Extreme Chemistry and the properties of Warm Dense Matter

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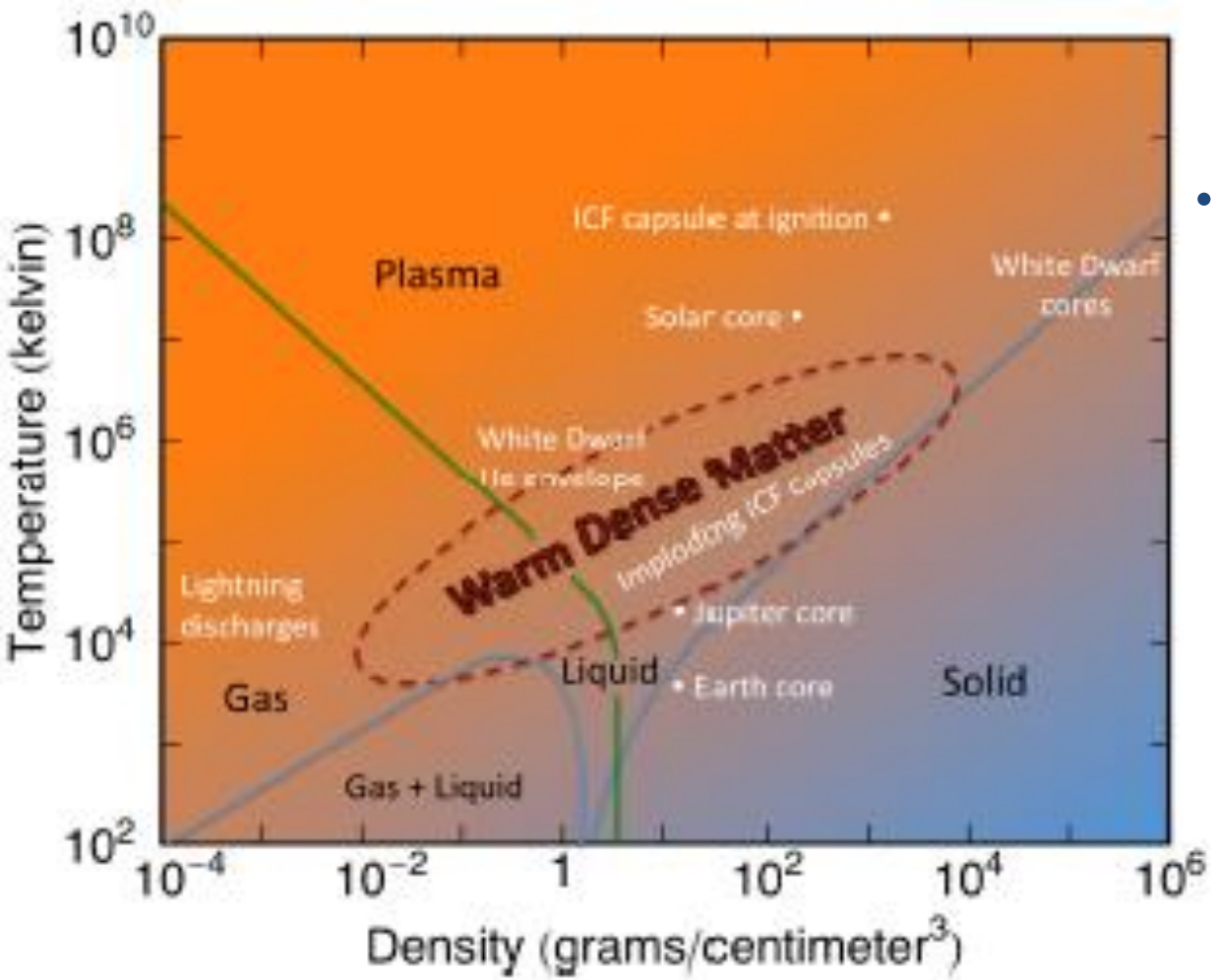
Extreme Chemistry and the properties of Warm Dense Matter

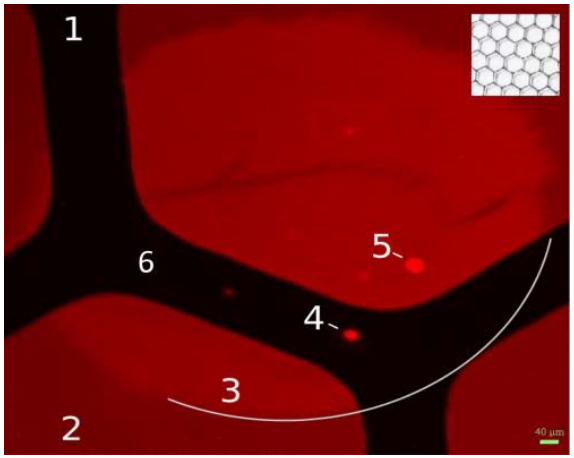


- What are opportunities for next 5 to 10+ years?
  - Drivers
  - Targets
  - Diagnostics
  - Theory and simulations

Extreme Chemistry and the properties of Warm Dense Matter

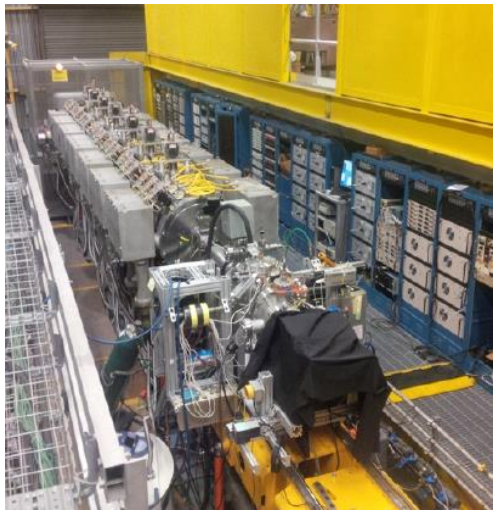
- **Warm dense matter** (~1 – 10 eV, ~1 Mbar, ~10^{11} J/m^3)
  - Ubiquitous in nature (e. g. large planets, …)
  - Underpinning for inertial fusion
  - And also in many laboratory and industrial settings
    - e. g. e-beam and laser processing
  - Transition regime with multi-phase characteristics, solid-liquid-vapor
  - **Very impressive progress, <u>and</u> large gaps in our knowledge of the equation of state of WDM**

- **Extreme Chemistry**
  - High temperature and pressure
  - Drive phase transitions and steer energy flow
  - Stable novel materials phases ?
    - Rapid heating and quenching
      - e. g. in micro/nano-structured targets



Extreme Chemistry and the properties of Warm Dense Matter

1. **Drivers**
   - Photons
     - See BELLA-I talk and white paper by Eric Esarey
     - See poster and white paper by Sven Steinke
   - Ions
     - See talk and white paper by John Barnard
     - See talk and white paper by Erik Gilson and Peter Seidl
   - …
2. **Targets**
   - Metals, Minerals, Hydrogen, …
   - Plus: micro/nano-structuring
3. **Diagnostics**
   - See talk and white paper by Cameron Geddes
4. **Theory and simulations**
   - See talk and white paper by Jean Luc Vay
   - See poster and white paper by Stepan Bulanov



Drivers for Extreme Chemistry and studies of Warm Dense Matter

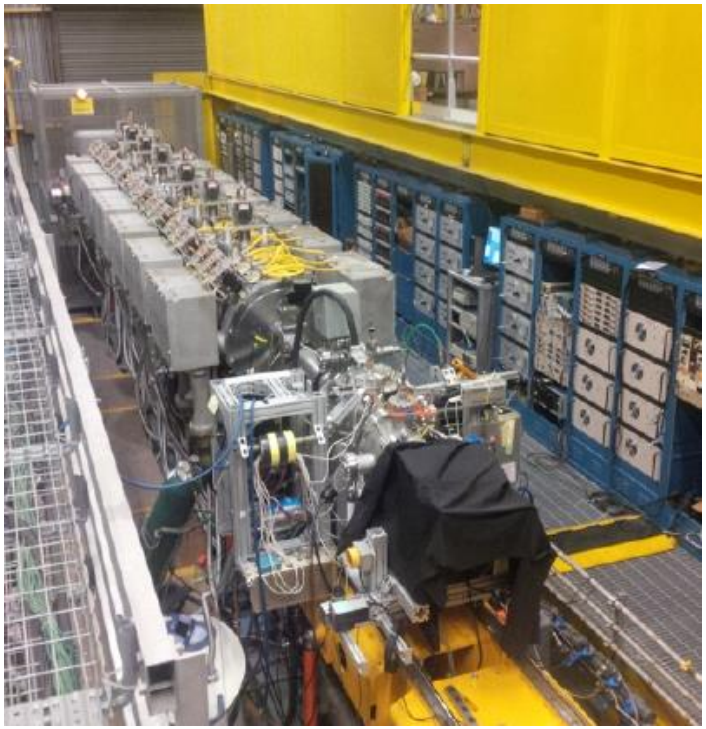
1. Drivers
   - Photons (optical, x-ray)
   - Electrons
   - Ions

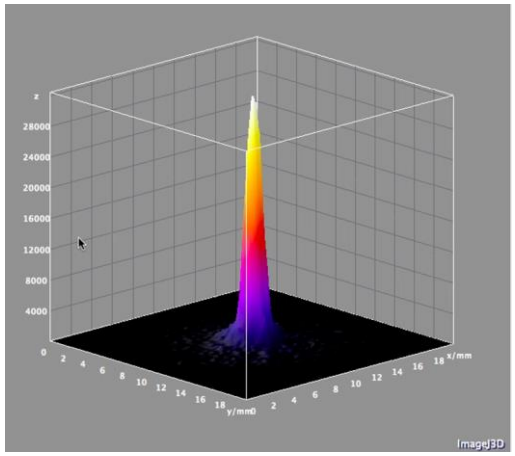
Driver properties
- Irradiance, power
- Energy and energy deposition profile
- Heated volume
- Radiation environment at target
- Access
- Pairing with diagnostics
- …

- Opportunity to enhance capabilities of diverse drivers and to increase access to drivers matched for specific experimental campaigns
  - X-ray FELs
  - Long pulse, high power lasers
  - PW lasers
  - Pulsed power
  - Pulsed ion accelerators

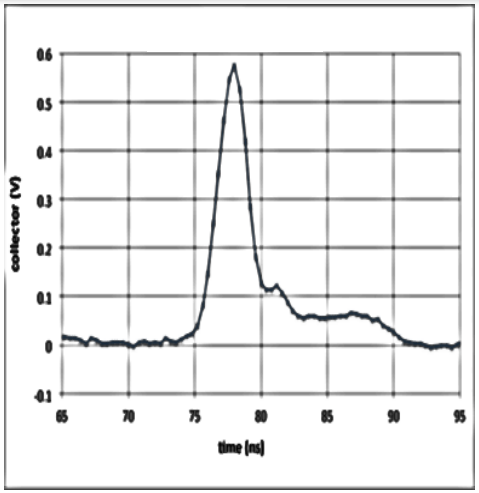
- Frontiers for WDM:
  - Uniform heating of large volumes
  - fs-scale synchronization of driver and probe beams
  - Easy access

