Russian Research Center" Kurchatov Institute"

Charge State Effects of Radiation Damage on Microstructure Evolution in Dielectric Materials under Neutron and Charge Particle Irradiations

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Joint ICTP/IAEA Advanced Workshop on Development of Radiation Resistant Materials

20-24 April 2009, Trieste, Italy

Materials for Fission and Fusion Reactors

Graphite Materials :
Graphite, C-C composits

Metallic Materials:
Austenitic Steels, Ferritic – martensitic Steels, ODS materials, V-alloys

Ceramic Materials:
SiC – composits, Al_2O_3, MgO, ZrO_2

Difference between metals and dielectrics

Metals:

- Point defects are neutral
- Electric field does not exist in the matrix

Dielectrics (Ceramic Materials):

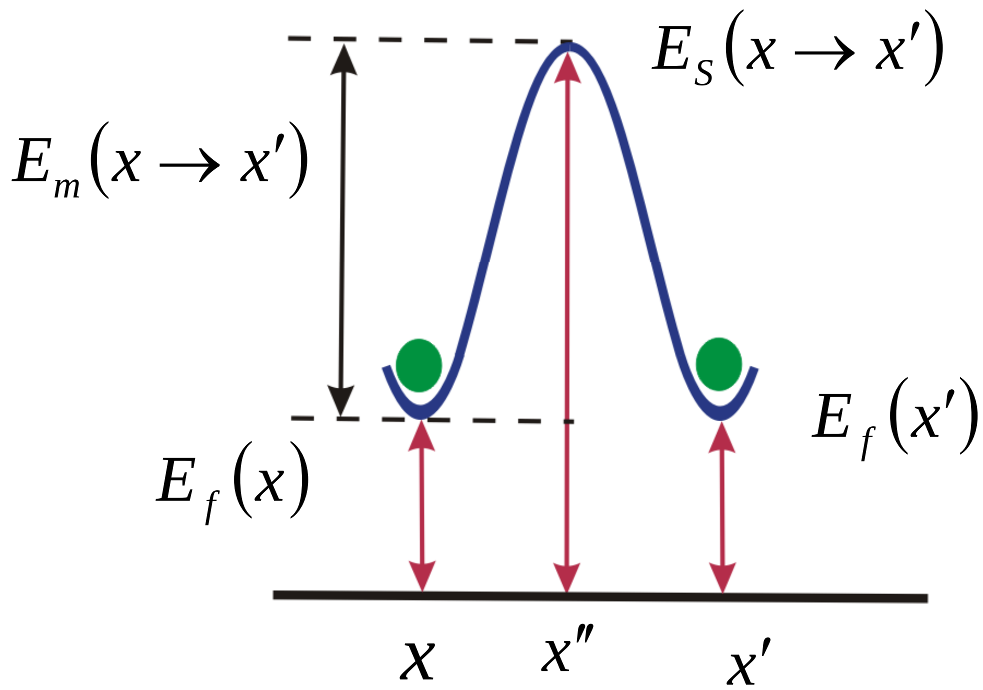
- Point defects can have effective charge
- Electric field exists in the matrix under the influence of an applied electric field
- Driving force due to an electric field can have a strong effect on diffusivity of charged point defects

Metals $(\mathbf{E}_0 = 0)$

Interstitial

Vacancy

$$q_I = q_V = 0$$



$$W_\alpha(x \to x') \sim e^{-\frac{E_S(x \to x') - E_f(x)}{kT}},$$

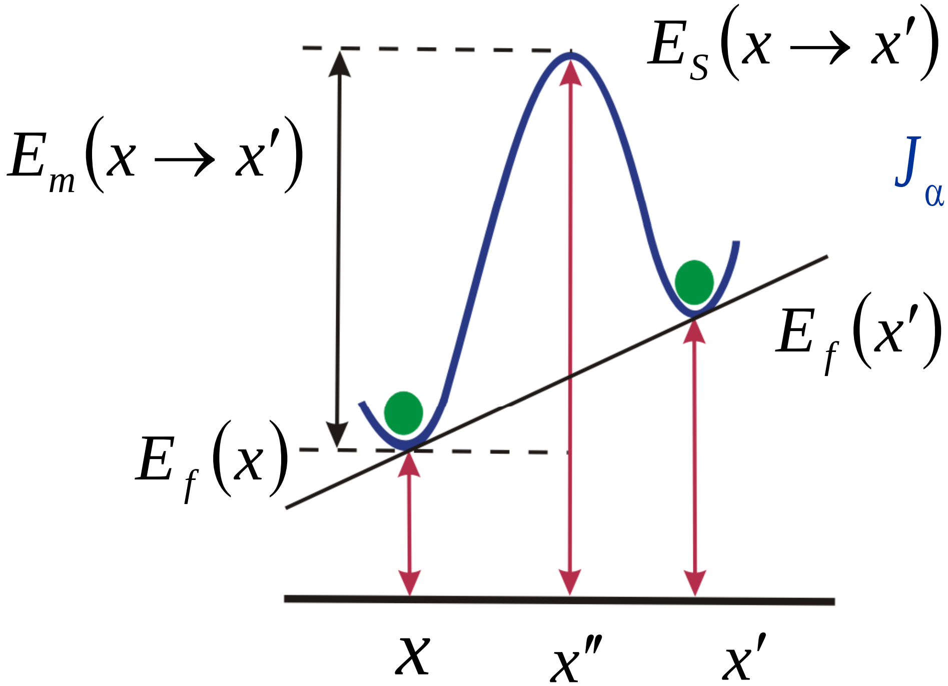
$$(\alpha = I, V)$$

$$J_\alpha(x) = C_\alpha(x) W_\alpha(x \to x') - C_\alpha(x') W_\alpha(x' \to x)$$

$$\mathbf{J}_\alpha = -D_\alpha \nabla C_\alpha, \quad (\alpha = I, V)$$

Dielectrics $(\mathbf{E}_0 \neq 0)$

Interstitial q_I Vacancy q_V



$$J_\alpha(x) = C_\alpha(x) W_\alpha(x \to x') - C_\alpha(x') W_\alpha(x' \to x)$$

$$W_\alpha(x \to x') \sim e^{-\frac{E_S(x \to x') - E_f(x)}{kT}},$$

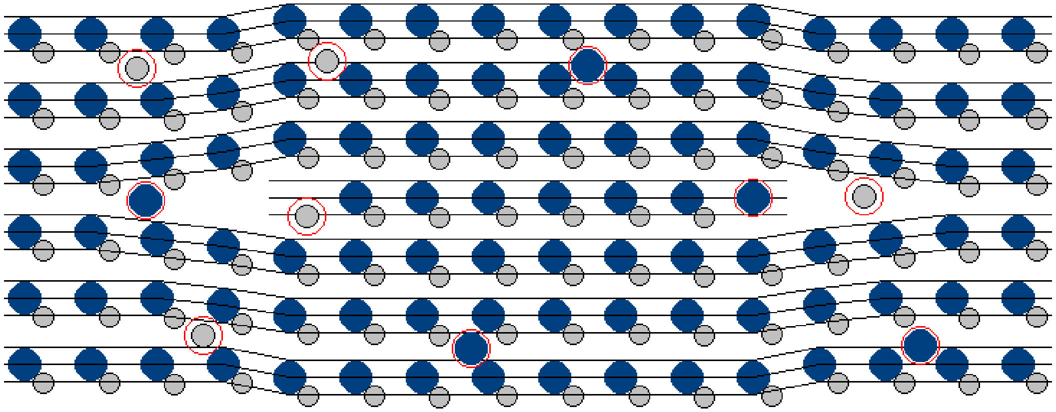
$$(\alpha = I, V)$$

$$E_{S\alpha}(x \to x') = E^0_{S\alpha} + q_\alpha \varphi(x) + q_\alpha (\mathbf{x}'' - \mathbf{x}) \nabla \varphi(x)$$

$$E_{f\alpha}(x) = E^0_{f\alpha} + q_\alpha \varphi(x)$$

$$\mathbf{J}_\alpha = -D_\alpha \nabla C_\alpha - \frac{q_\alpha}{kT} D_\alpha C_\alpha \nabla \varphi, \quad (\alpha = I, V)$$

Modeling of Dislocation Loops in Ceramics Materials (SiC)



System of Equations

$$D_m \Delta C_m + \frac{q\nu_m}{kT} D_m \nabla \left(C_m \nabla \varphi \right) = 0$$

$$\Delta \varphi = -\frac{4\pi}{\varepsilon\omega} \left(\sum_m q\nu_m C_m + \rho \right)$$

Boundary Conditions

$$C_m \big|_S = 0 \qquad C_m \left(r \to \infty \right) = C_{m0}$$

$$\varphi \left(r \to \infty \right) = 0 \qquad \sum_m \left(q\nu_m \mathbf{j}_m , \mathbf{n} \right) \Big|_S = 0$$

Physical model for radiation swelling

The radiation swelling (S_{tot}) in ceramic material is determined by the following relation

$$S_{tot} = \sum_{K}^{2} C_{IK} e_{IK} + \sum_{K}^{2} (C_{VK} - C_{VK}^{O}) e_{VK} + \omega \sum_{S,K} (n_{IK}^{S} e_{IK} + n_{VK}^{S} e_{VK}) \qquad (1)$$

Here $C_{\alpha 1}$ and $C_{\alpha 2}$ are concentrations of point defects for components: k=1= Si and k=2=C in two component (SiC) material;

C_{VK}^{O} is the thermal vacancy concentration of components (k=1 and k=2);

$n_{\alpha s}$ is the total number of point defects of the type α absorbed by sinks of the type s (dislocations, dislocation loops) in a unit volume;

$e_{\alpha K}$ is the dilatation of point defect type α (α = I for interstitial and α = V for vacancy) for k-th component

ω is the atomic volume. The summation is over all different sink types (dislocations, dislocation loops).

$$\frac{dC_{VK}}{dt} = G_{VK} - j_{VK}(\rho_D + \rho_L) - \alpha D_{IK} C_{IK} C_{VK}, \quad (k=1,2) \qquad (2)$$

$$\frac{dC_{IK}}{dt} = G_{IK} - j_{IK}(\rho_D + \rho_L) - \alpha D_{IK} C_{IK} C_{VK} = 0 , \quad (k=1,2) \qquad (3)$$

Here

ρ_D is the network dislocation density,

ρ_L is the dislocation density of dislocation loops ($\rho_L = 2\pi R_L N_L$);

G_{VK}, G_{IK} are the generation rates of vacancies and interstitials k-th components ($G_{V1} = G_{I1} = G_{Si}, G_{V2} = G_{I2} = G_C$),

α is the point defect recombination coefficient ($\alpha = 4/a^2$, a is the lattice spacing).

The total current of charged point defects of k-th component on the dislocation line taking into account stoichiometry and equality of the normal components of anionic and cationic interstitial and vacancy currents on dislocation core can be written in the following form

$$J_{IK} = 2\pi r_0 j_{IK}^{n} = \frac{2\pi r_0}{\ln(\frac{8R}{r_0})} \frac{D_{I1} C_{I1} D_{I2} C_{I2}}{D_{I1} C_{I1} + D_{I2} C_{I2}} \qquad (4)$$

The growth rate of dislocation loop in ceramic materials taking into account the absorption of two types of charged interstitial atoms and vacancies and remaining of stoichiometric of two components in dislocation loop is given by the following relation

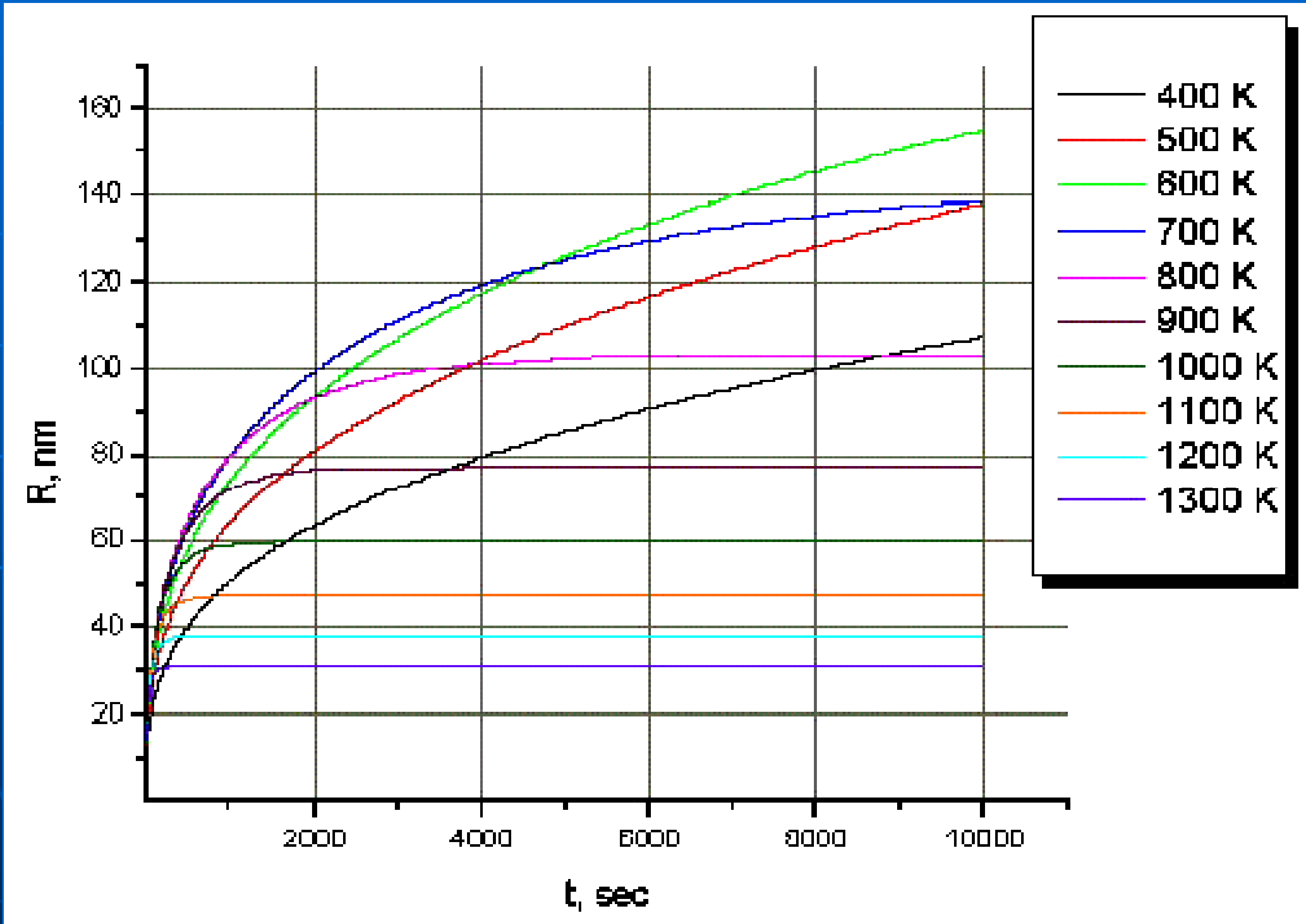
Main parameter values used for numerical calculations of radiation swelling in SiC

$G_1 = G_{Si}$	Point defect generation rate of Si atoms	3.10^{-3} dpa/s
$G_2 = G_C$	Point defect generation rate of C atoms	1.10^{-3} dpa/s
E_{mV}^{Si}	Silicon vacancy migration energy	2.3 eV
E_{mV}^{C}	Carbon vacancy migration energy	2.0 eV
E_{mI}^{Si}	Silicon interstitial migration energy	0.4 eV
E_{mI}^{C}	Carbon interstitial migration energy	0.3 eV
E_{FV}^{Si}	Silicon vacancy formation energy	2.5 eV
E_{FV}^{C}	Carbon vacancy formation energy	2.4 eV
ρ_D	Network dislocation density	10^{10} cm^{-2}
$e_{V1} = e_{V2}$	Vacancy dilatation	-0.1
a	Lattice parameter	5.14×10^{-8} cm

$D_{VK} = D_{VK}^{O} \exp(-E_{mV}^{K} / T)$,(where $D_{V1}^{O} = D_{V2}^{C} = 10^{-2} cm^{-2}$),

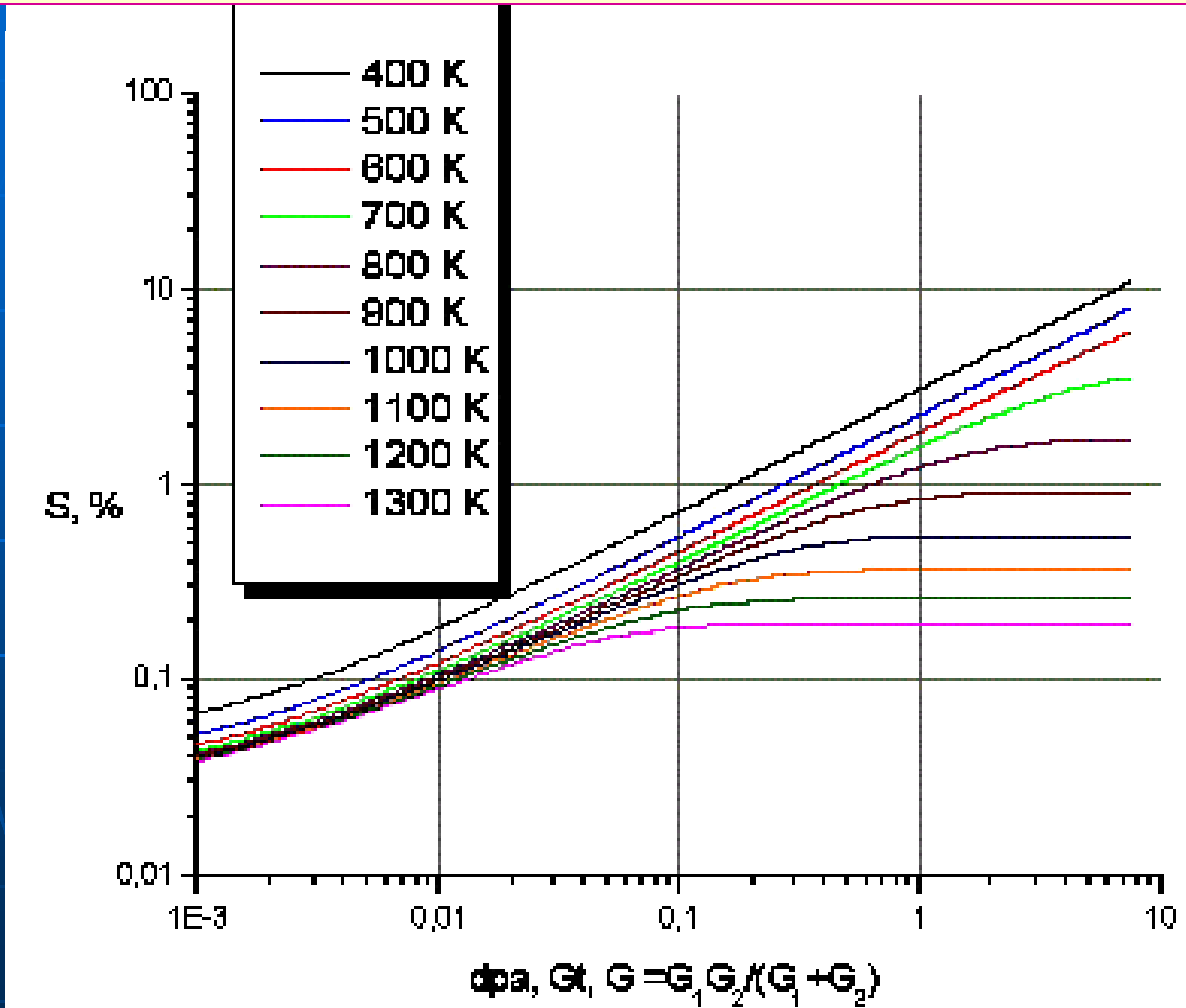
$N_L = N_L^{O} [\exp(E_{m1}^{1} / T) + \exp(E_{mI}^{2} / T)]^{1/2}$, (where $N_L^{O} = 3.10^{'2} cm^{-3}$).

