Welcome to
CHE 384T: Computational Methods in Materials Science

Defects in crystals

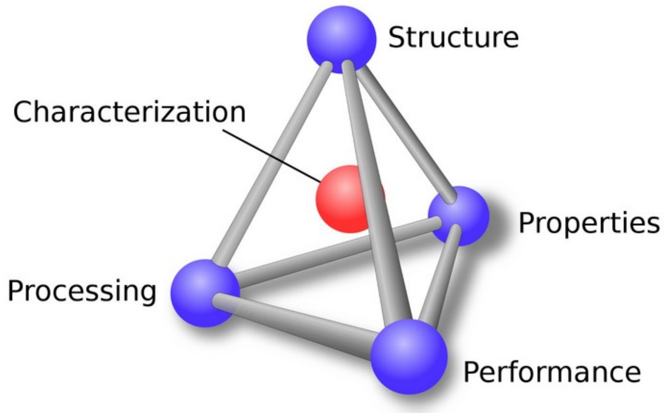
LeSar App. B1-B5

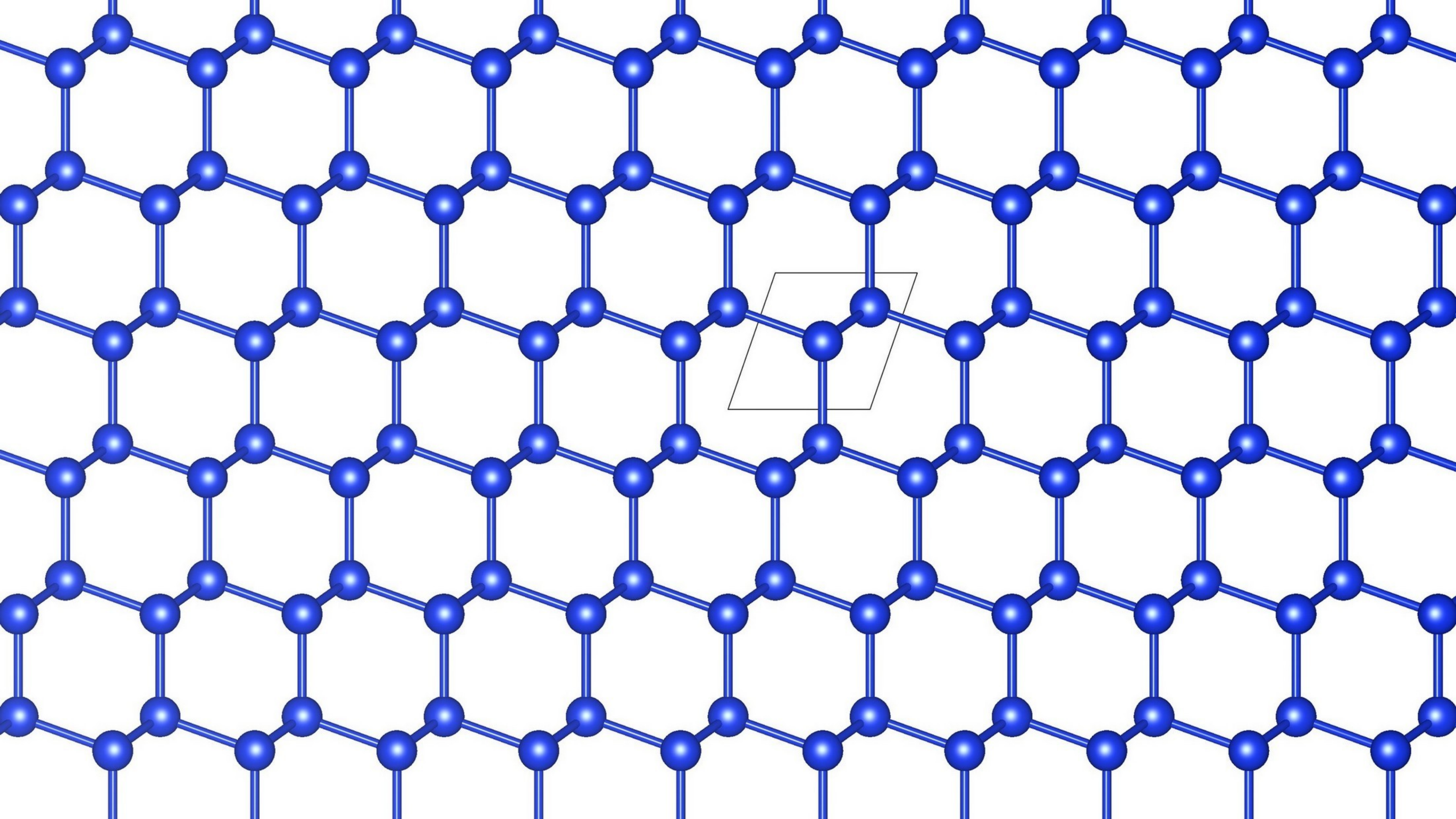
The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

