

Combined mechanism of diffusion in solids

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A new mechanism of diffusion, consisting in the simultaneous action of Shottky's vacancies and unstable pairs of point defects is described.

Описан новый механизм диффузии, состоящий в одновременном действии вакансий Шоттки и неустойчивых пар точечных дефектов.

*What is the sense, what for were we born?
Is it the same as of birds? No more?
Is it only to build nests
For leaving and incubating eggs?
I'm sure we are attending the World
To leave after us not an egg, but the WORD.*

V.K.

I'm sure Yakov Evseevech Geguzin had left his personality for the times in the Word precisely. His words were impressive and inspiring. At the style of his scientific life, colored by interest for all nontrivial. At the style of his questions to the Nature, which were simple and unexpected at the same time — at the Faraday like capacity of experiments statements. As well as in his desire to do transparently clear all the items in physics to which he touched. As well as in the style of his talent manifested at so great and so distant areas, which seems to be incompatible in one person. He was the talented scientist, that is known by a lot of those working at a field of solid state physics. He was the talented teacher of scientists, that is known for his numerous pupils — for hundreds of students, for tens of Ph.D., for some Doctors of Science, who were grown under Geguzin's ideas and Geguzin's care. He was the talented writer. He was talented! He possessed may be the most rare talent in a hostile world of inter — scientific human relations: he was well-wished person.

I am proud he had chosen me to be one of his younger (comparing ages) friends. But Ya.E. preserved a youth of his impres-

sions and expressions till the lasts of his earth days. He was a romantic in the science. May be one of last ones in the contemporainity. I was not his pupil. We had met when I was an "adult scientist". But the personal and scientific Geguzin's sharm is influencing me till now, during almost 30 years. Even now after a lot of years I had lost him. But till now I love the Geguzin's home, Sulamiph and Svetlana Geguzin's home. Now it is far from me in the United States. But I fill the relatives contact for ever. Even at a distance of 7 thousands of kilometers. That is nothing comparing to the distance to Ya.E. now.

I will not retell two papers which had been written by us together. I would like to describe the fate of the idea which had been supported by Ya.E. intellectually and emotionally at the moment of its birth [1]. One can understand just a belief at the Wiphleem moment is the most important! I have in a mind the idea of unstable pairs (UP), being dear for me. This is the third type of point defects in solids, an intermediate between small harmonic oscillations of an atom at a vicinity of its regular position in a lattice, and completely separated com-

ponents of Frenkel's pairs (FP), being the vacancy (v) and interstitial atom (i).

I have to deliver the short description of UP. Ya.I.Frenkel, the great scientist (which name had been one of the highest for Ya.E. as well as for me), being the author of the model of separated precisely Frenkel's pairs, had predicted the possibility of a "predissociation" of i and v , if i had not ran too far from the v left [2]. One of the first computer modelling of radiation damages in solids [3] had shown really there is a region in the vicinity of v within which any i is absolutely instable and recombines with v at any low temperature without any activation. A lot of experiments had confirmed this for metals, semiconductors and insulators. We had shown that the physical reason of the existing the instability zones (IZ) is the cutting off a periodical migration potential of interstitials by the interaction potential $i-v$ [4]. (By the way, this paper had been delivered to Professor Il'ya Mikhailovich Lifshits, who was the greatest scientific authority for Ya.E. as well as for me, just by Ya.E.. And the paper had been recommended by I.M.L. for the Proc. of USSR Academy of Sciences at his turn). The great number of empirical results shows that an amplitude of periodical potential mentioned (that is an activation energy of interstitials migration) is rather small, within 10^{-2} - 10^{-1} eV. This determines for a lot of crystals values of IZ radii like 2-12 Angstroms [4, 5] in a not a bad coincidence with experimental estimations for substances with different bonds types, different lattice types and different electronic properties. It had been shown that any kind of interaction of defects leads to such instability. Not only attractive potentials create instabilities, but repulsive ones as well. For the last ones IZ is a cross section of the absolute pushing out of mobile defects i , for the firsts IZ determines the probability of a recombination. These simple considerations lead to some not too trivial conclusions. I will list them without any proofs, focusing just at the recombination of point defects. Ones interested can learn the details in [5, 6]. The IZ are of a great importance for understanding and predictions of a lot of radiation phenomena. May be the most interesting at this field is the revealing of extremely high radiation stability of substances with lattices satisfying some crystallographic preconditions (see [4-7]). It was shown there are a lot of crystals of such type of behavior under ionizing irra-

