# Transitions in matter induced by intense X-ray radiation and their diagnostics.

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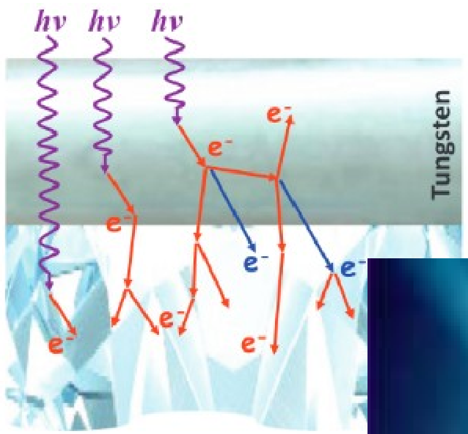


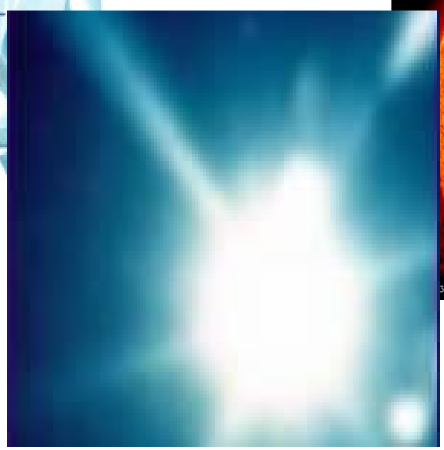

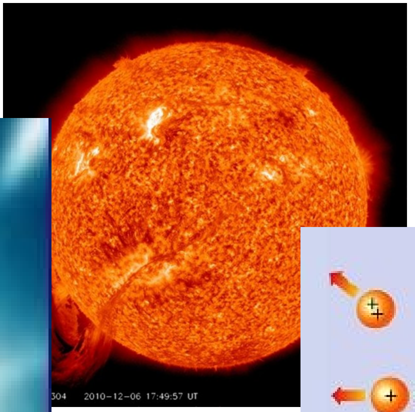


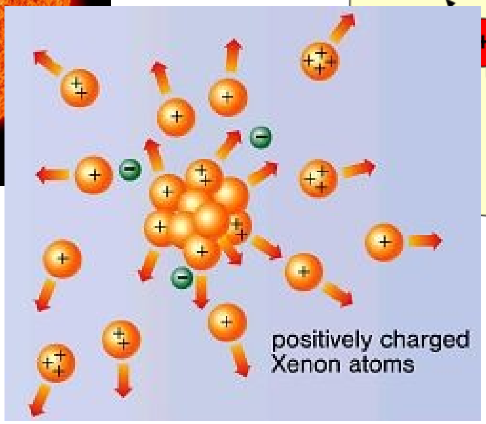


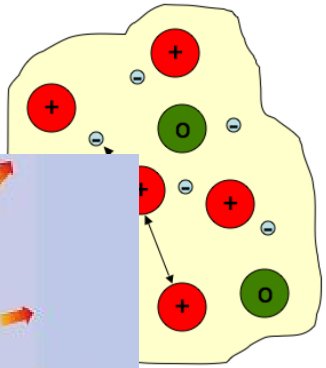

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# CFEL-DESY Theory Group
# at the Center for Free-Electron Laser Science

**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, Y.-J. Chen, O. Geffert, D. Gorelova, L. Inhester, Z. Jurek, A. Hanna, A. Karamatskou, M. Krishna, Z. Li, V. Lipp, M. A. Malik, P. K. Mishra, R. Santra (Group Director), 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 | V. Tkachenko | V. Saxena + J. Bekx

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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
...

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# Structural transitions in solids induced by X-ray radiation

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

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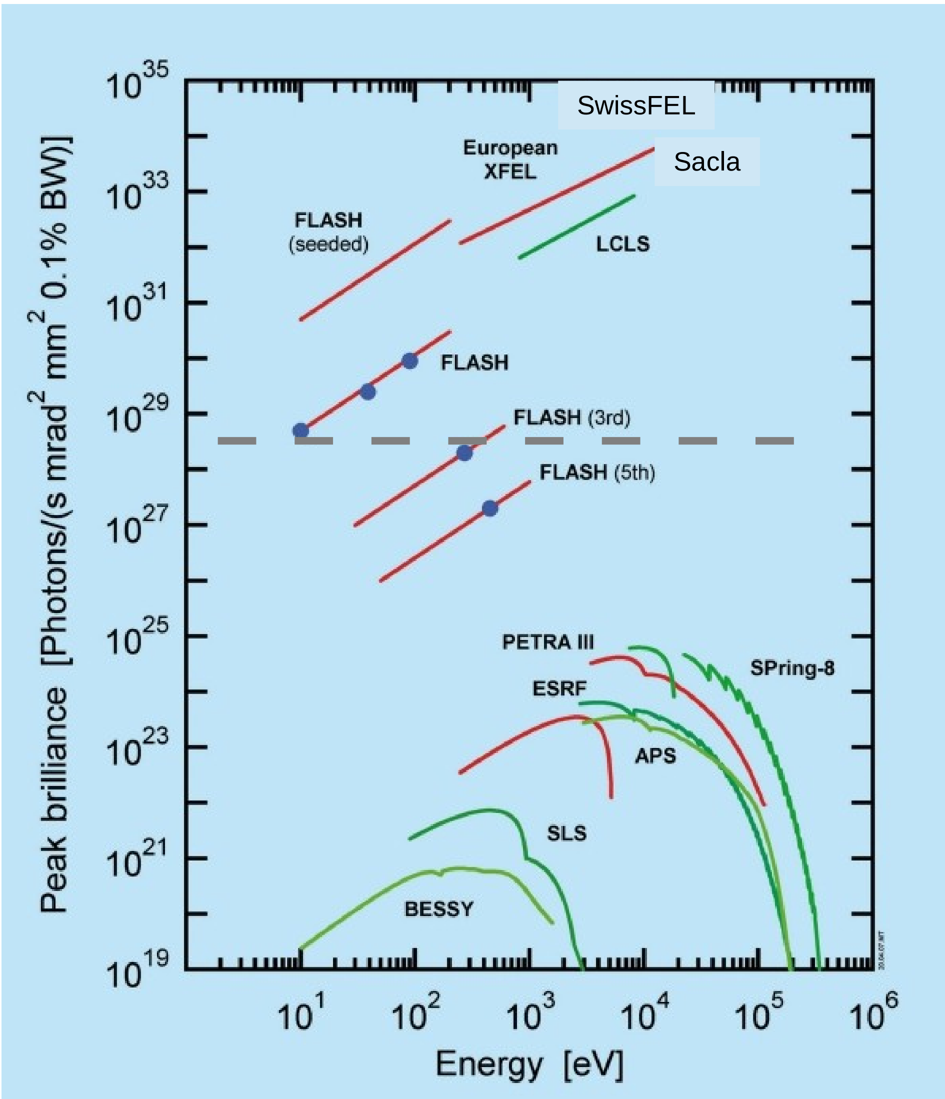
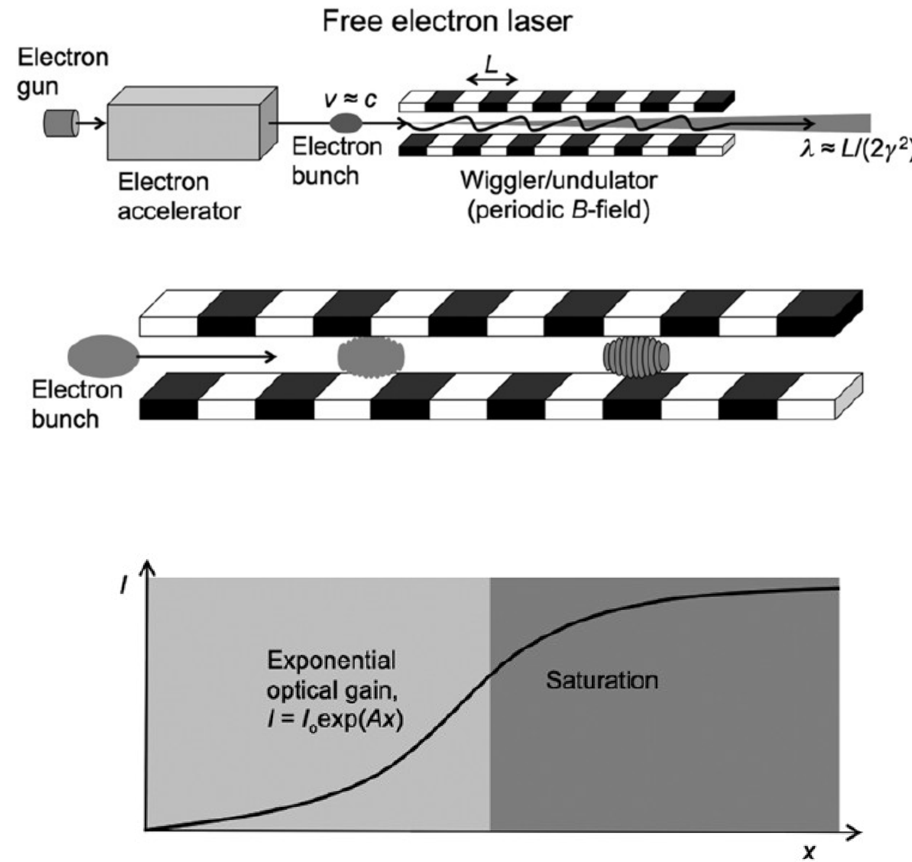
# FELs: 4th generation light sources




photon-science.desy.de



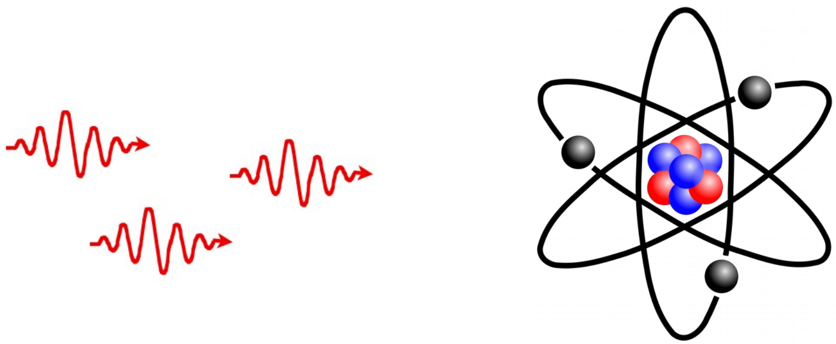

Ribic, Margaritondo, J. Phys. D **45** 213001 (2012)

