DEFECTS IN CRYSTALS

Instability zones and short-lived defects in the physics of crystals

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A review is given of the role played in the problems of solid-state physics by the various manifestations of instability zones for interacting defects and the presence of equilibrium and radiation-induced unstable vacancy–interstitial-atom pairs. The unstable pairs determine the features of the diffusion process and of a number of thermal properties of metals, semiconductors, and insulators, including superionic crystals, and also determine the radiation stability of solids. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1511716]

1. INTRODUCTION

This article presents a review of various processes in the physics of crystals from the standpoint of a model of short-lived unstable defect pairs consisting of a vacancy and interstitial atom. These processes result from the presence of zones of absolute instability of the interacting defects and, in turn, govern many of the equilibrium and radiation properties of metals, insulators, and semiconductors.

Equilibrium unstable pairs (UPs) are manifested mainly at temperatures quite close to the melting point but, generally speaking, can be observed at any temperatures.

The kinetics of the accumulation and healing of radiation defects, especially in pure substances, is governed by the instability zones (IZs), in particular, in low-temperature irradiation by low-energy particles, with energies only slightly above the Seitz threshold. In this paper we discuss the origin of the IZs and their role in the thermodynamics of the UPs, which are a third type of equilibrium defect in crystals, in addition to Schottky defects (SDs) and Frenkel pairs (FPs). Equilibrium UPs, together with SDs and FPs, determine the thermal properties and diffusion in solids. We consider the role of IZs in the accumulation of nonequilibrium (radiation-induced) defects. In particular, a crystallographic criterion of radiation stability is presented, along with a large number of experimental data for materials with extremely high radiation stability. The technical applications of radiation-stable metals, insulators, and semiconductors are discussed.

2. INTERACTING DEFECTS: ZONES OF ABSOLUTE RECOMBINATION AND ABSOLUTE SQUEEZING

2.1. The classic paper by Gibson, Goland, Milgram and Vineyard,[1] in which the methods of molecular dynamics were first applied to the study of radiation phenomena in metals, revealed an unusual phenomenon. It was found that if an interstitial atom i is located in the vicinity of a vacancy v, then i recombines with v without activation at any arbitrarily low temperature. In Ref. 1 these regions around v were called zones of spontaneous recombination or zones of instability of i with respect to v. The possibility of such an insta-

bility of defects was predicted by Frenkel some twenty years before, in 1943, but only by a single phrase in his famous book.[2] After the publication of Ref. 1 many authors reported both experiments and computer simulations confirming the existence of recombination instability zones (RIZs) in metals, semiconductors, and insulators, which appear during irradiation by high-energy particles. The characteristic radii of the IZs range from a few angstroms to tens of angstroms (see Refs. 3–5). The cause of these zones of absolute instability was elucidated in Refs. 3 and 6 and is as follows. The periodic potential of the lattice for an interstitial atom has an amplitude U_m which is the activation energy for the migration of i. Low-temperature experiments show that in the majority of crystals of the most diverse natures the values of U_m for an intrinsic i is of the order of $10^{-1}-10^{-2}$ eV, e.g., in copper it is 0.05 ± 0.02 eV, in germanium 0.02 ± 0.02 eV, in KBr and KCl from 0.03 0.06 eV for charged i to 0.1 eV for neutral i (see Refs. 3 and 5).

Vacancies are considerably less mobile, and the activation energies for their displacements are >1 eV in the majority of crystals. Now let i and v interact with each other, and superpose their interaction potential on the periodic migration potential of interstitials. It is easy to show that nearest energy minimum for an interstitial atom to a vacancy is found, generally speaking, not in the nearest interstitial position to v but far away from it: the interaction potential "cuts off" the nearest extrema up to a distance r_0 from v. In this region there are no extrema, and the interstitial atom (or ion) "slides down" toward the vacancy in an activationless manner. This is a recombination instability zone.

In the case of a Coulomb interaction

$$r_0^{\text{es}} = \alpha(q_i q_v a/\varepsilon U_m)^{1/2}, \tag{1}$$

where q_i and q_v are the charges of i and v, a is the interatomic distance, ε is the dielectric constant, and α is a factor of order unity which depends on the choice of the periodic potential.

A Coulomb IZ arises in insulators and semiconductors but not in metals, where the electrostatic interaction is

screened and only an elastic interaction, with a potential $U_{iv} = G\Delta V_i \Delta V_v / r^3$, is possible.[7] The radius of the IZ in that case is

$$r_0^{el} = \alpha^{1/2}(3G\Delta V_i \Delta V_v a/U_m)^{1/4}, \tag{2}$$

where G is the shear modulus, and ΔV_i and ΔV_v are the changes in the volume of the crystal upon the introduction of an isolated i or v. Interstitial atoms always expand the lattice, and vacancies almost always draw the matrix in toward them. The different signs of the displacements near the defects creates their attraction.

We should emphasize that while Eq. (1) is suitable for quantitative calculations, Eq. (2) is only good for estimates unless the radii of the elastic IZs are not more than 2–3 interatomic distances, but in most metals the IZs are larger than that.

Calculations according to Eqs. (1) and (2) describe the experimental data on IZs quite well.[3,5] Of course, everything is determined by small quantities—the migration energies of interstitial atoms or ions.

Let us estimate the lifetime of an ion found at the boundary of an IZ of radius r_0^{es} in the presence of a Coulomb i–v interaction.[3,8] The time required for i to return to its site is easily determined from the difference of the Coulomb potentials at the point r and in the initial position r_0^{es}, knowing the charges ($q_i = q_v$) and the mass M of the the ion, if it is assumed that within the IZ the ion moves as a free particle ($W(r)$ is the velocity of the particle):

$$\mathcal{T} = \int_{r_0}^{0} W^{-1}(r)dr = \frac{\pi}{2\sqrt{2}}\frac{\sqrt{M}}{q}r_0^{3/2}. \tag{3}$$

Estimates according to Eq. (3) for $r = 20$ Å and a mass of 60 amu give $\sim 10^{-11}$ s, which is only one or two orders of magnitude greater than the characteristic time for lattice vibrations. The calculations by Oksengendler[9] with allowance for the scattering of the moving particle on atoms inside the IZ give practically the same estimate for the lifetime of i.

2.2. The interaction of any defects will give rise to IZs. It should be noted that in the presence of repulsion between defects a zone of absolute squeezing (SIZ) arises in which, as in an RIZ, a mobile defect cannot be localized.[10,11] Of course, expressions (1) and (2) also describe SIZs around defects.

Instability zones also arise around dislocations. They, of course, have a cylindrical shape.

