7.3 Theory of a Quodon Gas with Application to Precipitation Kinetics in Solids Under Irradiation — V. I. Dubinko, R. V. Shapovalov (NSC Kharkov Institute of Physics and Technology), S.Y. Hu, Y.L. Li, C.H. Henager, Jr. and R.J. Kurtz (Pacific Northwest National Laboratory)

Extended abstract based on results that will be reported in the Springer Series on Wave Phenomena- Special Volume LENCOS [1] and NIMB_PROCEEDINGS-D-12-00109R1 [2].

OBJECTIVE

The rate theory of microstructure evolution in solids has been modified to account for the production of Schottky defects at surfaces of extended defects due to their interaction with the radiation-induced lattice excitations that primarily affect one-dimensional transport mechanisms. These modifications appear to be necessary in order to understand important radiation-induced rate processes, such as irradiation creep, radiation-induced annealing of voids, saturation of void growth under high dose irradiation, and void lattice formation.

SUMMARY

The difference in the ability to absorb point defects by extended defects is a main driving force of microstructural evolution under irradiation [3]. Another driver for radiation-induced microstructural evolution is based the forced atomic relocations resulting from nuclear collisions, a.k.a. ballistic effects [4] that have been taken into account for the explanation of the dissolution of precipitates under cascade damage. Later on it was recognized that the so-called “thermally activated” reactions may be strongly modified by irradiation resulting in the radiation-induced production of Schottky defects [3, 4-8], which has essentially the same physical nature as the ballistic effects, but, in contrast to the latter, it operates under both cascade and non-cascade damage conditions, including sub-threshold electron irradiation that does not produce stable Frenkel pairs. The underlying mechanisms for these processes are based on the interaction of extended defects with unstable Frenkel pairs, focusing collisions (a.k.a. focusons) and with lattice solitons. The latter can be mobile, and these are referred to below as quodons, which are stable quasi-particles that propagate one-dimensionally and transfer energy along the close packed directions of the lattice. Quodons may have more technological significance than focusons due to much longer propagation ranges expected from the nonlinear theory and demonstrated experimentally [8, 9]. This points to the necessity of the modification of the chemical rate theory to account for the quodon-induced energy deposition to the reaction area. Accordingly, the rate theory of microstructure evolution in solids has been modified to account for the production of Schottky defects at surfaces of extended defects due to their interaction with the radiation-induced lattice excitations [3, 5-8]. The modified theory predictions include important phenomena, which have not been properly understood before, such as irradiation creep [5, 6], radiation-induced annealing of voids [3, 7], saturation of void growth under high dose irradiation and void lattice formation [8].

PROGRESS AND STATUS

Introduction

Until recently the evidence for the existence of lattice solitons provided by molecular-dynamics simulations was restricted mainly to one and two-dimensional networks of coupled nonlinear oscillators with simple "toy" potentials (see e.g. [10]), whereas reports on their observation in three-dimensional systems using "realistic" molecular-dynamics potentials were scarce and restricted to alkali halide crystals [11]. The lattice solitons found in these simulations always drop down from the optical band(s) into the phonon gap, and hence become unstable. Consequently, it has been assumed that the softening of atomic bonds with increasing vibrational amplitude is a general property of crystals, and therefore lattice solitons with frequencies above the top phonon frequency cannot occur. However, in their recent paper, Haas et al [1] have provided a new insight on this problem by demonstrating that the anharmonicity of metals appears to be very different from that of insulators. As a result, in some metals, lattice solitons may exist with frequency *above the top of the phonon spectrum*. Using the known literature values of the pair potentials, Haas et al have found that in Ni and Nb this condition is fulfilled. Their molecular-dynamics simulations of the nonlinear dynamics of Ni and Nb confirmed that high-frequency lattice solitons may exist in these metals, and their corresponding energies may be relatively small, starting from threshold energy of 0.2 eV, just above the phonon band. These results allow us to look at the modification of the rate theory based on the quodon dynamics from a different perspective as compared to the one proposed in refs [3, 5-8]. Initially it has been assumed that the main difference between quodons and focusons is in their path lengths. Accordingly, it was postulated that (i) the quodon production rate was equal to the focuson production rate; and (ii) similar to focusons, quodons could eject vacancies from extended defects provided that their energies exceeded the vacancy formation energy. This mechanism is close to the classical ballistic mechanism of the precipitate dissolution under cascade damage [1]. However, in view of the new results [12], one can assume that irradiation may produce quodons with energies almost as low as that of phonons, which are lower than typical focuson energies by orders of magnitude. This assumption is the basis of the model proposed in [2], which has been applied in [1] for modeling of the nucleation and growth of copper precipitates in *FeCu* binary alloys under electron irradiation [13].

