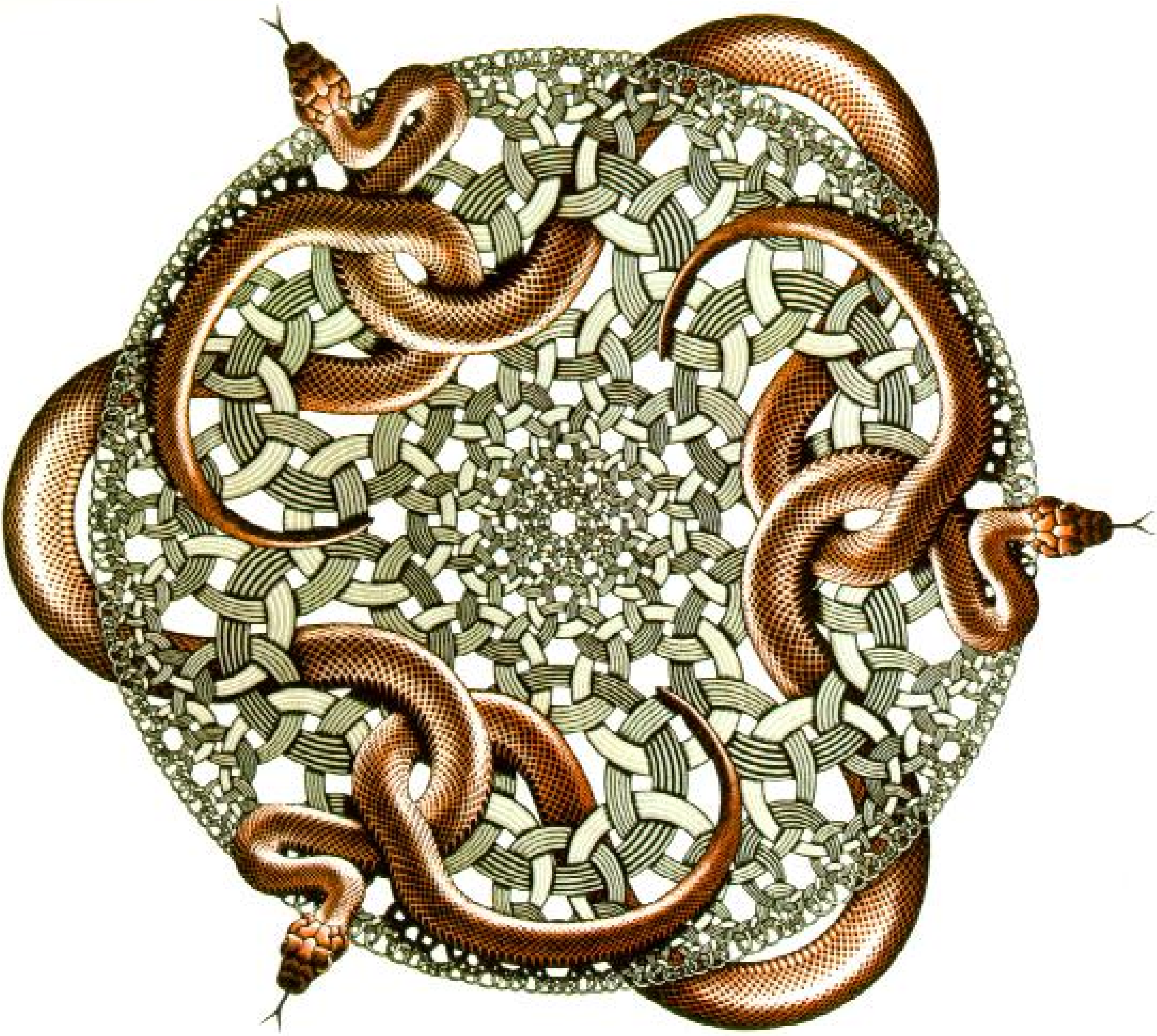
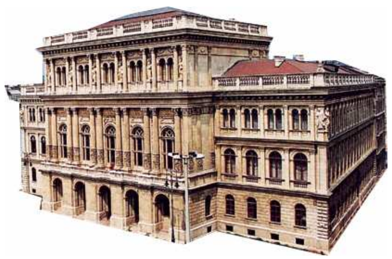