diation. These ones have to have loose lattice structures with empty positions at the regular lattice pattern. These emptinesses are not the defects (not the thermally activated vacancies, for example), but are the contents determined ordered voids. It had been shown that not only point defects instability is occurring, but the IZ for complex damages caused by heavy particles of high energy as well. This mechanism had been considered in Ref.[8] by Ya.E., Yu.R.Zabrodskii, and the author of this paper. It had been shown recently the radiation stability of some special kinds of metal alloys can be provided as well with quite more soft preconditions [9].

I will focus now to the thermal excitations of crystals. It had been shown there is the third type of equilibrium point defects in addition to the Frenkel's and Shottky's ones — precisely the unstable pairs (UP), see [4-6]. It was shown the UP at not too low temperatures can appear to be the most widespread equilibrium defects for a lot of solids. The statistical competitions of SV, FP and UP, taking place at any crystal, give the victory to one of them for different pristine characteristics of a given substance, but winners for different temperatures can be different for different crystals.

As to the properties of crystals with prevailing UP in equilibrium. I mentioned the UP excitations are short living defects and they recombine at the same point where they had been born. So the UP can not be quenched. This surprising phenomenon had been demonstrated experimentally for some semiconductors [5, 10] and than in [11] for metals, using comprehensive dates of the review [12]. Recently the role of UP in the equilibrium had been shown also by the excellent computer experiment [13]. In [11] I had estimated the contributions of FP, SV and UP into the heat capacity and thermal dilatation of metals. The model for the superionic phenomena at the base of UP conception appears to be successful as well (see [5]).

This brief review of the UP manifestations had been presented to describe an application of this model to the diffusion precisely being one of the most loving physical phenomenon for Ya.E.

It is clear UP can not cause the mass transfer directly because self i recombines with its v at the same point at which they had been born. But if the short living UP is appearing in the vicinity of a foreign atom, a competition between the native i , ran too far, and alien atom is appearing. If just the

last will be preferred by ν that will be the elementary diffusion act. Dr.V.M.Ekkerman and I had proposed the mechanism of diffusion using this idea [14]. Its main conclusion is the independence of diffusion activation energy on the kind of diffusing species. The migration energy of any foreign or self atom is excluded from the process as well as from the equations. This was confirmed experimentally in the collaboration with Dr.L.P.Gal'chinezki [15]. Of course this idea had been discussed in details with Ya.E.!

Now about the development of this idea. Ya.A.Kraftmakher had underlined in [12] there is a strange behavior of the diffusion activation energy of a lot of metals at high temperatures. It seems to be the rule for high temperature melting metals (such as tungsten, niobium or molybdenum) that at the high temperatures the diffusion activation energy increases sharply by about 1 eV. What is the reason of this? That is it. If an UP bursts in the vicinity of SV, the exchange of partners become possible. At this case the diffusion is determined by the meetings of UP and SV. The probability of these ones are determined by the product of UP and SV concentrations. Both of them are described for the first approximation by exponential functions of temperature of course with different activation energies E_{UP} and E_S subsequently. Thus the diffusion, determining by the probability of meetings these two types of defects have to be described by the activation energy being the sum of two activation energies mentioned above.

The analysis being done in [11] showed precisely this behavior of parameters mentioned. The combined mechanism of diffusion, determining by UP and SV both is presenting at a lot of solids.

Thus the competition between the lattice excitations mentioned can produce their effective collaboration as well.

Let me hope this will be the rule for the manhood as well.

The origin of these ideas had been described by Ya.E. in his brilliant semipopular book "The Living Crystal" [1]. I was and I am proud: that had been done just by him as the first. His criterion is of the highest validity for me.

Everyone have to depart from this life. That is natural and even not sad — it seems to me still living — if the kind memory is preserving. As to me I will remember the bright and kind personality of Ya.E. until I live.

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Комбинований механізм дифузії у твердих тілах

В.М.Кошкін

Описано новий механізм дифузії, складений з одночасної дії вакансій Шоттки та нестійких пар точечних дефектів.