Pulse duration ~ down to 10 fs
Wavelength ~ VUV- hard X-ray

**[This slide courtesy of Z. Jurek]**

# Structural transitions in solids induced by X-ray radiation

**Transition depends on the average absorbed dose ....**



egymbb.sk

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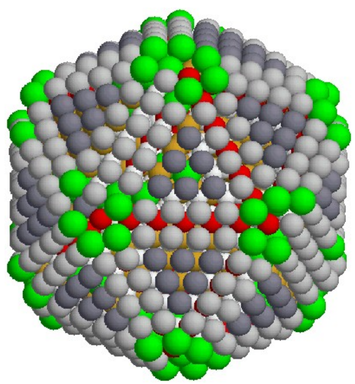
# Main interactions:

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

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

Ions: electrostatic repulsion → band modification → structural transition?



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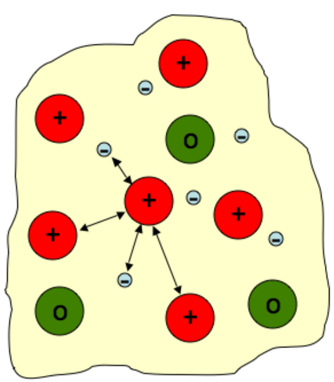
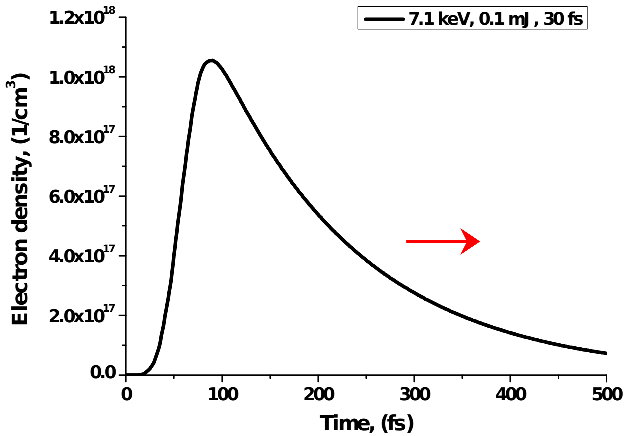


# Interaction of solids with low-fluence femtosecond X-ray pulses: → **Electron Kinetics**

**Low dose**

Radiation excites free electrons within solids which induce transient change of solid's optical properties (reflectivity, transmission) but no structural changes.

Example:
$SiO_2$

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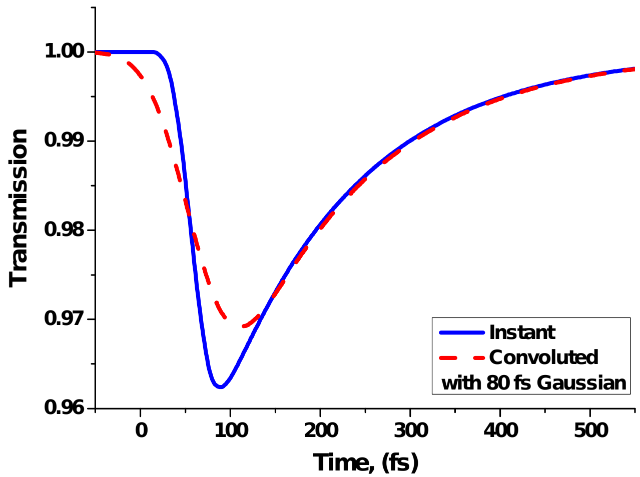



Electron density translates into transient change of optical properties with **Drude model** (or ab-initio calculated dielectric function)
[Medvedev et al., CPP 53 (2013) 347]

→ application for a non-destructive high-resolution FEL pulse timing tool
[Harmand et al. (Medvedev, Ziaja), Nat. Phot. 7 (2013) 215]
[Riedel et al.(Medvedev,Ziaja), Nat. Commun. 4 (2013) 1731]
[Finetti et al. (Medvedev, Tkachenko, Ziaja), PRX (2017) accepted]

**Damage Threshold**

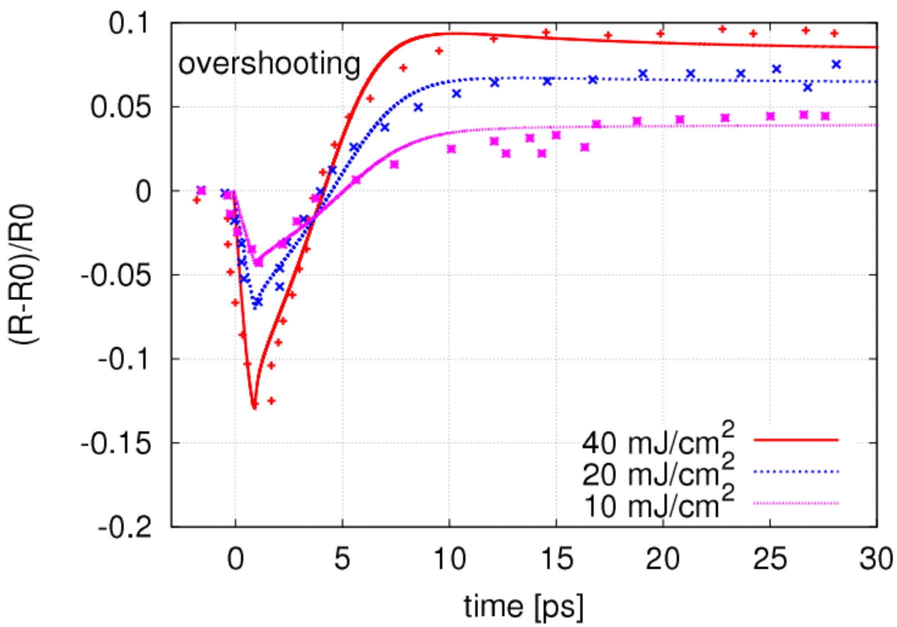
**[Images courtesy of N. Medvedev]**

# Interaction of solids with low-fluence femtosecond X-ray pulses → Electron Kinetics and Exchange with Lattice

**Low dose**

Reflectivity overshooting in GaAs

- **Reflectivity overshooting ← effect of band gap shrinking**
- **Timescale < 10 ps**
- **Observable at probe wavelength 800 nm (1.55 eV) ~ band gap width (1.43 eV) ← low absorption**




LCLS measurement (800 eV)

**Damage Threshold**

[B.Z., N. Medvedev, V. Tkachenko, T. Maltezopoulos, W. Wurth, *Sci. Rep*. **5**, 18068 (2015)]

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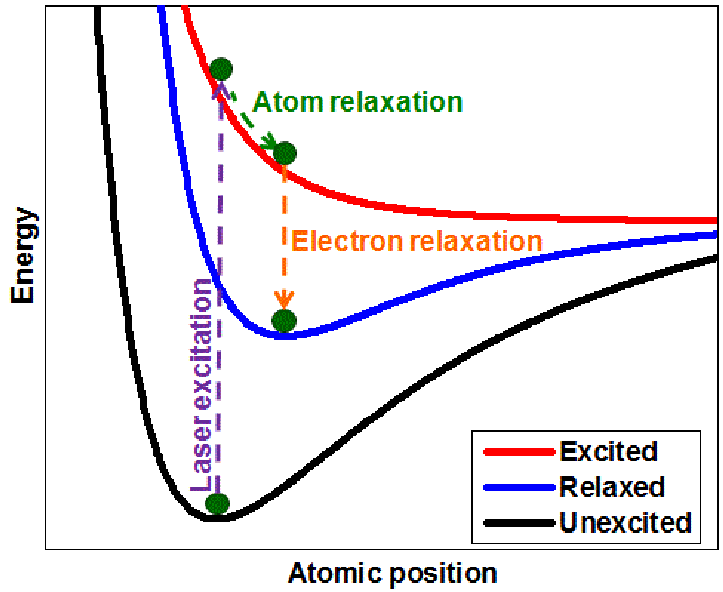
**[Images courtesy of V. Tkachenko]**