Swift heavy ion irradiation effects

in condensed matter

K. Havancsák

HAS-JINR Workshop 2004



Hungarian Academy of Sciences

Joint Institute for Nuclear Research

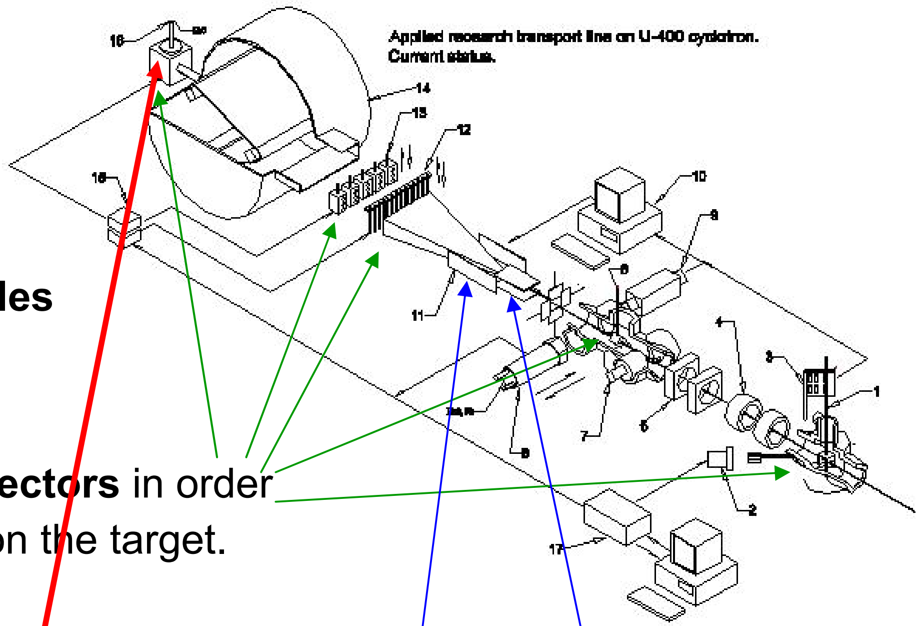
Use of heavy ions

- High energy **heavy ion beams** of the *U-400* cyclotron at the Laboratory of Nuclear Reactions, JINR, Dubna have been used since the early eighties for investigating irradiation effects in condensed matter.

- At first crystalline and amorphous **metals** were investigated.
  In the last years **polymers** and **ceramics** are in the focus of our interest, as well.

- This presentation is a **short review** of the results in the last years.

Ion beam transport line



- This heavy ion irradiation **facility** is suitable for irradiating **large** area polymer **films** just as **small** metal, semiconductor and ceramic **samples** in well controlled circumstances.

- The transport line is equipped with different **detectors** in order to control the beam current and its distribution on the target.

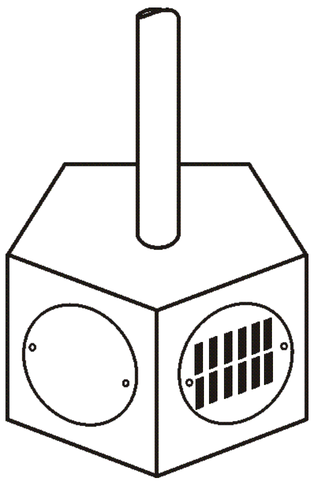
- The channel *10A* of *U-400* cyclotron is equipped by beam transport and diagnostical **units made** mainly by the **Hungarian party**.

- A homogeneous ion beam distribution has been achieved using horizontal and vertical high-frequency electrostatic or low-frequency electromagnetic **scanning systems**.
Ion beam homogeneity is better than *5%*.

- **Sample holder** for small sample irradiations.

Sample holder

- **Five-position** water or liquid nitrogen cooled **sample holder** is used for small sample irradiations. The surface of one side of the sample holder is as large as *32 cm*^{2}.



- The samples to be irradiated are **fixed** on this surface by **conductive glue**.
- During the irradiation the sample holder is in **vacuum** better than 10^{-6} *torr*.
- The ion current is measured by a **Faraday cup**.

Main parameters of the beam

- The attainable maximum **energy**: *3-5 MeV/nucleon*

- **Parameters** of the frequently used ions:

  $^{84}Kr^{+17}$, $E=246$ MeV, $I_{max} \approx 0{,}5\ \mu A$,

  $^{131}Xe^{+38}$, $E=600$ MeV, $I_{max} \approx 0{,}1\ \mu A$,

  $^{209}Bi^{+51}$, $E=710$ MeV, $I_{max} \approx 0{,}1\ \mu A$.

- To avoid overheating of the irradiated targets the **ion flux** density is usually maintained as **low** as $\sim 10^{8}$ *ions* $cm^{-2}s^{-1}$.

