Probing optical and electronic properties of individual defects through scanning transmission electron microscopy and first-principles theory

Stephen J. Pennycook

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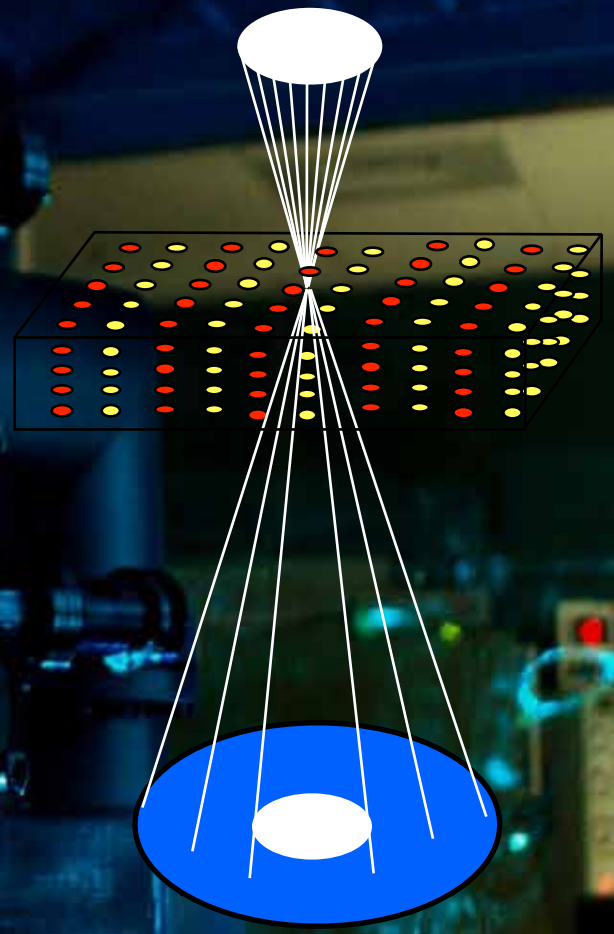
National University of Singapore

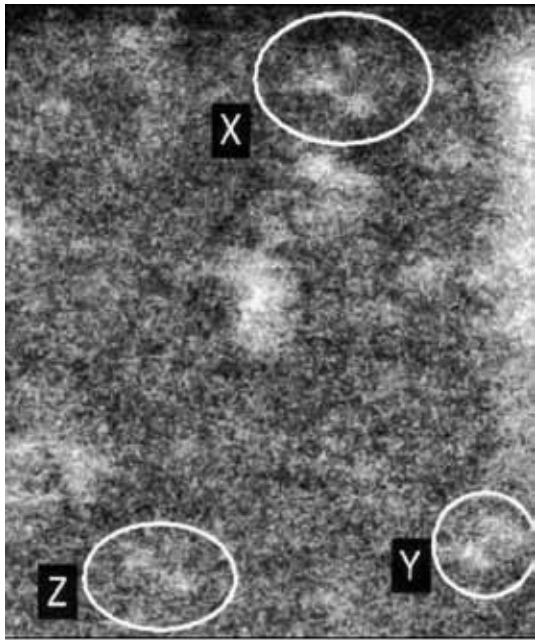
and

University of Tennessee



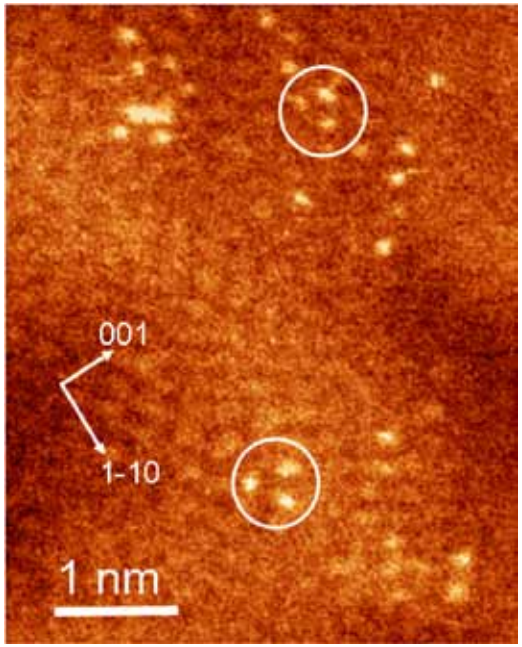
Advances in aberration correction

Pt on γ-Al_2O_3



P.D. Nellist 1996

Uncorrected

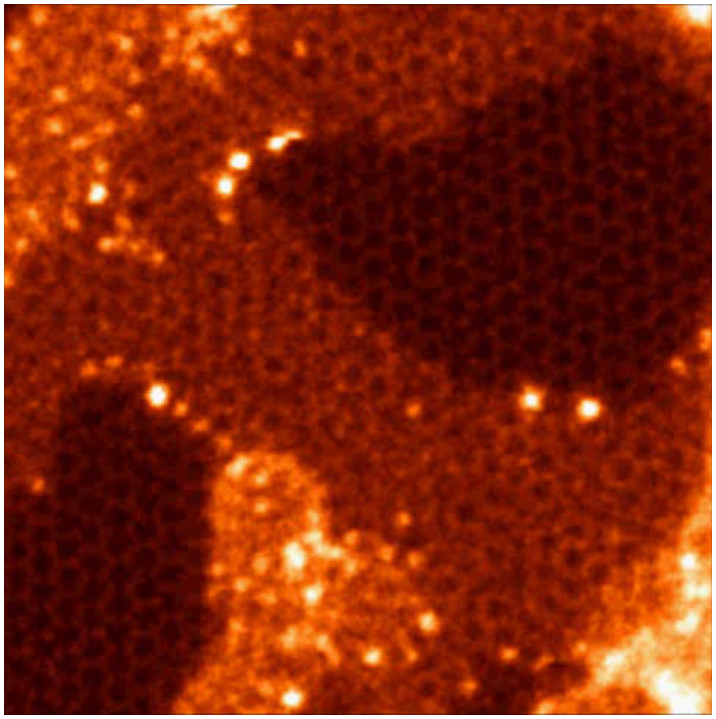


A. Y. Borisevich 2004

3rd order corrected

VG Microscopes HB603U 300 kV

Pt on graphene

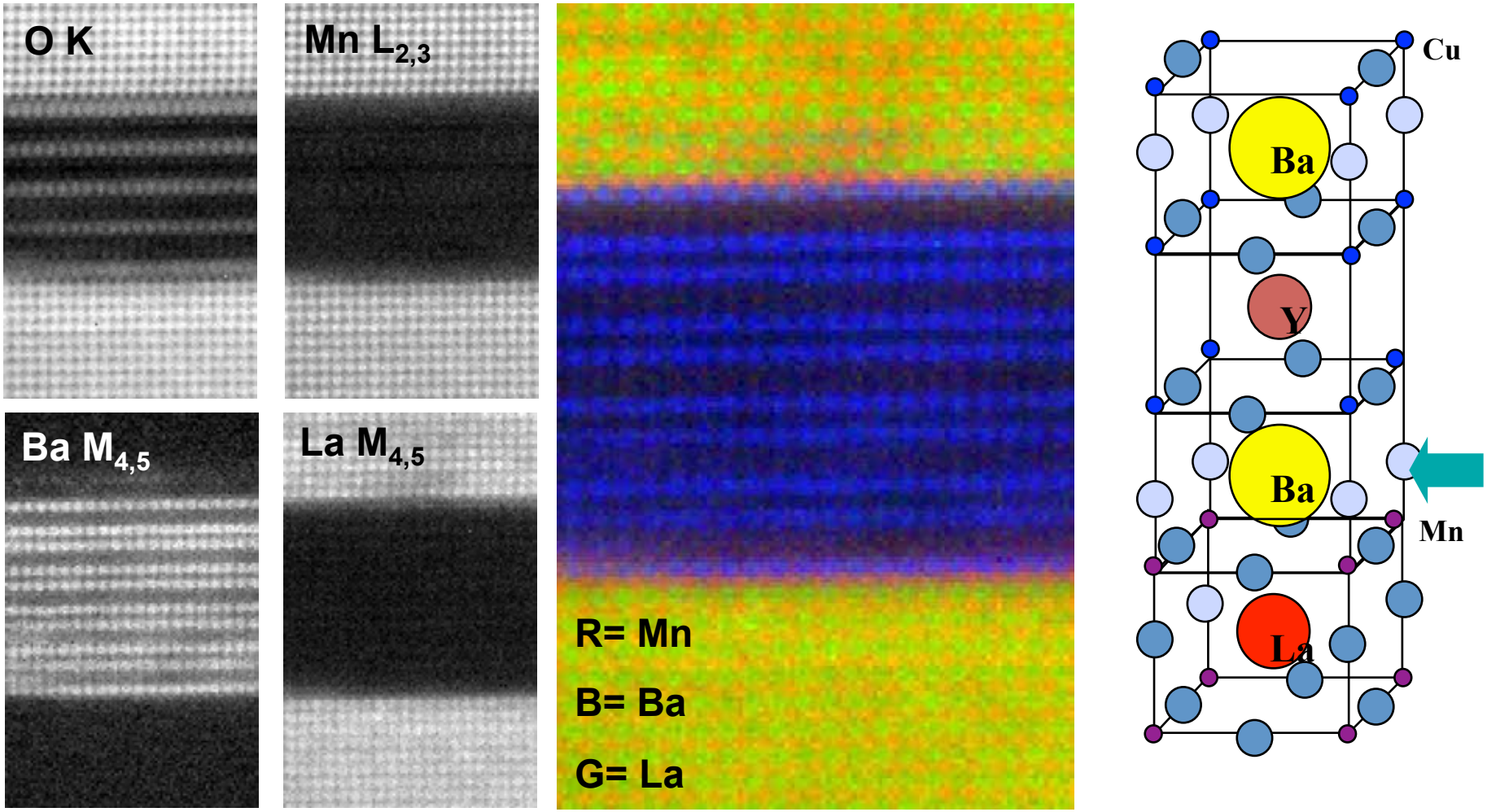


Wu Zhou 2012

5th order corrected

Nion UltraSTEM 60 kV

Stacking Sequence at Interfaces by STEM/EELS

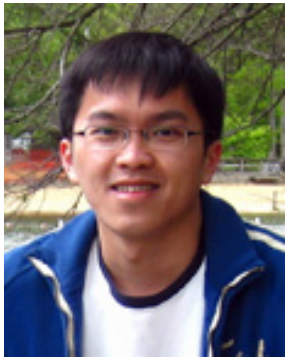


S. J. Pennycook and M. Varela, *J Electron Microsc*, 60, S213–S223 (2011).

Outline

- Point defects in graphene
  - Configuration
  - Bonding, electronic structure
  - Dynamics
- Optical properties
  - “Plasmons” in graphene
  - Atomic resolution valence EELS: optical properties defect by defect!
- Future directions
  - meV resolution EELS
  - 3D atomic resolution

Graphene team



Wu Zhou

Juan-Carlos Idrobo

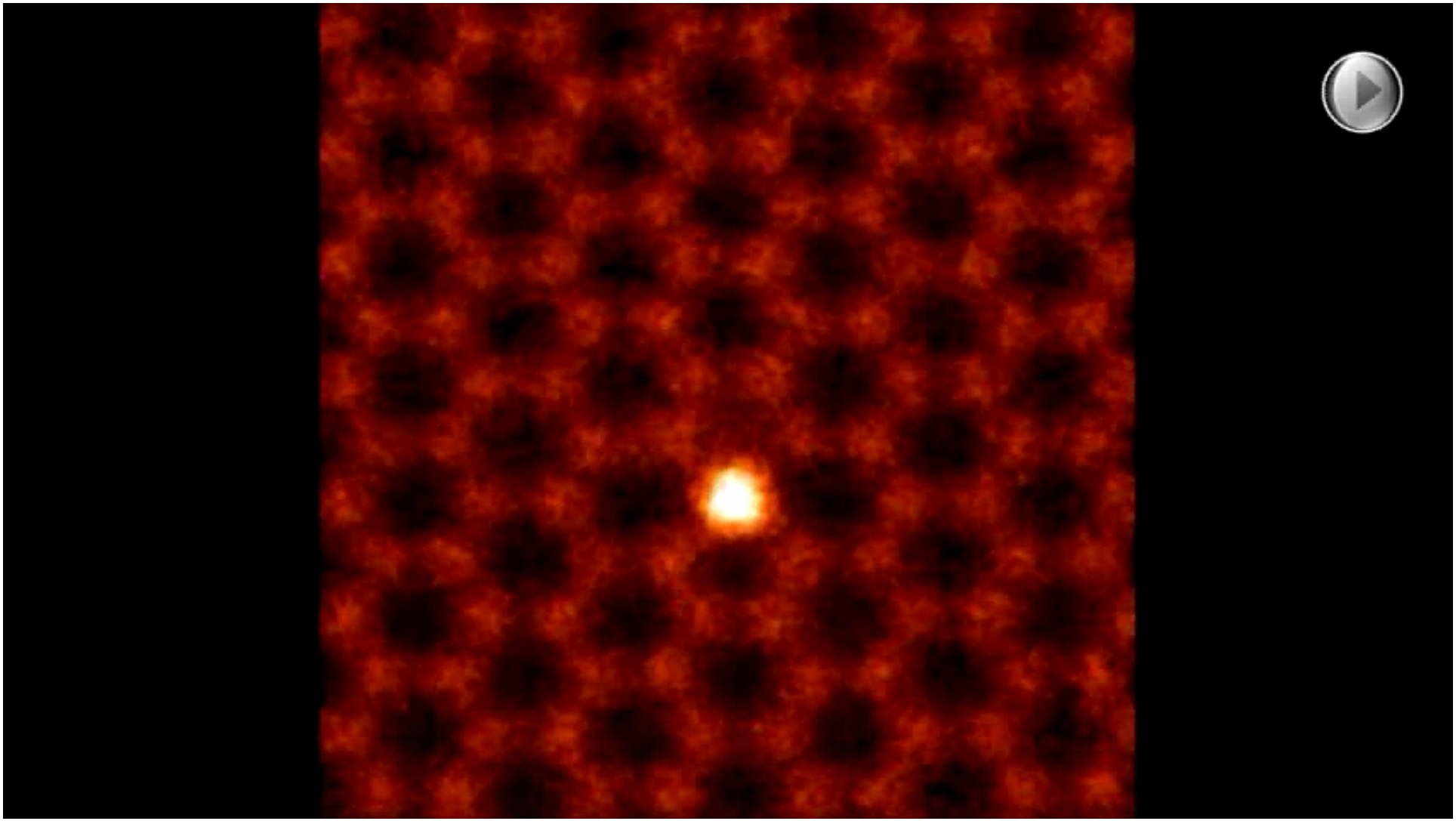
Myron Kapetanakis

Jaekwang Lee

Single atom microscopy: Bonding, Dynamics and Optical Properties

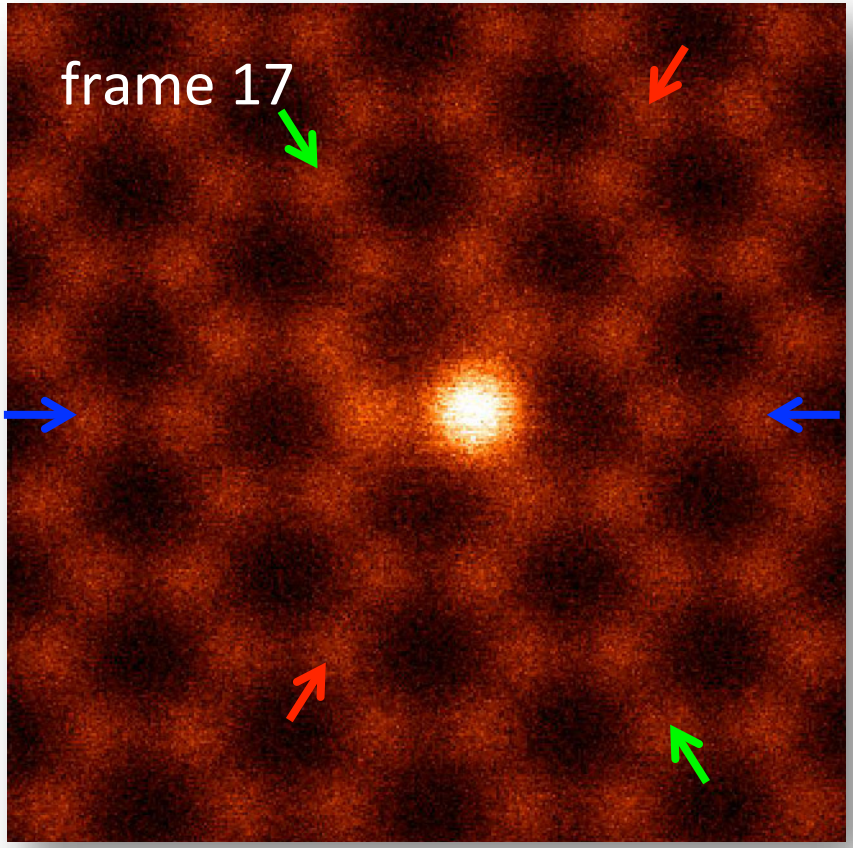
Sok Pantelides

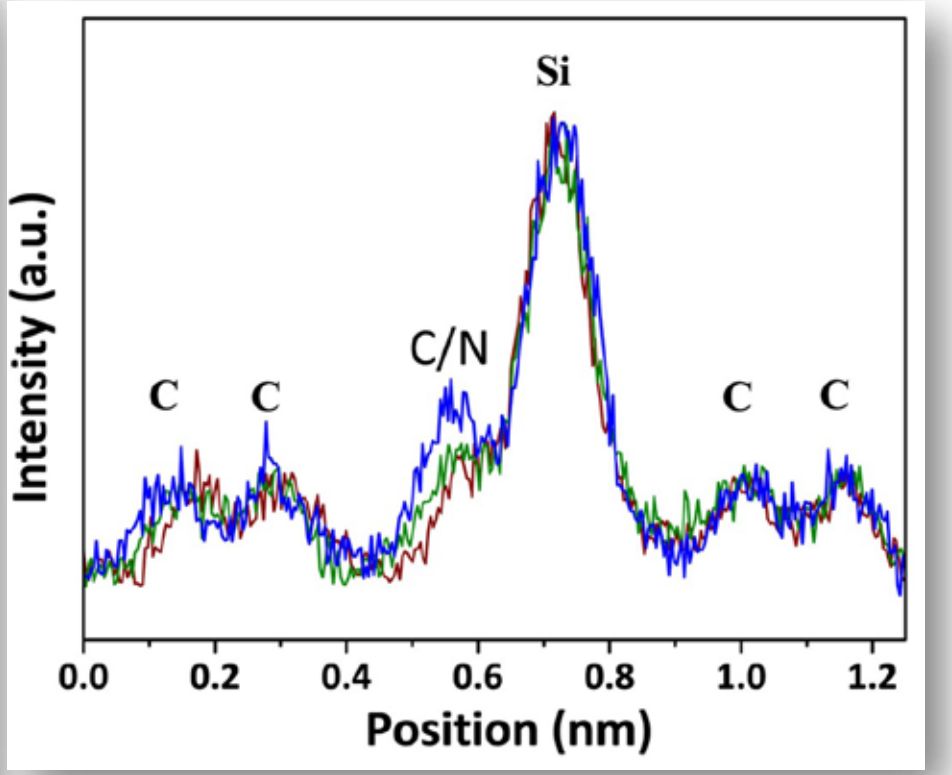
Tracking point defect dynamics



Zhou et al. *Microsc. Microanal.* (2012)

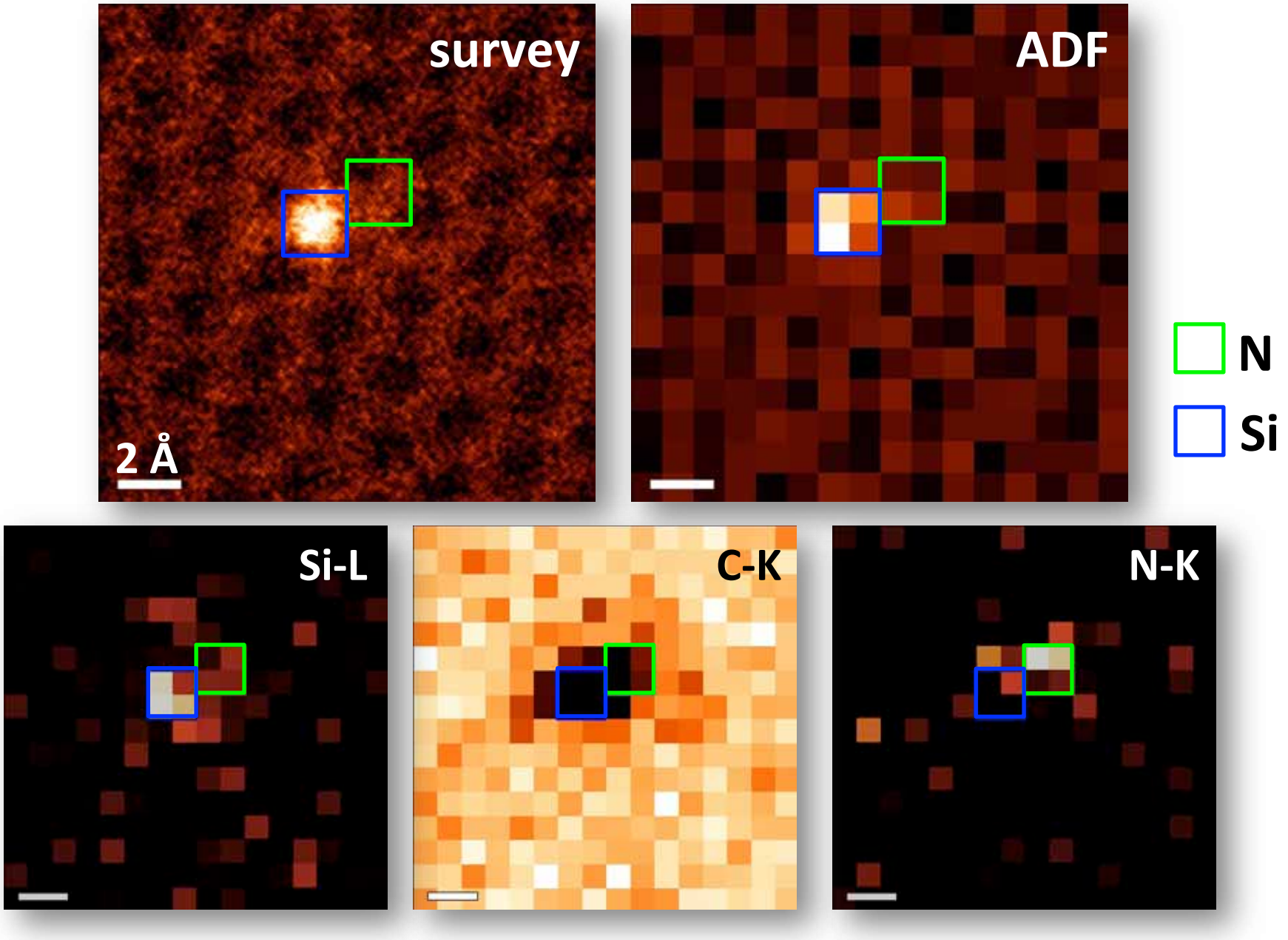
Direct identification of species from image intensity



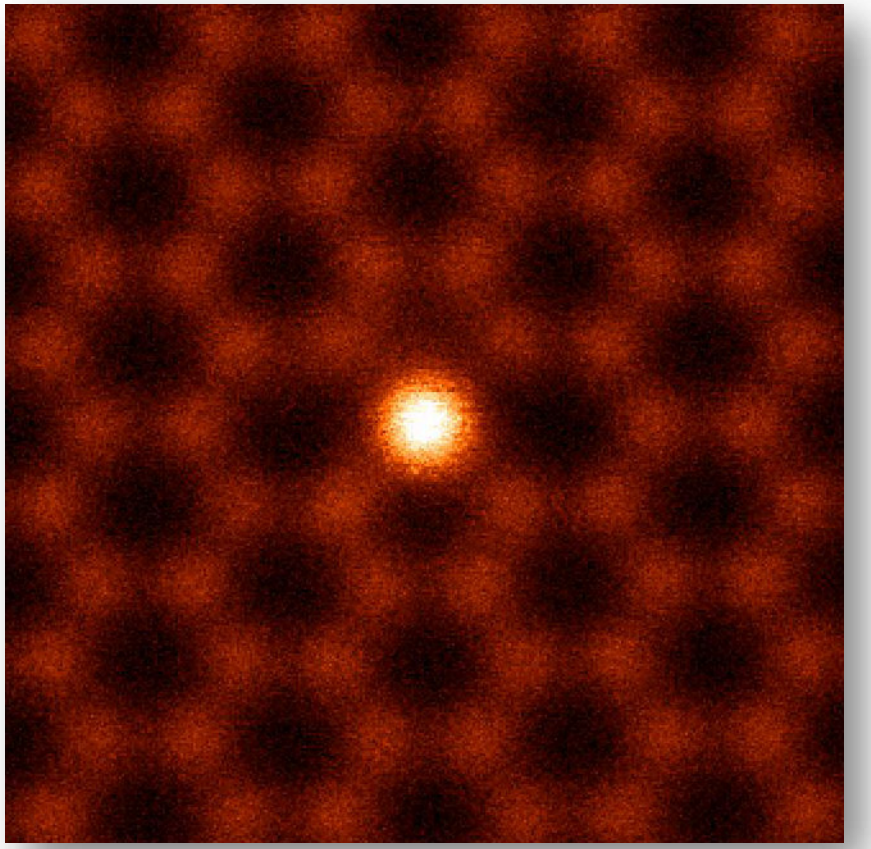


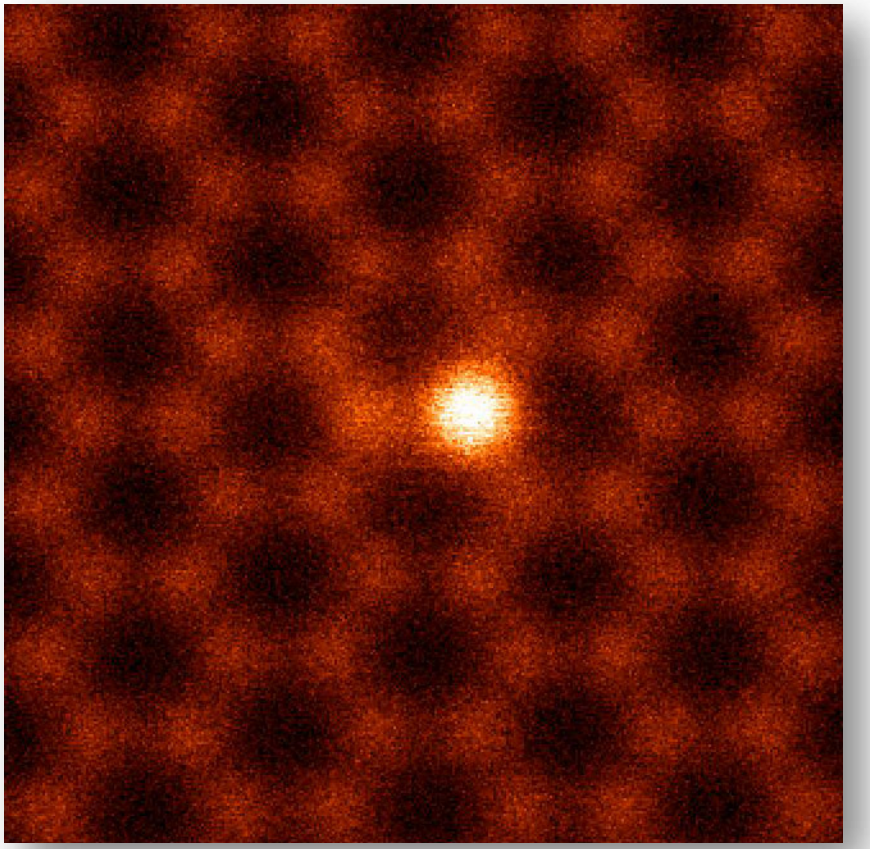
Zhou et al. *Microsc. Microanal.* (2012)