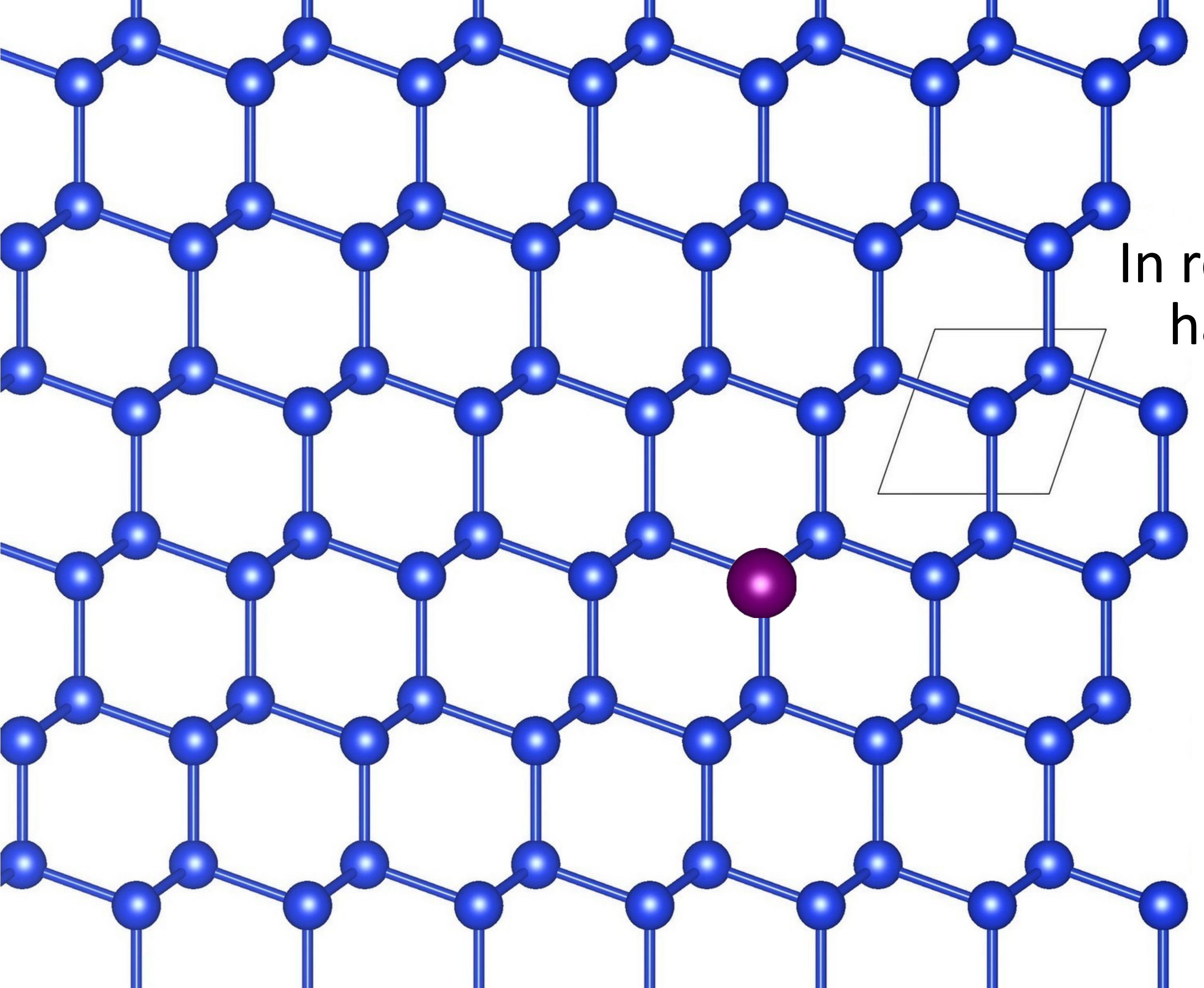
Lecture Outline

Crystal structure
- Unit cell
- Bravais Lattices
- Example Crystal structures from the cubic space group