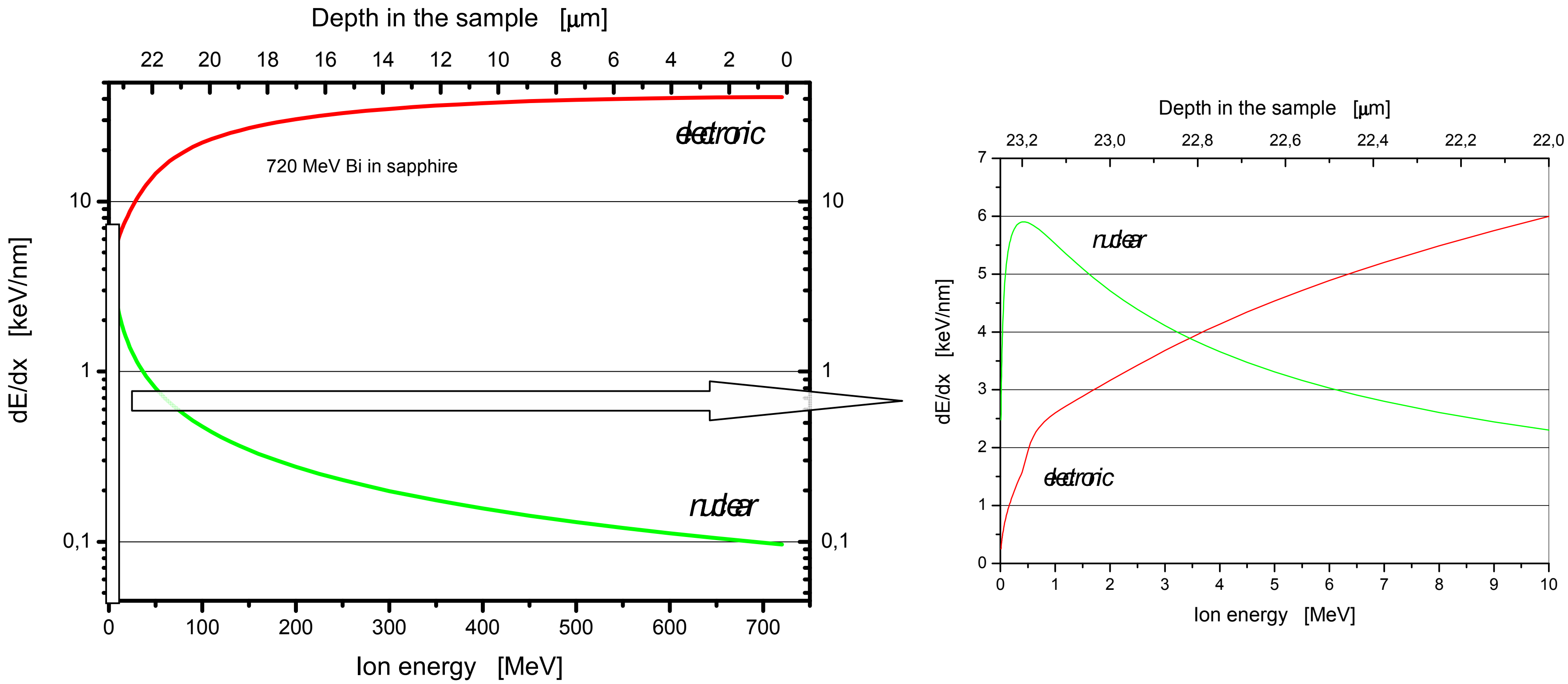
- With these fluxes **ion fluences of** $\boldsymbol{10^{8}\text{-}10^{14}}$ ***ions*** $\boldsymbol{cm^{-2}}$ can be attained in reasonable irradiation times.

Energy loss in solids

- Generally, slowing down of a swift heavy ion in solids results from

  1. **inelastic collisions** with electrons,
     (S_e *[keV/nm]*=electronic stopping power)

  2. **elastic collisions** with the nuclei of the target atoms
     (S_n *[keV/nm]*=nuclear stopping power).



It can be seen that with the exception of the low energy range (this is the end of the ion range) **the electronic loss dominates**, exceeding the nuclear one by 2-3 orders of magnitude.

Main features of the high energy heavy ion irradiation

- It can be seen that the **conventional ion** irradiation (energy less than a few *MeV*) produces electronic stopping power of a few *keV/nm* and therefore ion track damage does not occur and **nuclear collisions dominate**.

- **High energy heavy ion** irradiations create crystal demages through **inelastic electronic collisions**, as well.

As an example: heavy ion **stopping powers** at the entrance surface in sapphire:

Ion	Energy [MeV]	S_e [keV/nm]	S_n [keV/nm]
Kr	*250*	*17*	$2.3 \cdot 10^{-2}$
Xe	*600*	*29*	$3.4 \cdot 10^{-2}$
Bi	*130*	*25.3*	$3.9 \cdot 10^{-1}$
Bi	*275*	*34*	$2.1 \cdot 10^{-1}$
Bi	*720*	*41*	$9.6 \cdot 10^{-2}$

In case of high energy heavy ions electonic stopping dominates.

Crystal defects due to electronic stopping

- If the **heat conductivity is low** enough (insulators), then the energy of the exited electrons is transferred to the target atoms in the vicinity of the ion trajectory. As a result crystal defects are formed.

- This swift heavy ion collision displacement damage manifests itself in the form of

1. **Point defect** (defect cluster) generation and
2. **dislocation loop** formation at the periphery of the ion trajectory.
3. Disordered and even amorphous **ion track cores**.
4. High energy heavy ion collisions (elastic and inelastic) in a variety of solids create radiation **damage on the target surface**.

The aim of the investigations

- Questions to be answered:
  - The **physical mechanisms** responsible for **defect formation** (point defects, tracks) are still under debate (thermal spike vs. Coulomb explosion models).
  - The **threshold energies** of point defects, track and surface defect formation.
  - The **mechanism of amorphization** (if there is any) in the ion tracks.
  - The **mechanisms** of the **annihilation** of crystal defects during irradiation.
  - The **types of crystal defects** and their proportion depending on the type and energy of the ion.
  - The effect of crystal defects on the **macroscopical properties** of the materials, irradiation resistent materials and the defect production mechanisms in them.

- Besides the fundamental interest these investigations have practical interest as well. The densely ionizing **fission fragments** (e.g. *70 MeV I, Xe or Cs*) can create irradiation microstructures that are similar to **heavy ion created defect structures**. The fission fragments have important role in the construction materials of the fission reactors.

Tools for investigations

The different type of irradiation defects need different tools for their investigation.