Intense, pulsed ion beams at Berkeley Lab – NDCX-II



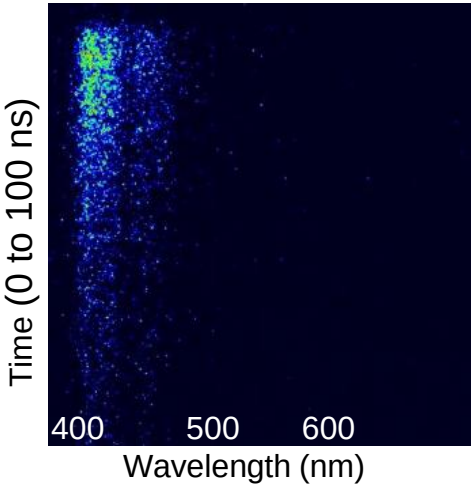


Beam spot 1.3 mm FWHM



Pulse length: 2 ns

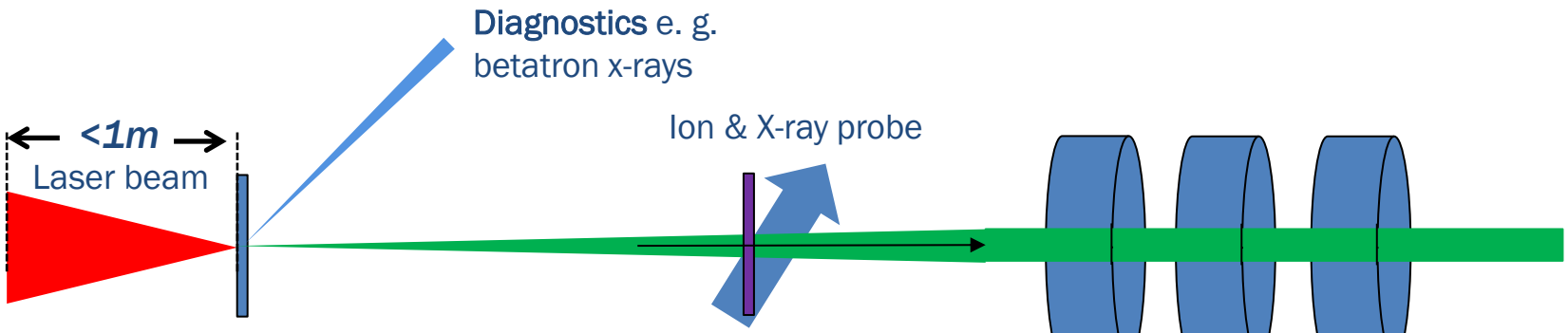
The Neutralized drift compression experiment.
Goal: uniform heating of materials to ~1eV with ion pulses, <1 ns, 1 mm, 1.2 MeV, **>50 nC**, up to 0.1 J.
Status: 2 ns, 1.3 mm, 1.2 MeV, ~**2 nC**, 2 shots/min.



Streaked ionoluminescence spectroscopy of YAP:Ce for a 1 A/mm^2 pulse of Li^+, 1.2 MeV. Decay time: 25 ns.

P. Seidl, et al., arXiv:1506.05839

A short focal lengths beam line at BELLA-i will enable unique access to HEDLP and laser-ion acceleration for users



Laser- matter interactions at >3x10^{21} W/cm^2

- Physics of laser-ion acceleration
- Onset of nonlinear QED

Laser accelerated ions for isochoric heating of WDM

Transport of laser accelerated ions in a beam line for applications in Hadron Therapy, Nuclear Physics, Active Interrogation, (Fusion)-

Frontier:

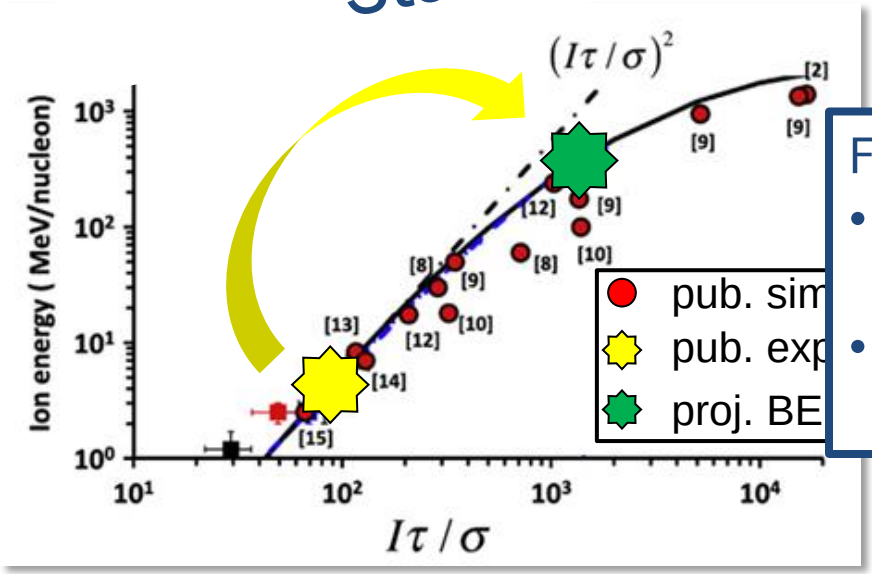
- High field physics at >3x1021 W/cm^2
- fs-synchronization of driver and probes
- Laser-ion acceleration
- See Bulanov and Steinke

- Acceleration fields ~10^{13} V/m (TV/m)
- Repetition rate 1 Hz
- Plasma mirror for very high laser contrast (<10^{-12})

Unique BELLA parameters allow exploration of new ion acceleration regimes, such as Light Sail Acceleration

Please see posters and white papers by Sven Steinke and Stepan Bulanov

Esirkepov et al. PRL 2004



Steinke et al. PRSTAB 2013

Initial Condition:

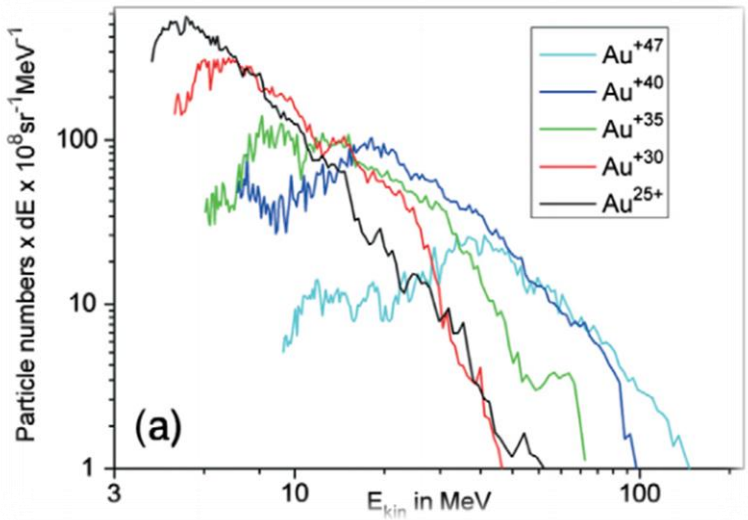
Frontier:

- Physics and technology of laser-ion acceleration
- Can we stage laser-ion acceleration to reach >>1 GeV, ...?

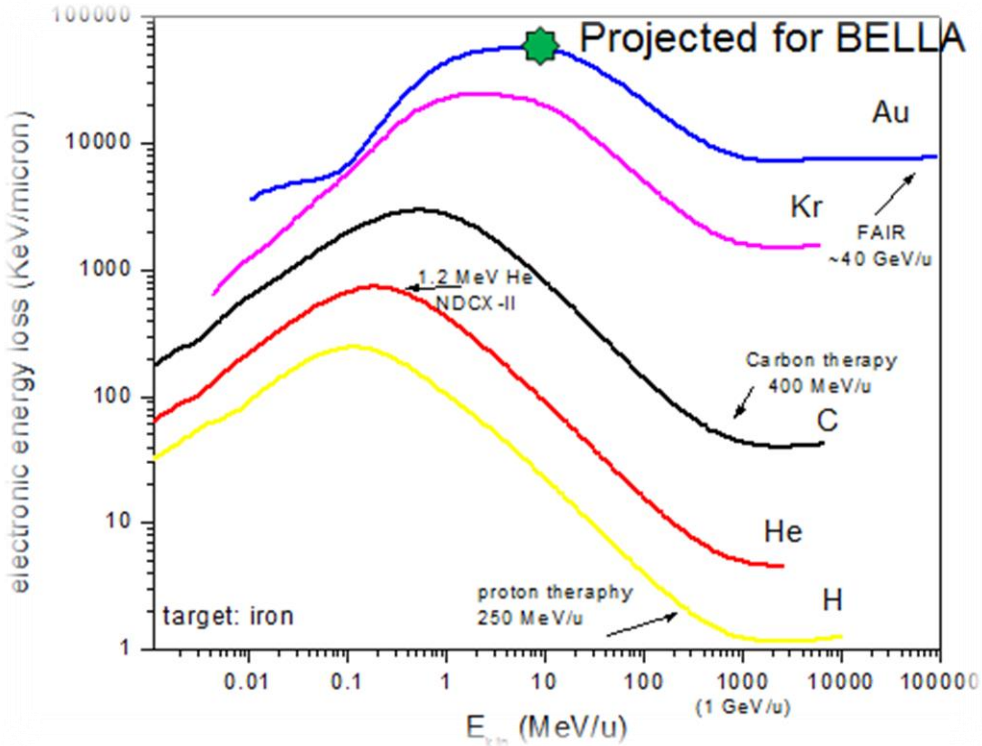
Can accelerate any target ion (D,Fe,Ti,Au,..., rare isotopes,...)

