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Structure of Defects and Microstructure Evolution in Oxide Ceramics - Role of Electronic Excitation and Selective Displacement Damage

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Fluorite- and spinel-type oxide ceramics, such as yttria-stabilized zirconia, ceria, magnesium aliminate spinel, are known to be exceptionally resistant to irradiation damage with energetic particles. Those oxide compounds, thereofore, have potential applications to advanced nuclear fuels and innert matrices of transmutaion targets. Fundamental understanding of radiation damage is apparently essential to assess the microstructure stability of fuel/target materials under the hostile environment. In this presentation, structure and stability of radiation-induced defects in the oxide ceramics is reported. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) is utilized to examine the following topics focucing on role of electronic excitation and selective displacement damage: (1) effects of selective displacement damage of oxygen sublattice in fluorite-type oxides, such as stabilided cubic ZrO_2, CeO_2 [1-3], (2) atomic structure of ion tracks in CeO_2 and $MgAl_2O_4$ induced by swift heavy ions, and microstructure evolution at high fluences under overlapping irradiation of high density electronic excitation damage [4-6], and (3) production and stability of defects in $MgAl_2O_4$ and alumina (α-Al_2O_3) under synergistic irradiation with dispacement damage and electronic excitation [7].

It is noted in fluorite-type oxides that there exists a significant difference in mass between cations and anions, and that the displacement energy of cation-sublattice is larger than the anion one. This leads to a higher displacement damage rate or selective displacement damage in oxygen sublattice in fluorite-type oxides. Figure 1 shows examples of TEM images in CeO_2 showing dislocation loops formed by electron irradiation with energies ranging from 200 to 1250 keV [1]. From contrast analysis and atomic resolution observations with TEM and STEM, those defects are found lying on {111} planes and have been discussed to be composed of solely oxygen ions formed under the selective displacement damage [1]. Similar defects were formed in yttria stabilized ZrO_2, in which entirely different growth process were observed compared to the normal (perfect) dislocation loops [2]. Molecular dynamic simulations in CeO_2, which showed the recovery process of multiple oxygen Frenkel pairs, revealed a tendency of oxygen interstitials for clustering on {111} planes, supporting the interpretation from the TEM and STEM observations [3].

Atomic resolution TEM and STEM observations in $MgAl_2O_4$ and CeO_2 irradiated with 200 MeV Xe ions have shown that the crystal structures are retained at the core region of ion tracks, showing their excellent resistance to high density electronic excitation [4,5]. Figure 2 is an example of atomic resolution image of ion tracks in CeO_2 with annular bright-field (ABF) STEM technique, showing that the crystal structure of Ce-cation column is retained at the core region of ion tracks, whereas O-anion column is preferentially distorted at the core region of ion tracks [5]. The atomic density inside the core damage region of ion tracks in both crystals was found to be decreased, which suggests the existence of high density of vacancies and/or small vacancy clusters inside the ion tracks [5]. Overlap of ion tracks at high fluence was found to develop dislocation structure in both $MgAl_2O_4$ and CeO_2. The development of dislocation structure also results in the formation of small sub-grains in CeO_2. Those microstructure evolution was discussed with the generation of interstitial atoms at the peripheral region of the core damage region of ion tracks [4,6].

It has been shown in $MgAl_2O_4$ and α-Al_2O_3 that synergistic irradiation with displacement damage and electronic excitation retards the nucleation of dislocation loops and enhance their growth [7]. Electronic excitation with 200 keV electrons makes small dislocation loops of interstitial-type unstable in $MgAl_2O_4$ and α-Al_2O_4. Dislocation loops were found to be disappeared during electron irradiation. Analysis of the temperature dependence of the elimination process leads to a conclusion that the dislocation loops are disappeared by dissociating into isolated interstitials. The elimination rate of loops was higher in $MgAl_2O_4$ than α-Al_2O_3, which indicates the high sensitivity of $MgAl_2O_4$ to electronic excitation, and this is considered to play a role for the radiation resistance of $MgAl_2O_4$.

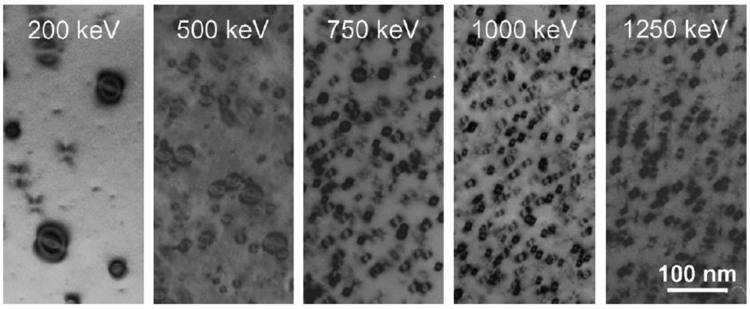

Fig. 1: Dislocation loops formed by electron irradiation ranging from 200 to 1250 keV at room temperature. Dislocation loops are considered to be interstitial-type loops consist of oxygen ions on {111} planes.

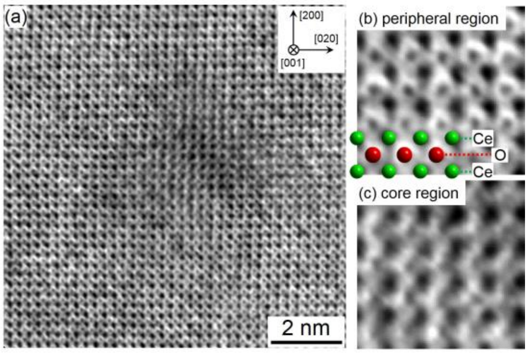

Fig. 2: Annular bright-field (ABF) images of ion tracks in CeO_2 irradiated with 200 MeV Xe ions to a fluence of $3x10^{12}$ cm^{-2}. An ion track is nearly at end-on condition parallel to [001] direction.

References

[1] K. Yasunaga, K. Yasuda, S. Matsumura, T. Sonoda, 'Electron-energy dependent formation of dislocation loops in CeO_2', Nucl. Instr. and Meth. B 266 (2008) 2877.
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[3] K. Shiiyama, T. Yamamoto, T. Takahashi, A. Guglielmetti, A. Chartier, K. Yasuda, S. Matsumura, K. Yasunaga, C. Meis, 'Molecular dynamics simulations of oxygen Frenkel pairs in cerium dioxide', Nucl. Instr. and Meth. B 268 (2010) 2980.
[4] K. Yasuda, T. Yamamoto, M. Etoh, S. Kawasoe, S. Matsumura, N. Ishikawa, 'Accumulation of radiation damage and disordering in $MgAl_2O_4$ under swift heavy ion irradiation', Int. J. Mater. Res., 102 (2011) 9.
[5] S. Takaki, K. Yasuda, T. Yamamoto, S. Mastumura, N. Ishikawa, 'Atomic Structure of Ion Tracks In Ceria', Nucl. Instr. and Meth. B 326(2014) 140.
[6] K. Yasuda, M. Etoh, K. Sawada, T. Yamamoto, K. Yasunaga, S. Matsumura and N. Ishikawa, 'Defect formation and accumulation in CeO_2 irradiated with swift heavy ions', Nucl. Instr. and Meth. B 314 (2013) 185.
[7] K. Yasuda, T. Yamamoto, S. Seki, K. Shiiyama and S. Matsumura, 'Production and Stability of Radiation-Induced Defects in $MgAl_2O_4$ under Electronic Excitation', Nucl. Instr. and Meth. B 266 (2008) 2834.

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Structure of Defects and Microstructure Evolution in Oxide Ceramics

– Role of Electronic Excitation and Selective Displacement Damage –

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MINOS 2nd Int. Workshop Irradiation of Nuclear Materials:

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KYUSHU UNIVERSITY

Oxide ceramics: fluorite- and spinel-type

□ Excellent radiation resistance

- Resistance to amorphization and volumetric swelling
- Successful achievements as LWR fuels: **UO_2, $(U,Pu)O_2$**
- Potential applications to inert fuel matrix, transmutation target: **stabilized ZrO_2**
- A surrogate of UO_2 : **CeO_2**

□ Radiation effects and radiation resistance

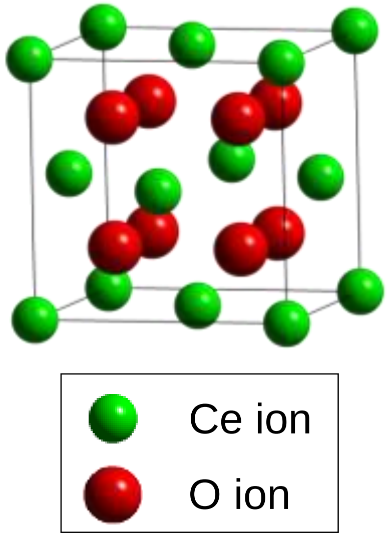
- Production rate of point defects
  - ⇒ difference between cations and anions
- Recombination rate of point defects
  - ⇒ structural vacancy: cation site (spinel), anion site (YSZ)
- Stability of extended defects: size of stable nuclei (ex. dislocation loop)
- Sensitivity to electronic excitation
  - ⇒ defect kinetics (rather low electronic stopping)
  - ⇒ ion tracks (high electronic stopping)

Topics

- Selective displacement damage of oxygen sub-lattice
- Structure of ion tracks
- Stability of dislocation loops under electronic excitation

☐ High production rate and mobility of oxygen defects (Fluorite-type)

CeO_2		Ce ion (cation)	O ion (anion)	Ref.
mass	[amu]	140	16	
Displacemend energy	[eV]	44～58	<30	[1]
V - migration enegy	[eV]	2.1～5.4	0.5～0.6	[1],[2]
I - migration energy	[eV]	6.1	1.1	[2]

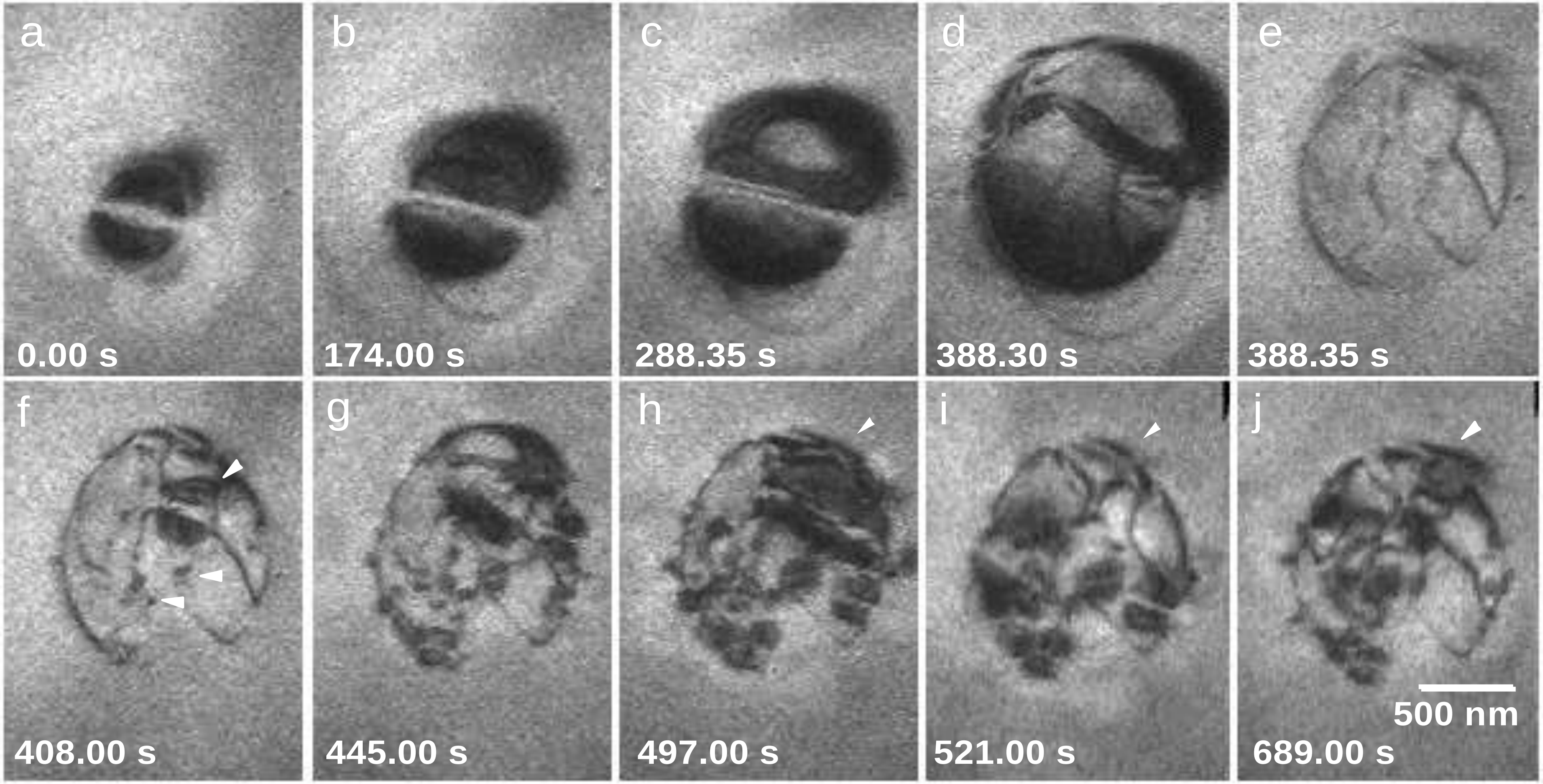


[1] K. Yasunaga, et al, *NIMB* 266 (2008) 2877.
[2] A. Guglielmetti et al, *NIMB* (2008) 5120.