Atom by atom spectroscopy



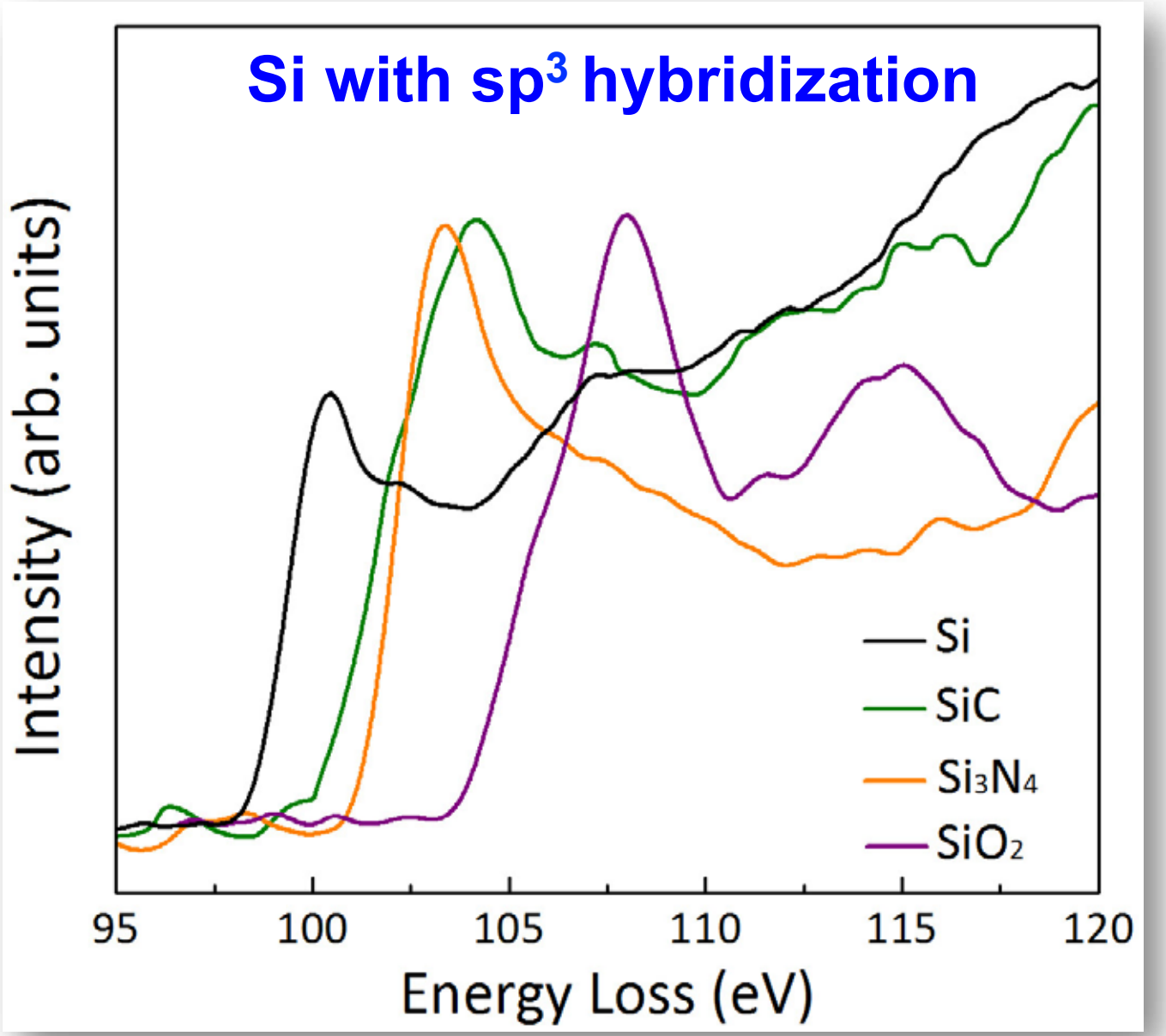
Revealing the nature of chemical bonding



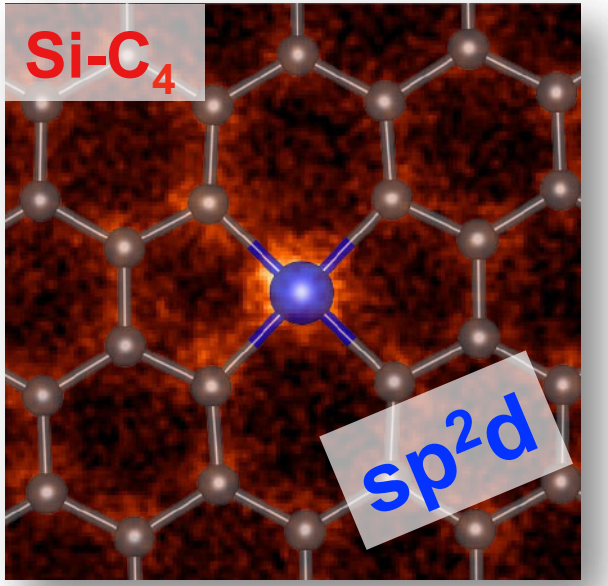


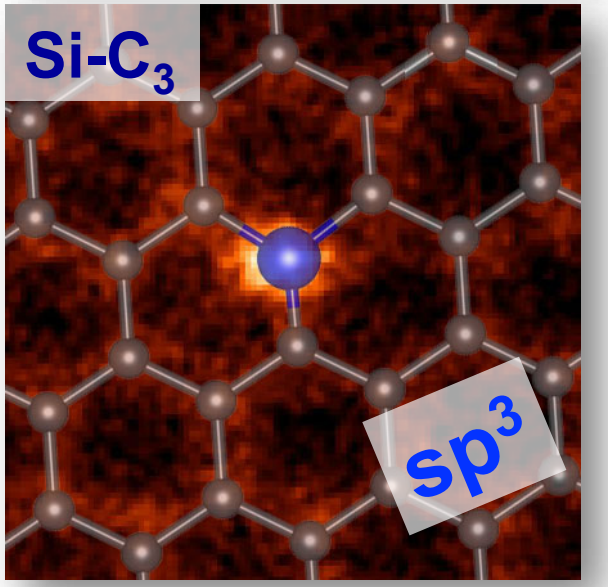
How do the Si atoms bond in the graphene lattice?

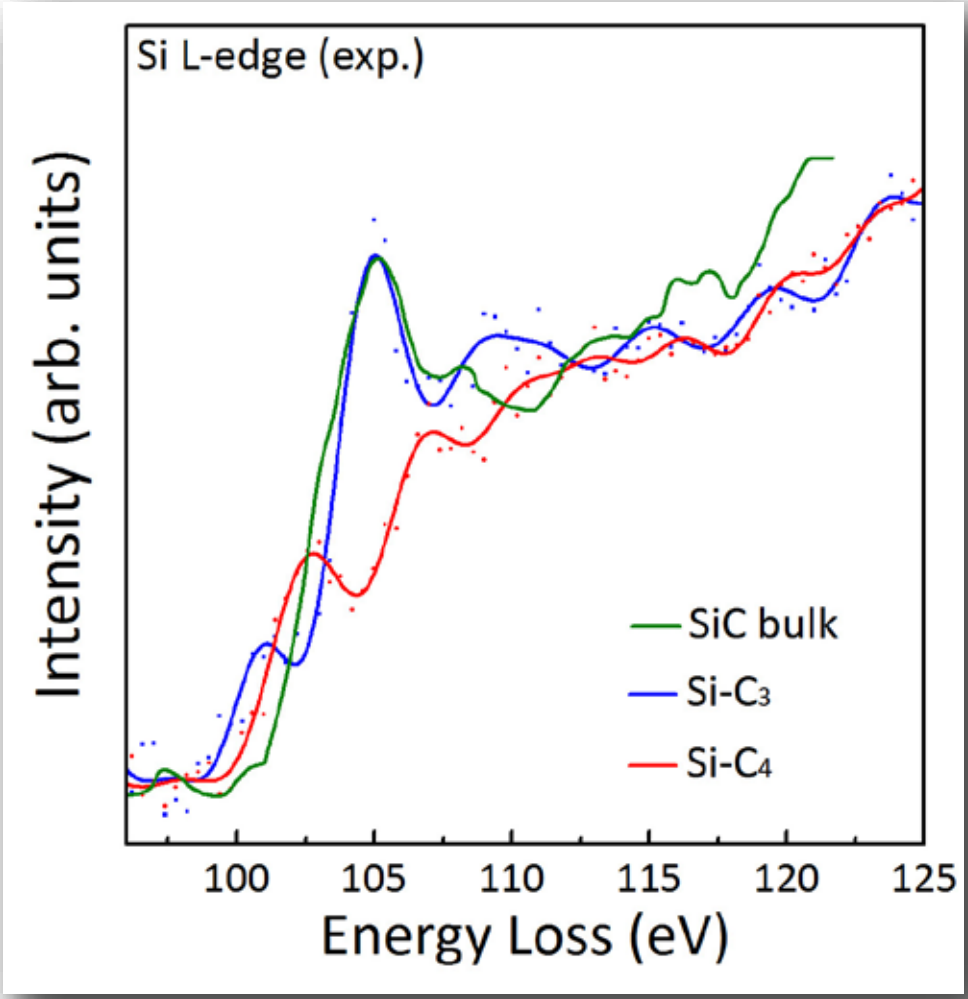
Reference spectra for the Si L-edge



Bonding of single Si atoms in the graphene lattice

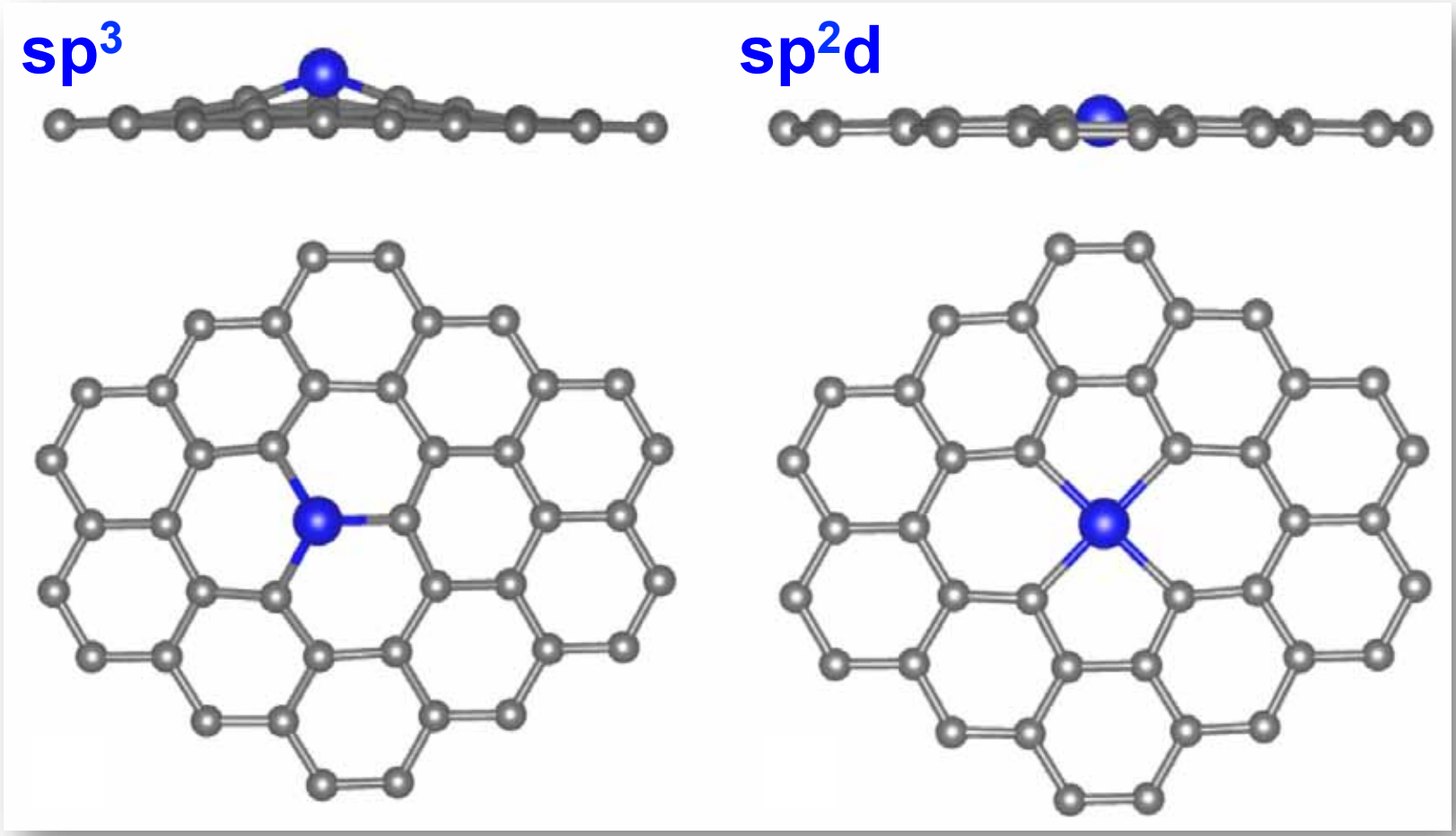






Some 3*d* states in Si-C_4 structure are missing!

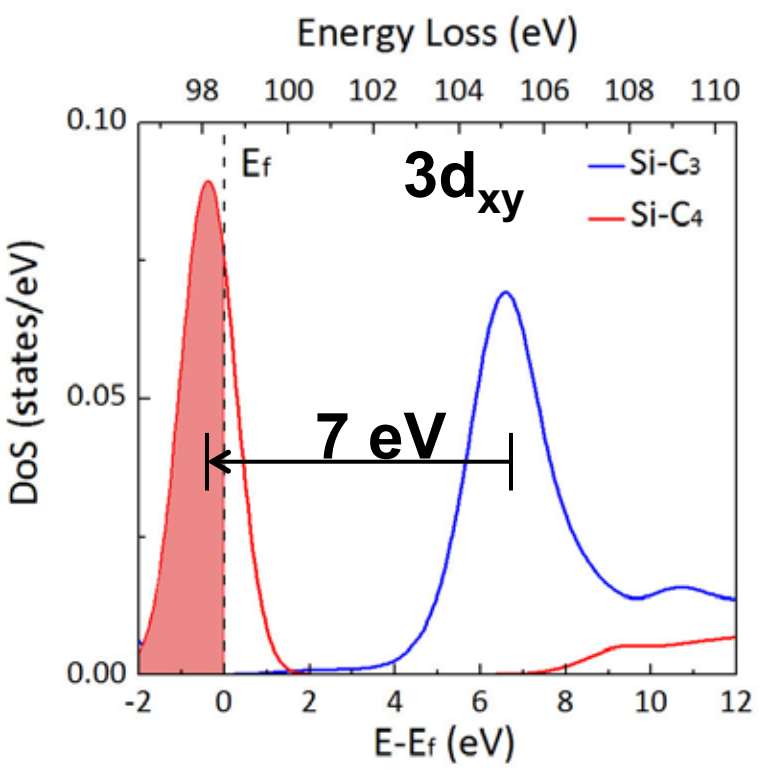
3D structure from DFT calculations

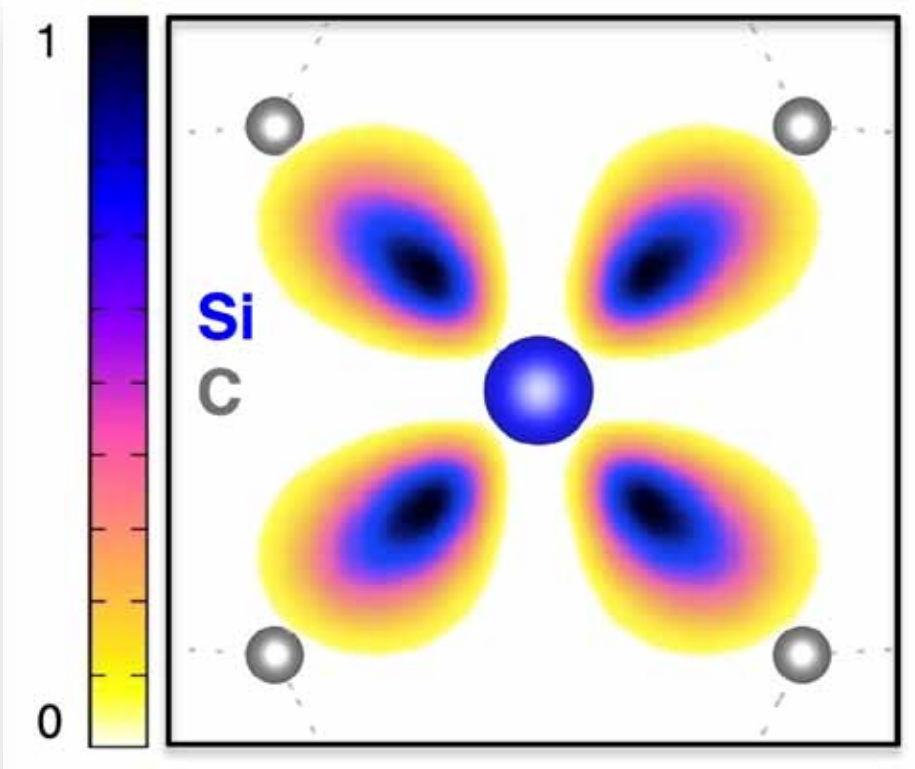


0.54 Å out-of-plane for Si-C_3
0.63 Å out-of-plane for SiC bulk ⇒ ***sp*^{3}-like hybridization for Si-C_3**

Myron Kapetanakis

Participation of d_{xy} states in chemical bonding of Si-C_4



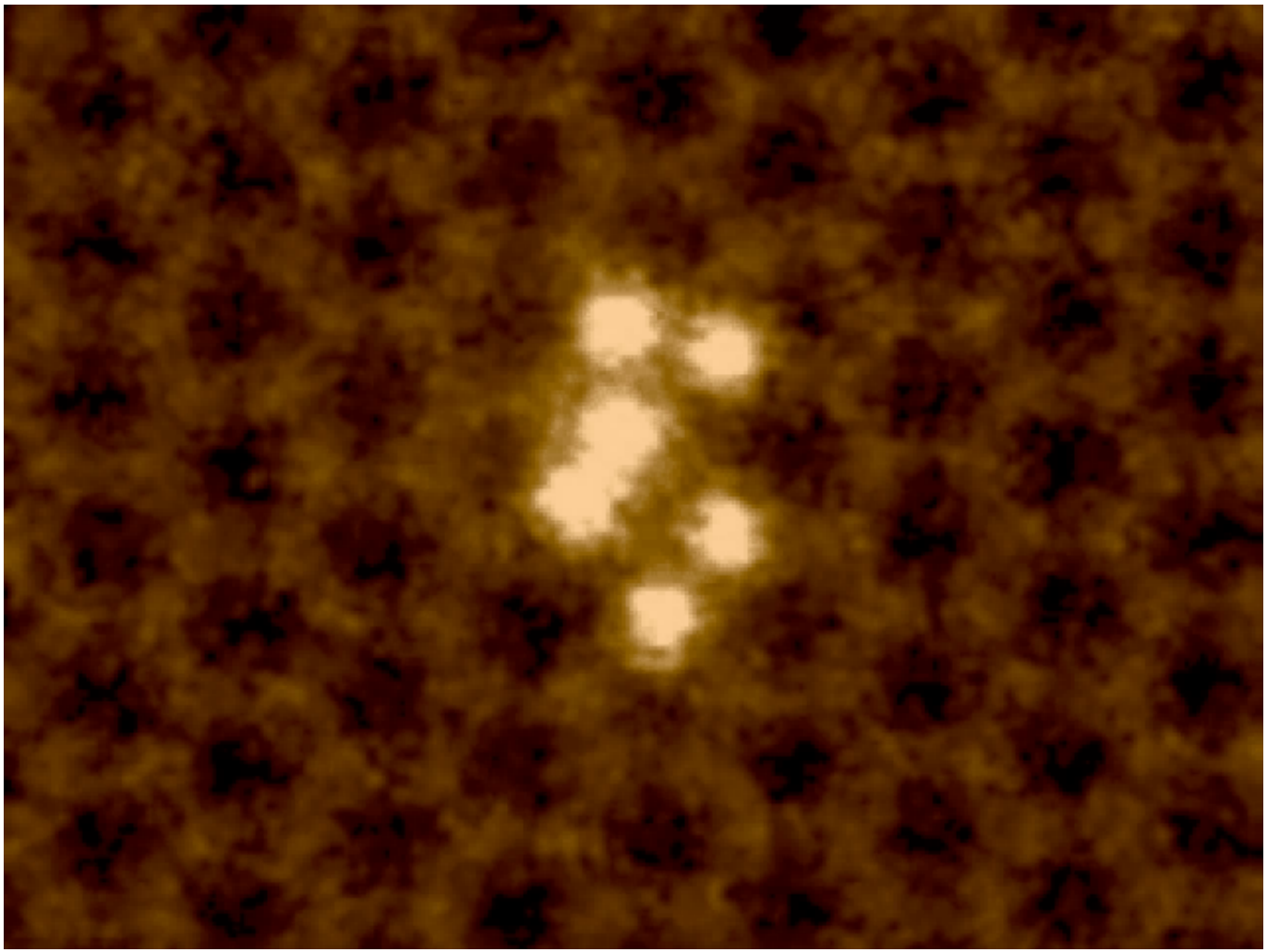


Si $3d_{xy}$ states participate in the chemical bonding of Si-C_4

***sp^2d* hybridization for planar 4-fold coordination**

W. Zhou, M. D. Kapetanakis, M. P. Prange, S. T. Pantelides, S. J. Pennycook, and J.-C. Idrobo *Phys Rev Lett*, 109, 206803 (2012).

