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ANOMALOUS KINETICS OF DIFFUSION-CONTROLLED DEFECT RECOMBINATION IN IRRADIATED OXIDE CRYSTALS

Abstract: The annealing kinetics of the primary electronic F-type centers (oxygen vacancies with trapped electrons) is analysed for three ionic materials (α-Al_2O_3, MgO and MgF_2) exposed to intensive particle irradiation by electrons, neutrons, and heavy swift ions. Phenomenological theory of diffusion- controlled recombination of the F-type centers with much more mobile interstitial ions (complementary hole centers) allows us to extract the migration energy of interstitials and pre-exponential factor of diffusion. It is demonstrated that with the increase of radiation fluence the migration energy decreases, and pre-exponent factor exponentially decreases for all three materials, irrespective of the type of irradiation. These two parameters satisfy the Meyer-Neldel rule [1] observed earlier in many areas of materials science in physics, chemistry and biology [2], which indicates for peculiarities of defect migration in ionic materials locally disordered by radiation (e.g. along incident ion tracks). This study demonstrates that in the quantitative analysis of the radiation damage of materials, the dependence of the defect migration parameters on the radiation fluence plays an important role and cannot be neglected.

Keywords: kinetic, diffusion - controlled defect recombination, α-Al_2O_3, MgO and MgF_2, Meyer - Neldel rule

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Introduction. α-Al_2O_3 (sapphire, corundum) is a promising material for fusion reactors, mainly for diagnostics as a general insulator or optical components. Another two important radiation-resistant ionic materials are MgO and MgF_2. It is very important to predict/simulate the kinetics of defect accumulation in sapphire under neutron irradiation as well as long-time defect structure evolution. As is well known, the F center mobility is much smaller than that of the complementary Frenkel defects – interstitial oxygen ions. Thus, at moderate radiation doses and temperatures, the kinetics of the F-type center annealing is controlled by their diffusion-controlled recombination with mobile oxygen interstitials.

Despite numerous experimental data on defect kinetics, very few theoretical efforts were devoted so far to the quantitative analysis of available data, in order to extract main kinetic parameters-interstitial migration energy Ea and diffusion pre-exponent D_0, necessary for further prediction of the secondary defect kinetics and radiation stability of sapphire and related materials.

Recently, we developed simple phenomenological theory of diffusion-controlled defect recombination and applied it to irradiated insulators [3,4]. As it was shown therein, the kinetics of bimolecular recombination of the primary radiation defects - F type centers and interstitial ions is controlled by the two parameters: the activation energy E_a for migration (diffusion) of more mobile component (interstitial) and the pre-exponential factor $X = N_0\ R\ D_0\ /\ ?$, where N_0 is initial defect concentration, R recombination radius, D_0 diffusion pre-exponent, and β heating rate. Assuming standard parameters $N_0 = 10^{17}\,cm^{-3}$, R = 10 //A, $D_0 = 10^{-3}\ cm^2\ s^{-1}$, β = 10 K/min, one gets the estimate $X = 10^8\ K^{-1}$ for normal diffusion. Our analysis has demonstrated that the diffusion energy of oxygen interstitials varied considerably from one experiment to another, very likely

due to difference radiation doses. This means in particular, that the diffusion energy is not unique parameter characterizing radiation defect kinetics.

Results and discussion.

The F-type center annealing analysis To ledlighter to the problem, we analyse first the F-type center annealing kinetics for α-Al_2O_3, MgO and MgF_2 irradiated by electrons, neutrons, and heavy ions with very different fluences, which are available from literature. All three materials have quite different crystalline structure and chemical bonding: MgO is cubic and ionic, MgF_2 has rutile structure and ionic, sapphire (α-Al_2O_3) has hexagonal structure and partly covalent. As is known, three types of radiation create point defects with very different spatial distribution: almost homogeneous under electrons, strongly correlated along neutron trajectory and in heavy ion tracks. We will demonstrate that diffusion coefficients of point defects in all these materials and likely, in many other heavily irradiated ionic solids could no longer be described by a simple relation: $D=D_0 \exp(-E_a/kT)$, D_0 is constant, but under heavy irradiation it looks more as migration in liquids with high mobility and low migration barriers.