⇒Role of oxygen point defects is important for defect kinetics in fluorite-type oxides.

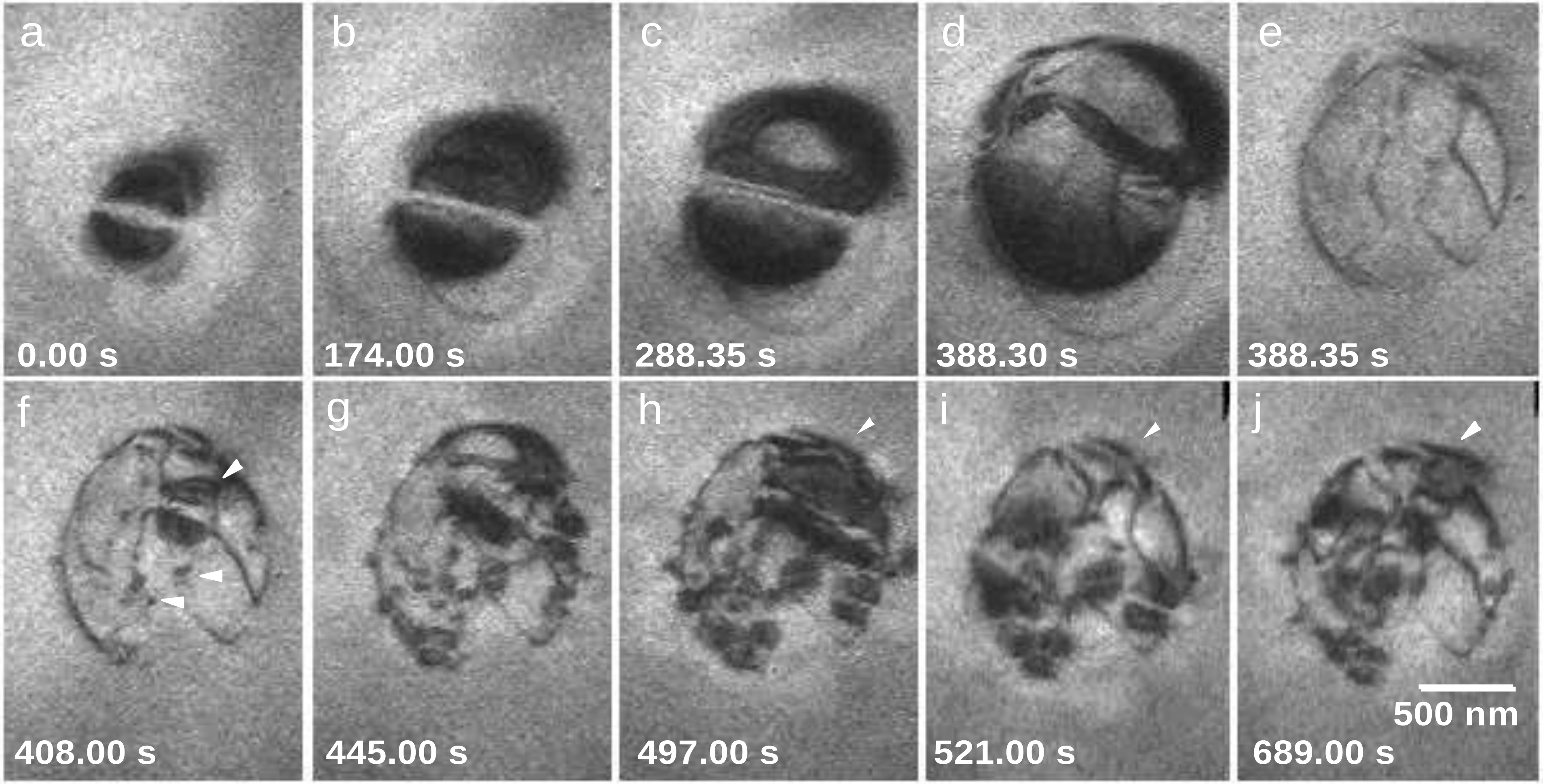
Anomalous defects in YSZ: selective displacement of O-ions

300 keV O ions ⇒ 200 keV electrons



K Yasuda et al, JNM 319 (2003) 74.

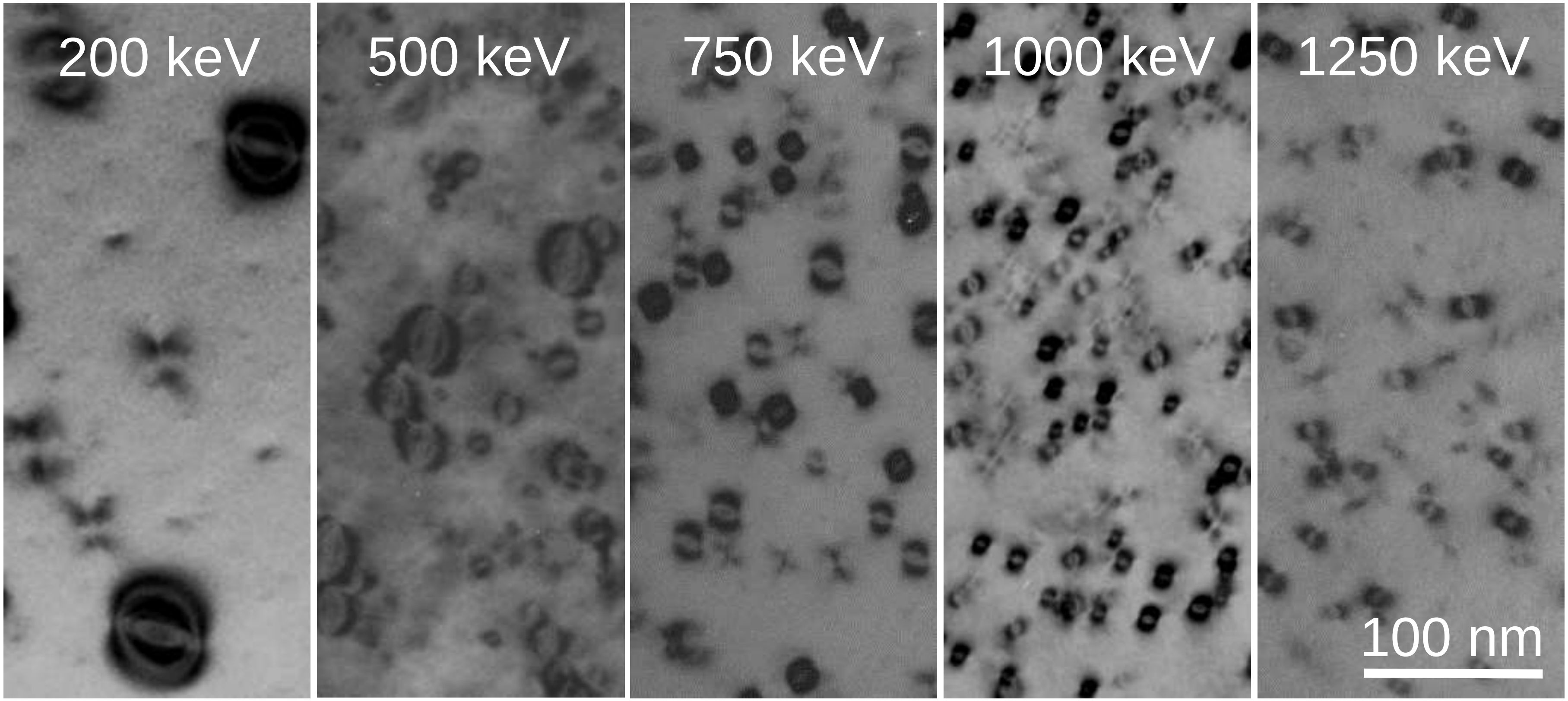
- Strong stress and strain field around the defect
- Entirely different growth process
- Multiplication of dislocations during the growth.



K Yasuda et al, JNM 319 (2003) 74.

Similar oxygen-type defects (loops) in CeO_2

(at 300 K. $\Phi \sim 3 \times 10^{26}$ e/m^2)



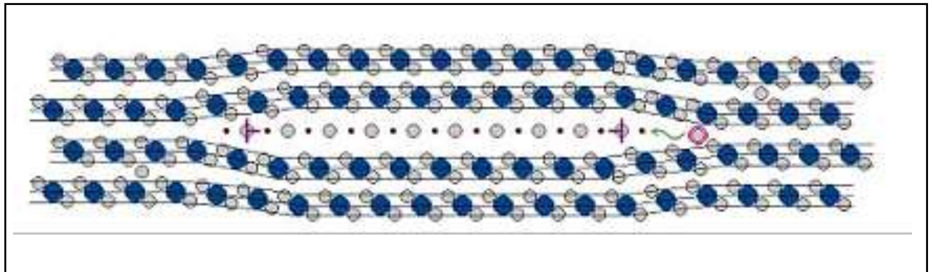
With decreasing e-energy, loop size is increased and density is decreased.

$\vec{B}$ *// <111>, on (111) planes*

K Yasunaga et al, NIMB (2008)

A model for charged disl. loop consist of O-ions

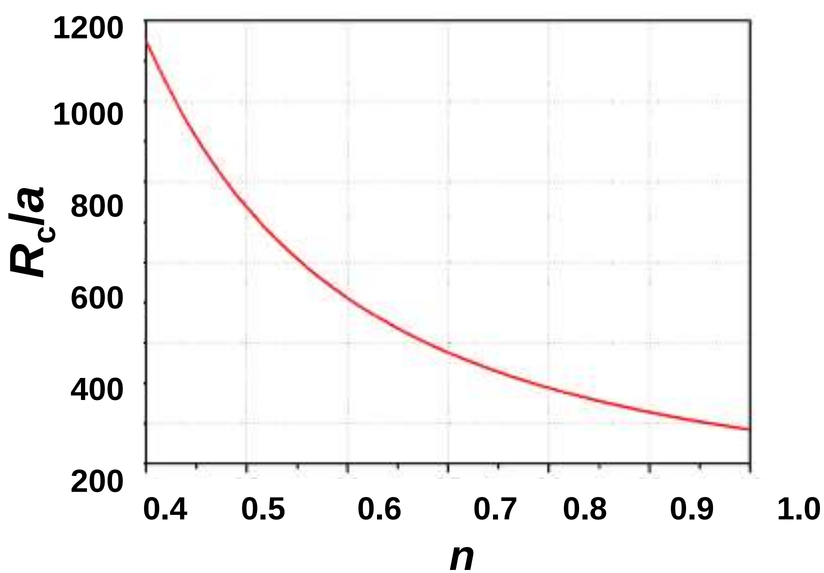
A. Ryazanov et al, JNM 323 (2003) 372.



$$\sigma_{ik} = \sigma_{ik}^{E} + \sigma_{ik}^{Y}$$

driven by an electric field | driven by an elastic strain

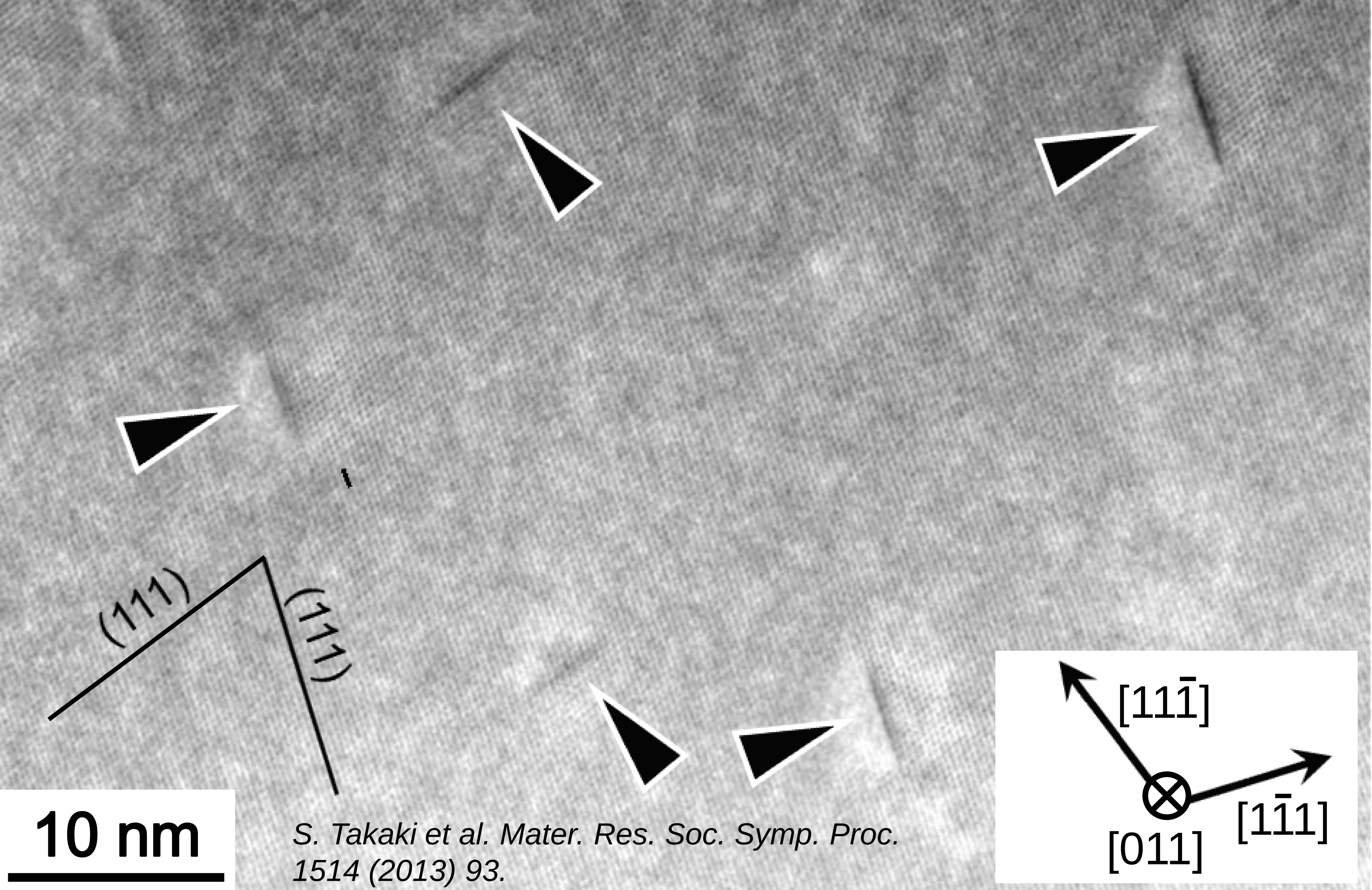
- accumulation of oxygen ions, preferentially at dislocations or invisible defect clusters
- oxygen ions are considered to lose electrons during diffusion process
- the defect clusters are considered to trap free electrons and grow as a charged dislocation loop



