Solids underway to warm dense matter state

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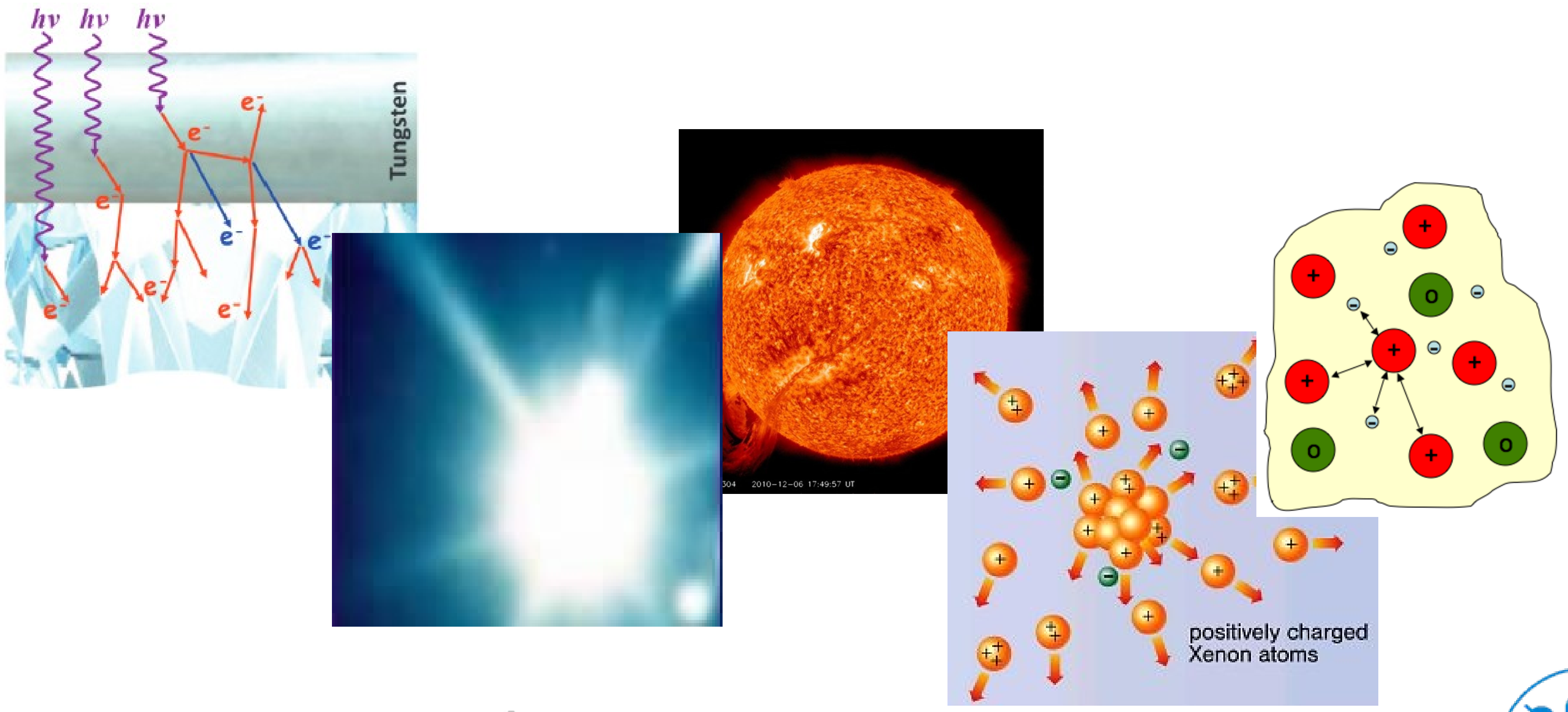

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CFEL-DESY Theory Group
at the Center for Free-Electron Laser Science

The CFEL Theory Group develops theoretical and computational tools to predict the behavior of matter exposed to intense electromagnetic radiation. We employ quantum-mechanical and classical techniques to study ultrafast processes that take place on time scales ranging from 10^{-12} s to 10^{-18} s. Our research interests include the dynamics of excited many-electron systems; the motion of atoms during chemical reactions; and x-ray radiation damage in matter.

Members of the CFEL-DESY Theory Group: C. Arnold, S. Bazzi, J. Bekx, Y.-J. Chen, O. Geffert, D. Gorelova, L. Inhester, Z. Jurek, A. Hanna, R. Kaur, D. Kolbasova, M. Krishna, Z. Li, V. Lipp, M. A. Malik, P. K. Mishra, R. Santra (Group Director), J. Schaefer, S.-K. Son, V. Tkachenko, K. Toyota, R.Welsch, B. Ziaja

3 subgroups:

'Ab-initio X-ray Physics' (S.-K.Son),
'Chemical Dynamics' (R.Welsch),
'Modeling of Complex Systems' (B. Ziaja)

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My excellent collaborators ...

V. Lipp

N. Medvedev

Now in Prague ...

V. Tkachenko

V. Saxena

Now in Delhi ...

J. Bekx

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Outline

1. **Transitions in matter triggered by X-rays**

2. **X-ray induced graphitization of diamond**

3. **Amorphization of diamond by intense X-ray pulse**

4. **Summary**

Outline

1. Transitions in matter triggered by X-rays

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Transitions in matter ...

Energy delivered to a thermodynamic system → transition into a different phase or state of matter

Examples:

Structural transition → leads to a change of a system structure
Magnetic transition → changes magnetic properties (e.g., demagnetization)
Superconductivity → superconducting phase
...

Or

Solid-to-solid → leads to a change of solid's structure
Solid-to-liquid → melting
Solid-to-plasma → ionization
...

Structural transitions in solids induced by X-ray radiation

... Femtosecond intense pulses from X-ray free-electron laser ...

Pulse duration ~ down to a few fs
Wavelength ~ VUV- hard X-ray

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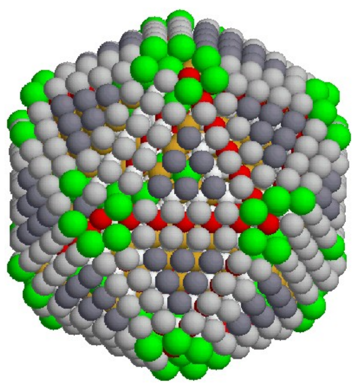
Main interactions:

X-ray photons: elastic scattering, Compton scattering, photoionization (valence band, inner-shell), Auger & fluorescence decays

Electrons: collisional ionization and recombination from/to bands, thermalization → band modification

Ions: electrostatic repulsion → band modification → structural transition?



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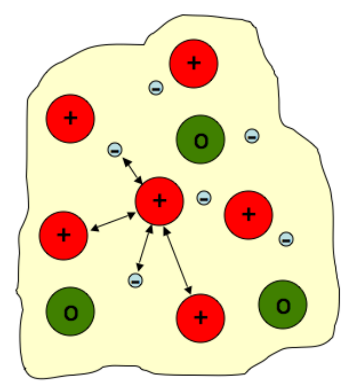

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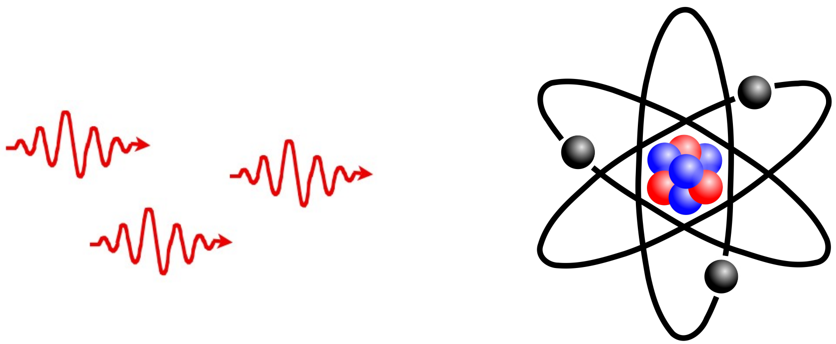
Structural transitions in solids induced by X-ray radiation

Transition depends on the average absorbed dose ....



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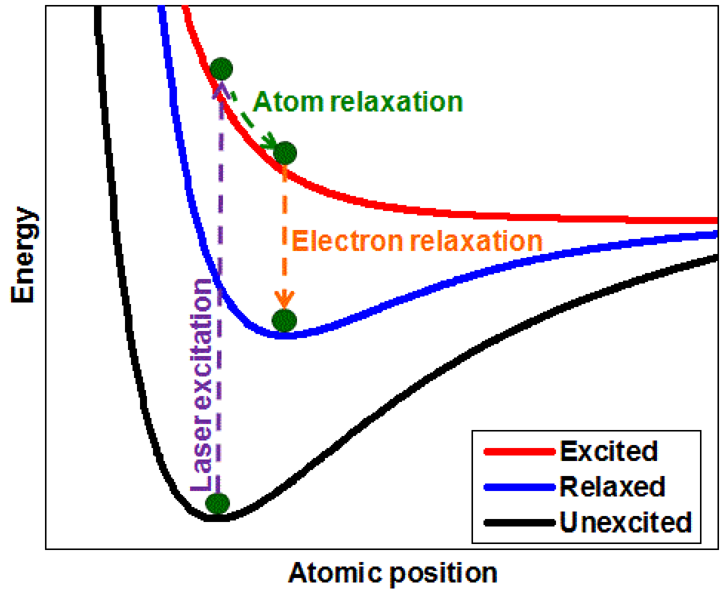
Interaction of solids with fs X-ray pulses of fluence above structural damage threshold