Point defects, defect clusters: *positron annihilation and luminescence measurements*

Tracks (discontinous and continous), dislocations, amorphization: *Mössbauer effect, electron diffraction and high resolution electron microscopy, CRBS.*

Internal stresses, phase transformation: *Mössbauer effect, X-ray diffraction.*

Surface defects: *scanning probe microscopy (STM, AFM).*

Cooperating participants

Departments of the Eötvös Loránd University, Hungary:

Department of solid state physics,
Department of general physics,
Department of Nuclear Chemistry

Methods: X-ray diffraction, Mössbauer effect, theoretical work.
Participating persons: J. Gubicza, K. Havancsák, E. Kuzmann, G. Szenes,
S. Stichleutner , Z. Illés

Institutes of the Hungarian Academy of Sciences:

Research Institute for Technical Physics and Materials Science (MFA),
Research Institute for Nuclear and Particle Physics (RMKI)

Methods: scanning probe microscopy (SPM), positron annihilation, RBS.
Participating persons: L.P. Biró, J. Gyulai, Á. Illés, Zs. Kajcsos

Laboratory of the Joint Institute for Nuclear Research (JINR), Dubna

Flerov Laboratory of Nuclear Reactions, Center of Applied Physics,

Methods: luminescence measurements, atomic force microscopy.
Participating persons: S. N. Dmitriev, V. A. Skuratov, A. Yu. Didyk,
O. M Ivanov, V. A. Kuzmin, A. E. Efimov

Cooperating participants

University of Bundeswehr, München, Germany
Institute for Nuclear Physics
Methods: pulsed, low energy positron beam facility
Participating persons: L. Liszkay, P. Sperr

University of Coimbra, Portugal
Department of Physics
Methods: positron annihilation (low energy positron beam)
Participating persons: P. M. Gordo, A. P. de Lima

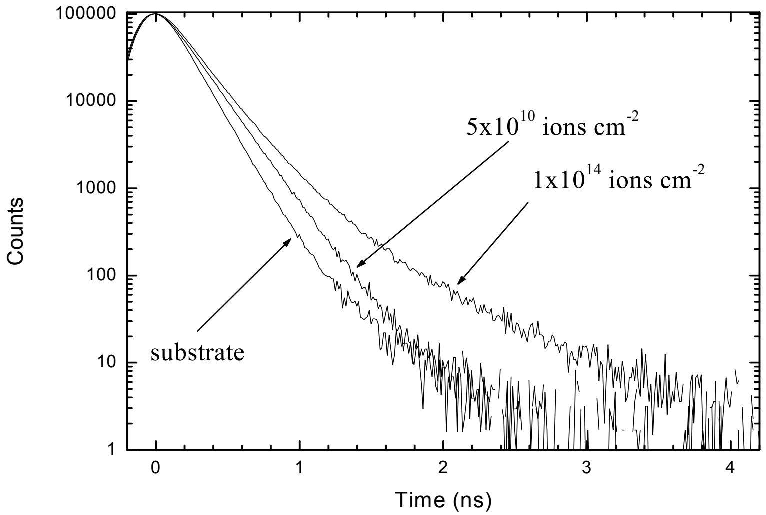
Oak Ridge National Laboratory, Oak Ridge, USA
Metals and Ceramics Division
Methods: electron diffraction and high resolution microscopy
Participating person: S. J. Zinkle

Positron lifetime study

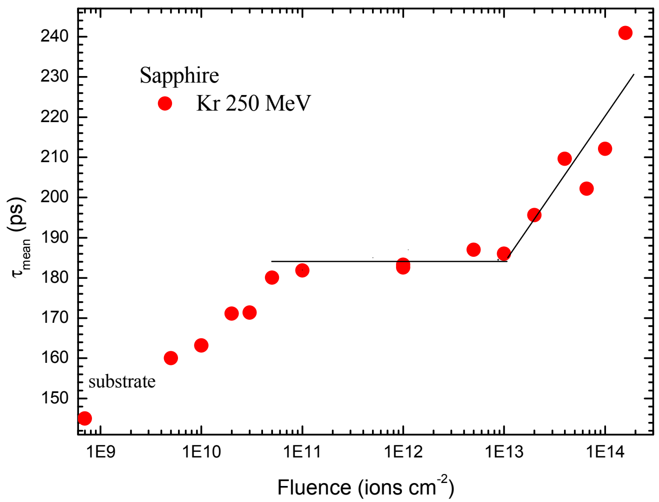
Positron annihilation spectroscopy has been extensively used in the study of implantation-induced defects.

Positrons are **extremely sensitive to vacancies, vacancy complexes and voids**. The mechanisms of creation of these defects, the dose dependences can be studied by this technique. Its use can yield complementary information to other spectroscopy methods.

Example: positron lifetime measurements can give information on the different stages of defect creation vs. ion dose.



Positron lifetime in sapphire before and after irradiation with different doses



The mean lifetime as a function of dose. The figure shows different stages of point defect creation.

L. Liszkay, P. M. Gordo, K. Havancsák, V. A. Skuratov, A. de Lima, Zs. Kajcsos:
Positron lifetime and Doppler broadening study of defects created by swift ion irradiation in sapphire
13th International Conference on Positron Annihilation, Kyoto, Japan, 7-12 September 2003.
Materials Science Forum 445-446, 138-140 (2004).

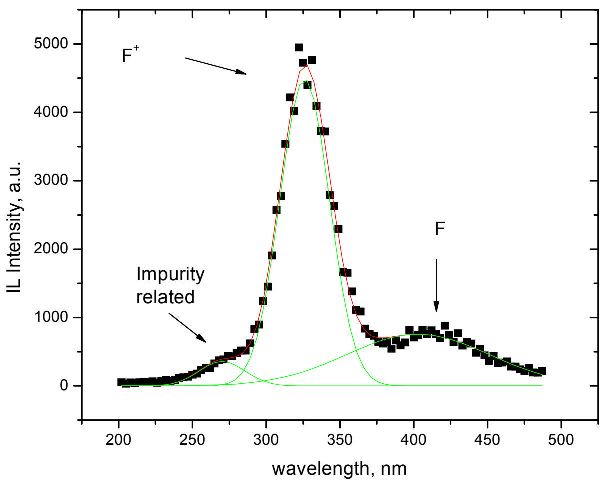
Luminescence measurements

Luminescence measurements have been **started recently** at LJAR.