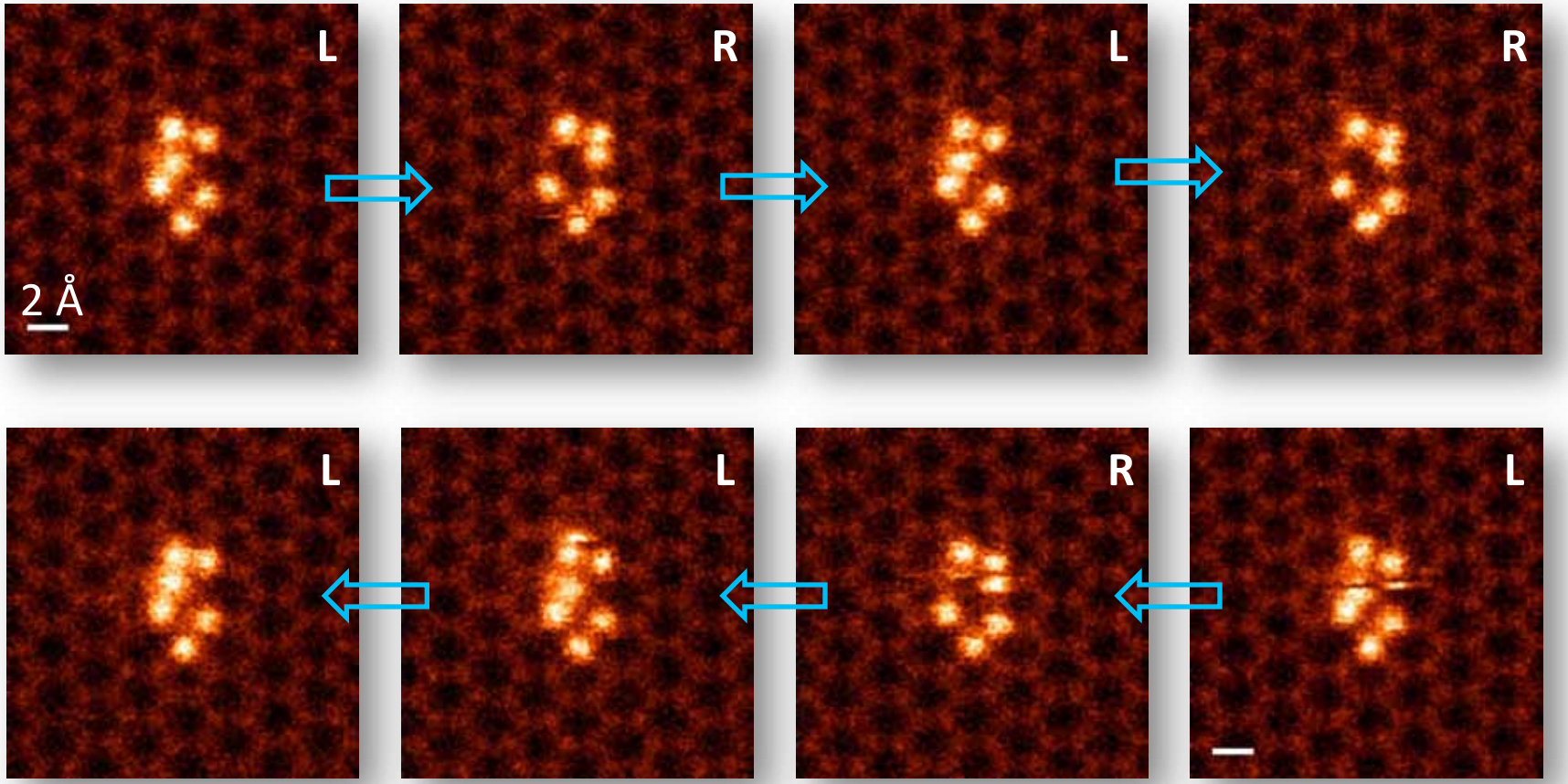
Si_6 magic cluster



UltraSTEM at 60 kV

W. Zhou, J-C Idrobo: Si on graphene

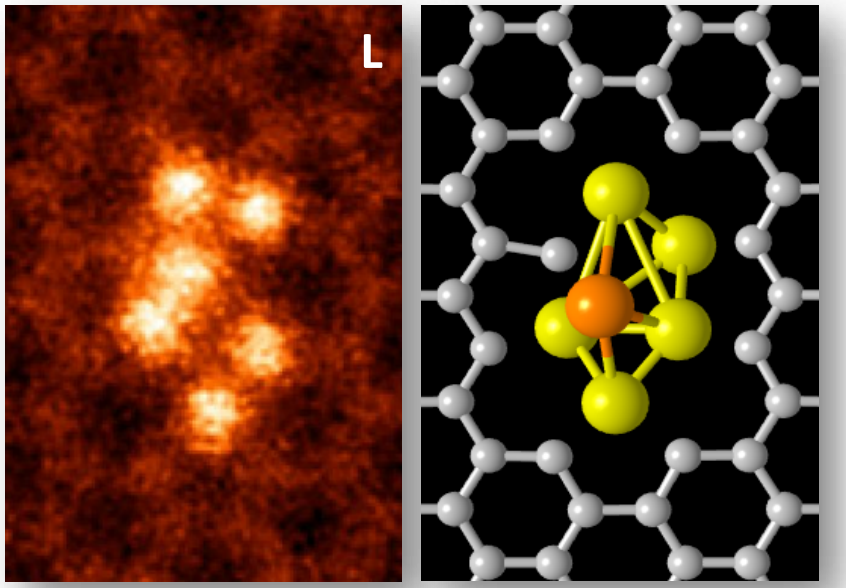
Reversible dynamics at the atomic scale

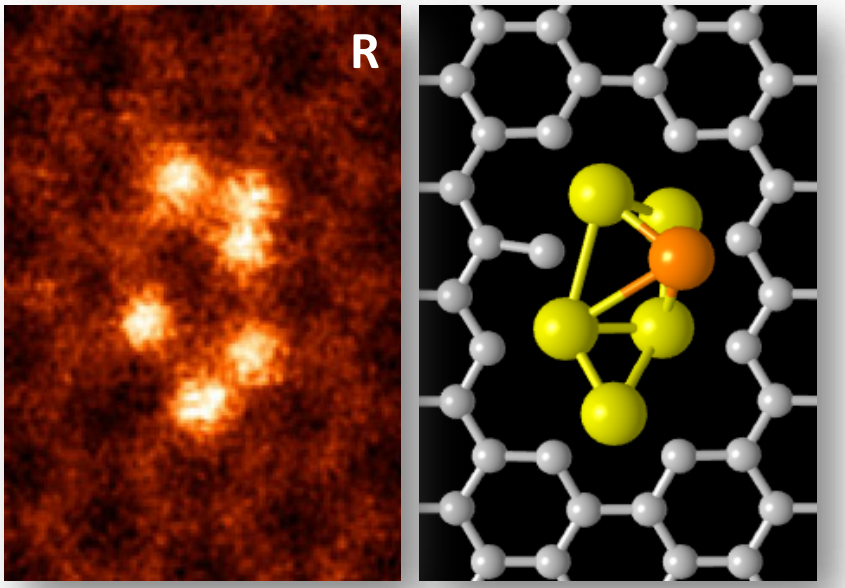


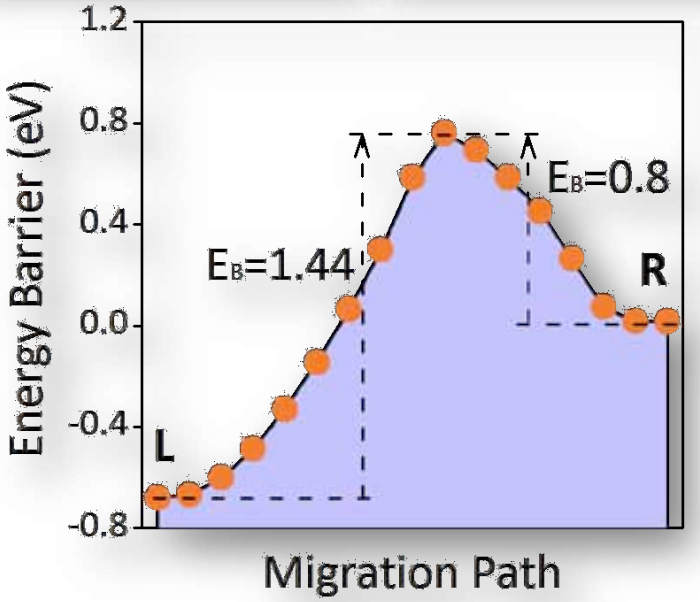
6 s/frame

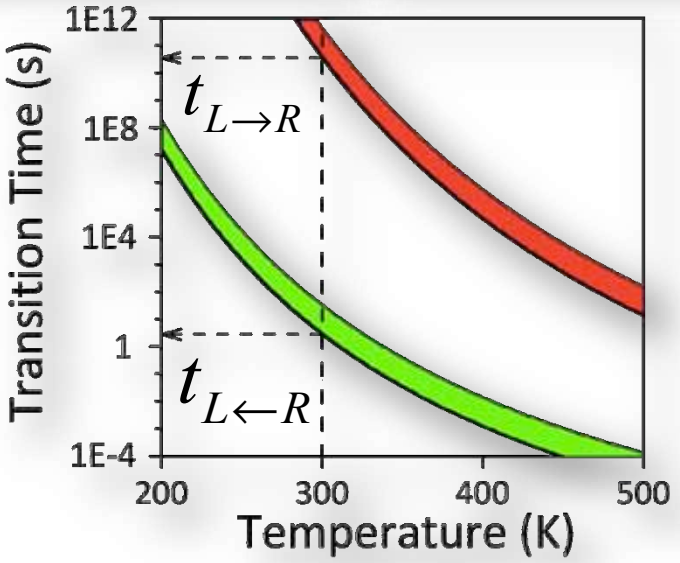
Turn to theory: Jaekwang Lee

Atomic scale molecular dynamics









J. Lee, et al. *Nature Commun*. (2012)

Optical properties from EELS

Energy loss: $\chi(E) = \mathrm{Im}\left(\frac{1}{\varepsilon(E)}\right)$

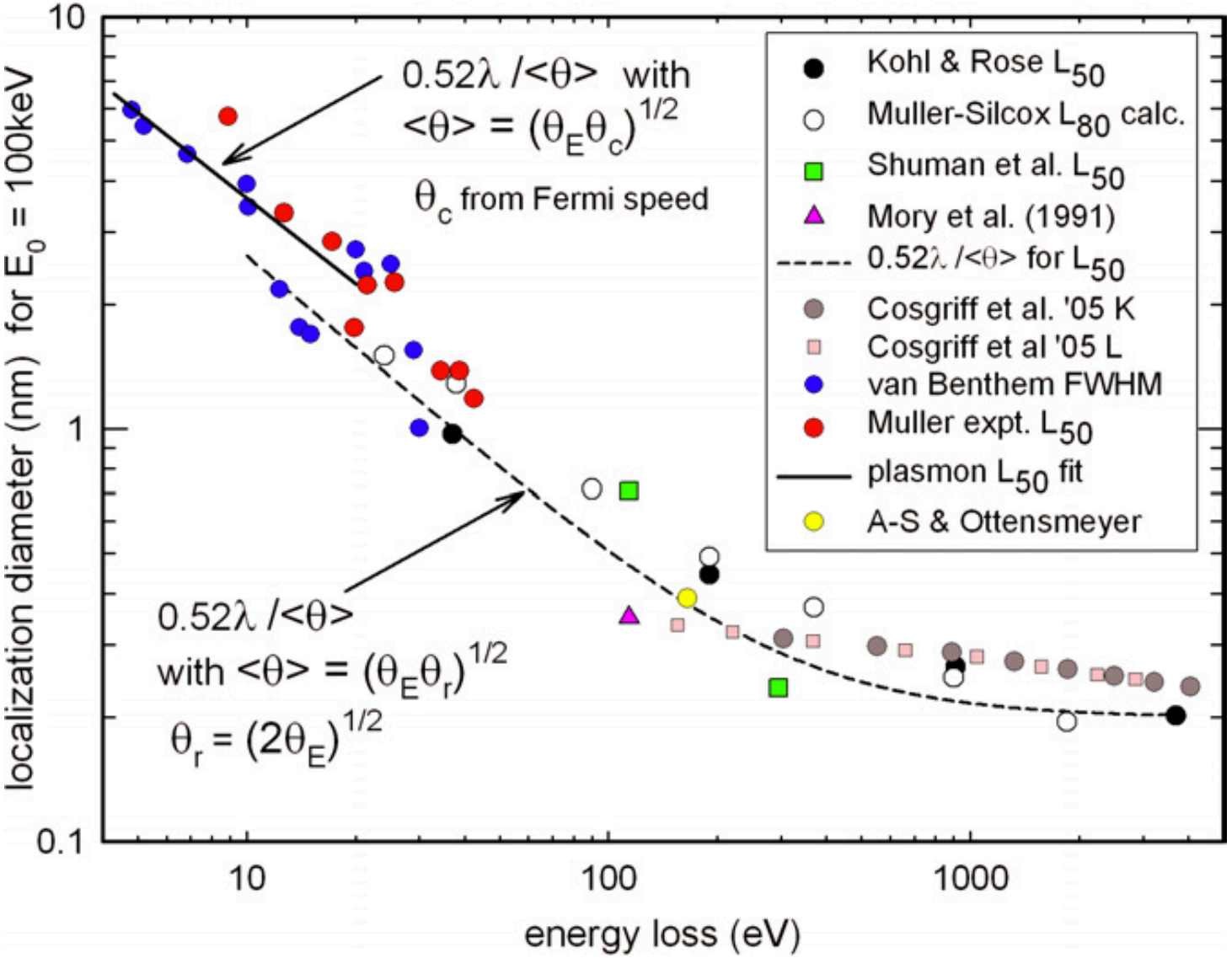
$$\chi(E) \rightarrow \varepsilon(E) \rightarrow \varepsilon_1(E), \varepsilon_2(E)$$

↑

Optical absorption

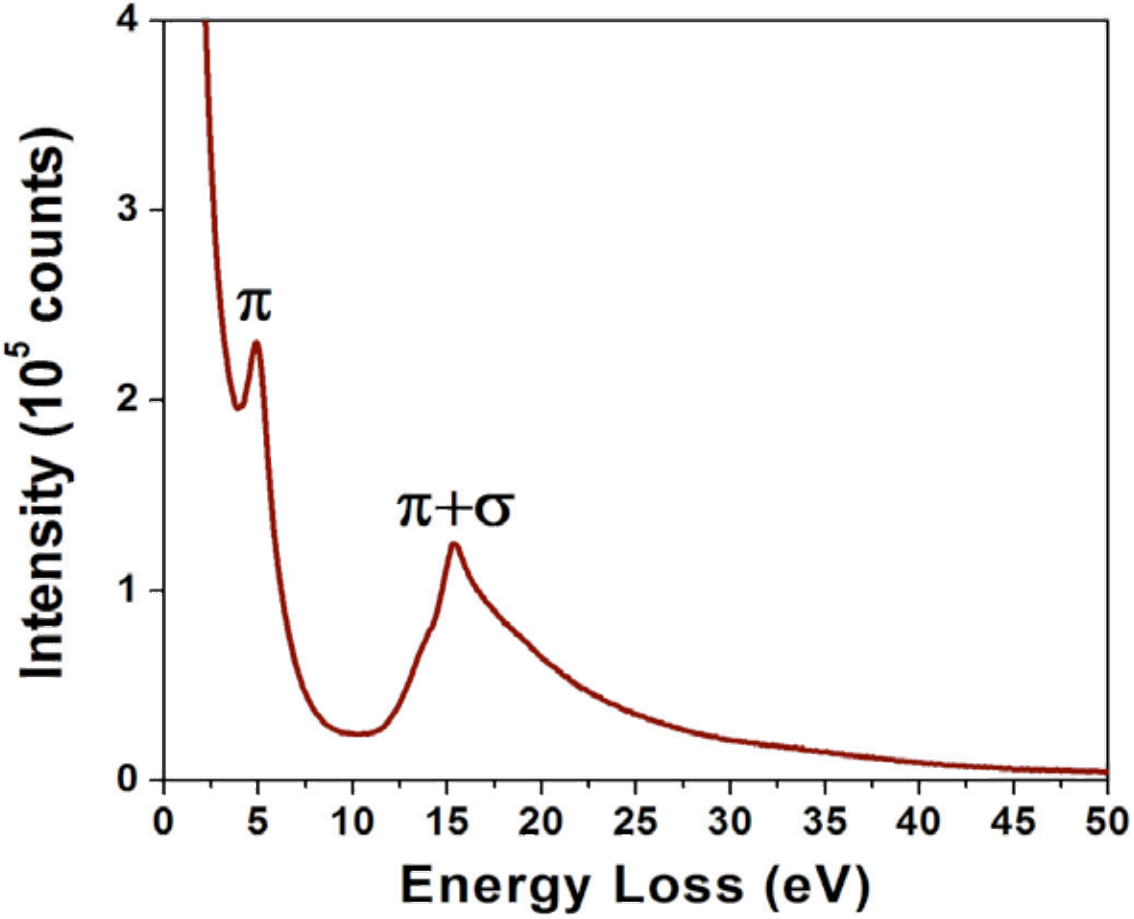
STEM-EELS: Optical absorption with atomic resolution

Delocalization is a problem?



R. F. Egerton, Rep. Prog. Phys. 72, 6502 (2009).

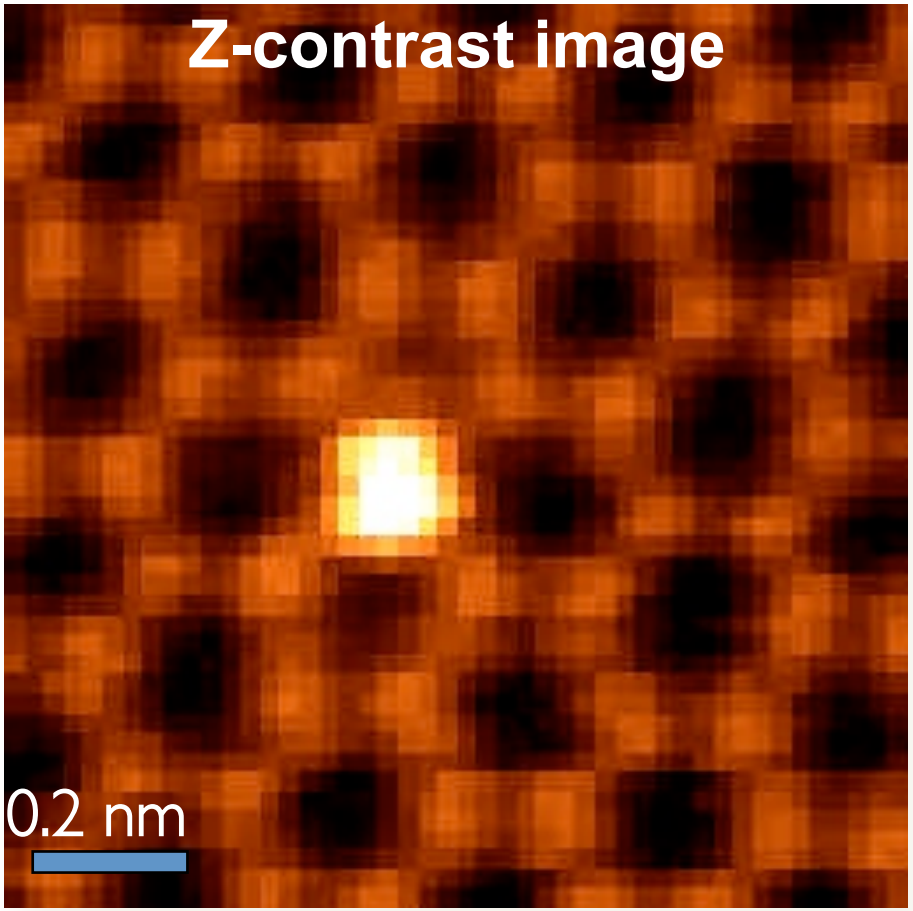
Typical “plasmon” peaks of monolayer graphene

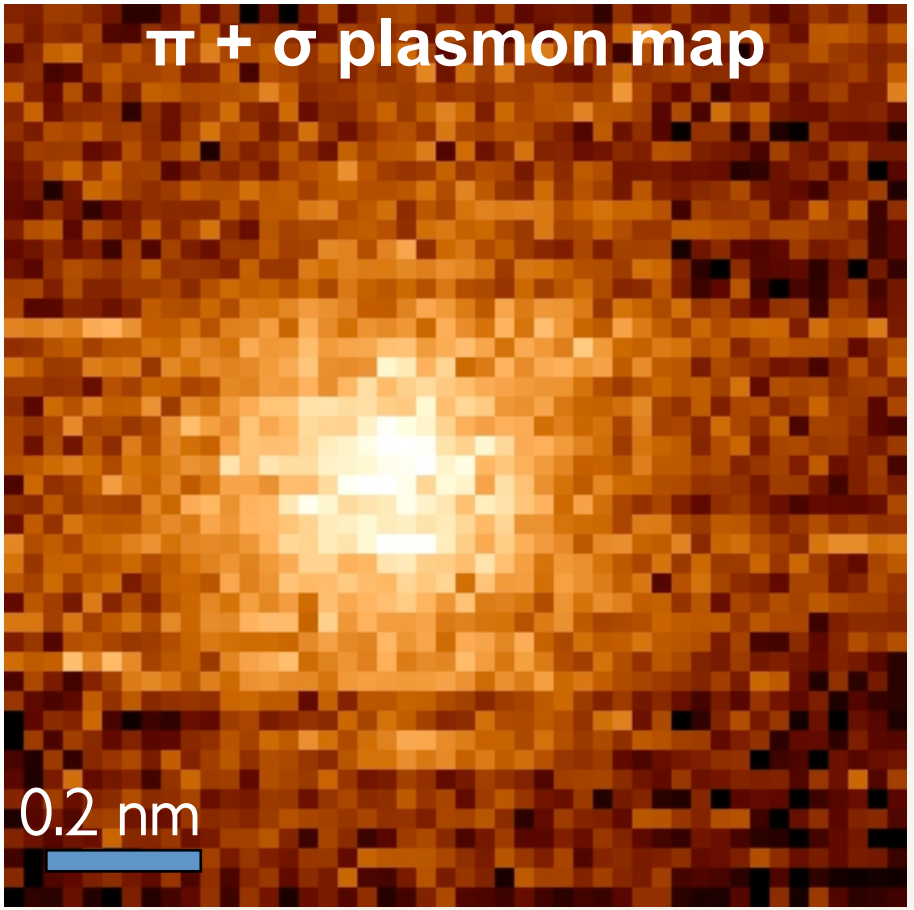


How do point defects affect the plasmon response?

Atomically localized plasmon enhancement

FWHM for enhanced plasmon: 0.43±0.05 nm (< λ/200)

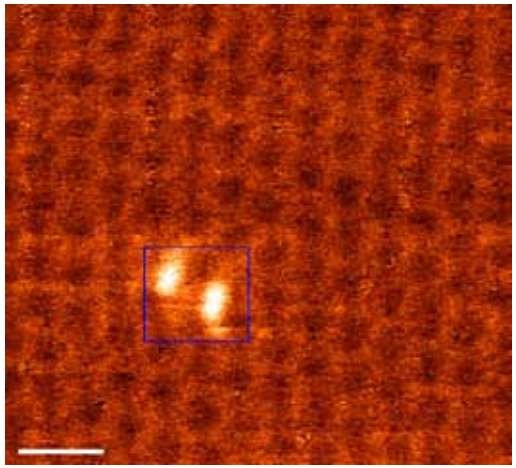




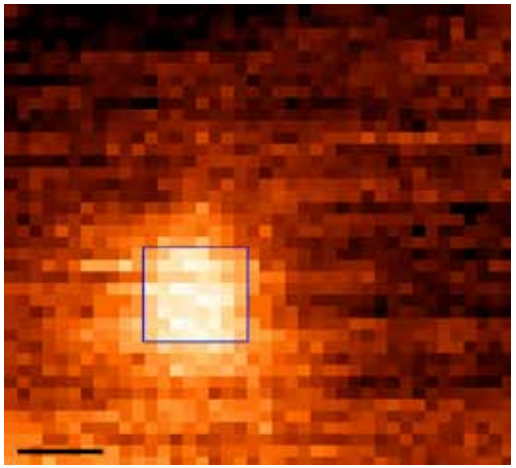
W. Zhou, J. Lee, J. Nanda, S.T. Pantelides, S.J. Pennycook and J.C. Idrobo
Nature Nanotechnology 7, 161 (2012).