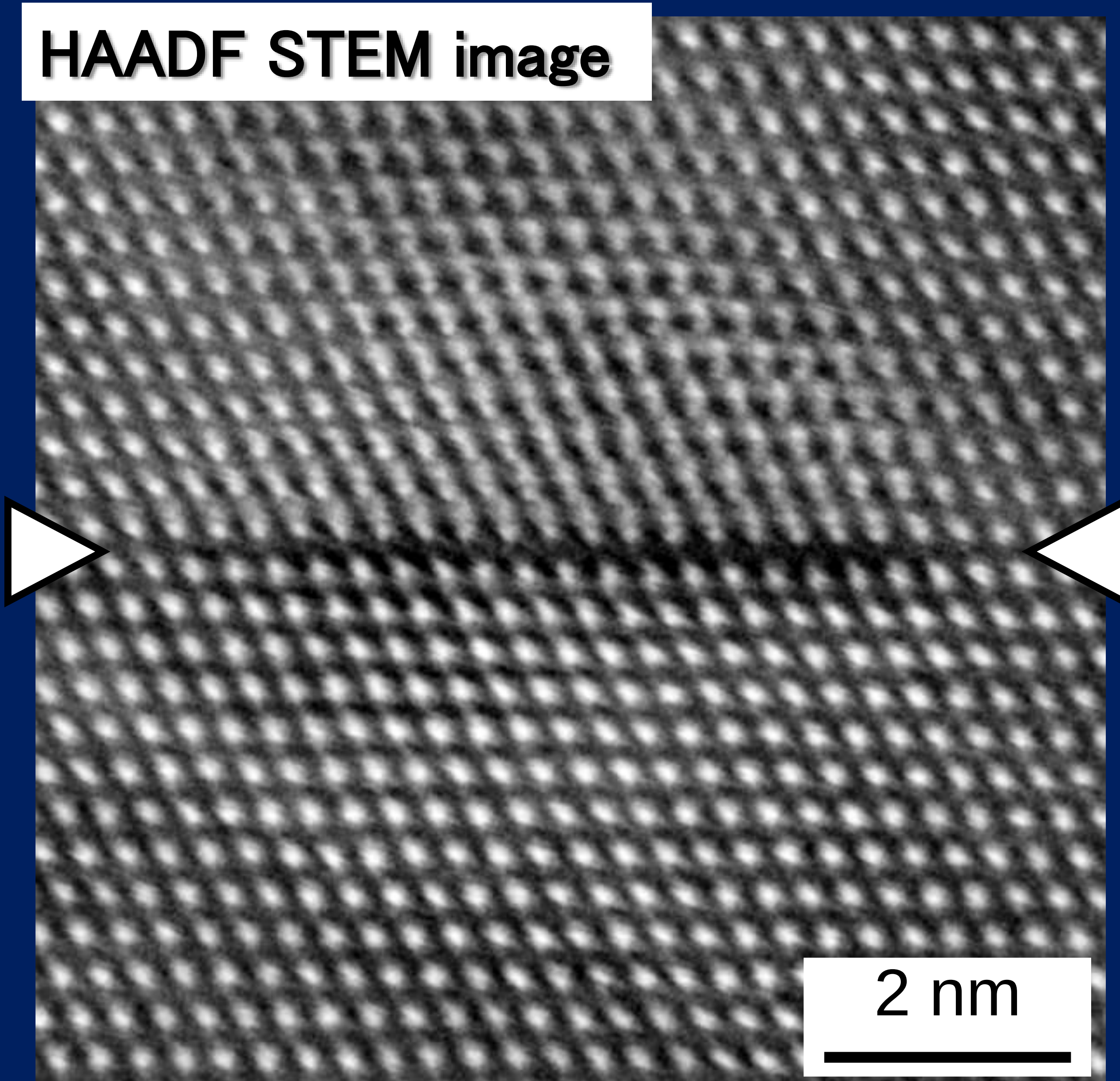
Charge of O^{-n} ions

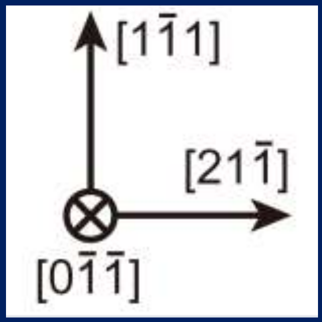
HAADF STEM image of Dislocation loops in CeO_2

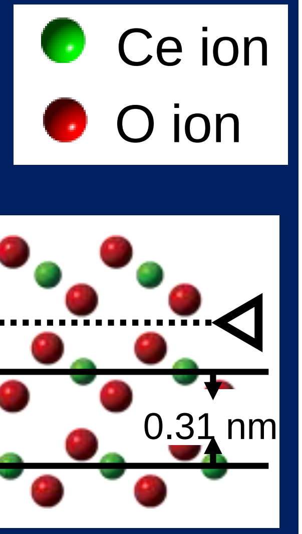
◆ 200 keV electron irradiation at 300 K



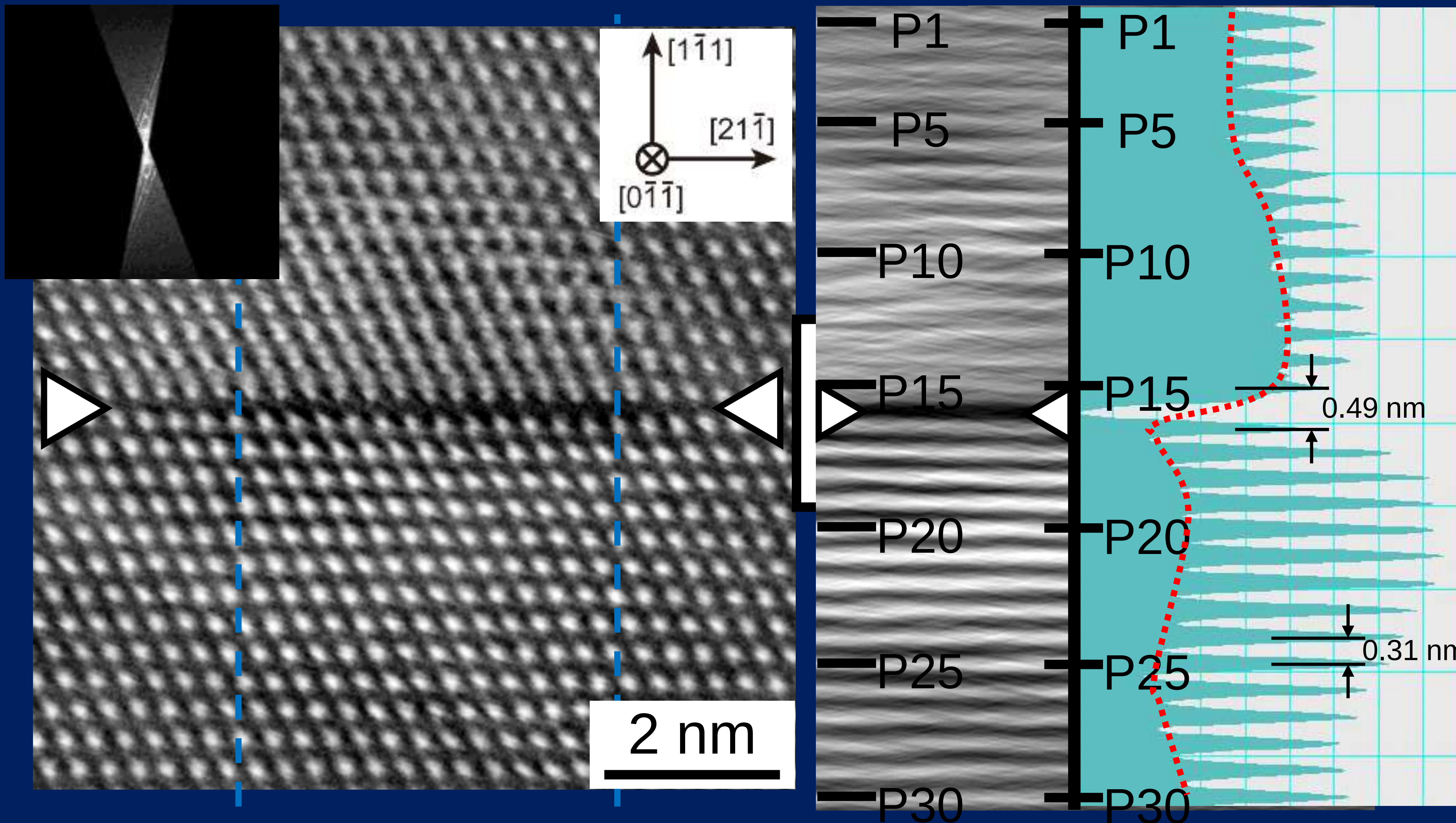
S. Takaki et al. Mater. Res. Soc. Symp. Proc. 1514 (2013) 93.







- Lattice planes are strongly distorted around the dislocation loop.
- No additional Ce-plane is inserted at the dislocation loop, indicating that this is not the perfect dislocation loop.



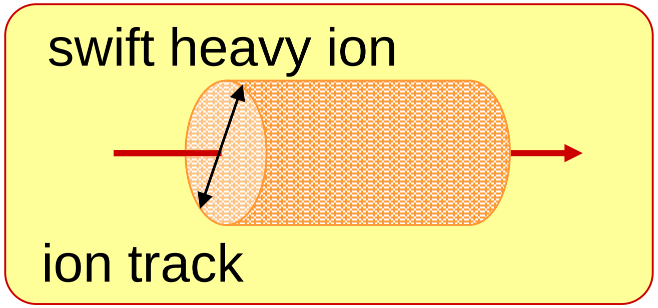
⇒The loop is suggested to be on a (111) plane consist of oxygen ions.

Topics

- Selective displacement damage of oxygen sub-lattice
- Structure of ion tracks
- Stability of dislocation loops under electronic excitation

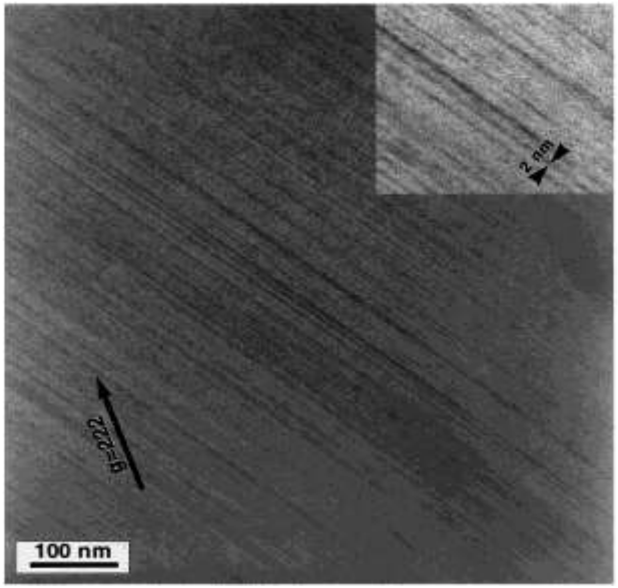
□ Fission fragments (E~70-100 MeV)

- high-density electronic excitation
  (S_e ~20 keV/nm)
- ion tracks



□ Ion tracks in fluorite and spinel-type oxides

- radiation resistant: no amorphization by individual ions
- threshold S_e for continuous track formation
  ~10 keV/nm: $MgAl_2O_4$, ~15 keV/nm: CeO_2
- At high fluence ⇒dislocation structure
  $MgAl_2O_4$: amorphization (10^{20} m^{-2})
  (Zinkle 2000)
  CeO_2: sub-grain formation
  (Sonoda 2010, Garrido 2009)

