic excitations were optically produced near impurities.<sup>27,76,103</sup> The use of low irradiation doses made it possible to investigate the formation and annealing of defects in the regime of isolated  $(\alpha, I)$  pairs, when the average distance between defect pairs exceeds appreciably the average distance between the complementary pair components (Refs. 14, 103, 106). Creation-correlated vacancies and interstitial atoms are annealed in accord with the theory of diffusion-controlled reactions.110 Figure 13 shows for KCl-Rb the annealing curves of the anion vacancies ( $\alpha$  centers) after optically producing near-impurity excitons by 7.6-eV photons. Annealing decreases the number of v<sup>+</sup> in the region of 18, 22, 28, and 32 K. The effect is due to hopping diffusion of the  $i^-$  and their recombination with the  $v^+$  that are located at various distances (5-10 a) from the i<sup>-</sup>. The interstitial halogen atoms produced in the KCl-Rb are annealed, as shown by pulsed annealing of ESR of H centers<sup>109</sup> (see Fig. 13), in the 35-55 K range. At 35-40 K, annealing takes place of (F, H) pairs with distance less than 5a

between defects. These pairs can be easily transformed into  $(\alpha, I)$  pairs by F-center optical excitation that stimulates radiative tunnel charge exchange of (F, H) pairs (see Fig. 13):

$$\mathbf{v}^+\mathbf{e}^- + \mathbf{i}^0 + h\mathbf{v}_{\mathrm{F}} \rightarrow \mathbf{v}^+ + \mathbf{i}^- + h\mathbf{v}_{\mathrm{L}}.$$
 (5.5)

For KCl we have  $hv_F = 2.3 \text{ eV}$  and  $hv_L = 3.0 \text{ eV}$ . Consequently  $hv_F < hv_L$ , and it is this which determines the possibility of tunneling charge exchange of (F, H) pairs:

$$v^{+}e^{-} + i^{0} \rightarrow v^{+} - i^{-},$$
 (5.6)

which was also observed in KCl and CsBr.95,98,105

The exciton mechanism of FP production in KCl crystals is highly efficient. At 5 K, 16% of the electronic excitations produced by the laser beams decay to produce shortlived (F, H) pairs, <sup>102</sup> and 6% of them constitute stable (F, H) pairs. The quantum yield of the radiative annihilation of the excitons in KCl is of the order of 3% at 4.2 K (Ref. 27).

# b) Mechanisms of exciton decay and electron-hole recombination accompanied by defect formation

Excitons exist in AHC in two qualitatively different states. At the instant of ultraviolet irradiation, free excitons  $(e^0)$  are produced whose states are separated by an energy barrier (10–40 meV) from the state of the self-trapped excitons  $e_S^0$ .<sup>111–114</sup> The hole component of  $e_S^0$  has the structure of a dihalogen molecule  $X_2^-$  (X = F, Cl, Br, I) located in two anion sites.

The lifetime of  $e^0$  on a crystal-lattice site is considerably shorter than  $\tau_D$ , therefore  $e^0$  that interact weakly with the lattice vibrations cannot create defects directly. At the instant when the exciton becomes self-trapped, the local exciton-phonon interaction becomes strongly enhanced, and if  $e_S^0$  has a sufficiently high energy, decay accompanied by defect production becomes possible.

The possible processes that produce Frenkel' defects in  $e^0 \rightarrow e_s^0$  transitions and in annihilation of various  $e_s^0$  states were considered in Refs. 12–16, 62, 84–96, and 115–124. It was proposed in Refs. 80, 117, and 11 that production of i<sup>-</sup> or i<sup>0</sup> occurs in nonradiative annihilation of  $e_s^0$  and when the system goes into the ground state ("recombination mechanism"). In Refs. 88 and 119 a dissociative model was considered of  $e_s^0$  decay with (F, H) pair production: one of the excited  $e_s^0$  states has a repulsive potential, and when the  $e_s^0$  goes over into this state its hole component can dissociate and the halogen can be displaced into an interstice.

Lushchik and Élango proposed<sup>62</sup> a model, subsequently greatly elaborated, <sup>120,121,123,124</sup> for the decay of an exciton with production of an FP via translation of a dihalogen  $e_S^0$ component from two anion sites into one, with formation of an (F, H) pair. The translation of the interstitial atoms of the halogen in the decay of  $e^0$  presupposes orientation of the effect along the (110) axes in KCl and KBr and along the (100) axes in CsBr. This effect was observed for CsBr<sup>14,125,106</sup>. Escape of the halogen from the crystal along the (110) axis was observed when KCl was irradiated by an electron beam or by a laser.<sup>128</sup>

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The inverse of exciton decay with FP production was observed experimentally for CsBr crystals.<sup>125,106</sup> Recombination of F and H centers by heating to 11 K or by illuminating the crystal in the H-band absorption region produced  $e_s^0$ that emitted their characteristic luminescence as a result of the reaction

$$\mathbf{v}^{+}\mathbf{e}^{-} + \mathbf{i}^{0} \to \mathbf{e}^{0}_{s} \to h\mathbf{v}. \tag{5.7}$$

In the body centered CsBr crystals, as shown by an investigation of the emission produced by stimulation with polarized light in the H-center absorption region, the ions are displaced along close packed rows of anions in the [100] direction.

Most (F, H) and  $(\alpha, I)$  pairs in KCl and KBr annihilate without radiating. This may be, as noted in Ref. 126, the cause of the "radiative jarring" in crystals: nonradiative recombination of interstitial atoms with vacancies is accompanied by acoustic waves that can act on spatially remote radiation defects and cause the latter to diffuse or to be restructured. Optical manifestations of this effect were revealed for the first time in Ref. 127 by the quenching of the  $e_s^0$ luminescence in KCl in which  $(v^+, i)$  pairs recombined.