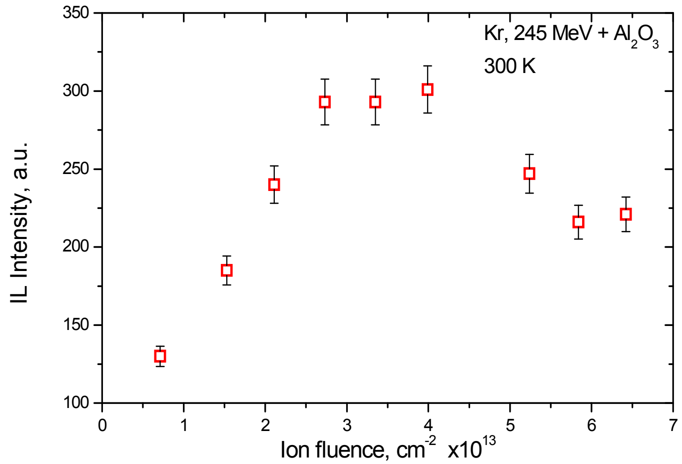
The luminescence spectrums are sensitive to **charged point defects**.

We hope that **luminescence** can be a useful complementary measurement to **positron results** in the study of irradiation induced point defects.

Demonstrative example: The luminescence intensity of F^+ centres (oxigen vacancy with one trapped electron), and F centres (oxigen vacancy with two trapped electron) changes as a function of ion fluence.



Typical luminescence spectrum measured on sapphire under 245 MeV Kr ion irradiation



Luminescence intensity in F^+ band (328 nm) as function of 245 MeV ion fluence

Scanning probe microscopy

Two measuring techniques: scanning tunnelling microscopy (**STM**),
atomic force microscopy (**AFM**).

Sensitive and informatic methods for **surface analysis**.

In case of appropriate apparatus and accurate experimentation even **atomic resolution** can be attained.

High energy heavy ion irradiation creates surface defects that can be investigated with STM and AFM.

In several publication we have studied the nature of surface defects on graphite, mica, and ceramic materials such as sapphire (Al_2O_3), *MgO*, spinel ($MgAl_2O_4$).

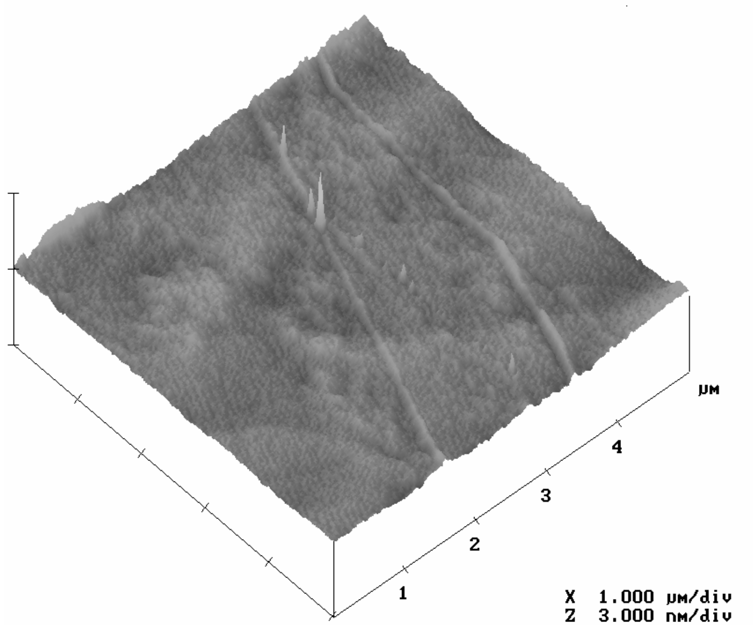
The aim of such investigation is defining:

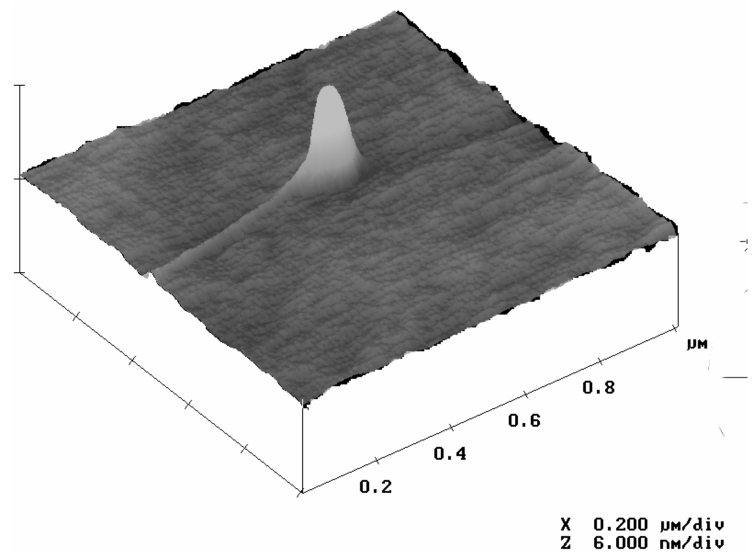
- **type of** surface **defects** in different target materials,
- **dependence** of their density **on the fluences**
- **threshold energy** of their formation
- **their dimensions** depending on the ion type and energy.