Theory

It is known that even in the case of displacement damage, only a small part of the energy of impinging particles is spent on generation of stable Frenkel pairs (that require 20-40 eV each) and their clusters (in energetic displacement cascades), while the major part of energy is dissipated into heat, or in other words, it is spent on generation of phonons.

The first main assumption made in [1, 2] is that *quodons are the transient form of the heat generation under irradiation*, which means that they are constantly generated by irradiation, and subsequently lose energy by generating phonons. Let K_q be the average rate of quodon generation (per atomic site per second), which should be proportional to the flux of impinging particles, F_{irr}, and the energy deposition density by one particle, dE_{irr}/dx, and inversely proportional to the mean quodon energy,

$\langle E_q \rangle$:

$$K_q\left(F_{irr}\right) = k_{eff}^q F_{irr}\left(\frac{dE_{irr}}{dx}\right)\frac{w}{\langle E_q \rangle}, \tag{1}$$

Where w is the atomic volume, and k_{eff}^q is the quodon production efficiency that depends on material and irradiation conditions and can range from zero (no quodon generation) to unity (e.g. under sub-threshold irradiation that does not produce stable defects).

Then the mean density of quodon gas under steady-state irradiation (the number of quodons per unit volume) will be given simply by the product of their mean generation rate and the lifetime, τ_q:

$$N_q\left(F_e, T_{irr}\right) = \frac{K_q\left(F_e, E_e\right)\tau_q}{w}, \; \tau_q\left(T\right) = \frac{l_q\left(T\right)}{c_q}, \tag{2}$$

Where c_q is the quodon propagation speed, which is assumed below to be close to the sound velocity, c_s, and $l_q\left(T\right)$ is the quodon propagation range before decay.

From a quantum theory of intrinsic localized modes it is known that they decay by generating phonons. Similar to that, quodons are assumed to lose energy in quodon-phonon collisions *by portions (or quanta)* ΔE_{qp}. Then the mean quodon propagation range may be written as

$$l_q\left(T, \langle E_q \rangle\right) = \frac{\langle l_{qp}\left(T\right) \rangle}{\varepsilon_{pq}}, \; \varepsilon_{pq} \equiv \frac{\Delta E_{qp}}{\langle E_q \rangle}, \tag{3}$$

where $\langle l_{qp}\left(T\right) \rangle$ is the mean length of quodon free path between collisions with phonons, which is determined by a well known formula for a 1-D propagating particle in a medium with scattering centers of a given density and cross-section:

$$\langle l_{qp}\left(T\right) \rangle = \frac{1}{\pi R_{qp}^2 \langle N_p\left(T\right) \rangle}, \; \langle N_p\left(T\right) \rangle = \frac{1}{w}\frac{1}{\exp\left(\frac{\hbar\omega_D}{k_B T}\right) - 1}, \tag{4}$$

Where R_{qp} is the effective quodon-phonon cross-section radius, $\langle N_p\left(T\right) \rangle$ is the density of phonons having a high-frequency ω_D (a.k.a. Debye phonons), k_B is the Boltzmann constant and *T* is the temperature. We assume here for simplicity that Debye phonons are the main contributors to the quodon decay due to the loss of energy in each collision between them represented by the energy coupling parameter $\Delta E_{qp} \approx \hbar\omega_D$. These and other material parameters used in the calculations are listed in ref [1].