The elementary act of translational displacement of the hole component from two sites into one as a result of strong exciton-phonon interaction was theoretically analyzed by Élango,<sup>124</sup> Toyozawa.<sup>120</sup> Song,<sup>121</sup> Stoneham,<sup>122</sup> and Kristofel'.<sup>123</sup> The energy, configuration, and dynamics of the "exciton + defect" system during various stages of its evolution in KCl crystals are schematically illustrated in Fig. 14.129 The ordinate is the energy of the system relative to the energy of the unexcited crystal. The abscissa is the displacement of the removed anion from its equilibrium position in the [110] direction. The curves are the adiabatic potentials of the "exciton + defect" system when an anion in the form  $X^-$  (1) or  $X_2^-$  (2) is removed from the site. The shaded region on the configuration schemes corresponds to the spatial distribution of the electronic component of the exciton.

The lowest-energy nonrelaxed intrinsic excitation in KCl is the  $\Gamma$  exciton. The absorption bands corresponding to its optical formation are located at 7.779 and 7.893 eV (1s state) and 8.465 and 8.575 eV (2s state). After its optical production, the  $e^0$  relaxes into the  $e_s^0$  states and its hole com-

Ş Energy, Distance, d

ponent acquires the configuration of the  $Cl_2^-$  quasimolecule. The energy of the lowest electronic state of a self-trapped exciton at thermal equilibrium is 6 eV.<sup>130</sup>

Among the defect states, the most reliably established are the energies of the relaxed charged Frenkel' defects. Calculation yielded for the ( $\alpha$ , I) pair in KCl a value  $E_{\alpha I} = 3.7$ eV.<sup>131</sup> To estimate the energy of the (F, H) pair in KCl (6.3 eV), a closed cycle of physical processes of known energy was considered.<sup>124</sup> The system energy at the instant when an anion passes between two neighboring cations was estimated in Ref. 132. For an anion in the ground electronic state, it amounts to 12–15 eV, and for the  $Cl_2^-$  quasimolecule the barrier is considerably lower (there may be none at all for an excited  $Cl_2^-$  quasimolecule<sup>133</sup>).

The dynamics of  $e_S^0$  decay with production of an (F, H) pair by the translational displacement mechanism was analyzed by Toyezawa, Song, and Kristofel'. 120, 121, 123 The instability produced at the instant when  $e_s^0$  goes over from a state with an excited electronic component 2p (excited state  $b_{3u}$ in Fig. 15) into a state with unexcited electronic component  $(a_{1,\alpha})$ . When an even intramolecular vibration is produced for  $X_2^-$  and "breathing vibrations" for the surrounding ions, interaction with odd  $b_{3u}$  vibrations (departure of the hole component to the [110] direction) produces instability of the state  $a_{1g}$ , analogous to that in the Jahn-Teller pseudoeffect (the adiabatic potential acquires a negative curvature), and displacement of  $X_2^-$  from two sites into one becomes possible. The electron is then adiabatically localized in the lowest state of the resultant anion vacancy. The bottleneck of the process is the  $2p \rightarrow 1s$  transition. Calculations<sup>121</sup> have shown that such a transition can occur within  $10^{-11}$  s, in agreement with experiment.<sup>102,134</sup>

The considered model of the decay of  $e_s^0$  with production of (F, H) pairs predicts the possibility of defect formation by optical excitation of the  $e_s^0$  that had until then an electronic component in the 1s state. This effect was observed by Williams et al. 102 and was studied in detail by Ito et al. 15, 134, 135 Figure 15 shows the spectra of the transition absorption of triplet  $e_{S}^{0}$  in KCl, produced by an electron-beam pulse. The region 1.5-3.0 eV corresponds to excitation of the electronic component of  $e_s^0$  (the transitions  $1s \rightarrow 2p$  and  $1s \rightarrow 3p$ ). The 3.1-4.2 eV region corresponds to excitation of

> FIG. 14. Energy of KCl crystal as a function of the displacement of the Cl<sup>0</sup> atom from its equilibrium position in the [110] direction (in units of the distance d between the ions). Model configurations of various states are shown.



the hole component of  $e_s^0$ . The electronic excitations were resolved in Ref. 136 by a polarization procedure. The spectrum for production of (F, H) pairs by radiation from a tunable laser contains all the excited states of the electronic component of  $e_s^0$  (Ref. 135).

It might seem that the spectra for the production of (F, H) pairs in KCl by UV radiation (see Fig. 12) do not agree with the Jahn-Teller mechanism of (F, H) pair production, since the defect-production efficiency is high not only when excitons are produced with n = 2 but also with n = 1. This contradiction is only a seeming one: it has been shown<sup>76,136</sup> that for vibrational relaxation the  $e_s^0$  state with n = 2 is lower than the  $e^0$  state with n = 1, so that free excitons with n = 1 are partially transformed into self-trapped excitons with n = 2, and this may be the cause of (F, H)-pair production via the Jahn-Teller mechanism. In Refs. 15 and 134 the mechanism is considered of  $e_s^0$  decay with (F, H)-pair production with allowance for the energy transfer from the excited  $e_s^0$  component to its hole component.

AHC can be divided into two groups with respect to the features of the  $e_{S}^{0}$  decay with (F, H) pair production. According to Ref. 137, the efficiency of this decay in KCl, KBr, RbCl, RbBr, and CsBr is high even at 4.2 K and depends little on temperature, while in NaCl, NaBr, KI, and RBI the decay efficiency is lower by several orders, but is strongly increased by heating to 100-200 K. This behavior was interpreted by Lushchik et al.<sup>138</sup> For the crystals of the first group, the intramolecular oscillations of the self-trapped holes and of the  $e_S^0$  hole component have frequencies higher than the limiting crystal-vibration frequencies, since they are slowly relaxing local vibrations. After the decay of  $e_s^o$ into F and H centers situated close by, the reserve of vibrational energy of the local vibration can contribute to further athermal departure of the H center from the F center even at 4.2 K. The intramolecular  $e_s^0$  oscillations in the crystals of the second group are superimposed in frequency on the crystal vibrations, being quasilocal and relatively short-lived. The hole component in these crystals "cools" rapidly and separation of the (F, H) pair calls for heating to 100-200 K.