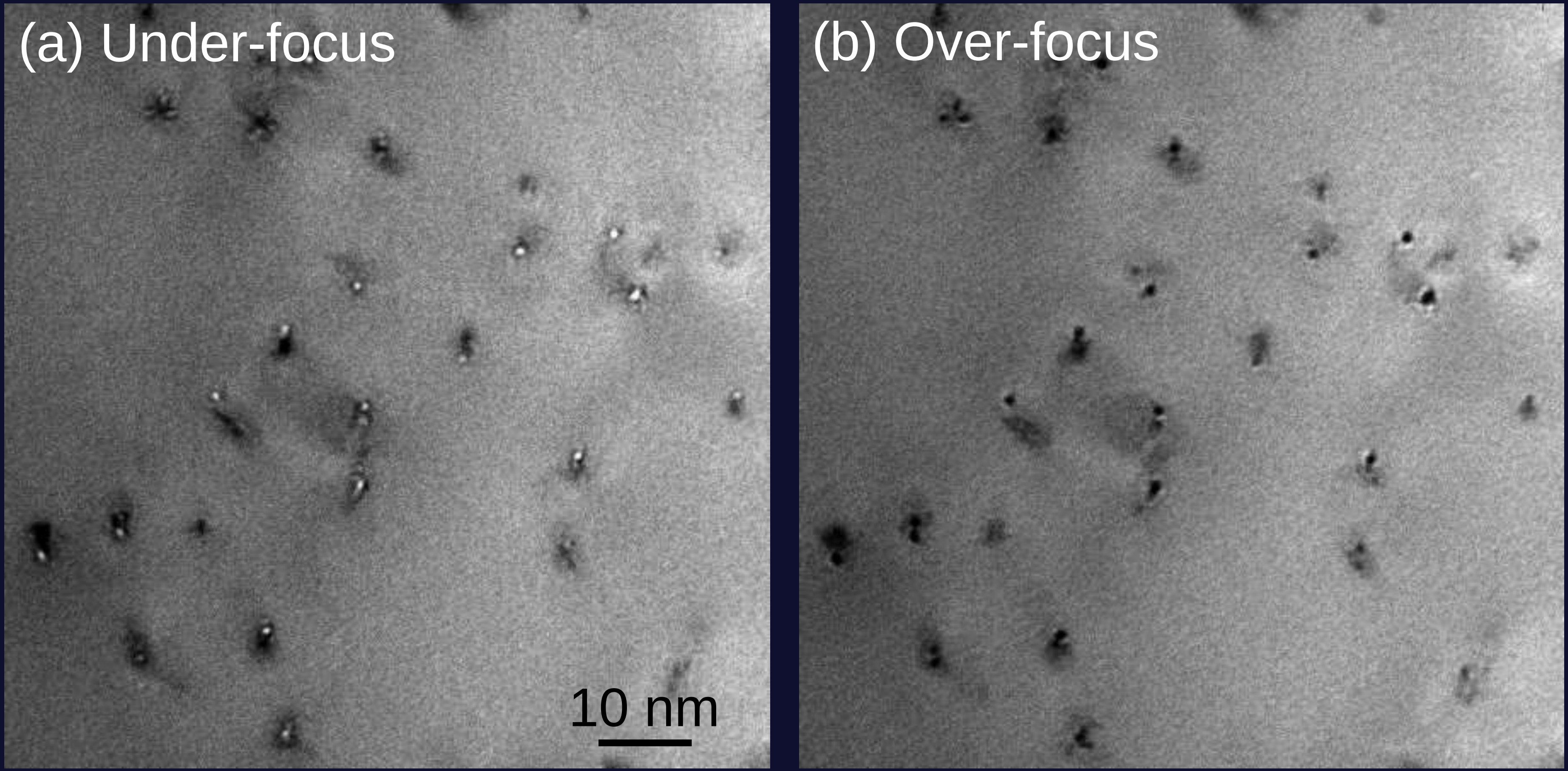


S.J. Zinkle et al., NIMB 141 (1998)

CeO_2 irradiated with 200 MeV Xe : S_e=27 keV/nm

Bright-field kinematical TEM images

3 x10^{11} (cm^{-2})

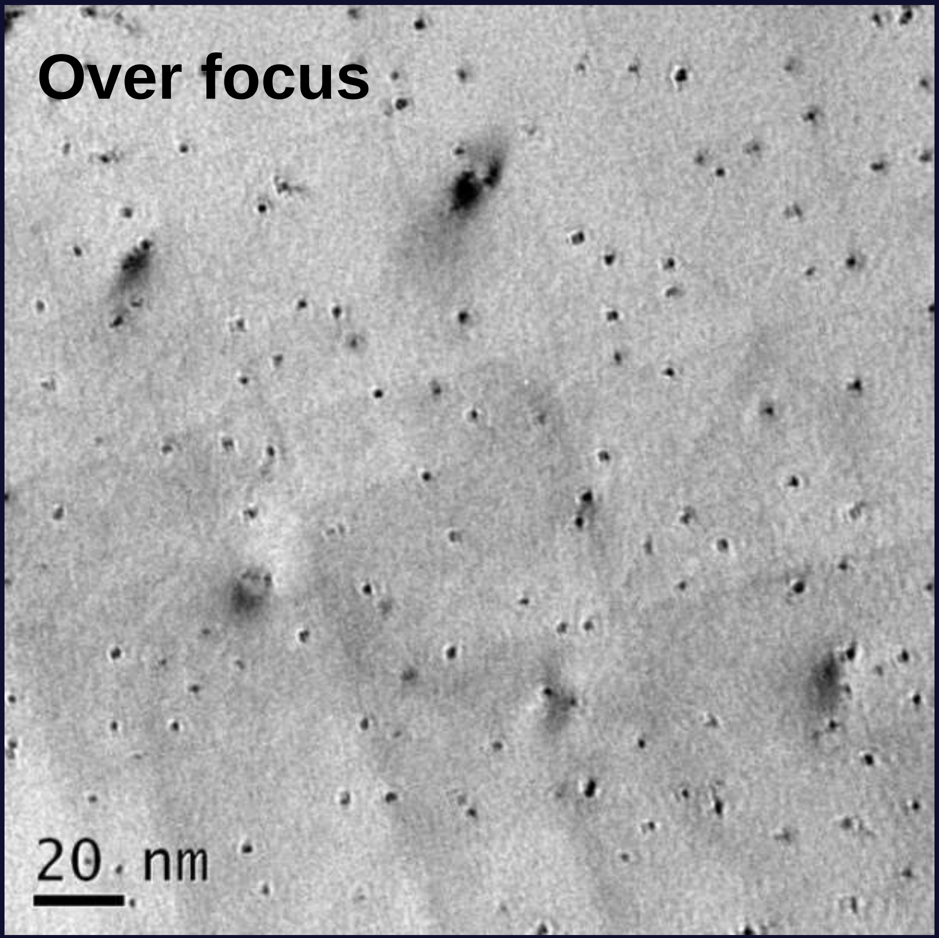


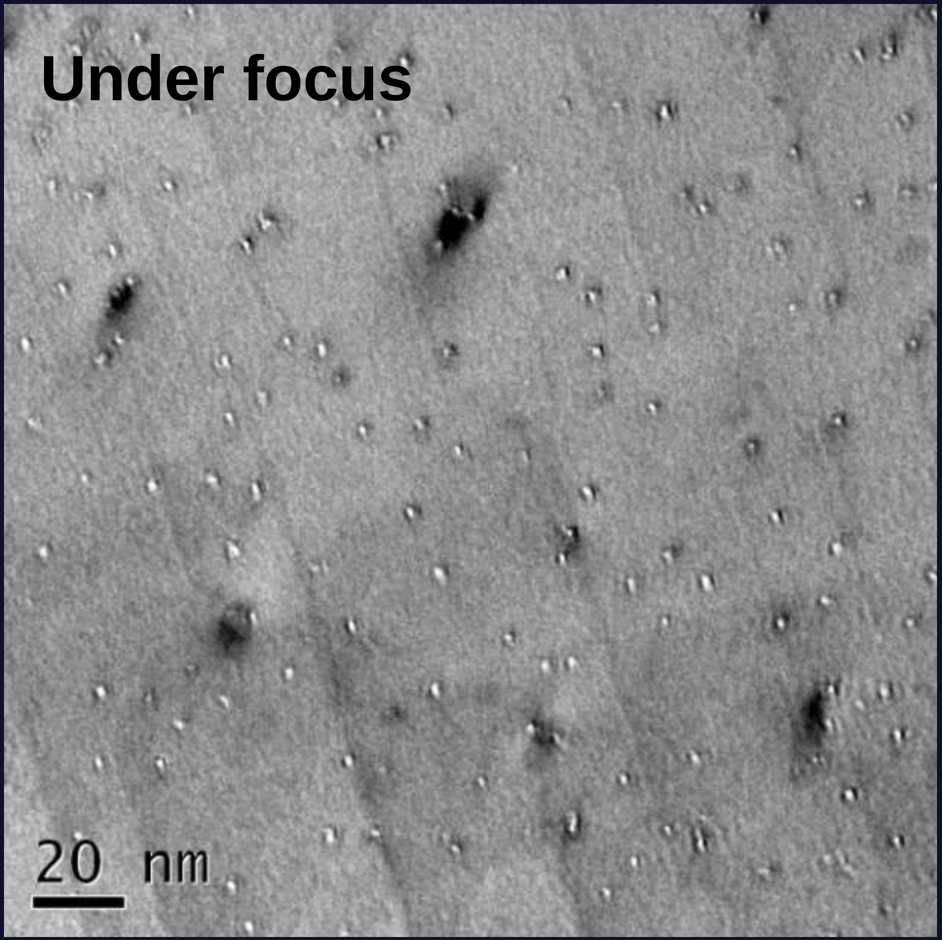
- Ion tracks appear as Fresnel contrast ⇒ decrease in atomic density.
- Fluorite structure is retained.

K. Yasuda NIMB 314 (2013) 185.

$MgAl_2O_4$: Bright-field TEM images

kinematical (off-Bragg) diffraction condition 5×10^{15} (m^{-2})



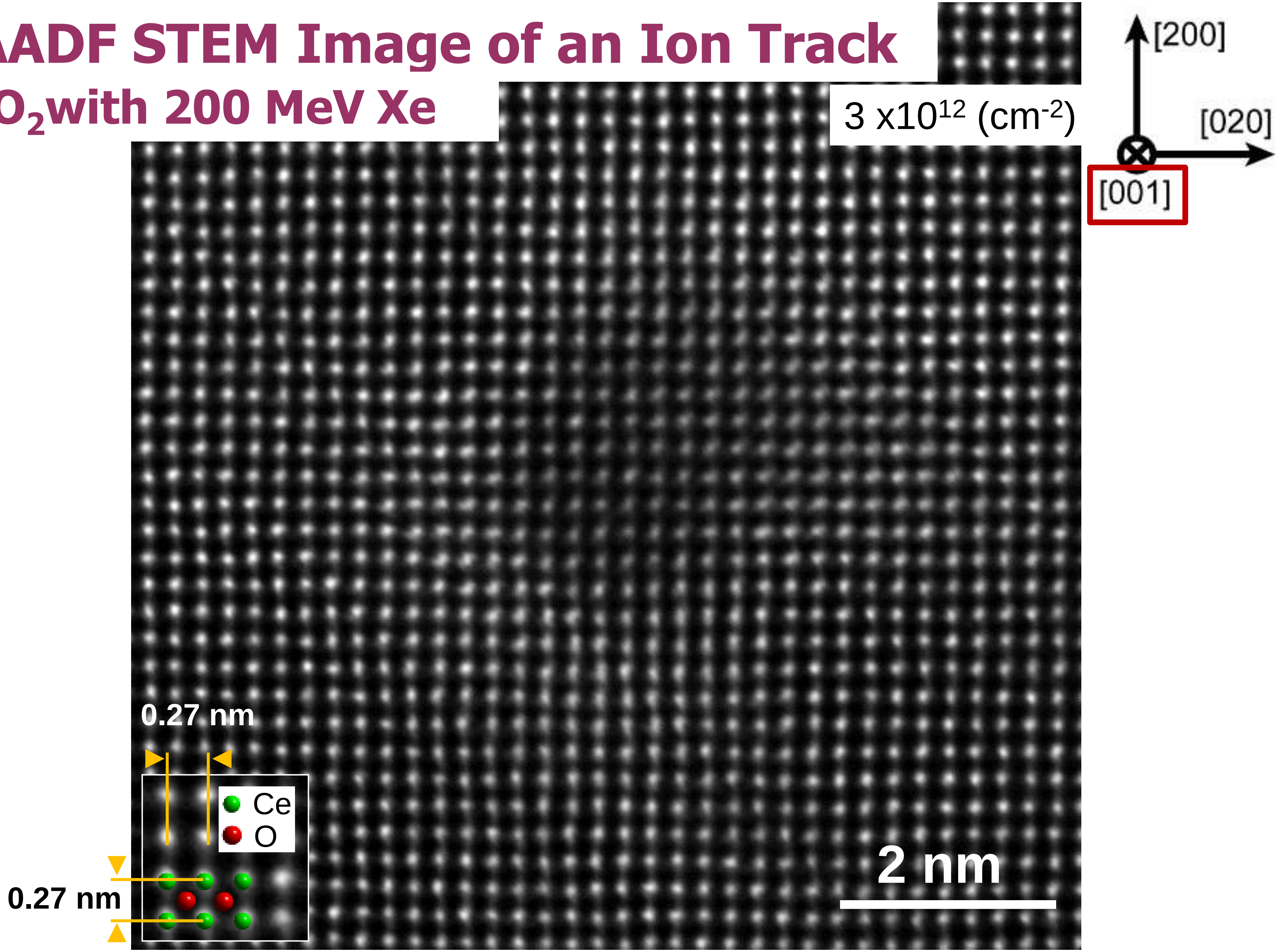


- Core damage regions (2-3 nm insize) show Fresnel contrast.