The quodon-phonon cross-section radius is extremely small (~10^{-12} m), and so the quodon propagation range can reach tens of centimeters (Fig. 1), which agrees with experimental data on tracks produced by quodons in mica muscovite [9]. These enormous ranges in real crystals that contain structural defects can be understood only assuming that quodons can both lose and gain energy in the scattering process with extended defects. So the <u>second main assumption</u> of the model [1, 2] is that in the collision events between quodons and extended defects, *quodons lose and gain energy with equal probability*.

As can be seen from Fig. 1, the quodon generation rate under irradiation conditions [13] can exceed the displacement rate by 6 orders of magnitude, and the density of quodon gas becomes comparable to that of Debye phonons at the electron flux of $10^{24}\,m^{-2}s^{-1}$, which corresponds to the displacement rate of ~5 x 10^{-3} s^{-1} that is a typical value for radiation damage studies using electron beams. So we may conclude that under irradiation a crystal contains a mixture of "gases" of quasi-particles, namely, almost equilibrium phonons and strongly non-equilibrium quodons, the densities of which may be comparable. After irradiation is switched off, quodons transfer their energy to phonons and disappear over a short relaxation time $\sim\tau_q \approx 7\times10^{-5}$ s, as the crystal attains a thermal equilibrium state. In the following section, we consider the effect of quodon gas on chemical reaction rates under irradiation.

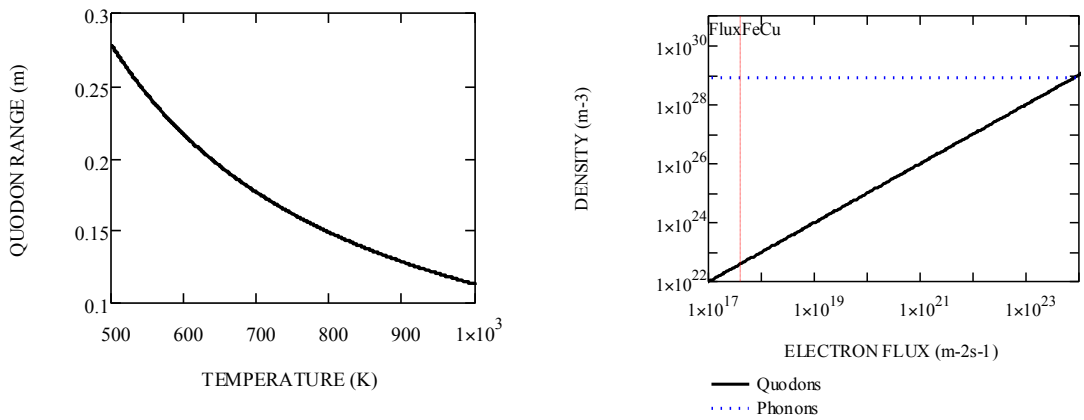

Figure 1. The temperature dependence of the quodon propagation range $l_q(T)$ and the density of quodon gas vs. electron flux, $F_{irr} = F_e$ at the irradiation temperature 563 K. The vertical dotted line corresponds to irradiation flux [13]. Density of the gas of Debye phonons at 563 K is shown for comparison.

RESULTS

It is known that the "gas" of phonons is responsible for the temperature effect on the reaction rates, $\dot{R}$, which is expressed by Arrhenius' law:

$$\dot{R} = \omega_p \exp\left(-\frac{E_a}{k_B T}\right), \tag{5}$$

Where ω_p and E_a are the frequency factor and the activation barrier, respectively. The reaction activation barrier is determined by the maximum *free energy change* of the system imposed by reaction (a.k.a. the free energy barrier). Phonons represent thermal fluctuations acting on a system (e.g. point defect and its surrounding) and helping it to overcome the barrier.