Recombination of electrons with relaxed holes (those having no excess vibrational energy) produces (F, H) pairs

FIG. 15. Absorption spectrum of dihalogen self-trapped electrons (1) and spectrum for production of short-lived centers by excitation of self-trapped excitons by a tunable lasers (2) for KCl crystals irradiated by electrons at 10 K.

with short distances between defects, and practically no  $(\alpha, I)$  pairs are produced. The non-equivalence of the exciton and electron-hole mechanisms for defect formation was considered in Refs. 14 and 94.

# c. Defect formation in wide-gap oxides

Radiative formation of defects by decay of electronic excitations has come into use recently for production of active centers in tunable lasers based on ionic crystals<sup>139</sup> and also to implement "interstitial-vacancion" memory mechanisms in various memory devices. Such a mechanism is used, for example, in halogen-containing sodalites, where excitation of the halide ion causes ejection of the halide atoms from the cavities of the rigid alumosilicate framework into neighboring cavities, so that F centers are produced.<sup>140</sup> More frequently, however, decay of electronic excitation accompanied by defect formation leads to highly undesirable phenomena such as aging and degradation of a great variety of solid materials.

Replacement of AHC by crystals made up of doubly and triply charged ions increases greatly the energy needed to produce FP (Refs. 12, 73, 141). If the exciton (electronhole pair) energy  $E_e$  is lower than the FP-formation energy  $E_{\rm dis}$ , the electronic excitations cannot decay and produce defects in the regular crystal-lattice sites. This is precisely why BeO, MgO, Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, and others are more resistant, by thousands of times, to the action of radiation than are KCl and KBr (Ref. 141).

One might assume that in crystals with  $E_e < E_{\rm dis}$  the defect-formation mechanisms could predominate as a result of elastic displacements of the ions. It has long been noted, <sup>142</sup> however, that in strongly irradiated wide-gap crystals the effective defect-formation mechanisms may turn out to be those with collective decay of two (or several) interacting electronic excitations (e.g., the (e<sup>0</sup>, e<sup>0</sup>) mechanisms). These processes are particularly probable in crystals such as MgO, for which  $E_e < E_{\rm dis} < 2E_e$  (Ref. 141). Annenkov *et al.* have shown recently that when MgO is irradiated by nanosecond pulses of subthreshold-energy electron beams (in the elastic-displacement mechanism), effective defect formation sets in when the critical power is exceeded. <sup>14,143</sup>

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#### 6. RECOMBINATION-STIMULATED AND ELECTRONIC-THERMAL MECHANISMS OF DEFECT TRANSFORMATION

Effects which manifest themselves in photoconductivity and in thermostimulated conductivity of semiconductors and which could presumably be attributed to the appearance of new centers or to vanishing of previously existing ones as a result of low-energy excitation (e.g., via interband transitions) were observed already back in the fifties.<sup>31,32</sup> The experimental proof, however, that such defect creation or annihilation processes do take place was obtained only in the early sixties by Sheĭnkman, Korsunskaya, and Markevich, with single-crystal CdS and CdSe as examples.<sup>37,38</sup> This was made possible by the fact that by then Lishkarev and Sheinkman have developed new methods for comprehensive investigation of the electric and luminescent properties of photoconductors.<sup>50</sup> These methods have made it possible to measure directly the basic parameters of different centers in semiconductors and trace the changes of their density and various transformations of different centers. Special methods have made it possible to distinguish between center creation (annihilation) processes and the typically electronic processes of their charge transfer and modulation of the energy barriers that surround the centers.37,38

The essential difference between the processes considered and those described in Secs. 4 and 5 is that the semiconductor-excitation energy, and accordingly the energy of the subsequent recombination of the carriers and of the annihilation of the excitons, turns out to be considerably lower than the energy needed to produce defects in an ideal lattice. Therefore, as shown by numerous experiments, the centers (defects) contained in semiconductors undergo transformations.

Starting in 1960, Sheĭnkman *et al.* investigated a number of similar processes (named photochemical reactions already back in Ref. 31) in pure and doped CdS, CdSe, ZnSe and  $In_4S_5$  crystals. These processes led to changes in the thermostimulated-conductivity spectra,<sup>37,38</sup> to an increase of the photosensitivity,<sup>37,38,144</sup> to a decrease of the photosensitivity,<sup>145</sup> and to changes of the photoluminescence spectra<sup>56,145,146</sup> as well as of the luminescence-excitation spectra.<sup>11,146,159,160</sup>

It turned out that the appearance of nonequilibrium carriers leads to dissociation of donor-acceptor pairs or of defect complexes, as well as to inverse processes such as reassociation of the centers initially in the complexes. Several types of reaction between defects were observed and studied:

1) Photothermal decay of an associated donor-acceptor (DA) pair (such as an interstitial  $\text{Li}_i^+$  ion + a cadmium vacancy, or an interstitial  $\text{Cd}_i^+$  + an acceptor) into a separate donor and acceptor. The cause of the decay is diffuse motion of the  $\text{Li}_i^+$  and  $\text{Cd}_i^+$  ions which move easily in the lattice after the Coulomb interaction between the donor and acceptor has stopped as a result of the hole capture by the acceptor.<sup>149</sup> As a result of this decay the photosensitivity increases, a new luminescence band due to capture of an electron by an acceptor appears, and a new peak of thermostimulated conductivity<sup>38,147</sup> due to the donor is produced (see Fig. 4). Similar DA-decay processes were observed lat-



FIG. 16. Decay of clusters of CdS,  $^+$  donors following their optical or thermal ionization. a—Level scheme in the band gap before (1), during (2), and after decay of the clusters in darkness (4) and on illumination by infrared from the region of the photocurrent quenching (5).