The time dependence of dislocation loop growth at different irradiation temperatures in SiC



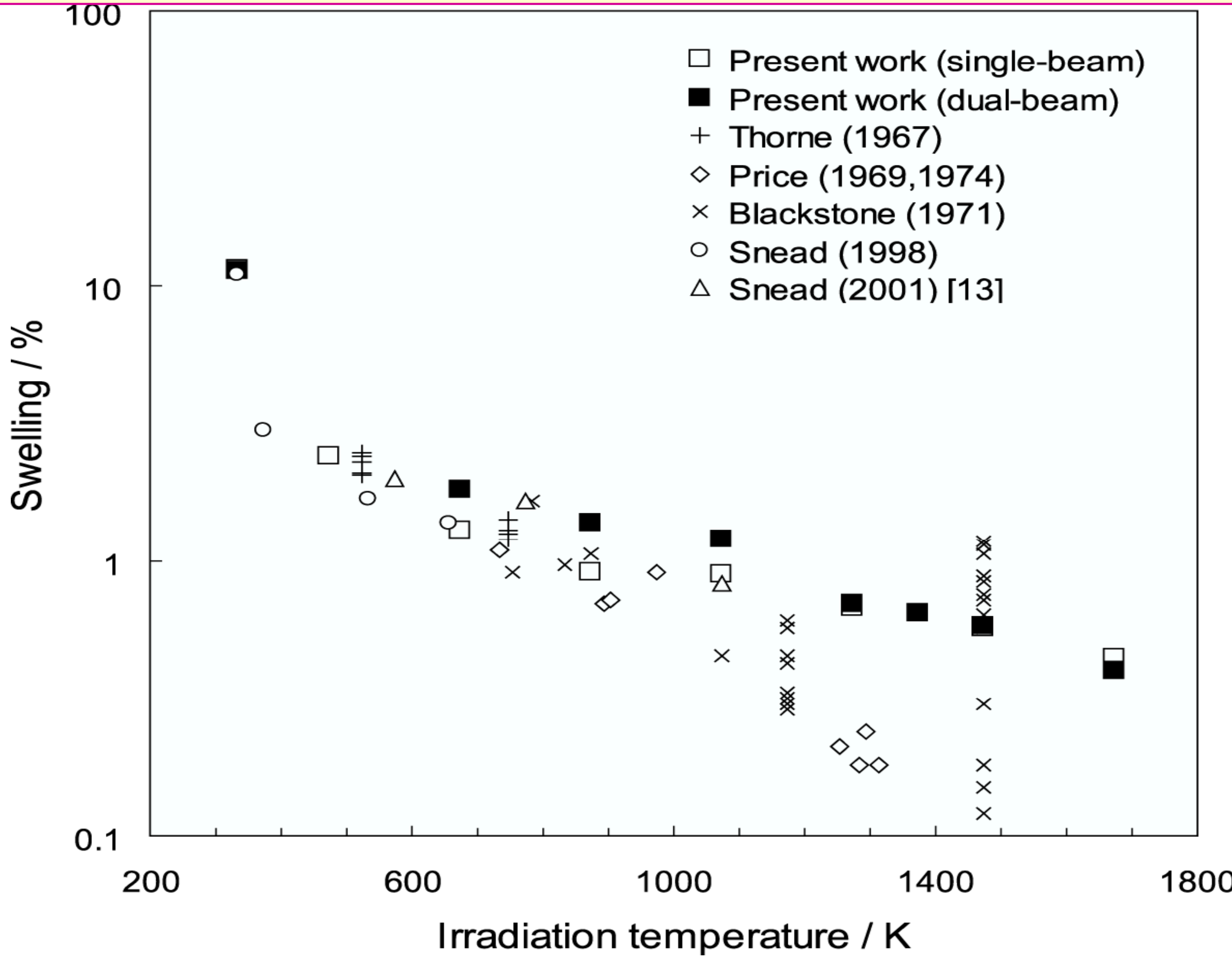
A.Ryazanov, A.Kohyama, 2002

Dose dependence of radiation swelling in SiC at different irradiation temperatures

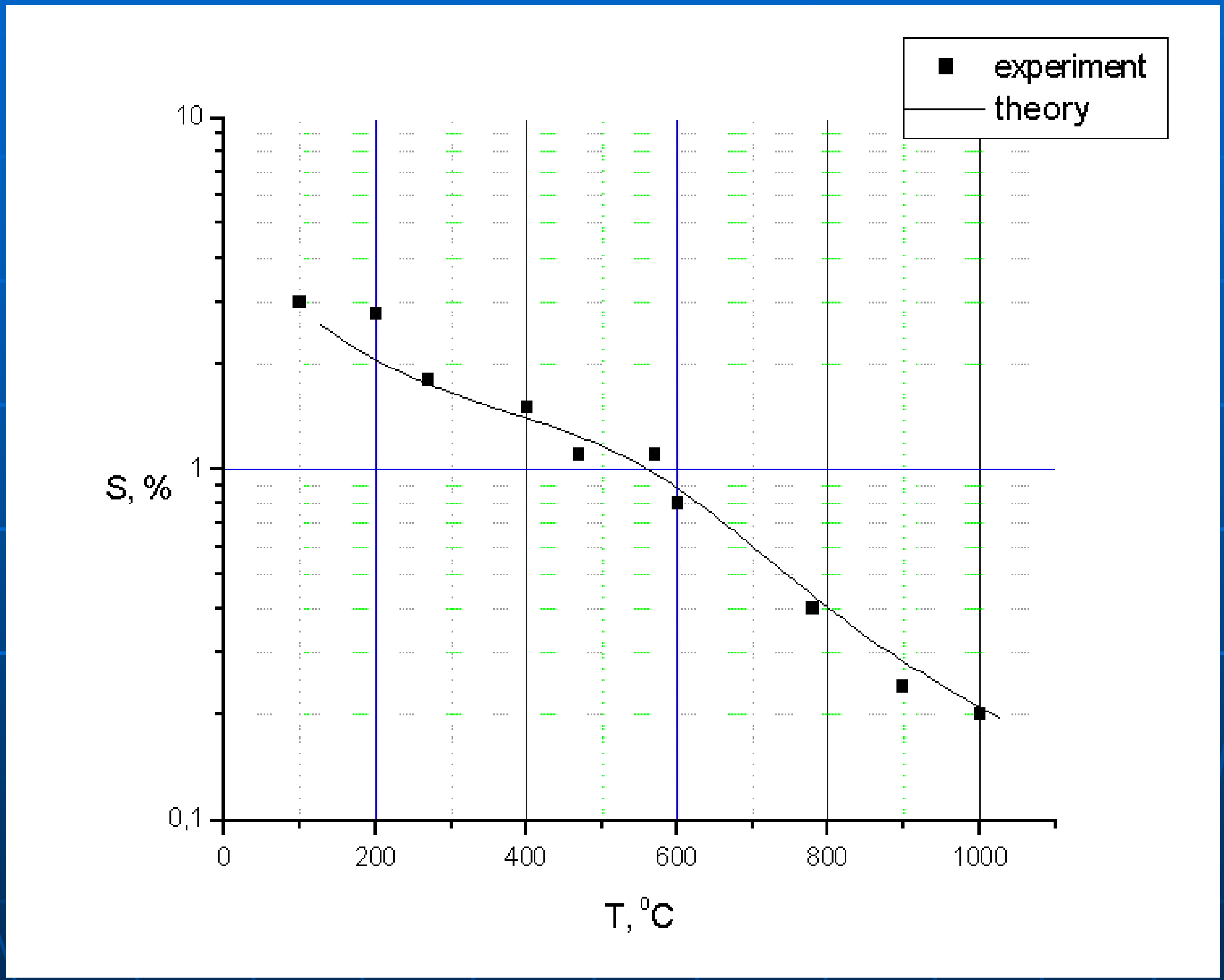


A.Ryazanov, A.Kohyama, 2002

Temperature dependence of swelling of SiC



The comparison of experimental and theoretical temperature dependencies of radiation swelling in SiC.



A.I.Ryazanov, A.V.Klaptsov, A.Kohyama (JNM,2002)

BACKGROUND

Oxide Ceramic Materials $(e.g. \alpha - Al_2O_3)$
in Fusion Reactors:

- *Insulating Materials*
- *RF Window Materials*

International Thermonuclear Experimental Reactor (ITER) Environment:

- *Electric Field: 0.1 –100 (kV/m)*
- *Temperature: 50 –700 (K)*
- *Damage Rate: 10^{-10}- 10^{-7} (dpa/s)*

DETERMINATION OF EFFECTIVE CHARGE STATES FOR POINT RADIATION DEFECTS IN FUSION CERAMIC MATERIALS

A.I. Ryazanov, A.V. Klaptsov, C. Kinoshita, K. Yasuda, 2004

Main Aim:

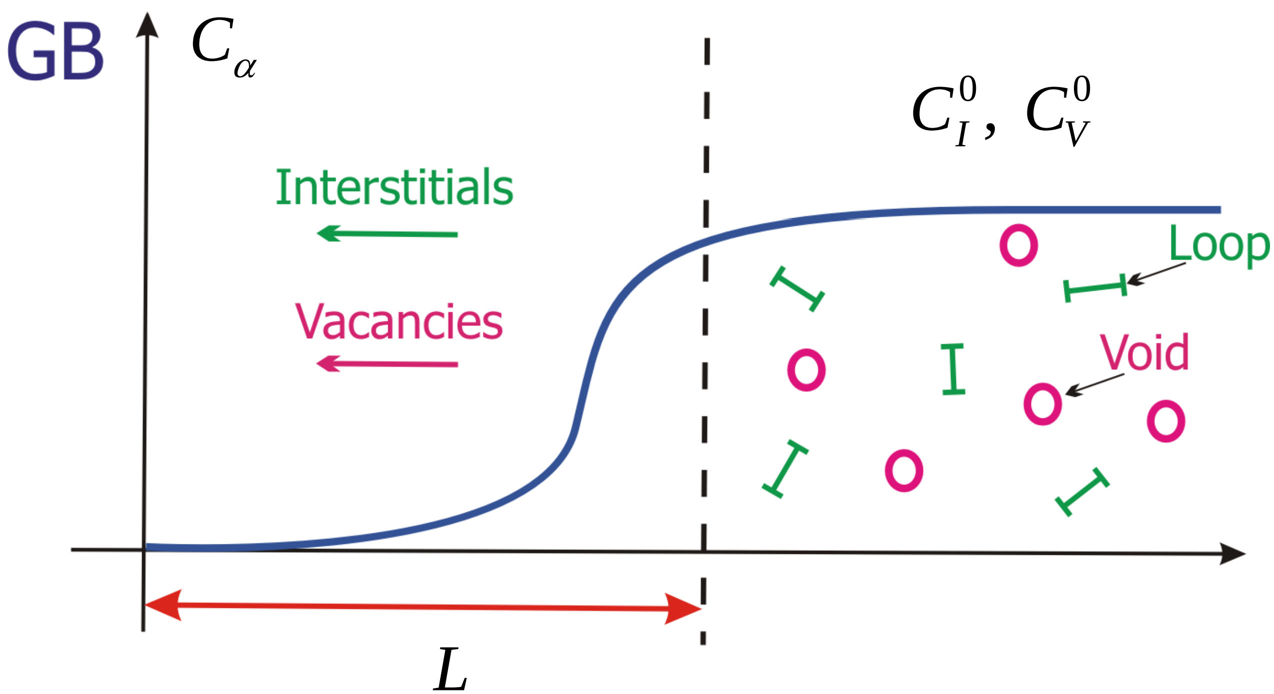
To suggest experimental method for measurements of an effective charge for point radiation defects in fusion ceramic materials

Content:

- Introduction
- Physical Model
- Main Equations
- Results
- Observations
- Conclusion

Physical Model of denuded zone formation in irradiated materials

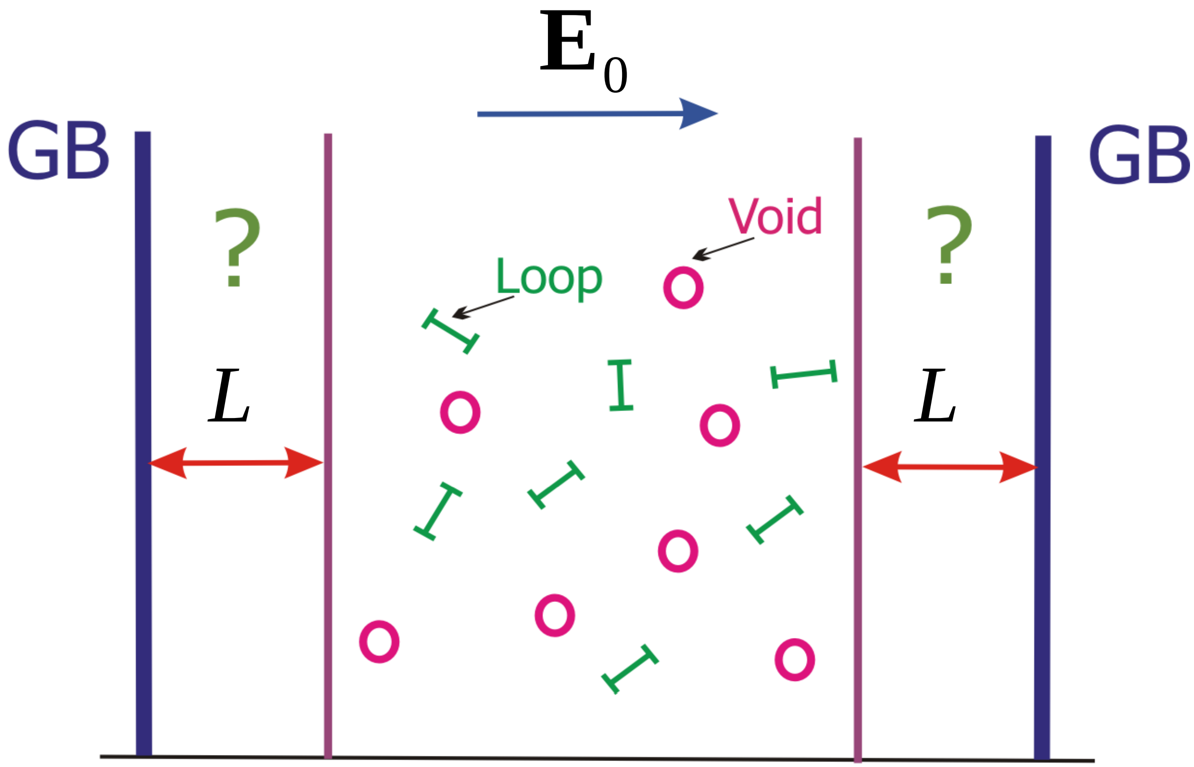
Denuded zone $\left(E_0 = 0\right)$



L **is the size of denuded zone**

Effect of an Applied Electrical Field ($E_0 \neq 0$)

A.I. Ryazanov, A.V. Klaptsov*, K.Yasuda**,
C. Kinoshita**, JNM, 2004



$$L = L(q, E_0) = ?$$

Main Equations:

