

Some General Questions Of Radiation-Chemical Stability Of Solids

L.T. Bugaenko*, Yu.A. Zakharov, S.M. Ryabykh, D.G. Yakubik

Kemerovo State University, Ul. Krasnaya, 6, Kemerovo, 650043, Russia

** Moscow State University, Russia*

Abstract – It is suggested two component composing of inorganic crystal reactivity (stability) in the radiation field:

- **fundamental reactivity (FR) characterizing chemical transformation in the ideal crystal lattice;**
- **structure-sensitive reactivity (SSR) taking into consideration the chemical transformations with admixture and macrodefects participation.**

In the frames of these ideas there has been carried out the FR analysis of inorganic crystals of different chemical composition according to the space criterion displacement in the crystal lattices of exciton decay fragments generated by the radiation. Besides the notions of "hard" (non-deformable) and "soft" (deformable) exciton decay products and their comparison with free volume value of the crystal lattice are introduced.

Analyzing reactivity (stability) of solids in the radiation field we suggest marking out two its components: fundamental and structure-sensitive.

Fundamental reactivity (FR) is a substance ability in the radiation field to undergo chemical transformations in a ideal crystal lattice where there are only original point ionic defects.

Structure-sensitive reactivity (SSR) is a substance ability to undergo chemical transformations the field of the ionizing radiation with admixtures and macrodefects participation.

In radiating physics and chemistry of solids the problem has developed by comparative analyzing of radiation-stimulated processes in of monovalent metals halogenides. Historically the law formation study of radiating defects made, basically, on the AMH, and cluster metal formation research under the influence of active light was on silver chloride and bromide. In the best photoemulsions on the basis of microcrystals of silver bromide quantum yield of photolysis reaches 1, i.e. a theoretical limit. Under the influence of radiation clusters of metal are not formed at all in large and purified from admixtures crystals of silver chloride and bromide, and besides the formation of the electronic centers is very ineffectively. At the same time in the AMH there is a radiolysis with the center formation of colouring with a constant yield up to deep fractional conversion.

At first sight, there was a paradoxical situation: clear and high perfect crystals of silver halides are

radiationally stable, and the AMH is not present, but there is for defect microcrystals on the contrary.

Thus silver halides are defective in a cationic sublattice by Frenkel, and AMH is by Shottky. It is connected with that alkali metal cations have closed external electronic shell and consequently are hard, not capable to deformation whereas silver cation has the distorted external layer and consequently can change its form. These distinctions are enough to explain a difference in radiatio-stimulated processes.

The basic process determining the FR is a decay of an exciton generated by radiation on a pair of point defects. The formation of the pair F-H-centers from an anionic exciton is most expressed in the AMH. Another situation is in silver halides: localization of hole on cation is possible in them because of the presence of silver cation condition with a charge +2. Moreover, on geometrical reasons such localization is probably more favourable: apparently in Fig. 1, it is not accompanied with cation moving. An exciton decay, whose hole making is a silver cation with a charge +2, has the displacement of this cation in interstice with formation of cationic vacancy and next capture of a free electron by this cation with an ordinary silver cation formation with a charge +1.

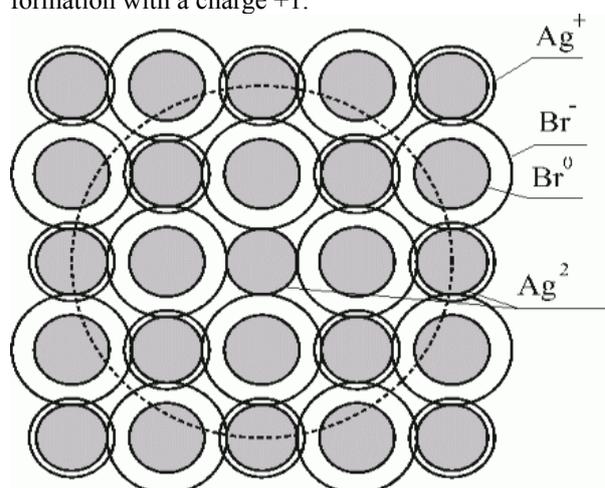


Fig. 1. A cationic exciton in crystal AgBr

The specified distinctions of the decay mechanism of excitons have far-reaching consequences. In the AMH it is possible the coagulation of F-centers with formation of the complex electronic-exceeded centers including X-centers which, as shown, can be transformed into metal colloids, but only after the warm-

up. It is an important point. It is not enough influence of one radiation supplying only energy for formation of colloid, it is still necessary the pulse supplied by the phonons. The H-centers are transformed to more stable hole centers and in halogen molecules. Such mechanism basically is impossible in silver halides: there are no anionic vacancies in them and they are not formed, and the only way for the pairs forming at the exciton decay "interstitial cation – cationic vacancy" is the recombination, but there should not be the formation of complex defects. That determines their high FR.