#### er also in ZnO-doped semiconductors GaAs and GaP.151

2) Decay of DA-complexes consisting of several donors and acceptors and manifesting itself in a change of the spectra of the luminescence and in its excitation.<sup>11,146</sup>

3) Decay of donor cluster consisting of shallow donors  $(Cd_i^+)$ ; this decay results from capture of a nonequilibrium hole or of an optical (thermal) excitation of an electron into the band 145 (Fig. 16).

4) Diffusion of interstitial donors, which have high mobility in the lattice, from their clustering places (e.g., decorated dislocations or other defect sinks) into the volume of the crystal as a result of the recombination that takes place at these sinks<sup>150</sup> (Fig. 17).

5) Clustering of shallow interstitial donors into complexes as a result of electron capture (Fig. 18). The produced donor clusters are centers of rapid nonradiative recombination.<sup>145</sup> This process lowers the photosensitivity and degrades photoresistors based on cadmium sulfide.<sup>152</sup> Process 3) restores the photoresistor.

The foregoing processes are due not only to the change of the Coulomb interaction between the components of the DA pair or of the complex, but also to the appearance or vanishing of the forces of the bonds due to the captured electrons.<sup>145</sup>

The processes described above were observed in II–VI crystals in the 150–350 K range determined by the activation energy of the interstitial-donor diffusion.<sup>153</sup> Special experiments have shown that  $Cd_i^+$  and  $Li_i^+$  drift easily in an electric field with the same activation energy.<sup>154</sup> Using the electric field to transfer the donors from one part of the CdS crystal to another, it was possible to simulate some of the photochemical processes, e.g., the process 4) (Ref. 150).

We have dealt above with restructuring of defects following the capture of a free electron or hole, which led to a transition of an atom between equivalent positions in a site and an interstice. In this case the diffusion activation energy in the investigated II-VI semiconductors was independent



FIG. 17. Photochemical reaction due to recombination-stimulated departure of the donors from the defect sink, and simulation of this reaction in an electric field. The CdS-crystal photoluminescence spectra measured in the region *ab* before (1) and after (2) departure of the donors from the sinks, and also after applying a  $10^3$  V-cm<sup>-1</sup> field at 350 K (3), when the region *ab* was the cathode.

of the presence of excitation (recombination) in the semiconductor.

Yet in semiconductors of other types, particularly in Si, GaAs, and GaP, the presence of recombination can influence substantially the diffusion coefficients of various impurities and defects, by significantly decreasing the activation energy of the diffusion and increasing its rate.<sup>155–159</sup> This fundamental process was discovered experimentally by Kimerling and Lang<sup>155</sup> and was named recombination-stimulated diffusion. It was shown that the diffusion barrier for GaAs and GaP is decreased by a value approximately equal to the energy  $E_{cap}$  for electron capture on the level of the diffusing center, which is the recombination center.<sup>156,157</sup>

The interpretation of the effect, proposed in Ref. 155 back in 1974, was based on the fact that the energy released in nonradiative multiphonon recombination on a center is transferred to the latter, and since it does not manage to go off to the lattice it contributes to diffusion hopping of the defect to a neighboring equivalent position in the lattice. A similar process, pertaining to defect formation, was consid-



FIG. 18. Clustering of shallow donors in CdS when an electron captures two free donors. a) Photoluminescence spectra of CdS-Cu crystals before (1) and after (2) clustering of the donors; b) level scheme in the band gap before (1) and after (2) the reaction.

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ered earlier (theoretically) by Vinetskii.5,63

The interpretation proposed was regarded as obvious for a long time.<sup>156,157</sup> A major difficulty of the proposed explanation is that the so-called receiving mode of the center (the excitation mode into which the energy goes over when an electron is captured from the excitation) and the reaction mode (e.g., the diffusion hopping) are in general not equal. The Kimerling model fails to explain why the energy has time to be transferred from one mode to the other without substantial dissipation in the lattice.

Sheĭnkman<sup>158,159</sup> proposed a new model of radiationstimulated processes in semiconductors, based on the fact that a process (e.g., diffusion jump) occurs not when the electron recombines, but when it is captured by a specific excited level of the center, a level corresponding to an antibinding orbital. It should be noted that Bourgoin<sup>160</sup> and Oksengendler<sup>161</sup> have explained the stimulated diffusion earlier by taking into account the possible existence of defect charge-exchanged states corresponding to inversion of the potential in the lattice. Eliseev *et al.*<sup>162</sup> considered the decay of a center as it captures an electron that lands on an antibinding orbital.

An essential feature of the model considered by Sheinkman is not only the assumption that the center must be excited, but also that this is precisely how the thermal equilibrium process (e.g., the considered diffusion of the defect) evolves. In the usually considered atom-diffusion mechanism it is assumed that the atom surmounts thermally the corresponding barrier in the lattice in the unexcited state. According to Ref. 158, a diffusion mechanism more effective for certain defects is thermal excitation of an electron to an antibinding orbital. When a semiconductor is excited (by illumination or by injection of minority carriers), the latter are captured by the center, and for this center to be in an excited state it suffices then that a majority carrier be captured by an excited level of the center. The activation energy of this capture, which is in fact the activation energy of the recombinationstimulated process, is  $E_{\rm T} - E_{\rm cap} = E_{\rm T}^*$ .

The practical value of the described processes of recombination-stimulated diffusion of defects (impurities) and of various reactions between them is that they serve as the basis of the mechanisms that degrade semiconducting (and mainly optoelectronic) materials and devices, viz., light-emitting diodes, photoresistors, photodiodes, solar-energy cells, and others.

The problem of degradation in semiconductors became particularly acute following the development, by Alferov *et al.*, of room-temperature cw heterolasers.<sup>163</sup> The ensuing situations were considered by Eliseev *et al.*<sup>64</sup> After 10<sup>3</sup> hours of operation, the number of recombination atoms in an injection laser is  $10^{33}$  cm<sup>-3</sup>, while the number of centers that cause degradation is increased by  $10^{16}$  cm<sup>-3</sup>. Although the efficiency of defect formation is low in this case ( $10^{-17}$ ), the total degradation is quite significant. Obviously, in such phenomena one must reckon not only with high-efficiency but also with low-efficiency defect-formation mechanisms.