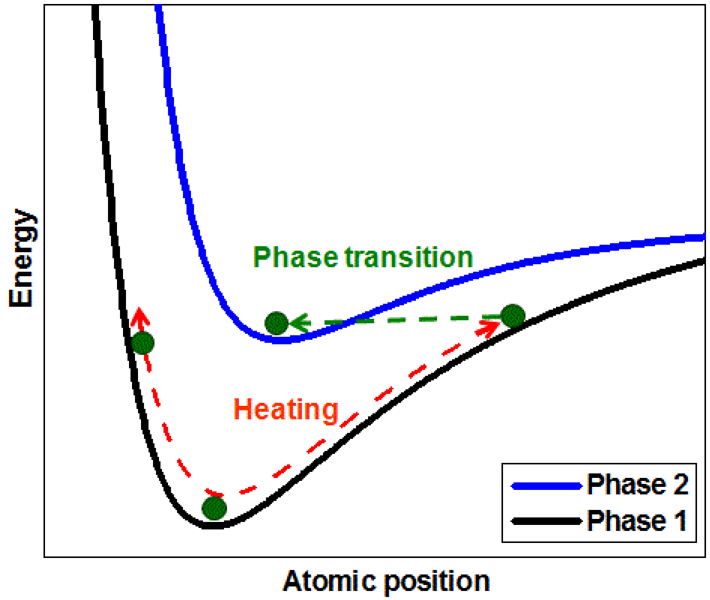
Damage threshold

Non-thermal melting (~100 fs)



Change of interatomic potential

Thermal melting (~ ps)



Heating of atomic lattice due to el-ph coupling within the same potential

Melting threshold

[Medvedev et al. (BZ): NJP 15 (2013) 015016; PRB 88 (2013) 224304 & 060101; PRB 91 (2015) 054113]

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[Courtesy of N. Medvedev]

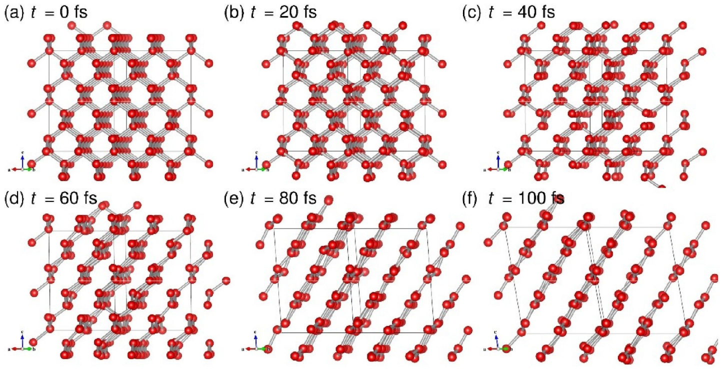
Interaction of solids with femtosecond X-ray pulses of fluence above the damage threshold:
→ Electron Kinetics + Atomic Relocations

Damage threshold

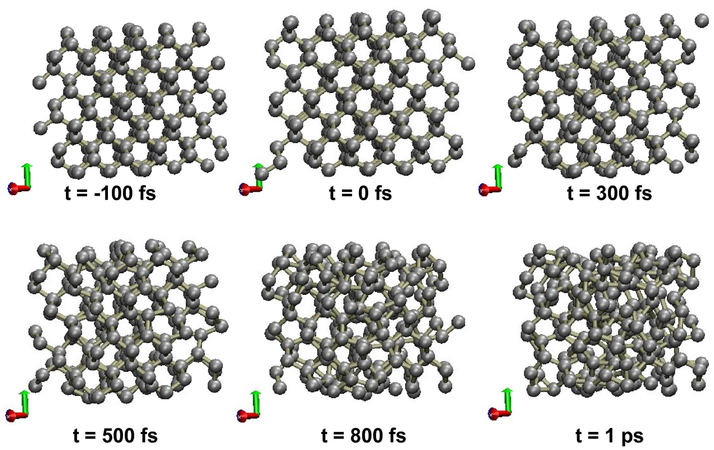
Structural transitions in solids:

Photon energy 92 eV, FWHM = 10 fs

→ graphitization of diamond
ultrafast non-thermal process modeled within Born-Oppenheimer scheme



→ amorphization of silicon
contribution of non-thermal and thermal melting (due to electron-phonon coupling); extended Born-Oppenheimer scheme



Melting threshold

[Medvedev et al. (BZ): NJP 15 (2013) 015016;
PRB 88 (2013) 224304 & 060101;
PRB 91 (2015) 054113]

Damage thresholds in good agreement with experiments!

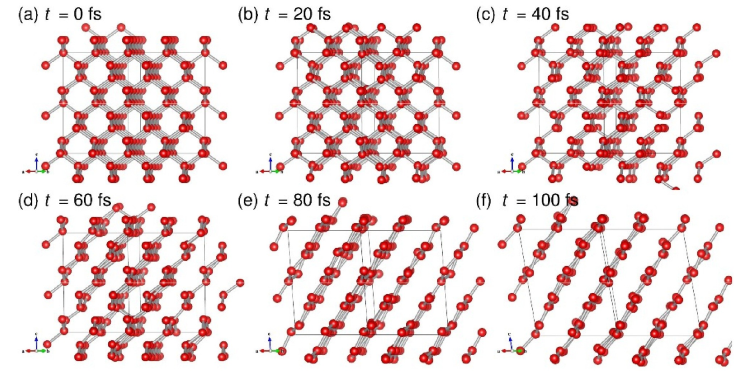
[Images courtesy of N. Medvedev]

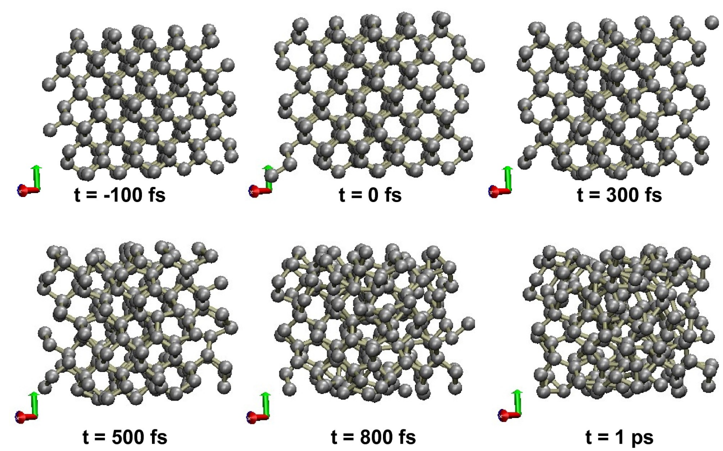
Interaction of solids with femtosecond X-ray pulses of fluence above the damage threshold:
→ **Electron Kinetics + Atomic Relocations**

Damage threshold

Simulations with dedicated code XTANT: X-ray induced Thermal and Non-Thermal Transitions →
[Medvedev et al.] →

Photon energy 92 eV, FWHM = 10 fs





Melting threshold

[Medvedev et al. (BZ): NJP 15 (2013) 015016;
PRB 88 (2013) 224304 & 060101;
PRB 91 (2015) 054113]

Damage thresholds in good agreement with experiments!

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[Images courtesy of N. Medvedev]

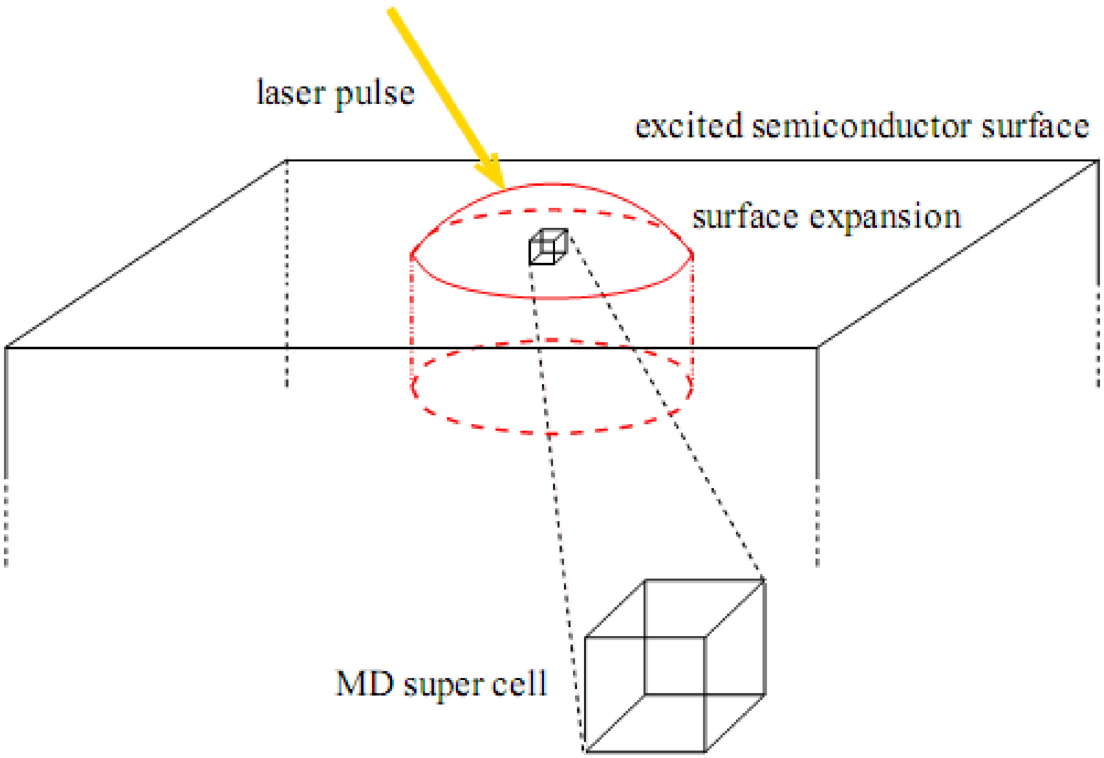
Our simulation tool XTANT: modular MD/MC/TB/Boltzmann approach