# Interaction of solids with femtosecond X-ray pulses of fluence above the damage threshold

**Damage threshold**

**Melting threshold**

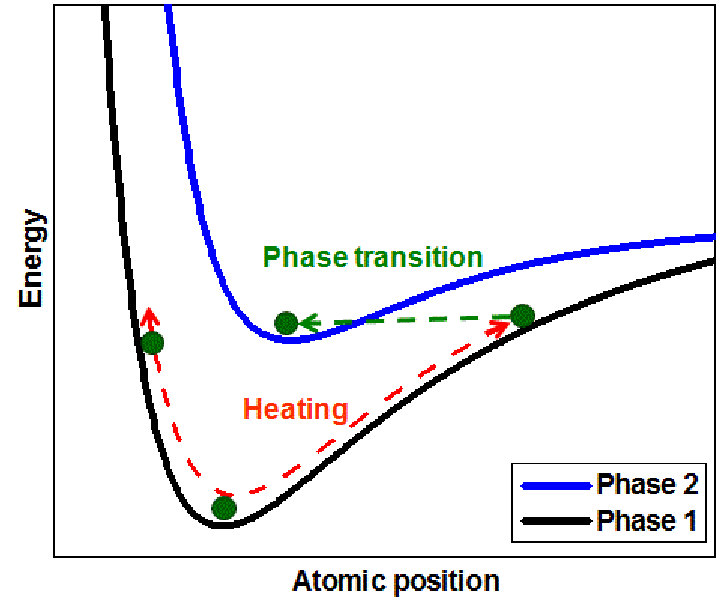
Non-thermal melting (~100 fs)




Change of interatomic potential

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

Thermal melting (~ ps)




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

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[Courtesy of N. Medvedev]

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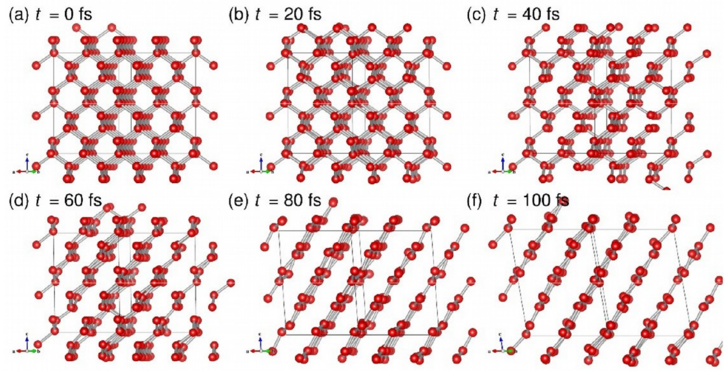
# Interaction of solids with femtosecond X-ray pulses of fluence above the damage threshold:
# → Electron Kinetics + Atomic Relocations

**Damage threshold**

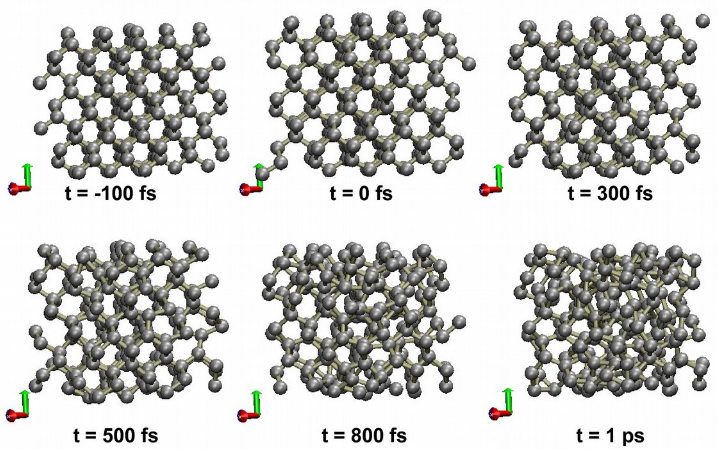
Structural transitions in solids:

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

**Photon energy 92 eV, FWHM = 10 fs**




→ 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 ]

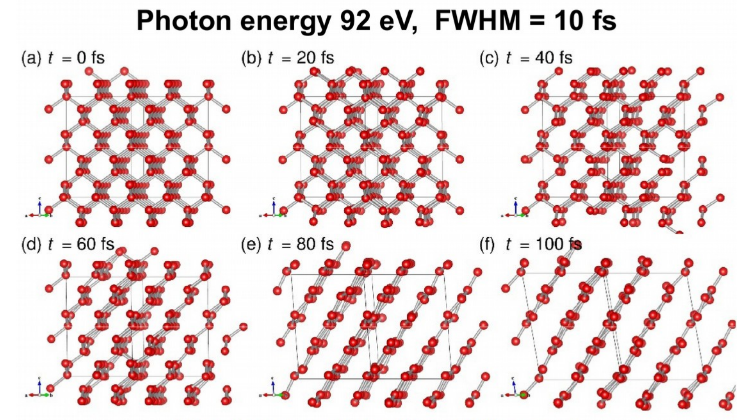
**Damage thresholds in good agreement with experiments!**

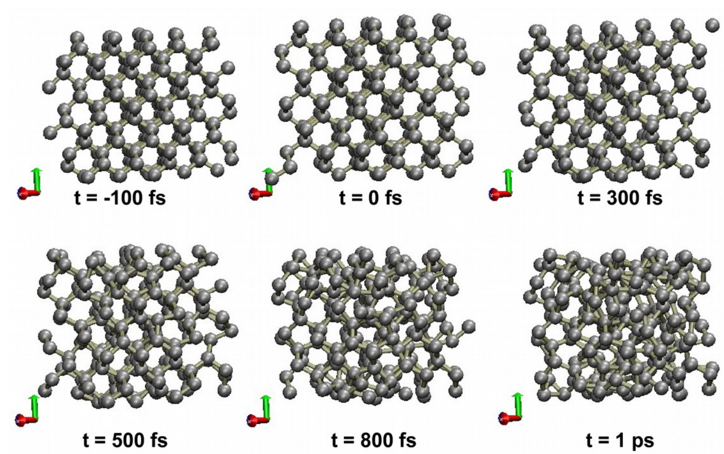
**[Images courtesy of N. Medvedev]**

# 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.]** →




**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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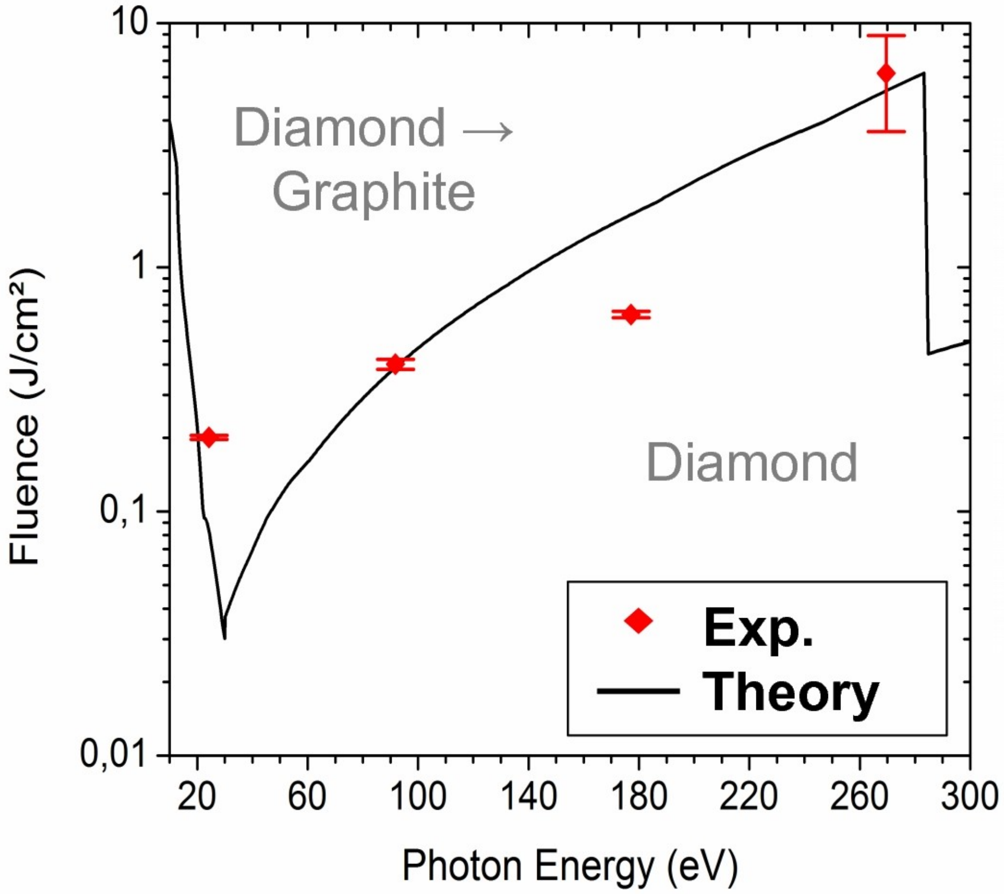
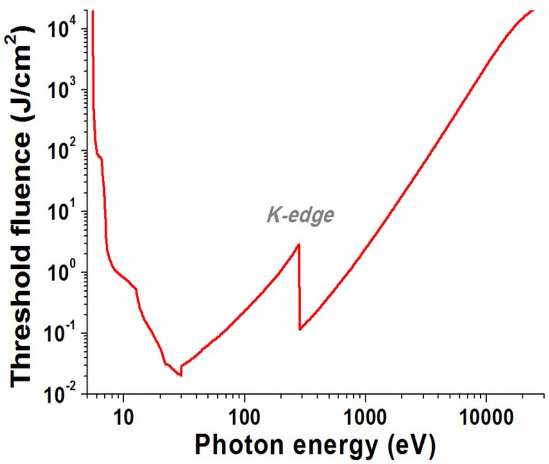
**[Images courtesy of N. Medvedev]**