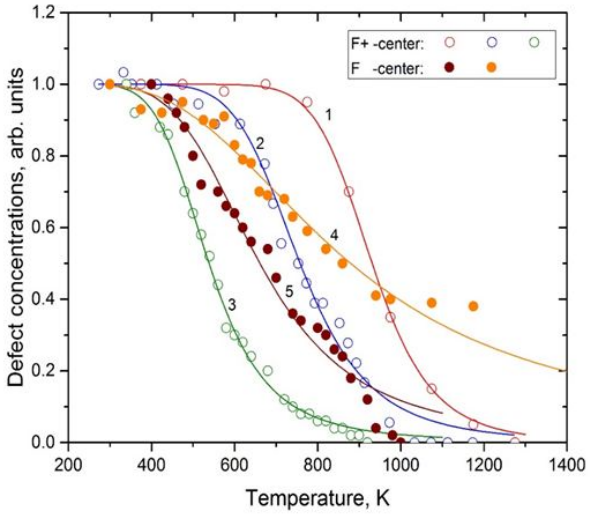

FIGURE 1 – The kinetics of the F or F^+ center annealing in α-Al_2O_3 (neutron irradiation)

Table 1 The explanation of curves 1-5 in Fig.3 and the obtained migration energy of interstitial ions E_a and pre-exponential factor X under different types of radiation and different doses

Nr.	Irradiation conditions	E_a (eV)	X (K^{-1})
1	electron irradiation, dose $1x10^{16}$ electrons/cm^2 [5]	1.60	$1.0x10^8$
2	electron irradiation dose $1x10^{17}$ electrons/cm^2 [5]	0.80	$8.4x10^3$
3	electron irradiation dose $2x10^{17}$ electrons/cm^2 [5]	0.35	$3.5x10^0$
4	neutronirradiation, 15 min [5]	1.24	$9.8x10^6$
5	neutronirradiation, 10 h [5]	0.56	$1.8x10^2$

Correlation of the diffusion energy and pre-factor The pre-exponent X is much smaller than the estimate for a regular diffusion in crystalline solids (see Table). Moreover, we have observed a strong correlation between the activation energy E_a and pre-exponent $X(E_a)$ which is no longer constant but fits very well to the exponential function of E_a.

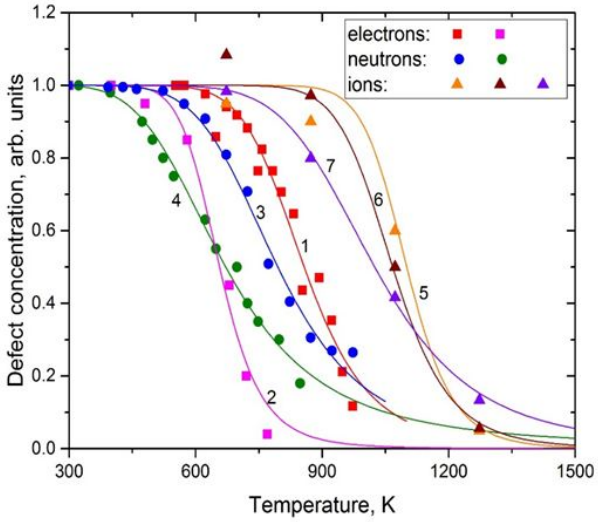

Figure 2 – The kinetics of the F centers annealing in MgO for different types of radiation