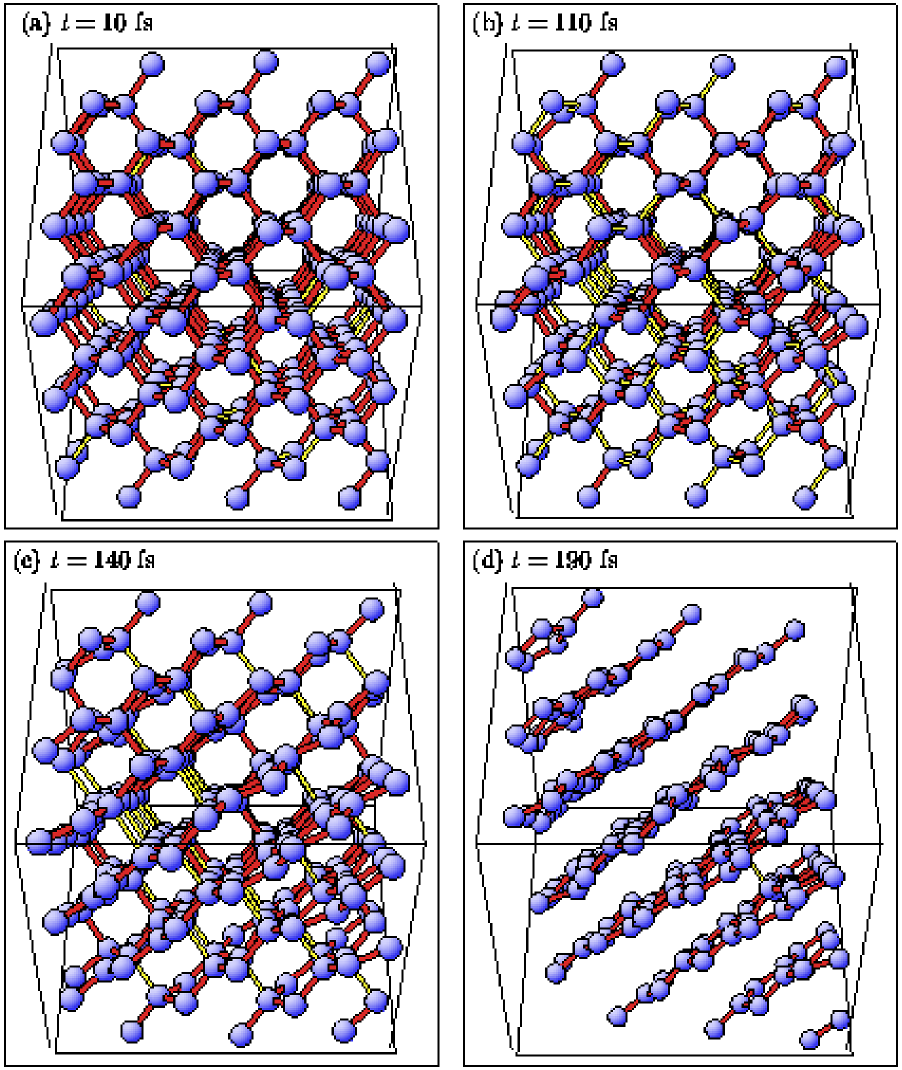
- MD (Parrinello-Rahman scheme) to describe dynamics of ions and atoms
- Boltzmann approach to describe dynamics of electrons within the valence and conduction bands
- Transferable tight binding method/DFT to describe changes of band structure and potential energy surface
- MC approach to describe dynamics of high energy free electrons in conduction band and creation and relaxation of core holes
- Scattering/ionization rates calculated from complex dielectric function updated at each time step

[Medvedev et al. (BZ): NJP 15 (2013) 015016;
PRB 88 (2013) 224304 & 060101;
PRB 91 (2015) 054113]

DESY

XTANT:
modular MD/MC/TB/Boltzmann approach





[H. Jeschke et al. PRL 2002]

Can be used to simulate both bulks as well as surfaces and thin layers

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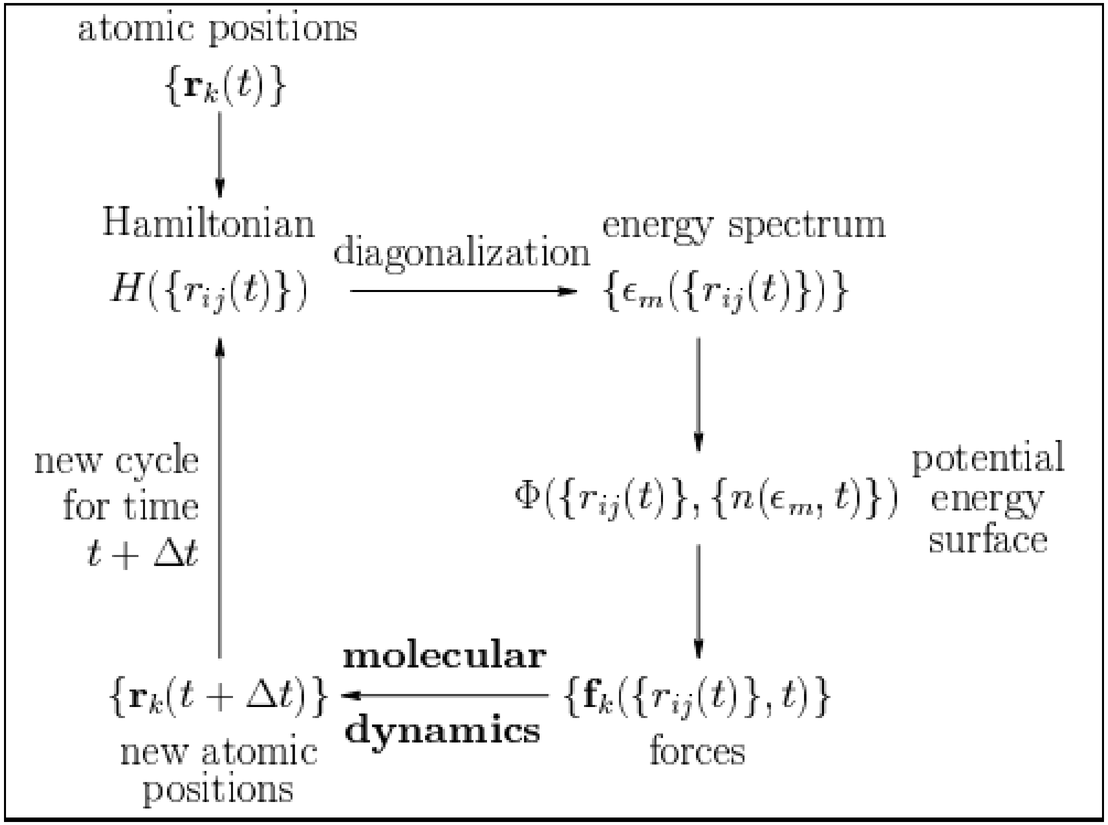
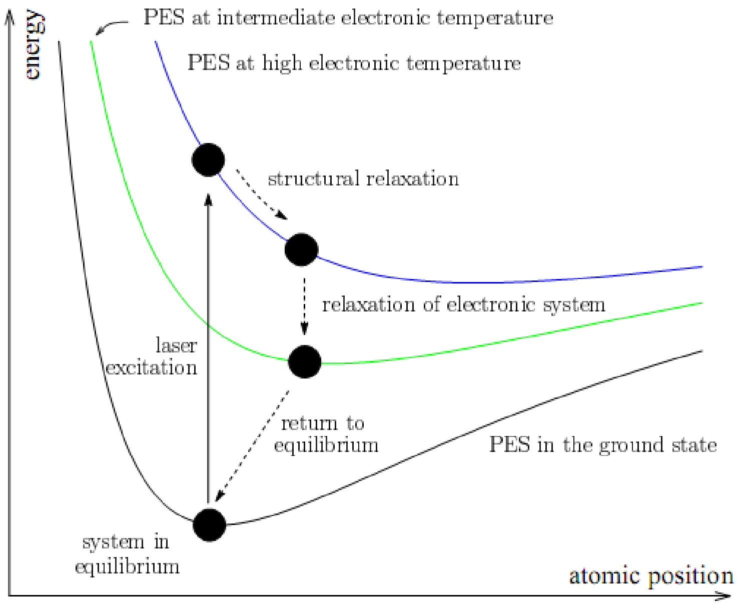
Tight binding method and molecular dynamics (TBMD)



[H. Jeschke et al. PRL 1999]

[This slide courtesy of N.Medvedev]

TB Method and molecular dynamics (TBMD)



$$m_k \ddot{\mathbf{r}}_k = -\frac{\partial \Phi(\{r_{ij}\}, t)}{\partial \mathbf{r}_k}$$

Electrons **Core**

$$\Phi(\{r_{ij}(t)\}, t) = \sum_m f(\epsilon_m, t)\epsilon_m + \frac{1}{2}\sum_{\substack{ij \\ j \neq i}} E_{\text{rep}}(r_{ij})$$

***f*(ϵ_m,*t*) - transient electron distribution function**

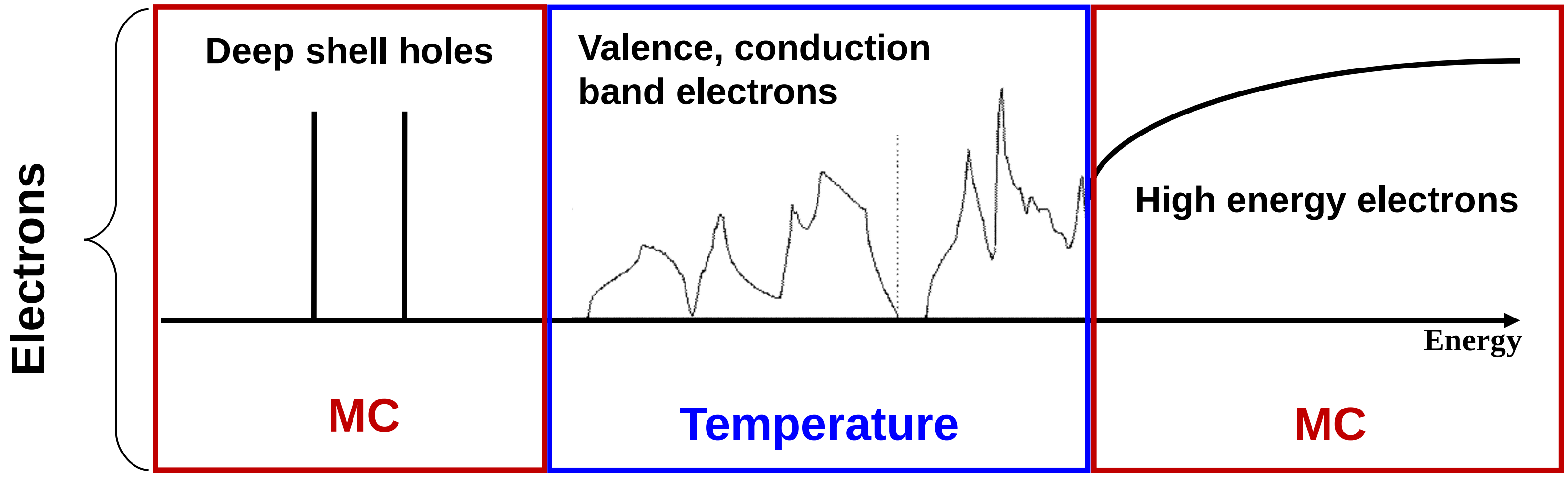
$\epsilon_m(\{r_{ij}(t)\}) = \langle m | H_{\text{TB}}(\{r_{ij}(t)\}) | m \rangle$ **- transient band structure**