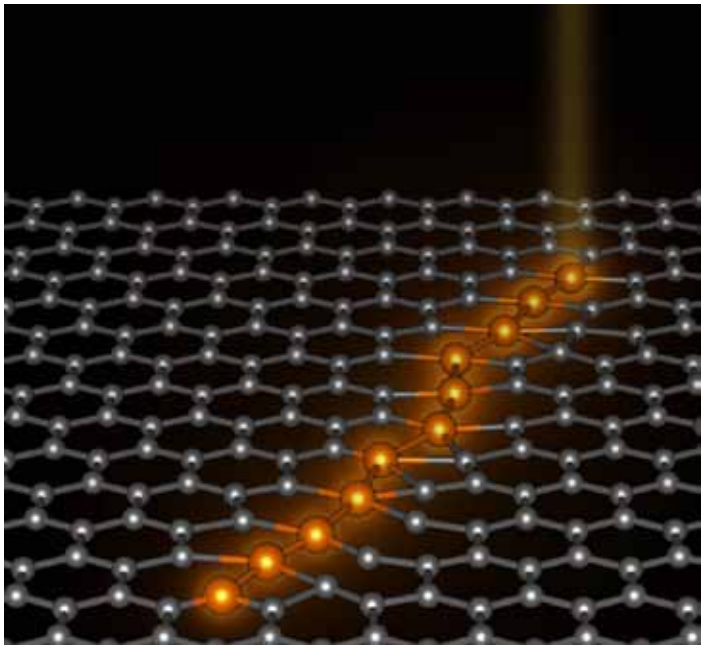
Atomically localized plasmon resonance

Z-contrast



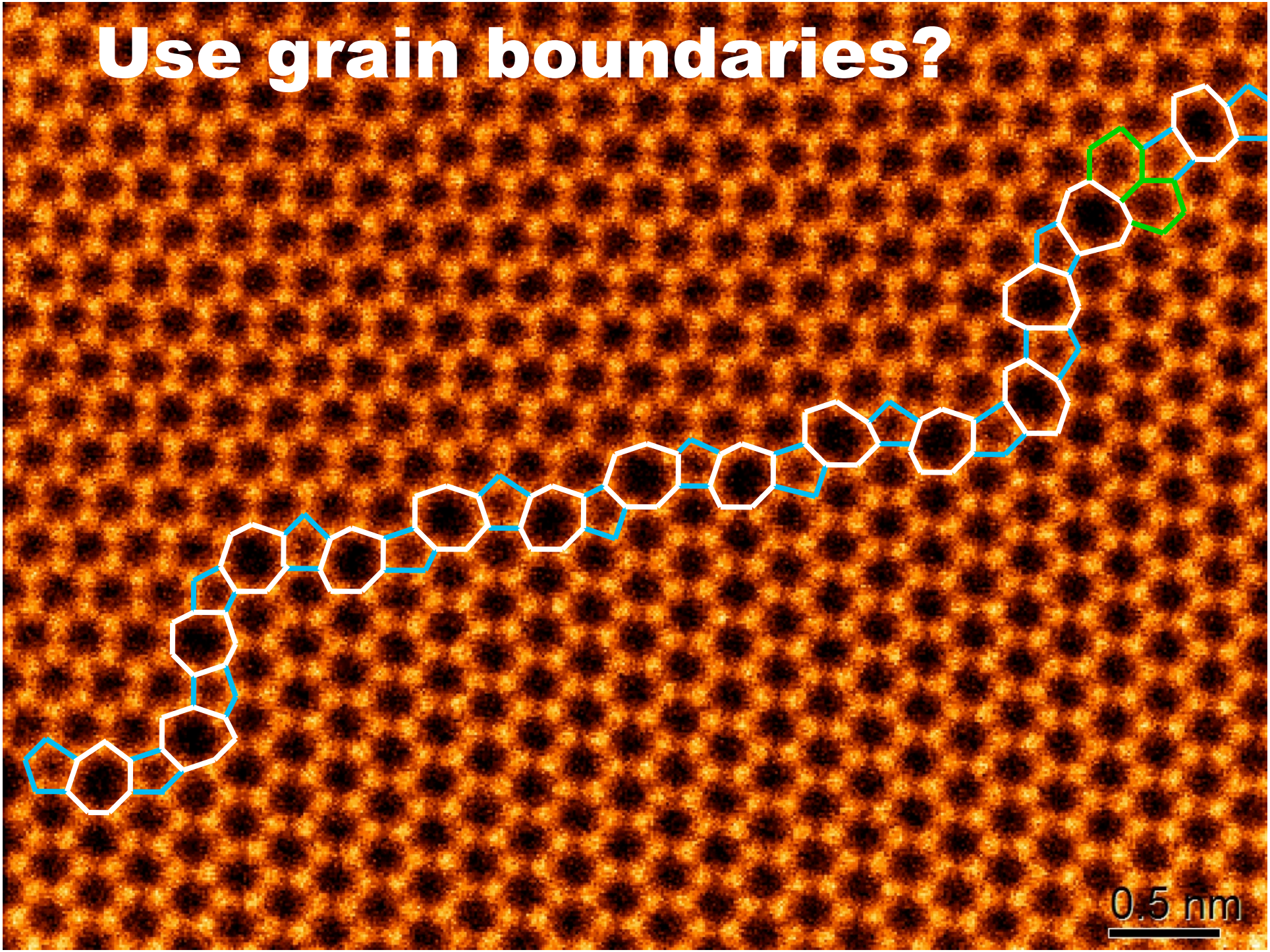
plasmon (11-18 eV)



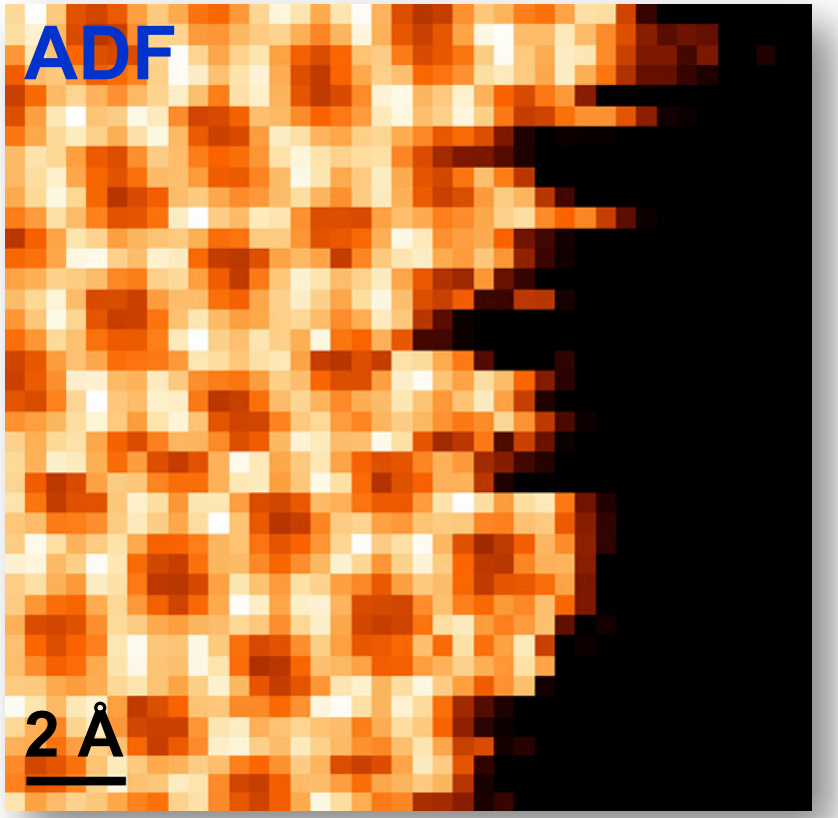


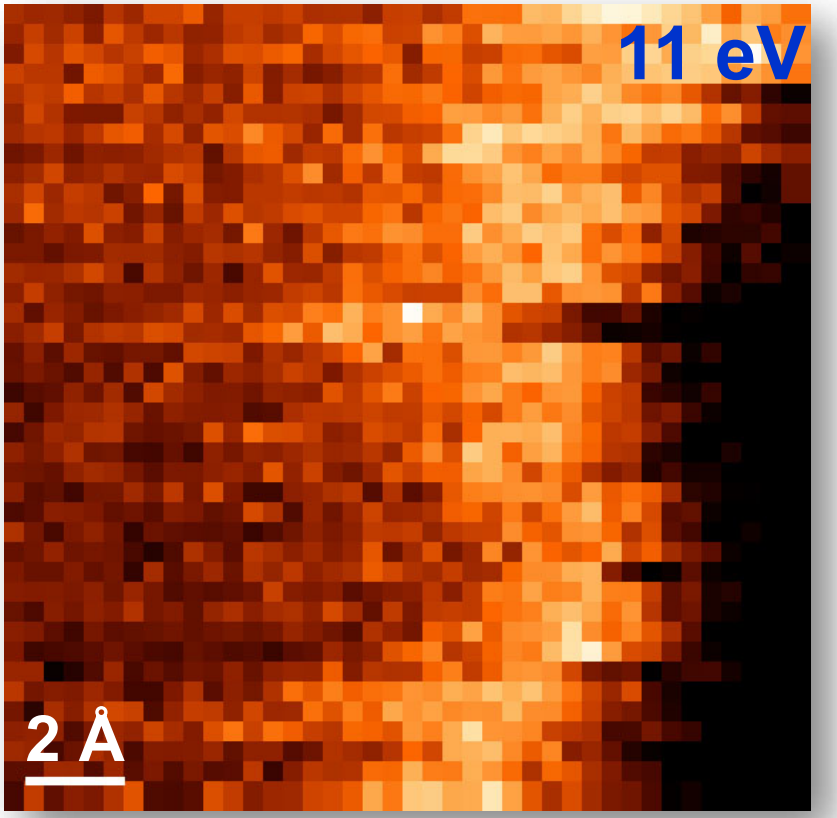
High frequency (10^{15} Hz) signals could be transmitted along atomically confined paths by assembling single atoms on graphene

*W. Zhou et al., Nat. Nanotech. 7, 161 (2012)


Use grain boundaries?
0.5 nm

1-D edge plasmon on graphene with 6Å localization

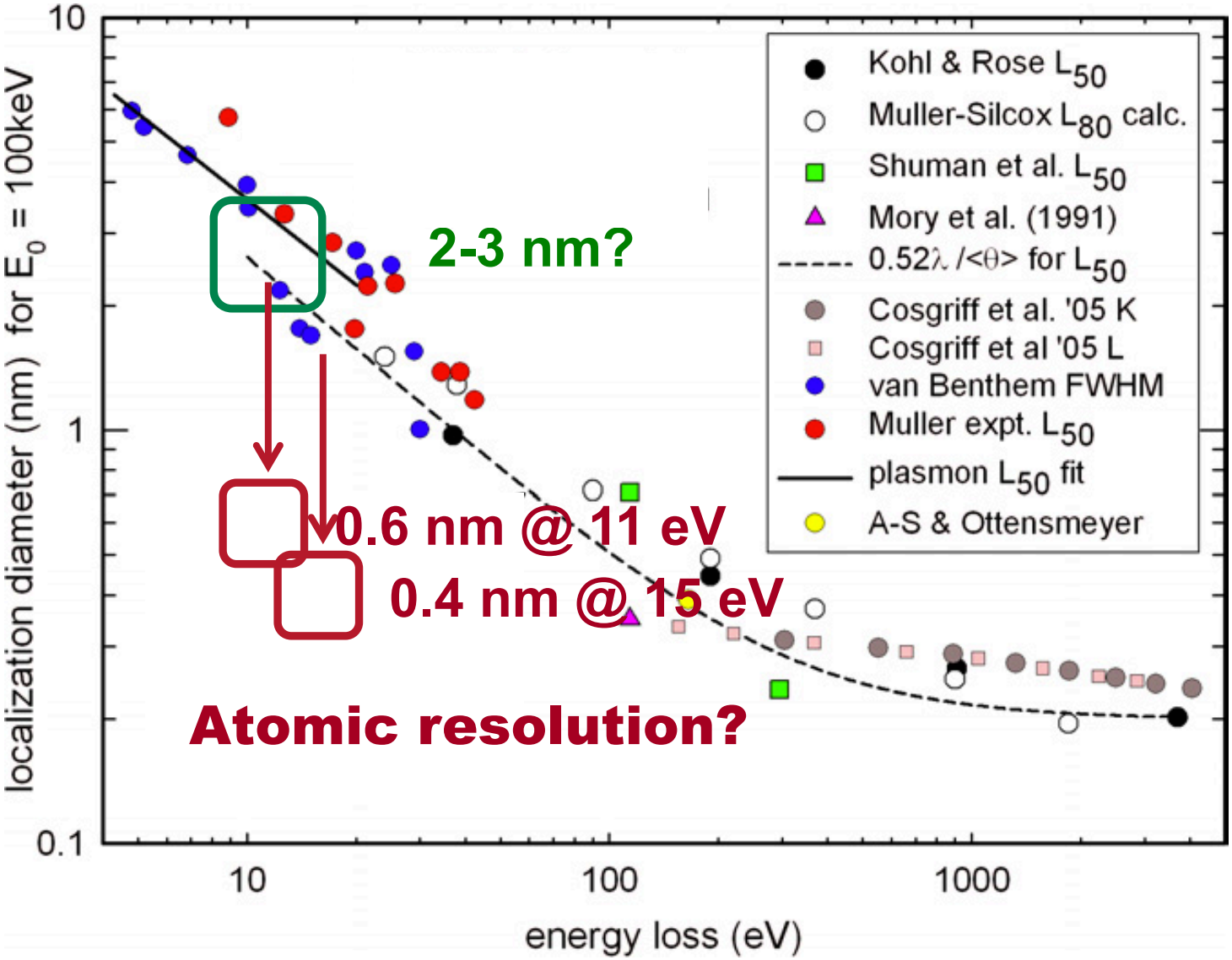




Localization depends both on the energy loss and the specific electron excitation mode contributing to the energy loss

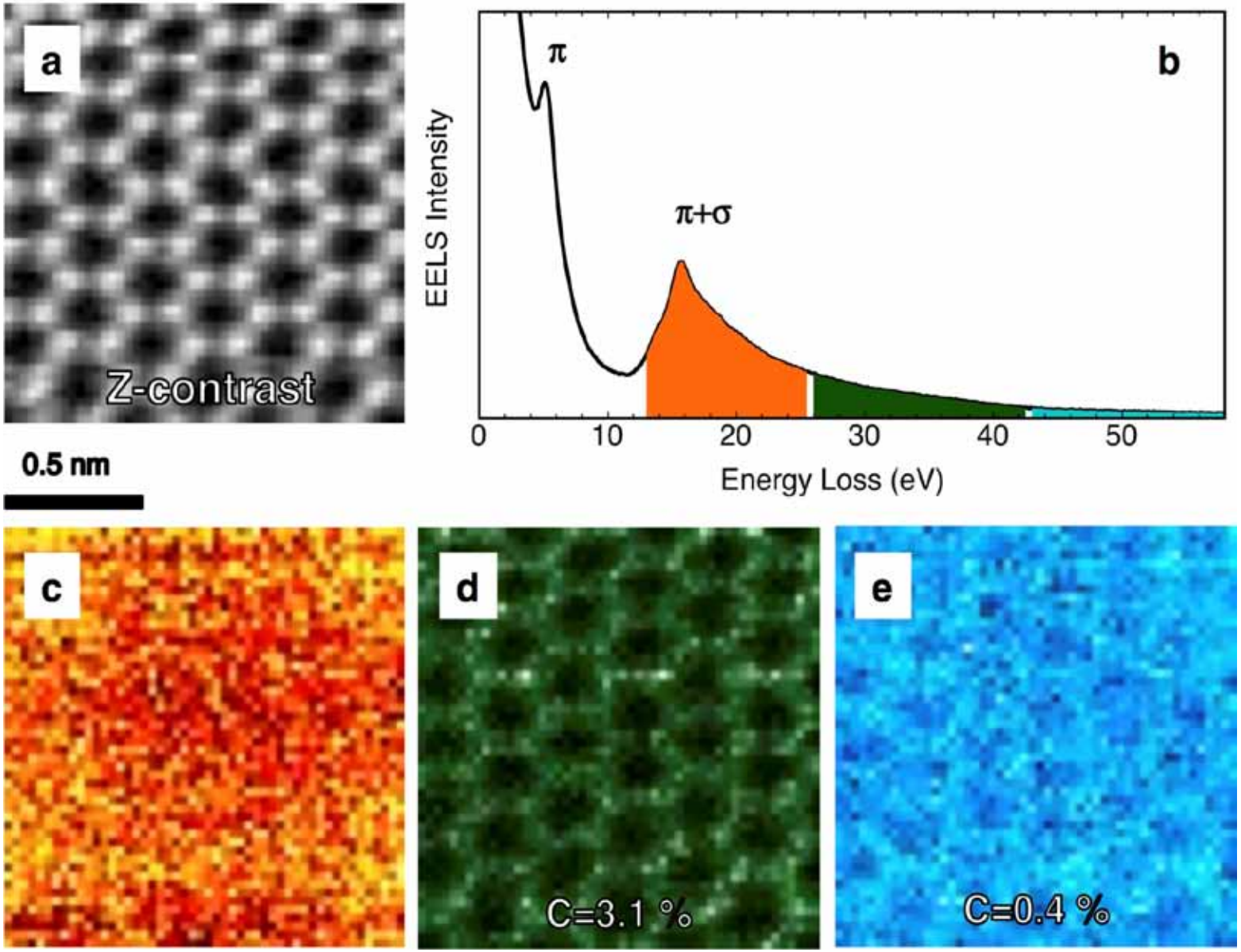
W. Zhou et al. Ultramicroscopy (2012)

Surprisingly localized



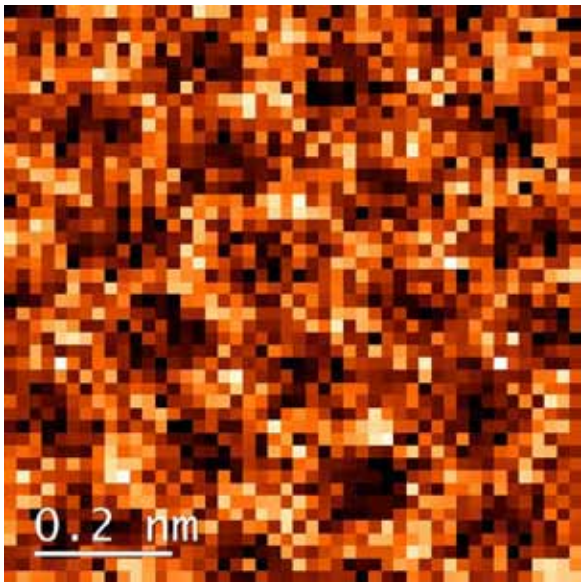
R. F. Egerton, Rep. Prog. Phys. 72, 6502 (2009).

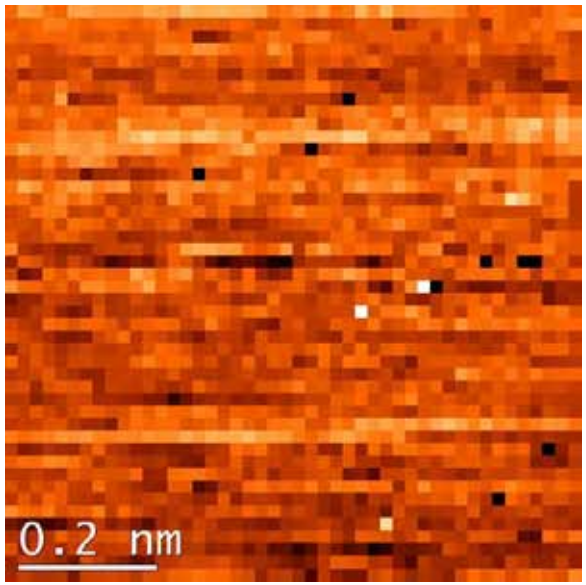
STEM-VEELS SPECTRA AND MAPS -- GRAPHENE



NOT preservation of elastic contrast

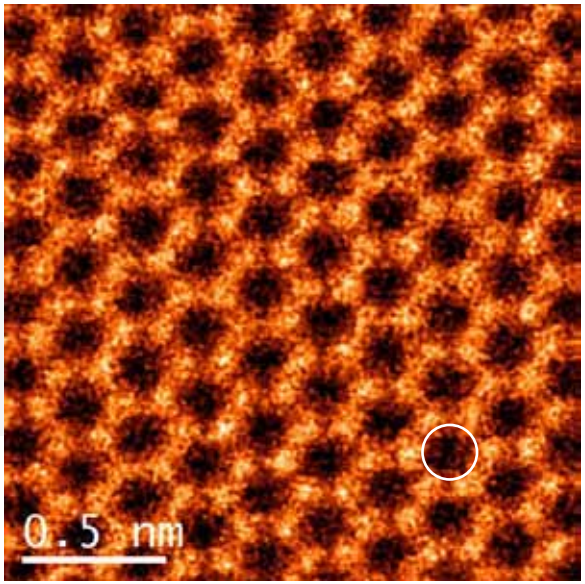
HAADF

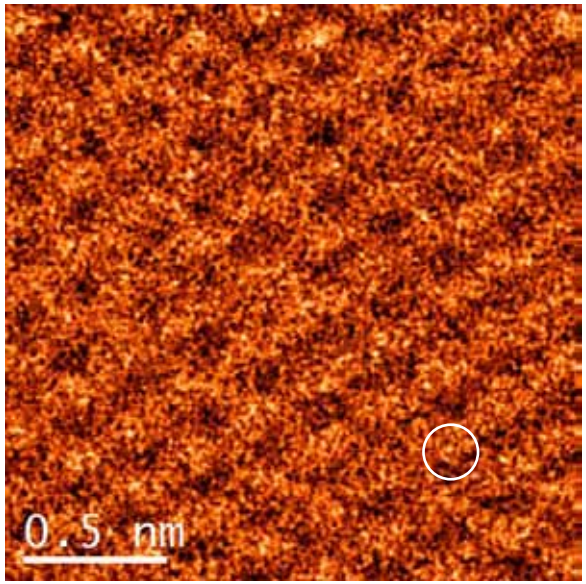




Zero loss

HAADF at optimum focus





Bright field shows reverse contrast

Definition of Plasmons

David Pines & David Bohm, *Physical Review* **85**, 338 (1952)

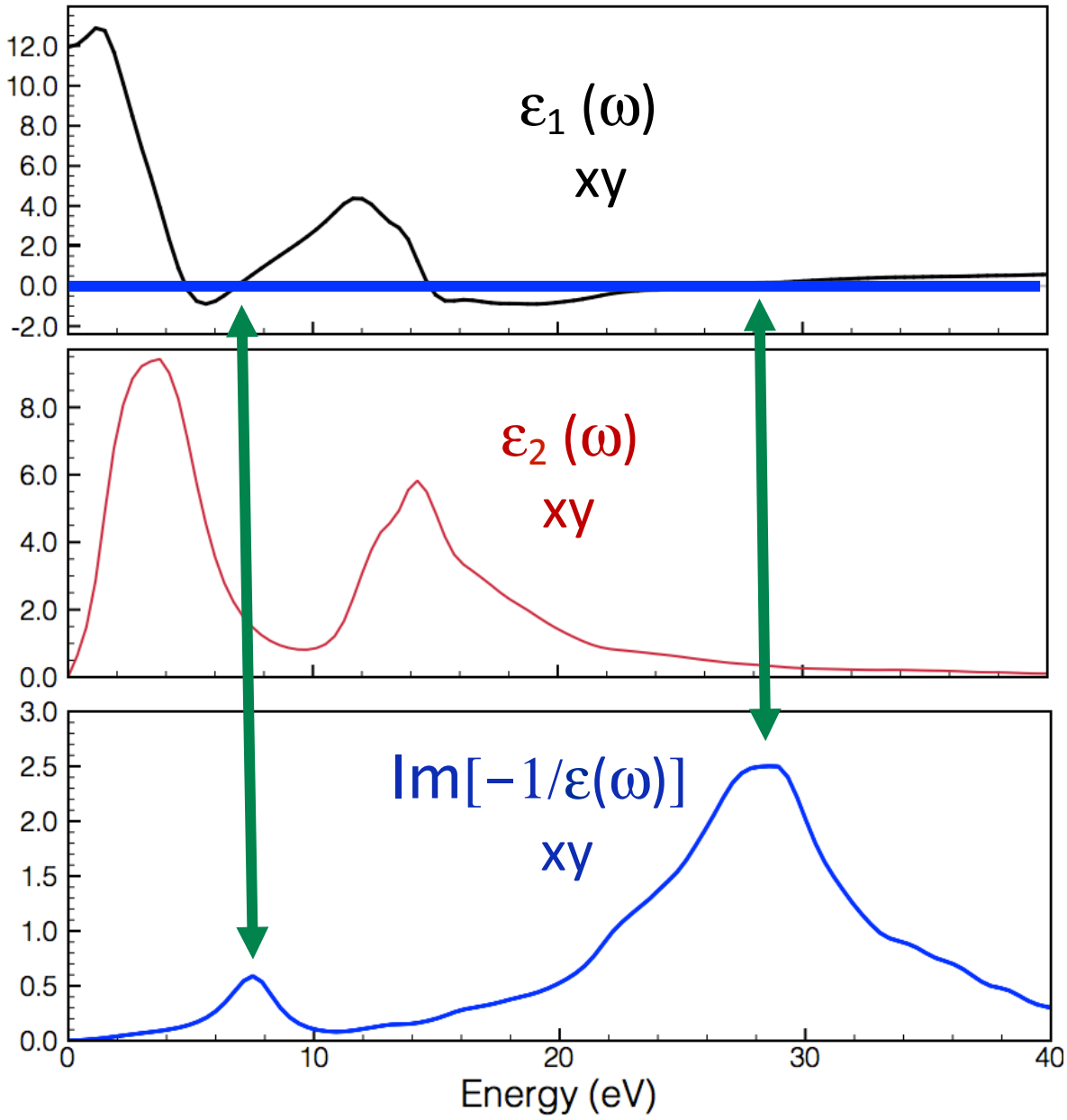
$$\mathrm{Im}\left(-\frac{1}{\epsilon(\omega)}\right) \quad \epsilon(\omega) \rightarrow 0$$

$$\frac{\epsilon_2(\omega)}{\epsilon_1(\omega)^2 + \epsilon_2(\omega)^2}$$

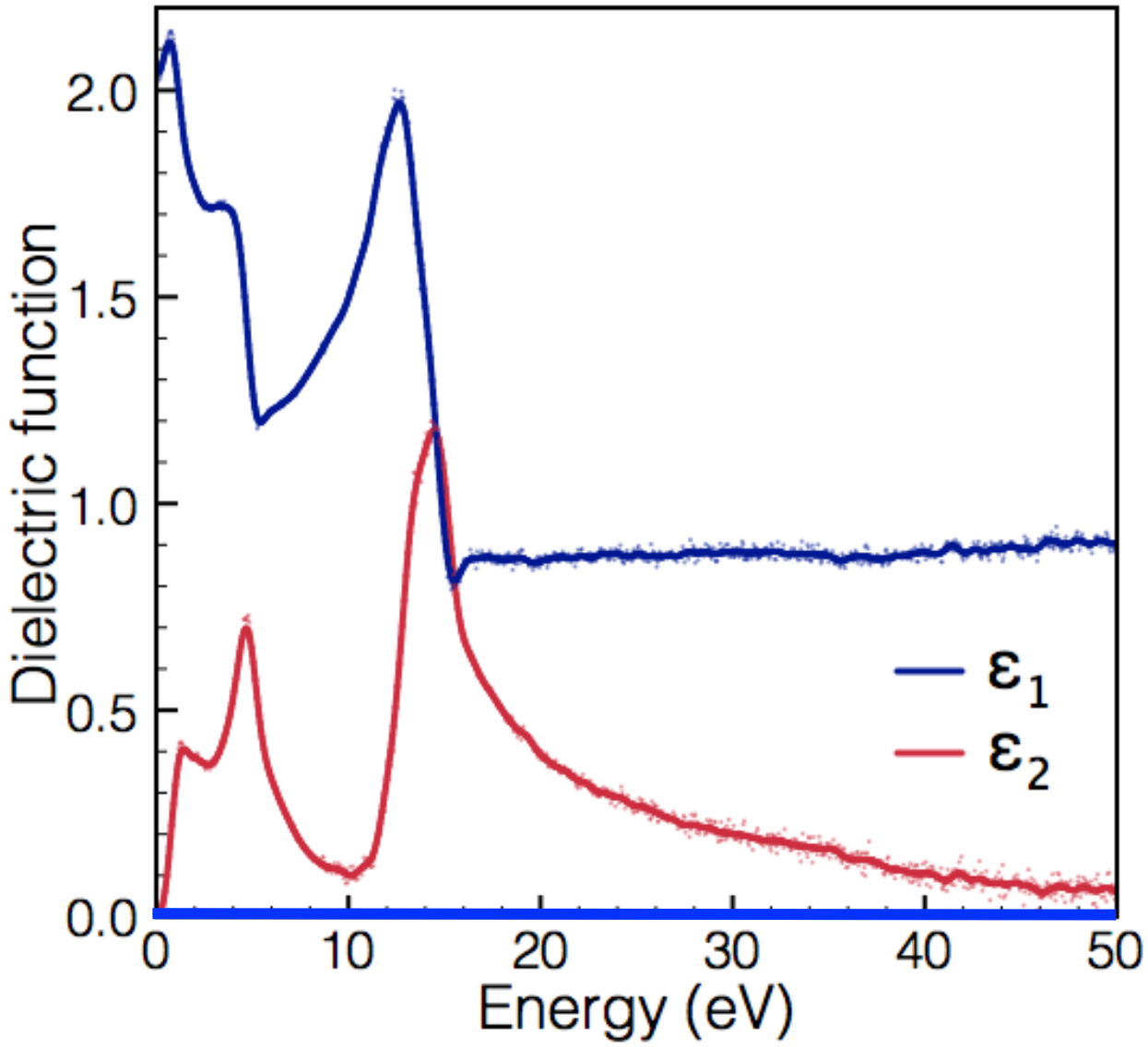
$$\epsilon_1(\omega) = 0 \qquad \epsilon_2(\omega) \approx 0$$

J-C Idrobo

Plasmons in graphite



“Plasmons” in graphene are *interband* transitions some of which are localized

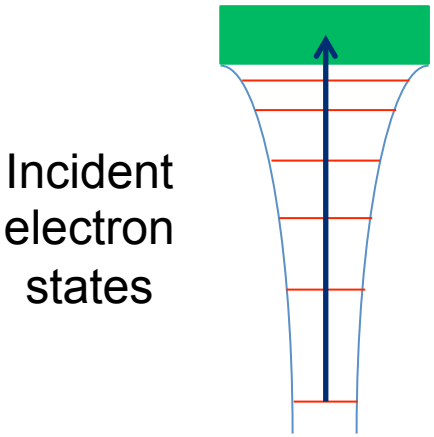


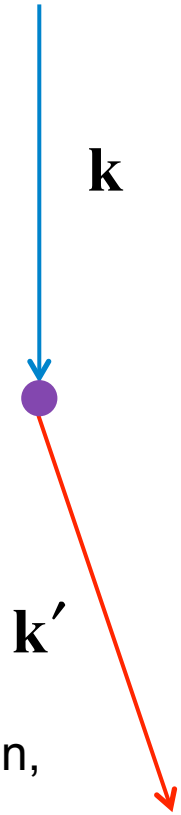
F. J. Nelson, J.-C. Idrobo, J. D. Fite, Z. L. Mišković, S. J. Pennycook, S. T. Pantelides, J. U. Lee, and A. C. Diebold, "Electronic Excitations in Graphene in the 1–50 eV Range: The π and π + σ Peaks Are Not Plasmons," *Nano Lett*, 14, 3827–3831 (2014).