In the case of charged dislocations D and defects d one has

$$r_{Dd}^{es} = \alpha^2(2e^2 a\sigma/\varepsilon U_m), \tag{4}$$

where e is the charge of an electron and $e\sigma$ is the linear charge density at the dislocation. In the case of an elastic interaction of D and d a somewhat more awkward expression is obtained.[3,12]

Instability zones also arise in the interaction of dislocations with each other, only instead of the energies of migration of i the relevant quantity is the height of the Peierls barrier, which for plastic solids, metals and many ionic crystals, is of the order of 0.05–0.1 eV.[3]

Estimates show that IZs around dislocations can extend for several tens of angstroms, and so the formulas can be used for quantitative calculations.

Below we shall trace the role of IZs in the physics of crystals.

3. THERMODYNAMICS OF UNSTABLE PAIRS AND THEIR PLACE AMONG OTHER EQUILIBRIUM DEFECTS

3.1. In spite of their very short lifetimes, there exists an equilibrium concentration of v–i pairs. If a thermally excited atom does not leave the RIZ of its vacancy, then it will return to its place in an activationless manner within its lifetime. The birth event of an UP is the same as for a Frenkel pair (FP), but, unlike the latter, when the v and i that are created become independent, in an UP the interstitial recombines with the same vacancy with which it is corrected by birth. The UPs die at the same point where they were born. Therefore, unlike the free energy of equilibrium FPs, in the partition function of a system with UPs it is necessary to take into account this strict correlation, viz: the number of states f of the interstitial in the IZ.[3,8,13] In the zeroth approximation at low temperature (i.e., for a small concentration of equilibrium defects) and small RIZs, the concentration of Frenkel defects and UPs are independent and are expressed as

$$C_{PF} = \beta^{1/2}\exp(-E_{PF}/2kT), \tag{5}$$

$$C_{UP} = f\exp(-E_{UP}/kT), \tag{6}$$

respectively, where E_{PF} and E_{UP} are the energies of formation of a Frenkel pair and an unstable pair, and β is the ratio of the number of lattice sites to the number of interstitial positions.

In the next approximation[3,8] it becomes obvious that FPs and UPs compete, and for large IZs the UPs prevail, provided, of course, that E_{UP} is not too much larger than E_{PF}:

$$C_{PF} = \beta^{1/2}[1 - f\exp(-E_{UP}/kT)]\exp(-E_{PF}/2kT). \tag{7}$$

The energy of formation of an equilibrium FP is equal to the sum of the energies of formation of the independent i and v. The energy of formation of an unstable pair is the sum of the same energies, but in view of the short distances between the interstitial atom and vacancy in an unstable pair, it is smaller by the amount of the interaction energy between them. Estimates of the lifetime of a UP (3) show that the relaxation of the lattice occurs before recombination, and one can therefore introduce an average energy of formation E_{UP}. In the case of the Coulomb interaction one has $E_{UP} = E_{PF} - e^2/\varepsilon r_{iv}$ (r_{iv} is the average i–v distance in the UP).

Then the concentration ratio is

$$\frac{C_{UP}}{C_{PF}} = f\exp\left[\frac{1}{2kT}\left(\frac{2e^2}{r_{iv}} - E_{PF}\right)\right]. \tag{8}$$

Estimates show that for sufficiently large RIZs the competition of FPs and UPs is won by the latter. It is this third type of defect (additional to Schottky and Frenkel defects) that turns out to be the predominant type of equilibrium defect in many crystals at high temperatures, where by "high" temperatures we mean temperatures not very far from the melting point of the substance. This can be a temperature of the order of a thousand (e.g., for copper or silicon) or tens of

kelvins (for frozen gases). A computer model for the investigating thermal excitations in metals, which was created recently by Nordlund and Averbak,[14] showed that UPs are in fact significant in copper at premelting temperatures.

3.2. What place do UPs occupy among the other equilibrium lattice defects (see Refs. 3, 4, and 7)? The lowest-energy defect is a lattice vibration: the excited atom executes small harmonic vibrations about its site. At a larger amplitude the vibration becomes anharmonic. When a very high energy is localized in the vicinity of a given site on account of fluctuations, the atom can go out to a distance of the order of the interatomic distance or more. If the atom remains within the RIZ and returns to the vacancy that it has left, then this excitation is similar to a vibration about the site, but its amplitude is so large that it would be senseless to describe the motion of such an interstitial atom in terms of an anharmonic correction. If the energy of the local excitation exceeds the threshold for formation of an unstable pair but is less than that necessary to leave the boundaries of the RIZ and form a Frenkel pair with independent i and v, then a short-lived unstable pair arises. Thus the UP is a special type of lattice defect intermediate between a harmonic vibration and the Frenkel pair.

Below we discuss the consequences of the presence of unstable pairs and the experimental data confirming their determining role in many equilibrium properties of crystals.

4. EQUILIBRIUM UNSTABLE PAIRS AND THE PHYSICAL PROPERTIES OF CRYSTALS

4.1. One of the fundamental differences between unstable pairs and other equilibrium defects (Frenkel pairs or Schottky vacancies) is that an unstable pair cannot be quenched. Indeed, unlike FPs and Schottky defects (SDs), the lifetime of an unstable pair is very short and is independent of temperature, and the interstitial atom and vacancy of a given unstable pair recombine specifically with each other. Therefore, in crystals where the predominant type of defect is unstable pairs, a rapid quenching should leave all the properties unchanged. This has been demonstrated for the example of the semiconductors In_2Te_3 and Ga_2Te_3 with a loose-packed crystal lattice,[3,15] where it was shown by investigations of the most diverse physical properties (see below) that UPs were the main type of equilibrium defects. In Ref. 15 careful estimations were made of the possibilities of defects escaping to sinks, and it was shown that at the quenching rates used (not less than 100 K/s) less than 1% of the defects would manage to escape to sinks if they were long-lived. Control experiments on the quenching of other semiconductors (Ge, CdTe, ZnSe), in which the predominant equilibrium defects are SDs, were done under the same conditions,[15] and it was found that the quenching of these other substances led to radical changes of all their measured parameters, in complete agreement with the known published data.

Kraftmakher[16] called attention to the fact that the quenching of the majority of metals, which, as we know, leads to the freezing of defects, reveals a paradoxical fact: the concentration of frozen defects turns out to be several orders of magnitude lower than the equilibrium concentration for the high temperature from which the quenching took place. Kraftmakher developed a unique modulation technique for determining the concentration of equilibrium defects at premelting temperatures and reliably showed that the aforementioned difference is a general effect for metals. Also presented in Ref. 16 were data on the large disagreement of the heat capacity and the stored enthalpy on quenching. This is the same effect.