Diffusion equations for point defects

$$G - \alpha C_I C_V - \frac{dj_I}{dz} = 0, \quad G - \alpha C_I C_V - \frac{dj_V}{dz} = 0, \qquad \textbf{(1)}$$

G **is the generation rate of point defects under irradiation**,

α **is the recombination coefficient,** $\alpha = \mu(D_I + D_V)$

D_I, D_V **are diffusion coefficients of intestinal atoms and vacancies**

Diffusion currents of point defects

$$j_I = -D_I \frac{dC_I}{dz} + \frac{qD_I C_I}{kT}\frac{d\varphi}{dz}, \quad j_V = -D_V \frac{dC_V}{dz} - \frac{qD_V C_V}{kT}\frac{d\varphi}{dz} \qquad \textbf{(2)}$$

φ **is the potential of internal electric field ,** $E = -\nabla\varphi$

kT **is the temperature**

Poisson equation

$$\Delta\varphi = -\frac{4\pi}{\varepsilon\omega}\left(qC_V - qC_I + eC_h - eC_e\right) \qquad \textbf{(3)}$$

Total electric current

$$J = -q\left(j_I - j_V\right) = q\left(D_I\frac{dC_I}{dz} - D_V\frac{dC_V}{dz}\right) + \frac{q^2}{kT}\left(D_I C_I + D_V C_V\right)E = J_0 \qquad \textbf{(4)}$$

Boundary conditions:

$$C_I\left(z=0\right)=0,\quad C_I\left(z\to\infty\right)=C_I^0,\quad C_V\left(z=0\right)=0,\quad C_V\left(z\to\infty\right)=C_V^0 \qquad \textbf{(5)}$$

$$J_0 = \left.\left(q\left(D_I\frac{dC_I}{dz} - D_V\frac{dC_V}{dz}\right) + \frac{q^2}{kT}\left(D_I C_I + D_V C_V\right)E\right)\right|_{z=0} = \sigma\omega E_0$$

Assumption:

$$C_I \approx C_I^0 + C_I^1 \left(|C_I^1| << C_I^0 \right), \quad C_V \approx C_V^0 + C_V^1 \left(|C_V^1| << C_V^0 \right) \qquad \textbf{(6)}$$

Equations (1)-(3) have the following form

$$\frac{d^2C_I^1}{dz^2} + \frac{qE_0}{\varepsilon kT}\frac{dC_I^1}{dz} - \left[\frac{\alpha C_V^0}{D_I} + \frac{4\pi q^2 C_I^0}{\varepsilon \omega kT} \right] C_I^1 - \left[\frac{\alpha C_I^0}{D_I} - \frac{4\pi q^2 C_V^0}{\varepsilon \omega kT} \right] C_V^1 = 0,$$

$$\frac{d^2C_V^1}{dz^2} - \frac{qE_0}{\varepsilon kT}\frac{dC_V^1}{dz} - \left[\frac{\alpha C_I^0}{D_V} + \frac{4\pi q^2 C_V^0}{\varepsilon \omega kT} \right] C_V^1 - \left[\frac{\alpha C_V^0}{D_V} - \frac{4\pi q^2 C_I^0}{\varepsilon \omega kT} \right] C_I^1 = 0 \qquad \textbf{(7)}$$

Solutions of equations (7) have the following form

$$C_I^1, C_V^1 \sim \exp(-\lambda_{\min} z) \qquad \textbf{(8)}$$

$\lambda_{\min}$ **is the minimum positive roots of the equation:**

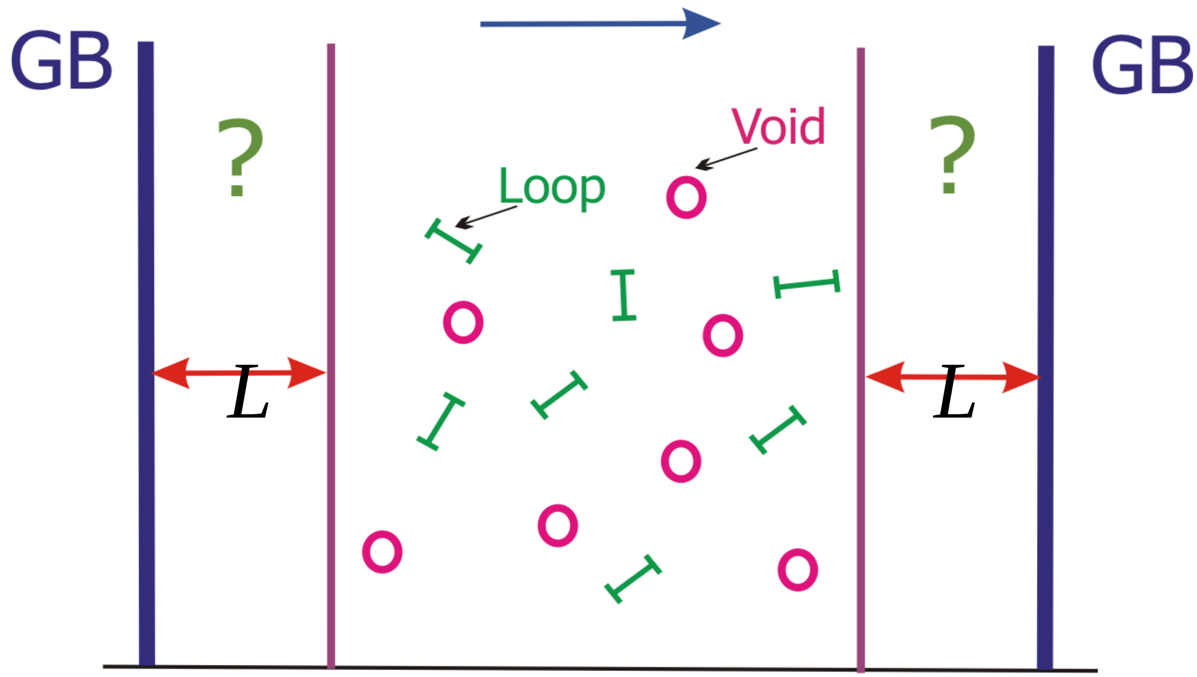
$$\left(\lambda^2-\frac{qE_0}{\varepsilon kT}\lambda-\frac{\alpha C_V^0}{D_I}-\frac{4\pi q^2 C_I^0}{\varepsilon\omega kT}\right)\left(\lambda^2+\frac{qE_0}{\varepsilon kT}\lambda-\frac{\alpha C_I^0}{D_V}-\frac{4\pi q^2 C_V^0}{\varepsilon\omega kT}\right)=$$

$$=\left(\frac{\alpha C_I^0}{D_I}-\frac{4\pi q^2 C_V^0}{\varepsilon\omega kT}\right)\left(\frac{\alpha C_V^0}{D_V}-\frac{4\pi q^2 C_I^0}{\varepsilon\omega kT}\right). \qquad \textbf{(9)}$$

Size *(L)* of denuded zone is equal

$$L=1/\lambda_{\min} \qquad \textbf{(10)}$$

1.Absence of an external electric field ($E_0 = 0$)



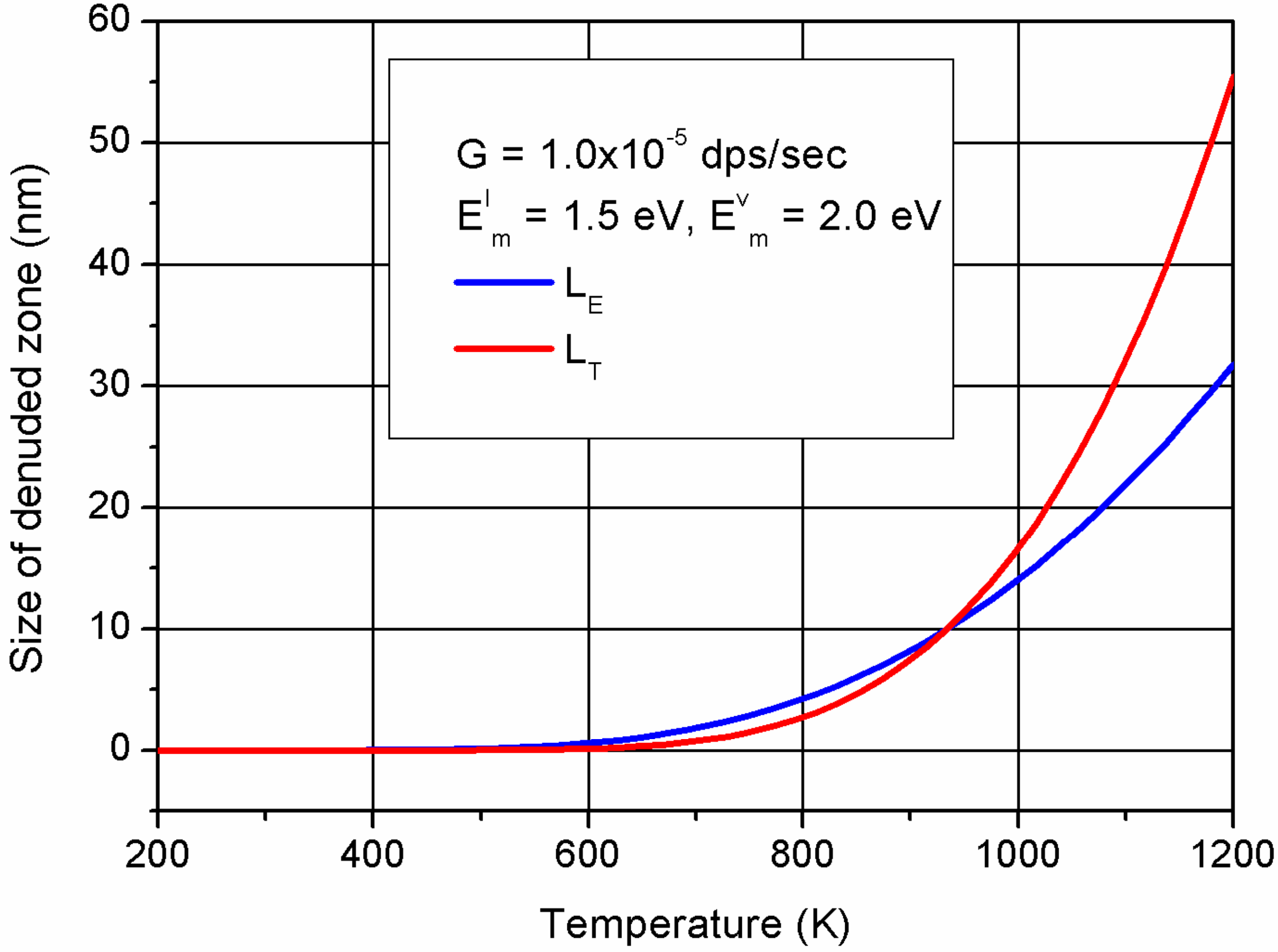
Denuded zone size in ceramics:

$$L_E \approx \sqrt{\frac{\varepsilon\omega kT}{8\pi q^2}}\left(\frac{\mu D_I}{G}\right)^{1/4}, L_T \approx \left(\frac{D_V^2}{\mu D_I G}\right)^{1/4}$$

Denuded zone size in metals:

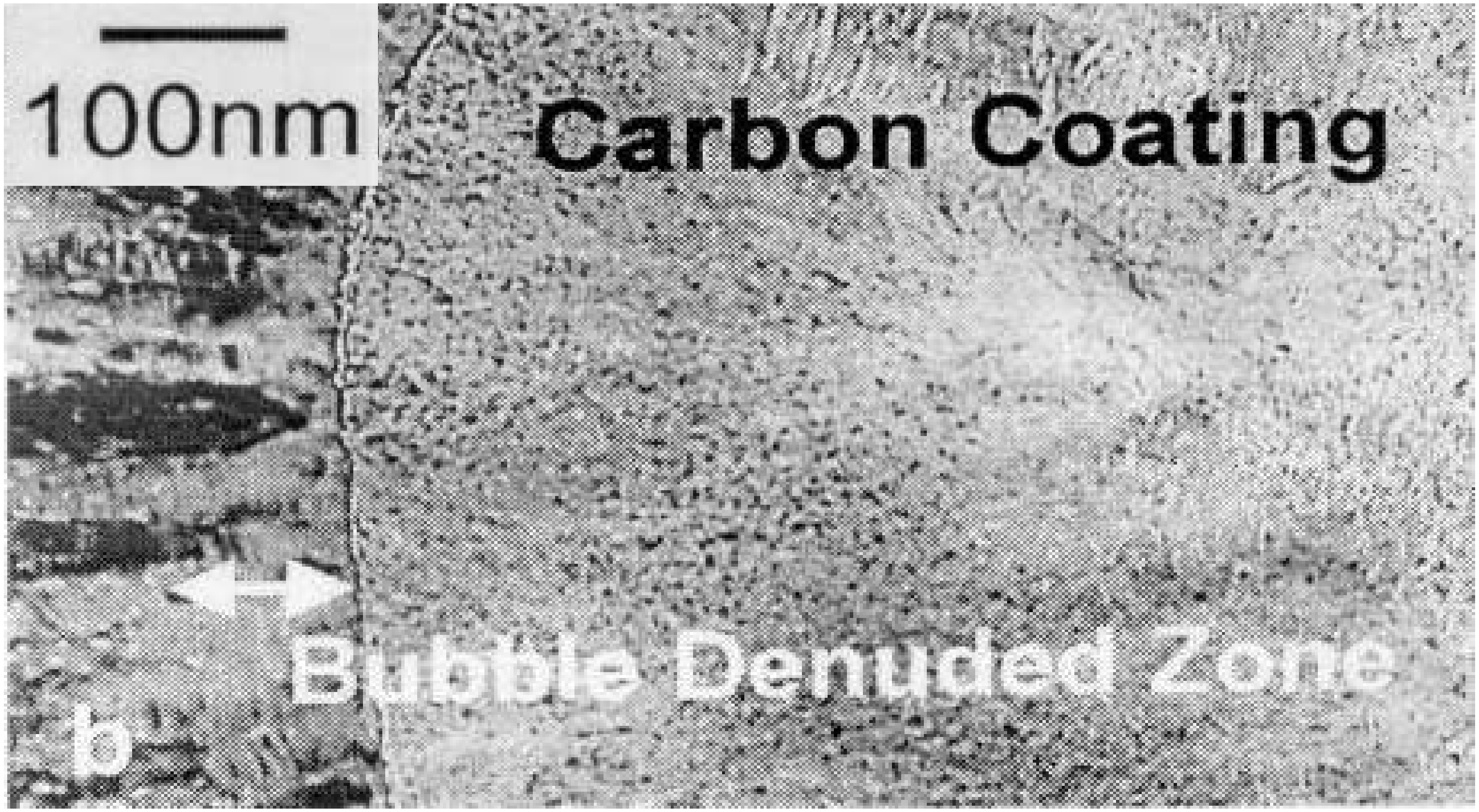
$$L_T \approx \left(\frac{D_V}{\mu G}\right)^{1/4}$$

Temperature dependence of denuded zone size



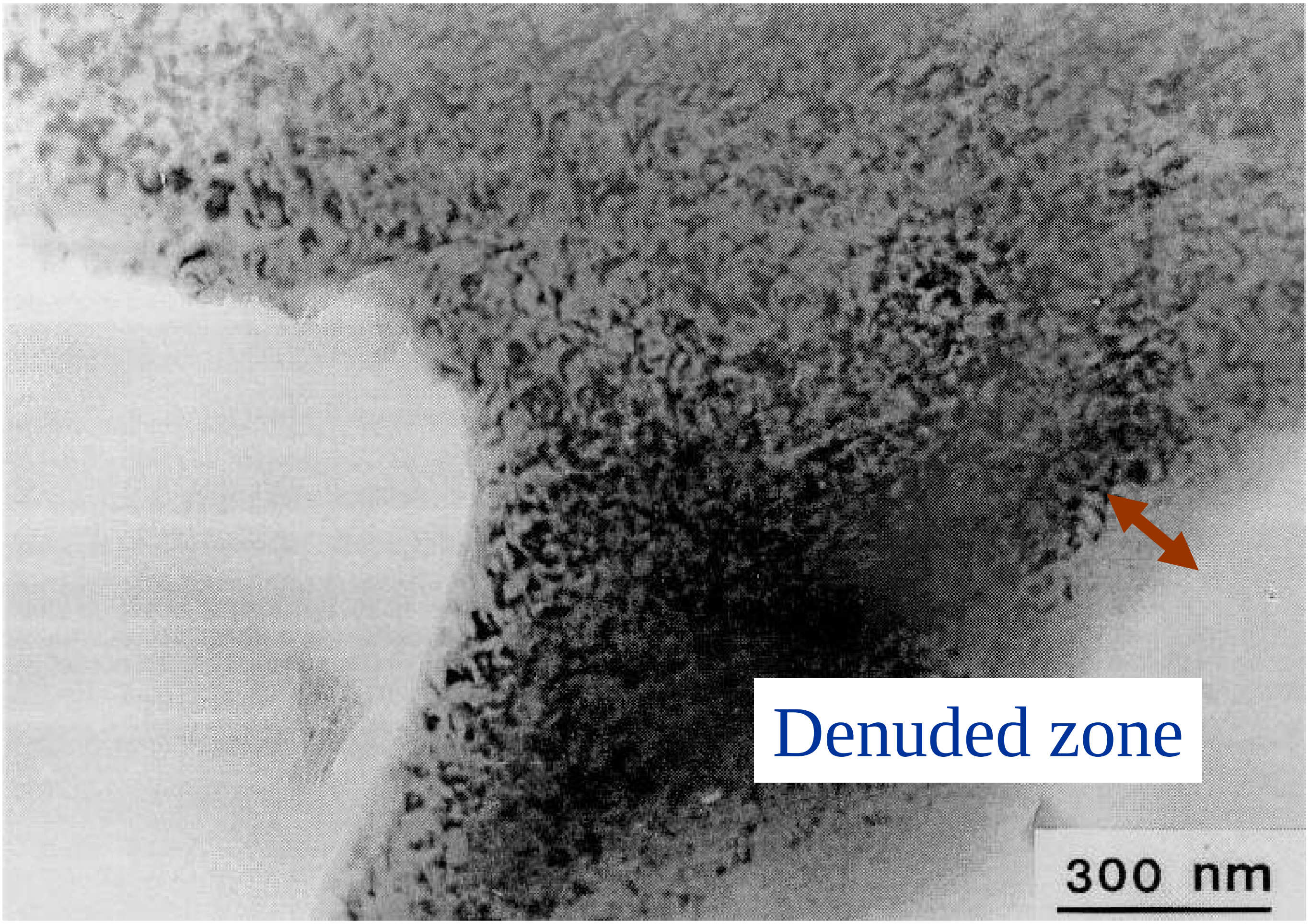
TEM micrograph of SiCf/SiC composites after implantation with 3 MeV helium and annealing at T = 1673 K for 1 h