EELS simulation at atomic resolution

Dynamical Electron Scattering

$$\psi(\mathbf{r}) = \sum_{\mathbf{g}} \Psi_{\mathbf{g}} e^{2\pi i(\mathbf{k}+\mathbf{g})\cdot\mathbf{r}}$$

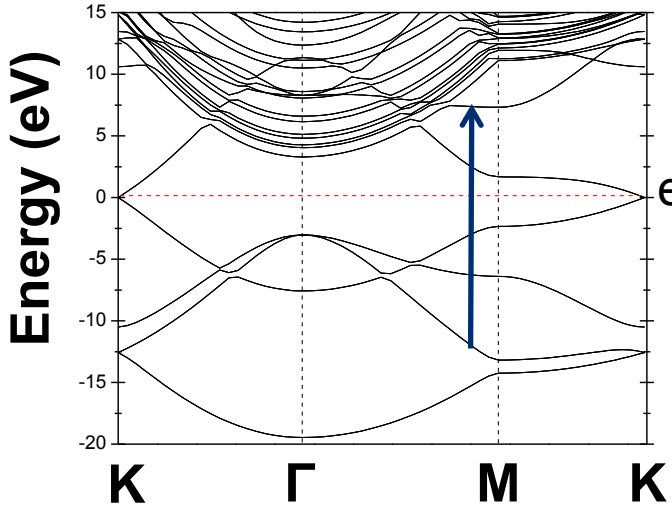




- **NO SOLID STATE BONDING**
- Detailed description of electron propagation (dynamical diffraction, channeling)
- Probe position dependence

Density Functional Theory

$$\psi = e^{2\pi i\mathbf{k}\cdot\mathbf{r}}$$



- **FULL SOLID STATE BONDING**
- Incident electron is a plane wave- magically appears at the atom
- No incident beam direction
- No detector
- No spatial information

M. P. Prange, M. P. Oxley, M. Varela, S. J. Pennycook, and S. T. Pantelides, "Simulation of Spatially Resolved Electron Energy Loss Near-Edge Structure for Scanning Transmission Electron Microscopy," *Phys Rev Lett*, 109, 246101 (2012).

Combining Electron Scattering & DFT

core state

final state

$$M_{if}\left(\mathbf{Q_g}\right)=\left\langle \varphi_i\left(\mathbf{r}\right)\middle|\exp\left(2\pi i\mathbf{Q_g}\cdot\mathbf{r}\right)\middle|\varphi_f\left(\mathbf{r}\right)\right\rangle$$

$$\mathbf{Q_g}=\mathbf{q}+\mathbf{g}=\left(\mathbf{k}+\mathbf{g}\right)-\mathbf{k}'$$ momentum transfer

We measure intensities: $\left|M_{if}\left(\mathbf{Q_g}\right)\right|^2=M_{if}\left(\mathbf{Q_g}\right)M^*_{if}\left(\mathbf{Q}_h\right)$

Mixed Dynamical Form Factor (MDFF) – needed for STEM probe

$$S^{i,f}\left(\mathbf{Q_g},\mathbf{Q_h},E_{\text{loss}}\right)=\left\langle i\middle|\exp\left(2\pi i\mathbf{Q_g}\cdot\mathbf{r}\right)\middle|f\right\rangle\left\langle f\middle|\exp\left(-2\pi i\mathbf{Q_h}\cdot\mathbf{r}'\right)\middle|i\right\rangle$$

Dynamical Form Factor (DFF) – only applies for plane wave

$$S^{i,f}\left(\mathbf{q},E_{\text{loss}}\right)=\left|\left\langle i\middle|\exp\left(2\pi i\mathbf{q}\cdot\mathbf{r}\right)\middle|f\right\rangle\right|^2$$

EELS: Inelastic Scattering Potential

Fourier Component

detector and beam direction

$$\mu_{\mathbf{h},\mathbf{g}}^{i,f} \propto \int_{\text{detector}} k' \frac{S^{i,f}\left(\mathbf{Q}_{\mathbf{g}},\mathbf{Q}_{\mathbf{h}},E_{\text{loss}}\right)}{\left|\mathbf{Q}_{\mathbf{g}}\right|^2\left|\mathbf{Q}_{\mathbf{h}}\right|^2} d\Omega_{k'}$$

The full inelastic scattering potential:

$$W^{i,f}\left(\mathbf{r},\mathbf{r}',E_{\text{loss}}\right) \propto \sum_{\mathbf{h},\mathbf{g}} \mu_{\mathbf{h},\mathbf{g}}^{i,f} e^{-2\pi i\mathbf{g}\cdot\mathbf{r}} e^{2\pi i\mathbf{h}\cdot\mathbf{r}'}$$

$$\text{DFF} \Rightarrow \mu_{0,0}^{i,f} \propto \int_{\text{detector}} k' \frac{\left|\left\langle i\left|\exp\left(2\pi i\mathbf{q}\cdot\mathbf{r}\right)\right|f\right\rangle\right|^2}{\left|\mathbf{q}\right|^4} d\Omega_{k'}$$

Mean value of the inelastic potential

The Inelastic STEM Image

The inelastic image as a function of probe position R.

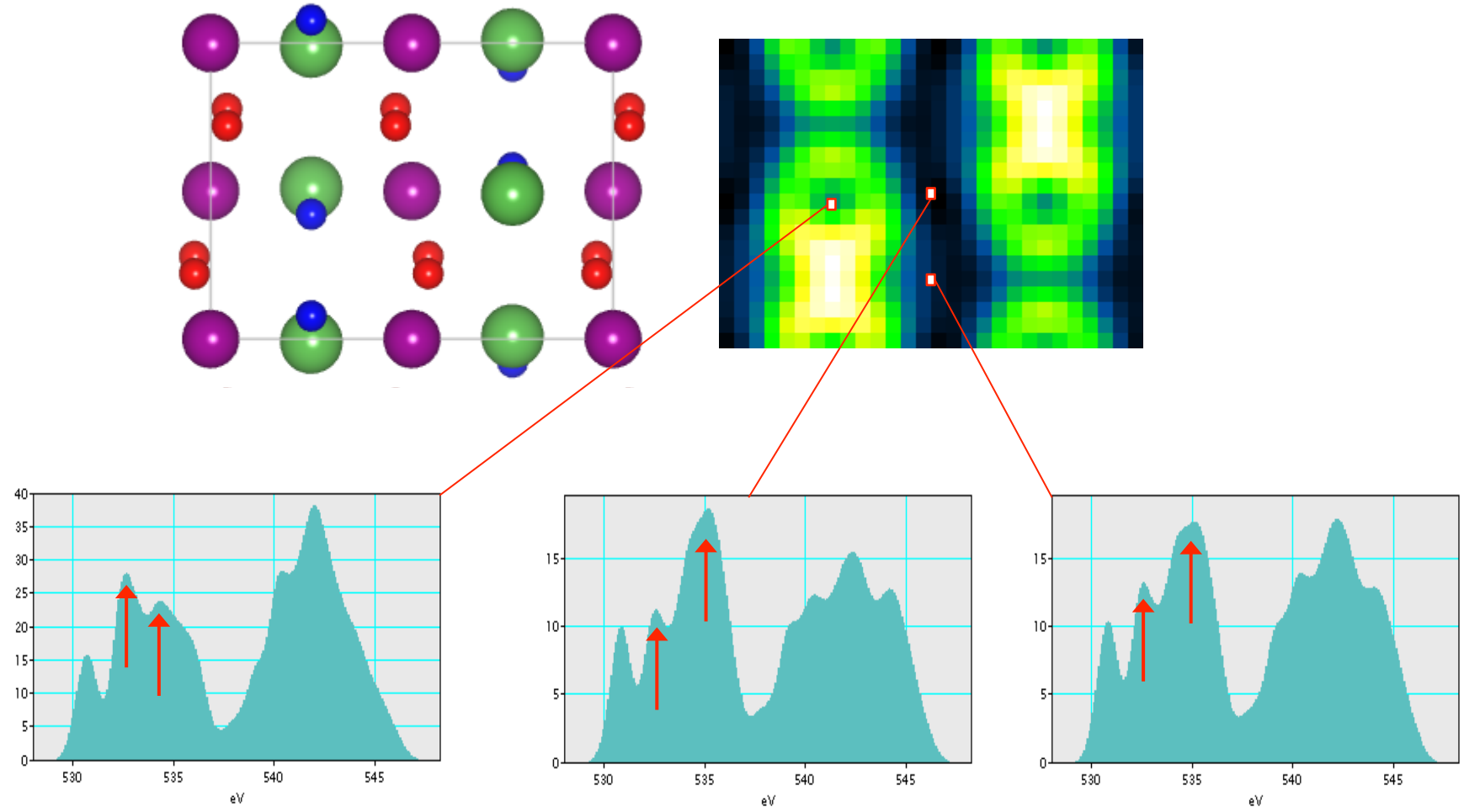
$$I^{i,f}\left(\mathbf{R},t\right) \propto \int_0^t \sum_{\mathbf{h},\mathbf{g}} \Psi_{\mathbf{h}}^{*}\left(\mathbf{R},\mathbf{r'}_{\perp},z\right)\Psi_{\mathbf{g}}\left(\mathbf{R},\mathbf{r}_{\perp},z\right)\mu_{\mathbf{h},\mathbf{g}}^{i,f}dz$$

$$\mathrm{DFF} \Rightarrow \mu_{0,0}^{i,f} \Rightarrow I \propto \left|\Psi_0\right|^2 \mu_{0,0}^{i,f}$$

The DFF contains no information about the probe position or propagation

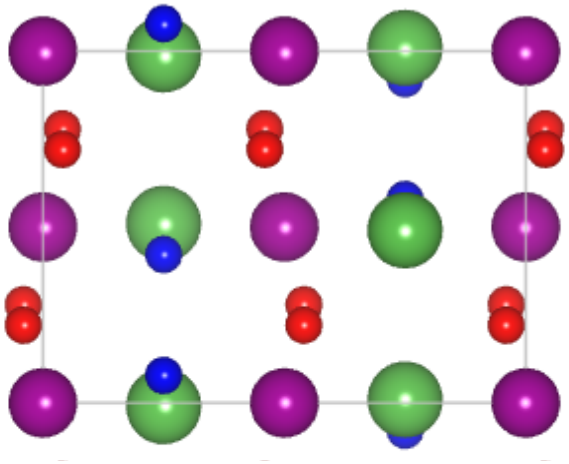
For a given transition, fine structure will not change shape, only intensity

Near Edge Structure as a Function of Probe Position: O1 signal in LMO

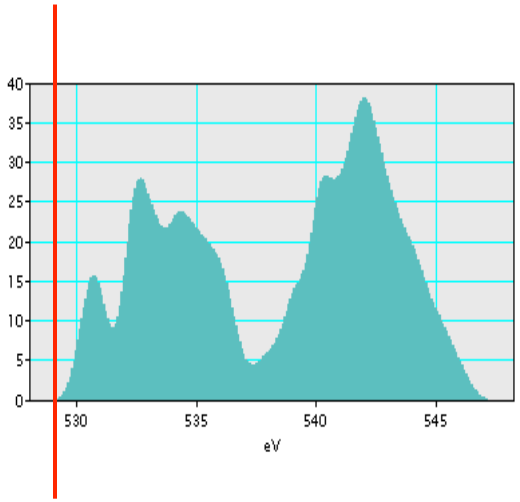


Fine structure varies with probe position – need full simulation

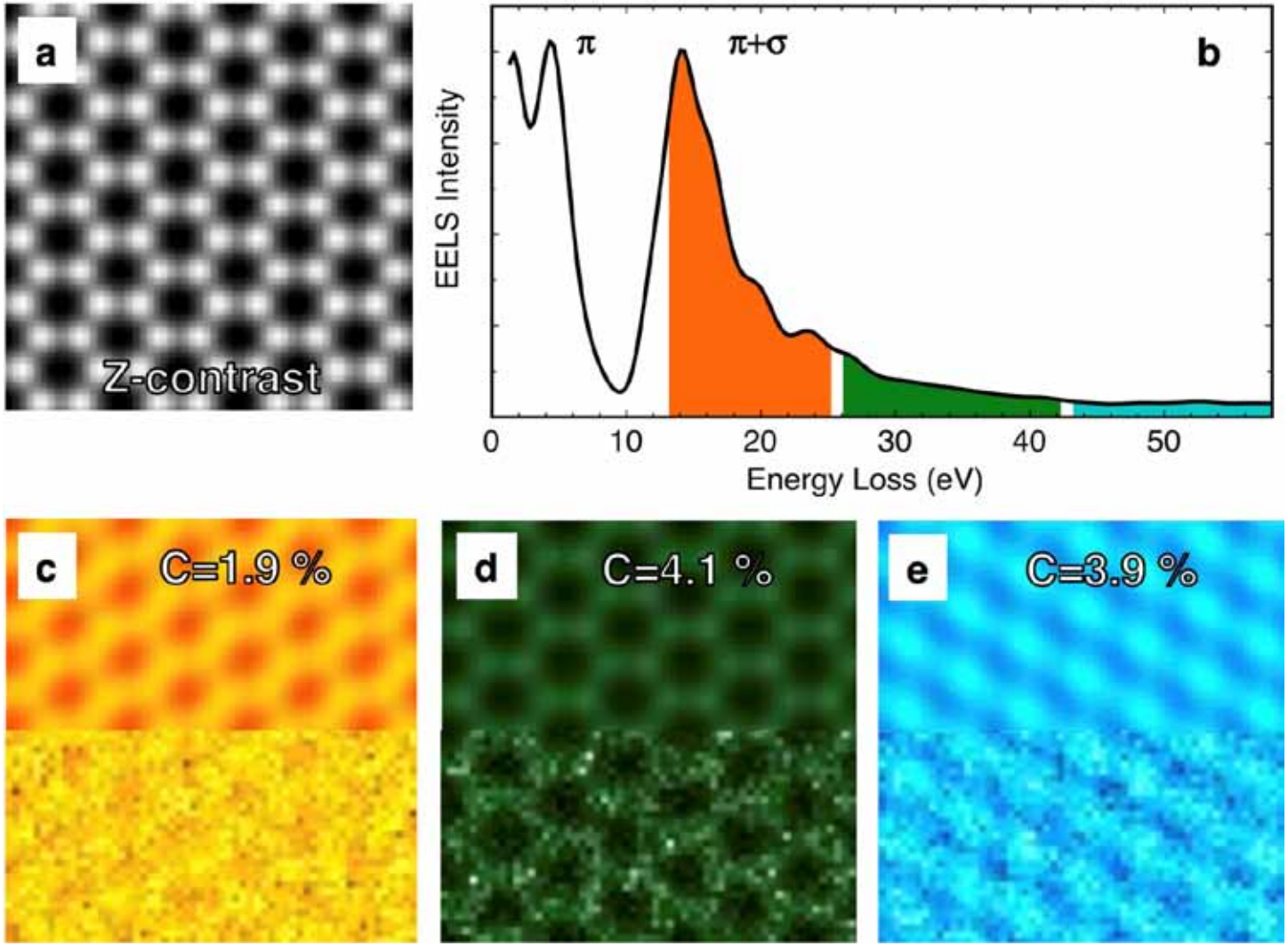
Near Edge Structure as a Function of Energy: O1 signal



- Fine structure varies with energy
- Delocalization changes for transitions < 5 eV apart
- DFF or simple d_{50} type expressions fail
- Need full simulation



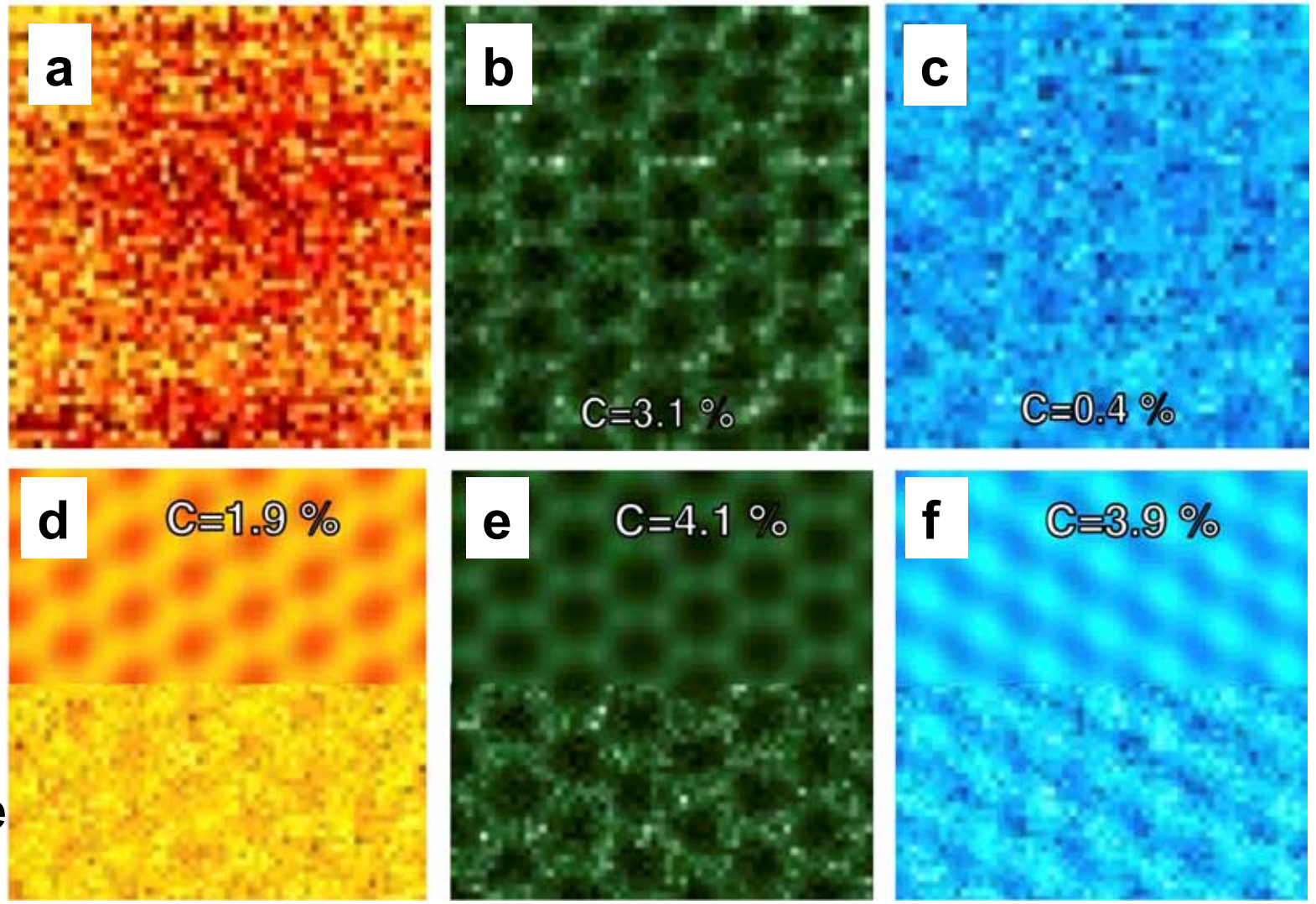
THEORETICAL VEELS SPECTRA AND MAPS -- GRAPHENE