It seems that the unquenchability of defects is a direct consequence of the fact that a significant fraction of the equilibrium defects consists of unstable pairs (see the detailed analysis in Refs. 17 and 18).

4.2. It is known that in the temperature region where the equilibrium concentrations of any point defect (FP, SD, or UP) is rather large, the contribution of their formation to the heat capacity becomes substantial.[16,19] Using the model of Refs. 3, 4, 8, and 13, which describes the coexistence of all three types of defects, it is possible to interpret this effect, keeping in mind that at high temperatures UPs and FPs come into play, with energies of formation that are larger than that of SDs, which are prevalent in metals at lower temperatures. Tere is another paradox in the thermal properties of metals, noted in Refs. 16 and 19: the concentrations of defects determined from dilatometric measurements and from the heat capacity under equilibrium conditions at a high temperature come out different. Kraftmakher showed[16] that these differences are indicative of the presence of interstitials. As we have seen above, in spite of the short lifetimes of UPs, the relaxation of the lattice around v and i does have time to take place, and therefore in the x-ray diffraction experiments the lattice constant is determined by the difference of the effects of i and v. Thus the UP model can also eliminate this paradox in the high-temperature physics of metals.[17,18]

4.3. Finally, diffusion. Of course, UPs cannot contribute directly to the mass transfer, since they die at the same point where they were born. Nevertheless, their participation in a diffusion event can play an important role. An elementary diffusion event in the case of a long-lived SD, for example, consists in the following. A marked atom "waits" until an already formed vacancy migrates into a position adjacent to it and then, with a certain probability, hops over into it. Therefore the activation energy for diffusion by the vacancy mechanism consists of two components: the formation energy of v and its migration energy. In the case of an UP, the situation is different. The marked atom "waits" until an unstable pair is formed near it, within a distance less than the size of the RIZ of this atom and vacancy. Then in competition with the interstitial atom i belonging to this vacancy, the atom gets a chance to hop over into the vacancy. This mechanism of diffusion, which was proposed in 1974,[20] eliminates the migration, and the activation energy for diffusion in crystals in which UPs are predominant should therefore be equal to the energy of their formation and should not depend on the jump energy of the diffusing atom. Studies of semiconductors of the In_2Te_3 type, where UPs are the predominant type of equilibrium defect, have shown that the activation energy for self-diffusion and heterodiffusion in them is always the same.[21] Later, similar diffusion mechanisms were proposed in Refs. 22 and 23, the authors of which also were forced to propose an instability of Frenkel pairs.

The anomalies in the temperature dependences of the

coefficients of self-diffusion in metals were also discussed in the brilliant review by Kraftmakher.[16] It turns out that in many metals at high temperature the activation energy for diffusion increases sharply without any phase transitions, and this activation energy can exceed the enthalpy of formation of defects, determined from the temperature coefficient of the heat capacity, by a factor of two or even three times.

This surprising fact can also be interpreted consistently on the basis of the UP model. Indeed, as the temperature increases, so do the concentrations of both SDs and UPs, and, consequently, the probability of an encounter, which is proportional to the product of their concentrations, increases as well. If an encounter does occur, then the interstitial atom belonging to the UP can hop over into the Schottky vacancy. The diffusion coefficient in this case will be

$$D \sim \exp[-(E_{\text{Sch}} + E_{UP})/kT], \tag{9}$$

i.e., the activation energy for diffusion at high temperature is the sum of the energies of formation of a Schottky vacancy and an unstable pair. A joint processing of the data on the temperature dependences of the heat capacity and of the diffusion coefficients shows quite satisfactory agreement.[17,18]

Thus the UP model can be used successfully to describe many phenomena corrected with the equilibrium concentration of defects in crystals.

5. UNSTABLE DEFECTS IN THE RADIATION PHYSICS OF CRYSTALS

5.1. As we have seen, all three types of point defects—Schottky vacancies, Frenkel pairs, and unstable pairs—are manifested in the equilibrium properties of crystals. The lowest energy of formation of all equilibrium defects is that of the SDs, and we need to demonstrate that the FPs and UPs can be predominant under certain conditions. In the case of radiation damage of a solid, everything is quite the contrary. The primary defects are now FPs and UPs, which are related in their origins. Indeed, the attacking high-energy particle, in transferring energy and momentum to an atom of the lattice and knocking it out of its site, of necessity creates v and i in equal numbers (see Ref. 24). Even if the formation of defects is a secondary result of the decay of optical excitation of an atom (so-called subthreshold effects), which takes place mainly in ionic and cryocrystals, again it is i–v pairs that are created.[25] The IZs turn out to govern the kinetics of the accumulation of radiation defects: the RIZ is the cross section for their recombination.[3,5,24]

One of the basic parameters in the radiation physics of crystals is the Seitz threshold E_S, which has a value of the order of 20–30 eV. This is the energy that the primary knock-on atom (PKA) must acquire in order to occupy a stable position in an interstitial site. For a long time it was assumed that this would be a position in the nearest coordination sphere of the vacancy created. The discovery of IZs made it necessary to modify the interpretation of E_S: it is the energy of a PKA necessary for the latter to leave the perimeter of the RIZ, since otherwise i would recombine with v in an activationless manner.[3,24]

The simplest kinetic equation describing the process of accumulation of point defects under the action of ionizing radiation with allowance for the number of positions f of the

interstitials within the RIZ and the fact that the concentration of radiation-produced i and v are equal[24] has the form

$$dC_d/d\Phi = \chi[1 - w_0 C_d], \tag{10}$$

where w_0 is the volume of the RIZ and χ is the number of defects introduced by a unit fluence Φ of defect-forming particles.

The solution to equation (10),

$$C_d = w_0^{-1}[1 - \exp(-w_0 \chi \Phi)], \tag{11}$$

shows that with increasing w_0 both the rate of accumulation of defects and their limiting concentration

$$C_{\text{sat}} = 1/w_0 \tag{12}$$

fall off. (In Eqs. (10)–(14) the concentration is the number of particles per unit volume.)

This is how things stand with the irradiation by particles of small mass and/or at not very high energies, when the PKA acquires an energy only slightly in excess of E_S. In this case only point defects form, and the meaning of Eq. (10) is that the rate of accumulation of defects is proportional to that volume of the crystal which remains free of the RIZs of those vacancies which have already accumulated by the given time. Saturation sets in when the RIZs of the accumulated v cover the entire volume of the crystal. (Below we shall recall the situation when the UPs initiated by irradiation can become stabilized at significantly higher concentrations.)