One of the main causes of degradation of injection lasers and light-emitting diodes is that the so-called dark-line and dark-spot effects are produced in the operating region of the device in the course of operation (see, e.g., the reviews<sup>164–166</sup>). These effects turn out to be three-dimensional dislocation grids caused either by displacement of the dislocations or by absorption of point defects that move rapidly towards the dislocations.<sup>167</sup> The cause of the rapid motion is recombination-stimulated diffusion of the defects with participation of the processes considered above.

Recombination-stimulated diffusion of defects (impurities) leads to intense formation in the working region of devices of complex centers such as donor-acceptor pairs and clusters. They can be either new radiating centers, or nonradiative-recombination centers in which the energy released upon capture of a carrier does not go into radiation but is transferred to another carrier bound to a neighboring center, and is subsequently dissipated by collision of the carrier with the lattice. These nonradiative processes were first considered in Refs. 168 and 169, were subsequently confirmed experimentally many times for various semiconductors, <sup>170</sup> and were explained theoretically.<sup>171</sup>

An analysis of the abundant experimental material on the degradation of semiconductor-based injection lightemitting diodes and lasers has led Torchinskaya *et al.*<sup>165</sup> to the conclusion that an active part is played in these materials, besides radiation-stimulated diffusion, by the other recombination-stimulated processes described above.

Vinetskiĭ and Kholodar' proposed and analyzed in detail electronic-thermal mechanisms for the production and transformation of defects in solids.<sup>5,59,172</sup> A defect captures an electron (hole) as it is produced by thermal fluctuations. The defect-production activation energy is then lowered  $(E_{\rm T} \rightarrow E_{\rm T}^*)$ , so that the range of temperatures in which defects are effectively produced can be substantially expanded towards lower temperatures. If the inverse of defect formation, viz., defect annihilation, takes place without activation, the thermodynamic relations lead to  $E_{\rm T} - E_{\rm T}^* = \gamma E_{\rm cap}$ , where  $E_{\text{cap}}$  is the capture energy and  $\gamma = 1$ . According to Ref. 173, this relation can be obtained from the theory of multiphonon transitions of an atom from a site to an interstice with participation of a conduction electron captured by the acceptor level that appears when the interstitial atom is produced. This mechanism can be effective if the fluctuating-defect lifetime is not too short compared with the multiphonon capture time,  $\tau_{cap} \gg \tau_D$ , and if the energy  $E_{cap}$  is high enough  $(E_{cap} \gg kT)$ .

Analysis of similar complicated processes (see, e.g., Refs. 174 and 78b) shows that an important role is played in them by long-lived local or quasilocal atomic-motion modes associated with the excitation modes  $Q_e$  (in the capture act) and the FP-formation reaction mode  $Q_d$ , modes whose binding parameter g is finite. Here  $\gamma$  depends on  $E_{cap}/E_T$  and g, so that  $0 < \gamma \leq 1$  at  $g \neq 0$  (or  $\gamma = 0$  at g = 0).

Electronic-thermal defect-production mechanisms, when effective  $(\gamma \neq 0)$ , lead to two results of importance to semiconductor physics.<sup>5,58,175-177</sup> One of them is stoichiometric self-compensation. This known phenomenon, which occurs when shallow donors are introduced into a semiconductor, leads to an irreversible deviation of the crystal from stoichiometry; stoichiometric self-compensation determines the reversible change of the equilibrium defect density, and at the same time the features of the equilibrium conductivity of a number of semiconductors. In particular, an exponential decrease of the carrier density when the temperature is raised is possible.<sup>176,177</sup> A distinct experimental manifestation of this effect was obtained in Ref. 176 for  $\beta$ -SiC. Another effect, intrinsic-defect conductivity of semiconductors, determines the character of the high-temperature equilibrium conductivity of a number of semiconductor compounds.5,59,60

Production and restructuring of defects with participation of carriers exert a strong influence on the magnitude and character of the temperature dependence of the nonequilibrium conductivity of semiconductors when used at high temperatures.<sup>5,178</sup>

# 7. NONRADIATIVE ELECTRONIC TRANSITIONS ACCOMPANIED BY DEFECT FORMATION

The foregoing results offer incontrovertible evidence that nonradiative transitions of a special type are realized in solids, whereby the decay of the electronic excitations leads not to excitation of small vibrations of many atoms but to large (compared with the lattice constant) displacements of individual atoms, i.e., to defect formation.

The actual mechanisms of these complicated processes were considered above for some simple cases. A common feature of processes of this type is the following: the elementary act is preceded by local-atomic-configuration instability determined by the decaying electronic excitation and by its interaction with the lattice. It is therefore possible to classify the process in a unified and sufficiently general manner in accordance with the ensuing instability.<sup>78b</sup> From this viewpoint, the following mechanism types can be distinguished:

1) Mechanisms with electrostatic instability or with an instability determined by the combined action of electrostatic interactions and thermal fluctuations (see Sec. 4).

2) Mechanisms with vibrational (more accurately, vibronic) instability determined by strong vibrational excitations (see Secs. 5 and 6).

Common to these mechanisms are the following properties:

1. The energy  $E_{\rm dis}$  needed to displace the atom (ion) from a site and produce a defect is in the case of electronicexcitation decay as a rule much lower than the threshold energy  $E_d$  of the elastic-displacement impact mechanism (usually 10 eV  $<\!E_{\rm d}<\!100$  eV as against 1 eV  $<\!E_{\rm dis}<\!10$ eV.)

2. The displacement time  $\tau_{\rm dis}$  is as a rule long,  $\tau_{\rm dis} \gtrsim \tau_{\rm D}$ , while for elastic displacement  $\tau_{dis} \ll \tau_{D}$ .

3. The decaying electronic excitation and the local configuration that becomes unstable should as a rule have low symmetries (lower than the lattice point symmetry).