(A.Hasegawa et. al. 1999)



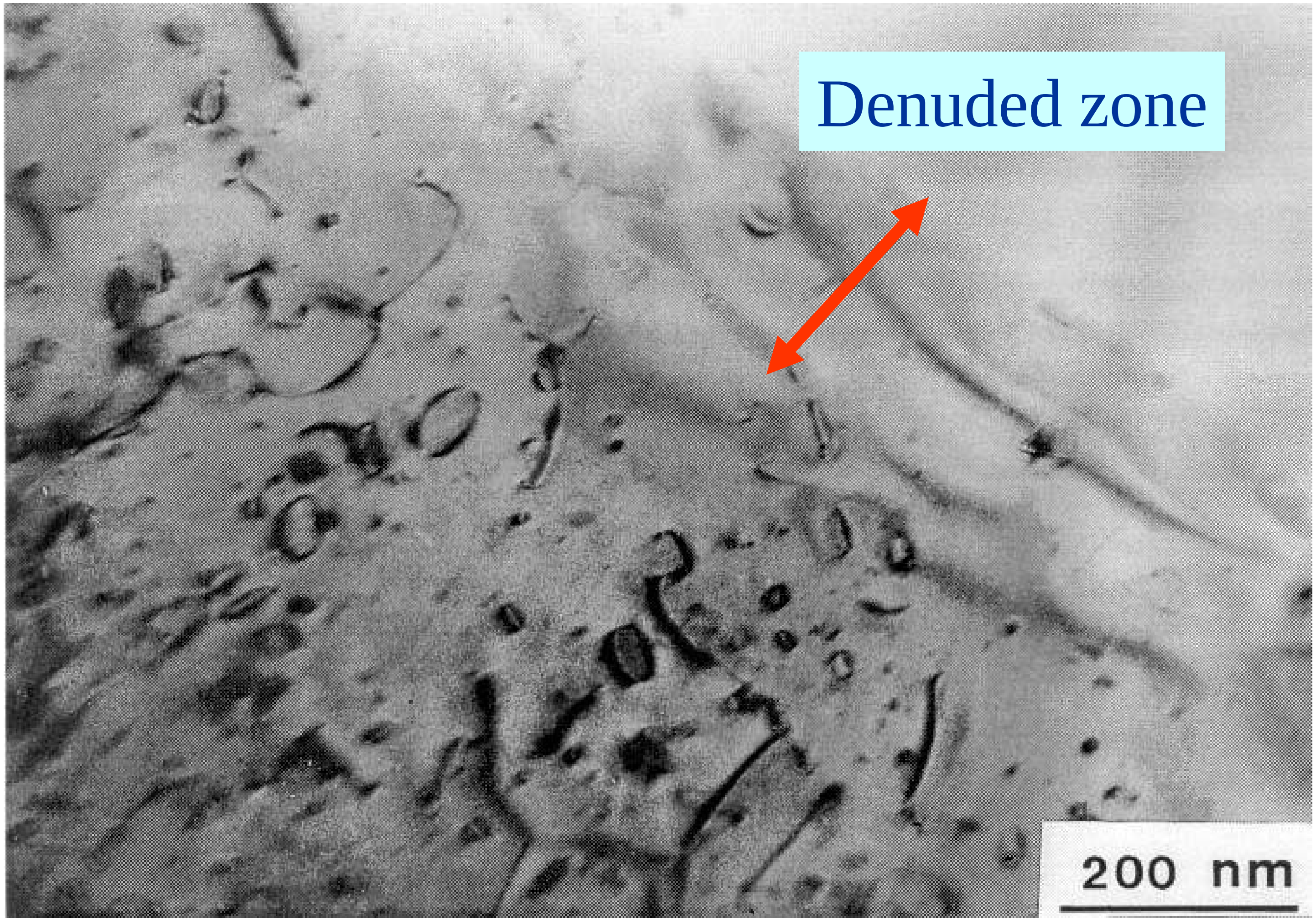
TEM image of neutron (HFR) irradiated Al_2O_3 (4.6×10^{25} m^{-2})

(R.J.M.Konings et. al. 1998)



TEM image of neutron (HFR) irradiated CeO_2 ($4.6x10^{25}$ m^{-2})

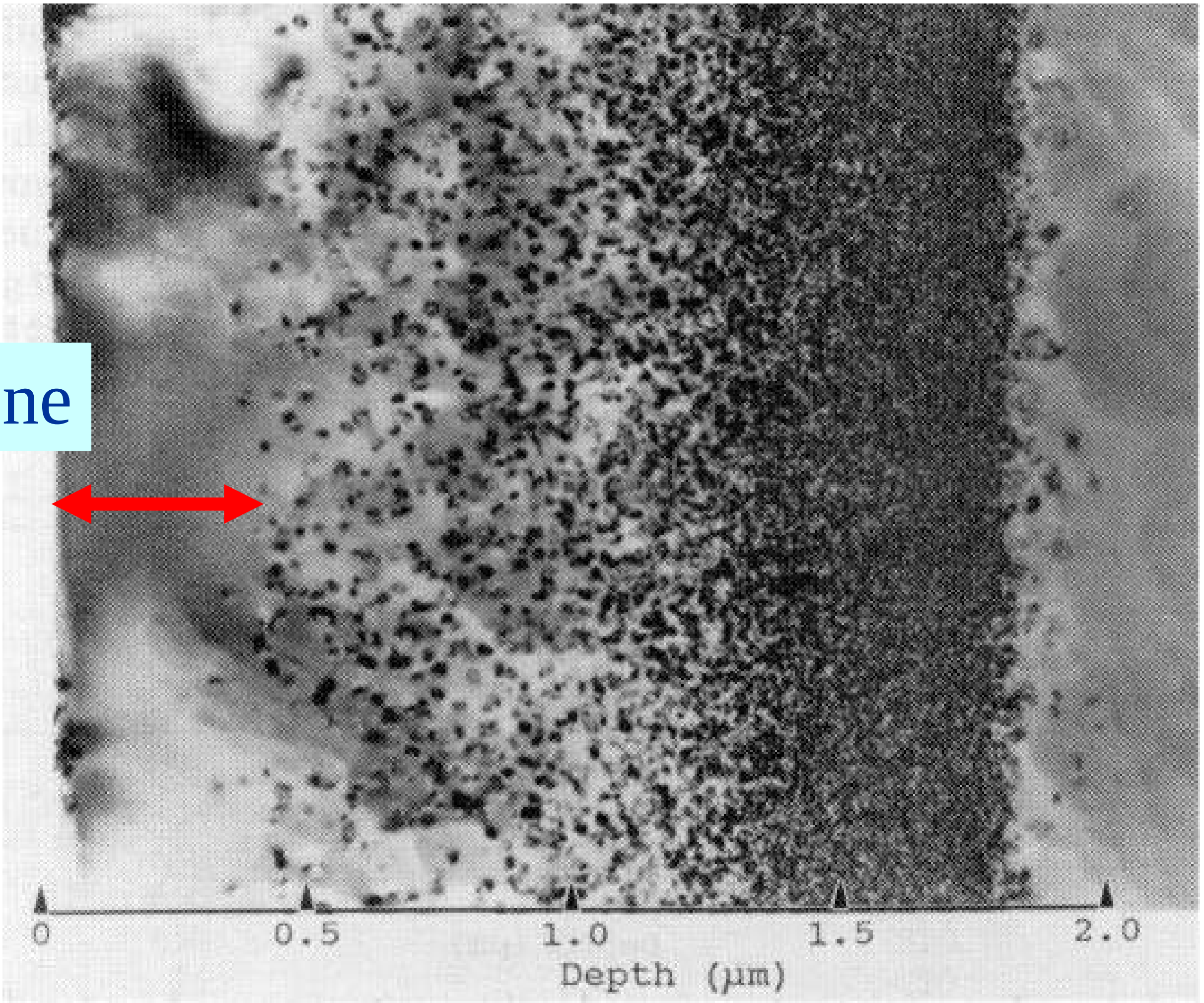
(R.J.M.Konings et. al. 1998)



Depth-dependent microstructure of $MgAl_2O_4$ (spinel) irradiated by 2 MeV Al^+ at 650 C to a peak damage 14 dpa

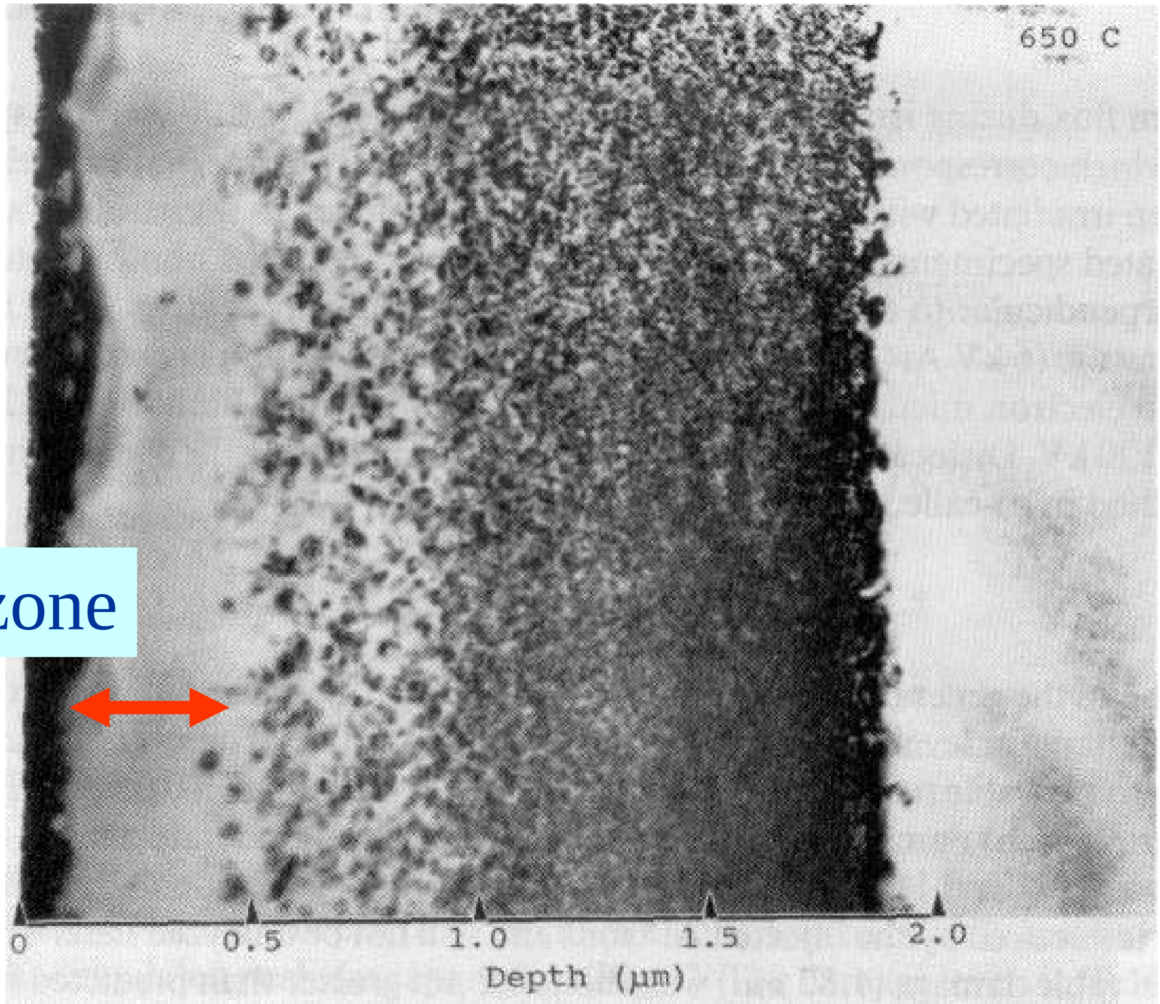
(S.J.Zinkle 1992)

Denuded zone



Depth-dependent microstructure of $MgAl_2O_4$ irradiated by 2 MeV Al^+ at 650 C to a peak damage 100 dpa

(S.J.Zinkle 1992)