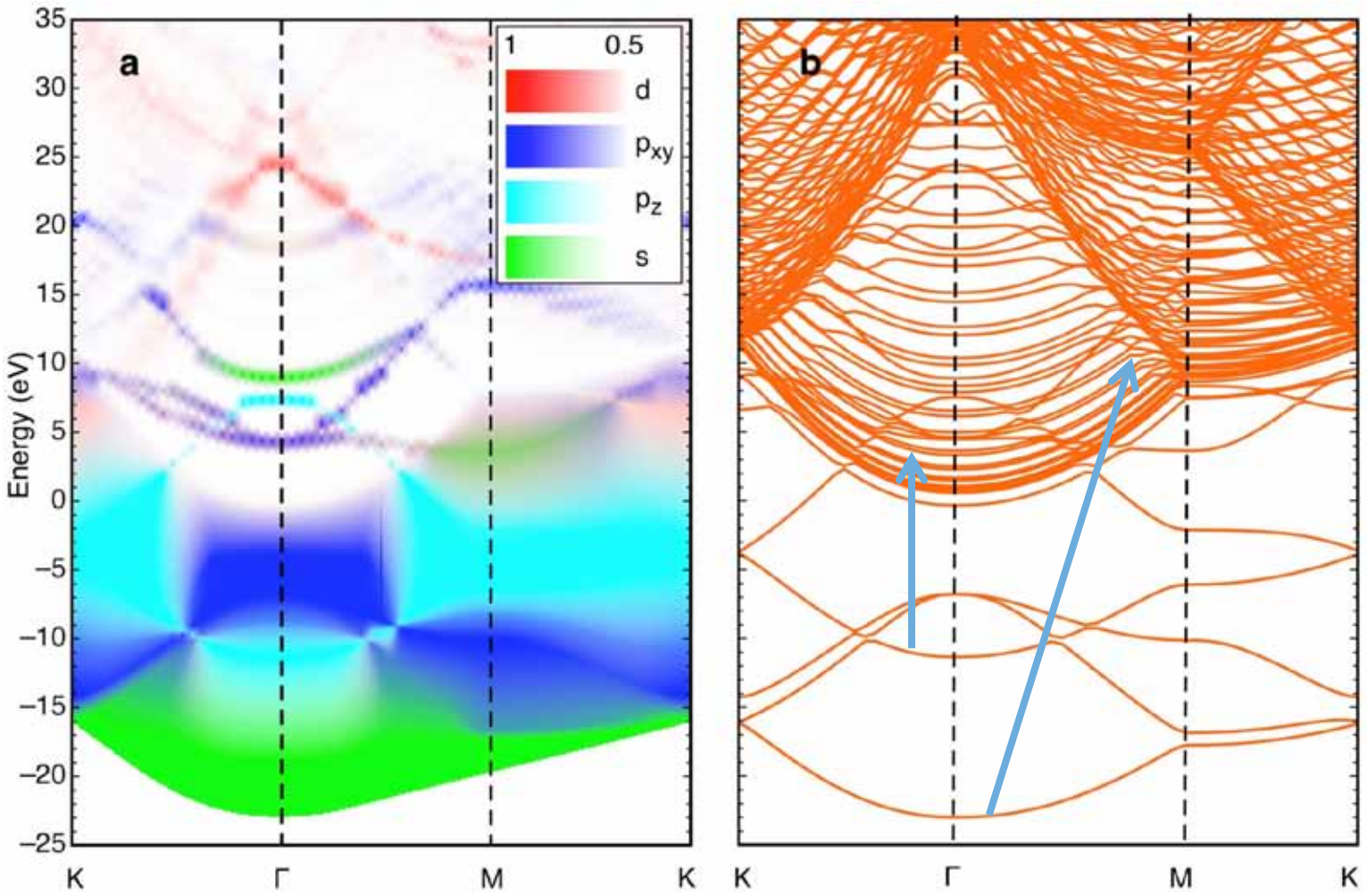
+1% noise

COMBINES DFT EXCITATION MATRIX ELEMENTS WITH DYNAMICAL SCATTERING

Experiment

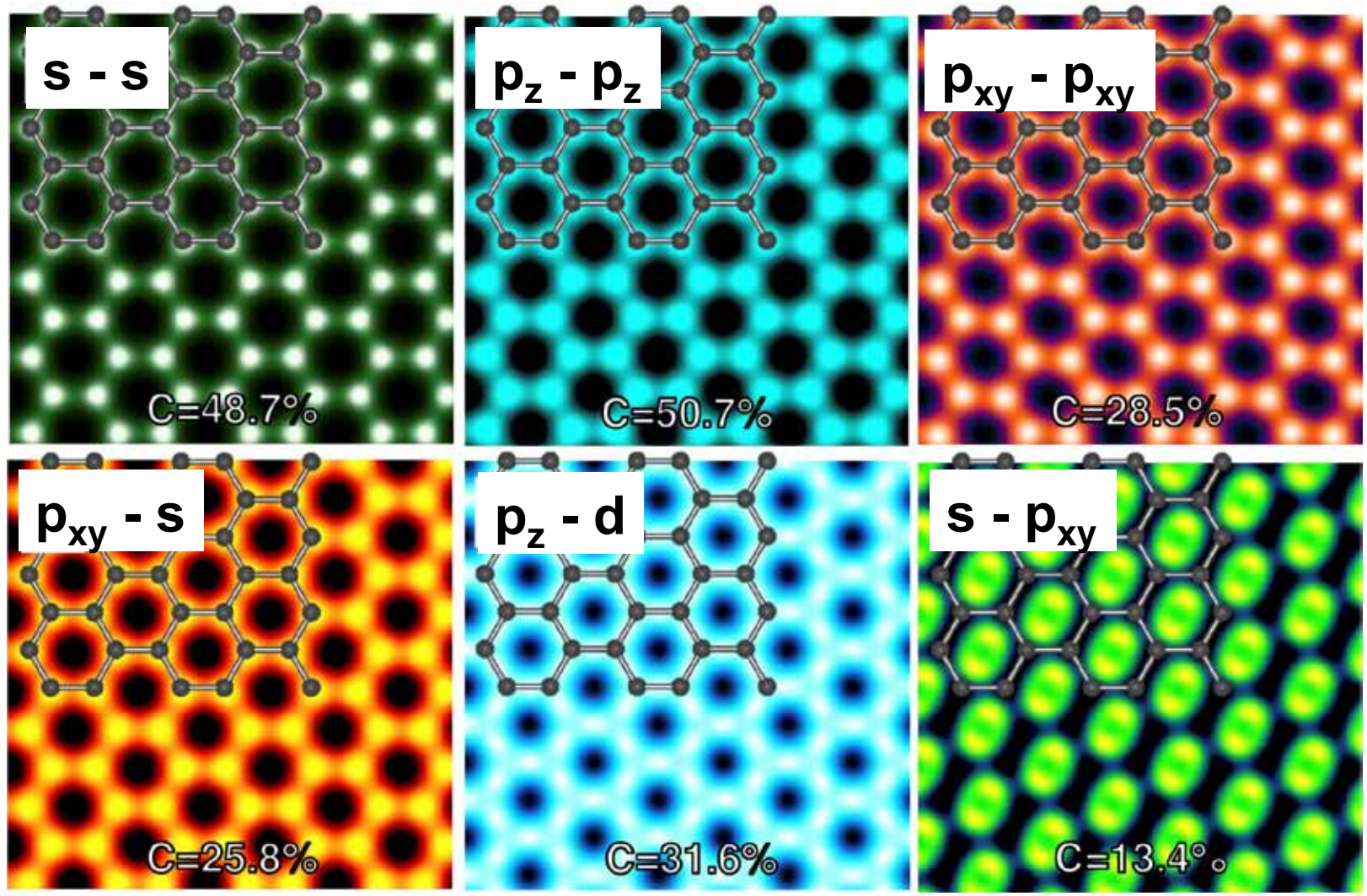


THE ATOMIC CHARACTER OF GRAPHENE STATES



SELECT ELECTRONIC EXCITATIONS AT k = 0

Images from states with maximum atomic character



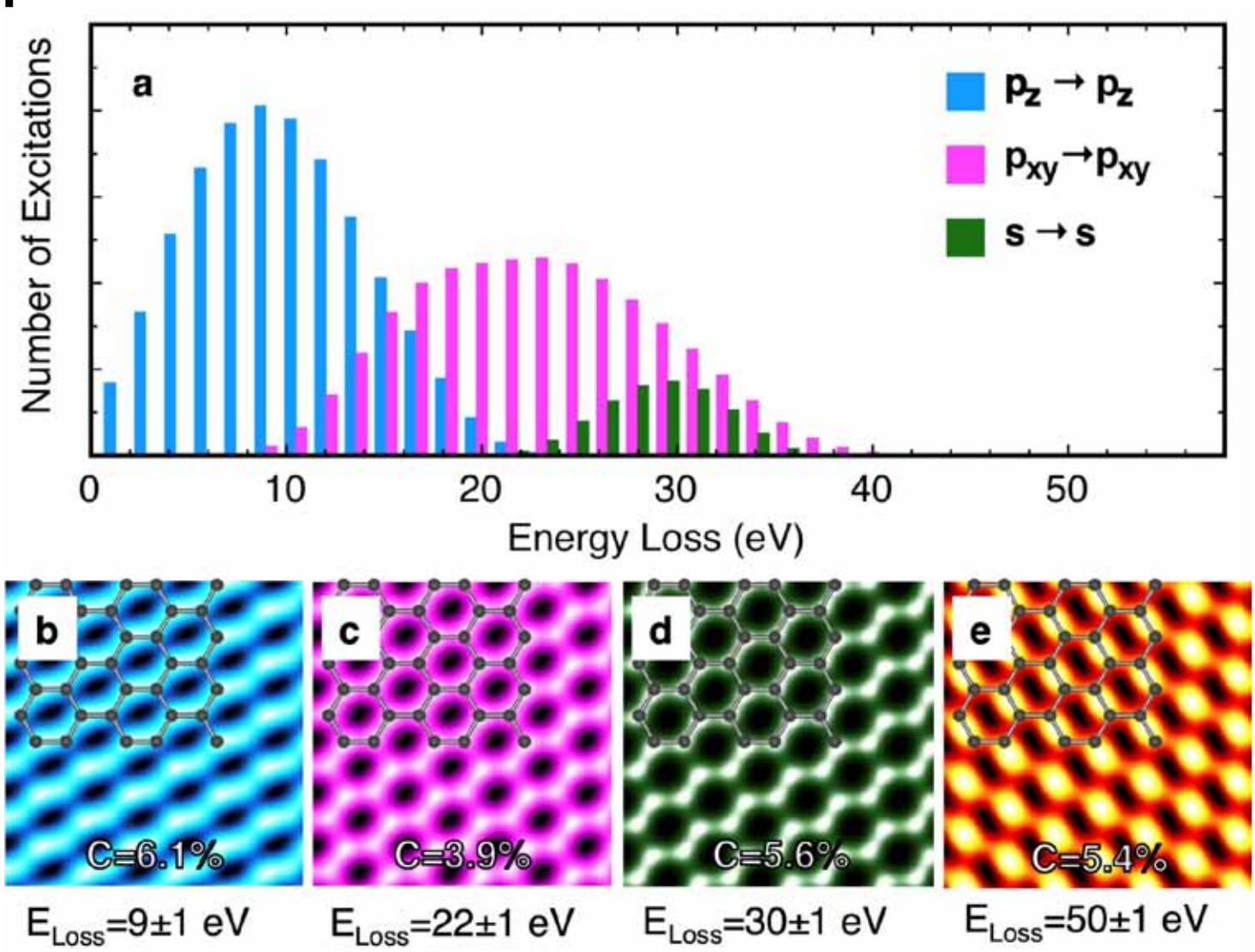
non-dipole allowed

dipole allowed

Reverse contrast

THE ORIGIN OF GRAPHENE-LIKE IMAGES

All k points



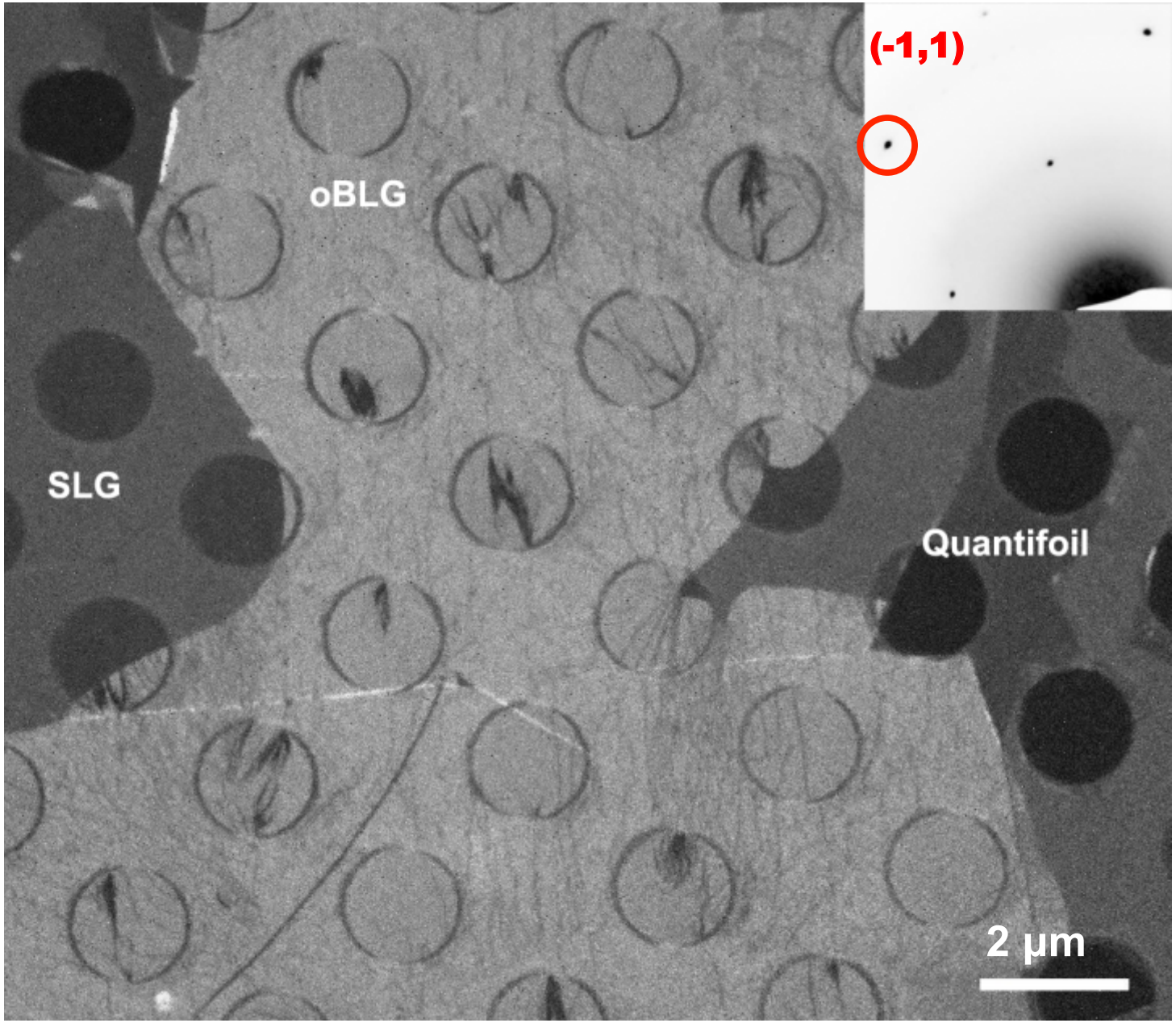
PROPOSED APPLICATIONS

- **THEORY: DEMONSTRATE THE POWER OF ATOMICALLY-RESOLVED VEELS**
  - **POINT DEFECTS**
  - **INTERFACES**
  - **MAGNETIC DICHROISM**
- **EXPT: NEED BETTER S/N RATIO AND ENERGY RESOLUTION**

Bilayer graphene: oriented BLG

Tilt: 0˚
Boundaries show dark

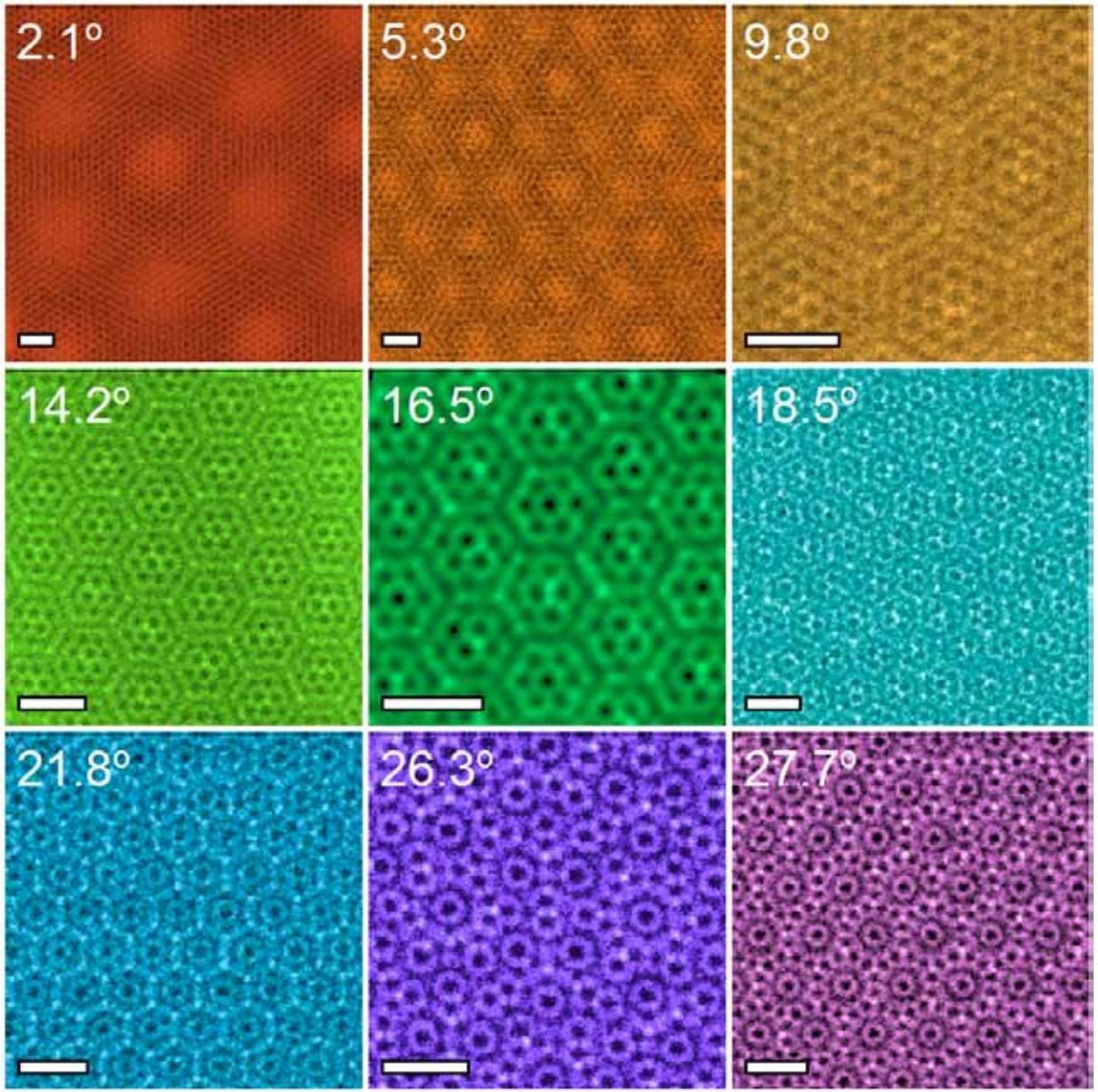
Width ~10 nm



Junhao Lin

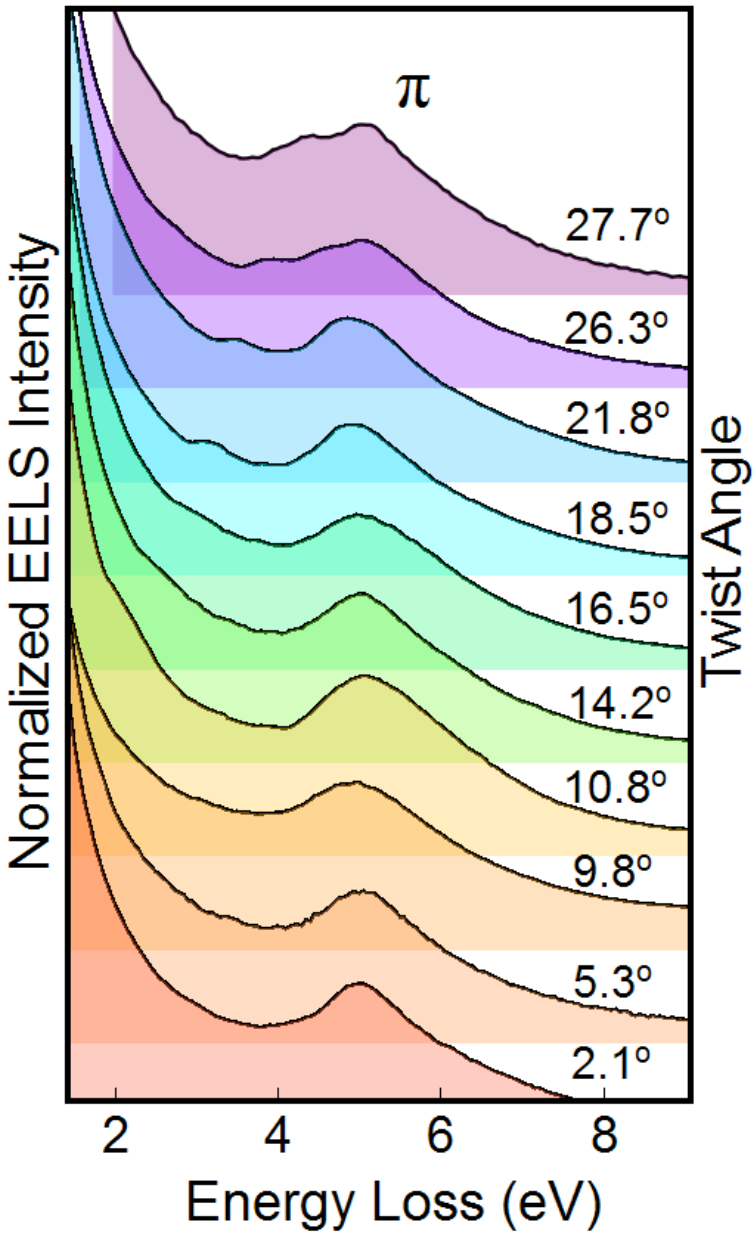
Sok Pantelides

STEM images of Twisted Bilayer Graphene



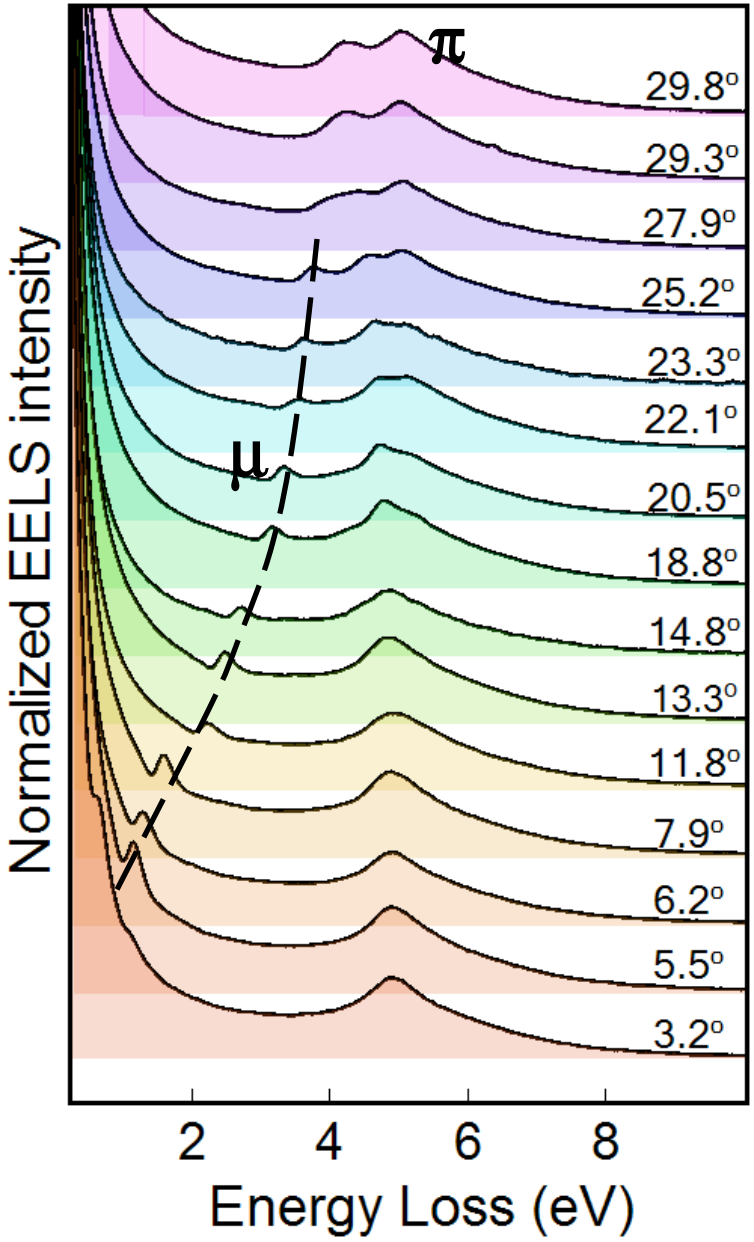
Scale bars are 1 nm

EEL spectra of BLG (350 meV energy



Experiments @ ORNL

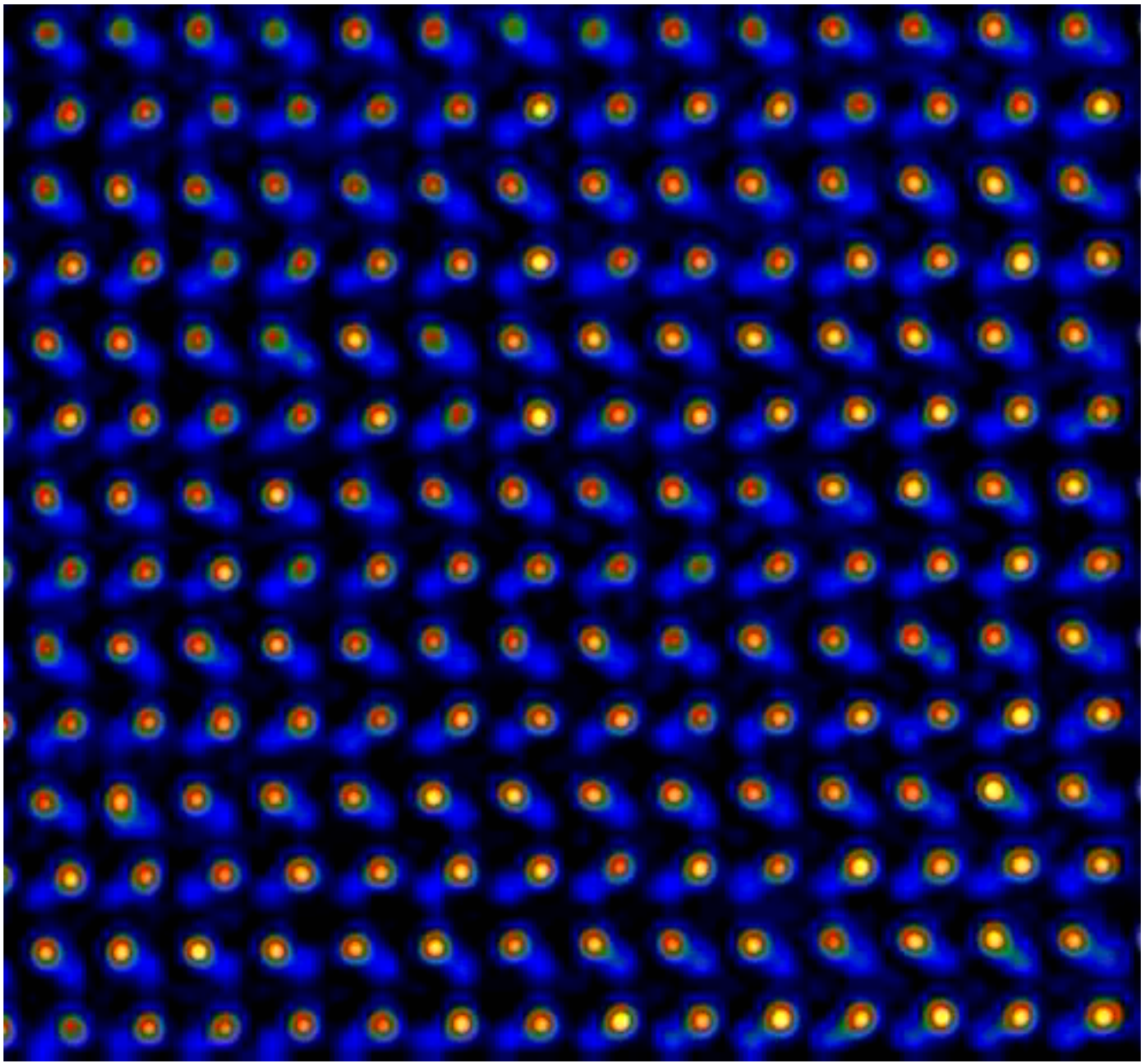
EEL spectra of BLG (60 meV energy resolution)



Experiments @ ASU

Dynamics of point defects...