5.2. One of the main ways of determining the RIZ volumes experimentally involves the processing of data with the use of Eqs. (10) and (11). A great number of data have been accumulated on the sizes of the IZs. The characteristic radii of RIZs in metals are often of the order of ten or even fifteen times larger than the atomic radii.[3,5,27,28] At the same time, as have seen, the RIZs in metals are determined exclusively by elastic v–i interactions, and such large sizes of the IZs cannot be described by means of Eq. (2). They can be interpreted quantitatively if not only the elastic attraction of v and i is taken into account but also the elastic repulsion potential of like defects, i–i and v–v.[10,11] The zones of absolute squeezing (SIZs) must be taken into account in order to explain the circumstance that the effective volume of a crystal available for localization of defects generated by the radiation should be decreased by that fraction of the volume in which the defects cannot coexist, not only because of recombination but also on account of expulsion. Two interstitials, for example, crowd each other out from the SIZ into the RIZs of vacancies, the attraction of which leads to mutual annihilation of two partners v and i. And the interstitial that has expelled its partner remains alive until another one expels it. Thus, there is a severe ultraspecific struggle.

Generalization of the linear Thompson equation (10) with allowance for the repulsion of like defects gives a saturation concentration

$$C_{\text{sat}} = 1/(w_0 + w_1), \tag{13}$$

where w_1 is the volume of the EIZ of the interstitials.

Since an interstitial i usually carries considerably larger elastic stresses than a vacancy v, the contribution of the i–i interactions exceeds the direct effect of the RIZ.[10] Thompson[24] showed that the general form of the dependence

of the concentration of accumulated defects on the fluence of irradiation remains formally the same as in the case described even when the crystal is irradiated by heavy particles at high energies (fast neutrons, protons, ions, highly relativistic electrons), which form not only isolated $v-i$ pairs but also cascades of atomic collisions with the multiple creation of such pairs. Generally speaking, expressions (10)–(13) describe an extremely perfect crystal containing such a small number of dislocations, grain boundaries, and blocks that the escape of point defects to those sinks can be neglected. Strictly speaking, this is the low-temperature limit, when the thermally stimulated migration (diffusion) of defects is not taken into account, but when it is taken into account it is obvious that the larger the RIZ and SIZ, the lower the saturation concentration C_{sat}, which characterizes the radiation stability of the structure. The larger the values of w_0 and w_1, which take into account both the RIZ and SIZ, the smaller the value of C_{sat}, and the fewer the lattice defects that manage to survive after the action of the ionizing radiation.

A most important characteristic of crystals, their radiation stability, is largely determined by the sizes of the instability zones of defects—the RIZs and SIZs.

6. RADIATION STABILITY: EXPERIMENTS AND CRITERIA

The radiation stability of materials is extremely important in the age of atomic energy and space flight. It is necessary to create materials which, when subjected to enormous fluxes of ionizing radiation, maintain their operational parameters, both functional and protective. Is this possible in principle? It is necessary only to find a way to ensure the self-healing of defects.

6.1. As we have seen, the radiation stability is determined by the sizes of the IZs. How will the radiation resistance change if vacancies are introduced in the crystal prior to irradiation, with each vacancy forming its RIZ for interstitials i? The kinetic equation (10) for the concentration of radiation defects takes the form[29]

$$dC_d/d\Phi = \chi[1 - w_0(C_{v0} + C_d)], \qquad (14)$$

where C_{v0} is the preirradiation vacancy.

It is clear from Eq. (14) that with increasing C_{v0} the value of C_{sat} decreases. This is a consequence of the recombination of i from the radiation-excited pairs with the previously existing vacancies. The physical meaning of Eq. (14) is that the i introduced by the radiation can recombine with structural vacancies v present in the sample, leading to the annihilation of these particles, so that a vacancy introduced by irradiation replaces the vacancy initially present, and their total concentration remains the same: the vacancies simply exchange places.

There are several classes of metallic alloys in which the concentration of vacancies is determined by the composition of the alloy, e.g., Hume-Rothery alloys in which the concentration of equilibrium vacancies C_{v0} is determined by the relationship between the electron concentrations and the filling of the states in the Brillouin zones in the corresponding alloy (alloys in the systems Ni–Al, Ni–In, Ni–Sn, etc.). In these alloys the concentration C_{v0} does not depend on temperature influences and therefore these alloys can serve as a basis for radiation-stable metal structures; it would seem that

the coalescence of defects and radiation swelling could be eliminated if the RIZs of the existing structural vacancies covered the entire volume of the crystal: recombination process occur immeasurably faster than diffusion processes. Estimates show that pre-irradiation vacancies in the amount of 0.1% would be sufficient to completely prevent the accumulation of radiation defects—their self-healing is practically complete.[29]

Equation (14) describes processes occurring upon the spatially uniform introduction of point radiation defects: the cascade damage by heavy particles lessens the attractiveness of this idea. However, this seems like a promising way of developing structural metals, particularly since the RIZs are substantial even in damage cascades (see below).

Let us mention an exceedingly important point concerning all radiation damage effects in crystals. Equations (10)–(14) describe the accumulation of those i which after excitation have overcome the Seitz threshold, i.e., have escaped to beyond an RIZ. In fact, a very large fraction of the PKAs that have acquired an energy less than E_S remain within an RIZ and, with a probability of unity, recombine with the vacancies they have left behind in a time of the order of 10^{-10} s. The fraction that these made up depends on the energy of the PKA and the size of the RIZs. Under any circumstances, the larger the RIZs, the higher the radiation stability of the crystal, both on account of instantaneous recombination and on account of the slower processes described by equations of the type (10) and (14), e.g., the behavior of those PKAs that have escaped to beyond the RIZ.

The destiny of the PKAs remaining within the RIZs, which recombine with their vacancies v and return the energy they have acquired back to the crystal, was investigated in Ref. 30 on the basis of the UP model:[3,13] Indenbom[30] assumed that the energy released in the recombination of i and v becomes a source of short-wavelength phonons, which stimulate the annealing of radiation defects.

Can radiation stability be ensured for semiconductors and insulators, whose properties are immeasurably more sensitive to the effects of radiation? In contrast to the metals considered above, in which the initial v are disordered, in nonmetallic compounds the exchange of places between different atoms or ions is ruled out altogether or it creates defects that radically alter all the physical characteristics. It would seem that the problem of finding radiation-stable semiconductors is hopeless.