Scanning probe microscopy

In an early publication on **graphite** (**conductive** in *c* plane) we have shown:

- There is **no** visible **trace of projectile ion** (the threshold energy of surface defects through electronic stopping is higher than *12 keV/nm*).
- The **knocked on *C* atoms** can travel as long as several *μm* parallel to the *c* plane.
- These ***C* atoms can produce nanoscale surface defects** (hillocks and craters) by **nuclear collisions**.





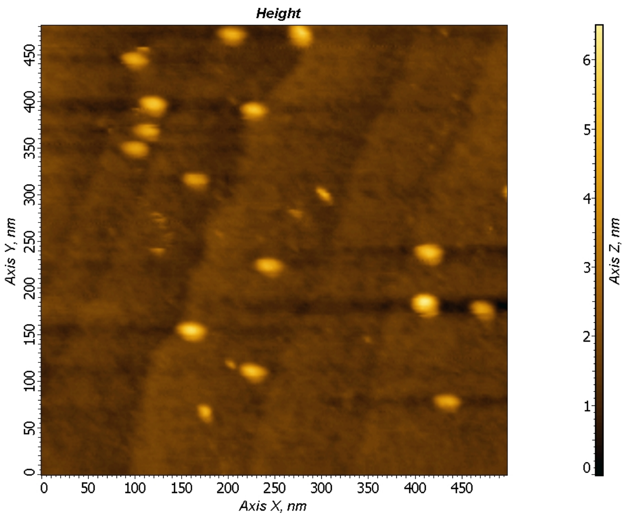
*K. Havancsák, L. P. Biró, J. Gyulai, A. Yu. Didyk: STM and AFM Observations of Damage Produced by Swift Ne and Kr Ions in Graphite, Radiation Measurements **28**, 65-70 (1997)*

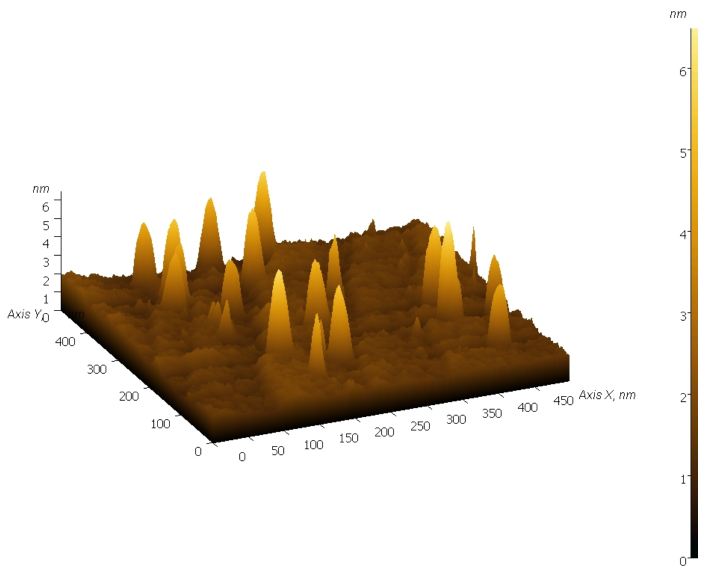
Scanning probe microscopy

In a recent work it was shown on **insulating ceramic** samples that:

- The **projectile ions produce nanoscale hillock** like surface defects above a certain threshold energy.
- These defects have **inelastic** collision (electronic stopping) **origin**.
- These properties depend on the **type and energy of ions**.

Example on **sapphire** irradiated with 720 MeV Bi ions at room temperature:





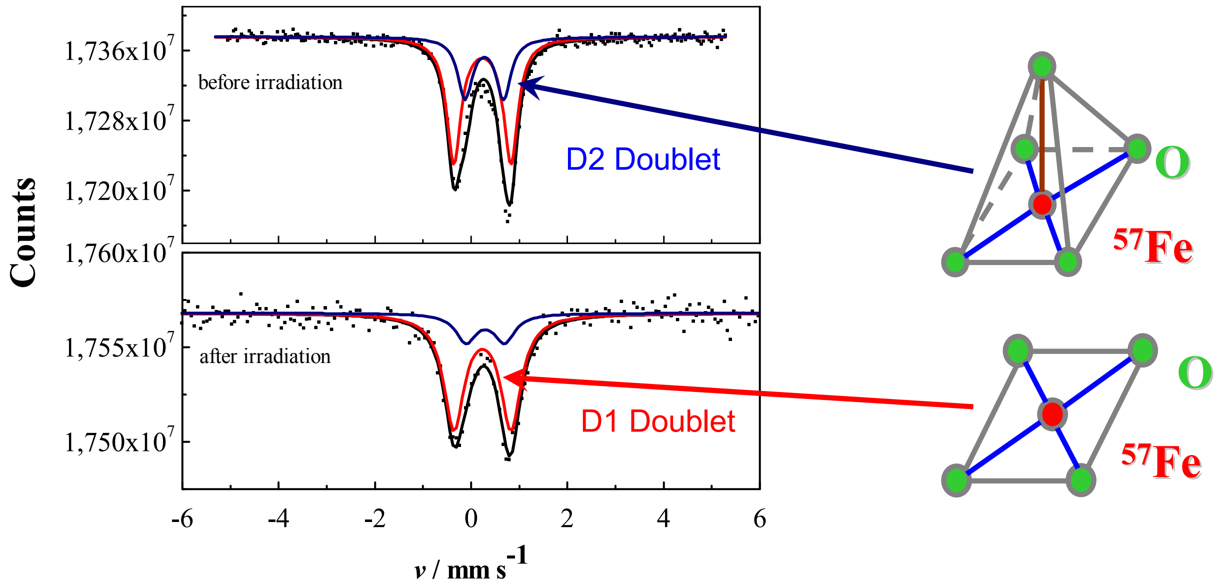
V.A. Skuratov, S.J. Zinkle, A.E. Efimov, K. Havancsák: Swift heavy ion induced modification of Al2O3 and MgO surfaces Nuclear Instruments and Methods in Physics Research B 203 (2003) 136-140.