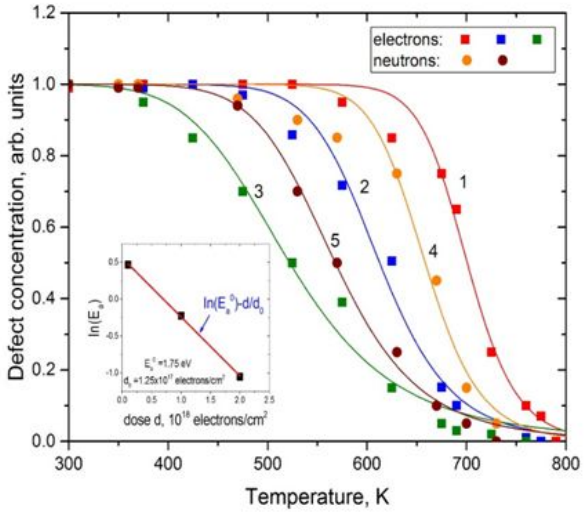

Figure 3 – The kinetics of the F centers annealing in MgF_2 for different types of radiation (see Table for details

In fact, as radiation dose increases, both the migration energy E_a and pre-exponent X decrease, as the result defect diffusion rate effectively grows. Moreover, we observed this correlation for several irradiated ionic materials - Al_2O_3, MgO and MgF_2 which indicates that this could be quite common phenomenon.

The presented results could be understood as a growing topological disordering of materials under irradiation with a continuous transition from a perfect crystalline structure to the amorphous-like one [6]. This could explain drastic reduction of the activation energy for diffusion. As is well observed [7,8], in liquids the main migration mechanism is not thermally activated overcome of the energy barrier between two lattice positions, but particle (molecule) penetration into nearest cavity due to density fluctuation when nearest molecules are collectively move apart opening the path for a random walk with a low activation energy. The characteristic feature of liquids and amorphous solids is a strong temperature dependence of the pre-exponential factor which is no longer a constant.

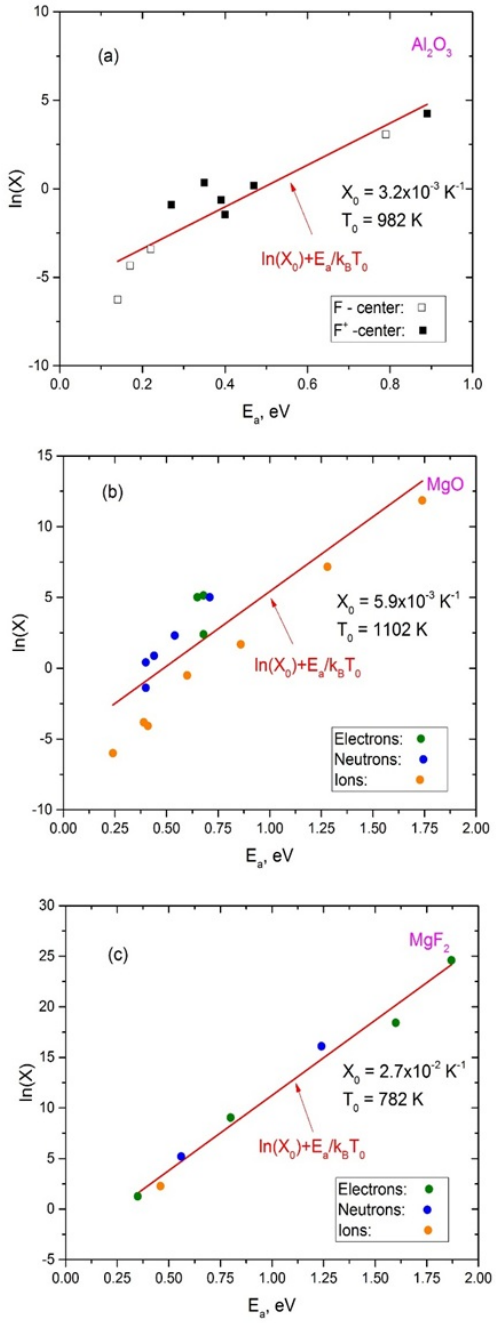

FIGURE 4 – Correlations for Al_2O_3 (a), MgO (b) and MgF_2 (c)