# 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)**

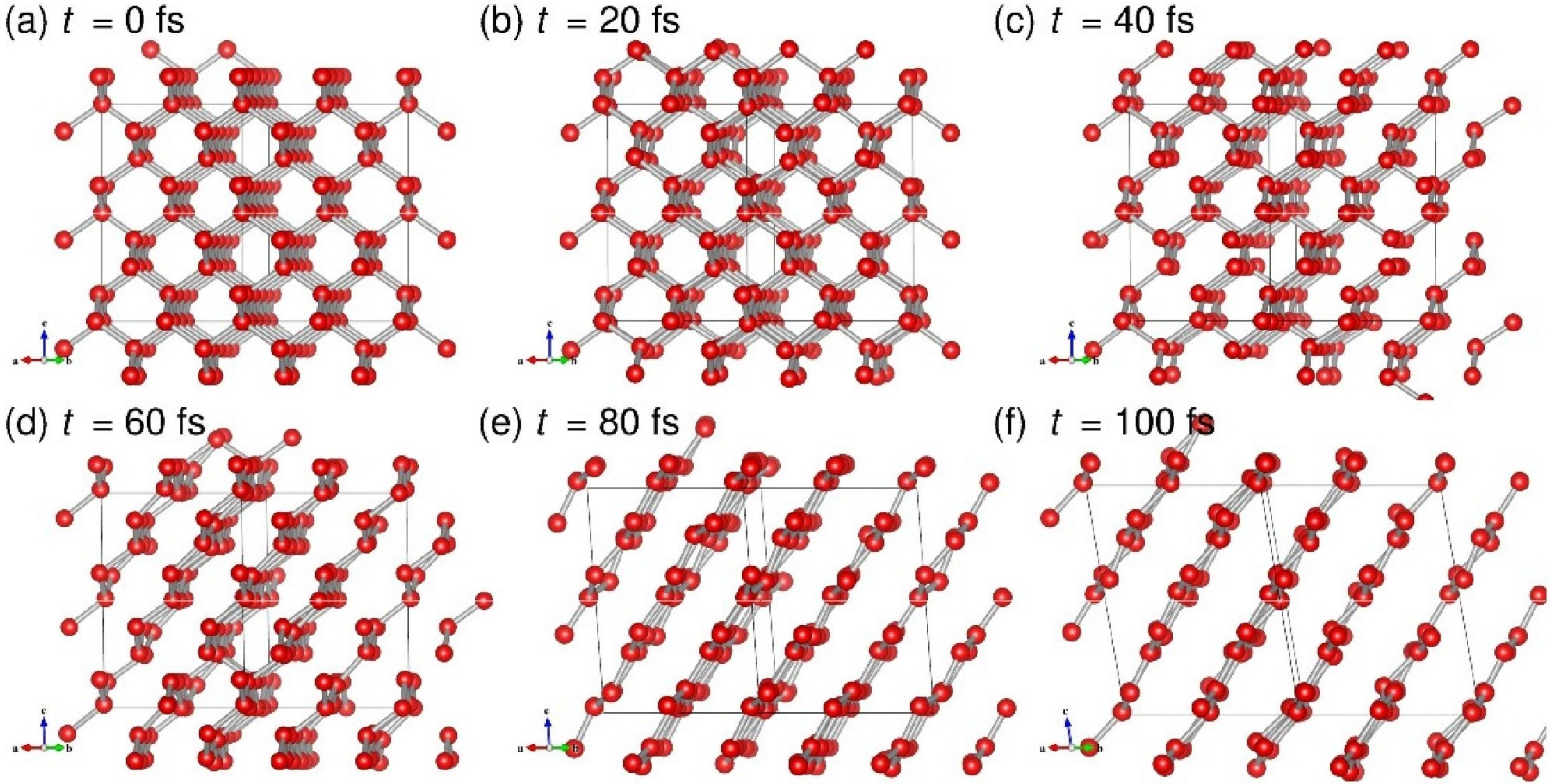
[J. Gaudin *et al.*, (2013) PRB, Rapid Comm. 88 (2013) 060101 (R)]