Mössbauer measurements

Our former Mössbauer measurements have demonstrated that this method is very **sensitive** to **structural changes** due to heavy ion irradiation.

In the last years we investigated:

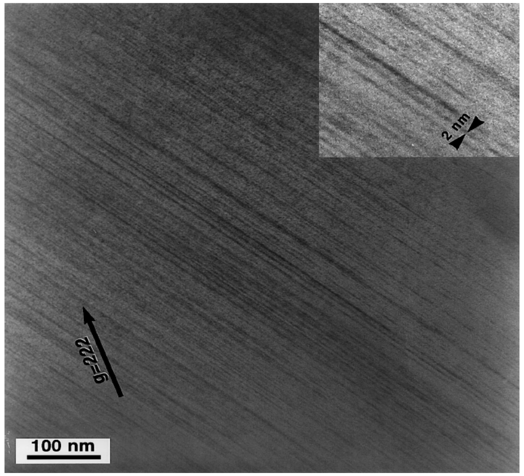
- **Thin Fe-layers** irradiated with *246 MeV* energy $^{86}Kr^{8+}$ ions at room temperature and **amorphous Fe phase** was found after irradiation.
- ***Fe-Ni-Cr* multilayers** (thickness of *5-10 nm*) irradiated with *246 MeV* energy $^{86}Kr^{8+}$ ions at room temperature **new non-equilibrium** ferromagnetic *Fe-Ni-Cr* and paramagnetic *Fe-Ni-Cr* **phases were found**, which never form in thermal preparation.
- **High temperature superconductive** $(Bi_{0.93}Pb_{0.17})Sr_{1.9}Ca_{2.05}(Cu_{1.02}{}^{57}Fe_{0.01})_3O_y$ **material** was irradiated with 246 MeV energy $^{86}Kr^{8+}$ and the **structural changes** were charcterized.



Electron microscopy

- **High resolution electron microscopy and electron diffraction** can be useful tools in studying latent tracks, structural changes and defect structure.
- Spinel ($MgAl_2O_4$), sapphire (Al_2O_3), MgO irradiated with Kr, Xe, and Bi ions were investigated. The latent **track parameters** and the **defect structure** in the vicinity of the latent track have been determined.

Examples:



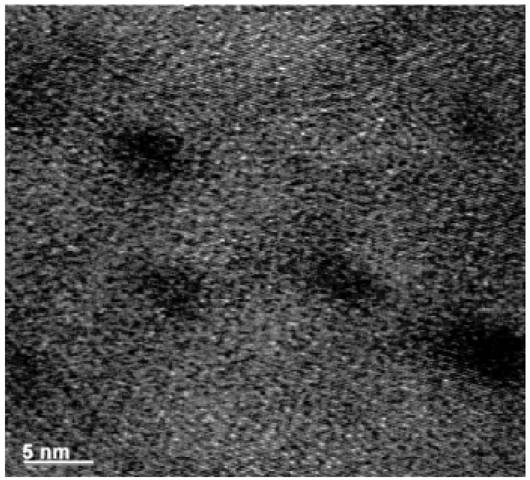
***Ion tracks in spinel** irradiated with 430 MeV Kr ions to a fluence of 1.1×10^{12} cm^{-2} at room temperature.*
*The average TEM **track diameter is ~2 nm**.*

V.A. Skuratov, S.J. Zinkle: Track formation and dislocation loop interaction in spinel irradiated with swift heavy ions Nuclear Instruments and Methods in Physics Research B 141 (1998) 737-746.

Electron microscopy

- **High resolution electron microscopy and electron diffraction** can be useful tools in studying latent tracks, structural changes and defect structure.
- Spinel ($MgAl_2O_4$), sapphire (Al_2O_3), MgO irradiated with Kr, Xe, and Bi ions were investigated. The latent **track parameters** and the **defect structure** in the vicinity of the latent track have been determined.