6.2. Meanwhile, back in 1969 (the first open publications were Refs. 13 and 31–33) it was revealed that semiconductors of the In_2Te_3 type have extremely high radiation stability both against to gamma radiation, which creates only point radiation defects, and to the action of fast neutron fluxes (in a nuclear reactor) and highly relativistic electrons with energies of up to 300 MeV. In recent years this phenomenon has been comprehensively investigated. It has been shown that the electrical conductivity of such semiconductors, its temperature dependence, the optical absorption in the ultraviolet, visible, and infrared regions, the the photoconductivity spectra, the lifetimes of photoexcited charge carriers, the thermopower, the thermally stimulated conductivity, and the mechanical properties suffer practically no changes after irradiation by fluxes of fast neutrons to fluences of

10^{18} cm^{-2} and of electrons with energy up to 300 MeV to fluences of up to 10^{17} cm^{-2}. (The fluxes indicated were those that were achieved in the experiments and by no means represent the limiting fluences for radiation stability of these semiconductors!) Both the irradiation and the measurements were done at temperatures ranging from 80 to 300 K. Measurements have also been made directly in the channel of a nuclear reactor. The stability of all the parameters of semiconductors of the In$_2$Te$_3$ type has been confirmed in all the experiments: radiation defects hardly accumulate, if at all, during irradiation.

"Effects of absence" require special experimental "hygiene." Therefore in all the experiments with the crystals mentioned, samples of the classic semiconductors CdTe, ZnTe, and Ge were irradiated and investigated under the same conditions. The data obtained, which are in splendid agreement with published sources, confirmed that the classic semiconductors are not radiation stable and are degraded when irradiated even by low fluences.

A detailed review of the data on radiation stability can be found in Refs. 3, 4, and 26.

6.3. What is the reason for such unusual radiation stability of the semiconductors In$_2$Te$_3$, Ga$_2$Te$_3$, and Ga$_2$Se$_3$? It lies in the crystal structure of these substances. They all have the sphalerite lattice, the same as for II–VI and III–V semiconductors, but with a fundamentally important structural feature: one-third of the sites of the cation sublattice of the compounds III$_2$–VI$_3$ are vacant. Even without delving into the quantum chemistry of these compounds (see Ref. 3), it is easy to see that for the same sphalerite structure, the number of cations and the number of anions in II–VI and III–V are equal, while in II$_2$–VI$_3$ there are three anions for every two cations. The presence of stoichiometric vacancies (SVs) is determined by the valence relations and is independent of temperature. It would seem that if there is an enormous concentration of vacancies, everything will reduce to the problem of metals with inherent vacancies, which was considered in paragraph 6.1. But let us not be hasty with conclusions. In fact, it is likely that a cation knocked out of its site will fall into a SV and set up a chemical bond, while the vacancy of a radiation origin left behind will become stoichiometric. This would amount to only disordering of the SVs and the cations in the cation sublattice of III$_2$–VI$_3$. This apparently is what happens in experimental reality; there is indirect evidence of it. But what happens in the anion sublattice? The mechanism considered in paragraph 6.1 cannot be used to interpret the anomalously high radiation resistance of these semiconductor compounds. It has a different physics (see below).

6.4. Concerning the accumulation of radiation defects and radiation resistance under irradiation by heavy particles. Of course a very large fraction of the radiation defects created are annihilated immediately after creation, as is confirmed by the results of Ref. 34, in which the damage to a lattice under irradiation by heavy ions was simulated and, at the same time, from the data of diffuse x-ray scattering, experimental evidence was found of a very large UP fraction, whose annihilation time is independent of temperature. If we are talking only about the SVs of III$_2$–VI$_3$ in relation to irradiation by gamma rays or electrons with energies of the

order of a few MeV, when the energy transferred to the PKA is only slightly larger than E_S and only point radiation defects form, the high radiation resistance could be completely explained by the large sizes of the RIZs and instability of FPs, both cationic and anionic, which is in fact observed in these loose-packed crystal structures (see Sec. 4) by virtue of the rather large IZs in these crystals. However, the radiation resistance against fast heavy particles, neutrons in particular, requires a completely different interpretation, of course, using the presence of RIZs.

The collision of a fast neutron with the nucleus of a lattice atom transfers to the atom an energy E many time larger than E_S. The simplest estimate, according to Kinchin–Pease (see Ref. 24), shows that the number of defects formed in this case is E/E_S. As was shown in the classic papers of Lindhard,[24] the average distance between the vacancy v formed and the PKA i, because of multiple scattering on the surrounding atoms of the lattice, is not large; in copper crystals, e.g., it is not more than 3–5 Å. This value is considerably smaller than the radius of a RIZ, and it would seem that all of the radiation defects could recombine at the time of creation. If this were the case, then there would be no problem of the radiation stability of materials in nuclear power technologies. In actuality the situation is different. There is the Silsbee effect: a focusing of atomic collisions (see Ref. 24). This is a classical effect that goes back to the billiard rules formalized by Coriolis and Sommerfeld. If a chain of billiard balls is arranged in a line and is struck by another ball strictly along the line, then the whole row is shifted by one interball distance and (almost!) all of the energy and momentum is acquired by the last ball in the chain. It will go far, in accordance with the force of the impact. Silsbee discovered the same thing in atomic chains: as it advances, losing energy, the PKA can initiate an interstitial atom far from the place where it initiated the focusing, leaving a vacancy at that point. The mean free path $L\,[hkl]$ of such an excitation (crowdion) can amount to tens of interatomic distances (h, k, and l are the Miller indices denoting the crystallographic direction of propagation of the crowdion). Torrens and Chadderton[35] showed that focusing can also occur along chains of different atoms if the mass of the atoms is not too different. Thompson and Nelson showed that the Silsbee effect is enhanced substantially in a lattice on account of the focusing "atomic lenses" consisting of symmetric atomic triangles and (more rarely) squares surrounding a given crystallographic direction. These lenses do not allow the advancing crowdion to deviate from its line of travel, restoring deviating atoms to the correct path. This is the so-called "additional focusing" effect, which is much more effective than the simple focusing effect: an interstitial atom can end up at a distance of several tens of atomic distances from the place where the vacancy due to its creation is located. There is no hope that defects so far apart will be within a RIZ and recombine with each other.

It would seem that radiation stability is unachievable...