[This slide courtesy of N.Medvedev]

[H. Jeschke et al. PRL 1999]

DESY

Combined MC-TBMD



$$m_k \, \ddot{\mathbf{r}}_k = -\frac{\partial \Phi(\{r_{ij}\}, t)}{\partial \mathbf{r}_k}$$

Electrons Core

$$\Phi(\{r_{ij}(t)\}, t) = \underbrace{\sum_m \boldsymbol{f}(\epsilon_m, t)\epsilon_m}_{\text{Electrons}} + \underbrace{\frac{1}{2}\sum_{\substack{ij \\ j \neq i}} E_{\text{rep}}(r_{ij})}_{\text{Core}}$$

[This slide courtesy of N.Medvedev]

[B. Ziaja, N. Medvedev, HEDP 8, 18 (2012)]

Processes considered

1) Photoabsorbtion by deep shells and VB

2) Scattering of fast electrons:

- Deep shells ionization

- VB and CB scatterings

3) Auger-decays of deep holes

4) Thermalization in VB and CB

} - MC

5) Lattice heating (e-phonon coupling) - Temperature & Boltzmann equation

6) Atomic dynamics

7) Changes of band structure

8) Changes of scattering rates

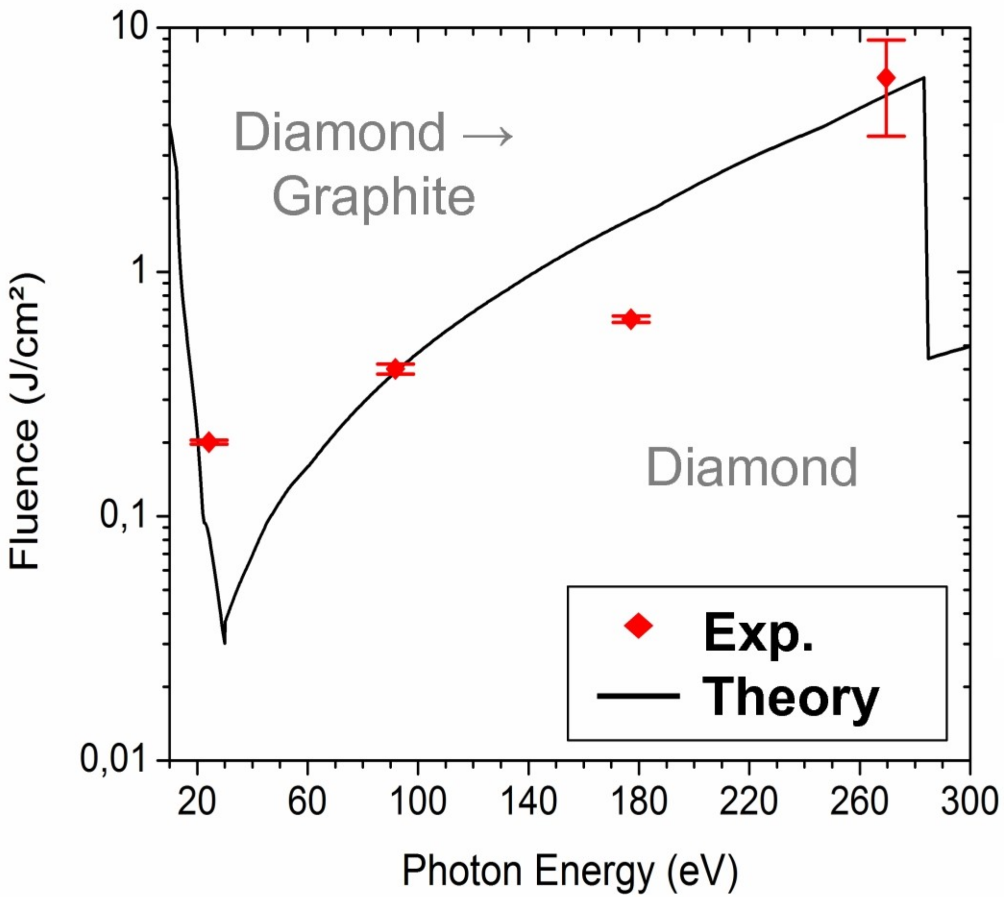
} - TBMD

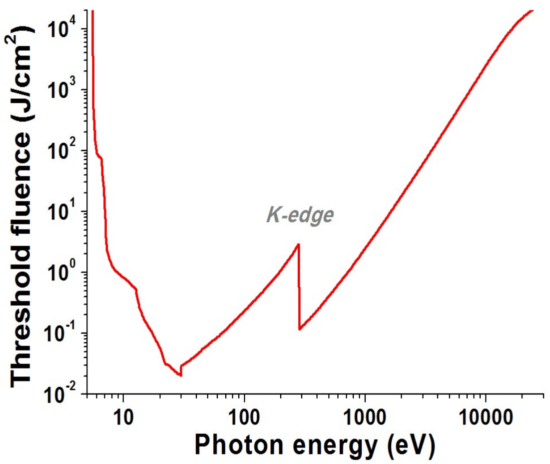
DESY

[This slide courtesy of N.Medvedev]

Graphitization Damage threshold

Irradiated diamond turns into graphite if the fluence is high:





Extrapolation to hard X-rays

Damage threshold is in a good agreement with the experiments by J. Gaudin *et al.* (FLASH)

≈ 0.7 eV/at

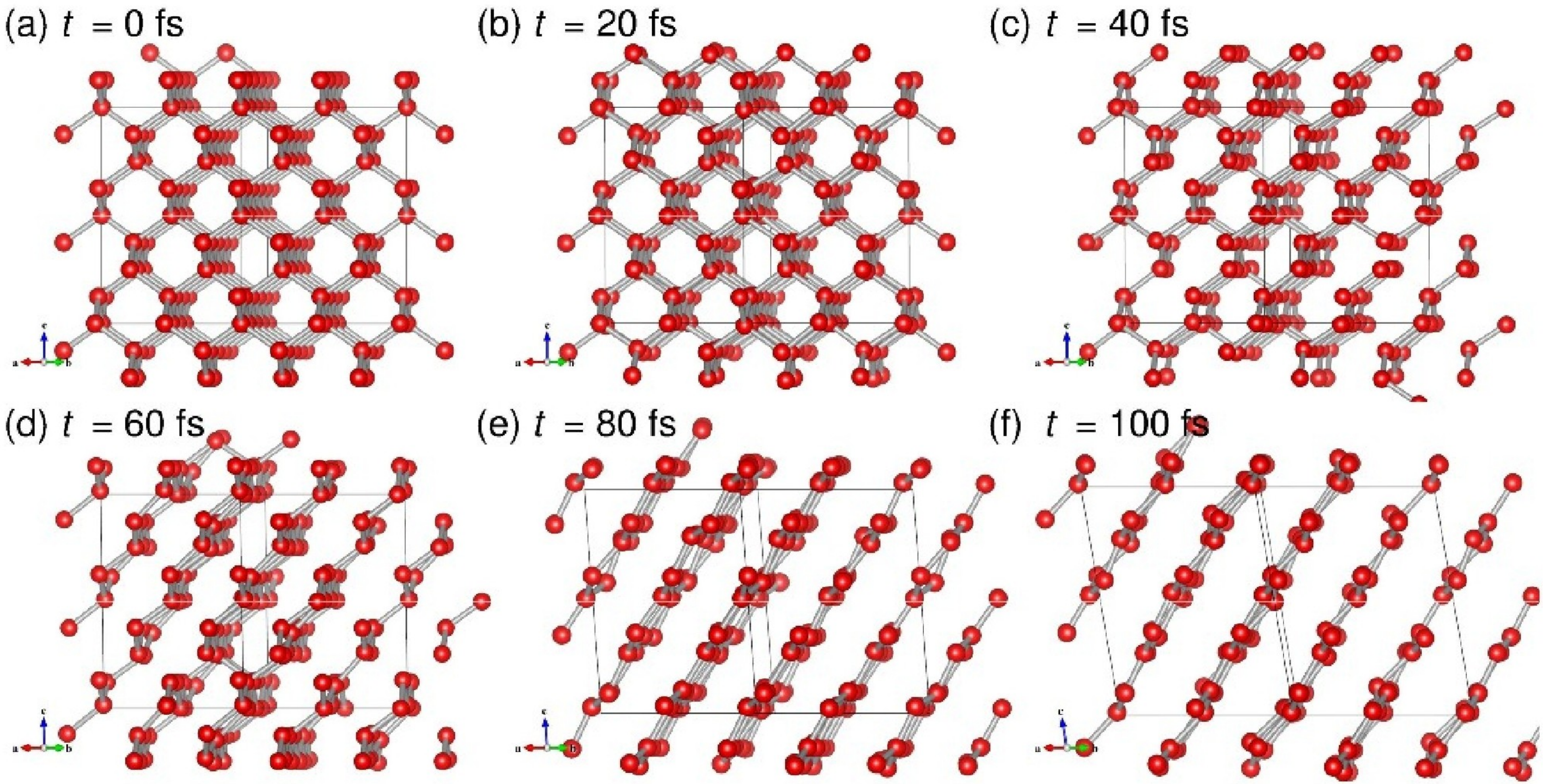
[J. Gaudin et al., PRB, Rapid Comm. 88 (2013) 060101 (R)]