Generally speaking, these processes require that at least two conditions be met:

1. The electronic excited state of the local configuration should be strongly enough localized, and the local deformation of the initial structure must be large enough.

2. Preferred long-lived local or quasilocal atomic-motion modes corresponding to the excitation process  $(Q_e)$  and to the defect-formation act  $(Q_d)$  (with lifetimes  $\tau_l(Q_e) \gg \tau_D$ and  $\tau_l(Q_d) \gtrsim \tau_R \gg \tau_D$ ,  $\tau_R$  is the reaction time) must exist and interact.

These two conditions can be met for the nonradiative electronic transitions considered here, which lead to large atom displacements (to formation or transformation of defects), generally speaking, in one of the following two situations<sup>78b</sup>:

a) the electronic excitation is self-trapped, in which case the process can be realized in a regular (defect-free) lattice (see Sec. 5);

b) in the absence of self-trapping (as in ordinary semiconductors), a suitable defect must be present beforehand in the crystal if the excitation is to be localized (see Secs. 4 and 6).4)

Note that for the alternative nonradiative vibronic transitions that lead in a solid to heat release, the need for localization (self-trapping) of the electronic excitations and for

considerable displacement of the equilibrium positions of atoms and of their vibration frequencies for various electronic states was noted already in the pioneering papers of Frenkel'<sup>179,180</sup> and Peierls.<sup>181</sup> This idea was quantitatively developed by Seitz,<sup>182</sup> Huang and Rhys,<sup>183</sup> Krivoglaz,<sup>184</sup> and others. It can be made clear by considering adiabatic potentials of three types.

Figures 19a-c show in simplified form the dependences of the ground- and excited-state potentials of three types on the generalized configuration coordinate of heavy particles. Nonradiative  $2 \rightarrow 1$  transitions result either from thermal fluctuations that cause the adiabatic potentials of the system to come closer together (above-barrier nonradiative transitions), or (even at T = 0) from tunneling nonradiative transitions due to the overlap of the wave functions in states 2 and 1.

It was noted long ago<sup>182</sup> that the adiabatic-potential arrangement shown in Fig. 19b is possible in principle. This case corresponds to nonluminescent centers (not counting the weak hot luminescence). Once the system is excited to state 2, one can have either a transition to the ground state with release of heat, or formation of a metastable configuration 2' from which tunneling into state 1 is possible. It was not assumed in Ref. 182 that heavy-particle displacements in a phototransition can exceed the lattice constant, and only the conversion of the absorbed energy into heat was considered. Now that there is no doubt of the possibility of electronic excitations with (v, i) pair production, it is clear that the metastable configuration 2' can correspond to vacancies and interstitial atoms that are closest to one another and can afterwards be separated (the states 2").

With  $F_A$  centers in KCl–Li as the example, Luty<sup>185</sup> found that adiabatic potentials of a third type (see Fig. 19c) can exist in solids. In this case optical excitation of an  $F_A$ center leads to a vacancy jump to a neighboring anion site, and to an F<sub>A</sub>-center orientation change accompanied by a radiative transition.

The recombination-stimulated-process model pro-

e) for ground (1) and excited (2) electronic states in solids [the three right-hand maxima in Fig. b correspond to (2'), (2"), and (2")].



FIG. 19. Possible types of adiabatic potentials (a-



posed in Ref. 158 was used to consider the situation when the excited-state adiabatic potential is below the activation barrier for thermal transitions in which an unexcited atom takes part (Fig. 19a).

Dexter et al.<sup>186</sup> were the first to point out that nonradiative transitions with heat release (see Fig. 19a) can occur in crystals not only after vibrational relaxation of an excited center, but also during vibrational relaxation "from above," when the system goes through the region where the adiabatic potentials come close together. The role of the ensuing "optical quenching" was analyzed in Refs. 187–191. The probability of nonradiative  $2\rightarrow 1$  transitions during vibrational relaxation was found to depend on the rate of the vibrational relaxation. In the absence of local vibrations and accordingly of fast vibrational relaxation, there is practically no optical quenching of the emission (e.g., in KCl–Pb, Ref. 187). Optical quenching was observed<sup>188</sup> in the presence of local vibrations and of a low relaxation rate (e.g., in KCl–NO<sub>2</sub>).

Obviously, nonradiative transitions can be produced in vibrational relaxation also when lattice defects are created (see Fig. 19b). Lushchik et al. have shown experimentally that in this case the presence of local vibrations (e.g., for  $e_S^0$ in KCl) enhances greatly the effectiveness of low-temperature formation of stable Frenkel' pairs.<sup>138,191</sup> In the presence of quasilocal vibrations (e.g., for  $e_S^0$  in KI), decay of an electronic excitation produces only Frenkel' defects that are little separated (state 2'), and additional thermal fluctuation is needed to separate them further (Refs. 138, 191). A system having the excess of vibrational energy needed for decay with defect formation stays in a state with local vibrations long enough to choose the optimal (with respect to energy and other parameters) path for negotiating the complicated potential relief to a new stable equilibrium position. This is most probably the mechanism for the low-temperature athermal decay of  $e_S^0$  with production of Frenkel' defects in KCl crystals.<sup>12,148,191</sup> In the mechanisms discussed, the mode  $Q_e$ corresponds to the excited state of a self-trapped exciton (or of a captured electron, etc.), while the mode  $Q_d$  corresponds to collective displacement of the atoms with FP production.

For the mechanisms with electrostatic instability in a low-symmetry excited configuration, the decisive role is played by the mode  $Q_0$  of the relative translational atomic motion, a mode made preferred by an electrostatic interaction (Coulomb repulsion, etc.). In a certain sense the situation corresponds qualitatively to that illustrated by curve 3 of Fig. 19b (Ref. 71). Following the Auger process, the system configuration corresponds to a very high value of the adiabatic potential, and its "rolling down" separates the defects by several interatomic distances. For low-symmetry electrostatic defect-formation mechanisms, the excitation mode  $Q_e$  and the reaction mode  $Q_d$  practically coincide,  $Q_e$  $\approx Q_0 \approx Q_d$ , and the FP formation process reduces to a real displacement of a definite atom from a site to a spatially remote interstice.