[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



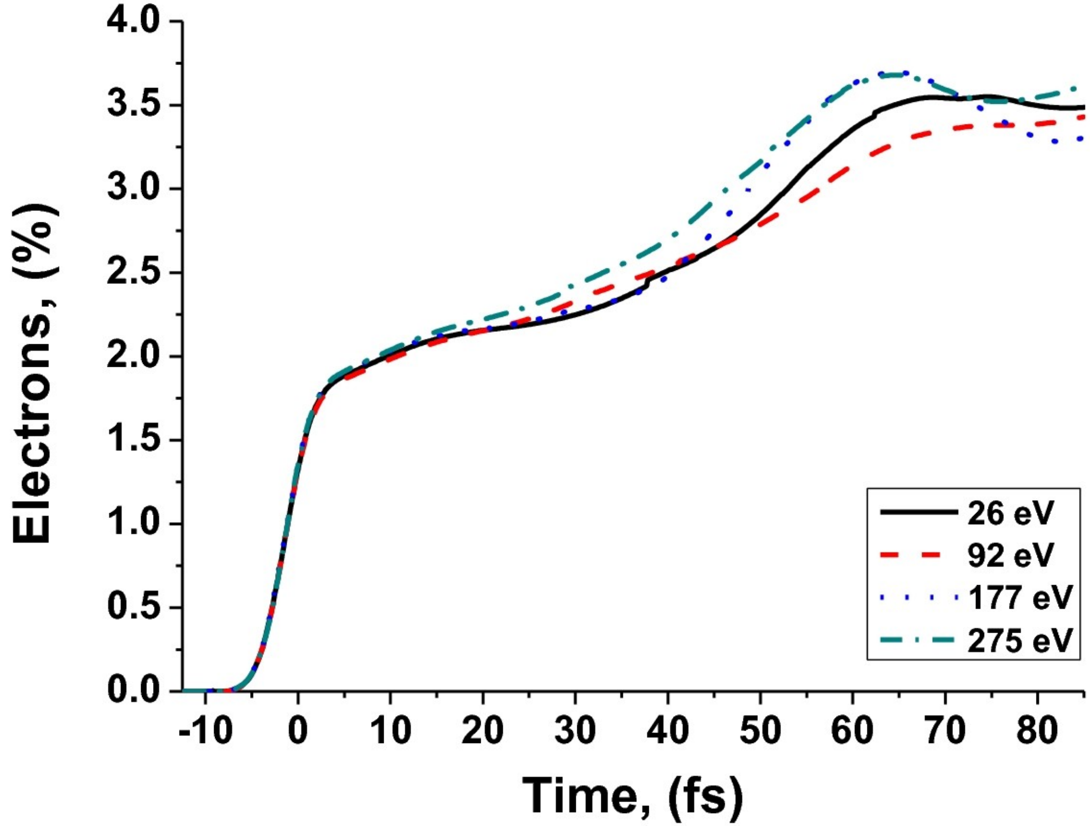

**Ultrafast graphitization of diamond**

[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**

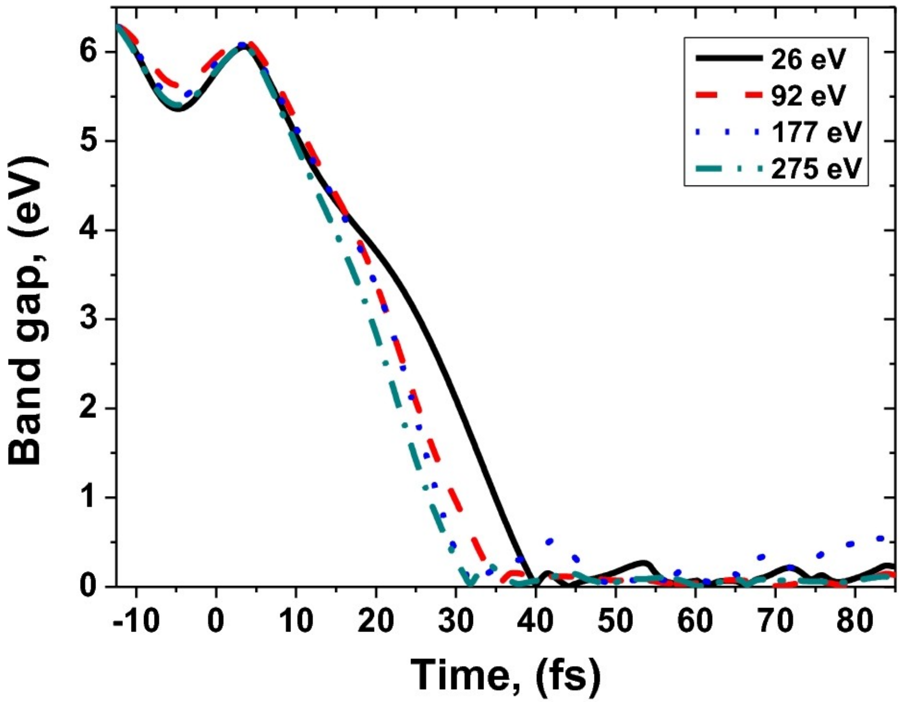


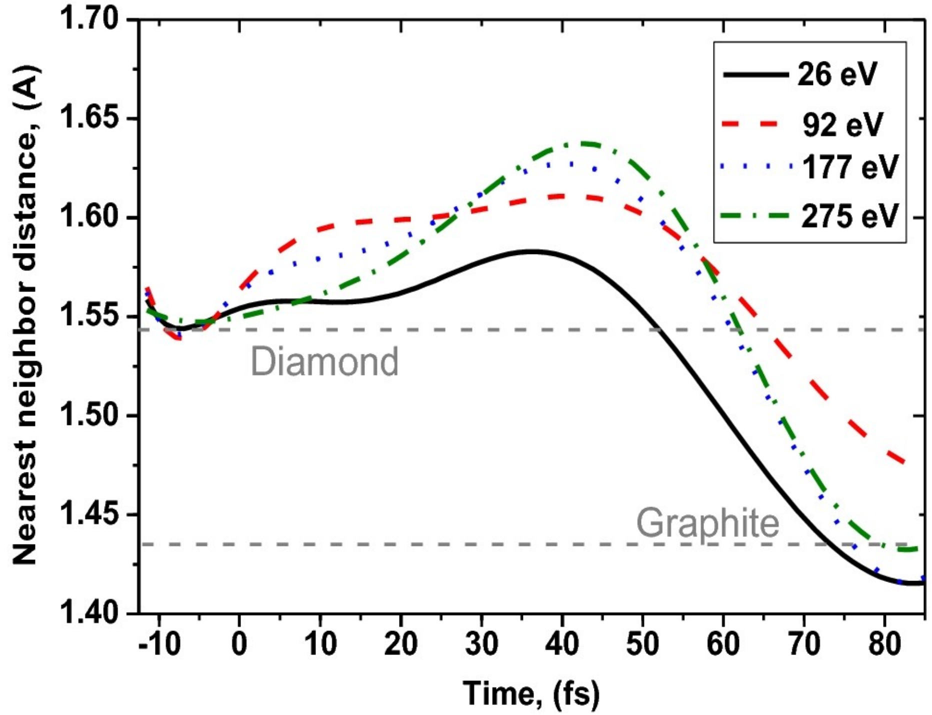

**When electron density overcomes threshold value of 1.5 %, phase transition occurs**

[This slide courtesy of N.Medvedev]

# Results: Bandgap collapse

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

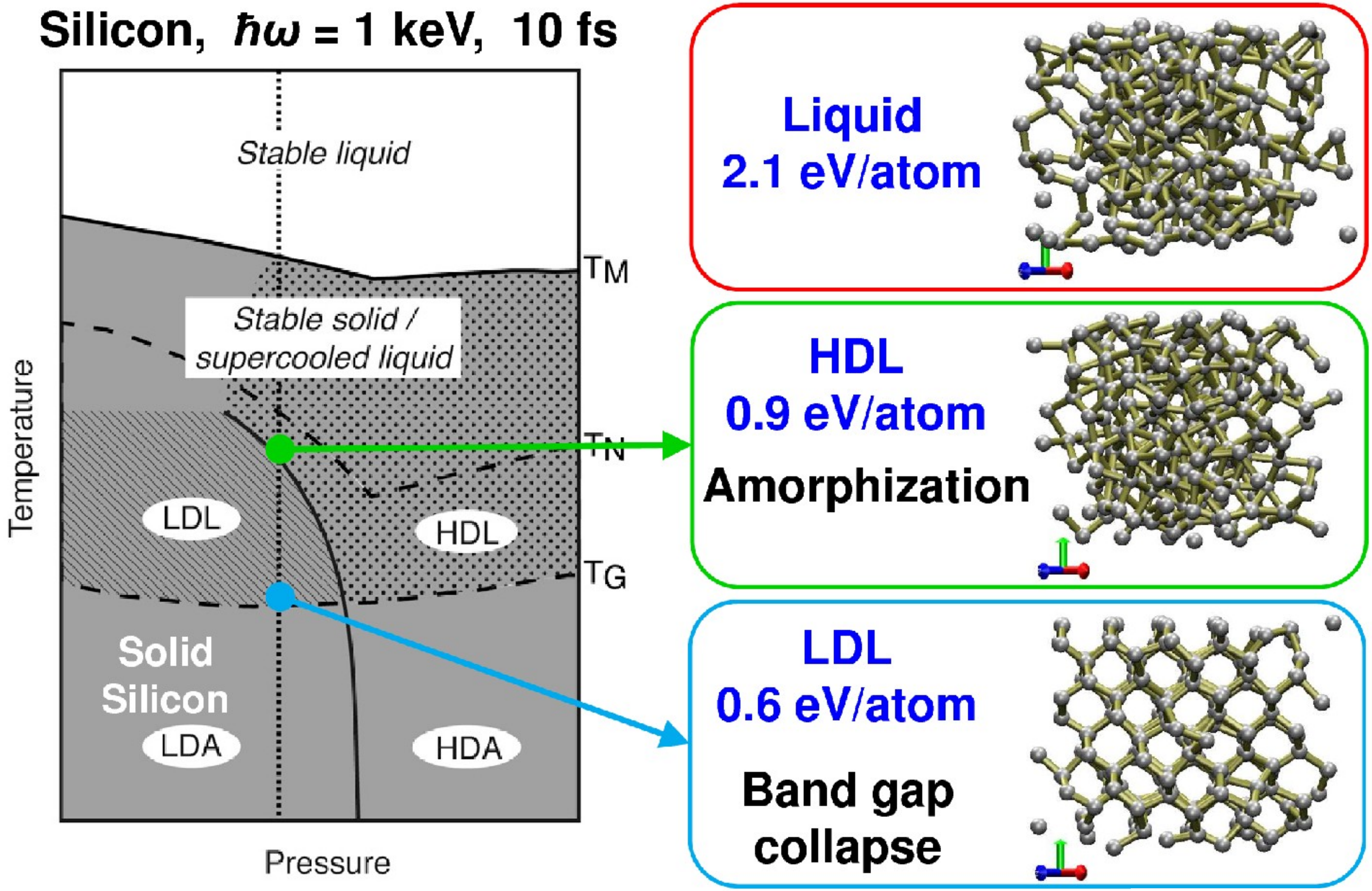



**Bandgap collapse induces ultrafast phase transition**

[This slide courtesy of N.Medvedev]

# Structural transition in Si: interplay of thermal and non-thermal processes




M. Beye, *et al.*, *J. of El. Spectr.* 188 (2013) 172

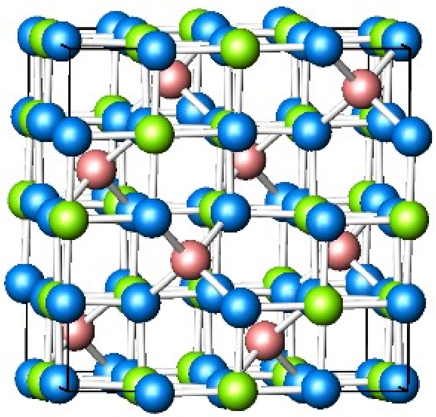
N. Medvedev, Z. Li, B. Ziaja, PRB 91 (2015) 054113

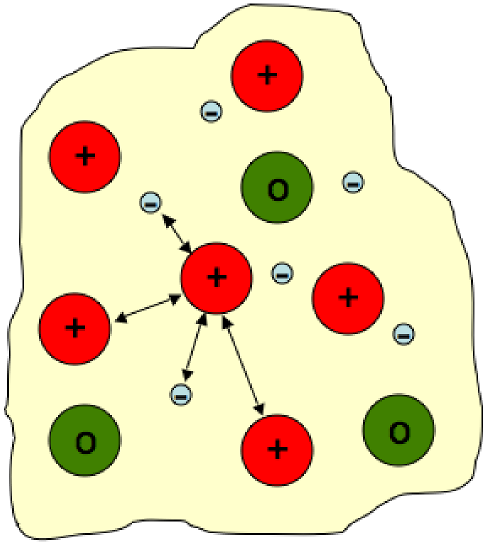
**[This slide courtesy of N.Medvedev]**

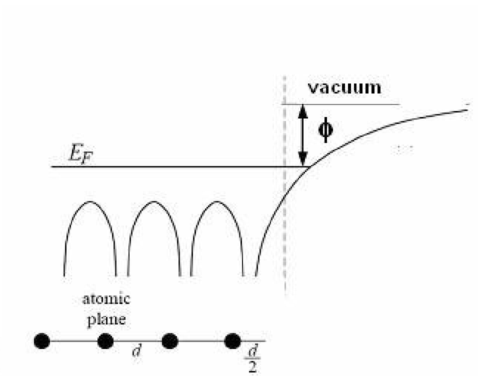
# Interaction of solids with high-fluence femtosecond X-ray pulses:
# → Transition to Warm Dense Matter or Plasma