K. Yasuda et al. Int. J. Mater. Res. (2011) 140.

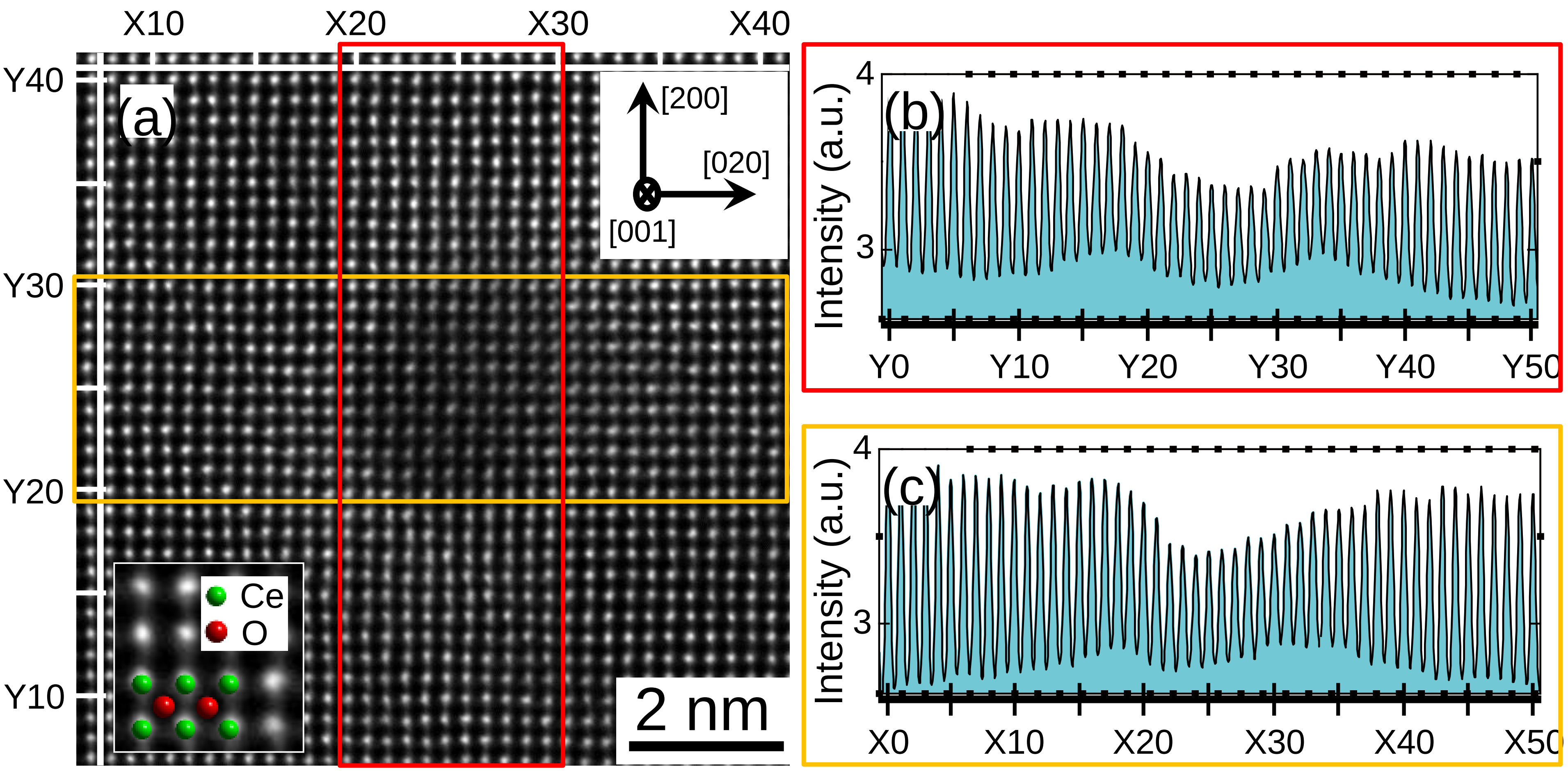
HAADF STEM Image of an Ion Track

CeO_2 with 200 MeV Xe



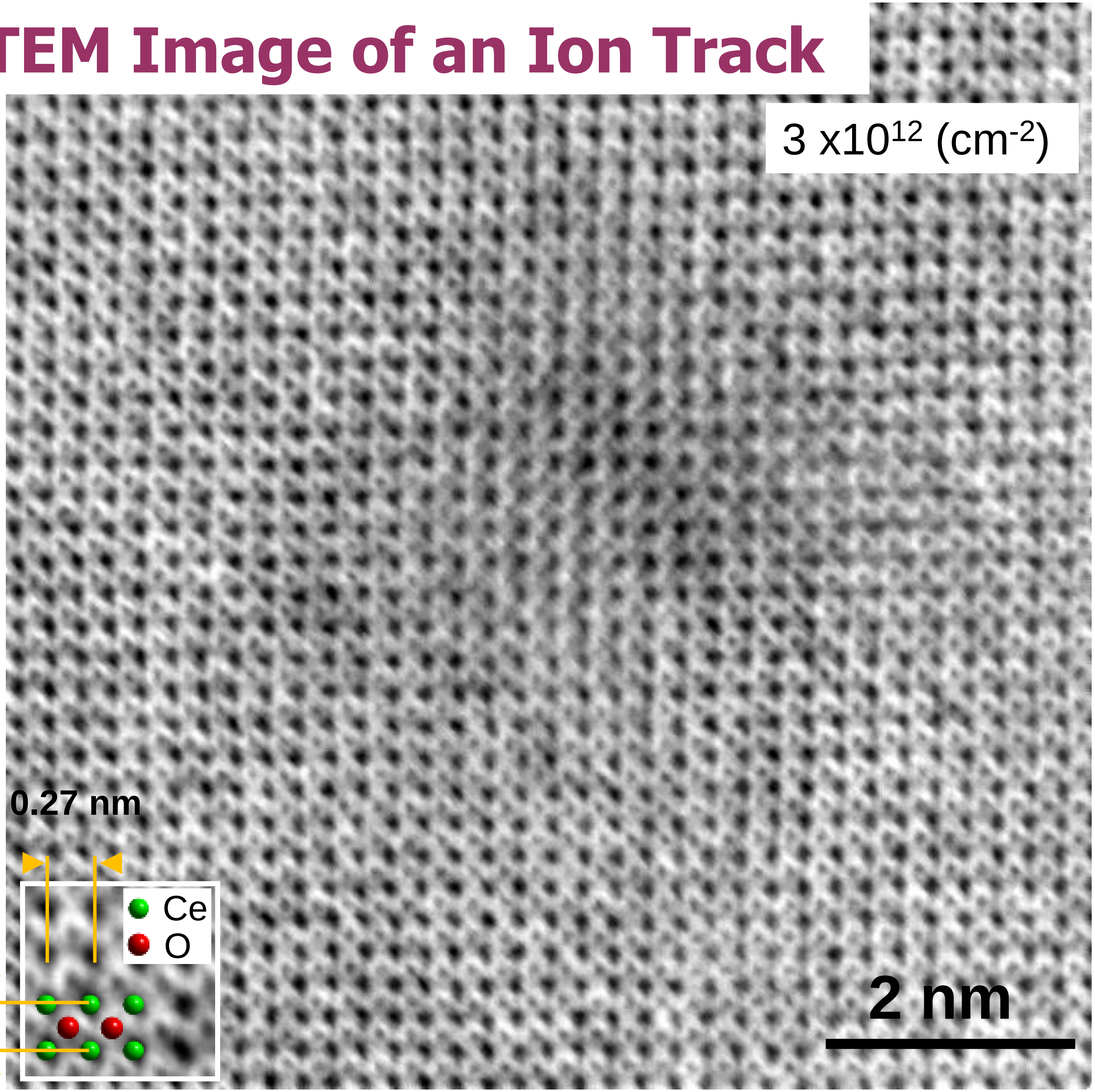
S. Takaki et al. NIMB 326 (2014) 140.

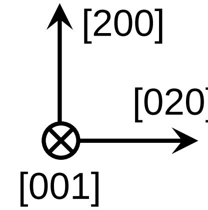
Signal intensity profile around the ion track



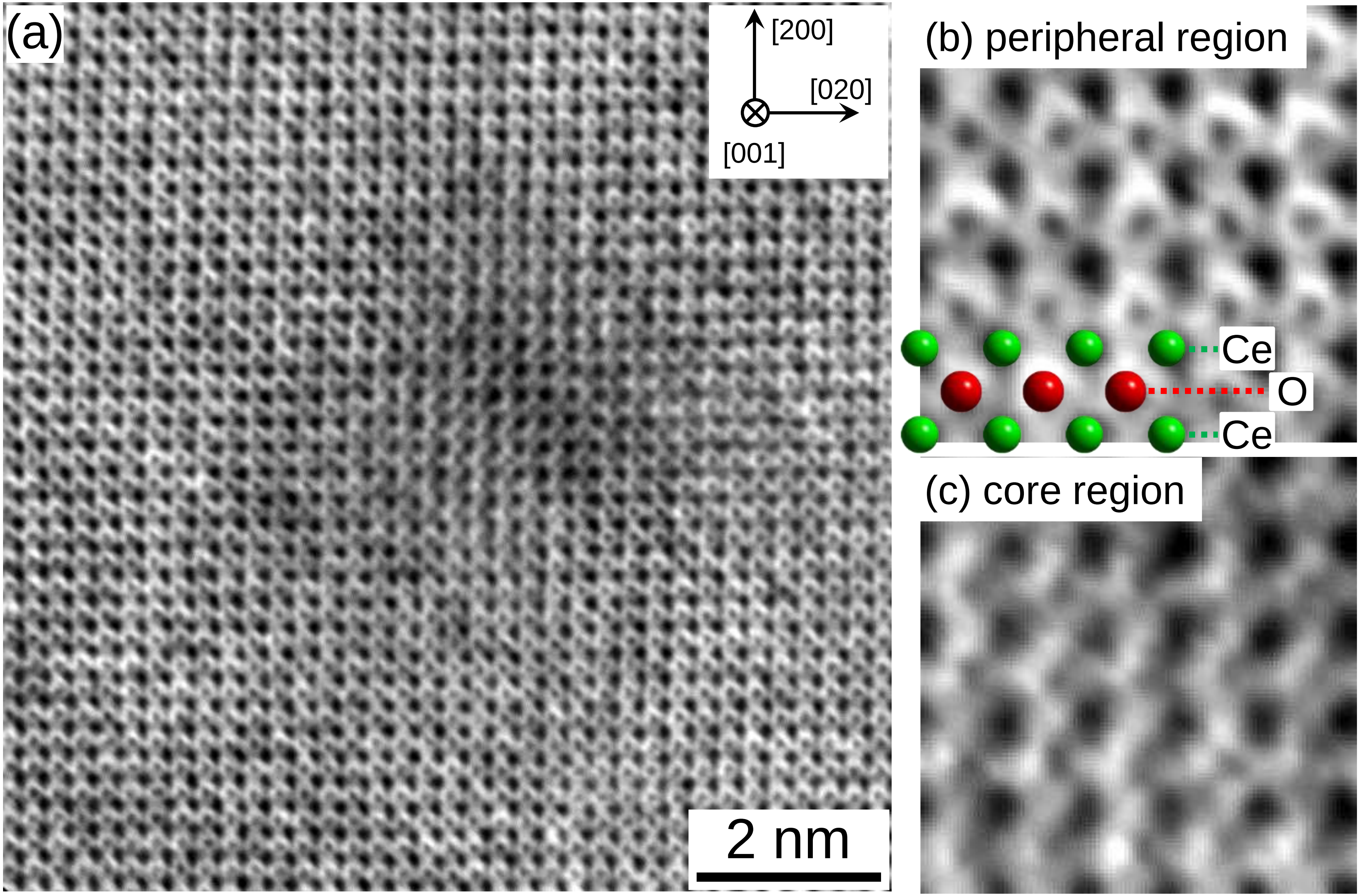
- Ce-signal intensity decreases at the center of ion track (~2-3 nm).
- The size, where the Ce signal intensity is decreased, is comparable to the size of Fresnel contrast in BF image .