But nature has also provided the inverse effect, the possibility of asymmetric, defocusing atomic lenses.[4,3,36] Such lenses occur in crystal structures where there is asymmetry of the local environment—not of a given atom, but of a given crystallographic direction in the lattice. It is therefore

clear that crystallographically anisotropic crystals are more radiation stable than are isotropic crystals, and this has been confirmed experimentally.[37] The asymmetry of the lenses is strongest in crystal structure, which, even macroscopically isotropic, have local asymmetry in the short-range "coordination cylinders" of a given crystallograpic direction (cylinders and not spheres, since we are talking about the propagation of crowdions). In crystals with stoichiometric vacancies the latter create an exceedingly strong asymmetry of the lenses, which instead of three identical atoms in a given lens have one of the atoms missing. Such a lens is defocusing: at such a place the advancing crowdion breaks up, and a classical interstitial i is formed. Such lenses suppress focusing. This was demonstrated in Ref. 36 with the aid of a very simplified modification of the molecular dynamics method. The criteria of radiation stability of an initially defect-free single crystal is[9,3,36]

$$L_{\langle hkl \rangle} < r_{0 \langle hkl \rangle}, \qquad (15)$$

where $L_{\langle hkl \rangle}$ is the mean free path of the crowdion, and $r_{0 \langle hkl \rangle}$ is the size of the RIZ for the $i-v$ interaction in the crystallographic direction $\langle hkl \rangle$. In the presence of defocusing lenses the maximum distance between i and v is the distance between these lenses. In crystals of the In_2Te_3 type, as a result of the presence of SVs, the defocusing lenses along the principal focusing direction $\langle 111 \rangle$ are located at distances not exceeding two interatomic distances. It is clear that in III_2-VI_3, even a focused interstitial i will remain within the RIZ of the vacancy it has left. In such lattices, defocusing lenses are present for all directions with low Miller indices, i.e., the directions for which focusing is even possible. There are three-component semiconductors, e.g., $ZnIn_2Te_4$ and $Hg_3In_2Te_6$, which also have lattices close to the sphalerite lattice but with a lower concentration of SVs (1/4 and 1/6 of all the cation sites, respectively). It was shown in Ref. 38 that the radiation resistance of such crystals is also substantially higher than for classic semiconductors without SVs.

Of course, the class of crystals with a loose-packed lattice does not exhaust all semiconductors with SVs. In particular, there is an enormous number of oxides whose structures have the same defocusing lenses. If the distance between these lenses is smaller than the radius of the RIZ in any of the possible focusing directions, then those crystals should also have very high radiation resistance, especially in view of the fact that the dielectric permittivity in oxides is lower than in covalent semiconductors, and this [see Eq. (1)] will tend to increase the size of the RIZs. Experimental data on the irradiation of a number of substances in a reactor have shown that the radiation resistance is in fact high in such crystals (e.g., Y_2O_3 and In_2O_3).[36] Criterion (15) can be used to propose a classification of crystals according to radiation resistance: if defocusing lenses are present at distances of not more than 3–4 interatomic distance in all crystallographic directions (for cubic crystals there are three of them), then the radiation stability will be especially high; if defocusing is absent in one of the three directions, then the radiation stability is lower; if absent in two directions, it is lower still. Crystals in which focusing is not suppressed at all have the lowest radiation resistance. Such a classification and a numerical radiation resistance scale were introduced in Ref. 39. On the basis of this classification one can choose substances for applications in radiation technologies.

Thus the radiation stability of crystals is determined by IZs and UPs.

7. COLLECTIVE EFFECTS WITH THE PARTICIPATION OF UNSTABLE PAIRS

7.1. Let us begin with phenomena in radiation physics. At very high intensities of the defect-forming radiation, short-lived UPs, by interacting with each other, can create long-lived defects. Indeed, if the spatial density of the UP excitations is so high that the RIZs overlap, then a situation can arise in which the interstitial i from one UP is simultaneously located in the RIZ of another. Then this i can annihilate with the vacancy from another UP, and the i from the latter, together with the v from the former, find themselves at a distance greater than the size of the RIZ. In this case a long-lived FP has been created from two UPs. However, the FPs that have arisen also interact with other raditation defects. As a result, with increasing concentration of nonequilibrium PKAs introduced by radiation per unit time (in the case of a uniform distribution of them, which is realized, for example, in the case of intense gamma irradiation), the overall concentration of FPs nevertheless decreases, and the concentration of UPs, which are not preserved on quenching, increases, reaching a nearly constant value at extremely high intensities.[40] This is rather unexpected: with increasing intensity of the introduction of radiation defects, the probability of accumulation of stable radiation defects can decrease. Such a scenario is also observed in cascades of radiation defects created by heavy particles, when the local concentration of radiation defects in a volume of the order of several hundred atomic volumes is huge, and collective effects arise; by the way, some aspects of the physics of these collective effects find agreement with the above-described features of the kinetics of the accumulation of radiation defects at a large but uniformly distributed concentration of them.

As was shown 40 years ago (see Ref. 24) and is confirmed by present-day studies,[34] the lattice damage after the impact of a heavy particle when the energy of the PKA is many times greater than E_S leads to a nonuniform distribution of defects: at the center of a cascade there are predominantly vacancies v, and at the periphery there are excess interstials i. If i and v in a radiation defect are charged, then the higher concentration of v at the center of the cascade will create an excess charge, so that the i on the periphery are found in an electrostatic field created by the excess v at the center, the total charge Z of which is the difference of the charges of v and i inside a sphere of any radius centered at the center of the cascade. It is easy to see that the RIZ of any i in such a field increases, according to (1), by a factor of $\sqrt{Z}$. This is the size of an instability macrozone.[41] It is clear that recombination of radiation defects in cascades is stimulated by this distribution of the defects. The overall picture is the same for cascade damage occurring in metals or in covalent semiconductors like Ge and Si, in which case the total elastic stress field around the core of the cascade creates a corresponding macro RIZ by analogy with (2). It is clear that this mechanism acts the more strongly the larger the ordinary

RIZs (1) and (2). We note that such a distribution of i and v in the cascades for which the distance between i and v in the central regions is substantially smaller than the RIZ does not, however, lead to complete annihilation, partly because the numbers of i and v are not equal. This limits the radiation resistance even for those crystals which meet criterion (15). A much stronger limitation is the probability of formation at the center of the cascade of amorphous regions or new crystalline phases that may have equilibrium analogs or may be particularly nonequilibrium.[42,43] As was shown by Bakai,[44] even the state diagrams of multicomponent alloys under steady defect-forming irradiation acquire different topological forms. This is apparently equivalent to the introduction of an additional quasi-thermodynamic degree of freedom, corresponding to the steady-state concentration of i and v.