[N. Medvedev , H. Jeschke, BZ, PRB 88 (2013) 224304]

[This slide courtesy of N.Medvedev]

Graphitization: Atomic snapshots

Photon energy 92 eV, FWHM = 10 fs



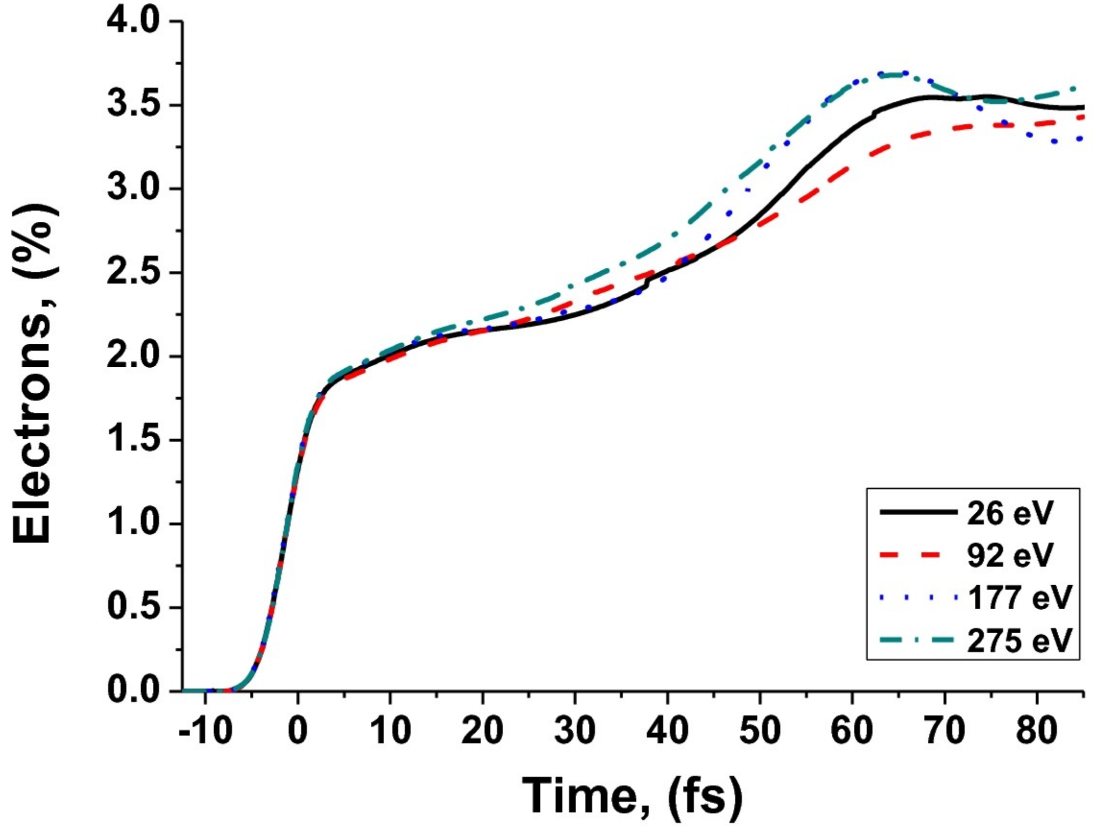
Ultrafast graphitization of diamond

[N. Medvedev, H. Jeschke, B. Ziaja, NJP 15 (2013) 015016]

[This slide courtesy of N.Medvedev] **Increase of electronic density → band gap collapse**

Results: Conduction band electrons

Different photon energies: 26 eV, 92 eV, 177 eV, 275 eV

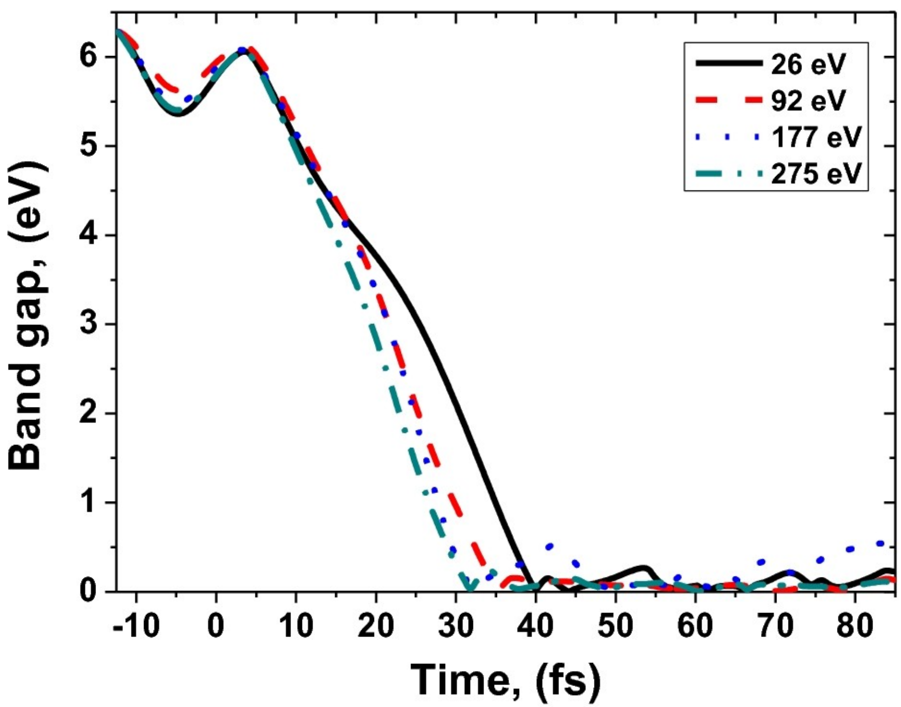


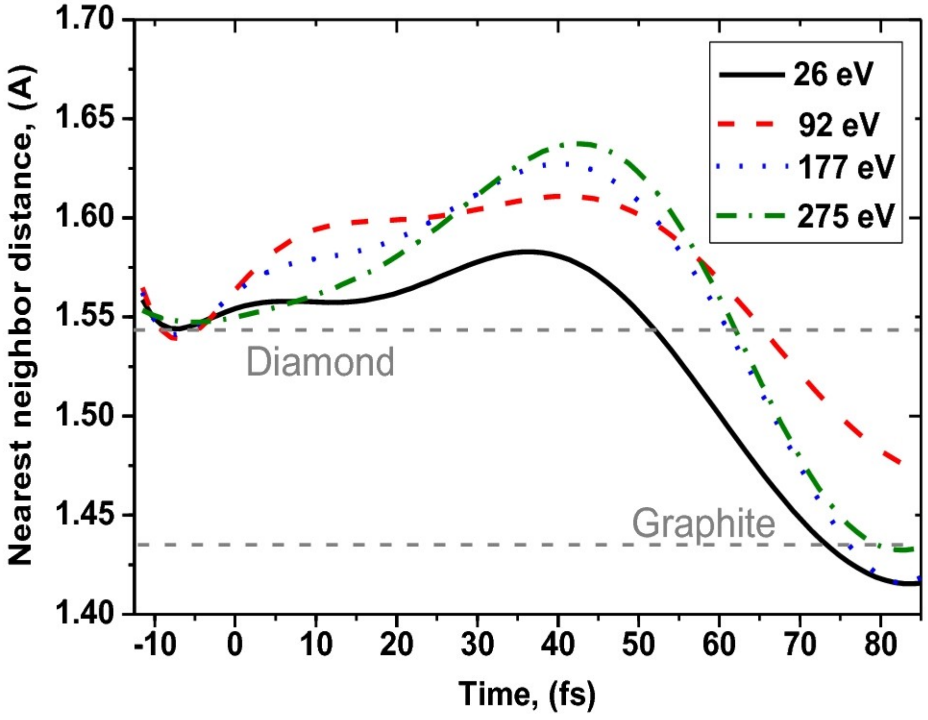
When electron density overcomes threshold value of 1.5 %, phase transition occurs

[This slide courtesy of N.Medvedev]

Results: Bandgap collapse

Different photon energies: 26 eV, 92 eV, 177 eV, 275 eV





Bandgap collapse induces ultrafast phase transition

[This slide courtesy of N.Medvedev]

Diagnostics of transitions?

Damage thresholds → post mortem measurements on samples

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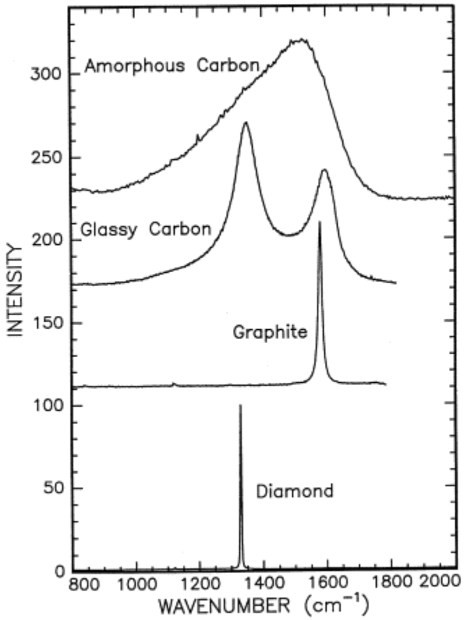

matsci4uwi.wordpress.com

Diagnostics of transitions?

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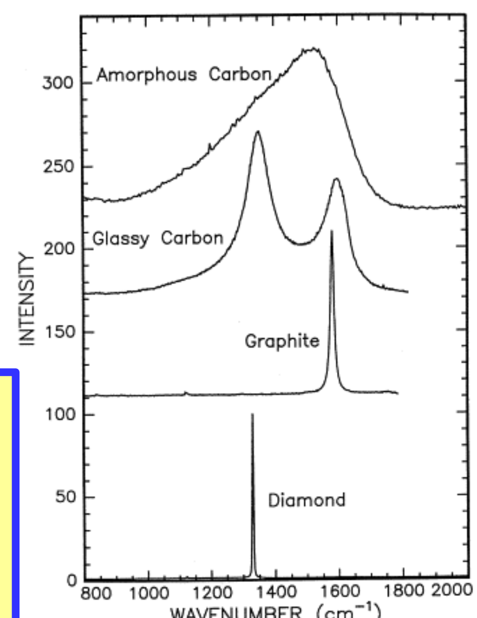


matsci4uwi.wordpress.com

Challenge: long-time large-scale simulations needed for comparison to post-mortem measurements

←

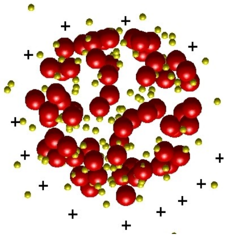
long time-span between ultrafast excitation and final relaxation of the material: lattice heating, diffusion, recrystallization ...