ABF STEM Image of an Ion Track

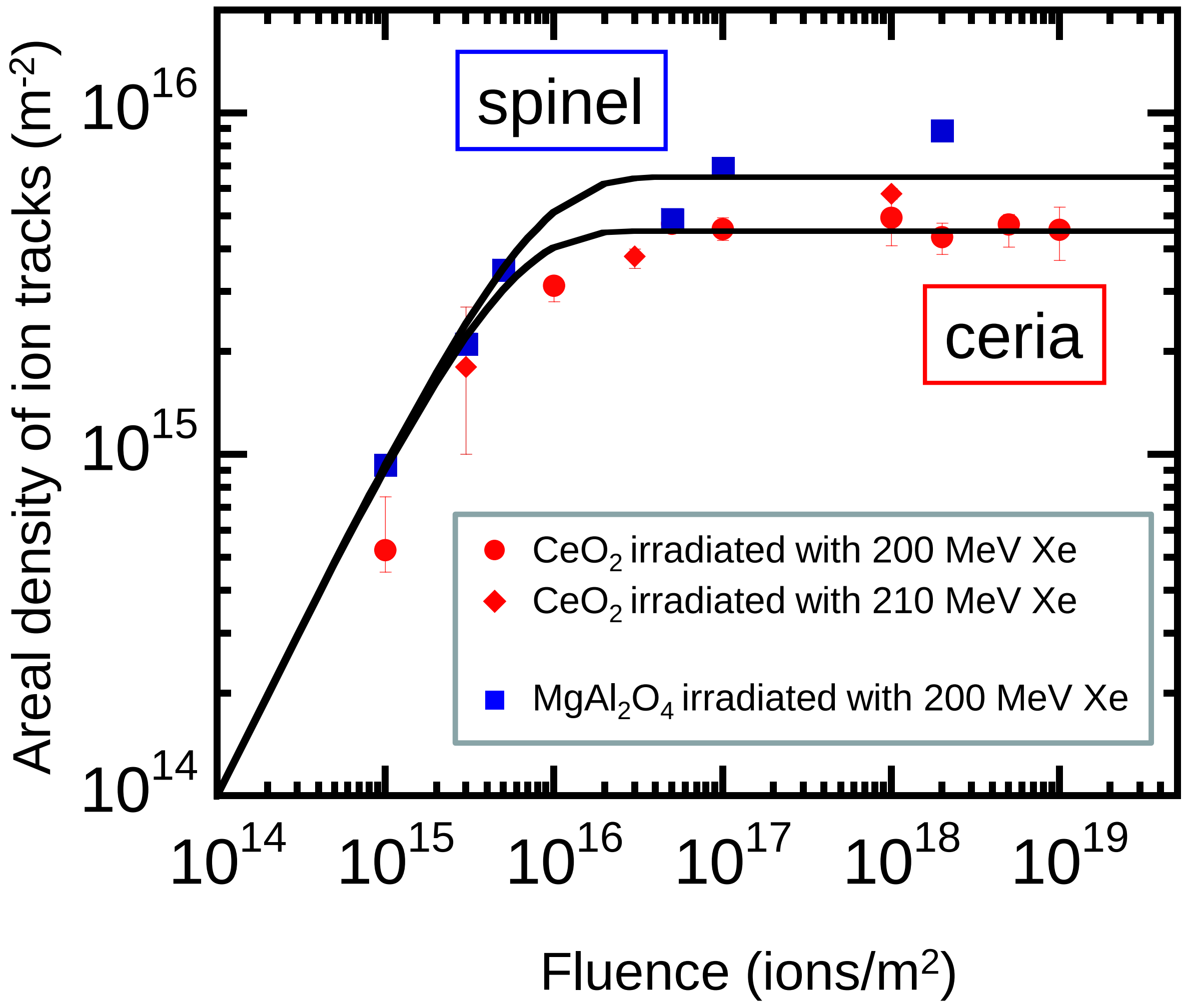




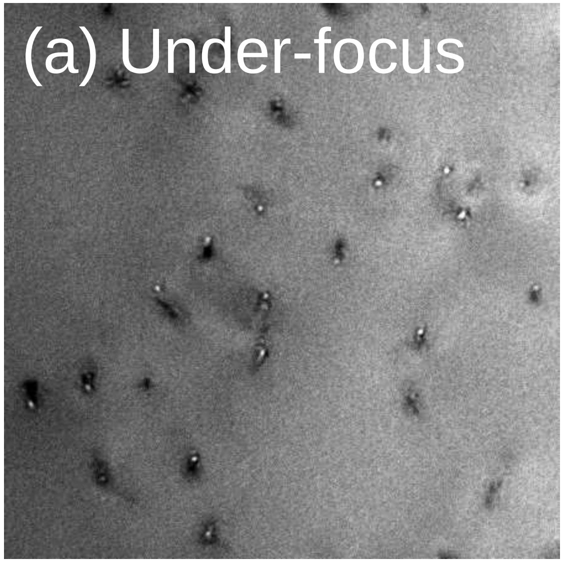
S. Takaki et al. NIMB 326 (2014) 140.


(a)
[200]
[020]
[001]
2 nm
(b) peripheral region
Ce
O
Ce
(c) core region

Accumulation of core damage region

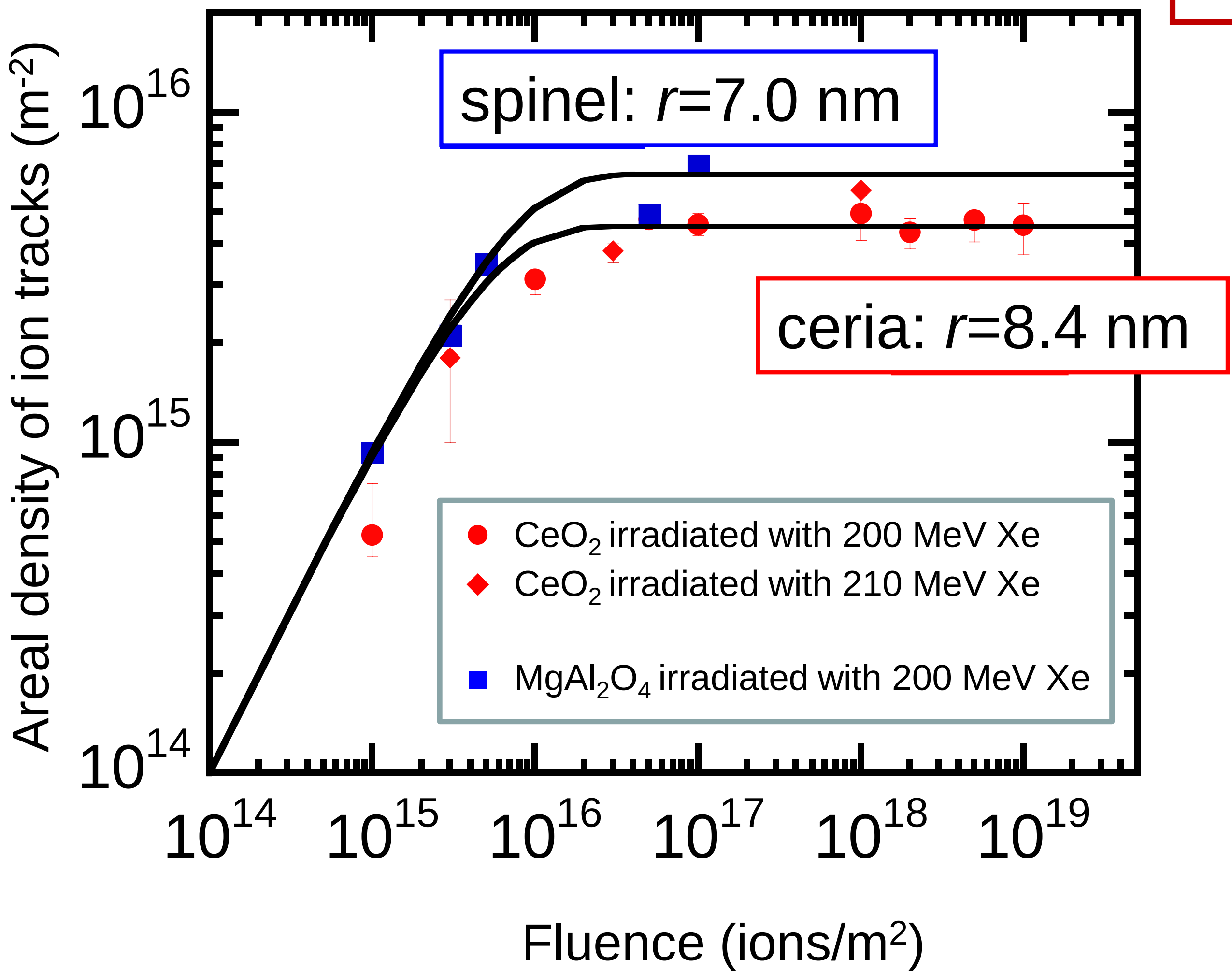


BF-TEM Fresnel contrast

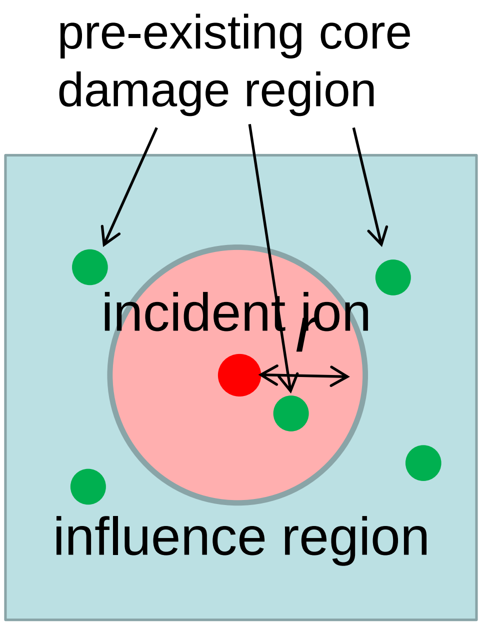


- The density is saturated at high fluence, although damage area does not covers the whole region. ⇒ balance between the production and recovery

Accumulation of core damage region



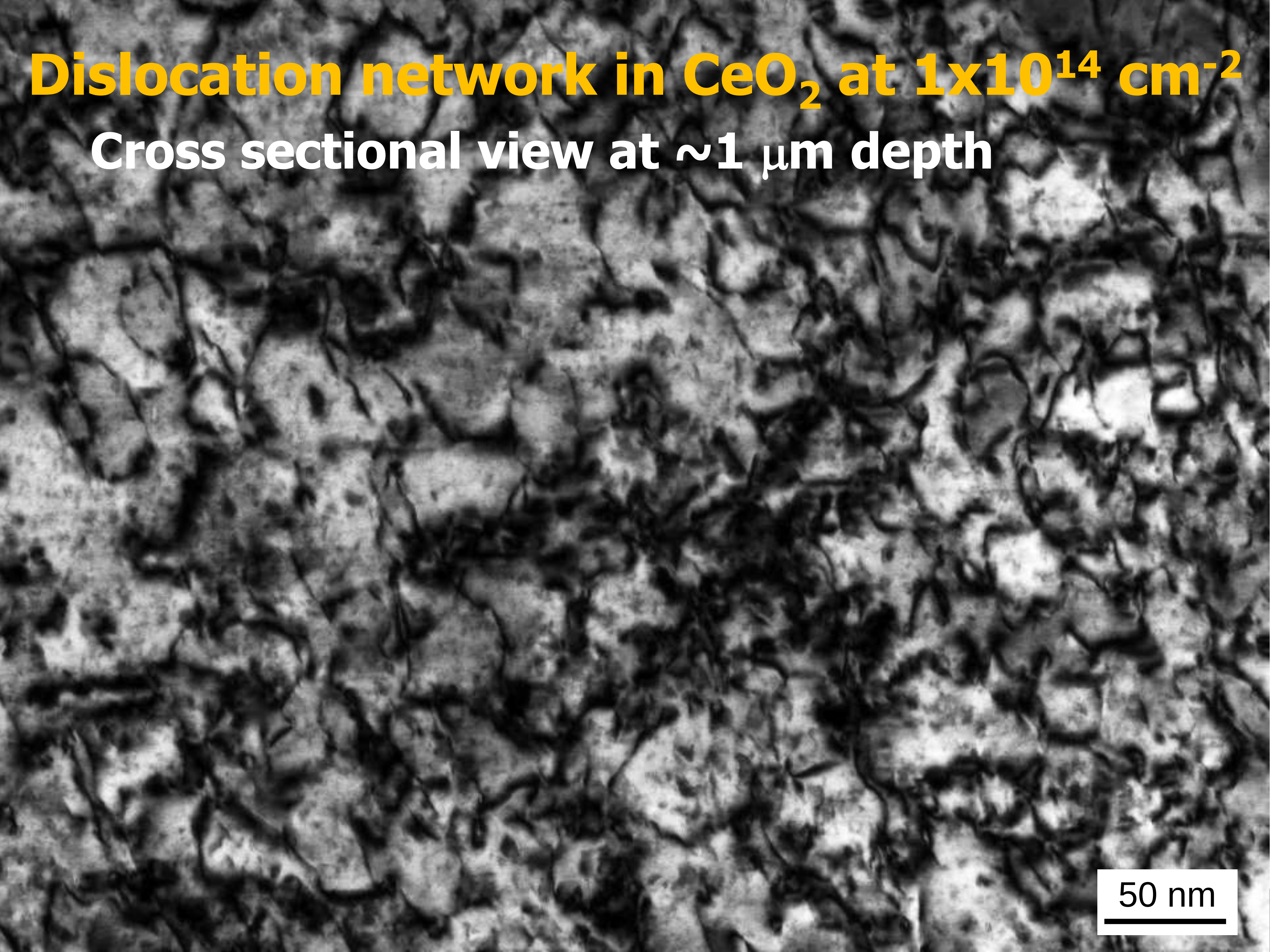
BF-TEM Fresnel contrast



- Interstitials are generated during the recovery process in the influence region to create core damage regions with high concentration of vacancy.