Denuded zone

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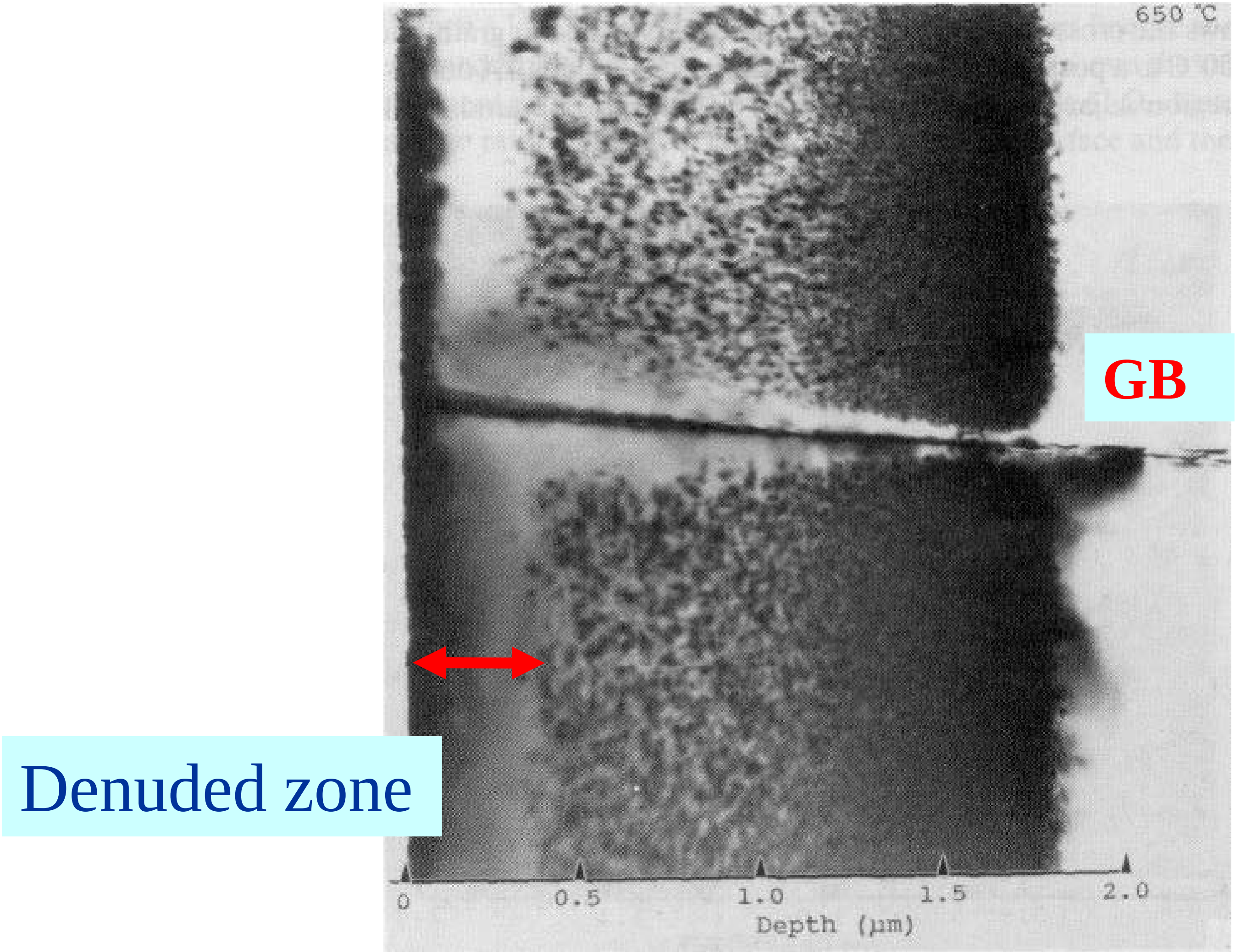
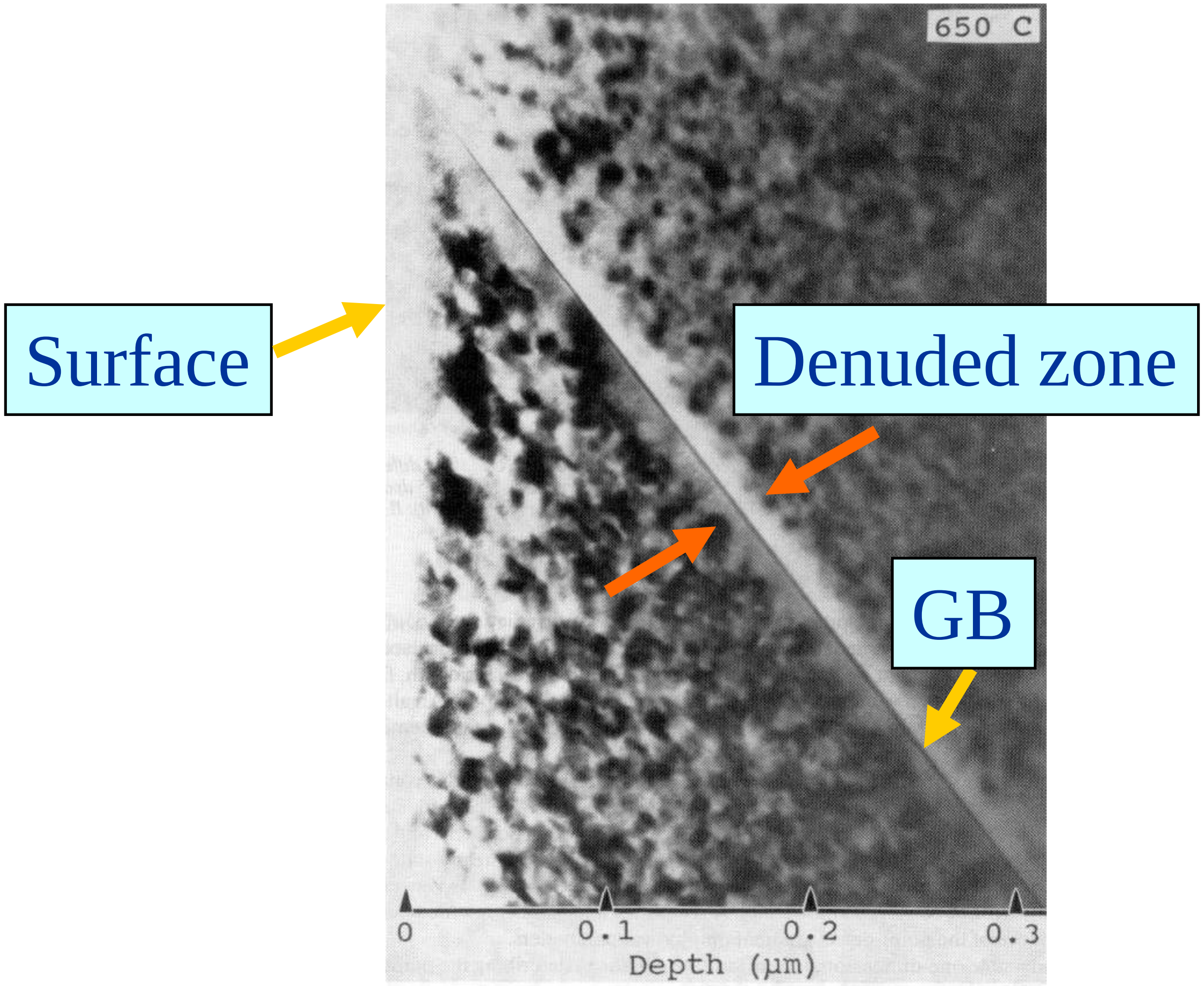
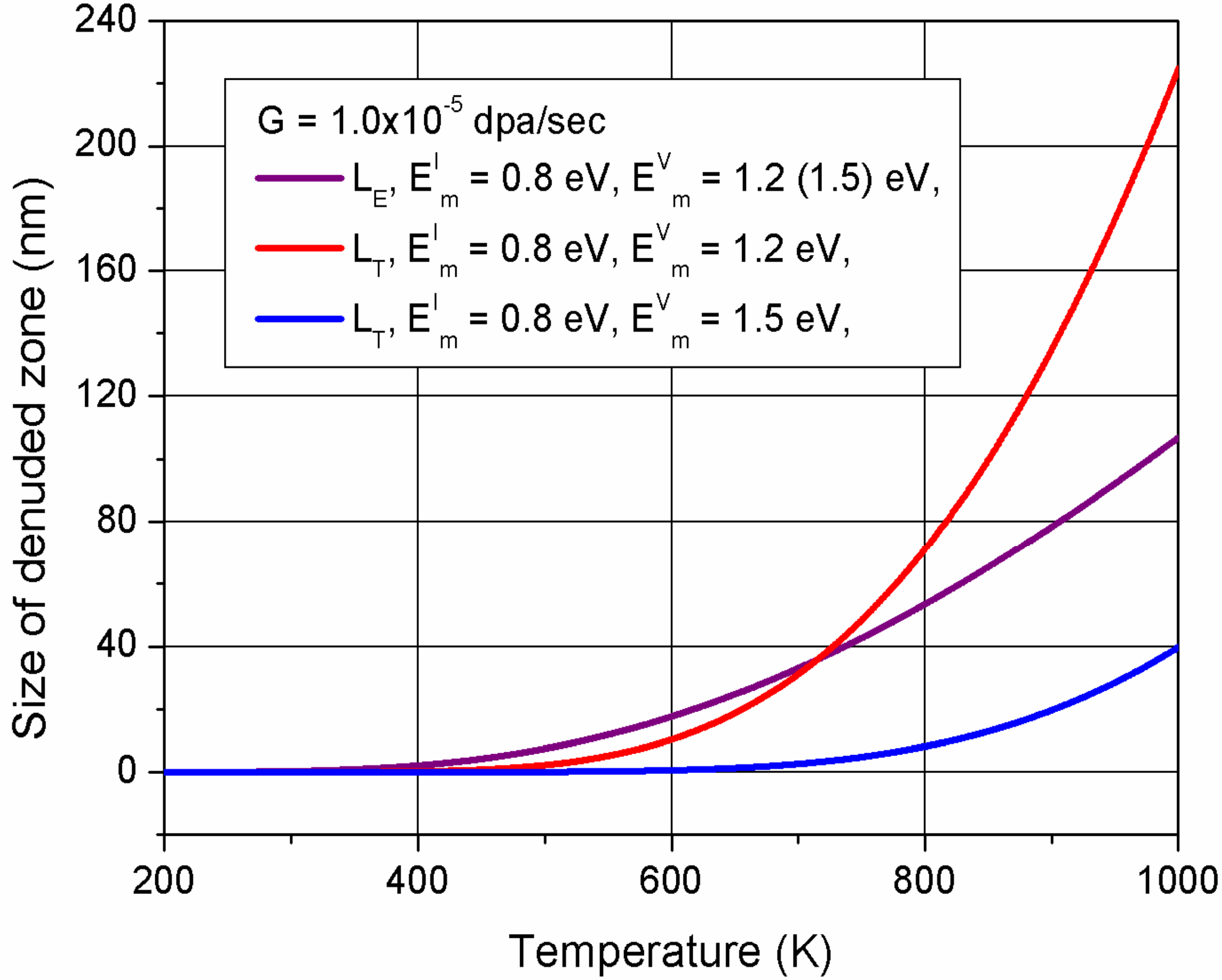
Defect free zones near surface and grain boundaries in $MgAl_2O_4$ (spinel) irradiated by 2 MeV Al^+ at 650 C to a peak damage 14 dpa (S.J.Zinkle 1992)



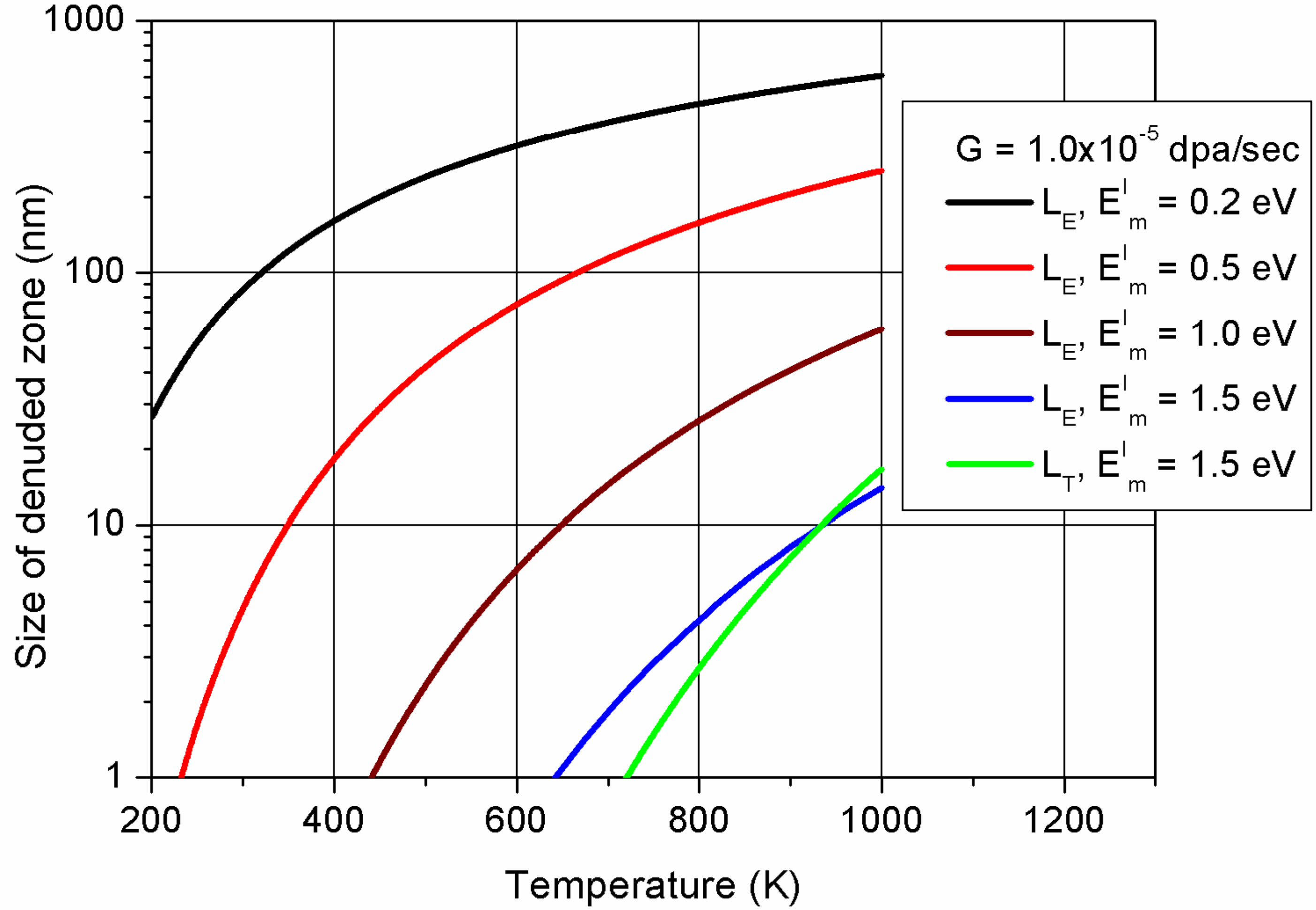
Microstructure of Al_2O_3 in the vicinity of surface and grain boundary irradiated by 2 MeV Al^+ at 650 C to a peak damage 1 dpa (S.J.Zinkle 1992)



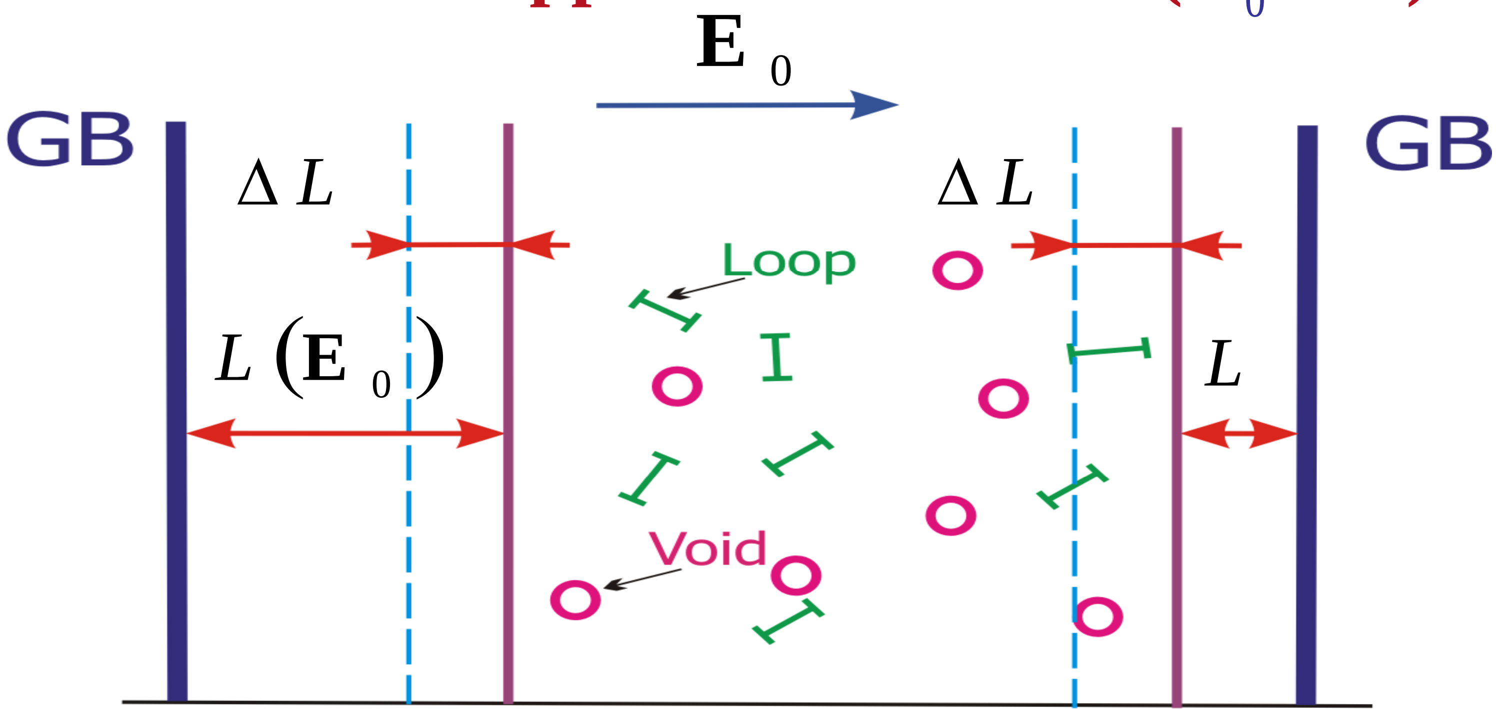
Temperature dependence of denuded zone size



Temperature dependence of denuded zone size



2.Effect of an applied electric field ($E_0 \neq 0$)