**Melting threshold**

'Ensemble' of bonded atoms → 'Gas' of free ions and electrons



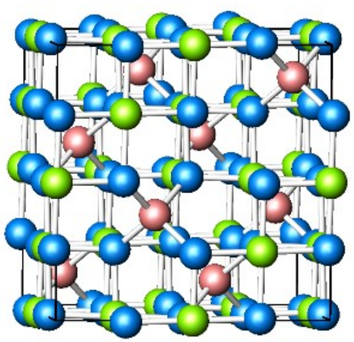


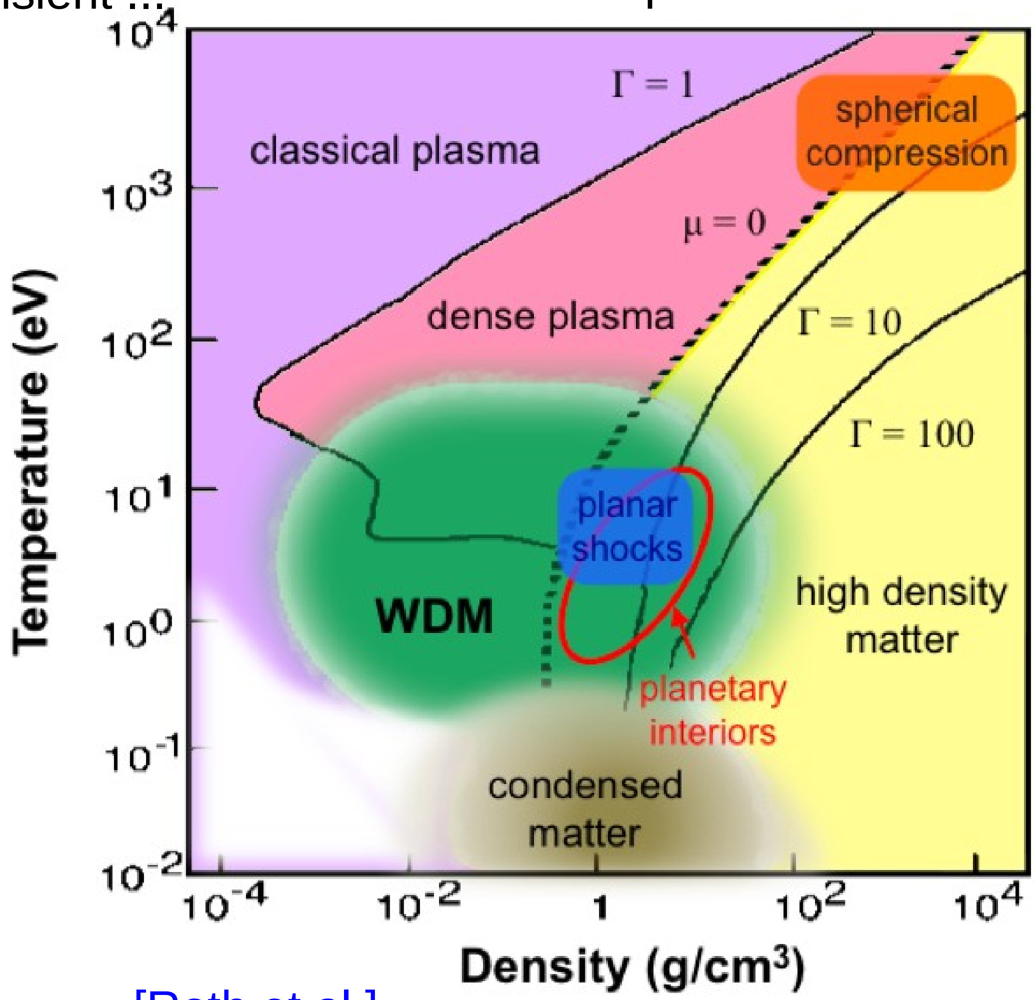


# Matter in warm dense matter (WDM) state

Located between solid state and plasma state. Because of its extreme temperatures and pressures, WDM tends to be drastically transient ...

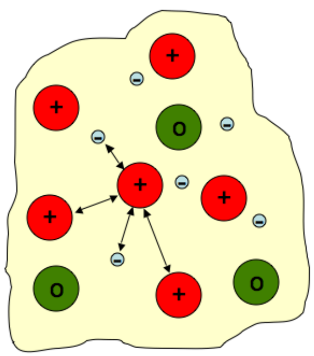
Y






[Roth et al.]

WDM defined by Γ, Y ≈ 1.



Γ – Coulomb coupling parameter =

potential energy/
kinetic energy

Y – degeneracy parameter =

Fermi energy/
kinetic energy

# Diagnostics of transitions?

Damage thresholds → post mortem measurements on samples

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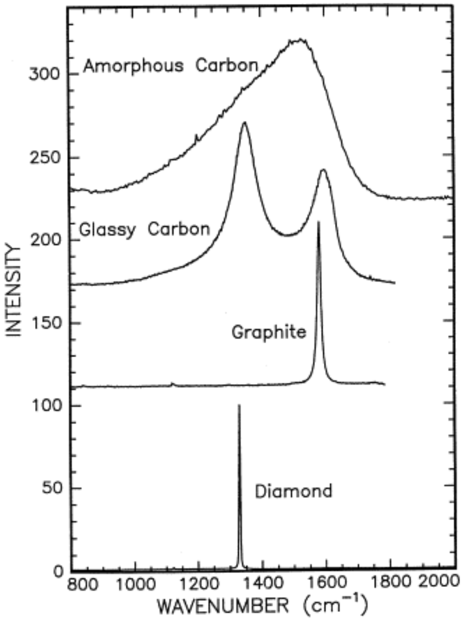


matsci4uwi.wordpress.com

# Diagnostics of transitions?

Damage thresholds → post mortem measurements on samples

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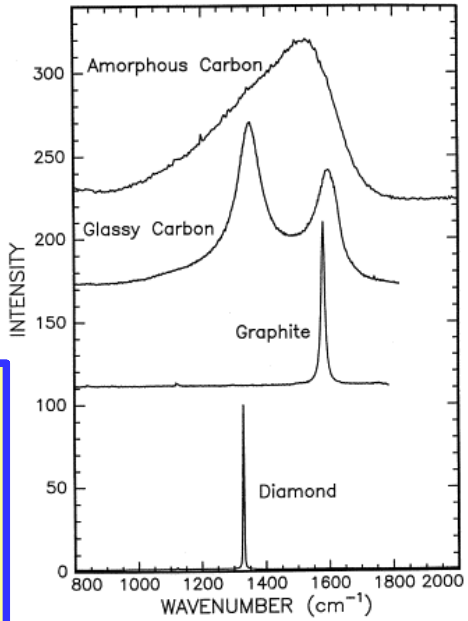


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Challenge: long-time large-scale simulations needed for comparison to post-mortem measurements

←

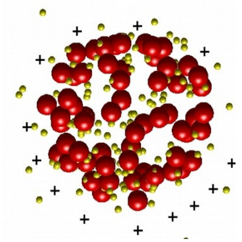
long time-span between ultrafast excitation and final relaxation of the material: lattice heating, diffusion, recrystallization ...

# Time-resolved diagnostics of transitions:

Pump-probe experiments:

- pump pulse initiates transition ...

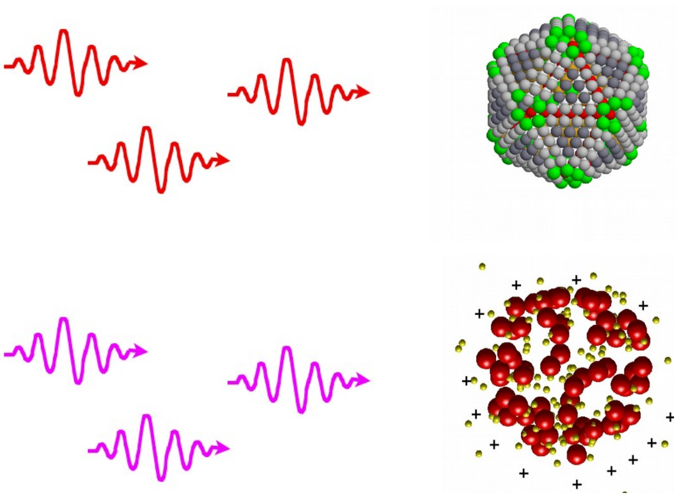
- probe pulse probes it at varying time delay ...



# X-ray diffraction as diagnostics of structural transitions

Example: diamond melted into plasma ...

Pump



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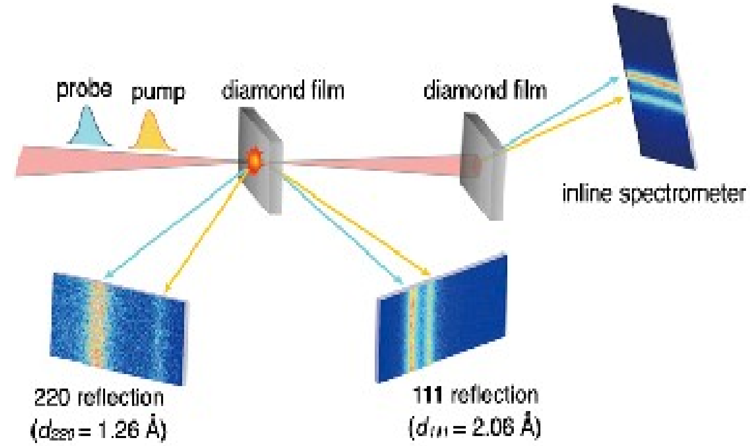
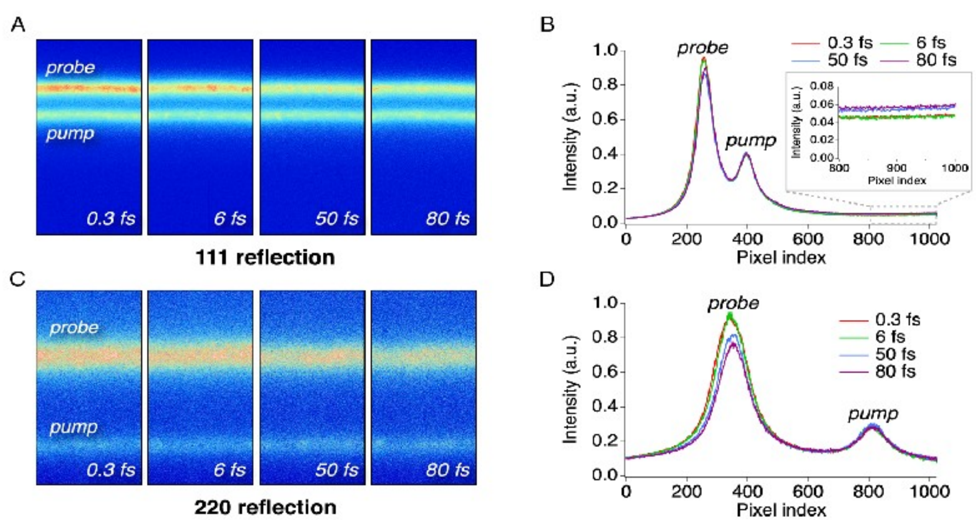