For  $e_S^0$  decay in an ionic crystal, the displacement of an atom from a site to a remote interstice is a collective process of the crowdion type.

## 8. RADIATIVE EFFECTS IN NONMETALLIC GLASSES

We have considered so far the decay of electronic excitations, accompanied by defect formation, in crystals. When it comes to amorphous condensed media such as glasses, the situation acquires new features.

Subthreshold formation of radiative defects has been investigated in the last few years in crystalline and glassy silicon dioxide. <sup>192-194</sup> Irradiation of these materials results in self-trapped excitons<sup>195</sup> whose energy is in principle sufficient to produce defects. Conversion of  $e_S^0$  into stable radiative defects was actually recorded for glassy SiO<sub>2</sub>. This effect remained unobservable in wide-gap ( $E_g = 12 \text{ eV}$ ) crystalline SiO<sub>2</sub> for a long time. It was shown recently<sup>184</sup> that action of electrons having an energy that is subthreshold for elastic displacements can produce in SiO<sub>2</sub> crystals defects that manifest themselves in a change of the crystal volume, but these are short-lived defects similar to unstable (v, i) pairs in AHC.

In glassy semiconductors (As<sub>2</sub>S<sub>3</sub> and others) characterized by much narrower gaps in the energy spectrum of the single-particle excitations ( $E_g \approx 2-1 \text{ eV}$ ), irradiation by visible light leads to particularly unique phenomena that have no counterparts in crystals. Thus, tremendous long-lived photostructural changes are observed, corresponding to very high density of peculiar point defects that cannot be described in terms of Frenkel' pairs,  $c_d \leq 0.1$ . The optical properties (e.g., the width of the optical gap) are then greatly altered, together with a number of physico-chemical and other characteristics, but the electric and magnetic properties remain almost unchanged (see, e.g., Ref. 196). Kolobov et al.<sup>197</sup> proposed a phenomenological model of the photostructural changes, based on the following assumption: the local atomic configuration in a glassy semiconductor has essential electronic ground and metastable excited states, and the aggregate of radiative and nonradiative transitions between them leads to a restructuring of the interatomic bonds. A somewhat different phenomenological model was developed in certain papers (see, e.g., Ref. 198). These models, especially that of Ref. 197, have been compared in detail with experimental data in a number of studies (see, e.g., Ref. 199).

Klinger recently proposed microscopic mechanisms and a theoretical model of such phenomena within the framework of the developed general theory of electronic states of the gap for the mobility of glassy semiconductors<sup>80,200,212</sup> (see also Ref. 79). This theory established two phenomena that determine in many respects the behavior of such amorphous substances: 1) the presence of a high density  $c_a$  ( $\leq 0.1$ ) of small-size ( $\approx a$ ) easily restructured "soft" atomic configurations with anomalously small quasielastic constants  $k(\ll M\omega_D^2 \approx 10-30 \text{ eV} (\text{\AA})^{-2})$  with respect to a chosen anharmonic "critical" mode  $Q_c$  of the atomic motion<sup>80,200,201</sup>; 2) the presence of a high density  $c_{\pm}$  ( $\leq 0.1c_a$ ) of zero-spin electron ( $e^-$ ,  $e^-$ ) and hole ( $e^+$ ,  $e^+$ ) pairs of small size ( $\approx a$ ), which are self-trapped on "soft" configurations and have a negative correlation U < 0 of anomalously large magnitude  $|U| \simeq E_g/2(1 \text{ eV} \gtrsim |U| > 0.5 \text{ eV})$  and with energy levels (per particle) near the center of the gap<sup>80,200-202</sup> (cf. Ref. 79). In such a system, the absorption of photons, including visible light of frequency  $\omega \gtrsim \hbar^{-1} E_{g}$ , leads to excitation of such pairs (and of "soft configurations with electron terms in the gaps), viz., radiative centers and metastable nonradiative centers. A feature of the latter, as a rule, is a radical restructuring of the initial atomic configuration and appreciable structural changes that can be set in correspondence with the high values of the possible densities of the produced radiation defects,  $c_d \leq (c_d)_{max} \leq 0.1-0.01$ . From this viewpoint, such defects are determined by the "structural" instability of the local configuration with respect to the critical mode  $Q_c$ , relative to the change of the electronic state, and in fact  $Q_e \approx Q_c \approx Q_d$  (see Fig. 19b). The corresponding elementary act of defect formation may be activated by a nonthermal mechanism, i.e., its probability  $W_0(\omega,T) \neq 0$  as  $T \rightarrow 0$  (in the appropriate region where  $\hbar\omega > E_{g}$ ). This leads, in particular, to suppression ("fatique") of the luminescence (see also Refs. 78b, 80, 200, 201), and can also be essentially correlated with changes of the optical properties of the material.5)

At low-temperature irradiation of the semiconductor with visible light having  $\hbar\omega \leq E_g$ , a finite contribution to the defect formation can be made by the electrostatic low-symmetry mechanism (4.1)-(4.4) (Ref. 77), which correlates more weakly with the optical properties. This occurs (see Sec. 4) because the lifetime  $\tau_l^{(v)}$  of the photoproduced charge can be determined here by the hopping mechanism, so that  $\tau_l^{(v)} > \tau_{dis}$  at low temperatures  $(\tau_l^{(v)} \rightarrow \infty \text{ as } T \rightarrow 0)$ , while the intrinsic (e<sup>-</sup>, e<sup>-</sup>) and (e<sup>+</sup>, e<sup>+</sup>) pairs play the role of preexisting charge centers with high density  $c_{+} \leq 0.01$ . The contribution of this mechanism to the photostructural changes, however, can be substantial only at sufficiently low temperatures and at  $\hbar\omega \leq E_g$  such that  $W_0(\omega,T) \rightarrow 0$  as  $T \rightarrow 0$ . On the other hand, the contribution of such electrostatic low-symmetry mechanisms to defect formation in such materials may be in general substantial when they are exposed to radiation of higher energy (x or  $\gamma$  rays, fast electrons, etc.). The experimental situation, however, is here on the whole much less clear than in a material exposed to visible light. In particular, experiments have shown that in a weak x-ray field the defect formation is much less correlated with the changes of the optical properties than under the action of high-power sources (synchrotron x rays, fast electrons, etc.), although the changes of the physico-chemical properties still remain noticeable.203,204