Ce in AlN



R. Ishikawa and
A. R. Lupini

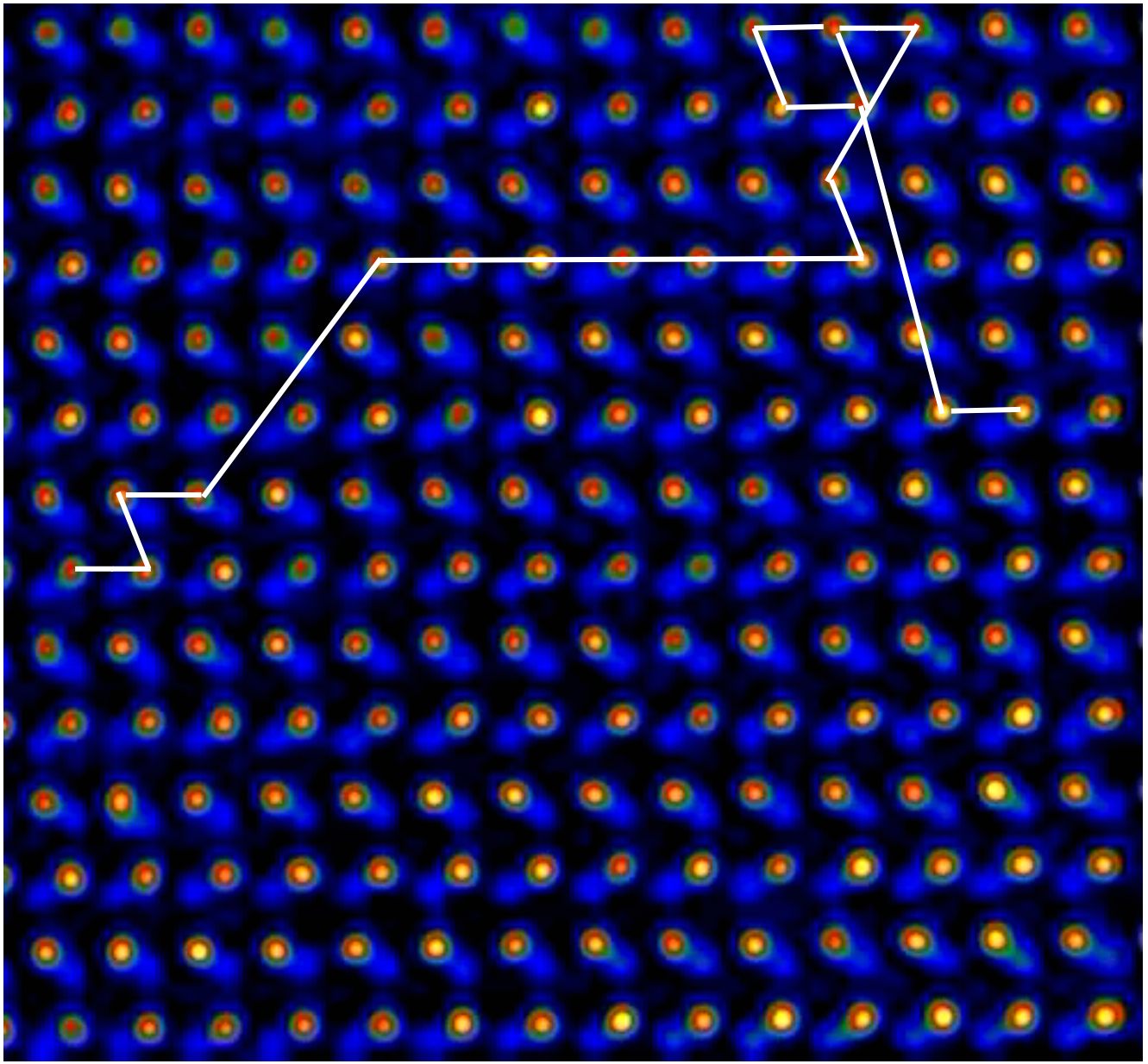
UltraSTEM200

We can see atomic diffusion…

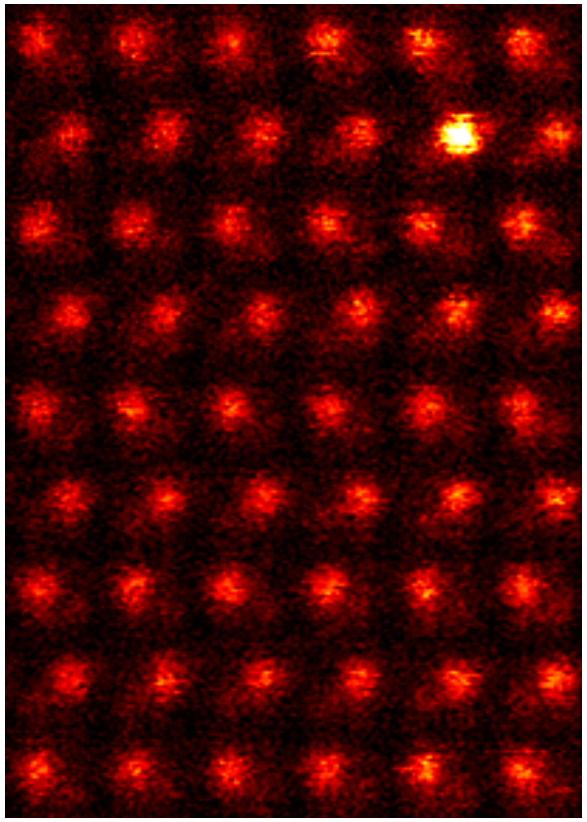
Ce in AlN

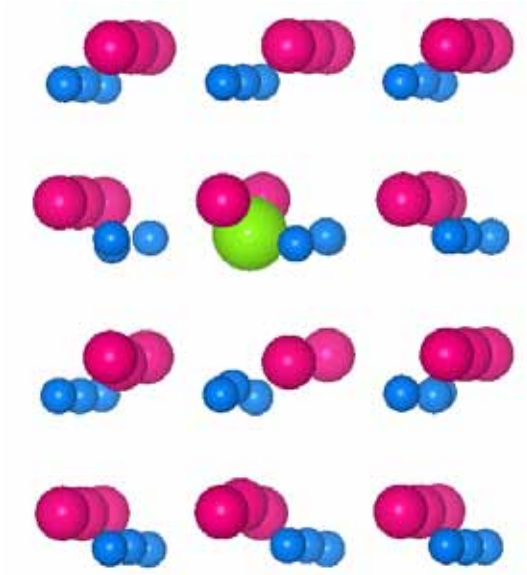
R. Ishikawa and A. R. Lupini

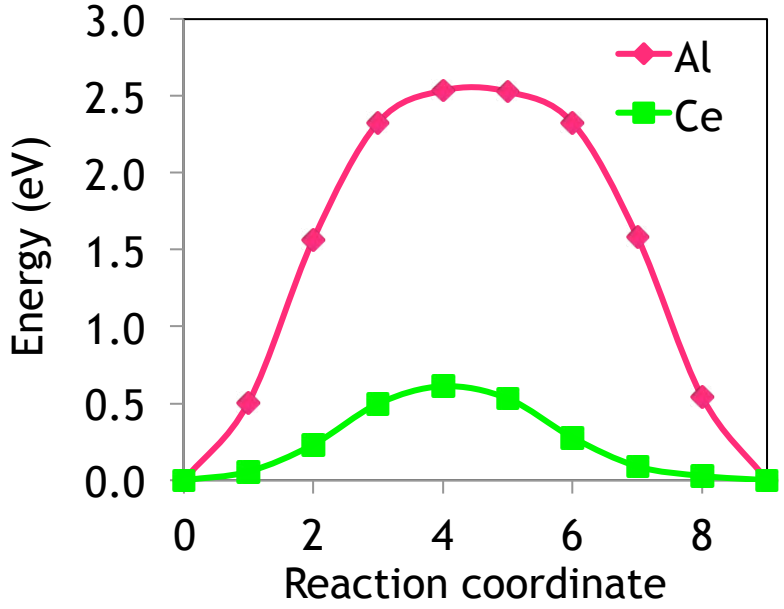
UltraSTEM200



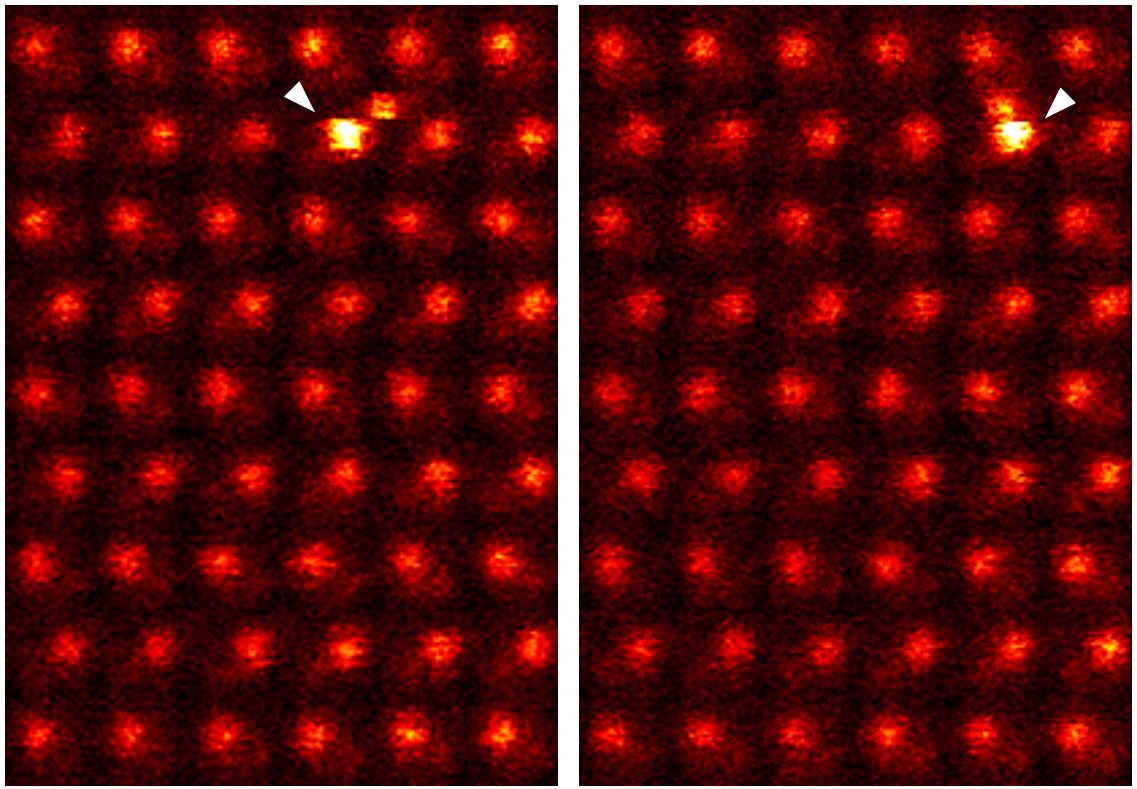
Correlated vacancy-dopant motion







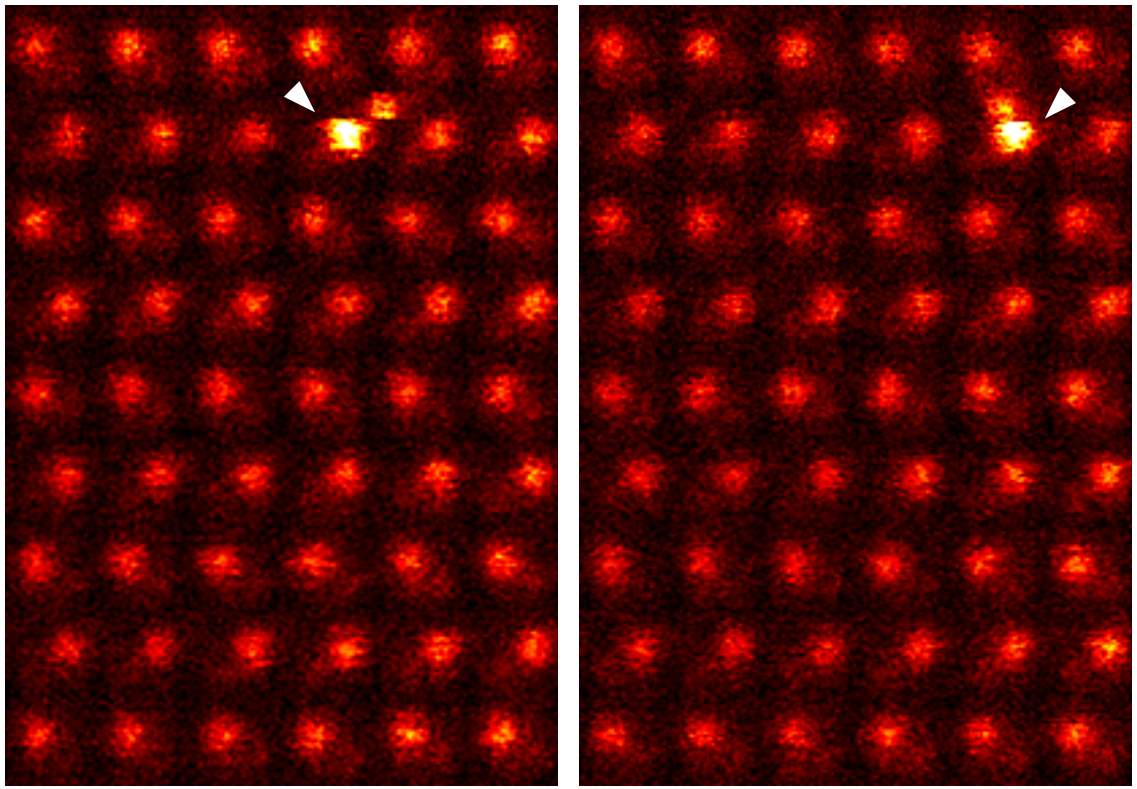
Interstitial “Kick-out” mechanism



Ce atom at interstitial sites

Simulate higher-temperature diffusion events!

Interstitial “Kick-out” mechanism



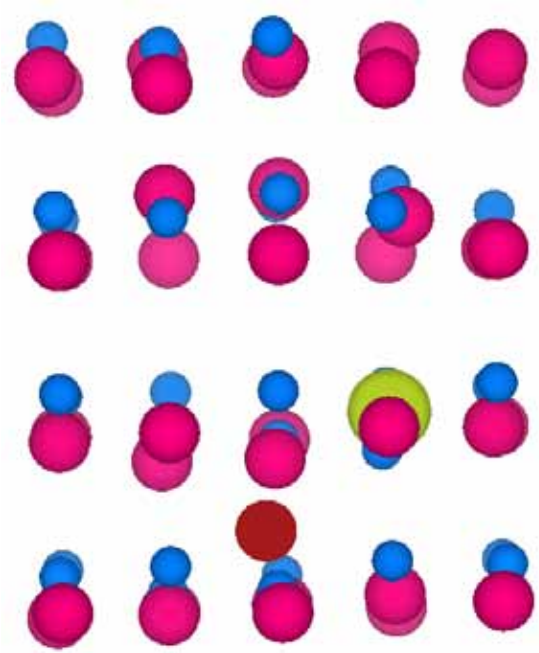
Ce atom at interstitial sites

Simulate higher-temperature diffusion events!

Kick-out mechanism

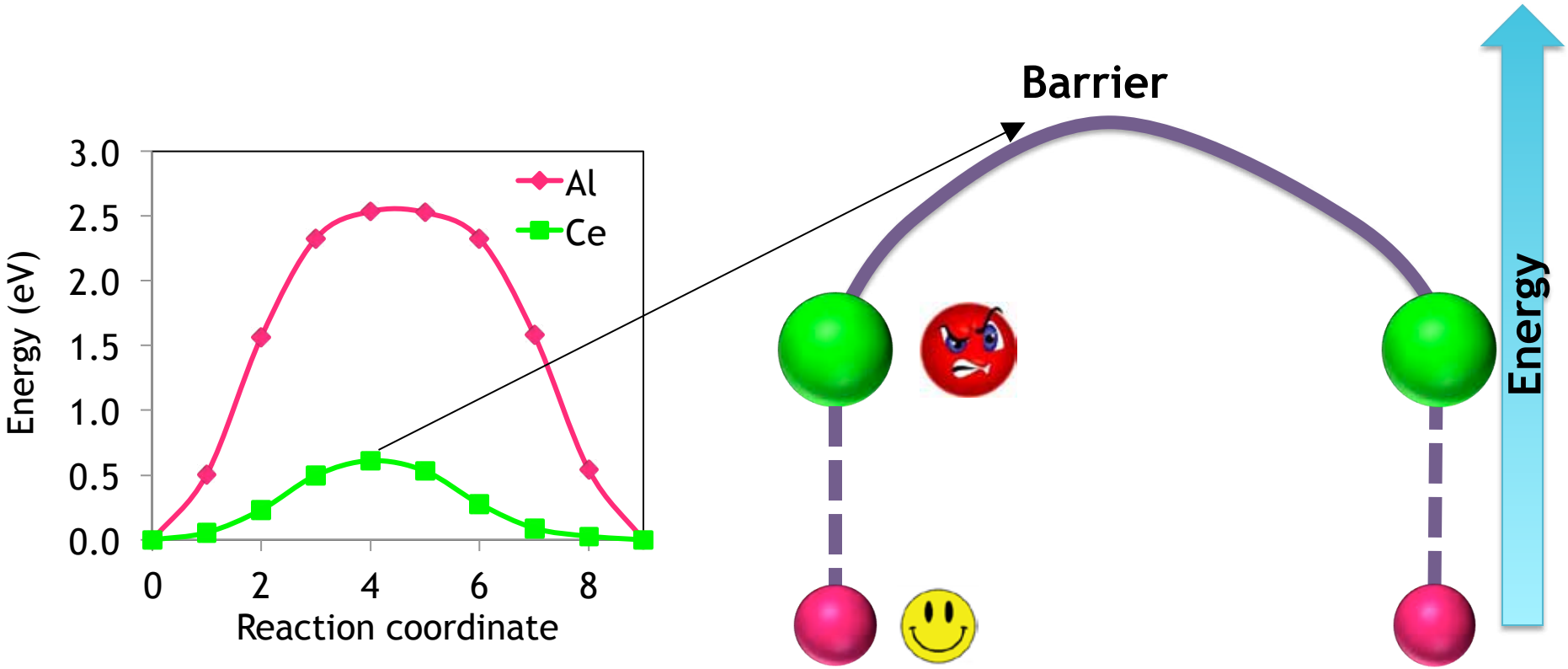
$$X_s + I \rightleftarrows X_i$$

X_s : Substitutional dopant
X_i : Interstitial dopant
I : Self-interstitial



Barrier : 3.7 eV

Why is the Ce barrier so low?



Large Ce atom is highly strained in a small AlN lattice

nature International weekly journal of science

Hasten high resolution

Build precision microscopes to map atoms, say **Stephen J. Pennycook** and **Sergei V. Kalinin**.

Feynman's goal = 0.1Å!

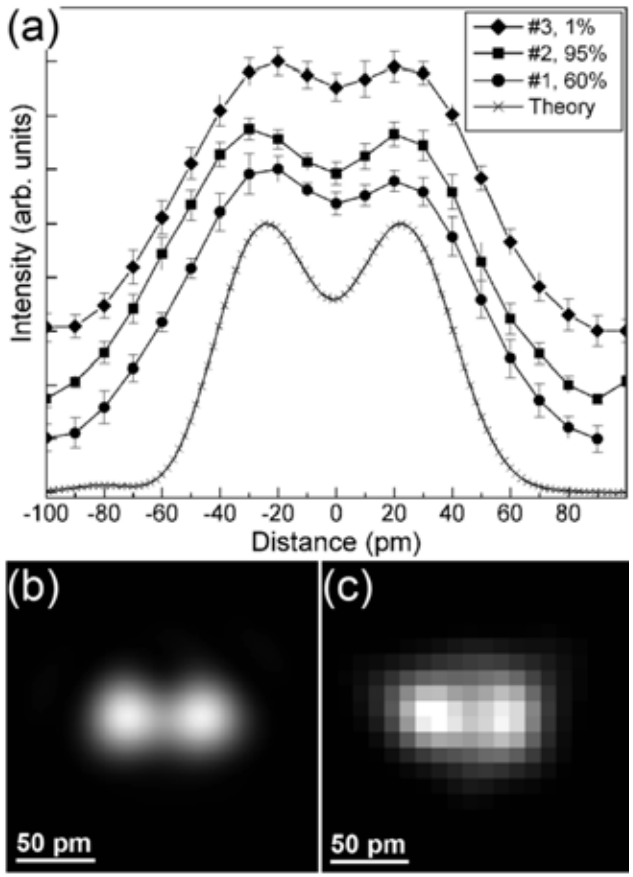
"just look at the thing!"

"I would like to try and impress upon you while I am talking about all of these things on a small scale, the importance of improving the electron microscope by a hundred times. It is not impossible; it is not against the laws of diffraction of the electron."

1. S. J. Pennycook and S. V. Kalinin, "Hasten high resolution," Nature, 515, 487–488 (2014).
2. S. J. Pennycook, "Fulfilling Feynman's dream: "Make the electron microscope 100 times better"—Are we there yet?" *MRS Bull*, 40, 71–78 (2015).

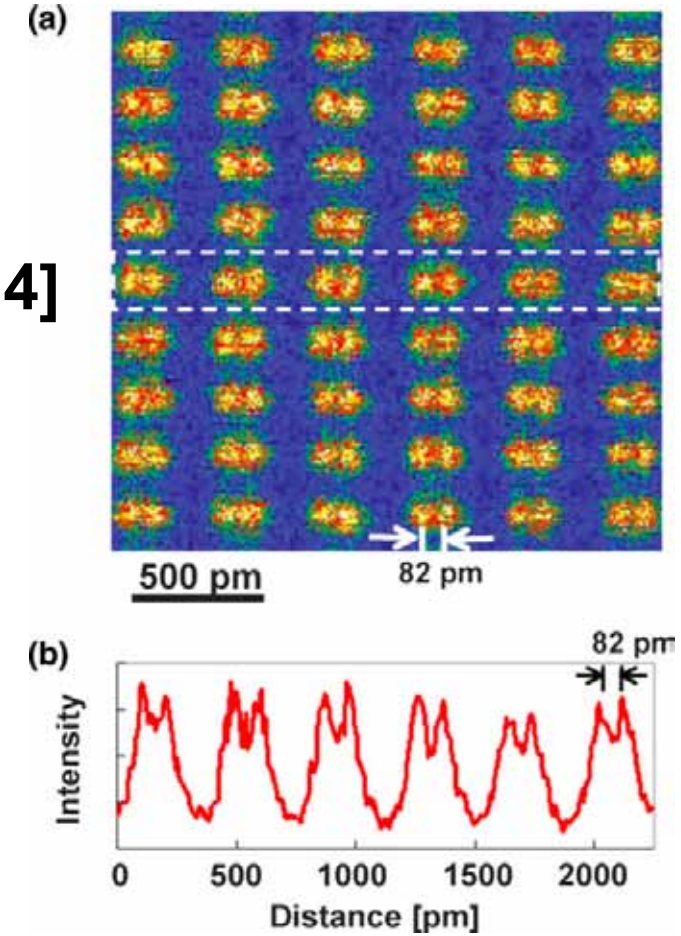
STEM achieves 0.5 Å resolution

5th order aberration correction, 300 kV



Erni, R. et al., *Phys Rev Lett* 2009, *102*, 96101; TEAM project

Ge [114]