The Meyer-Neldel rule The above observed correlation of the migration energy E_a and pre-factor X (Fig.4) fits quite well to the relation known as the Meyer-Neldel rule [1,2]:

$$ln(X) = ln(X_0) + E_a/k_BT_0, \tag{1}$$

where X_0 is a constant and T0 some characteristic temperature. Eq. (1) shows how reduction of the activation energy with growing disorder is compensated by orders of magnitude decrease of the pre-factor X. Fig. 4 demonstrates that this relation indeed is well satisfied for all three materials,

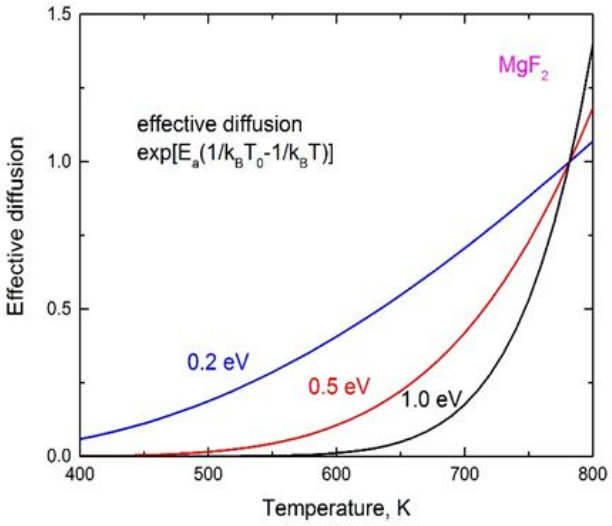

FIGURE 5 – The effective diffusion coefficient in MgF_2 for three different values of activation energies

and the more so, for different types of irradiations (and initial defect spatial distributions). Note that all experimental points lie below the characteristic temperature T_0.

Eq. (1) could be also interpreted as the diffusion coefficient with exponentially dependent pre-exponent

$$D \sim exp\left(\frac{E_a}{k_B T_0} - \frac{E_a}{k_B T}\right), T < T0, \tag{2}$$

Fig. 5 shows how the effective diffusion coefficient depends on the activation energy E_a: the smaller energy, the larger diffusion coefficient and defect mobility, which shifts the recombination region to lower temperature side (see Figs. 1-3).

Note that this effect [1] is well known in chemistry, biology, even semi-conductor physics [2,9]. The foundations of this empirical rule are still not fully understood. One of possible phenomenological models (Dyre1986) [10] claims that eq. (1) holds in disordered systems with exponential probability distribution of energy barriers of localized quasi-particles, and parameter T0 could have the meaning of glass transition. The relation (1) was observed also in multicomponent systems (metallurgical slags [11]) containing tens of oxides, and in glasses under irradiation [9,12].Recently, by applying high pressure or changing the Ce content in Y-doped $BaMO_3$, it has been shown that the proton conductivity in these materials follows the Meyer - Neldel rule well [13]. It has also recently been established in detail that the nature of the conduction spectra in oxide and chalcogenide systems is different, which should indicate different mechanisms of conduction through polaron hopping [14]. This has been well studied using the Meyer - Neldel rule, which provides microscopic information about the behavior of conduction in various systems [14]. In particular, using the example of New chalcogenide glassy system, xAg_2S - (1-x) (0.5Se - 0.5Ge), it was found that DC conductivity shows a thermally activated nature, while AC conductivity via the Meyer-Neldeldemonstrates the correlated nature of hopping conduction across the barrier [15]. In [16] , as a first step, the authors relate the so-called Meyer-Neldel behavior in ionic conductors to phonon occupations. On the other hand, in [17], the nested Bi_2S_3 nano-networks with different morphologies were synthesized using topotactic transformation and used using the Meyer-Neldel relation to reveal the nature of its trap distribution (type and width). The fact that the temperature dependence of ac conductivity obeys the Meyer - Neldel rule was shown using the example of borate glasses doped $BaTiO_3$ for energy storage devices [18]. Finally, it turns out that the entropy of a material is critical for ionic conductivity [19].