With intense ion pulses we can drive large volumes of targets uniformly into WDM states

With 1.3J laser energy



Braenzel, et al., PRL 2015



- Bragg peak heating with heavy ions for large volumes of uniformly heated WDM (depth up to ~10 micron) to 10 – 30 eV and >10 Mbar pressures
- Recently 0.5 MeV/u Au ions from a 1 J laser, $8*10^{19}$ W/cm^2 via Coulomb Explosion mechanism (Braenzel, et al., PRL 2015)
- Importance of target nano-structure, high contrast optics, support from theory and simulations
- **With BELLA-i we will be able to push for ~6 MeV/u gold ions !**

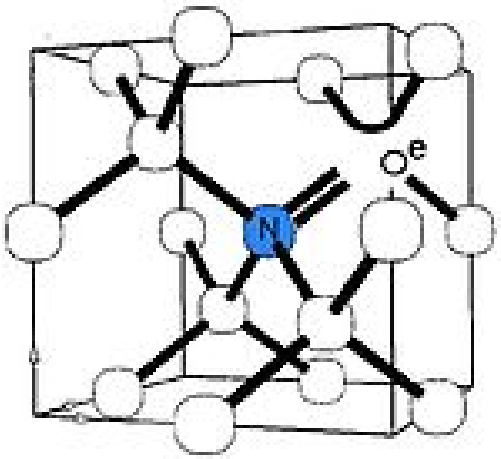
Extreme Chemistry and the properties of Warm Dense Matter

2. Targets

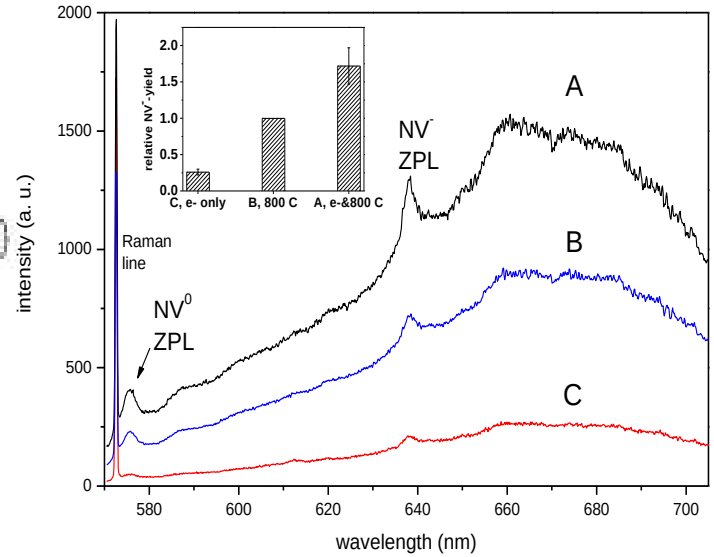
- Metals
- Minerals, silicate perovskite
  - $(Mg, Ca, Fe)SiO_3$
- Hydrogen
- …
- **Plus: now routine micro/nano structuring**

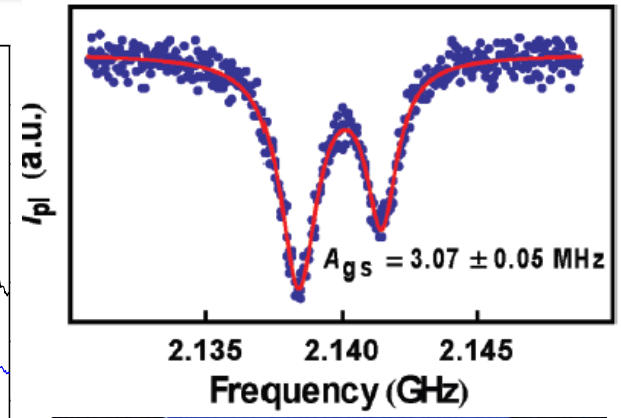
- Long, rich history of extreme materials science and materials synthesis
  - high pressure (e. g. from anvil cells) plus lasers or swift heavy ions, …, plus x-ray probes, …
  - See e. g. P. F. McMillan (2010); V. E. Fortov and V. B. Mintsev (2013); M. Lang, Nat. Mat. 2009

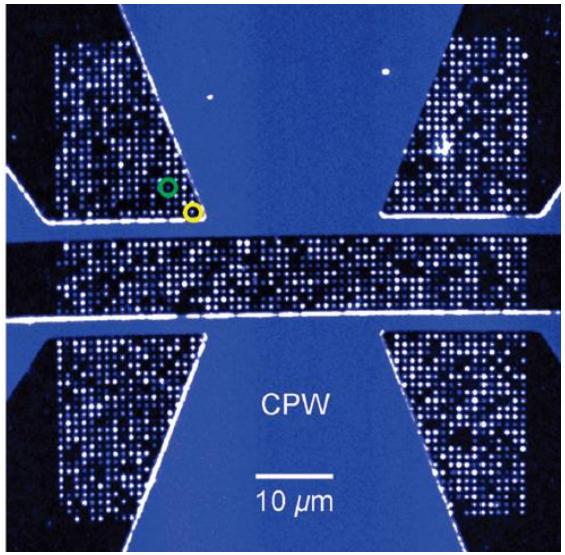
Example: The Nitrogen-Vacancy center in diamond – an (almost ideal) color center for magnetometry and spin – photon qubit integration



https://en.wikipedia.org/wiki/nitrogen-vacancy center



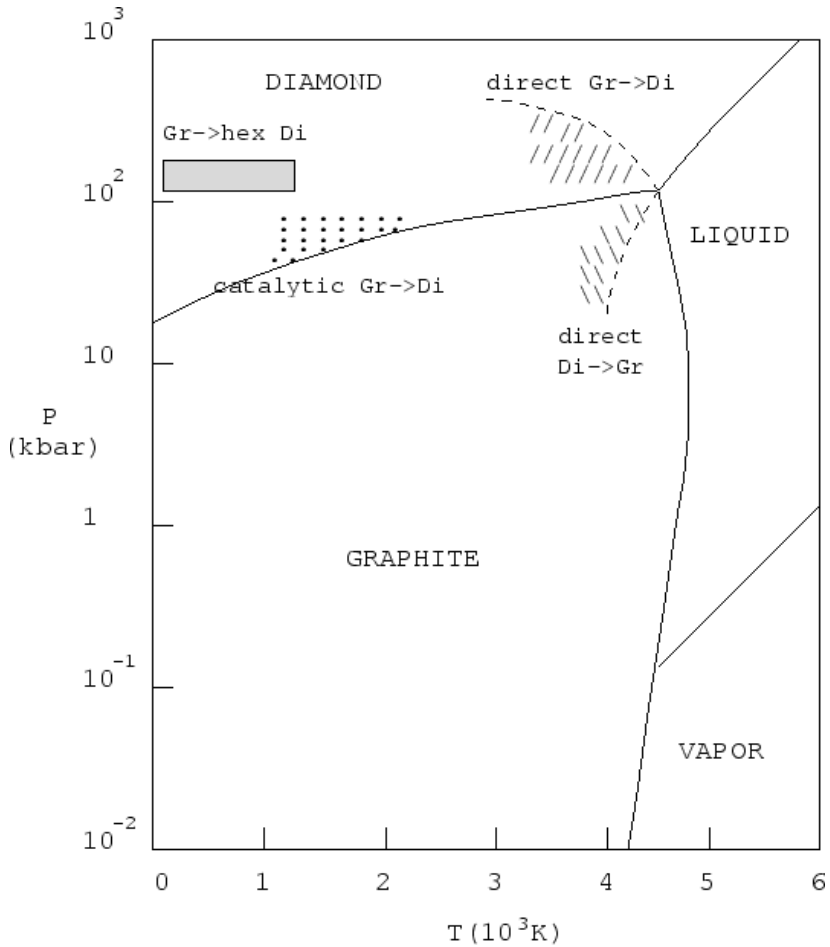




- up to ms spin coherence time at room temperature
- optical single spin read-out/manipulation (optical detection of magnetic resonance)
- single spin physics, entanglement and few-qubit control has been demostrated with e- and nuclear spins
- **but for multi-qubit integration we need to reliably form high quality NV-centers**

D. Toyli, et al., NanoLett. 2010
G. Fuchs, et al., Nat. Phys. 2010
J. Schwartz, et al., NJP, 2012

Materials physics of radiation in the time domain, defect dynamics, extreme chemistry and access to warm dense matter at ~1 eV



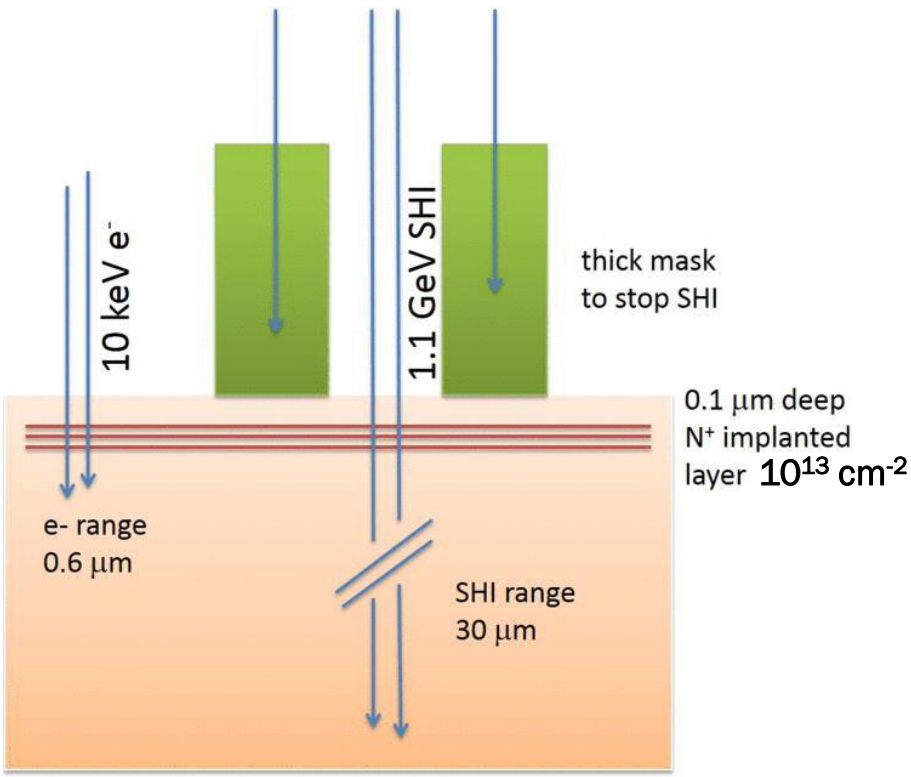
F.P. Bundy, Physica A **156**, 169 (1989)

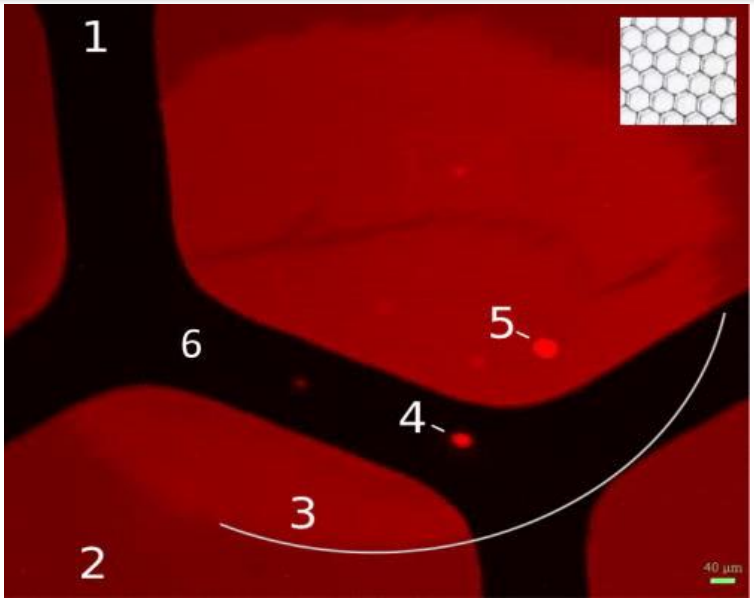
- Example: Phase diagram of carbon
- With pulsed ion beams, we can tickle materials along phase transitions
- Relatively large volume, heated uniformly
  - NDCX-II: ~1 μm*mm^2
- Equation of state studies up to ~1 eV
- Can we freeze-in metastable phases by rapid quenching with patterned excitation?