Examples:



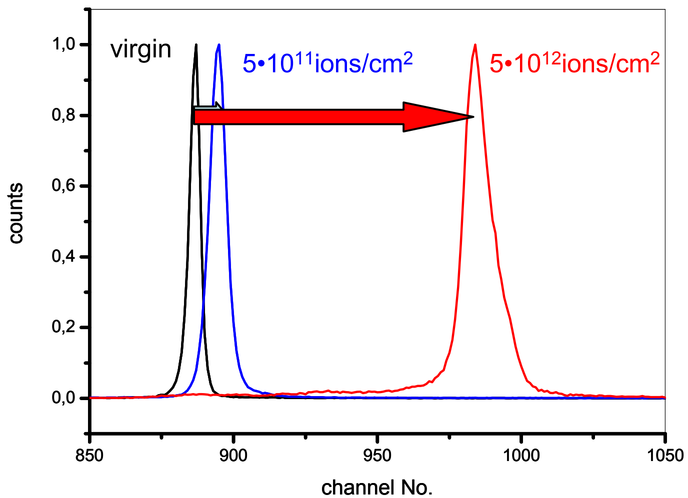
*High-resolution **lattice image of α-Al_2O_3** irradiated with 710 MeV Bi ions a fluence of 7×10^{12} cm^{-2} at room temperature.*
*The average TEM **track diameter is ~3 to 4 nm**.*

V.A. Skuratov, S.J. Zinkle, A.E. Efimov, K. Havancsák: Swift heavy ion induced modification of Al_2O_3 and MgO surfaces Nuclear Instruments and Methods in Physics Research B 203 (2003) 136-140.

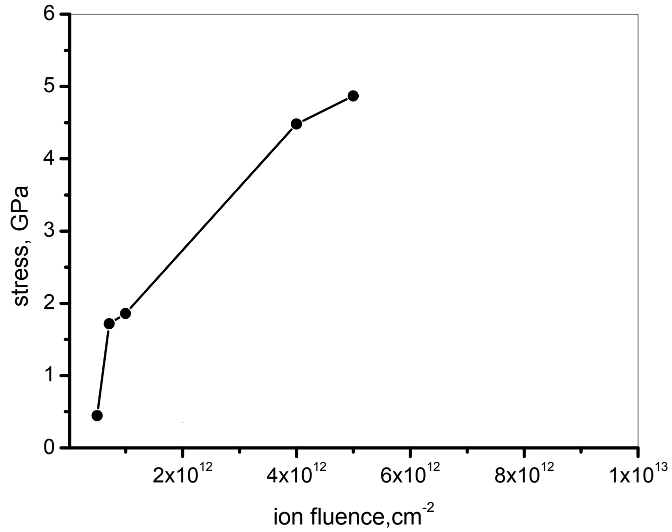
X-ray measurements

- X-ray diffraction measurements are sensitive to
  -changes in crystal-plane distances (internal stresses),
  -phase transformation (amorphization).

Example on internal stresses due to Bi ion irradiation in sapphire:



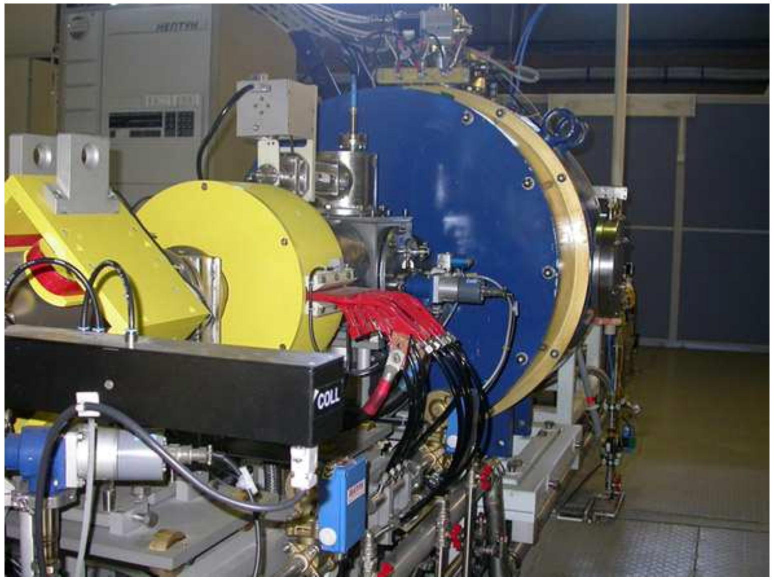
X-ray line shifts as the Bi ion-fluence increases.



The change of the internal stress as a function of Ion irradiation fluence.

Plans for the future

- To continue complex measurements on ceramic and semiconductor samples to clarify the adequacy of the competing theoretical models.
- To use molecular-dynamical computer simulation of defect creation in amorphous and crystalline materials due to heavy ion irradiation.
- To clarify the correlation between surface and bulk radiation damage induced by heavy ions.
- To broaden the range of ceramic materials which are candidate reactor construction materials ($MgAl_2O_4$, MgO, Al_2O_3, ZrO_2, SiC, ZrC, AlN, Si_3N_4).
- Intense use of the new accelerator IC-100 in the future. The energy of ion beams of this accelerator is close to the energies of fission fragments.



Conclusions

- In the last years a **wide international cooperation** was built up in order to study swift heavy ion irradiation defects in crystalline and amorphous condensed materials.

- The measuring **methods** used proved to be **successful**.

- In the period *2000-2004* the participants of this project published ***15* papers**, and had ***18* conference** contributions in the form of invited talks, oral lectures and poster demonstrations. In addition, in this field **one diploma work** and **two *PhD* dissertations** have been succesfully finished, and **one *PhD* dissertation** is still under work.

- After this overview four **more detailed lectures** on different subjects:
  - -G. Szenes: Swift heavy ion induced **tracks in** some III-V **semiconductors**.
  - -V. A. Skuratov: **Scanning probe microscopy** on heavy ion irradiated oxides.
  - -Zs. Kajcsos: **Positron lifetime and Doppler broadening** study of defects created by swift heavy ion irradiation.
  - -S. Stichleutner: **Mössbauer study** of heavy ion iradiated *Fe-Ni-Cr* multilayers.