On the other hand, unlike phonons, which are delocalized, quodons are strongly localized on several lattice sites, and in the collision event between a quodon and an extended defect (ED), the latter can gain (or loose) some portion of energy at the place of collision, and so the resulting energy of the system including the ED will undergo stochastic deviations from its average value. Accordingly, the Arrhenius' law (5) can be rewritten with account of the energy exchange between quodons and the "reaction area":

$$\dot{R} = \omega_0 \exp\left(-\frac{E_a^q}{k_B T}\right),\ E_a^q \equiv \langle E_a \rangle - \Delta E_a,\ \Delta E_a \equiv \frac{\langle V_q^2 \rangle - \langle V_q \rangle^2}{2k_B T}, \tag{6}$$

Where the brackets $\langle\ \rangle$ designate the integration over the Gibbs ensemble so that $\langle E_a \rangle$ is simply the average activation energy, while the second term in eq. (6) is always negative and it is proportional to the square of the energy dispersion due to quodon-induced fluctuations. This result means that under irradiation all reaction barriers in a crystal may be decreased by a value that depends on the statistics of the "gas" of quodons and their coupling with structural defects. It can be shown that at steady state the energy dispersion in eq. (6) can be expressed via the quodon propagation range l_q and generation rate K_q, which is proportional to the flux of impinging particles F_{irr} (see eq. (1)). Accordingly, one can express the modified reaction rate as follows [1, 2]:

$$\dot{R} = \dot{R}_0 A\left(f_{irr}\right),\ A\left(f_{irr}\right) = \exp\left(\frac{k_{mat} F_{irr}}{\left(k_B T\right)^2}\right), \tag{7}$$

where $\dot{R}_0$ is the reaction rate in the ground state (no irradiation) and $A\left(f_{irr}\right)$ is the reaction amplification factor due to the interaction with quodon gas, while k_{mat} is the coefficient determined by quodon statistics and material parameters.

The modified rate theory is applied to modeling of copper precipitation in *FeCu* binary alloys under electron irradiation characterized quantitatively by Mathon et al. [13] who described not only evolution of copper precipitates but also the time dependence of the concentration of copper atoms in the matrix, $\bar{C}_{Cu}\left(t\right)$, both under thermal annealing at 773 K and under electron irradiation at 563 K. It appears that $\bar{C}_{Cu}$ at the end of the precipitation process, which corresponds to the copper *solubility limit*, is of the same order of magnitude in both cases. This result is in a marked disagreement with Arrhenius law that predicts the copper solubility limit at 563 K to be several orders of magnitude lower than observed.

In the present view, this contradiction is a very principal one, since the solubility limit value practically determines the rate of the nucleation and growth, and a failure to evaluate it in the classical rate theory makes it impossible to describe correctly the precipitation kinetics under irradiation. In all up to date models, the solubility limit under irradiation is assumed to be determined only by temperature, similar to the thermal case (see e.g. [14, 15], which is a misleading assumption.

In ref. [1], the rate theory of the precipitation kinetics is modified to account for non-equilibrium thermodynamics of "quodon gas" and its results are compared with results of the classical model (without quodon-induced effects) and with experimental data [13] as shown in Figs. (2, 3). One can see that the classical model disagrees strongly with experimental data on all precipitation parameters, and this discrepancy is especially pronounced for the copper solubility limit (Fig. 3). In contrast, the quodon-modified model describes quite well both the evolution of precipitates and the matrix concentration of copper measured by different methods. The latter fact seems to be of particular importance, since it reflects the principal difference between the two concepts, namely, the "classical" and the new one, in relation to the mechanisms of production of Schottky defects. In the classical theory they are assumed to be emitted by ED's exclusively due to thermal fluctuations, which, in our language, are driven by phonons. In the modified rate theory we have taken into account essentially athermal fluctuation mechanisms based on the interaction of ED's with radiation-induced quodons.