Interesting photoinduced phenomena are observed in ferroelectrics (see, e.g., Refs. 205 and 206). It is possible that in ferroelectrics of the "order-disorder" type, in which hydrogen and hydrogen bonds play a significant role, these processes are determined by local restructurings of "soft" atomic configurations, which are related in some manner to the photostructural changes in the theoretical model proposed by Klinger.<sup>200,201</sup>

#### 9. CONCLUDING REMARKS

The extensive experimental material cited in this review is evidence that in dielectrics and semiconductors the excitation of the electronic subsystems leads to formation and transformation of point defects. The existing theories deal only with the most general features of these complicated phenomena, viz., electrostatic, vibronic, and "structural" instabilities, whose analysis calls for a unified consideration of electronic excitations and of structural "defects" in solids.

From the viewpoint of the experimental material, there is a particularly acute shortage of information on the spectra of the single-phonon and two-phonon production of defects in the most important solid materials (particularly in semiconductors), with coverage of a large spectral region that includes the vacuum ultraviolet and the x-ray regions. More promising are the recently initiated investigations of the specific properties of defect formation in solids at high irradiation powers (see, e.g., Ref. 20).

The topics discussed in this review have not yet attracted the attention of those specializing in radiation physics of metals, although it is in metals that excitation of the electron subsystem can lead in principle to formation of defects (see Ref. 209) other than the thoroughly investigated ones produced by elastic displacements. It is necessary also to speed up research into the specific features of nonradiative electronic transitions accompanied by defect formation, in various bodies having different degrees of ordering.

Processes that are to some degree related to the defect formation considered above are the photoplastic effect in semiconductors and dielectrics, whose mechanism is attributed to recombination of electron-hole pairs photoproduced on centers that are simultaneously dislocation-pinning centers,<sup>210</sup> and also laser annealing processes (see Ref. 211).

We have attempted in this review to consider certain elementary mechanisms of the decay of electronic excitations with formation and transformation of defects in dielectrics and semiconductors. We had neither the possibility nor the intent to discuss the enormous factual material on other radiation effects in solids, particularly the macroscopic phenomena that accompany defect formation. The filling of the wide gaps in our knowledge of the elementary acts of defect formation in solids and of their macroscopic manifestations is one of the important problems of solid-state physics. This is all the more necessary since it is precisely the methods of solid-state physics that are needed to solve one of the most complicated problems of modern science, that of producing radiation-resistant materials.

At the present time the development of physics and chemistry of solids is in a stage in which it is possible and necessary to find ways of purposeful control of the properties of solids by methods of radiation physics. The reviewed processes of defect formation and transformation in decay of electronic excitations in solids offer much promise in this respect.

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<sup>&</sup>lt;sup>15</sup>The concept of this type of equilibrium conductivity of semiconductors<sup>61</sup> (intrinsic-defect conductivity) was developed for CdS crystals by Böer

et al., although no proof was obtained of the intrinsic-defect character of the high-temperature conductivity of CdS.

<sup>2</sup>In the alternate case  $U_c > D_v$  the width of the band corresponding to coherent displacement of pairs of "unseparated" holes in a regular crystal is equal to  $D'_{v} \sim D^{2}_{v}/zU_{c} < D_{v}$  (z is the coordination number); see, e.g., Ref. 79b and also 208. At the values  $D_v \gtrsim 3 \text{ eV}$  encountered in practice in diamond-like semiconductors (z = 4) if  $U_c \leq 5-10$  eV, we have  $1 > D'_v D_v^{-1} > 0.1$  and hence  $\tau_l^{(v)} \simeq \tau'_v \approx \hbar/D'_v < 3 \cdot 10^{-15}$  s, so that  $\tau_{dis}^{(v)}/\tau'_v$ can still be large, and the defect formation mechanism in question can be exponentially weak (albeit stronger than if  $U_c \leq D_v$ ). Actually, however, in such semiconductors we have more readily  $U_c \leq 1 \text{ eV}$  (see Refs. 80 and 200).

<sup>3)</sup>The section in which the cross section grows slowly at low densities is well accounted for by assuming that the probability of separating the vacancy from the interstitial atom depends on the location of the Fermi level.

<sup>4)</sup>The low-symmetry electrostatic defect-formation mechanism (4.1)-(4.4) is highly effective ( $W_{(V)} \approx 1$ ) in the indicated semiconducting compounds of transition or rare-earth elements if  $D_{\rm V} \leq 0.1$  eV and  $\tau_{\rm V}$  $\gtrsim \tau_{\rm dis}$  (a), and is practically athermal (at  $c_{+} = {\rm const} < 1$ ) even in a crystal in which the valency shell of the atom is (photo)ionized.<sup>78</sup> As noted in Ref. 78b, however, defects can be effectively produced in such substances in a regular lattice via the mechanism with vibrational instability, since the carriers, usually holes, can become self-trapped.

<sup>5)</sup>This structural-change mechanism, as well as in general the role of the self-trapped electron (e<sup>-</sup>, e<sup>-</sup>) and hole (e<sup>+</sup>, e<sup>+</sup>) pairs with negative correlation energy, should be much weaker in oxide glasses, in which  $E_{\rm g}$ is very large  $E_g \approx 5-10$  eV and  $E_g > |U| \sim 1$  eV.

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