Time-resolved diagnostics of transitions:

Pump-probe experiments:

- pump pulse initiates transition ...

- probe pulse probes it at varying time delay ...



Transient optical properties
as diagnostics of X-ray induced transitions

Low material excitation
below and around damage
threshold → band structure
evolution accurately described
with transferable tight binding
method

Long-wavelength limit (q → 0), **Tight-binding (TB) model**

Optical **dielectric function** within the random-phase approximation (Lindhard formula) [3]:

$$\epsilon^{\alpha\beta}(E) = \delta_{\alpha,\beta} + \frac{4\pi e^2\hbar^2}{m\Omega}\sum_{n,n'}(\eta_{n'} - \eta_n)\frac{F^{\alpha\beta}_{n,n'}}{E_{n,n'}}\left[\frac{1}{E - E_{n,n'} + i\gamma}\right]$$

$$F^{\alpha\beta}_{n,n'} = \frac{2\langle n|\hat{p}_\alpha|n'\rangle\langle n'|\hat{p}_\beta|n\rangle}{mE_{n,n'}}$$

- the oscillator strength [3]

Calculated within tight-binding model by F. Trani et al, as: $\mathbf{P}(\mathbf{R},\mathbf{R}') = \frac{m}{i\hbar}[\mathbf{R} - \mathbf{R}']H(\mathbf{R},\mathbf{R}')$

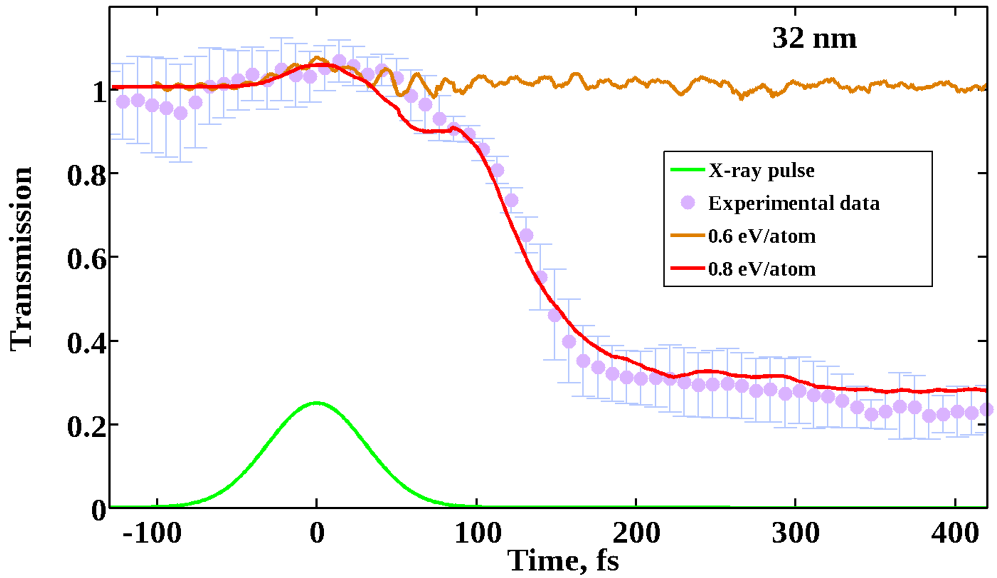
Dielectric function → refractive indices n, k

[Courtesy of V. Tkachenko] [V. Tkachenko, N. Medvedev et al. (BZ), *Phys. Rev. B* 93 (2016) 144101]

Transient optical properties as diagnostics of X-ray induced transitions

Damage threshold

First observation of time-resolved graphitization



Absorbed dose = 0.8 eV/atom

FEL pulse duration = 51 fs

FEL photon energy = 47.4 eV

Probe pulse duration = 32.8 fs

Probe wavelength = 630 nm

Angle of X-ray pulse incidence = 20°

Experiment performed by Sven Toleikis, Franz Tavella, Hauke Hoeppner, Mark Prandolini et al. at FERMI facility

-- Characteristic drop of transmission is observed during the experiment on fs time-scale
-- Evidence of phase transition within ~150 fs.
-- Very good agreement with our theoretical predictions for the absorbed dose of 0.8 eV/atom (above graphitization threshold)

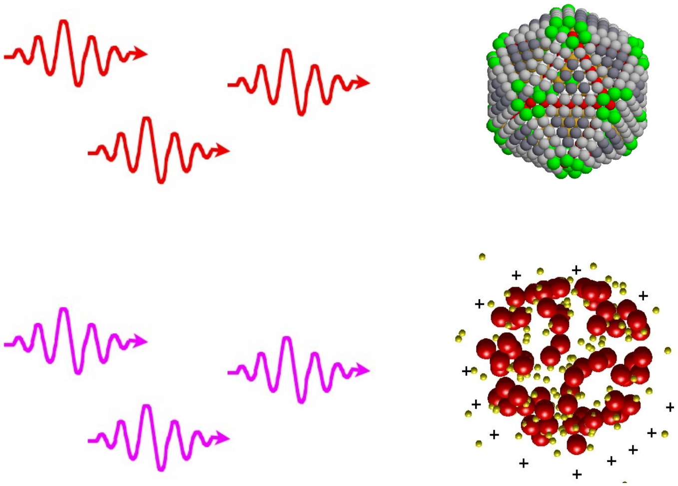
Melting threshold

[F. Tavella et al. (V.Tkachenko, N. Medvedev, BZ), HEDP 24 (2017) 22]

[Courtesy of V. Tkachenko]

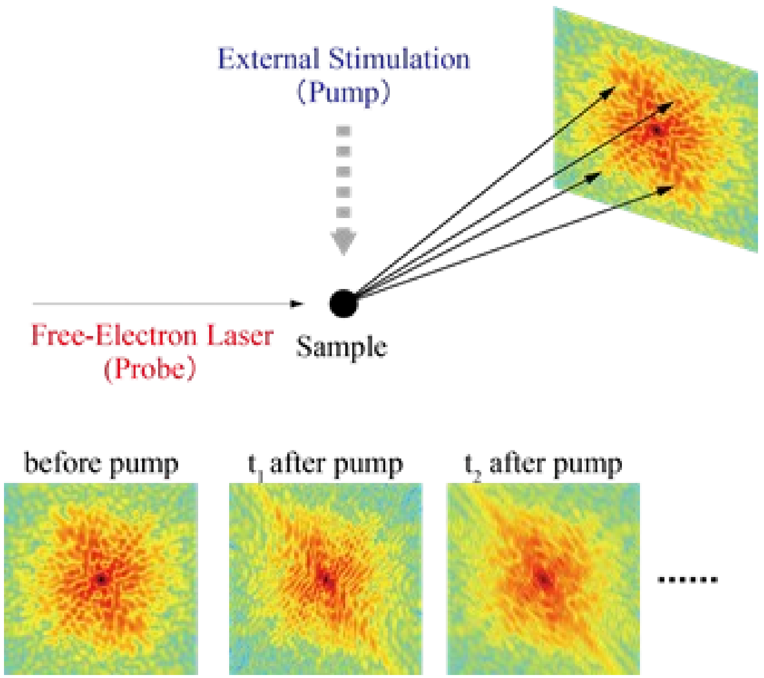
X-ray diffraction as diagnostics of structural transitions?

Pump



XFEL

→



[cxo-www.es.hokudai.ac.jp]

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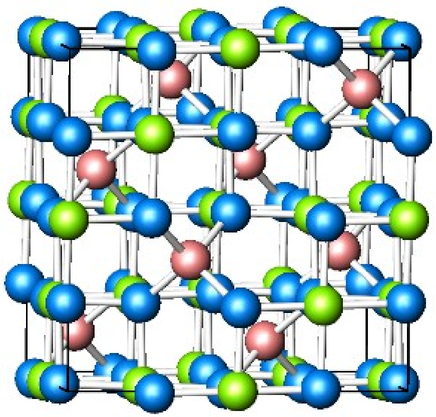
Impact of high-fluence fs X-ray pulses:
→ Transition to Warm Dense Matter or Plasma