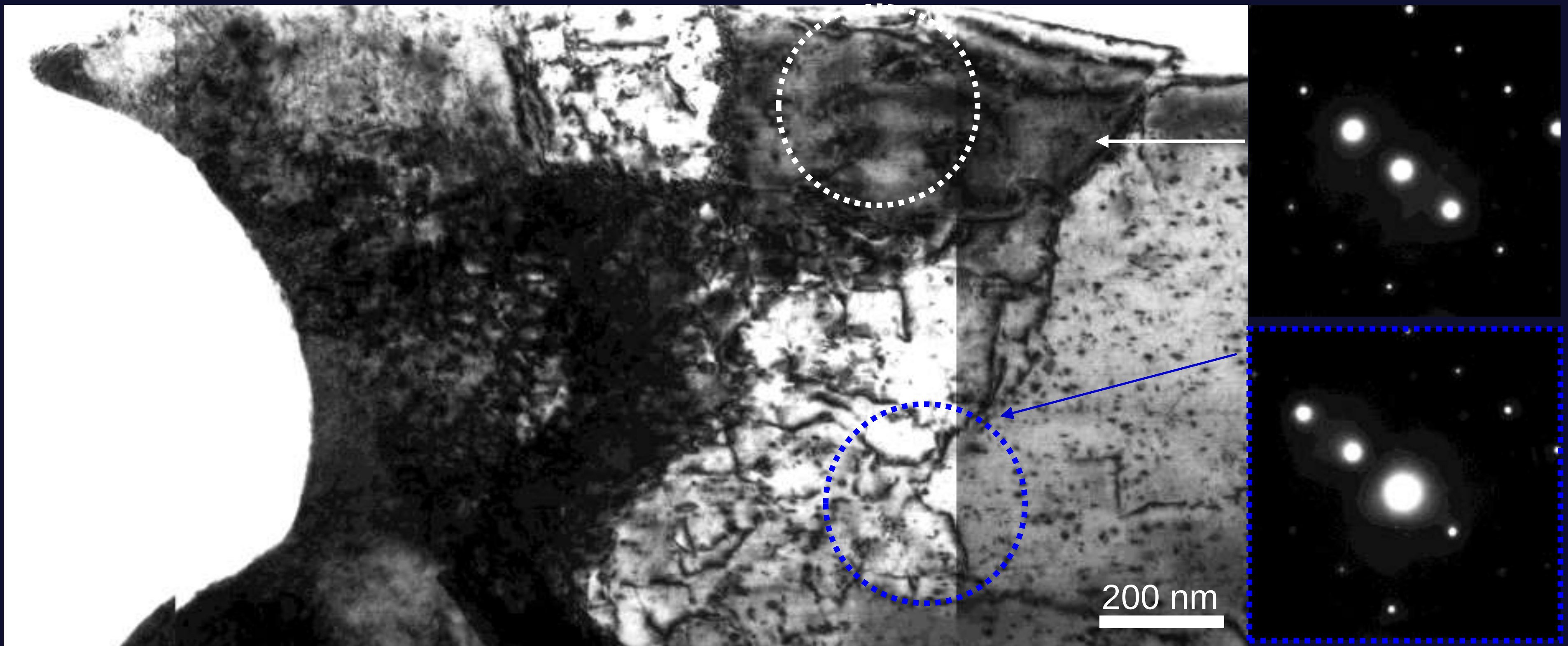
Dislocation network in CeO_2 at 1×10^{14} cm^{-2}

Cross sectional view at ~1 μm depth



Formation of subgrains at near surface region

210 MeV Xe ions: 1×10^{16} ions/cm^2 at 573 K ⇒ overlap with ~10^4 times

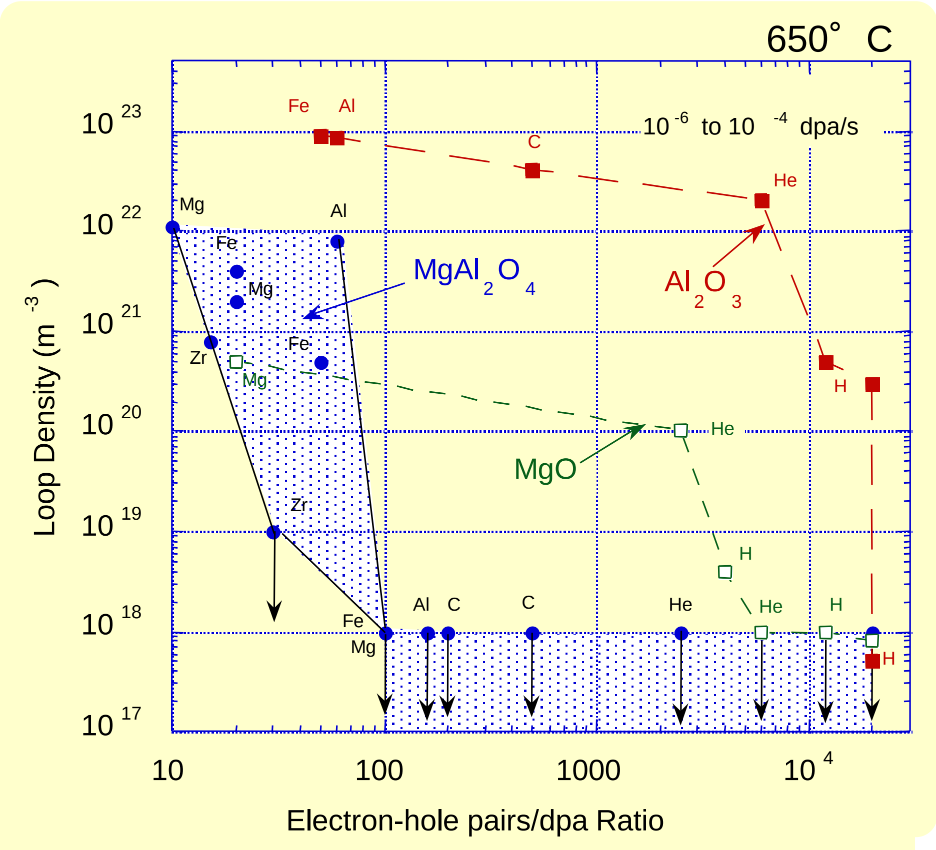


K. Yasuda NIMB 314 (2013) 185.

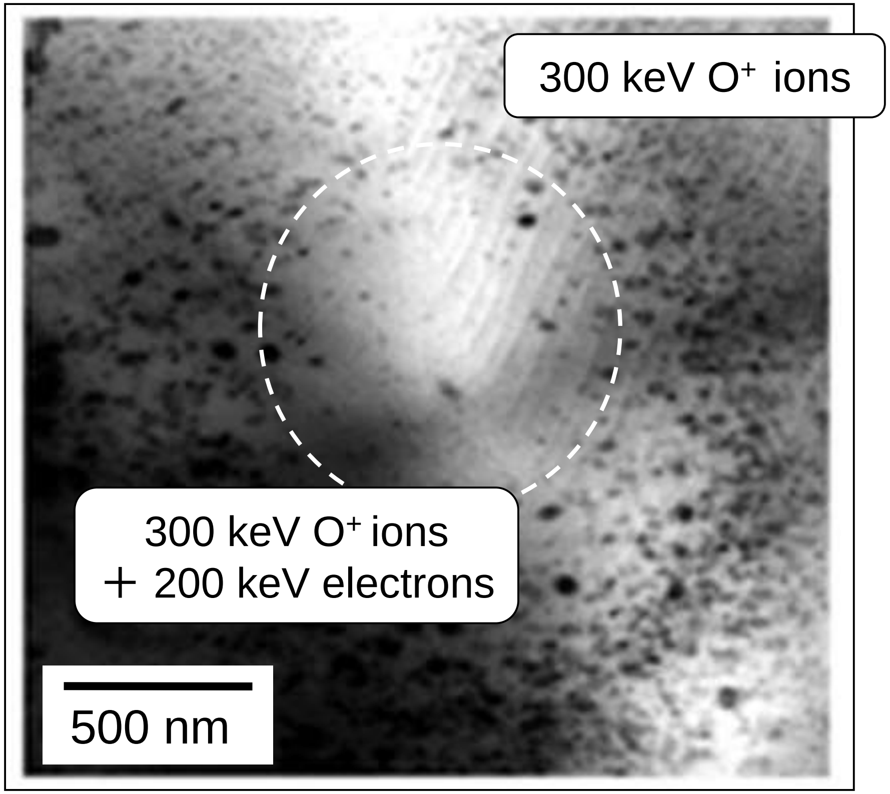
Topics

- Selective displacement damage of oxygen sub-lattice
- Structure of ion tracks
- Stability of dislocation loops under electronic excitation

Displacement damage and electronic excitation



S.J. Zinkle, MRS Symp. Proc. 439 (1997)



K. Yasuda, Philos Mag.78 (1998)

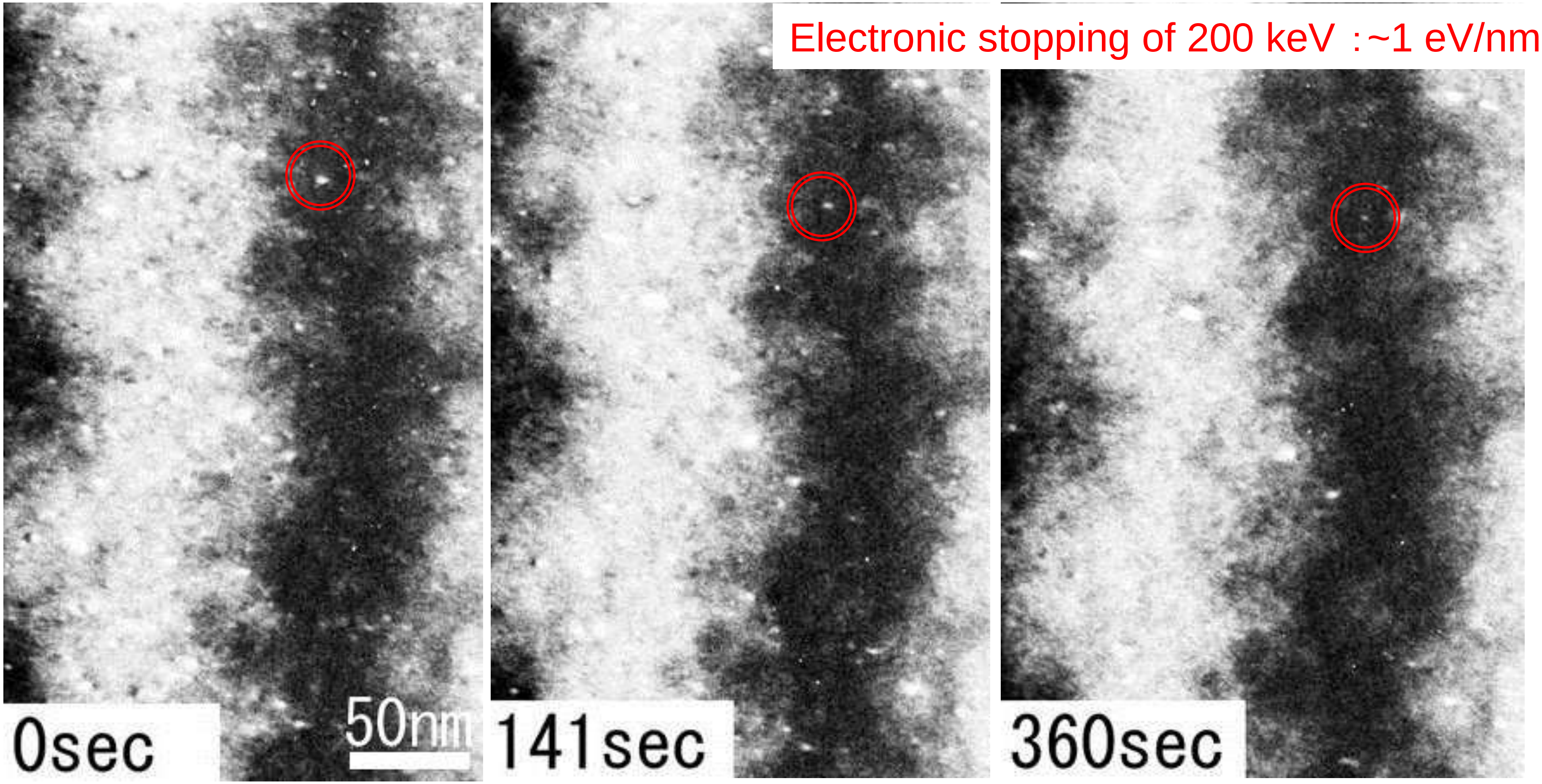
- Loop formation is suppressed by electronic excitation.
- Spinel is most sensitive to electroic exciation.