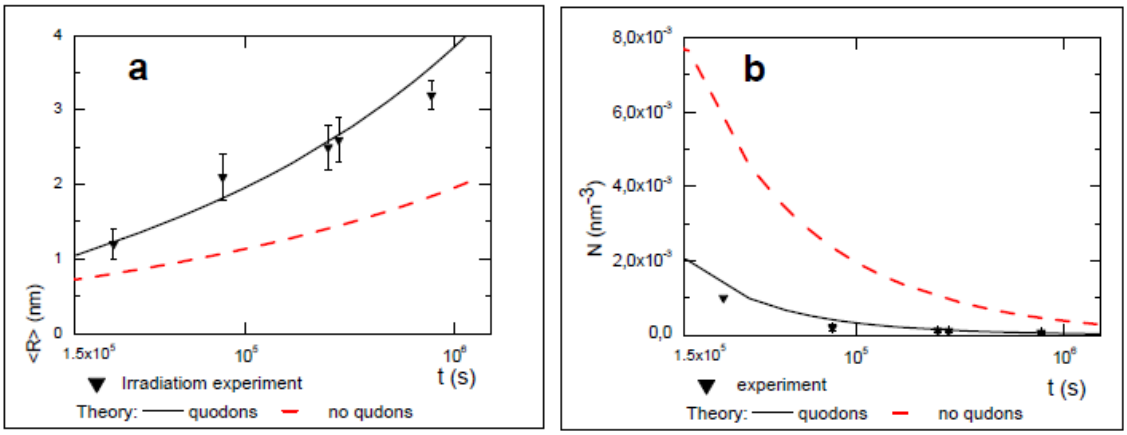

Figure 2. Time evolution of the Cu precipitate mean radius <R> and concentration N under irradiation vs. experimental data [13].

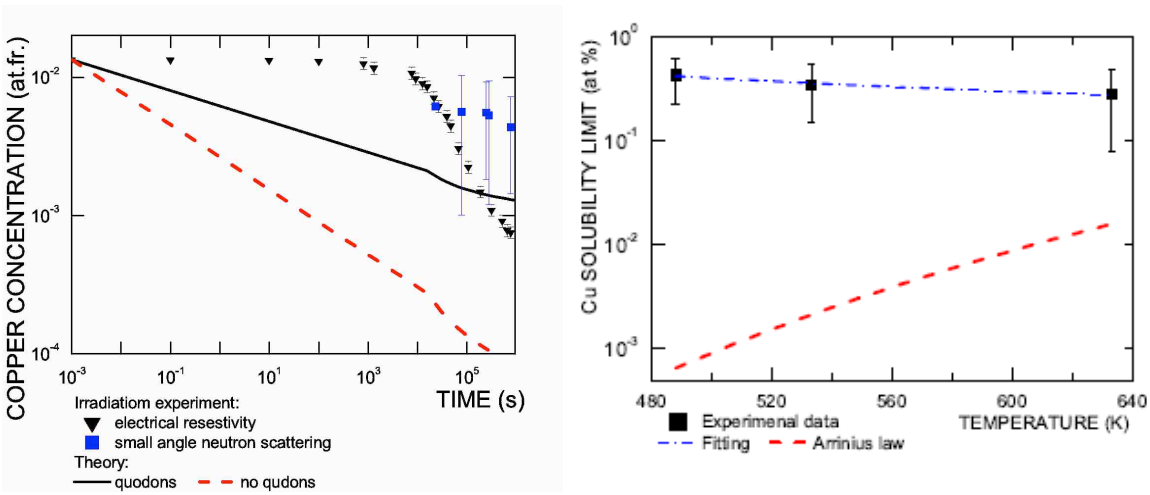

Figure 3. Time evolution of the concentration of copper atoms (left) and temperature dependence of the copper solubility limit under irradiation vs. Arrhenius law (right).

From a methodological side, the proposed concept of the radiation-induced "gas" of quodons offers a new insight on the radiation-induced processes in solids. It appears that *quodons are the transient form of the heat generation under irradiation* that subsequently transfers energy to phonons. The quodon gas may be a powerful driver of the chemical reaction rates under irradiation, the strength of which exponentially increases with irradiation flux and may be comparable with strength of the phonon gas that exponentially increases with temperature. Phonons obey the lows of equilibrium thermodynamics, such as the minimization of a system free energy, and the latter could not be defined for a crystal under irradiation in the classical framework. The proposed method of the free energy modification by taking into account non-equilibrium fluctuations of the potential landscapes for chemical reactions offers a new insight on the phase-field modeling (PFM) of radiation-induced processes in solids. Until now, PFM could not be applied to strongly non-equilibrium systems such as a crystal under irradiation, because it is based on minimization of a system free energy, which could not be defined for an irradiated crystal. Our method of the free energy modification by taking into account non-equilibrium fluctuations of potential energy landscapes for chemical reactions offers a way for development of a modified PFM, which will be able to describe the radiation-induced evolution of the microstructure.

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