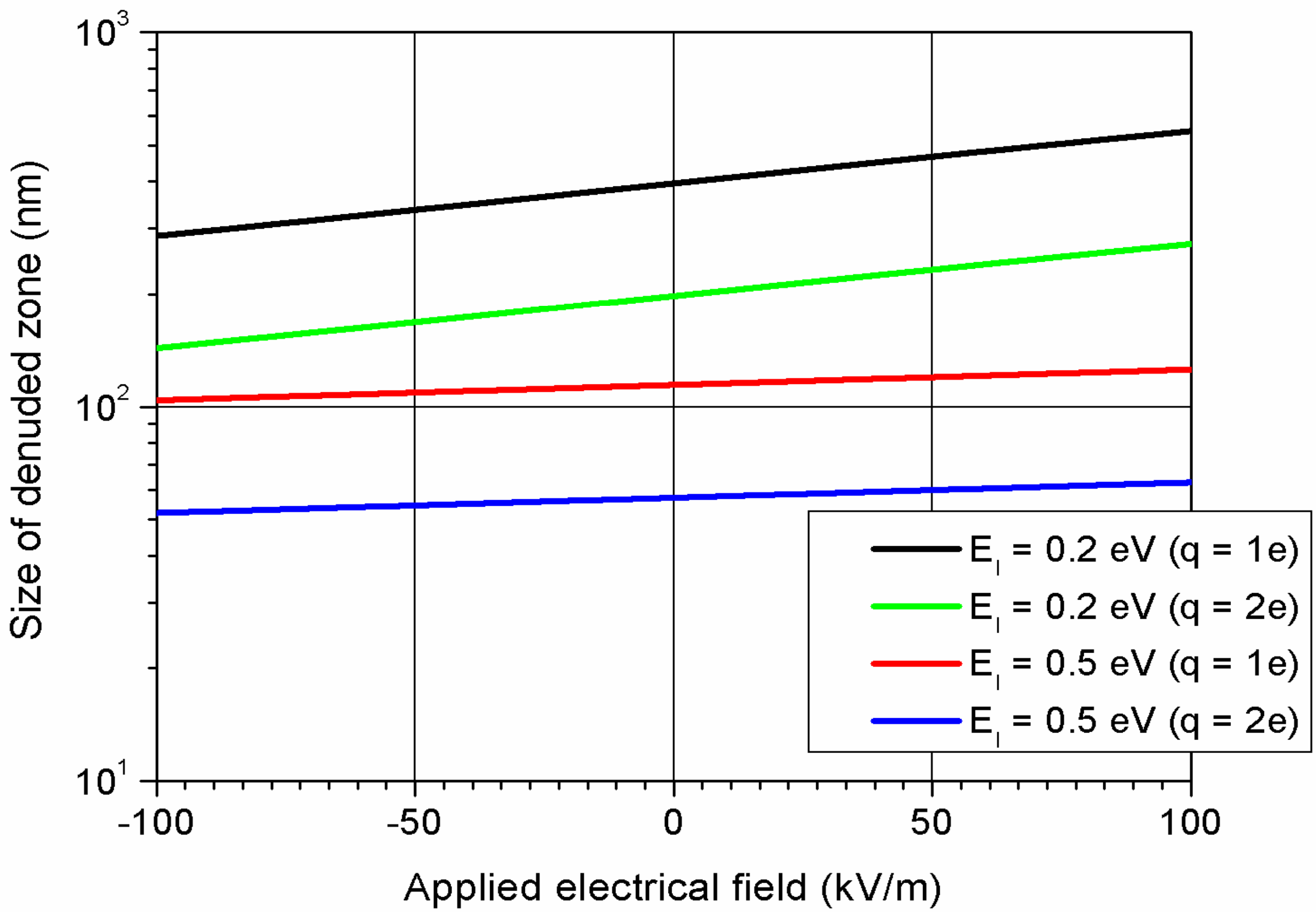


$$L \approx L_E(1-\alpha E_0+\frac{1}{2}\alpha^2 E_0^2), L_E >> L_T$$

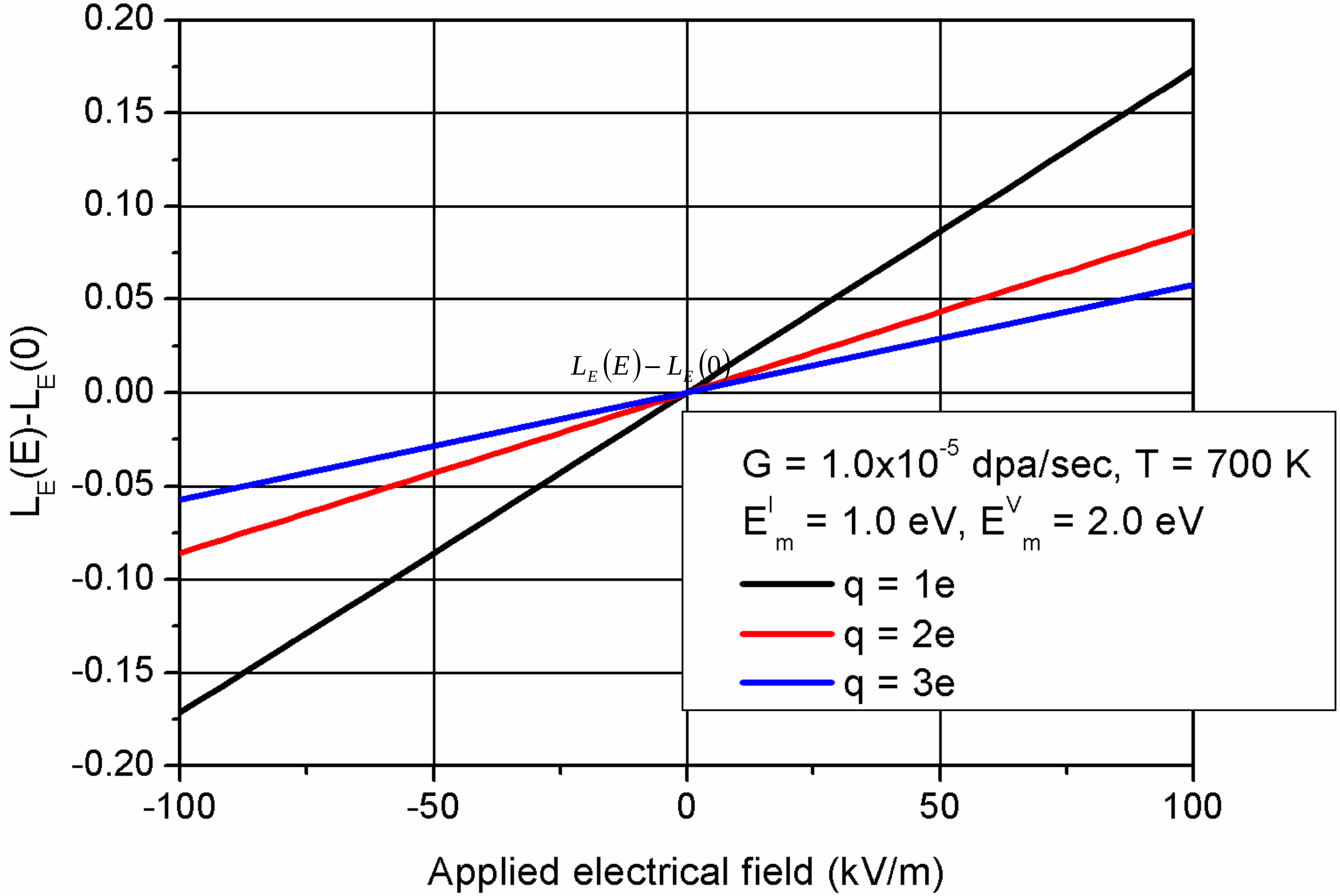
$$L \approx L_T(1-\beta E_0+2\alpha^2 E_0^2), \quad L_T >> L_E.$$

$$\Delta L(E_0) = -\frac{\omega}{16\pi q}\left(\frac{\mu D_I}{G}\right)^{1/2} E_0$$

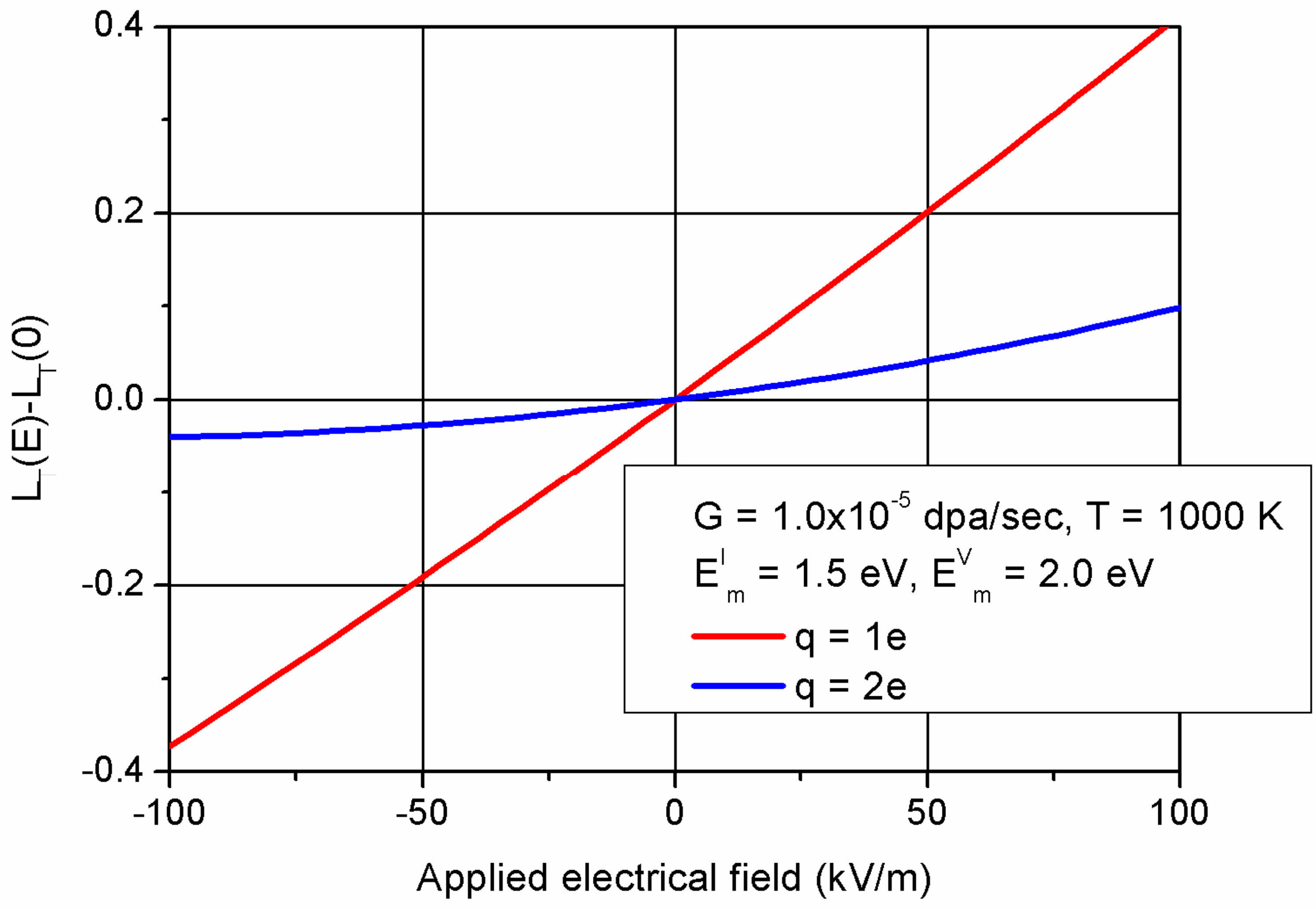
Dependence of denuded zone size on an applied electric field



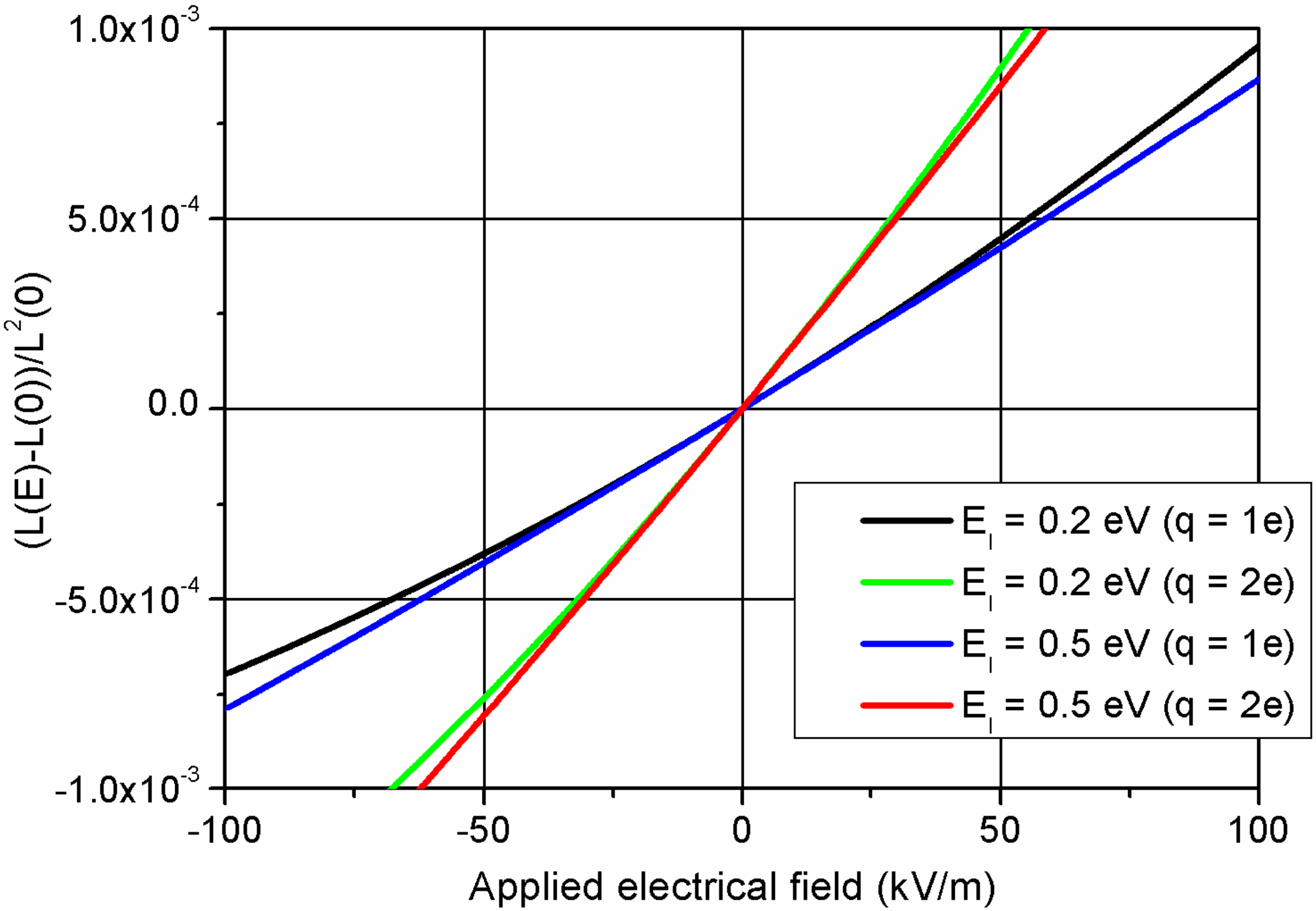
Dependence of $\Delta L_E(E)$ on an applied electric field