→ **Frontier of materials synthesis in the extreme chemistry regime**

→ **E. g. opportunity to find novel color centers, … spin-photon qubits in the telecom band at room temperature, …**

NV formation by electronic excitation from passage of ions through diamond ?





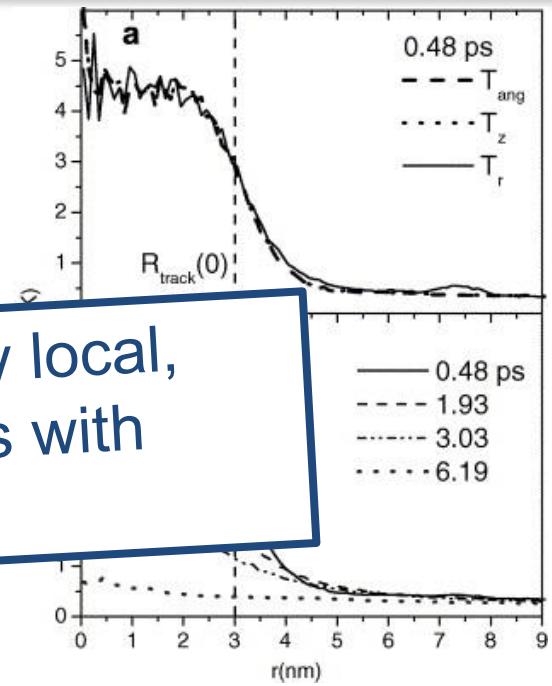
	Nitrogen implant	heavy ions	e^- beam	See NVs ?
1	No	No	No	No
2	No	Yes	No	No
3	**Yes**	**Yes**	**No**	**Yes !**
4	Yes	No	Yes	Yes
5	**Yes**	**Yes**	**Yes**	**Yes**
6	Yes	No	No	No

- Swift heavy ions, 5 MeV/u Uranium-ions, 5×10^{11} cm^{-2}
- GSI Helmholtz Center for Heavy Ion Research, special thanks to C. Trautmann, M. Tomut, M. Bender and D. Severin
- Electronic stopping power: 50 keV/nm (Bragg peak)
- delta-electrons up to ~10 keV
- J. Schwartz, et al., J. Appl. Phys., 2014

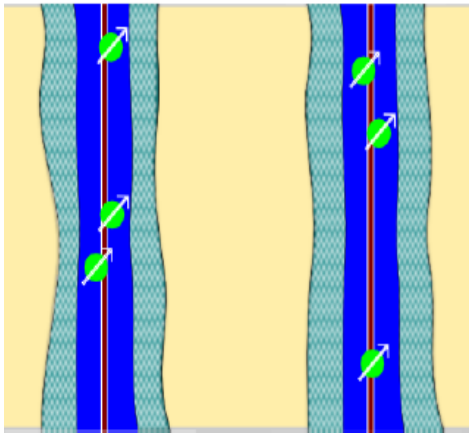
What are mechanisms of swift heavy ion induced NV-formation?

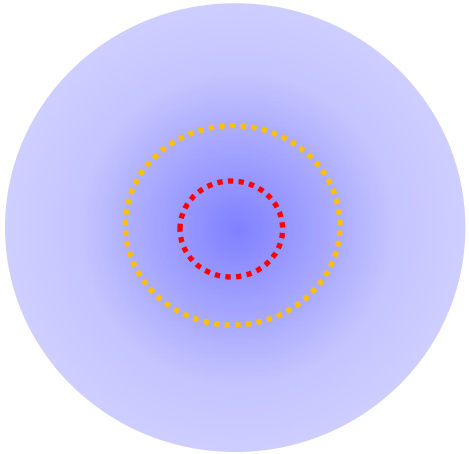
- Mechanisms of NV formation by swift heavy ions:
  - Thermal spike
    - Heating up to ~5000°K, few nm radius, few ps, partial melting and re-crystallization of a latent track
  - Electronic excitati
    surround
  - Conditio

Frontier: Extreme chemistry by local, volumetric heating of materials with intense, pulsed ion beams



Schwen and Bringa, 2007



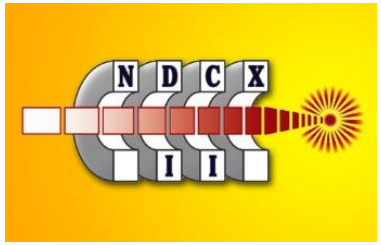


- Hot center, ~3 nm, melting and re-crystallization
- In surrounding cylinder, 3-5 nm, NVs from annealing and electronic excitation ?
- Further out, range of δ-electrons ~10 to 100 nm, NVs from electronic excitation?

Summary and outlook

- **Driver frontiers**
  - Complementary advantages of drivers matched to specific experimental campaigns
  - Advocacy for a vibrant and diverse domestic program with a mix of large and mid-scale facilities

- New opportunities in **extreme chemistry** are enabled by maturation of drivers, diagnostics, theory/simulations and nanotechnology tools
  - Can we steer phase transitions far from equilibrium and stabilize novel materials phases with tailored properties ?
    - Basic plasma-materials physics, connection to planetary science and applications
    - e. g. better color centers for sensing and quantum information processing, …



BELLA-i

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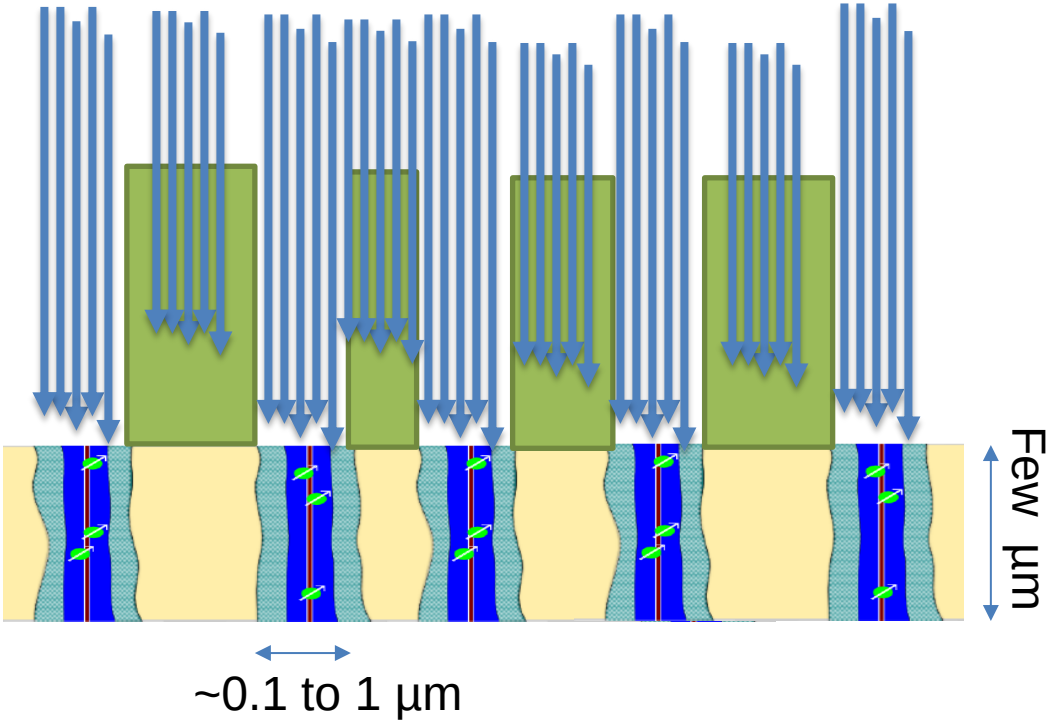
Extra slides

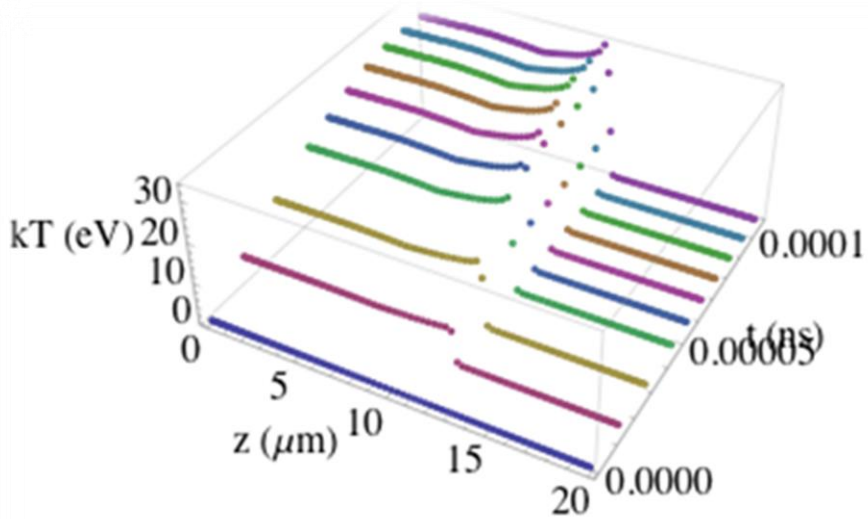
Frontier: Extreme chemistry by local, volumetric heating of materials with intense, pulsed ion beams

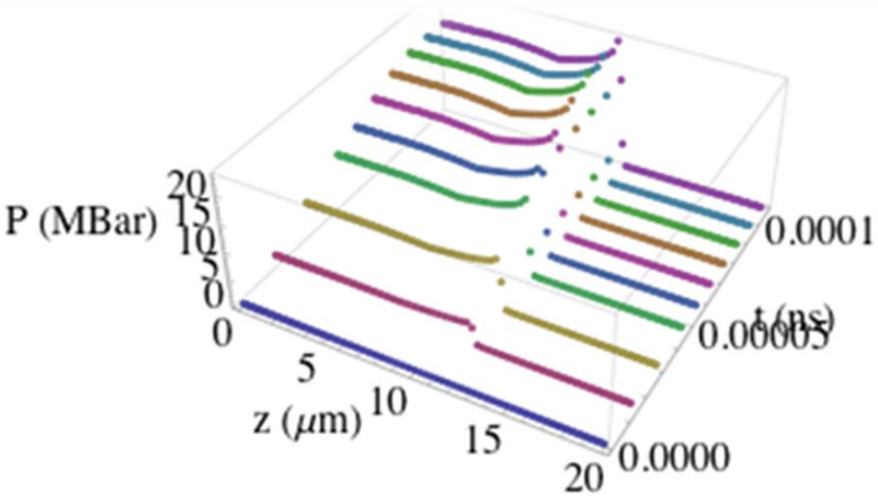


- Choice of materials and dimensions for masking of intense, pulsed ion beams
- Drive targets into extreme conditions
- Track phase transition *in situ, and*
- Stabilize phases by rapid quenching

→ **Frontier of materials synthesis by "extreme chemistry"**

Hydra simulations show isochoric heating of 10 μm thick gold targets to 8 – 30 eV by intense ion pulses (10^9 to 10^{10} Au^{q+})