In the cases of efficient colloid-formation in microcrystals of silver halides, the mechanism with participation of mobile interstitial cations and demanding presence of free volume can be realized. In the scientific photography such mechanisms are well-known and present consequent capture on a growing cluster of free electrons and mobile interstitial cations.

But in these mechanisms the ideal crystal was examined and deviations rejections from an ideal crystal lattice in substantial crystals were not taken into account. In fact, the silver atom is packed neither in interstice, nor in a normal lattice site of silver halides and it is not found accidentally out in silver halides as well as the diatomic single charged cation, though they are certainly identified in porous systems with adsorbed silver nitrate by ESR (for example, on silica gels basis). At the same moment the real times of metal cluster formation in silver halides have been measured resorting to the pulse methods with nanosecond resolution. They are appeared to be about 10^{-8} seconds less than it was expected if to calculate the duration of an ionic stage, proceeding from ionic conductivity value of a crystal. There are some other moments aggravating the situation: they are an apparent low-temperature photosensitivity and its increase at doping by two-valent cations.

The possible way out of the problem is in the account of substantial crystal features, i.e. in concept SSR. Besides, the electronic-microscopic supervision has shown that metal clusters are placed on a surface of a silver crystal azide (pseudo-halogenide) not equal; they gravitate to macrodefects (cracks, pits, surface pimples and crystallites, etc.). The possible reason is the increased concentration of interstitial cations because of lower barriers of their migration in comparison with ideal volume. Thus reactivity grows by two reasons: high local concentration and low barrier of interstitial cations migration. This area has positive charge and is an efficient trap of free electrons (if electrostatic section of capture is equal to the size of a microcrystal, the probability of capture is close to 1).

The role of multiply charged cations is reduced to that they are in a condition to grasp two electrons and then to transfer them to two silver cations with formation as a result of a metastable molecule made from two silver atoms.

Thus, the FR and the SSR introduction allow solving a problem in this case. There is a lawful question: whether this concept can be distributed on other objects?

Let's take as an example the nitrates of alkali metals investigated in details. As it is shown in series of works, radiolysis of these salts is led to the decay of an anionic exciton on the nitrite which remains in the unit, and the oxygen going to the interstice and forming gas-filled cavities. It is a fundamental process of exciton decay on defects with the light fragment eliminating, and the radiation-chemical yield of such process is determined only by the basic substance properties, instead of any defects presence.

Another situation is in the heavy metals azides case. At silver azide radiolysis of divalent cations additions of copper, cadmium, lead increase greatly the speed of radiolytic metal formation. As it turned out, these cations are the centers of cluster formation, and only after heterogeneous system "radiolytic metal – a parent crystal" forming the speeds of the preparation radiolysis containing impurities of the different nature and concentration are improved. Thus, we see firstly SSR and only then, in the generated heterogeneous system – the FR.

Fundamental process in a ideal crystal lattice of inorganic metal azides is the decay of an anionic exciton with eliminating and a nitrogen atom yield in interstice. Thus diatomic ion-radical which found out by ESR remains in the unit. Besides, there are the second processes of a tetratomic azotic ion-radical as a result of atom nitrogen interaction with azide-anion, molecular nitrogen formation and finally the formation of the complex radiation defect presenting highly relax anionic sublattice and consisting from nitrogen molecules or their predecessors, and a cationic sublattice in which cations have turned into atoms, but preserved the place as in a parent crystal. Particles of metal are formed only at this area destruction during disolution or at warm-up.

Formation of three nitrogen molecules at a bimolecular reaction of two azides-radicals is energetically very favourable and accompanied with evolving 10.4 eV of energy, but theoretically it is impossible: in a crystal the azide-radical is the located hole, and holes have efficient positive charge and, naturally, push from each other away. Their interaction is possible if to lead into the intermediate localization of hole on negative-charged defect, for example, on cationic vacancy with the neutral center formation. Then the process is possible. But there is one more obstacle. The free volume is needed for an activated hexatomic complex formation. It can not be found in a ideal crystal lattice, but it is found on a surface. So it is responsible for the gas-making and goes not only at radiolysis, but also at a thermolysis. This process can be related to fundamental one when the intermediate localization goes on cationic vacancies – its own defects, and to structure-sensitive when this process goes on impurities.