Dependence of $\Delta L_E(E)$ on an applied electric field

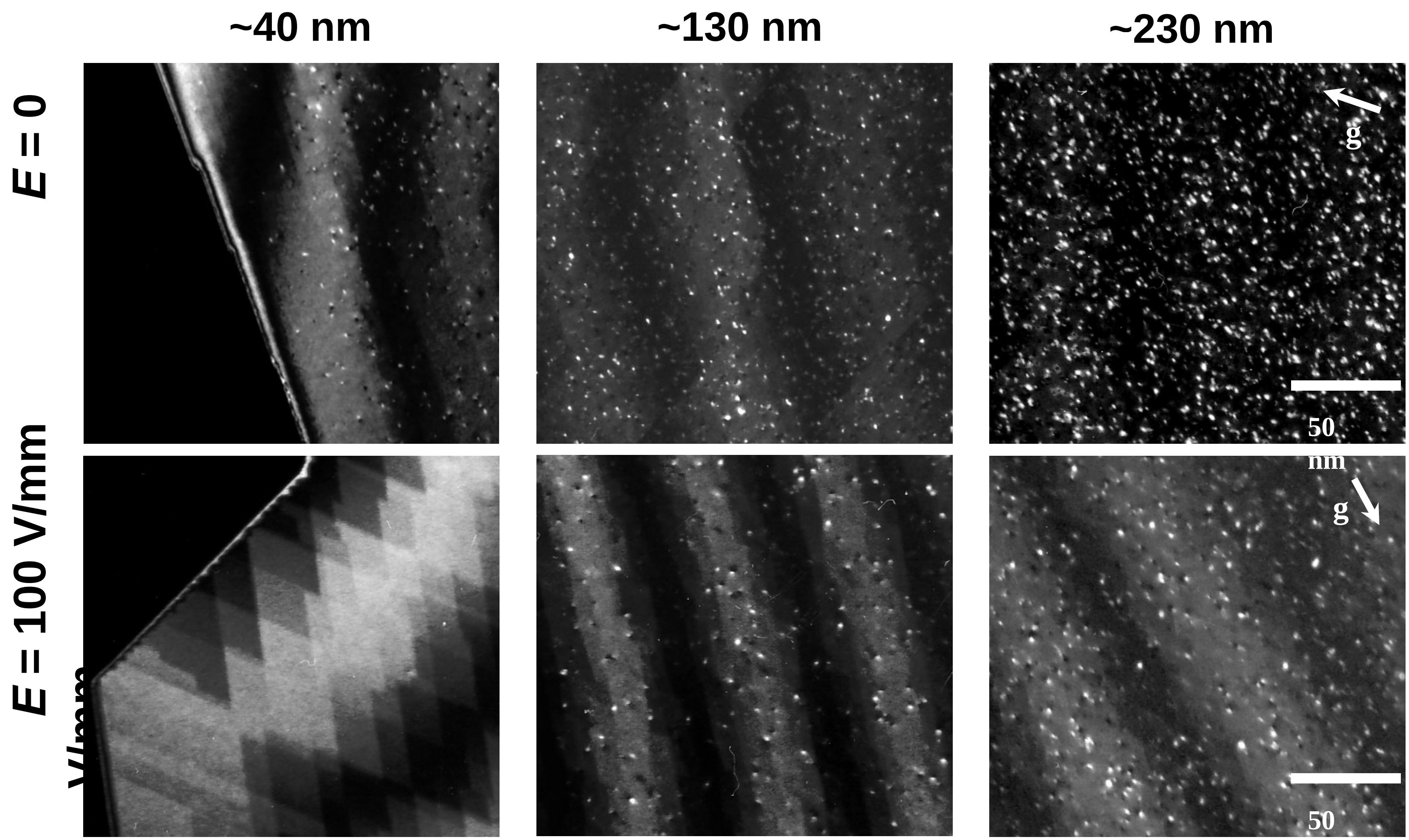


Dependence of $\Delta L_E / L_E^2$ on applied electrical field



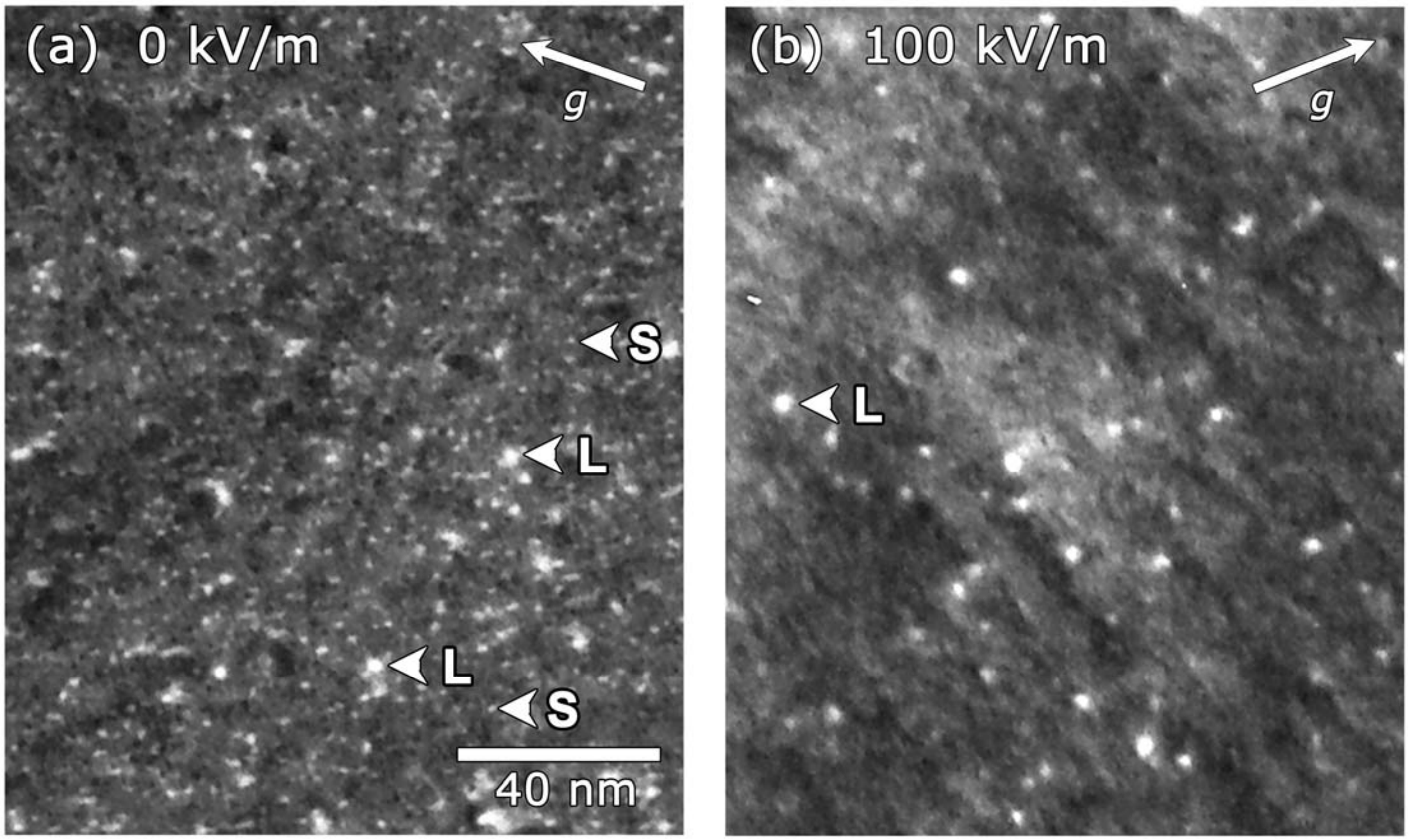
Experimental observation of dislocation loop density in Al_2O_3 irradiated at 760 K with 100keV He^+ ions to a fluence of $1x10^{20}$ m^{-2} with and without electric field of 100 kVm^{-1}

(K.Yasuda, K.Tanaka,C.Kinoshita 2002)



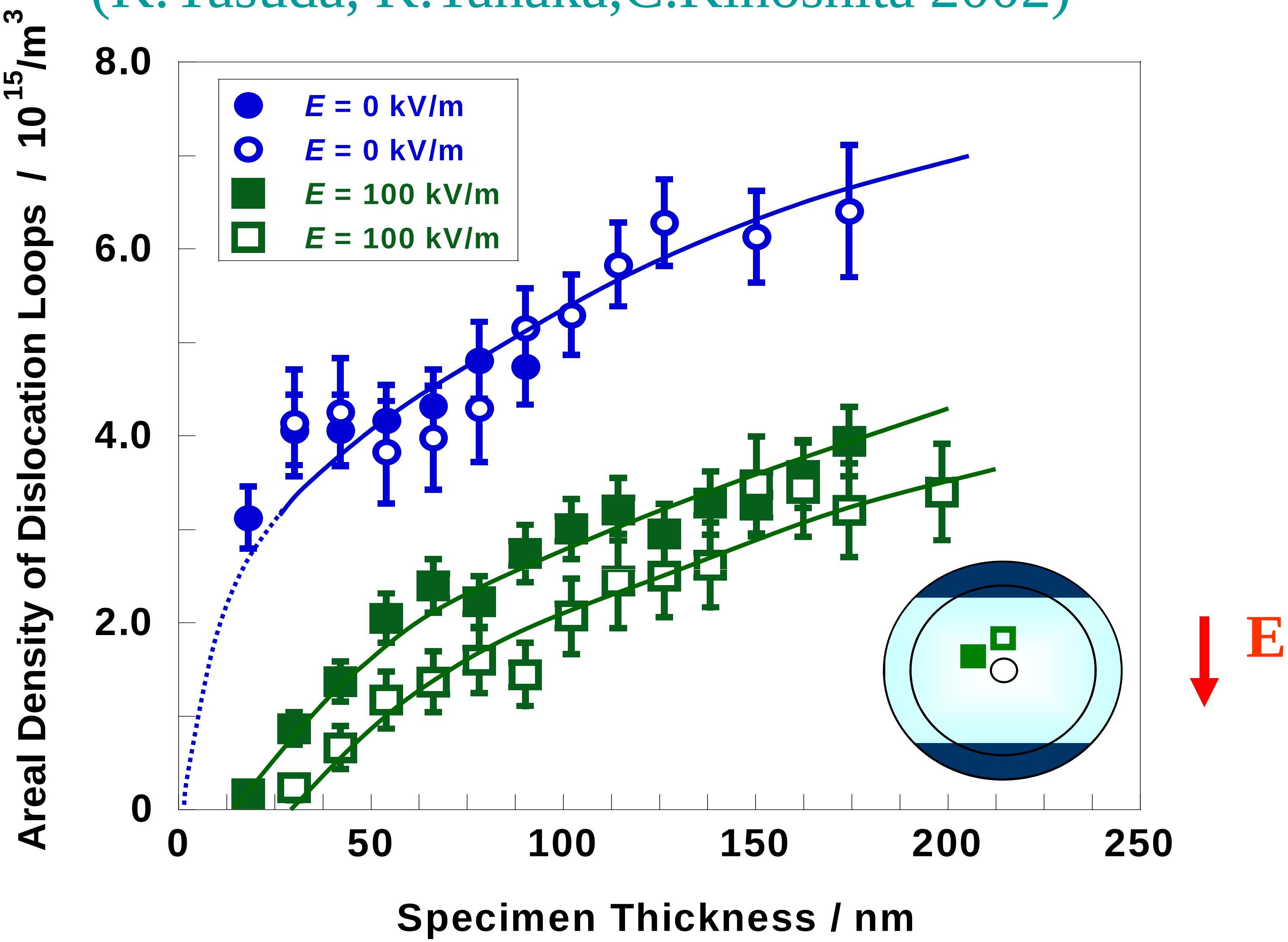
TEM data in α-Al_2O_3 irradiated with 100 keV He^+ ions at 870 K

(K.Yasuda, K.Tanaka,C.Kinoshita 2002)



Specimen thickness; 100 nm

(K.Yasuda, K.Tanaka,C.Kinoshita 2002)



INSTABILITY OF INTERSTITIAL CLUSTERS UNDER ION AND ELECTRON IRRADIATIONS IN CERAMIC MATERIAL

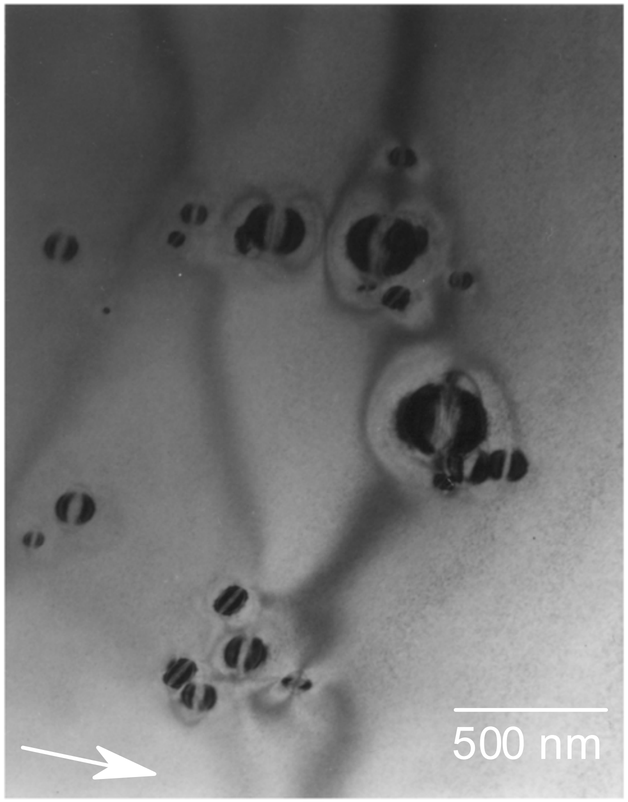
A.I. Ryazanov, A.V. Klaptsov, C. Kinoshita, K. Yasuda, 2004

Experimental

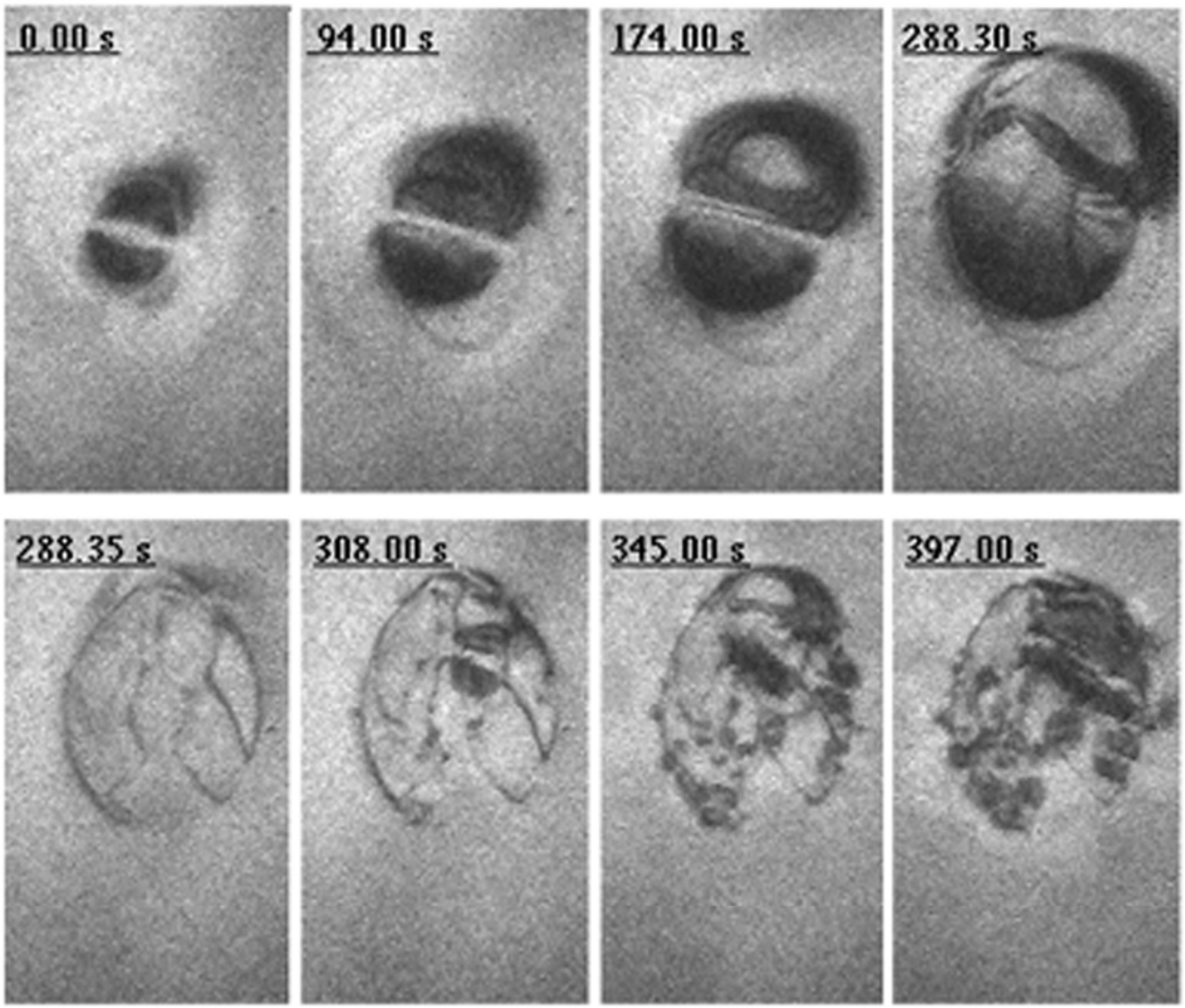
- Specimens: 13mol% Y_2O_3-ZrO_2 single crystal (Earth Jewelry Co.)
- surface orientation: (111)
- Irradiation:
  - ions: 100 keV He^+ at 870 K, up to 1×10^{20} ions/m^2
    - 4 keV Ar^+ at 300 K
    - 300 keV O^+ at 470-1070 K, up to 5×10^{19} ions/m^2
  - electrons: 1000 keV at 470-1070 K, up to 1.4×10^{27} e/m^2
  - electron irradiation subsequent to ion irradiation:
    - 100-1000 keV electrons at 370-520 K
- Observations:
  - in situ and ex-situ TEM
    - HVEM (JEM-1000, HVEM lab., Kyushu University)
    - TEM (JEM-2000EX, HVEM lab., Kyushu University)
    - TEM-accelerator facility (JEM-4000FX, TIARA, JAERI-Takasaki)

Defect clusters in yttrium-stabilized zirconia

-300 keV O+ions: 5.1x1017 ions/m2 at 470 K
-200 keV electrons at 370 K



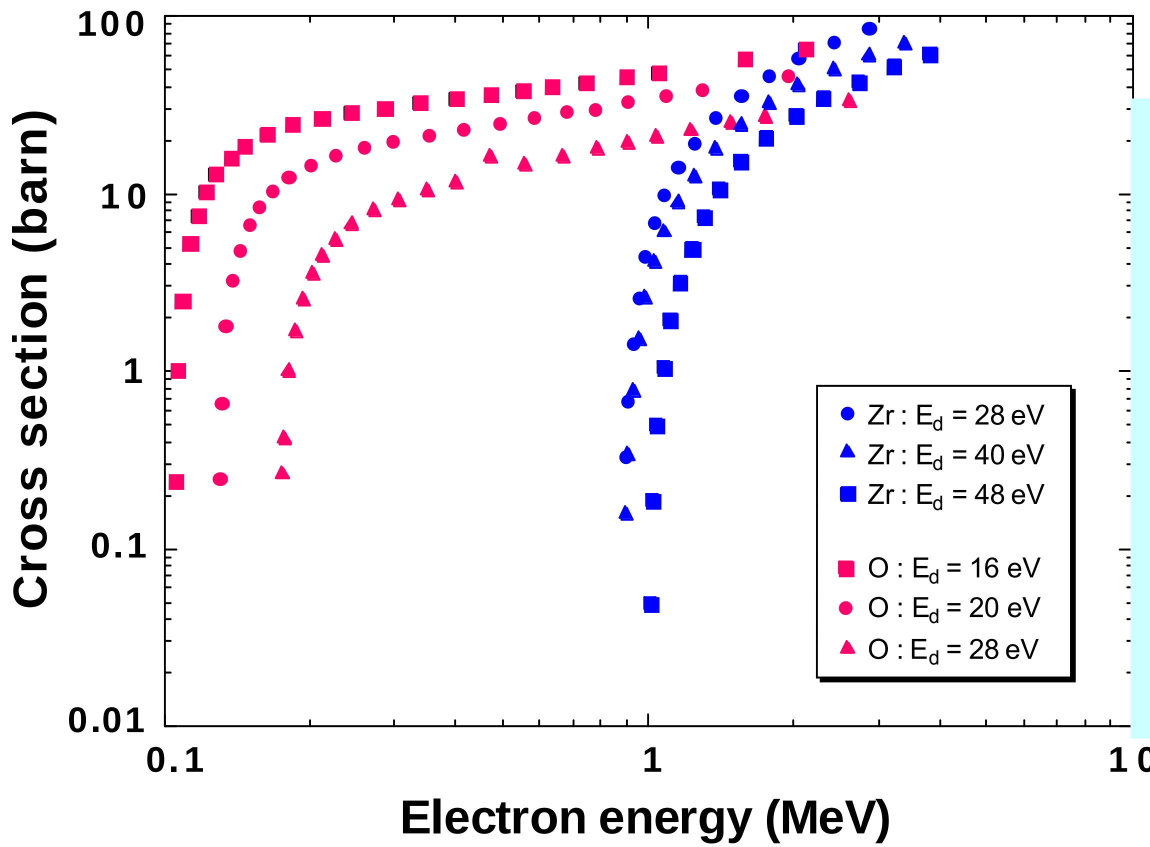
Instability of Interstitial Clusters



Characteristic features of the extended defects in yttrium stabilized zirconia

- irradiation condition: under 100-1000 keV electron irradiation subsequent to ion irradiation (100 keV He^{+}, 300 keV O^{+}, 4keV Ar^{+})
- strong strain and stress fields
- very high growth rate ≈ 1-3nm/sec
- preferential formation around a focused electron beam
- preferential formation at thick regions
- critical radius: 1.2 μm
  - sudden conversion to the dislocation network
  - repeat nucleation, growth and conversion to dislocation structure on dislocation lines