- Hydra simulations assuming an ion pulse energy of 2 J (5% of BELLA)
- 10^{10} gold ions, kinetic energy of 6 MeV/u
- a 25 μm thick gold target, spot diameter: 200 μm
- ion energy fluence: 6 kJ J/cm^2
- ion pulse duration: 100 fs (faster than electron – ion equilibration time)
- For 10^9 ions, the peak temperature is 8 eV, peak pressure 2 Mbar
- **Simulations by John Barnard, LLNL**

nature materials
LETTERS
PUBLISHED ONLINE: 6 SEPTEMBER 2009 | DOI: 10.1038/NMAT2528

Nanoscale manipulation of the properties of solids at high pressure with relativistic heavy ions

Maik Lang[1], Fuxiang Zhang[1], Jiaming Zhang[1], Jianwei Wang[1], Beatrice Schuster[2], Christina Trautmann[2], Reinhard Neumann[2], Udo Becker[1] and Rodney C. Ewing[1]*

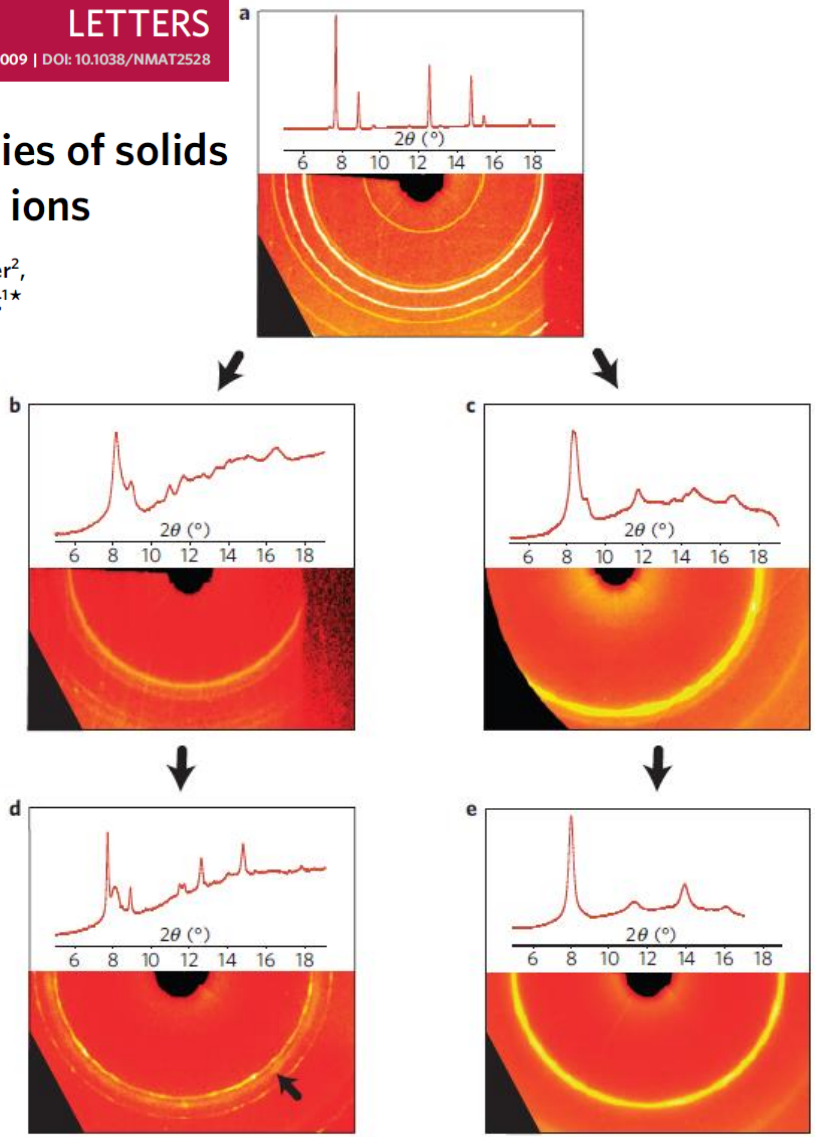


Figure 1 | Synchrotron XRD images and integrated patterns of $Gd_2Zr_2O_7$ obtained at different combinations of pressure and irradiation. **a–e**, Pyrochlore-structured $Gd_2Zr_2O_7$ starting material (**a**) on releasing pressure without (**b**,**d**) and with (**c**,**e**) irradiation ((**c**) 4 GeV xenon and (**e**) 7-GeV uranium ions of fluence 3×10^{12} cm^{-2}). The sample structure at the specific pressure is cotunnite-like high-pressure phase at 20.2 GPa (**b**), cotunnite-like high-pressure phase at 21.5 GPa (**c**), defect-fluorite structure with some remnants of X-Phase (arrow) 10 h after quenching (**d**) and pure X-phase 50 h after quenching (**e**).

For WDM, the thermal energy of the electrons is comparable to the binding energy of the molecules themselves, and chemistry needs to be redefined and broadened.

By extreme chemistry, we mean that chemical bonding by conventional outer-orbital (valence) electrons is superseded by core-electron interactions, which are very complex.

phase transitions to complex solid and liquid structures, or to new plasma states; and transitions between distinct liquid states.

- Why is this important ?

- Discovery potential ?

- Impact potential ?

- Planetary science
- Underpinning of inertial confinement fusion and inertial fusion energy
- Exciting opportunities for materials synthesis and materials discovery

- What has changed since report from 2009 workshop ?

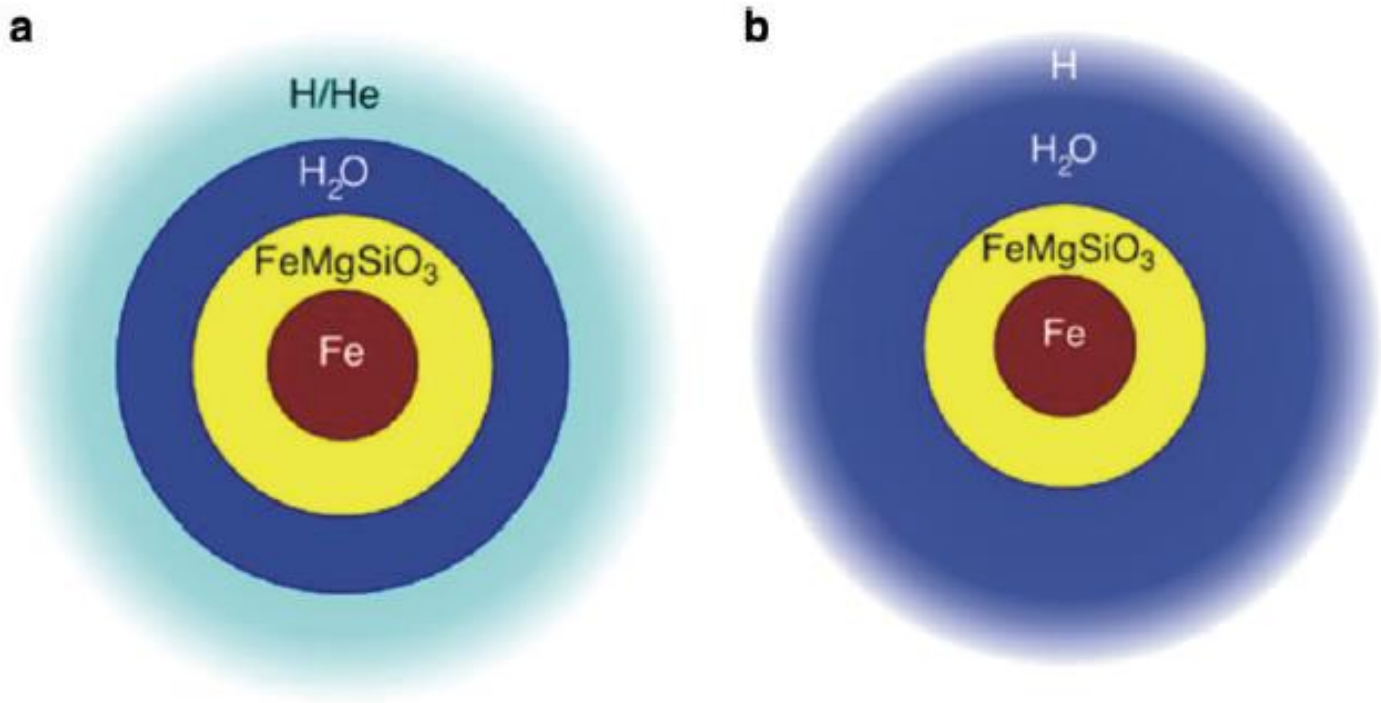
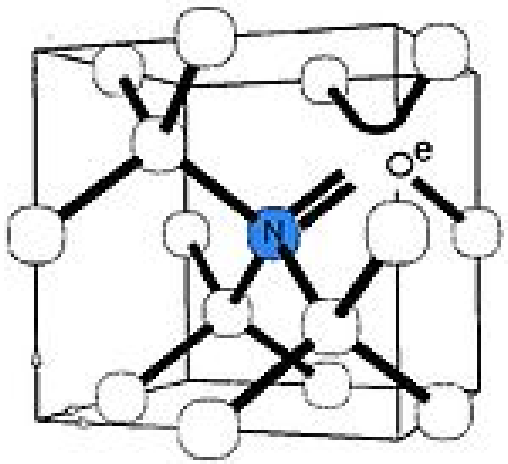
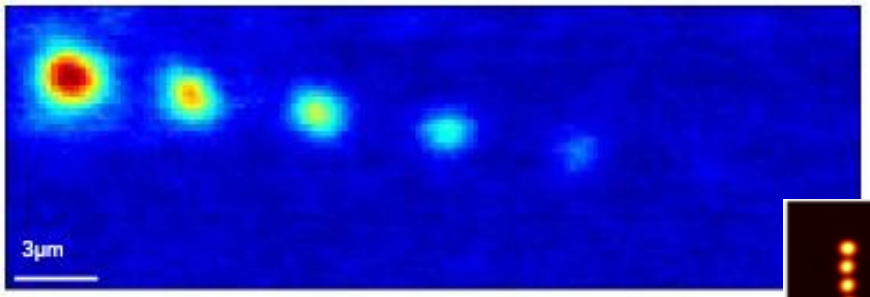


FIG. 1. Illustration of two possible scenarios for the structure of the low-density super-Earth GJ 1214, which can be derived from the radius-mass relation within the present uncertainties. Left scenario (**a**) would correspond to a mini-Neptune with a dense core that is surrounded by a primordial or outgassed dense hydrogen envelope. Right scenario (**b**) corresponds to a low-density core that is surrounded by a huge amount of H_2O and a thin hydrogen envelope (courtesy of D. Charbonneau). Color images available online at www.liebertonline.com/ast

Materials physics of radiation in the time domain, defect dynamics, extreme chemistry and access to warm dense matter at 1 eV