We have discussed the possibilities of the annihilation of radiation defects. It must be kept in mind, however, that there are mechanisms that act to stabilize the unstable radiation defects. These are the aforementioned overlap of the RIZs, the formation of metastable states of electrons with the participation of UPs, and also the formation of complexes of components of the UP with impurities.[27,34,40]

The formation of metastable phases and the amorphization at the center of cascades, as well as the phenomena listed above which stabilize the unstable radiation defects, spoil radiation stability, so that any euphoria as to the prospects for radiation-stable materials, even for those materials whose crystal structure is favorable for radiation stability, must be tempered by these factors. Nevertheless, there is a quite definite way of creating and selecting materials with enhanced radiation stablility.

7.2. Collective interactions of UPs determine effects in superionic (SI) crystals. The phenomenon of SI conduction consists in the fact that in a number of nonmetallic crystals, a wide class of substances called solid electrolytes or superionic crystals, a phase transition occurs in which the ionic conduction increases in a jump by several orders of magnitude, sometimes reaching values of up to $1 \ \Omega^{-1} \text{cm}^{-1}$, and the activation energy for conduction decreases sharply. The fundamental review[45] discusses both the experimental physics and theoretical models of SI crystals. In the final analysis, any model of ionic conduction rests on the concepts of mobile interstitials originating from FPs. However, theories based on the idea of an interaction of FPs and explaining many effects in SI crystals (in particular, the preservation of one of two sublattices nearly unchanged, while the other undergoes disordering) encounter substantial contradictions. Indeed, the FPs and their interactions are fundamentally isotropic. Meanwhile experiments show that the defects responsible for the SI phase transition have a spatial orientation. It is found, in particular, that the temperature of the phase transition depends strongly on the external electric field, and in a number of SI crystals there is not only a phase transition to a SI state but also a phase transition to a ferroelectric state. SI domains have been detected (see Refs. 45–49). Unlike the Frenkel pairs, the UPs are invariably anisotropic, and in ionic crystals this is expressed in the formation of short-lived dipoles. The observed domains are short-lived, with a lifetime of 10^{-11} s, which agrees with the estimate of the lifetime of UPs in ionic crystals which we made at the beginning of this paper.

Anisotropy of the excitations is observed, in particular, in the study of NMR and neutron scattering: ions very rarely go far from their regular positions in the lattice; the majority of them execute very large-amplitude oscillations but around "their own" site. In Refs. 50 and 51 the microwave absorption of a number of SI crystals was studied, and it was shown that "the ions jump out and immediately jump back," and the lifetime of these lattice excitations is of the order of 5×10^{-11} s, a value which also agrees exactly with the lifetime of UPs estimated in paragraph 2.1 [Eq. (3)].

Skipping a little ahead, let us point out that the theory of the SI state presented below, which is based on the UP model, successfully describes not only the lifetime but also the features of the absorption spectra of SI crystals in the far infrared and microwave regions.[52] We should mention an interesting paper[53] in which the dielectric features of SI crystals were described successfully, but a number of other effects could not be described without taking the IZs into account.

Here is the basic idea of the theory of SI crystals based on the UP model.[52] Unstable pairs in an ionic crystal are short-lived dipoles. These dipoles are born independently and are oriented randomly in the lattice. Fluctuations in which there arises a certain local predominance of a parallel orientation of short-lived dipoles are probable. In such a region an average electric field arises which stimulates the formation of new UPs with the same orientation of the dipoles. It is easy to see that it is sufficient to have a predominance of only the projections of the dipole moments of the UPs on some direction, so that a one-dimensional model is adequate. The mean field approximation gives the following expression for the energy of formation of an individual UP in the collective field of all the other UPs, which comprise dynamic (and not static) dipoles:

$$E = (x_1 + x_2)E_{UP} - \varphi(x_1 - x_2)^2. \tag{16}$$

It is clear that, depending on the value of the second term in (16), the formation energy of an unstable pair can be decreased substantially. In Eq. (16) φ is the total field that would arise if all the dipoles formed and were oriented in each cell of the lattice; x_1 and x_2 are the relative number of projections of the dynamic dipoles oriented in opposite directions; $(x_1 + x_2)$ is the total concentration of UPs; $(x_1 - x_2)$ characterizes the predominance of one of the two orientations, which is what causes a nonzero total field of all the existing UP dipoles and lowers the energy of formation of each UP in the traditional orientation—along the total field. The origin of the nonlinear term in (16) of a given UP is as follows: the value of the self-consistent field increases with increasing fraction of the the UPs which are oriented, but even the birth of a "correctly" oriented UP has been stimulated by this collectively determined field. In a collective interaction the traditional orientation, as expected, is thermodynamically more favorable, even if the pairs are unstable. $Z = (x_1 - x_2)/(x_1 + x_2)$ is a dimensionless orientational order parameter of the unstable dipoles, and it characterizes the predominance of the parallel orientation. Minimizing the free energy with respect to the total concentration of UPs and also

with respect to Z gives equations for determining the equilibrium values of the UP concentration and Z. The main parameter of the joint solution of these equations, $\gamma = 2\varphi/E_{UP}$, gives a relation between the energy of the UP dipoles in the self-consistent field and the energy of their formation in the absence of this field. In the region $0 < \gamma < 2$ the theory predicts two possible phase transitions, one of which must invariably be second-order. The higher-temperature transition may not actually be realized if the crystal melts before reaching it. The general regularities of the phase transitions in SI crystals demonstrate just such behavior (see Ref. 45). One rather unusual result:[52] at low temperatures the order parameter $Z = 0$ (reflecting the absence of the objects of the ordering, since their concentration is thermally activated), and as the temperature is raised and the concentration of interacting particles increases, their ordering occurs due to the predominance of the potential energy of interaction over the kinetic energy ($Z > 0$), but at still higher temperature, when the average energy of the lattice vibrations becomes larger than the average interaction energy, the ordering is suppressed and again $Z = 0$. A result with a similar physical meaning was obtained by Freiman *et al.*[54] in a study of the orientational degrees of freedom in molecular cryocrystals. The theory of Ref. 52 also permits interpretation of the superionic–ferroelectric phase transition: such a transition occurs when the interaction of the UPs in their self-consistent field is sufficiently strong in comparison with the energy of formation of the UPs ($\gamma > 2$). Then the UPs become stable ordered dipoles. In Ref. 52 the state diagram was constructed for systems in which both insulator–superionic-crystal transitions (one or two phase transitions are possible) and superionic-crystal–ferroelectric transitions occur. Thus the phase transition to the SI state is determined by the UPs and their interaction.

However, the high ionic conductivity, the most distinctive property of SI crystals, is governed by the transfer not only of charge but also of mass, and it cannot be due to UPs, since, as we have seen, the UPs die at the same point where they were born, and are unable to migrate during their short lifetimes.