XFEL

[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

# 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: $\mathbf{P}(\mathbf{R},\mathbf{R}') = \frac{m}{i\hbar}[\mathbf{R} - \mathbf{R}']H(\mathbf{R},\mathbf{R}')$

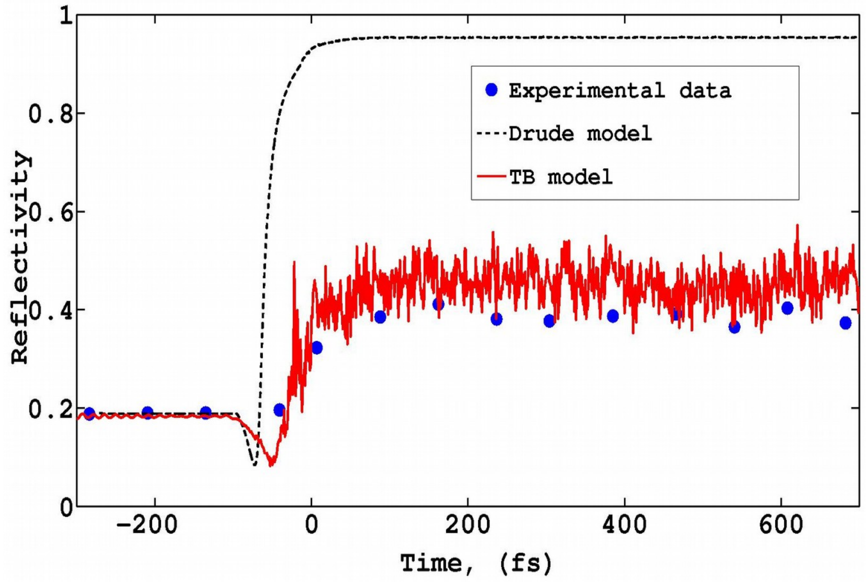
Dielectric function → refractive indices n, k

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

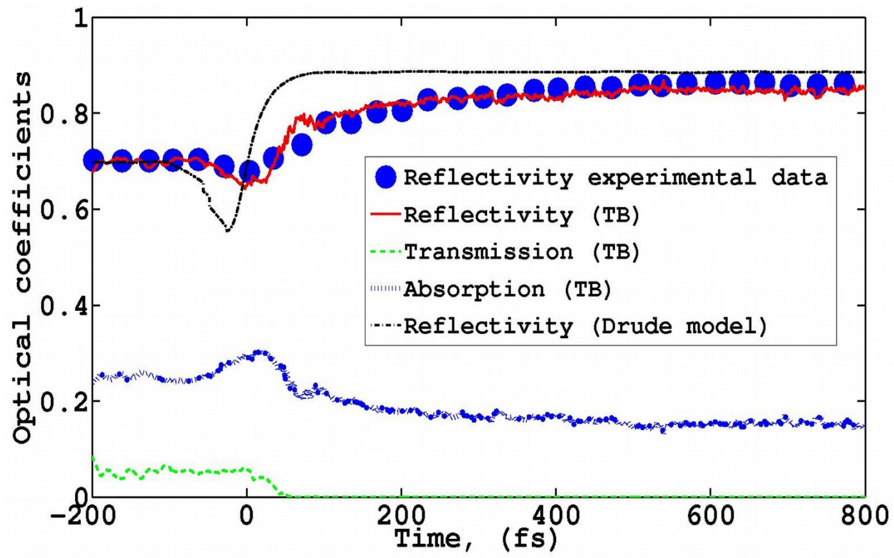
# Transient optical properties as diagnostics of X-ray induced transitions

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

-Diamond and silicon are excited with a laser pulse ...
-Transient optical properties are probed with the optical laser pulse ...
-Complex dielectric function calculated from an ab-initio scheme ...




**Diamond**




**Silicon**

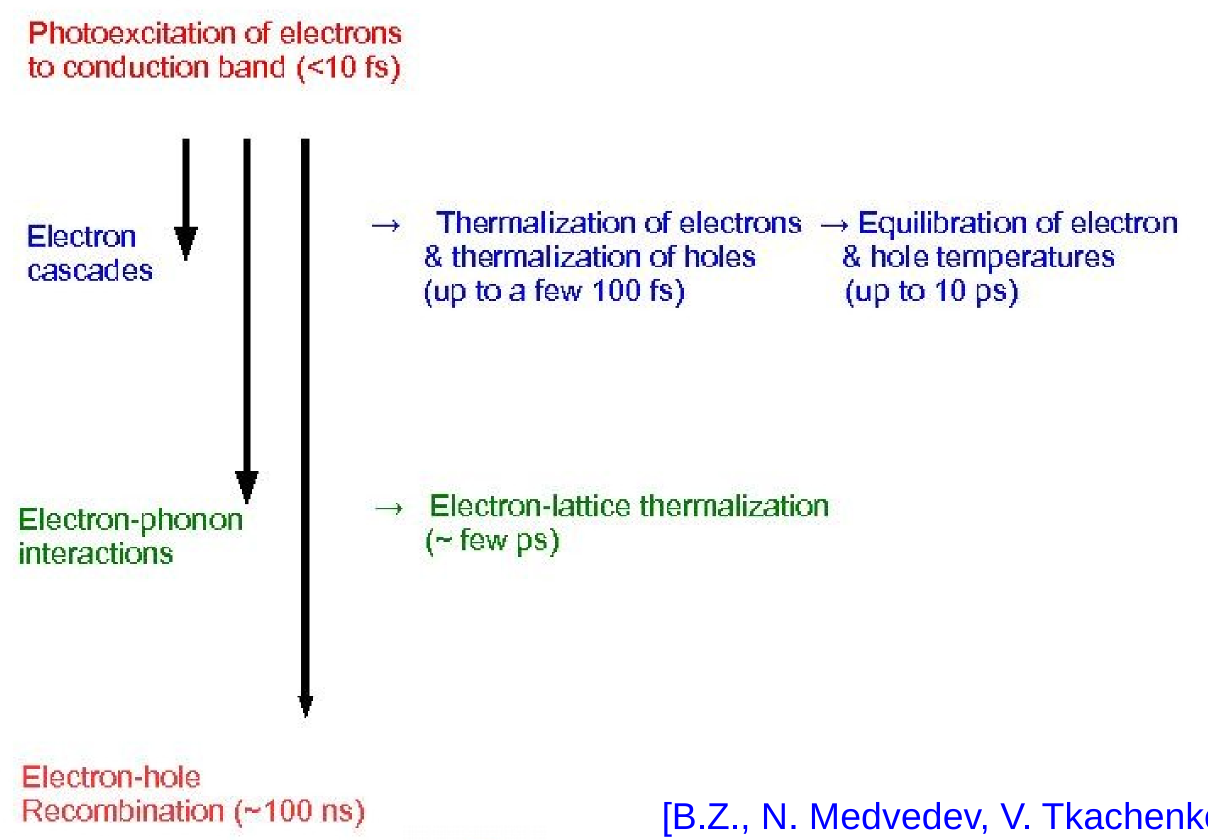
**[Courtesy of V. Tkachenko]** [V. Tkachenko, N. Medvedev et al. (BZ), *Phys. Rev. B* 93 (2016) 144101]

# Transient optical properties as diagnostics of picosecond transitions within irradiated systems

**Low dose**

**Reflectivity overshooting in GaAs ← effect of band gap shrinking**

Timescales of relaxation and excitation processes.




**Damage Threshold**

[B.Z., N. Medvedev, V. Tkachenko, T. Maltezopoulos, W. Wurth, *Sci. Rep*. **5**, 18068 (2015)]

**[Courtesy of V. Tkachenko]**

# Transient optical properties as diagnostics of picosecond transitions within irradiated systems

**Low dose**

**Reflectivity overshooting in GaAs**

- Rate equations → the evolution of free-carrier densities as a function of time [5];

$$d\,n_{e-h}(t)/dt \;=\; \gamma_{e-h}(t)$$ ← Before ΔR/R minimum

$$d\,n_{e-h}(t)/dt = -\gamma_{rec}\cdot n_{e-h}(t)$$ ← After ΔR/R minimum

- Two-temperature model → electron-lattice equilibration [5];

$$d\,T_{latt}(t)/dt \;=\; +G_{latt}(T_{e-h}(t) - T_{latt}(t))$$

$$d\,T_{e-h}(t)/dt \;=\; -G_{e-h}(T_{e-h}(t) - T_{latt}(t))$$

- Drude model → follows the transient reflectivity (extended for interband transitions) [5].