It was also noted that the search for anti - Meyer - Neldel rule materials with a highly distorted structure would have great potential [19]. Recently, much research has focused on the extraordinary characteristics of ionic conductors with the deepgoing comprehending about the reasons for Meyer - Neldel rule lacked [19]. This is important for the research and development of new materials for potential solid electrolytes.

Conclusion. It is demonstrated for the first time that in strongly irradiated ionic solids of different crystalline structure and chemical nature, the pre-exponential factor of diffusion is strongly related to the migration energy. In other words, the defect recombination kinetics is not characterized uniquely by the activation energy for diffusion with a constant pre-exponent but instead these parameters depend on the radiation fluence which considerably complicates analysis of the radiation-induced kinetic processes.

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АНОМАЛЬНАЯ КИНЕТИКА ДИФФУЗИОННО-КОНТРОЛИРУЕМОЙ РЕКОМБИНАЦИИ ДЕФЕКТОВ В ОБЛУЧЕННЫХ ОКСИДНЫХ КРИСТАЛЛАХ

Аннотация. Кинетика отжига первичных электронных центров F-типа (кислородных вакансий с захваченными электронами) анализируется для трех ионных материалов (Al_2O_3, MgO и MgF_2), подвергнутых интенсивному облучению электронами, нейтронами и быстрыми ТЯЖЕЛЫМИ ионами. Феноменологическая теория диффузионно-контролируемой рекомбинации центров F-типа с гораздо более подвижными интерстициальными ионами (комплементарными дырочными центрами) позволяет определить энергию миграции интерстициалов и предэкспоненциальный фактор диффузии.Эти два параметра удовлетворяют правилу Мейера-Нельделя [1], наблюдавшемуся ранее во многих областях материаловедения в физике, химии и биологии [2], которое указывает на особенности миграции дефектов в ионных материалах, локально неупорядоченных излучением (например, вдоль треков падающих ионов). Данное исследование показывает, что при количественном анализе радиационного повреждения материалов зависимость параметров миграции дефектов от флюенса излучения играет важную роль и им нельзя пренебрегать.

Ключевые слова: кинетика, диффузионно-контролируемая рекомбинация дефектов, α-Al_2O_3, MgO, MgF_2, правило Мейера-Нельделя

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СӘУЛЕЛЕНГЕН ОКСИД КРИСТАЛДАРЫНДАҒЫ АҚАУЛАРДЫҢ ДИФФУЗИЯЛЫҚ - БАСҚАРЫЛАТЫН РЕКОМБИНАЦИЯСЫНЫҢ АНОМАЛЬДЫ КИНЕТИКАСЫ

Аннотация. F-типті (қармалған электрондары бар оттекті вакансиялар) бастапқы электронды орталықтардың босаңдату кинетикасы, электрондармен, нейтрондармен және ауыр жылдам иондармен қарқынды сәулеленуге ұшыраған, үш иондық материалдар (Al_2O_3, MgO және MgF_2) үшін талданады. F-типті орталықтардың анағұрлым жылжымалы интерстициалды иондармен (комплементарлы кемтік орталықтарымен) диффузиялық басқарылатын рекомбинациясының феноменологиялық теориясы интерстициалдардың миграциялық энергиясын және экспоненциалдыға дейінгі диффузия факторын анықтауға мүмкіндік береді. Бұл екі параметр бұрын физикада, химияда және биологияда материалтанудың көптеген салаларында байқалған [2], Мейер-Нельдель ережесін қанағаттандырады [1], бұл сәулеленудің әсерінен жергілікті реттелмеген, иондық материалдардағы ақаулардың миграциясының ерекшеліктерін көрсетеді. (мысалы, түскен иондардың ізінің бойымен). Бұл зерттеу, материалдардың радиациялық зақымдалуының сандық талдауы барысында ақаулардың миграция параметрлерінің сәулелену флюенсіне тәуелділігі маңызды рөл атқаратынын және оны елемеуге болмайтынын көрсетеді.

Түйін сөздер: кинетика, ақаулардың диффузиялық басқарылатын рекомбинациясы, α-Al_2O_3, MgO, MgF_2), Мейер-Нельдель ережесі

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