The geometrical approach to the account of the substantial sizes atom ions, molecules and their fragments making a crystal, as well as their structures – the sizes of these particles in other charging conditions gives the valuable information about radiation-stimulated processes in solids. Thus deformability is determined by electronic density of corresponding layer. In a particle "rigid frame" i.e. the internal area is practically unable to the deformation. It allows carrying out the process classification. The process is impossible if it is necessary to displace the "rigid frames" from an equilibrium state at its passing and the process can be allowed if it is run only due to the external "soft" layers deformation. We call this requirement as "geometrical criterion" and its introduction is appeared to be productive for the process description in many systems.

Let's take as an example F-H- pairs formation in the AMH. It is necessary for its formation that the atom of halogen "has squeezeed" through corresponding minimum section. On Fig. 2 it is shown for sodium chloride. This section can be reduced by the compression. It is shown, that the efficiency of F-H – pairs formation is being decreased sharply at axial compression when the minimum section becomes less than the cation size.

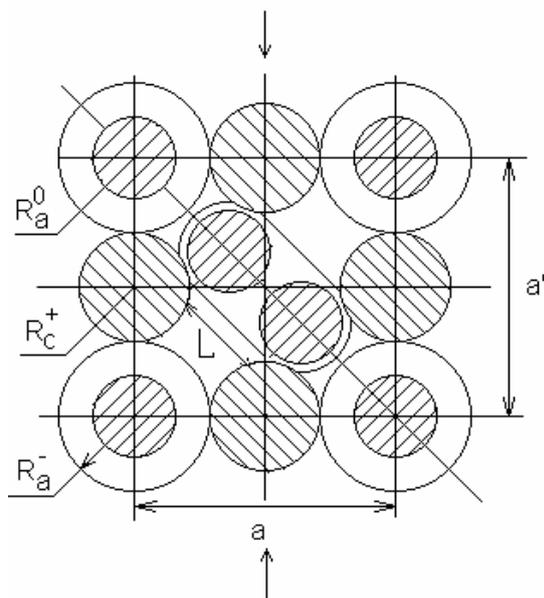


Fig. 2. Change of the H-center geometry under the line compression action

In silver halides the atom of halogen does not pass in minimum section even without compression that makes the anionic exciton decay on F-H – pairs impossible. And cationic exciton decay on an interstitial

atom and vacancy is allowed and corresponded to the experiment.

Certainly, the present model is only a convenient approaching. With its help it is possible to make calculations and estimations, using table values of atom and ion radiuses. But its usage is much wider, not only in radiation chemistry of solids. The atoms and ions presentation as a superposition of "rigid frame" and external distorted layer or several layers depending on number of steady valent states is appeared to be rather perspective in other areas of physics and chemistry of solids. In particular, due to this use the phenomena of ion transfer (electric conductivity and diffusion) are convincingly interpreted.

The real "rigid frame" is the atom or cation with the filled electronic shell. For elements of the second period it is the cation containing two electrons, i.e. lithium +1, beryllium +2, etc. up to fluorine +7. Their radiuses are easy to count up. Transition elements are considered to be multilayer; the number of layers is determined by number of steady valent states. For example, chlorine has conditions with charges -1, 0, +1, +3, +5, +7. We evolve for it "rigid frame" – cation with a charge +7 and five layers.

The basic process in the FR is an exciton decay on a pair of ionic point defects. For its passing it is necessary to spend energy on tearing up of chemical bonds and on overcoming of a barrier migration of corresponding ionic defect. An exciton has exceeded energy; there is the only question, whether it is enough for ionic defects formation (i.e. whether the energy criterion is observed). The silver halides probably have the anionic exciton energy near by the width of the band gap, i.e. 2.5 – 3 eV. It is not enough for halogen atom displacement (chlorine or bromine) because they cannot "squeeze" through minimum section between two clusters of a crystal lattice without of "rigid frames" displacement only due to external layer deformation. The cationic exciton has another pattern: its energy is higher, and movable two-valent silver cation has the smaller sizes that lets overcome minimum section. It also determines the different mechanism of excitons decay in the AMH and silver halides.

Another radiolysis feature is the reactions with participation of "hot" electrons. Anionic ions- radicals with a charge – 2 are formed at nitrates and azides radiolysis. Obviously, they have been got at interaction of an electron and anion, and this process is impossible. The similar reactions can pass only with participation of the "hot" electrons having the necessary exceeded energy.