The charge carriers in a SI crystal are free interstitials, i.e., components of FPs which, as we have seen, coexist at low concentrations but compete statistically with UPs. At large concentrations of UPs these short-lived dipoles in the field of isolated i and v turn out to be oriented, and they lower the energy of an isolated interstitial and vacancy. This is a sort of solvation, as, for example, for ions in water. Thus the growth of the concentration of UPs leads to a decrease of the activation energy for FP formation, i.e., to growth of the concentration of FPs, which is one of the main distinctive features of SI crystals.[45,52]

Let us discuss the mobility of interstitial ions in a SI crystal. The mean free path of i is determined by their annihilation on encountering v belonging to either FPs or UPs. In either case the cross section of the process is the same—the sizes of the RIZ (Eq. (1)). The classic Drude model with the use of the above considerations not only is capable of describing the temperature dependence of the conductivity of SI crystals but can also be used to calculate the absolute value of the highest conductivity observed in SI crystals experimentally, which is actually close to the theoretical limit (of the order of $1\,\Omega^{-1}\,\mathrm{cm}^{-1}$). The model can also be refined by taking into account the interaction of the interstitials with each other, with a scattering cross section equal to the size of the SIZ.

Thus the UP model can give a consistent and quantitative interpretation of many collective phenomena in the physics of cyrstals.

8. UNSTABLE DEFECTS AND MATERIALS FOR TECHNOLOGY

8.1. In paragraph 6.1 it was shown that UP concepts permit one to propose a criterion for choosing metallic alloys which would have exceptionally high radiation stability—these are alloys with inherent structural vacancies. Of course it must be kept in mind that their plastic parameters are much inferior; they are more brittle than the construction materials used in today's nuclear reactors. However, their advantage is that their operating characteristics should be less affected by particle fluxes than those of contemporary structural alloys. It appears that the use of the method developed by Bakai[44] for constructing state diagrams of multicomponent systems under ionizing irradiation can give a realistic prognosis for the use of such alloys with allowance for the sharp decrease in the generation of stable FPs. It is quite probable that these alloys with structural vacancies will be the construction materials for nuclear reactors of the future. It can be hoped that taking the IZs associated with dislocations into account will provide the prerequisites for a microscopic theory of point defect sinks.

8.2. In paragraphs 6.2–6.4 we stated a criterion for choosing semiconductors and insulators with a high radiation stability. These are loose-packed crystal structures with rather large RIZs and with suppressed focusing of atomic collisions. The crystallographic criterion (15) now enables one without any special calculations to make a selection of crystalline materials having a high radiation stability. For insulators everything is clear (Y_2O_3, In_2O_3, etc.), with the restrictions mentioned in paragraph 7.1, of course.

It has been shown that semiconductors of the In_2Te_3 type, whose crystal structure, as we have seen, satisfies criterion (15) and whose exceptionally high radiation stability has been subjected to comprehensive experimental verification, can be used as detectors of extremely high intensities and fluences of high-energy particle radiation,[3] where the use of classic semiconductors is completely ruled out. Can one create a radiation-stable electronics based on In_2Te_3 and structurally related semiconductor compounds? It turns out that it is not a simple task. The problem is that semiconductors of the In_2Te_3 type have one more unusual property: their electronic parameters, unlike those of other semiconductors, are practically independent of impurity concentration. This is also a consequence of the presence of structural vacancies. It has been found that the impurities are localized at structural vacancies, which they remain in an un-ionized, atomic state.[3] Therefore it is almost impossible to influence the electronic properties of such semiconductors by doping: they remain intrinsic at any doping level. How can one make active elements of electronics (diodes and transistors) with a high radiation resistance? In Ref. 55 it was shown theoretically that

heterostructures based on two intrinsic semiconductors have a pronounced nonlinearity of the current–voltage characteristic, and with the aid of some physical and constructional contrivances one can even create a transistor. Estimates shown[55] that both the rectifying coefficient and the signal-amplifying capabilities in heterostructures based on intrinsic semiconductors of the In_2Te_3 type are inferior to those of all such devices based on classic semiconductors. They have only one advantage: devices made from them can operate stably even in a nuclear reactor, in storage units for radioactive wastes, and on long missions in outer space. The radiation-stable electronics will be cruder but ultimately more reliable.

8.3. In the previous paragraphs of this Section we have discussed the technical capabilities of unconventional crystalline materials selected solely on the basis of their exceptionally high radiation resistance. At the same time, there is another technical problem: to look for radiation-resistant crystals among those which have already proven their practical value. Their radiation resistance might not have record values, but it would be high enough for specific applications. Some very efficient scintillators based on ZnSe isovalently doped with tellurium, which substitutes for Se in the anion sublattice, were described in Ref. 56. It was shown that the centers responsible for the luminescence are complexes: Te in a substitutional position with a zinc vacancy in the nearest coordination sphere (a doublet) and a doublet with an interstitial Zn ion attached to it (a triplet). The excitonic luminescence in pure form was immeasurably weaker than the emission on the impurity complexes, in complete agreement with what Broude, Eremenko, and Rashba showed back in the 1950s.[57] Of course, today it is possible to determine in detail what defects and defect complexes are responsible for the luminescence,[56] how to increase the equilibrium concentration of triplets, which are the most advantageous in respect to the scintillation parameters,[56,58] and to establish which II–VI compounds are better than others at maintaining their parameters under ionizing irradiation in accordance with the general concepts of the UP model.[11] In one way or another, the ideas of the 1950s are still relevant today.

The author is happy to be able to emphasize this point in connection with the jubilee of Prof. V. V. Eremenko.

9. SUMMARY

—Unstable pairs consisting of a vacancy and interstitial atom are present in crystals, representing a third type of equilibrium defect in solids along with Schottky defects and Frenkel pairs. The unstable pairs are responsible for features of the heat capacity and diffusion and for anomalies in relation to the concentrations of defects in equilibrium and upon quenching, especially at pre-melting temperatures. In equilibrium the UPs are manifested mainly at temperatures close to the melting point.

—The equilibrium concentration of UPs is determined by instability zones of interacting defects. The instability zones exist in all solids, without exception, from cryocrystals to refractor metals, and are important not only in the interaction of point defects but of any other interacting lattice defects.

—The instability zones govern the behavior of crystals under high-energy irradiation: the larger the instability zones, the higher the radiation stability of the material. We have formulated a crystallographic criterion of radiation stability and stated the limits of its applicability.

—We have indicated some possible uses for the consequences of the instability zone and unstable pair models in physics and engineering.

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Translated by Steve Torstveit