Sawada, H. et al., *J Electron Microsc* 2009, *58*, 357; CREST project

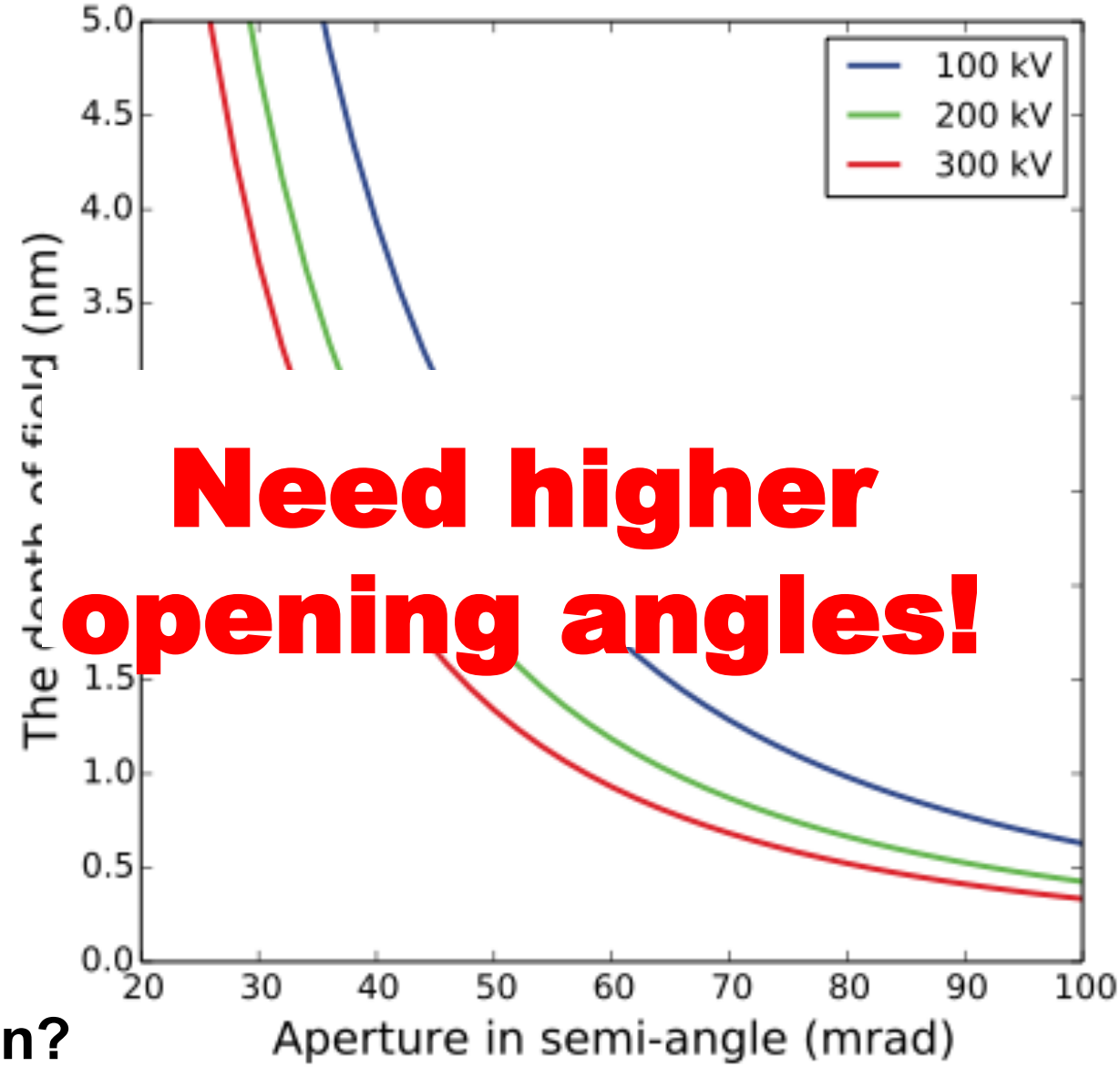
But depth resolution is still on the *nm*-scale

$$d_{x,y} = 0.61\frac{\lambda}{\theta}$$

$$d_z = 2\frac{\lambda}{\theta^2}$$

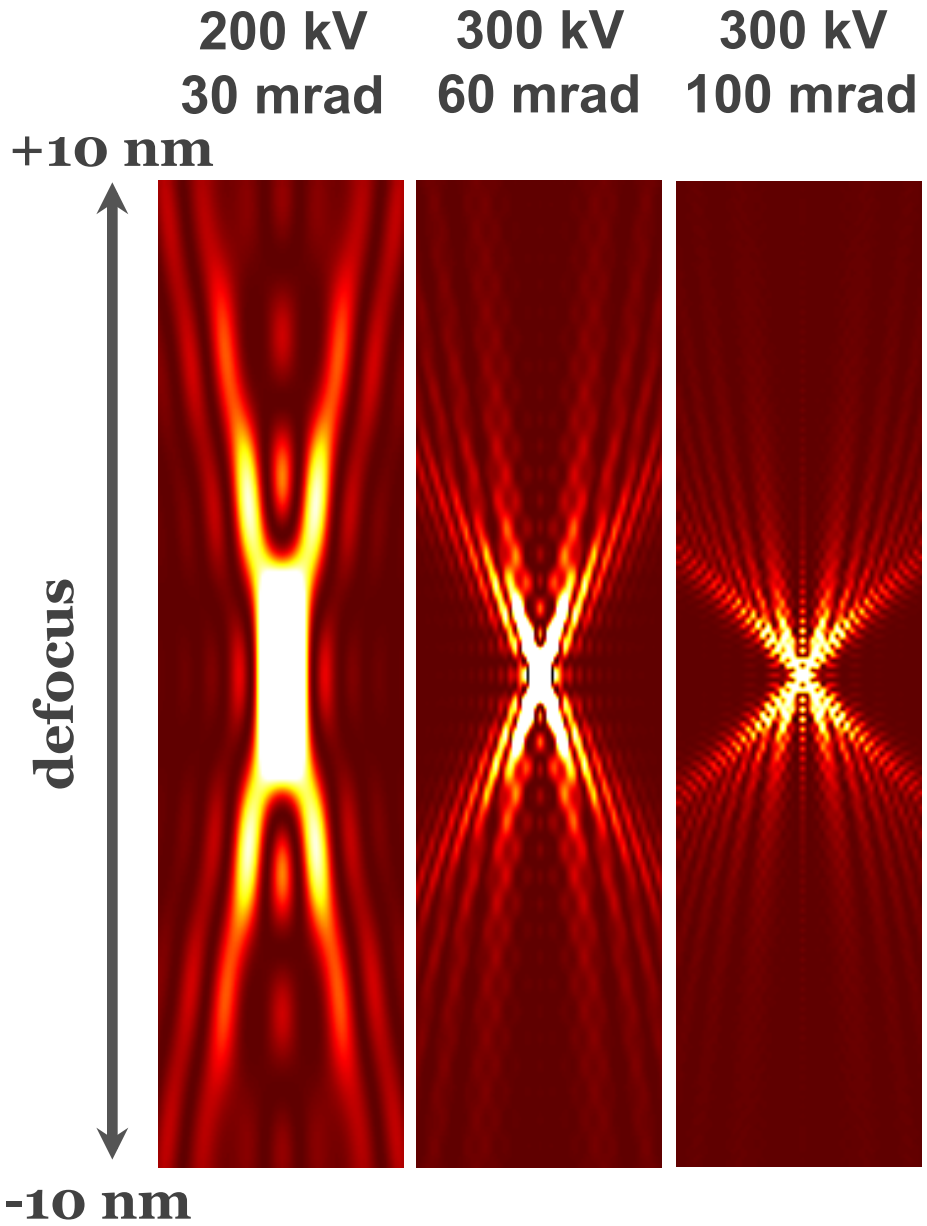
30 mrad:
few nm @ 300 kV

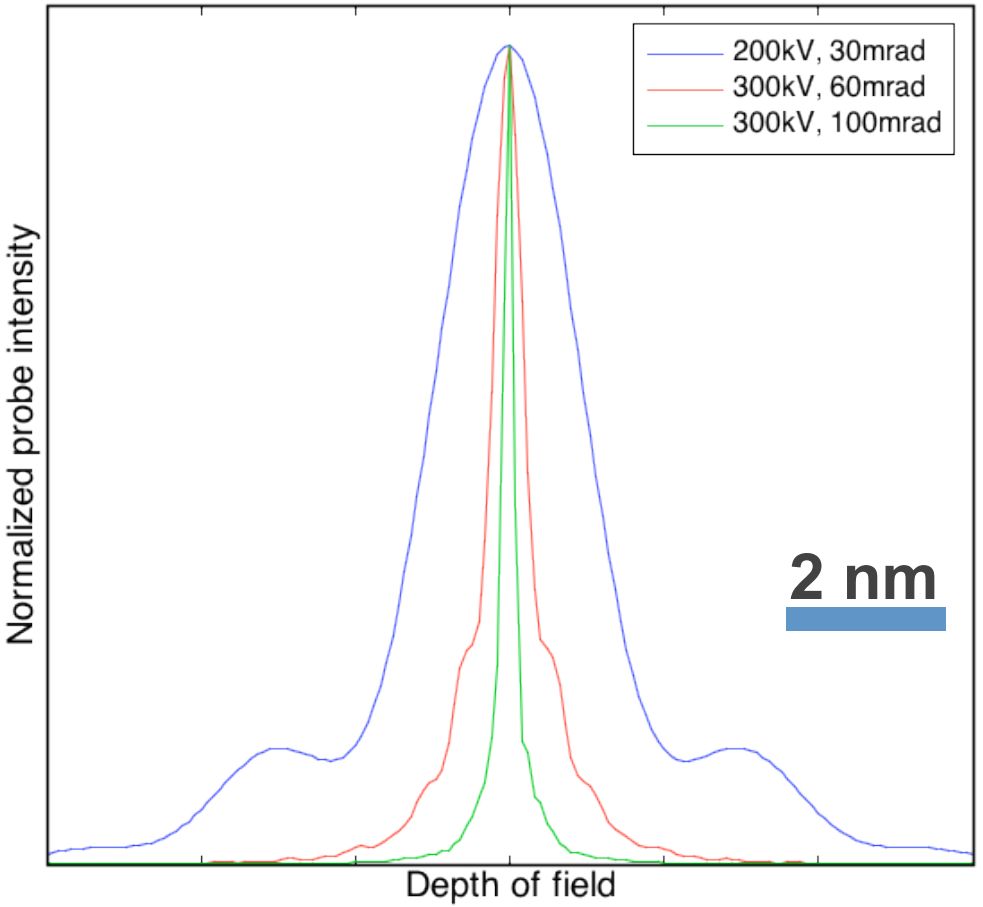
100 mrad:
4 Å @ 300 kV
Sub-unit cell resolution?



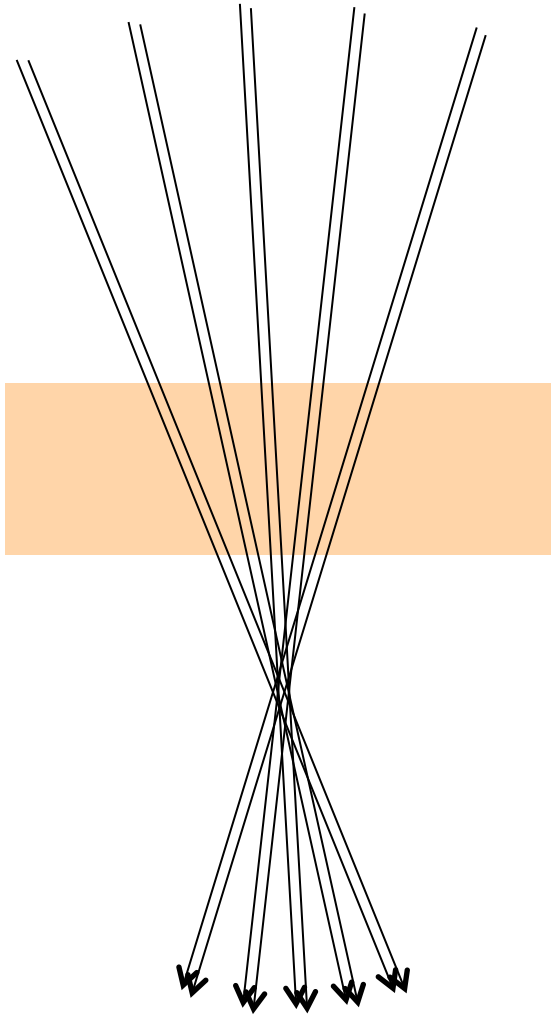
Need higher opening angles!

Depth resolution at unit cell level…

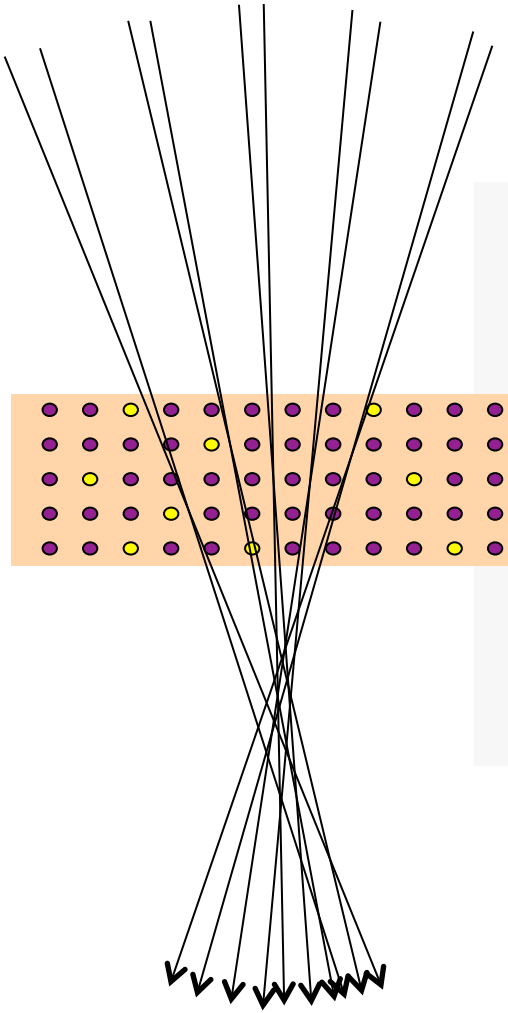




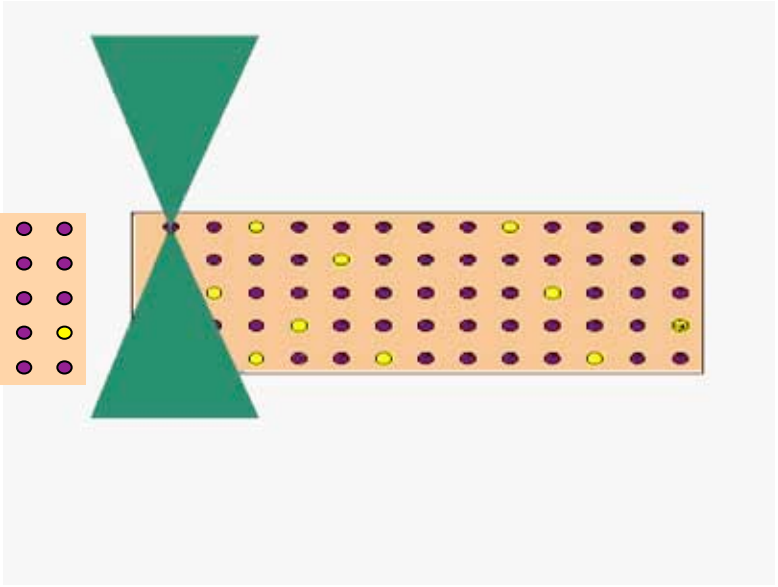
Resolution in the 3rd dimension?



Tomography requires direct projection eg HAADF at low resolution

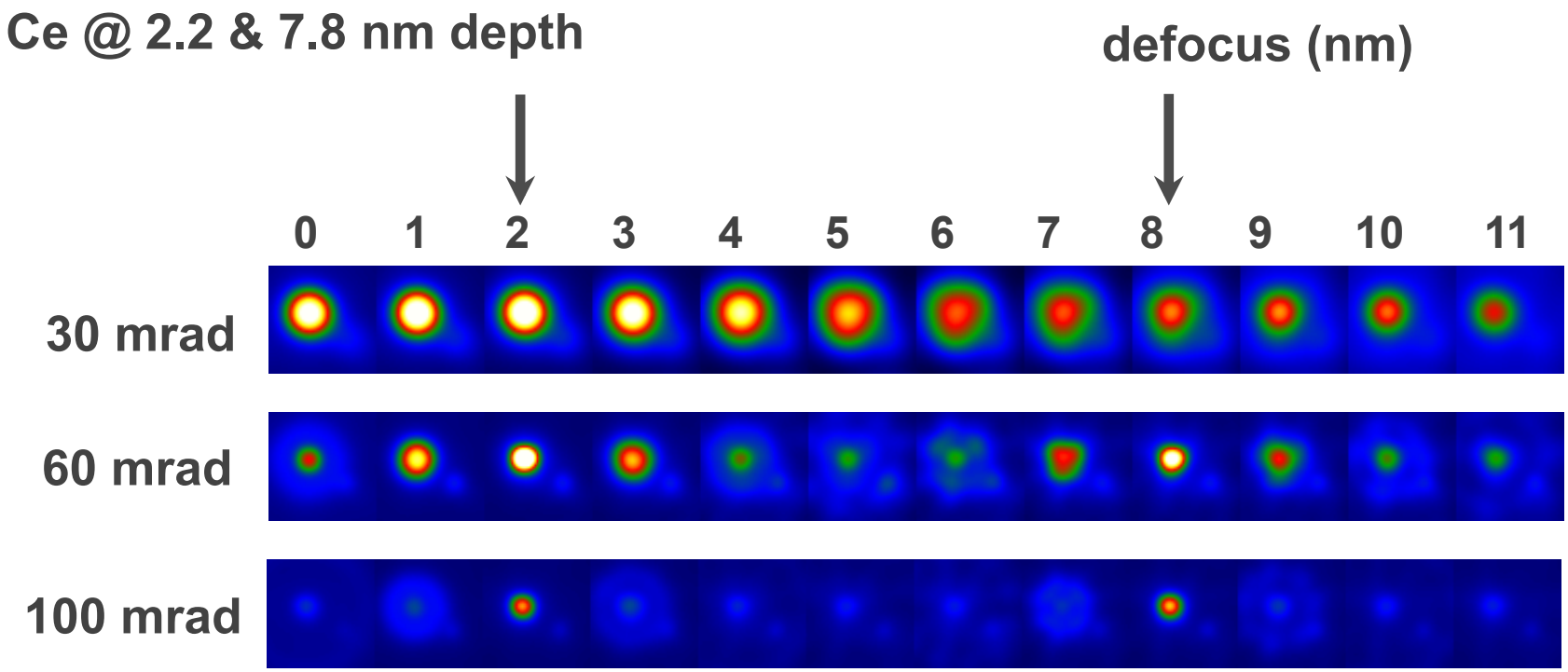


At high resolution direct projection breaks down Stability?



Natural transition to depth sectioning

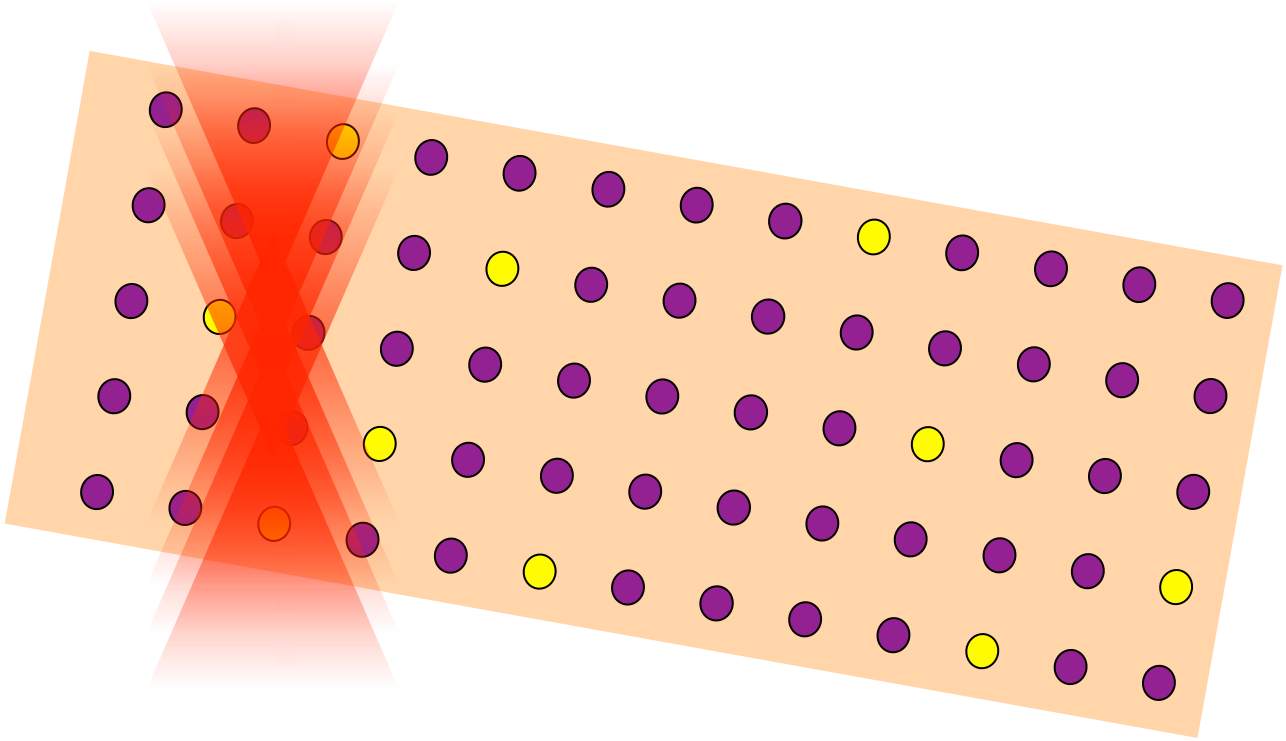
Substitutional Ce dopants in AlN



thickness = 12.4 nm

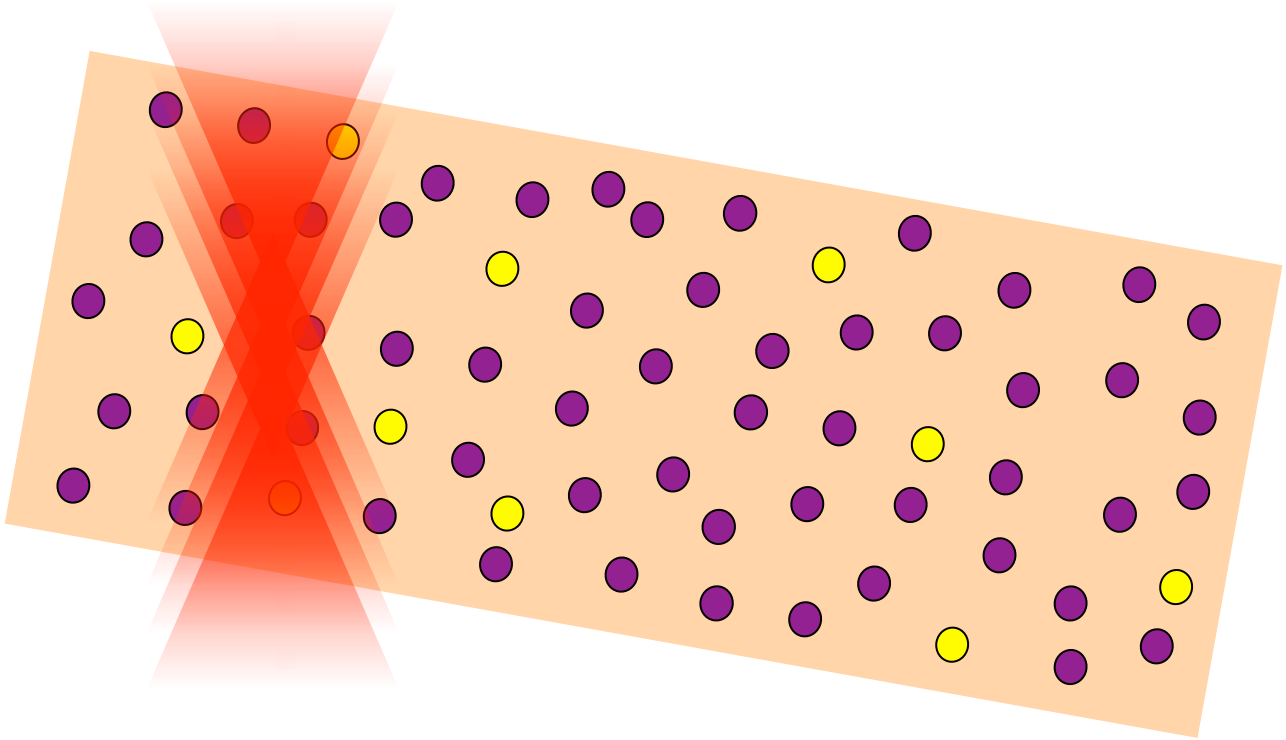
Simulation by Ryo Ishikawa

No need to align the sample!



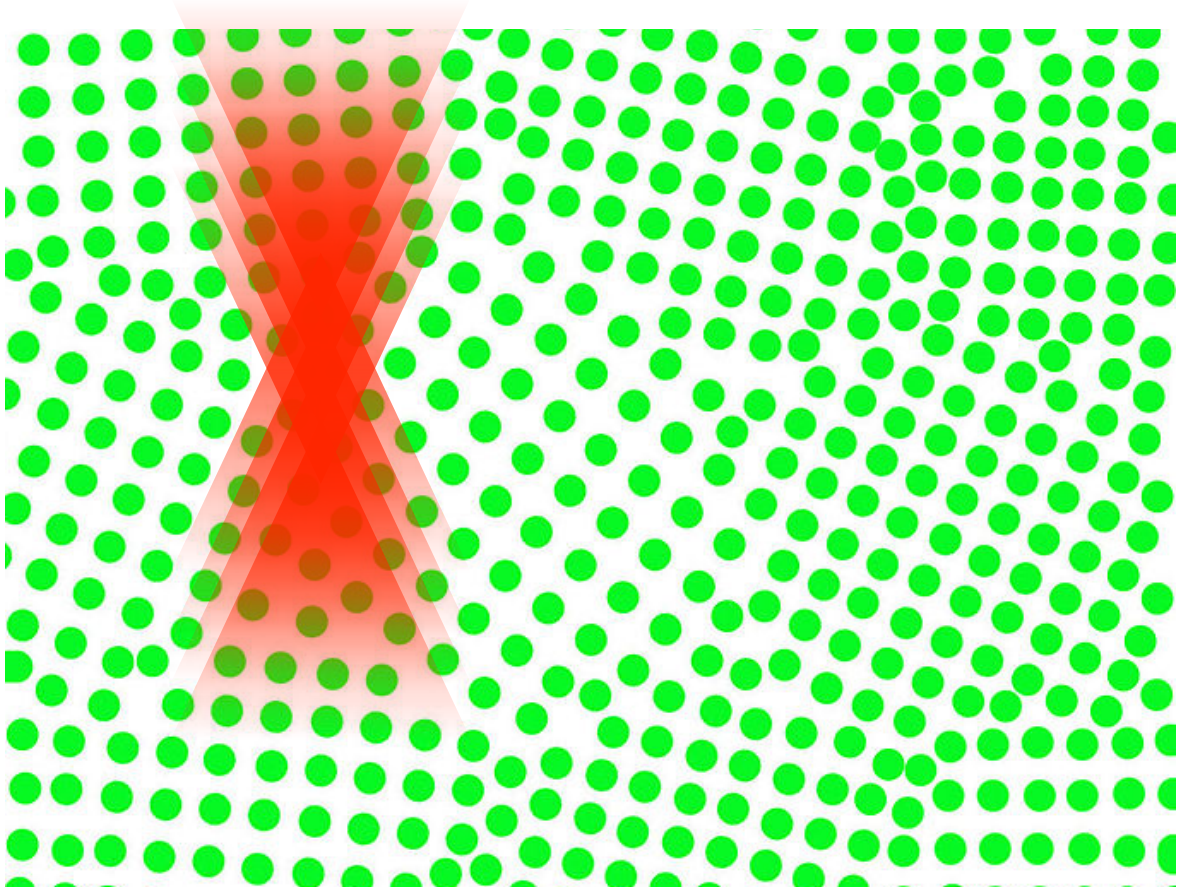
3D atomic structure!

We could look at glasses!



3D atomic structure!

We could see grain boundaries in polycrystalline materials!



3D atomic structure!

There's still plenty to see at the bottom!

- Next generation corrector
  - 300 kV, CFEG, 60-100 mrad probe angle
  - ~0.2-0.12 Å diffraction limit
- Improved signal to noise ratio
- Optical properties with atomic sensitivity
- Improved precision of atomic positions
- 3D atomic resolution