Elimination of dislocation loops under electronic excitation

300 K **$MgAl_2O_4$**

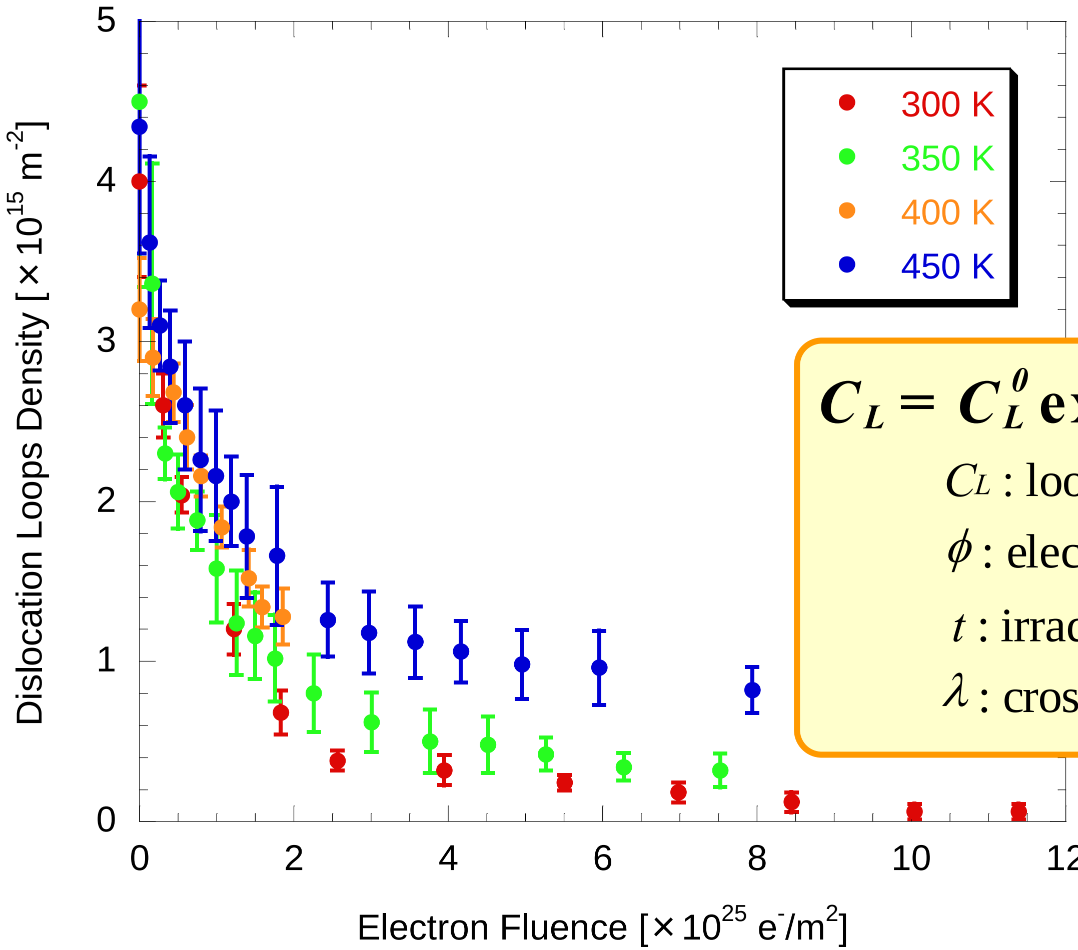
Electron flux：7.0×10^{22} e/m^2s

Electronic stopping of 200 keV ：~1 eV/nm



K. Yasuda NIMB 266 (2008) 2834.

Are e



$$C_L = C_L^0 \exp(-\lambda \phi t)$$

C_L : loop density,

ϕ : electron flux,

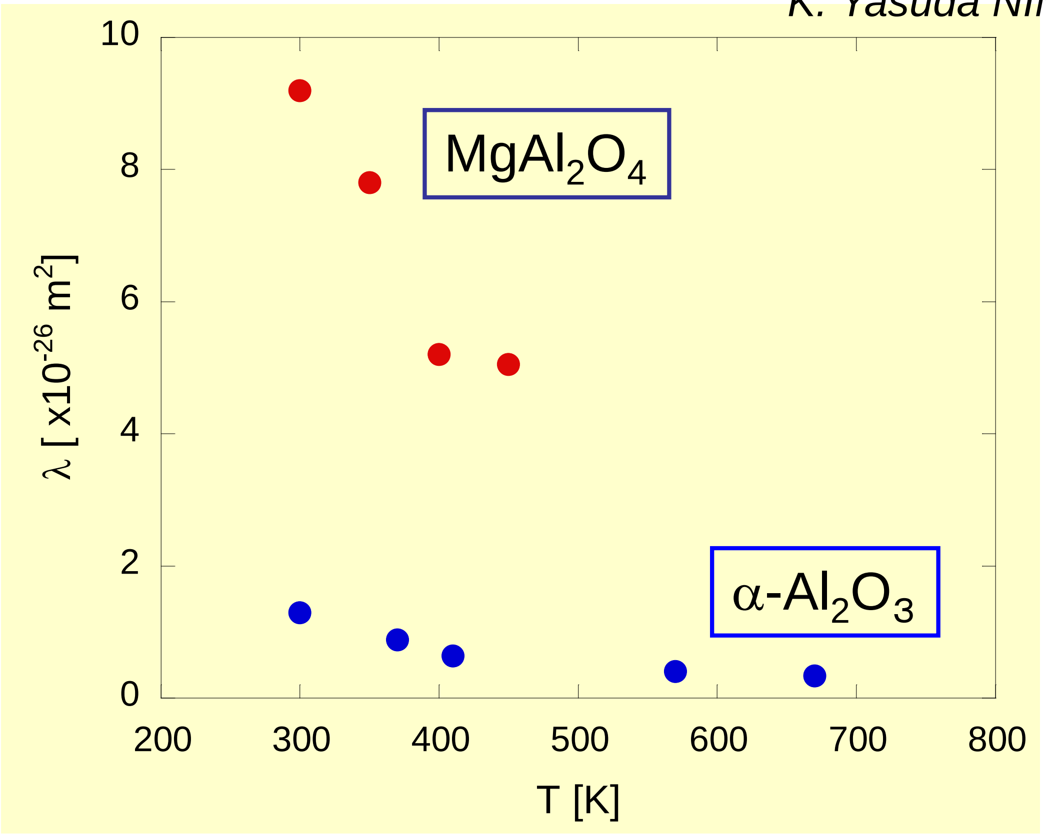
t : irradiation time ,

λ : cross section

⇒ *Evaluation of elimination cross section: λ*

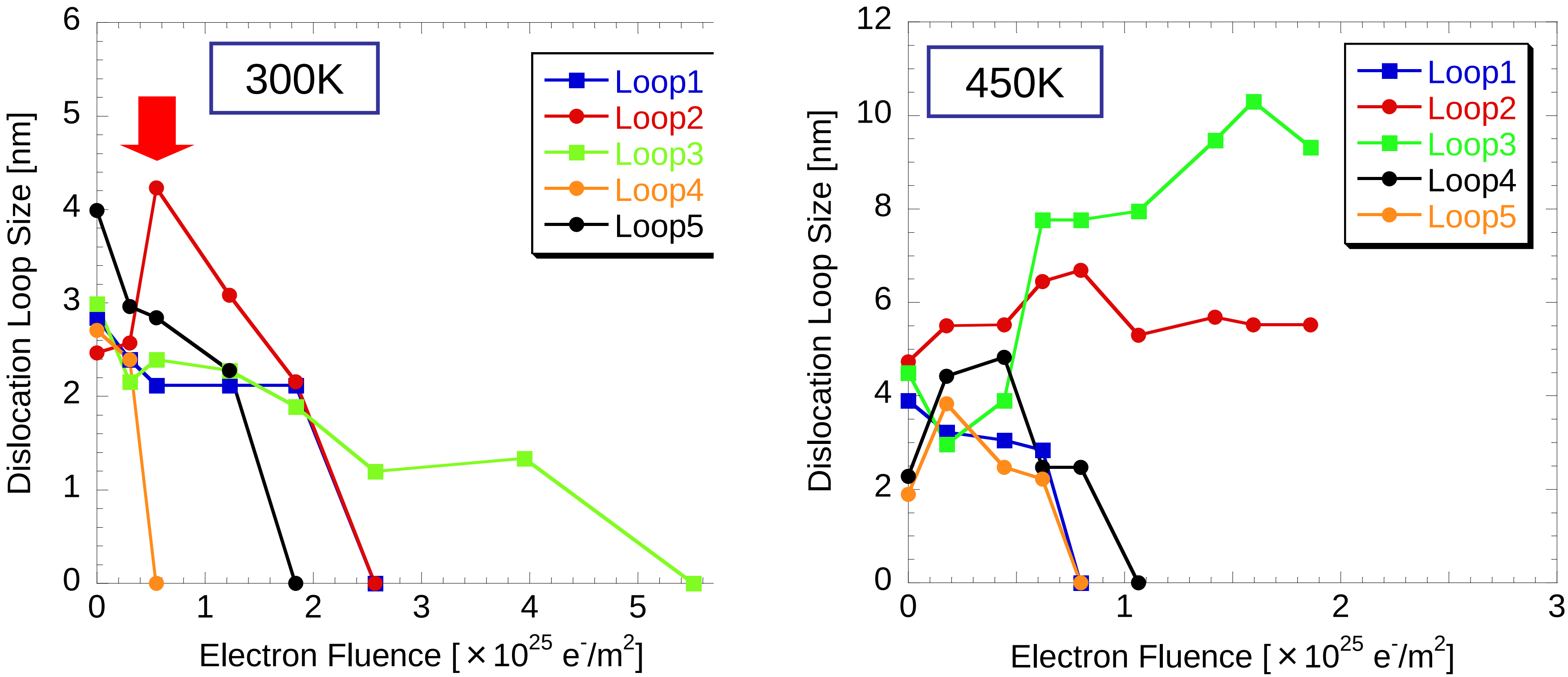
Cross section (λ) for elimination of loops

K. Yasuda NIMB 266 (2008) 2834.
K. Yasuda NIMB 191 (2002) 559.

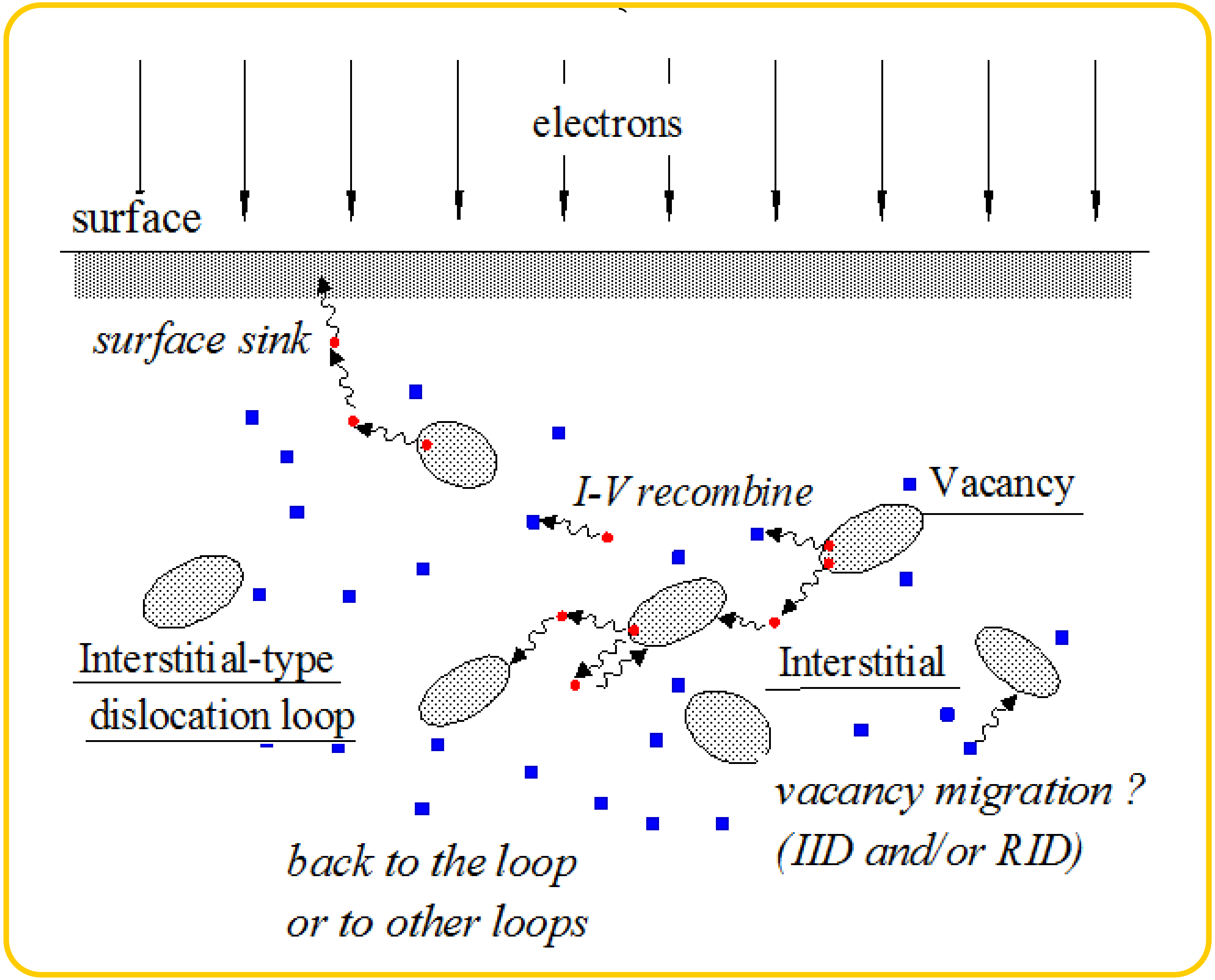


- Same temp.dependence⇒same mechanism：
  loops dissociate into isolated interstitials
- Loops in spinel is more unstable than alumina

□ Size variation vs. electron fluence



Schematic showing for the elimination of loops



Summary

- Selective displacement damage in fluorite-type oxides:
  - Charged dislocation loops with oxygen ions are formed on (111) planes
- Ion tracks in fluorite- and spinel-type oxides:
  - the core region is underdensed (with vacancies).
  - influence region ~15 nm in diameter (invisible in TEM)
  - interstitial generation to develop dislocation structure
- Instability of dislocation loops under electronic excitation:
  - dissociate loops into isolated interstitials
  - stability of loops: $MgAl_2O_44<Al_2O_3$

Thank you for your attention