Melting threshold

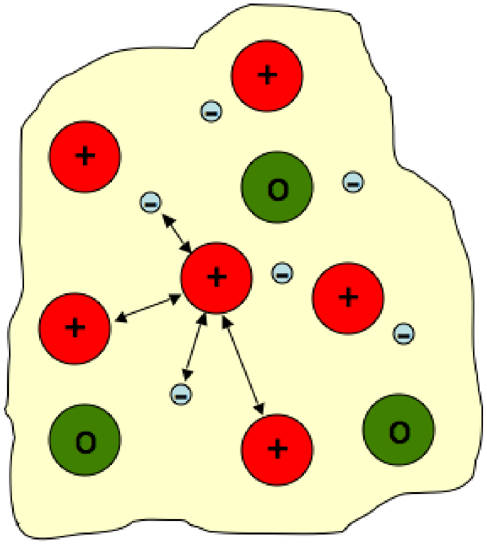
'Ensemble' of bonded atoms



→

WDM

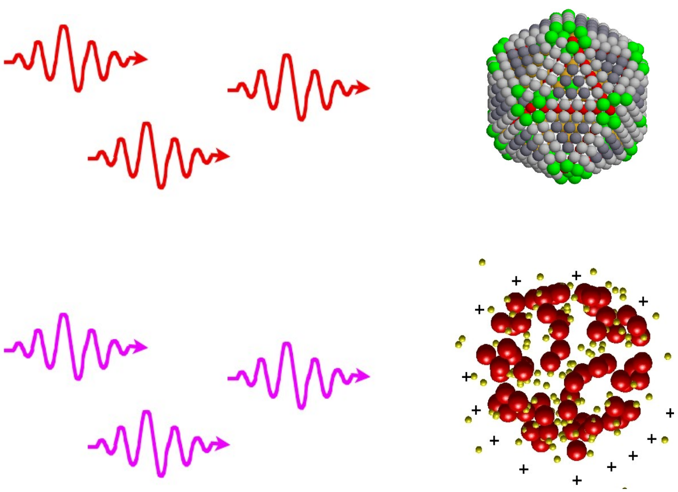
'Gas' of free ions and electrons



X-ray diffraction as diagnostics of structural transitions

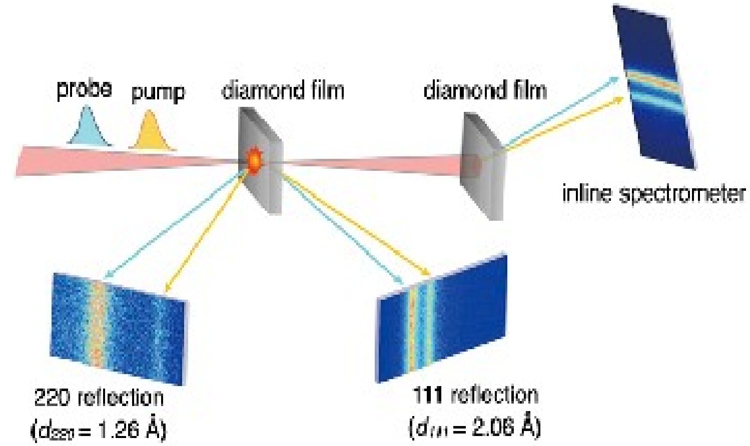
Example: diamond melted into plasma ...

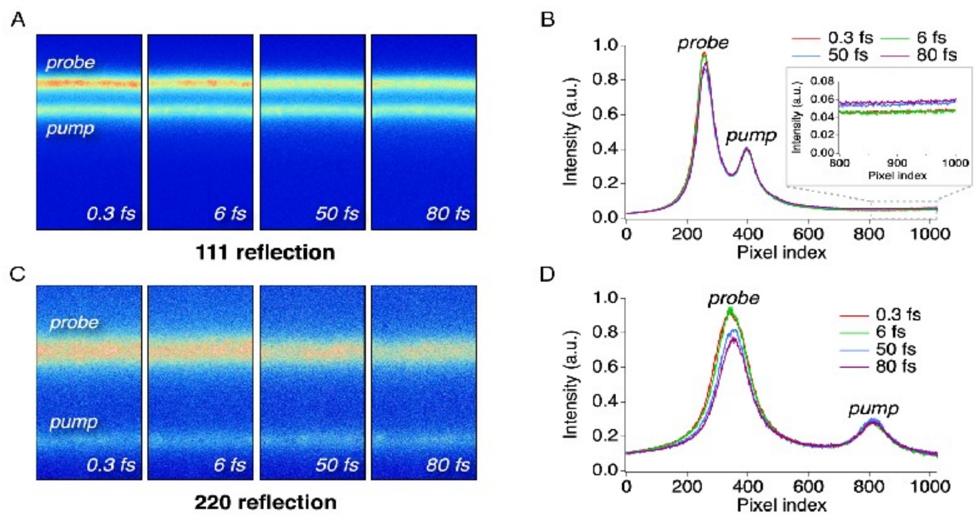
Pump



XFEL

→





[I. Inoue et al., PNAS 113 (2016) 1492]

SACLA pump/probe scheme:

3 / 7 J/cm^2

5 / 5 fs

6.1/ 5.9 keV

Amorphisation of diamond: atomic snapshots

Irradiation of diamond crystal with 5 fs-long pump pulse:

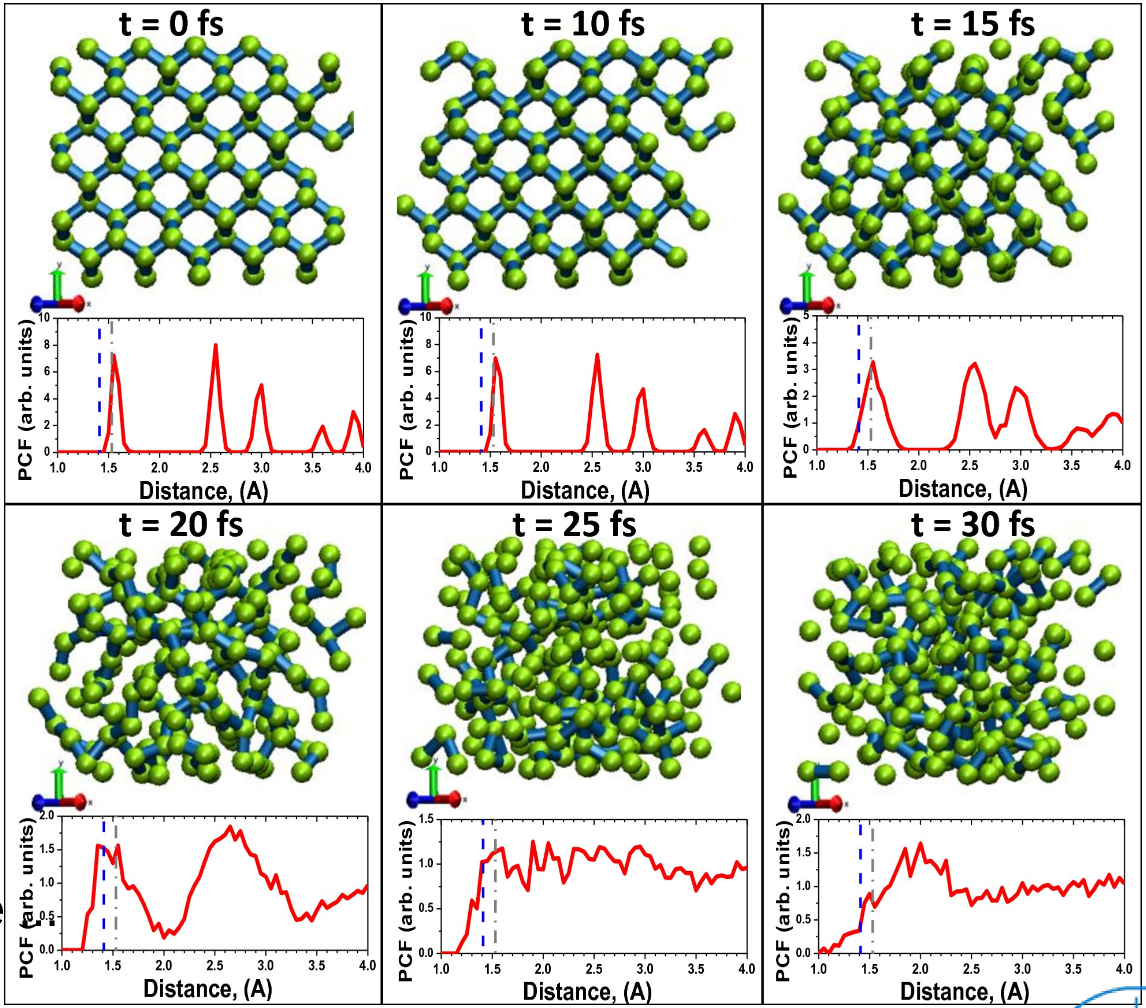
X-ray photons: 6.1 keV energy
Fluences: 2.3 - 3.1· 10^4 J/cm^2

↓

Average absorbed dose/atom:
19-25 eV/atom

↓

Intermediate graphitization phase at ~ 20 fs with overdense graphite

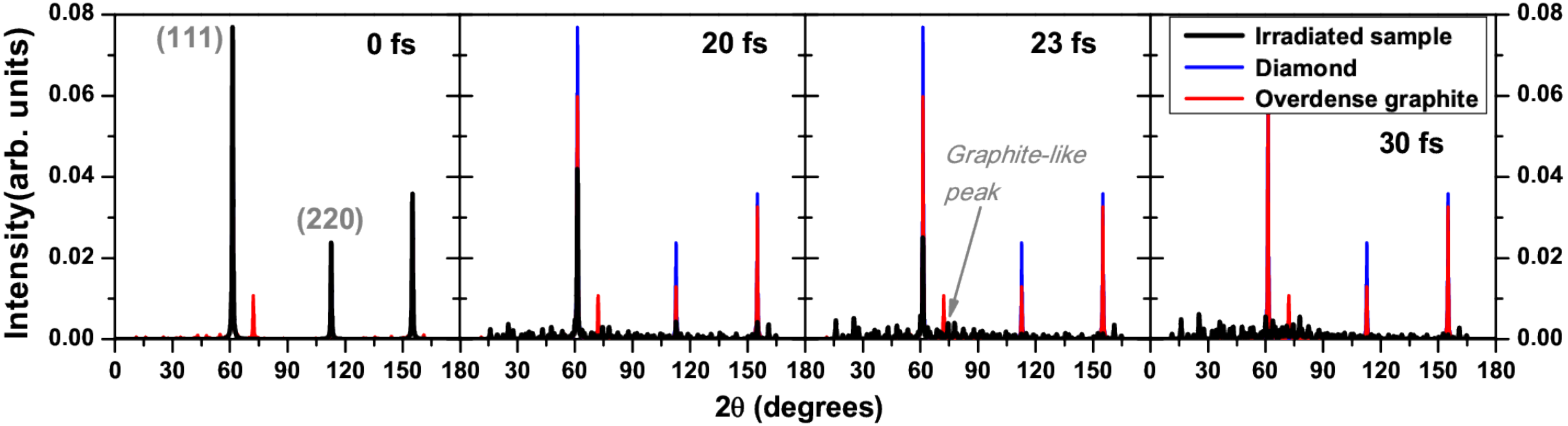


[N. Medvedev, B. Ziaja, Sci. Rep. 8 (2018) 5284]

XTANT simulations by N. Medvedev

Amorphisation of diamond: transient graphitization phase?