**Damage Threshold**

**[Courtesy of V. Tkachenko]**

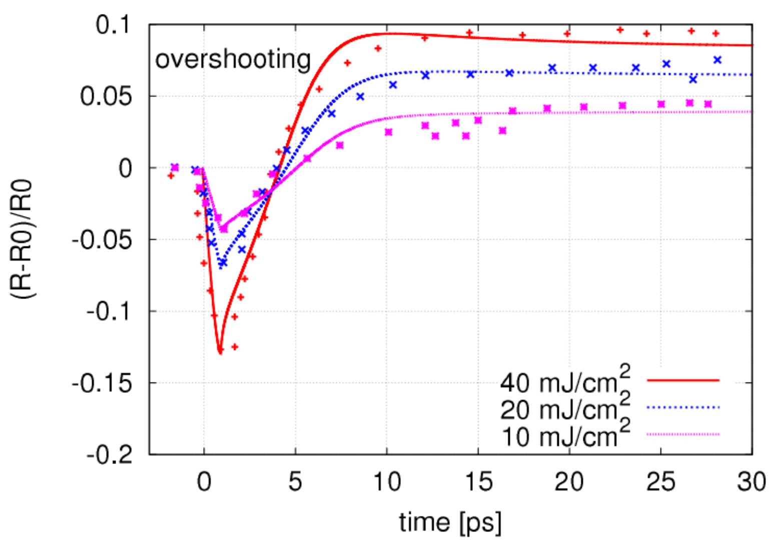
[B.Z., N. Medvedev, V. Tkachenko, T. Maltezopoulos, W. Wurth, *Sci. Rep*. **5**, 18068 (2015)]

# Transient optical properties as diagnostics of picosecond transitions within irradiated systems

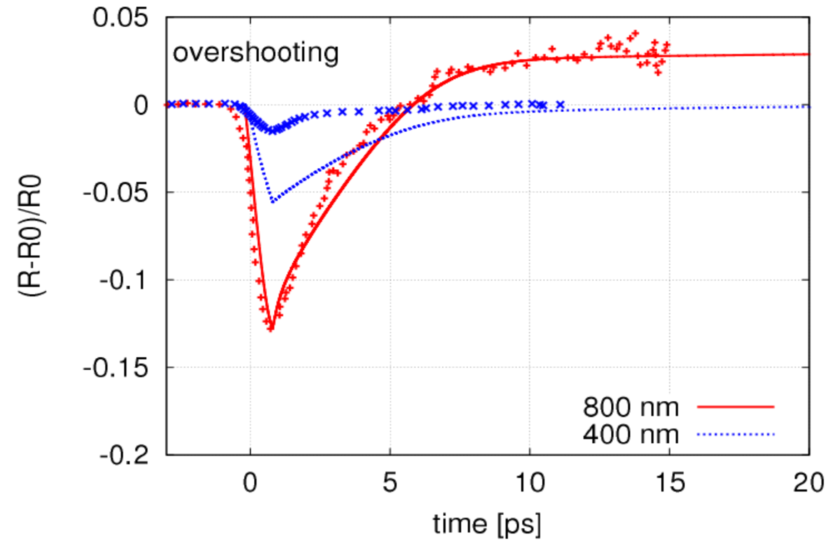
**Reflectivity overshooting in GaAs ← effect of band gap shrinking**

**Low dose**

- Timescale of a few ps
- Observable at probe wavelength ~ band gap width (low absorption)
- Measurement of electron-phonon coupling with femtosecond resolution ($\tau_{el\text{-}latt}$~ 2-3 ps) and transient electronic temperatures (~ 2-3 eV)
- Expected for other narrow band-gap semiconductors




LCLS measurement (800 eV)




FLASH measurement (40 eV)

**Damage Threshold**

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[B.Z., N. Medvedev, V. Tkachenko, T. Maltezopoulos, W. Wurth, *Sci. Rep*. **5**, 18068 (2015)]

DESY

**[Courtesy of V. Tkachenko]**

# Summary

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

**-below damage threshold – non-equilibrium electron kinetics**

**-below melting threshold – also rearrangement of atomic structure**

**-above melting threshold – amorphization; plasma, warm-dense matter formation**

**Diagnostics of transitions:**

**- transient optical properties ← time-resolved**

**- X-ray diffraction ← time-resolved**

**- post mortem measurements**

# Applications so far ...

Low fluence material excitation below and around damage threshold.
**Transient optical properties** can follow:

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

- Electron kinetics ~ 100 fs → application for FEL pulse diagnostics

[M.Harmand et al. (Medvedev, BZ), *Nat. Phot.* 7 (2013) 215;
R. Riedel et al.(Medvedev,BZ), *Nat. Commun*. 4 (2013) 1731,
P. Finetti et al. (Medvedev, Tkachenko, BZ), *Phys. Rev. X* (2017) accepted ]

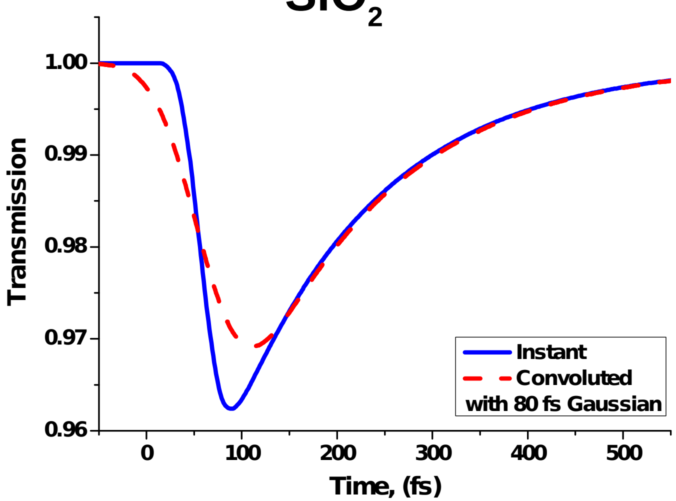
- Structural transitions ~ 100 fs - ps → application for damage studies in FEL optics

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

- Lattice heating ~ few ps → application for material studies

[B.Z., N. Medvedev, V. Tkachenko, T. Maltezopoulos, W. Wurth, *Sci. Rep*. 5, 18068 (2015)]

**$SiO_2$**




**Diamond**

Electron kinetics follows temporal pulse profile ...

Time-resolved non-thermal graphitization ...

[F. Tavella et al. (V.Tkachenko, N. Medvedev, BZ), 2016 submitted]

# Development of diagnostic tools ....

- Laser pulse properties (IR to X-ray): their quantitative temporal and spatial characteristics → pulse diagnostics

- Signatures of magnetic transitions → fundamental, material science

- Long-timescale simulations to unveil long-timescale relaxation processes within excited material → material science

- Going above low excitation limit: diagnostics of warm dense matter and plasma formation

↓ ↓ ↓

fundamental understanding and practical applications

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# Thanking my collaborators and the CFEL-DESY Theory Group

V. Lipp | N. Medvedev | V. Saxena | V. Tkachenko + J. Bekx

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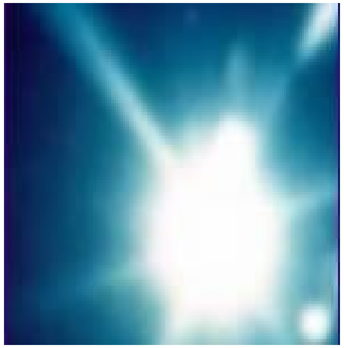
Thanking the Institute of Nuclear Physics, Polish Academy of Sciences in Krakow for the years of continuous support and inspiration

# Thanking our external collaborators...



J. Gaudin (CELIA, Bordeaux)

H. Jeschke (U. Frankfurt ), Z. Li (LCLS), P. Piekarz (INP, Kraków)

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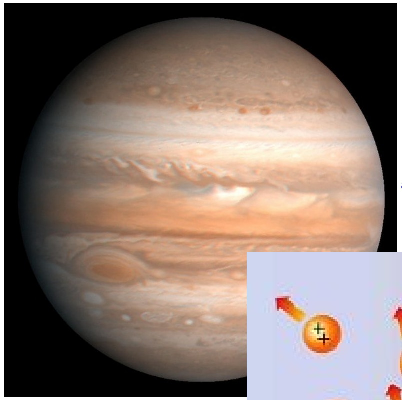
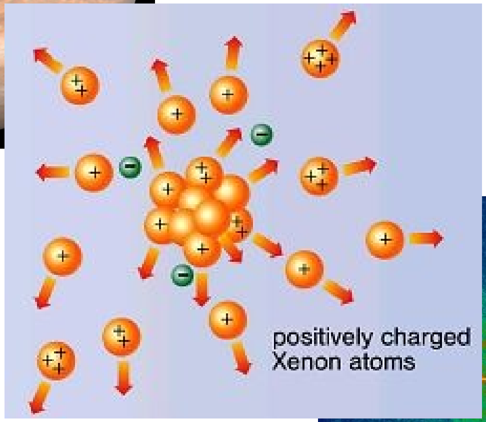
H.-K. Chung (IAEA, Vienna), R. W. Lee (LBNL, Berkley)



M. Harmand (LULI,CNRS), M. Cammarata (U. Rennes)

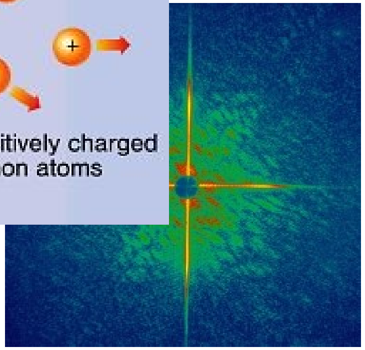
A. Ng (U. British Columbia), Z.Chen, Y.Y. Tsui (U. Alberta), V. Recoules (CEA, DAM)




F. Tavella (LCLS), U. Teubner (U. Oldenburg) and FERMI team

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

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **R. Santra** | B. Ziaja | S.-K. Son | Z. Jurek | N. Medvedev | V. Saxena | L. Inhester | K. Toyota | V. Lipp | M.M. Abdullah | V. Tkachenko |
| 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 !