Cross section for displacement in ZrO2 under electron irradiation



Displacement damage by elastic collisions

E_d(O)~20 eV,

E_d(Zr)~40 eV,

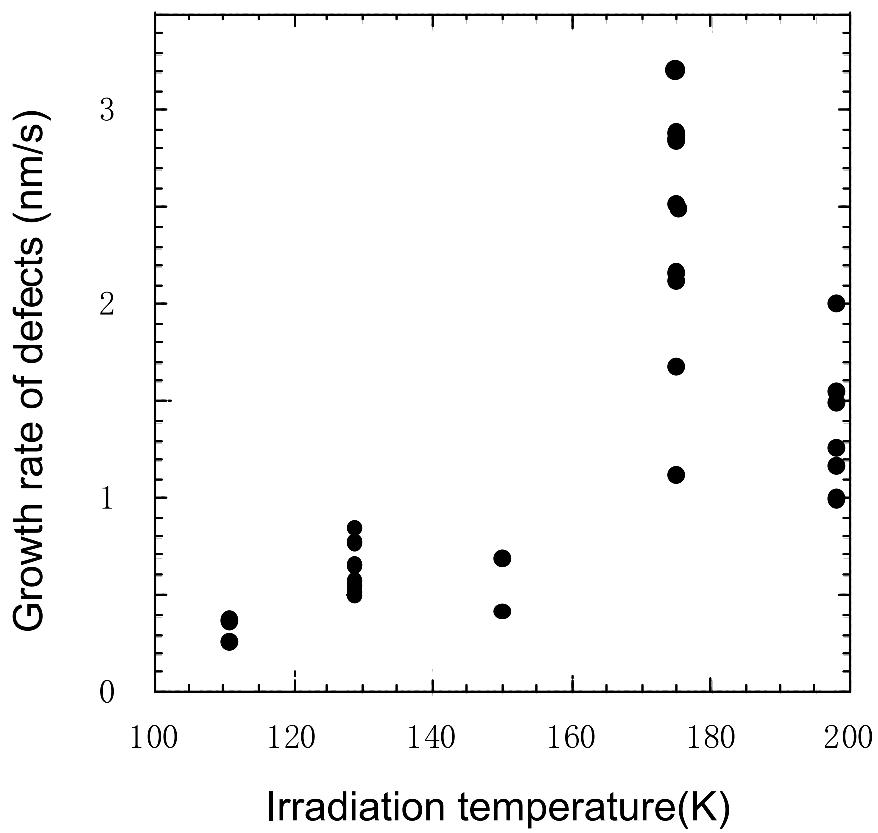
➔ 200 keV electrons :

σ(O) ~10~30 barn

➔ Φ = $10^{21} e^-/m^2 s$:

~ 10^{-6} dpa/s

Growth rate of radiation defects in ZrO_2



- Irradiation fluence of 300 keV O^+ ions:
  5.1×10^{17}(ions/m^2)
- Irradiation flux of 200 keV electrons:
  8.0×10^{21}(e/m^2s)
- Displacement rate of oxygen sub lattice: ~10^{-5} dpa/s
- Growth rate of defects：1-2 nm/s

Theoretical model

Growth rate of electrostatic charge (*Q*) on the dislocation loop with *R* radius is equal

A.Ryazanov, V.Klapzov, JETP Letters, 2005

$$\frac{dQ}{dt} = N\langle\sigma\rangle_I \Phi \approx \frac{\pi R^2}{a^2}\langle\sigma\rangle_I \Phi$$

$\langle\sigma\rangle_I$ is the cross-section of electron-electron elastic Reserford scattering

Φ is the electron flux, ***a*** is the lattice spacing

$$\langle\sigma\rangle_I = \int_I^{E_0} \frac{d\sigma}{dE}\, dE = 4\pi a_0^2 \frac{E_R^2}{IE_0}\left(1 - \frac{I}{E_0}\right),$$

$E_R = 13.6$ эВ - is the Ridberg energy, a_0 **= 0.53 A** is the Bohr radius

E_0 is the electron energy

Electrical field (*E*) near the charged dislocation loop is equal

$$E \approx \frac{Q}{\varepsilon R}\sqrt{\frac{1}{2\rho R}},$$

Elastic stress field due to polyarization of a matrix with the disribution of electrical field (*E*) is equal

$$\sigma_{ik} = \frac{\varepsilon}{4\pi}\left(E_i E_k - \frac{E^2}{2}\delta_{ik}\right), \quad \sigma \le \sigma_{th} = \frac{\mu}{2\pi}$$

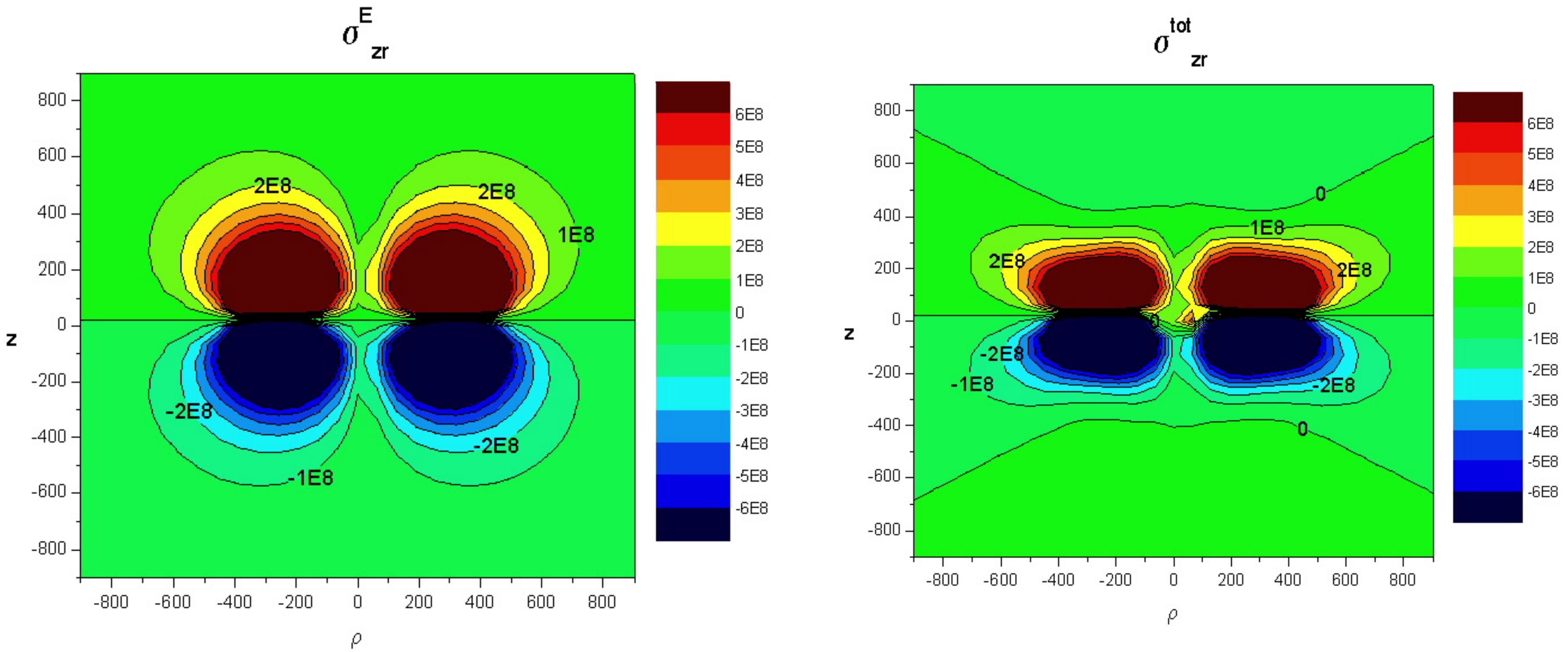
Time dependence of elastic stress field near charged dislocation loop

$$\sigma \approx \frac{Q^2}{16\pi\varepsilon\rho R^3} \approx \left(\frac{3}{20}\right)^2 \frac{\pi R}{\varepsilon\rho a^4}\langle\sigma\rangle_I^2(\Phi t)^2.$$

$\sigma_{th} = \mu/2\pi \approx 6 \times 10^{10}$ dyn / см^2 $\Phi = 10^{11}$ е/м^{2}сек

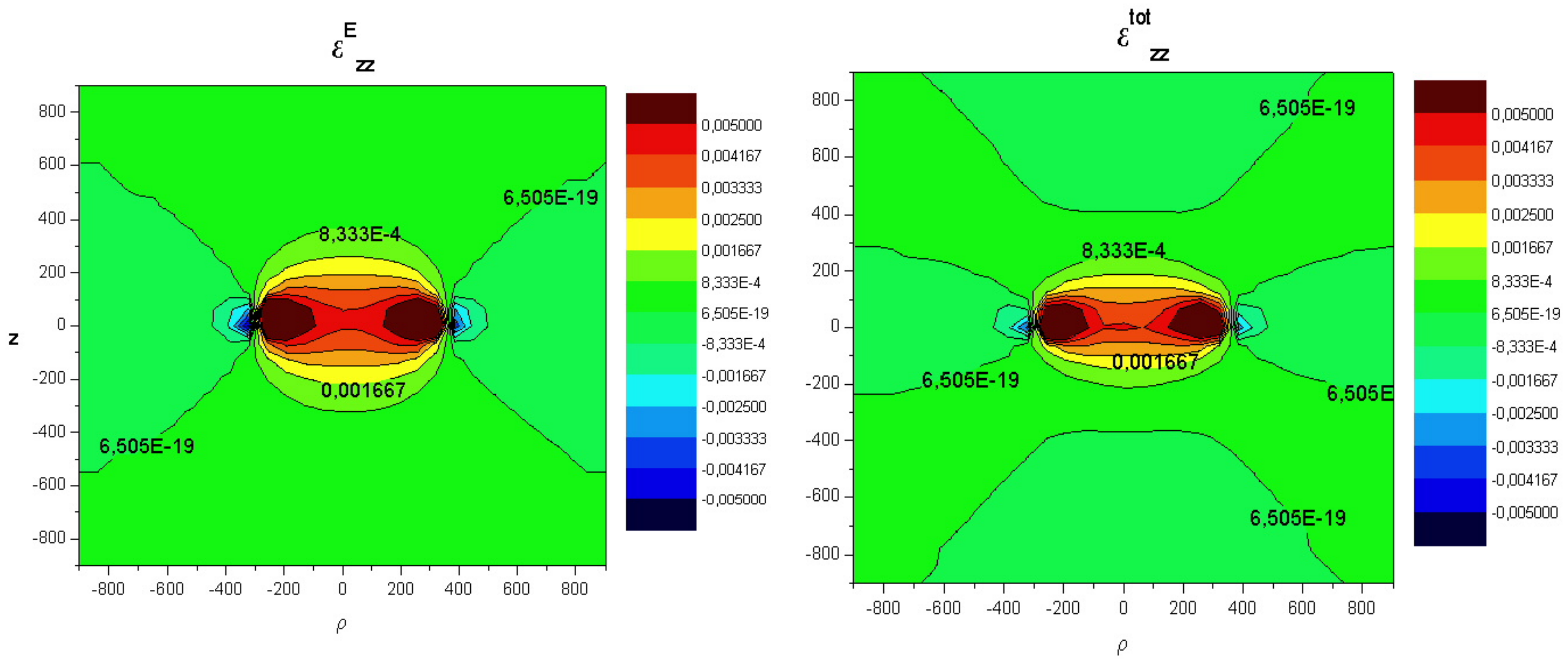
R = 600 nm, E_0 = 200 KeV, t = 280 sec

Shear stress component induced by charged dislocation loop

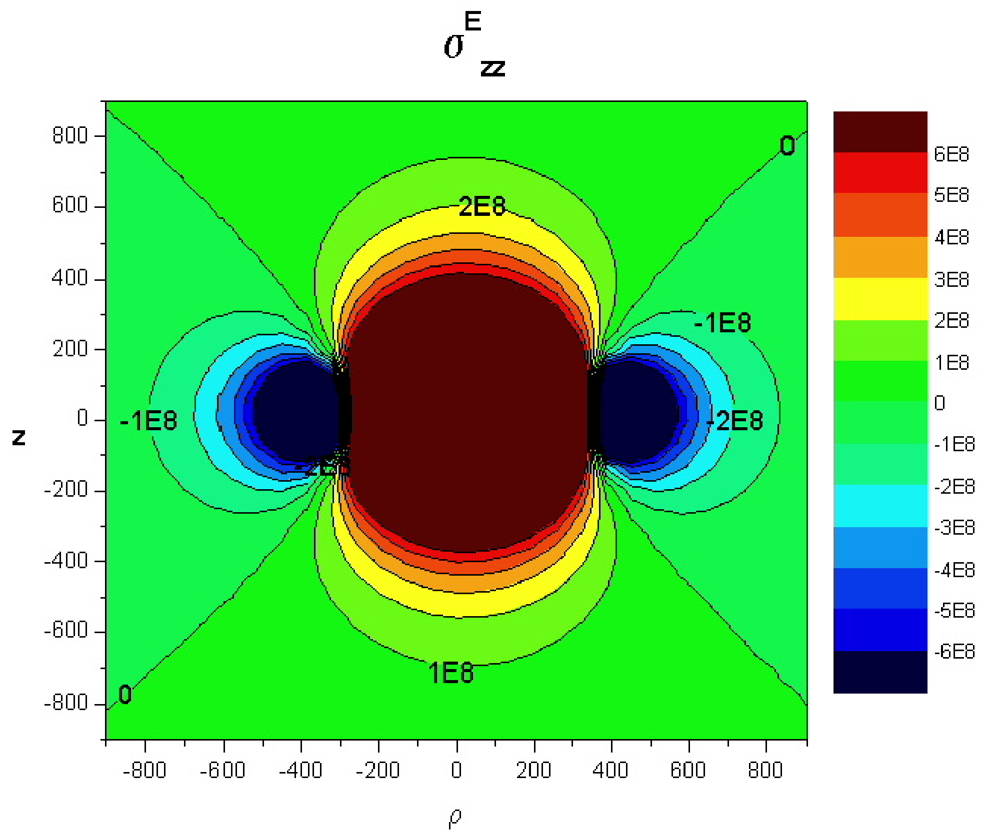


$$\sigma_{ik} = \frac{\varepsilon}{4\pi}\left(E_i E_k - \frac{E^2}{2}\delta_{ik}\right), \quad \sigma \approx \sigma_{th} = \frac{\mu}{2\pi}$$

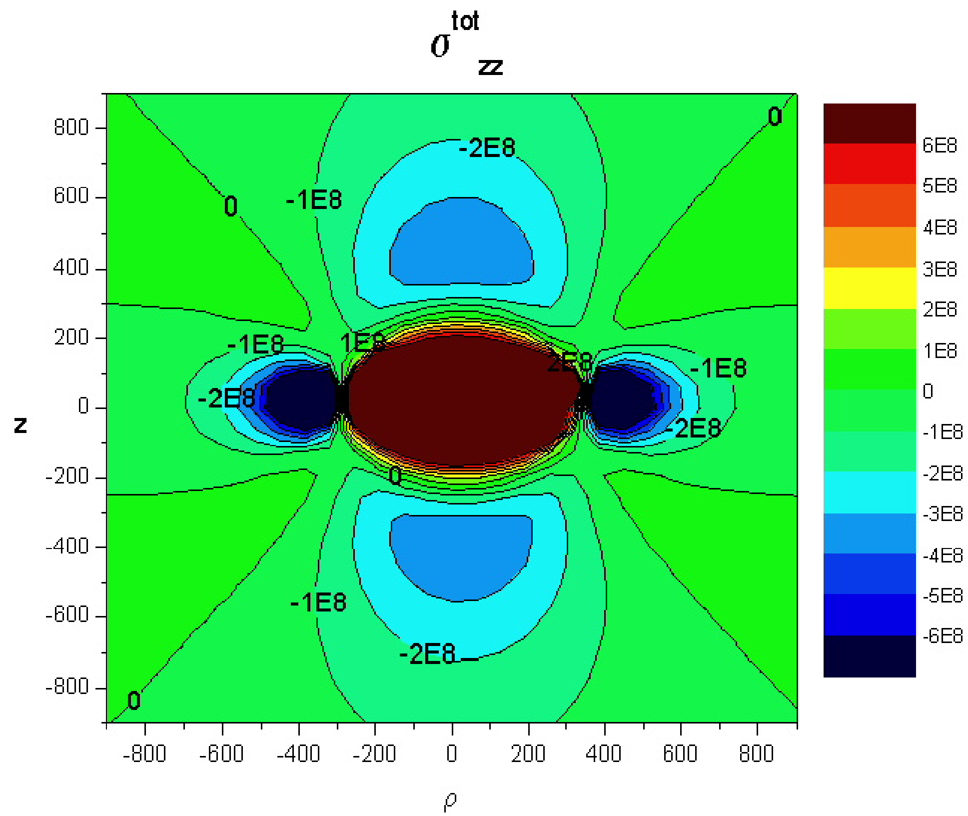
Strain-field induced by charged dislocation loop



Normal stress component induced by charged dislocation loop



Total normal stress component induced by charged dislocation loop



Summary

- Electron-irradiation subsequent to ion-irradiation induces anomalous large defect clusters with strong stress and strain filed in yttria-stabilized cubic zirconia (YSZ).
- Such defect clusters are considered to be oxygen clusters (platelets), which are formed due to the production of displacement damage in oxygen sublattice in multi-component ceramic: Y_2O_3-ZrO_2.
- Under irradiation, the growth of charged defect clusters can result in multiplication of dislocation network in fusion ceramics due to ionization processes and charge accumulation on dislocation loops.