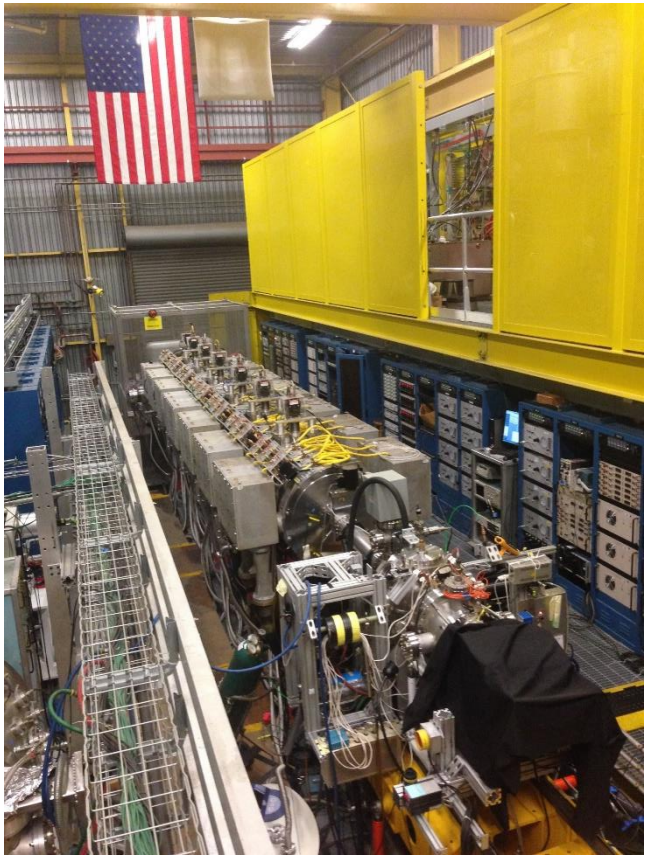


- With pulsed ion beams from NDCX-II we can
  - access the materials physics of radiation in the time domain
  - drive phase transitions and
  - process materials with unique control over the mix of electronic excitations, elastic collisions and heating

- Effects of low-energy electron irradiation on formation of nitrogen–vacancy centers in single crystal diamond, J. Schwartz, S. Aloni, F. Ogletree, T. Schenkel, New J. Phys. 14, 043024 (2012)
- Excited-state spin coherence of a nitrogen-vacancy centre in diamond, G. Fuchs, V. Dobrovitski, D. Toyli, J. Heremans, C. Weis, T. Schenkel, D. D. Awschalom, Nature Physics 6, 668 (2010)

Plasma Science at Berkeley Lab

- Ion beam – plasma processing of materials (color center qubits, …), warm dense matter
- **Challenges and opportunities**
  - Extreme chemistry, novel materials synthesis paths
    - e. g. for color center qubits in diamond, SiC, …
    - relatively low throughput, only for high impact applications
  - Extreme radiation hardness testing



http://atap.lbl.gov/research.html
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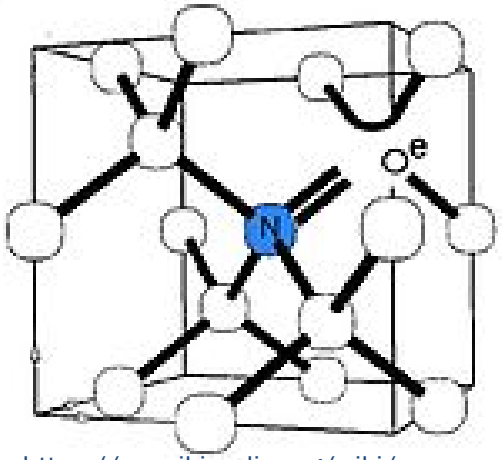
Special thanks to

- C. D. Weis, M. Ilg, J. Schwartz, A. Persaud, P. Seidl, LBNL
- I. Rangelow, Technical University Ilmenau
- C. Trautmann, M. Tomut, M. Bender, D. Severin, GSI
- staff of the Molecular Foundry at LBNL (S. Aloni, D. F. Ogletree, and E. Chan)

This work was supported by the US Department of Energy and by Darpa

Local Formation of Nitrogen Vacancy Centers in Diamond by Electronic Excitation



https://en.wikipedia.org/wiki/nitrogen-vacancy center

Goals

- To form high quality NV centers in diamond with
  - High spectral stability
  - Long coherence times
    → High formation efficiency, NV/N
  - High spatial resolution
    - For nearest neighbor coupling, device integration, …

Approach

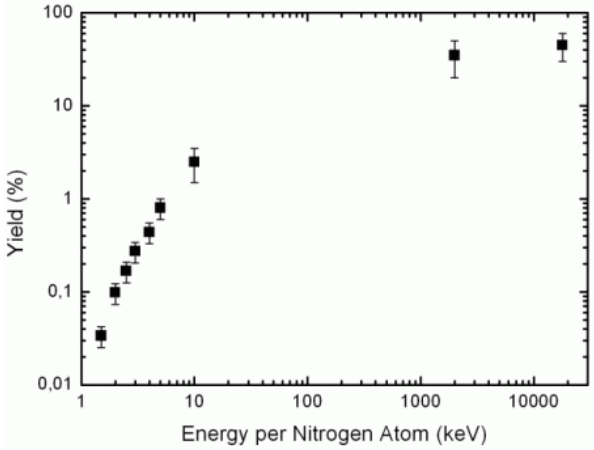
- Implantation of nitrogen ions into diamonds with low nitrogen background
- Annealing
- …

Findings

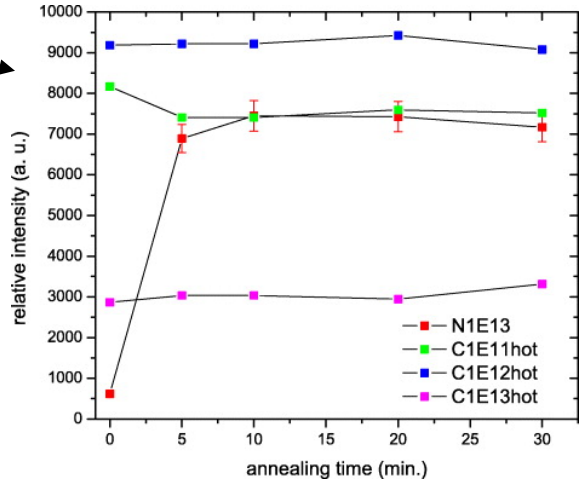
- It is easy to make some NVs based on nitrogen ion implantation, …
- And NVs also form following local electronic excitation, without thermal annealing
- A better understanding of NV-formation mechanism could lead reliable formation of high quality NV-centers

How do NV-centers form ?

- N + V → NV ?
- **Formation efficiency: $NV^{+,0,-}/N$ vs.**
  - Nitrogen ion implant energy
  - Addition of vacancies by co-implantation
  - Annealing temperature, pressure
  - Electronic excitation
  - Surface treatment for charge state control



S. Pezzagna, et al., NJP, 2010



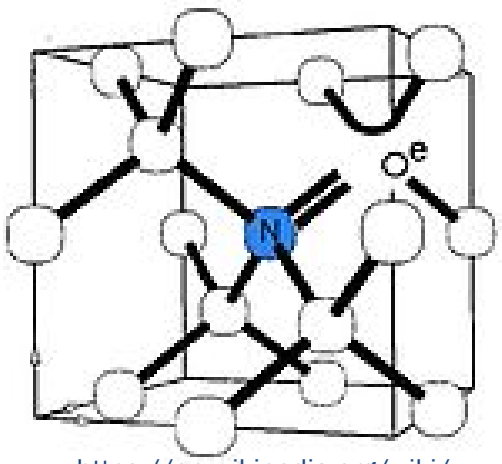
J. Schwartz, et al., NJP, 2011

How do NV-centers form ?

- following ion implantation, most N are on interstitial sites, and a few have replaced carbon atoms on lattice sites

1) $N_{substitutional} + V \rightarrow NV^{0,-}$

- Thermal annealing >600°C
- Two steps:
  - Nitrogen becomes substitutional (P1 center)
  - Vacancies diffuse and get trapped at substitutional Nitrogen sites
- Charge state controlled by local Fermi level (N bath, surface, …)

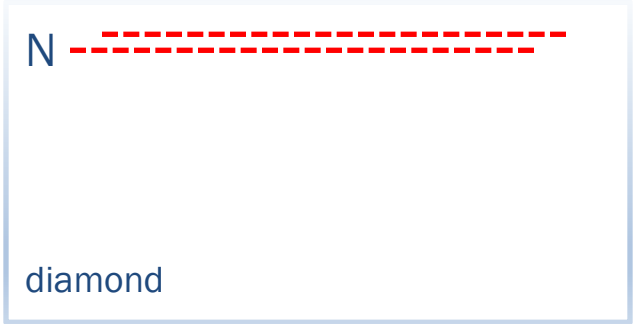


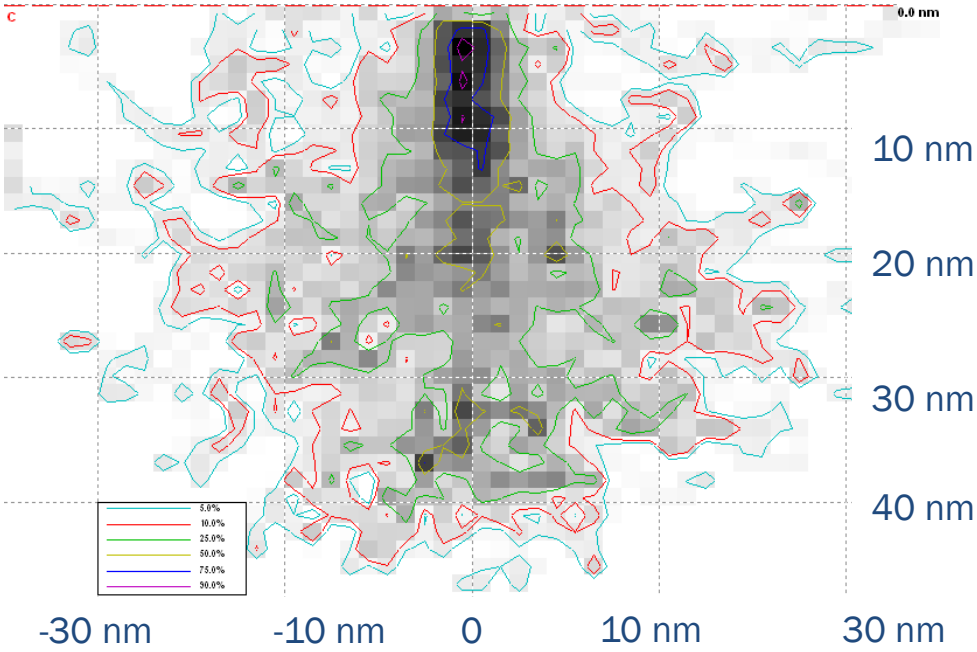
https://en.wikipedia.org/wiki/nitrogen-vacancy center

2) $N_{interstitial} + V_n \rightarrow NV^{0,-}$

- NV-formation can be induced by local electronic excitations at room temperature
- Defect complex with interstitial nitrogen and vacancies ?
  - Dissolves above 600°C
- Is an interstitial nitrogen – vacancy complex always required to form NVs ?