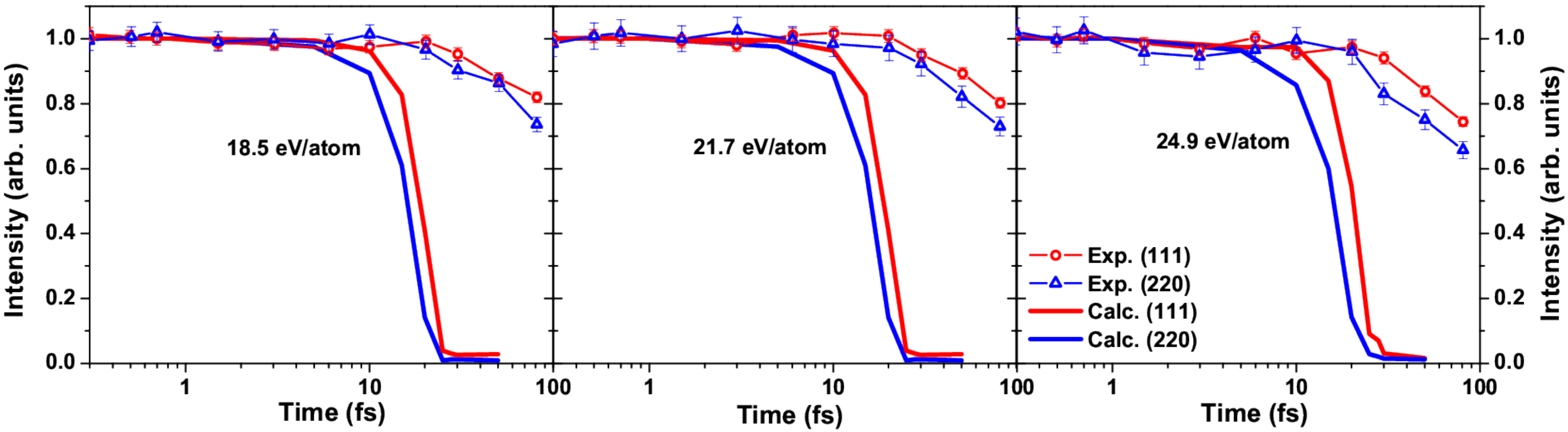
Intermediate few-fs long graphitization phase:
simulated powder diffraction peaks



Powder diffraction patterns in diamond irradiated with an X-ray pulse of 6.1 keV photon energy, 5 fs FWHM duration, at the average absorbed dose of 24.9 eV/atom at different time instants after the pump pulse maximum.

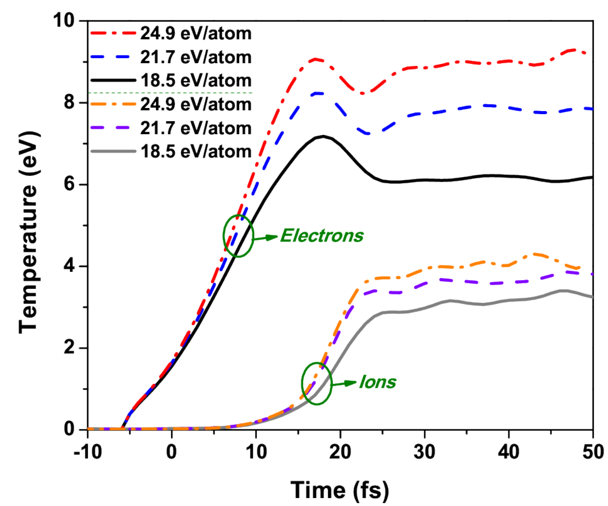
[N. Medvedev, B. Ziaja, Sci. Rep. 8 (2018) 5284]

Comparison with experiment



Integrated diffraction peak intensities (111) and (220) in X-ray irradiated diamond →
Too fast intensity decrease predicted

Temperatures of electrons and ions in X-ray irradiated diamond →
Timescales of the T_i increase in agreement with DW fit from experiment



[N. Medvedev, B. Ziaja, Sci. Rep. 8 (2018) 5284]

Necessary model improvements

Quest for an ab-initio model to describe accurately and efficiently WDM formation after solid's irradiation with X-rays.

XTANT could be a possible hybrid solution if some current shortcomings are addressed:

- correct description of atomic orbitals and impact ionization cross sections in dense plasmas

- impact of K-shell holes

- band structure description underway to dense plasma → transferable tight-binding model we use breaks down at high densitites of excited electrons (i.e., times > 20 fs)

[N. Medvedev, B. Ziaja, Sci. Rep. 8 (2018) 5284]

Necessary model improvements

Quest for an ab-initio model to describe accurately and efficiently WDM formation after solid's irradiation with X-rays.

XTANT could be a possible hybrid solution if some current shortcomings are overcome:

- correct description of atomic orbitals and impact ionization cross sections in dense plasmas → work on-going (J.Bekx, S.-K. Son, R. Santra, BZ)

- impact of K-shell holes→ turns out to be not critical in this case (photoionization degree ~ 0.003-0.004 per atom)

- band structure description underway to dense plasma → tight-binding model we use breaks down at high densitites of excited electrons (i.e., times > 20 fs) → ab-initio model under construction (XMOLECULE → J.Bekx, V. Lipp, N. Medvedev, R. Santra, S.-K. Son, V. Tkachenko, BZ; or DFT module)

[N. Medvedev, B. Ziaja, Sci. Rep. 8 (2018) 5284]

Outline

1. Transitions in matter triggered by x-rays

2. X-ray induced graphitization of diamond

3. Amorphization of diamond by intense X-ray pulse

4. Summary

Summary

Transitions in solids induced by X-ray radiation depend on material properties and pulse parameters:

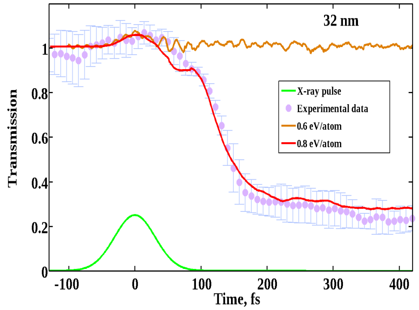
-below damage threshold – non-equilibrium electron kinetics → XTANT

-below melting threshold – also rearrangement of atomic structure ↑

-above melting threshold – amorphization; plasma, warm-dense matter formation → model developments on-going!

Diagnostics of transitions:

- transient optical properties ← time-resolved



- X-ray diffraction ← time-resolved

- post mortem measurements

Thanking my collaborators and the CFEL-DESY Theory Group

V. Lipp

N. Medvedev

V. Saxena

V. Tkachenko

+

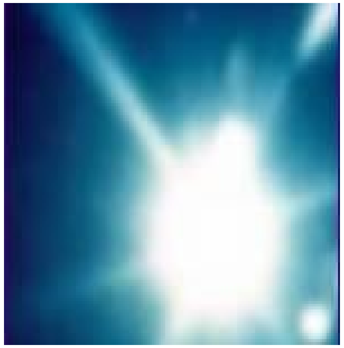
J. Bekx

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

CFEL SCIENCE

DESY

Thanking our external collaborators...



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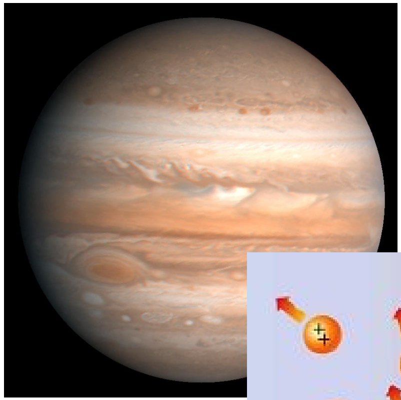

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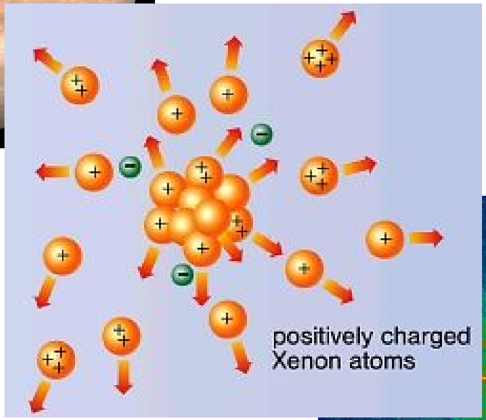
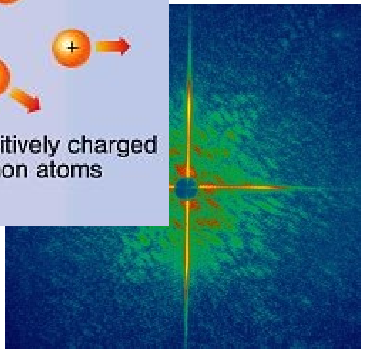


S. Toleikis, H. Hoeppner, M. Prandolini, T. Takanori (DESY)

and ...



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XTOOLs of the CFEL-DESY Theory Group

- **XATOM**[1]: an ab-initio integrated toolkit for x-ray atomic physics
- **XMOLECULE**[2]: an ab-initio integrated toolkit for x-ray molecular physics
- **XMDYN**[3]: an MD/MC tool for modeling matter irradiated with high intensity x-rays
- **XHYDRO**[4]: a hydrodynamic tool for simulating plasma in local thermodynamic equilibrium
- **XSINC**[5]: a tool for calculating x-ray diffraction patterns for nanocrystals
- **XTANT**[6]: a hybrid tight-binding/MD/MC tool to study phase transitions
- **XCASCADE**[7]: MC tool to follow electron cascades induced by low x-ray excitation
- **XCALIB**[8]: an XFEL pulse profile calibration tool based on ion yields

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1-5, 8	3,4,6,7, Boltzmann-code	1,2,3,8	3,5,8	6,7 (now in Prague)	4 (now in India)	1,2	1,2,8	6,7	3,5	6,7

Released versions of XATOM and XMDYN available at http://www.desy.de/~xraypac

[Slide courtesy of Z. Jurek]

Thank you for your attention !

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