Following implantation of nitrogen ions, NV-centers form during exposure to low energy electrons at room temperature

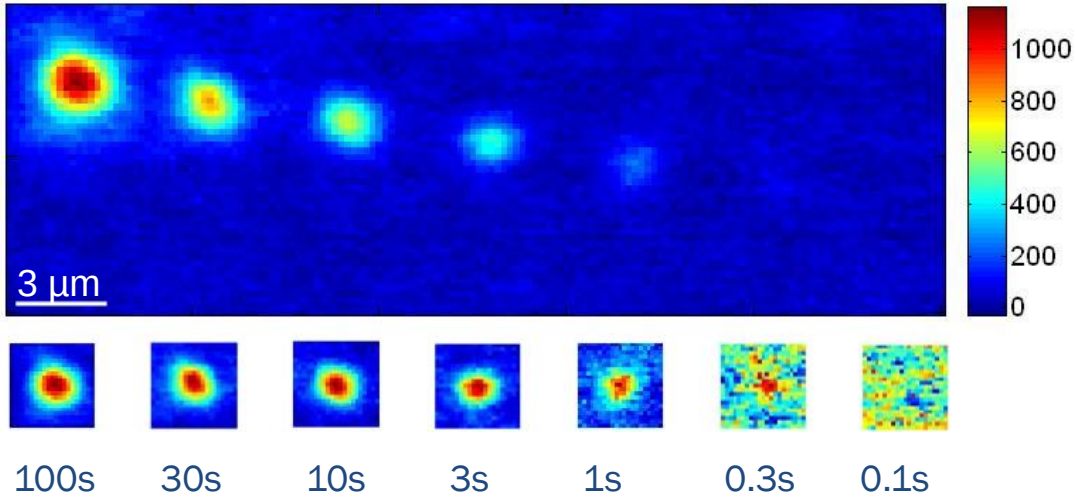




- Single crystal diamond with low nitrogen background
- Implanted with nitrogen ions, 7.7 keV, (100), fluence: 10^{12} cm^{-2} , at room temperature
- ~10 nm peak depth

- Casino simulation of electron (2 keV) trajectories in diamond

Following implantation of nitrogen ions, NV-centers form during exposure to low energy electrons at room temperature



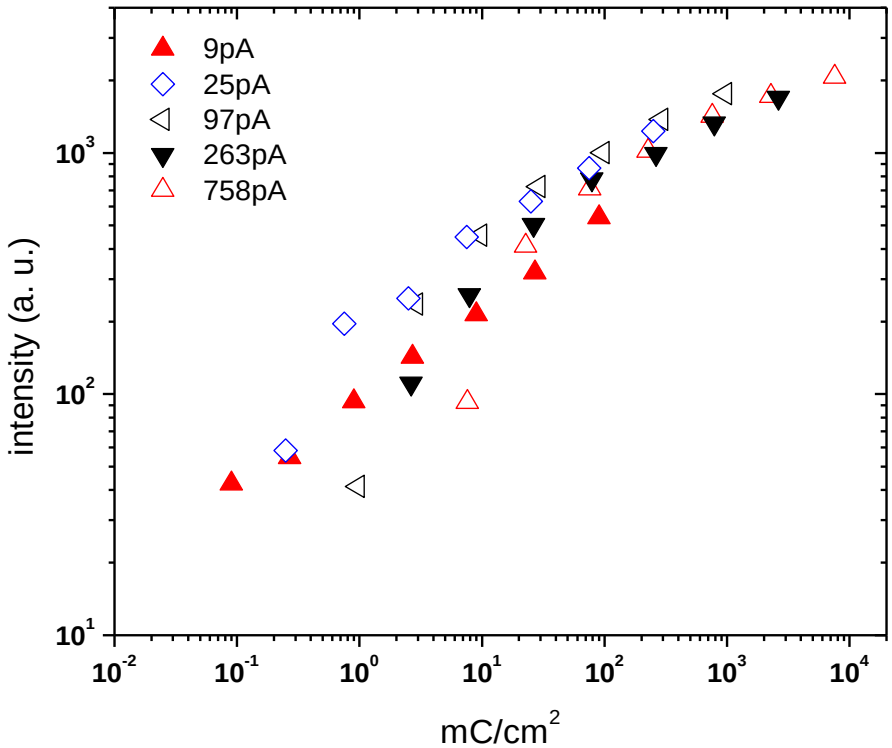
- Confocal PL image of NV− centers (635–642 nm) at room temperature, recorded following exposure of 1 µm squares to a 9 pA, 2 keV electron beam. Insets show locally auto-scaled spots.

- NV-spot increases with electron fluence

→ role of excited carriers (electrons, holes), which diffuse out of the e-beam spot

J. Schwartz, et al., NJP 2012

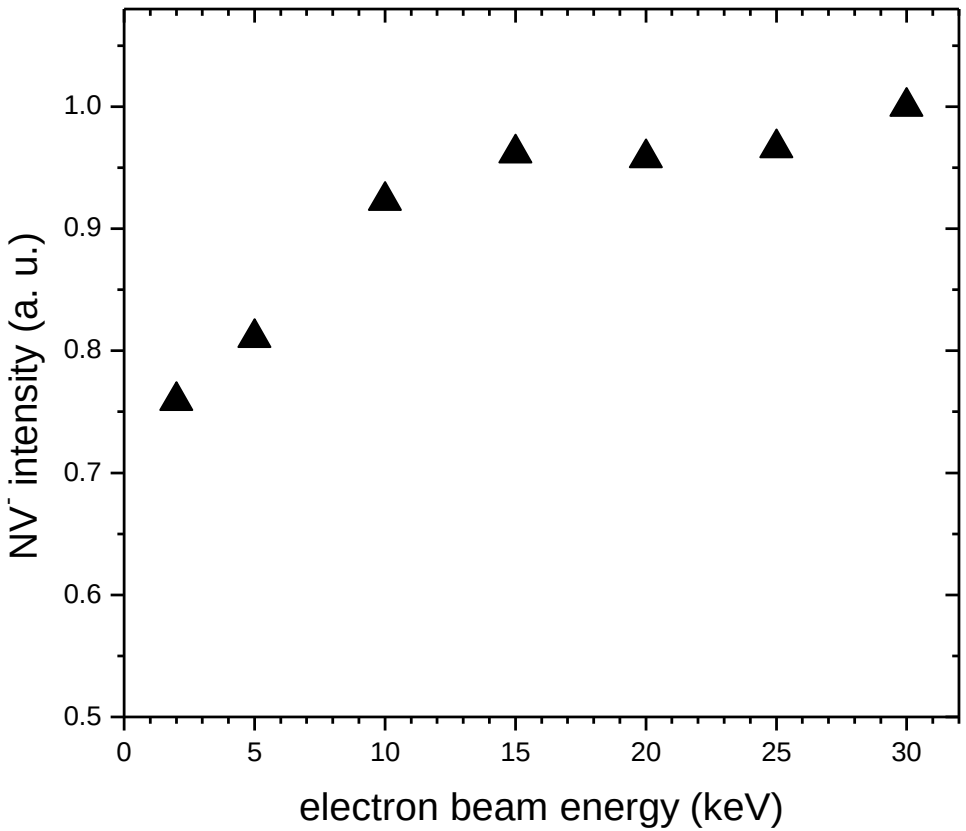
Mechanism of e-beam induced NV-formation – heating by the e-beam can be ruled out due to similar NV-intensities from very different e-beam dose rates



- NV^-PL intensity from 1 μm squares exposed to 2 keV electrons as a function of accumulated dose (1 mC/cm^2=10 pC/μm^2=6.2×10^{15} e$^-$/cm^2). The symbols correspond to different beam currents and exposure times.
- Electron beam heating estimate assuming energy is uniformly deposited in a sphere of radius R~30 nm at 2 kV, then $\delta T=(I\cdot V)/(\pi\cdot k\cdot R)$
  - K: thermal conductivity of diamond (2000 W/m·K)
  - Thus $\delta T < 1$ °K/nA at 2 keV, and less at higher E_{kin} since $R\sim E_{kin}^{1.75}$

J. Schwartz, et al., NJP 2012

Mechanism of e-beam induced NV-formation - no threshold observed in NV-intensities vs. e-beam energy and this rules out a dominant role of momentum transfer



- NV^--PL-intensity as a function of electron beam energy. 3x5 μm^2 areas were exposed to 40 nA electron beams with a fluence of 0.8 mC/cm^2 each. The energy threshold for e-beam induced displacement damage is ~80 keV.

J. Schwartz, et al., NJP 2012

What are mechanisms of e-beam induced NV-formation?

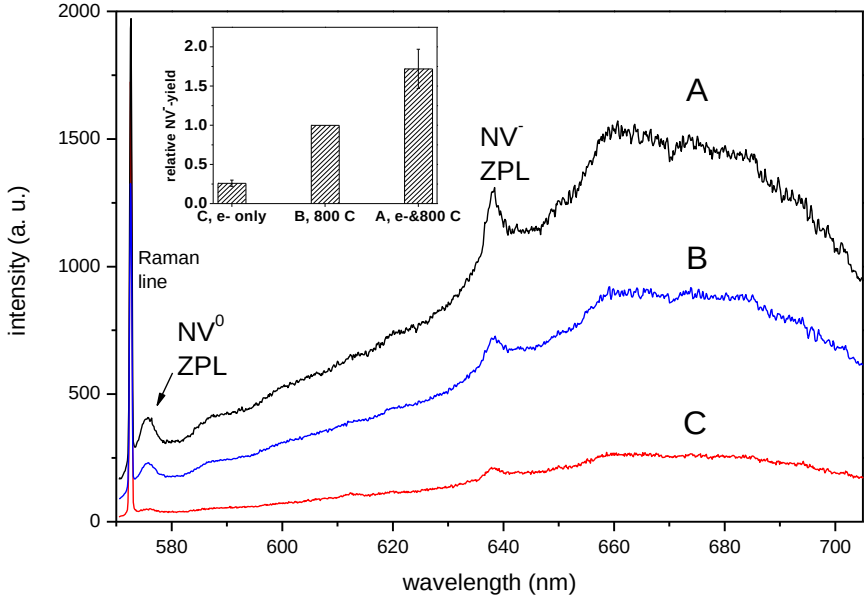
- Not momentum transfer
- Not local heating

- NV/N yield from e-beam exposure 0.25 of yield from thermal annealing, absolute yield <1%

- e-beam exposure, followed by thermal annealing increases NV-count by 1.8x

- But thermal annealing, followed by e-beam exposure has no effect

→ Is there a "pre-curser defect complex" present after nitrogen implantation ?
  → interstitial N with several vacancies in vicinity (or one di-vacancy) ?



- room temperature PL spectra of nitrogen implanted diamond
- A: e-beam, then thermal annealing
- B: thermal annealing only (800°C, 15 min.)
- C: e-beam only

J. Schwartz, et al., NJP 2012

What are mechanisms of e-beam induced NV-formation?

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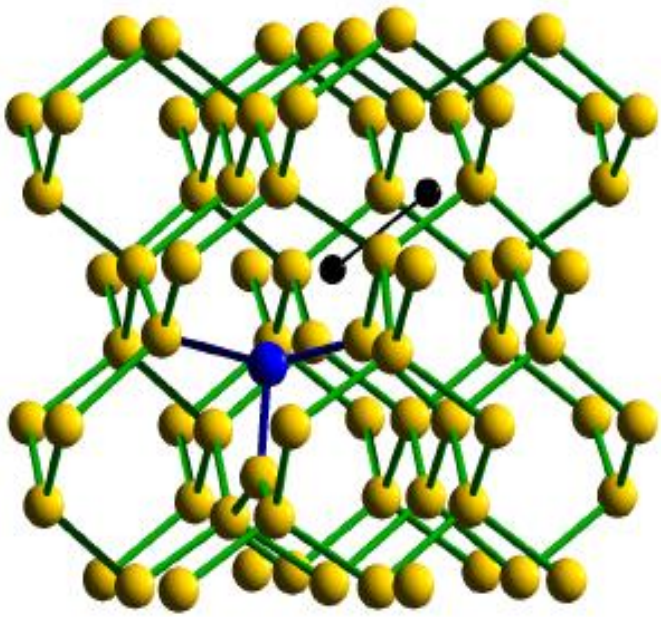


$$N_{substitutional} + V \rightarrow NV^{0,-}$$

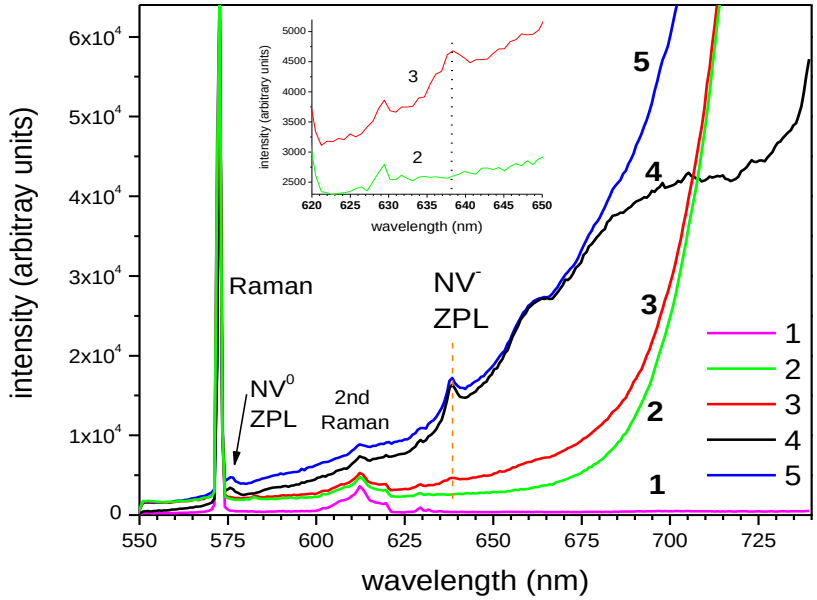
vs.

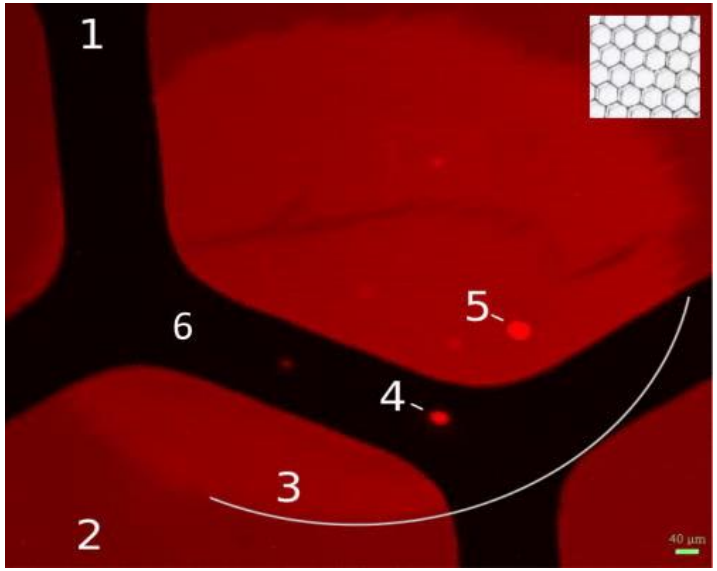
$$N_{interstitial} + V_n \rightarrow NV^{0,-}$$

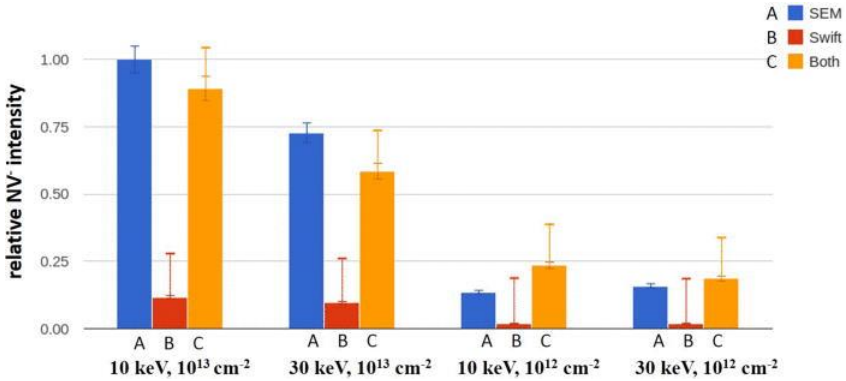
- A nitrogen atom on a split interstitial site (blue), close to two vacancies (black). Carbon atoms in yellow. NV's form during annealing at >300°C
  - J. Adler, R. Kalish, et al., J. of Physics, 2014
- P. Deak et al. PRB 2014: di-vacancy formation favored over NV formation during annealing of N rich diamond after vacancy producing irradiation

J. Schwartz, et al., NJP 2012

Local NV-center formation by electronic excitation from swift, heavy ions, without thermal annealing

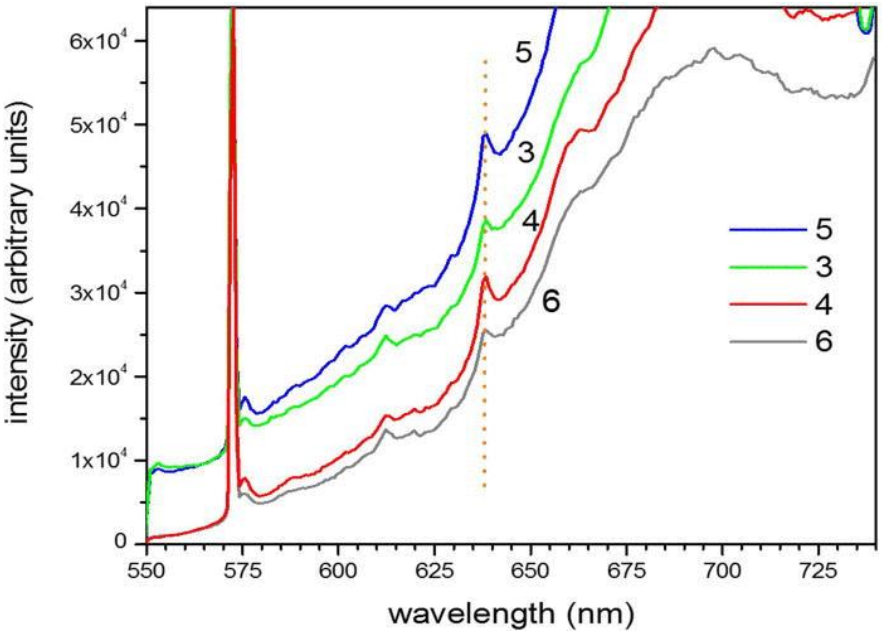


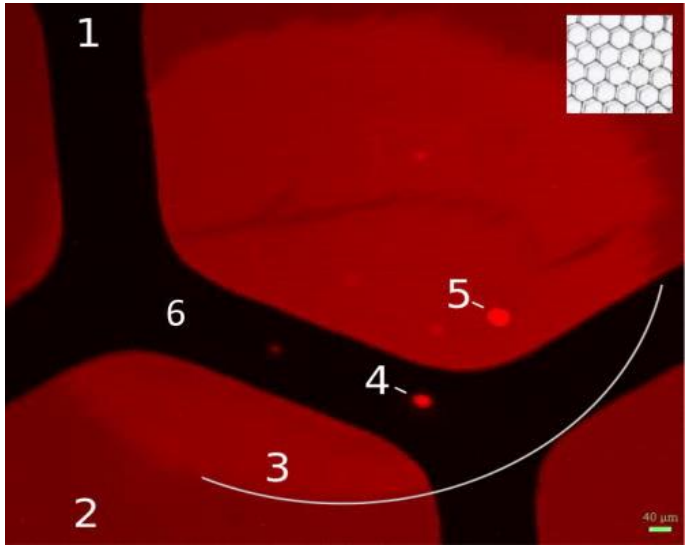


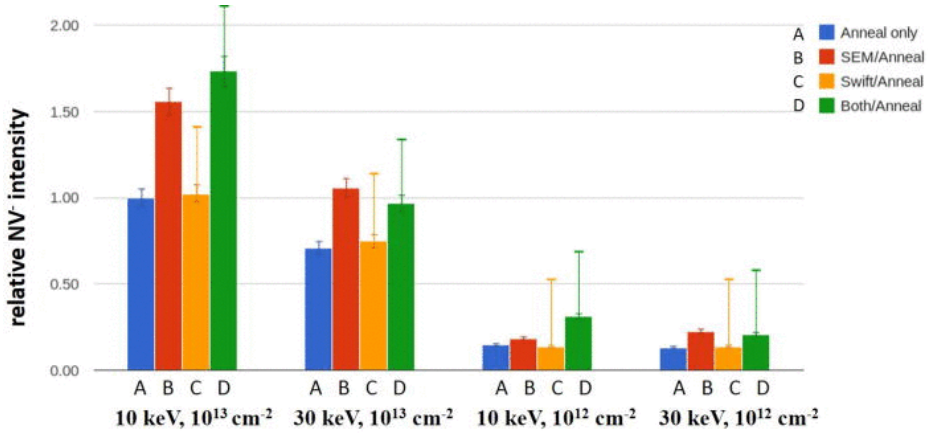


- NV's form in the nitrogen implanted layer during the passage of swift heavy ions
- Formation yield is ~0.1 of yield from high fluence e-beam and ~0.02 of yield from thermal annealing
- Low absolute NV/N ~ 10^{-4}–10^{-3}
- Not clear if effects of swifts and e-beam are additive

Local NV-center formation by electronic excitation from swift, heavy ions – yields after thermal annealing







- NV yields higher by factor 1.7x for e-beam and then thermal annealing vs. thermal annealing alone (850°C, 1 h, in vacuum)
- But no evidence for additive effect of swifts and thermal annealing
- Formation yield is ~0.1 of yield from high fluence e-beam and ~0.02 of yield from thermal annealing
- absolute NV/N ~ 10^{-4}–10^{-3}