Brief on Crystallographic notation







In reality, we often don't have perfect crystals

Defects can alter the properties of the host material

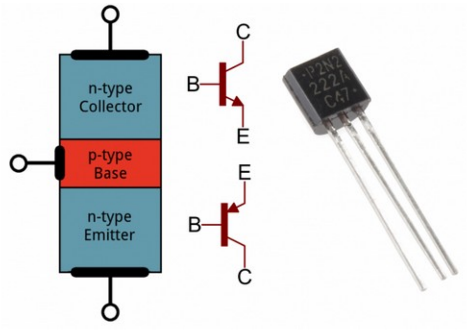
Optical Properties- colored diamonds

J.E. Shigley & C.M Breeding. Gems & Gemology, Summer 2013, Vol. 49, No. 2

Mechanical Properties

S.E. Merzlikin et al. Practical Metallography. 48, 365-375 (2011)

Electrical Properties



https://learn.sparkfun.com/tutorials/transistors/all

Types of Defects

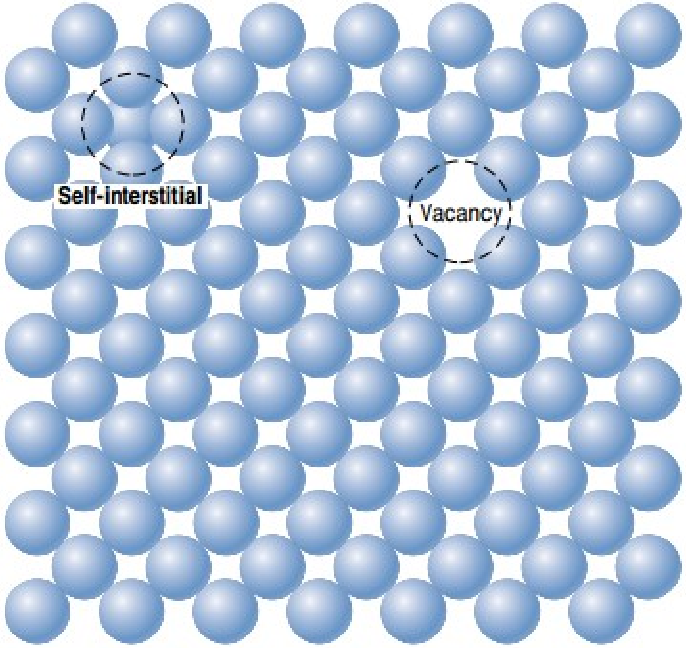
0D Point Defects: Impurities, Vacancies, Interstitials

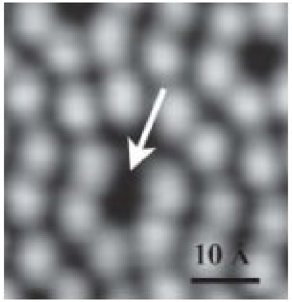
1D Line Defects: Edge and Screw Dislocations

2D Interfacial Defects: Grain boundaries

Point defects in crystals (monatomic)

Figure 4.1 Two-dimensional representations of a vacancy and a self-interstitial.
(Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 77. Copyright © 1964 by John Wiley & Sons, New York, NY. Reprinted by permission of John Wiley & Sons, Inc.)





Scanning probe micrograph that shows a vacancy on a (111)-type surface plane for silicon.

Point defects in crystals (monatomic)

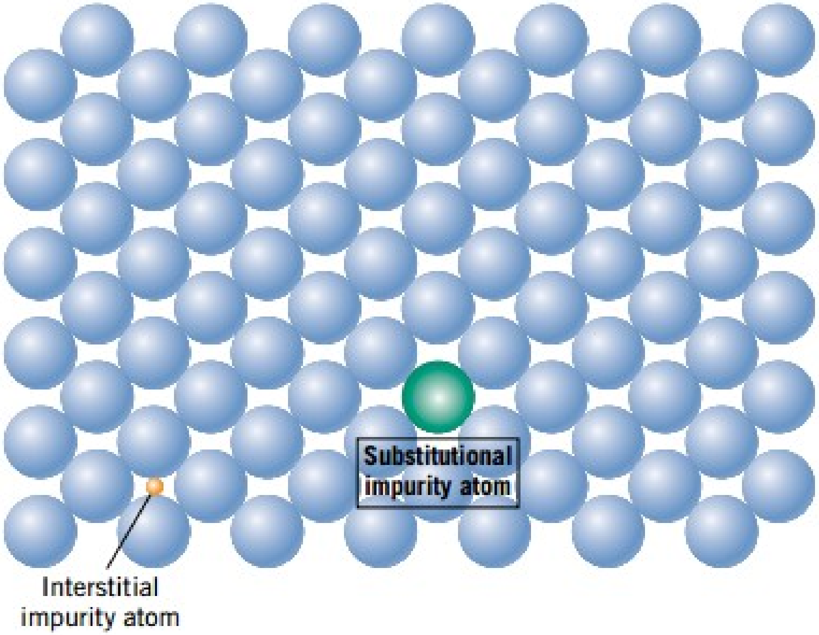
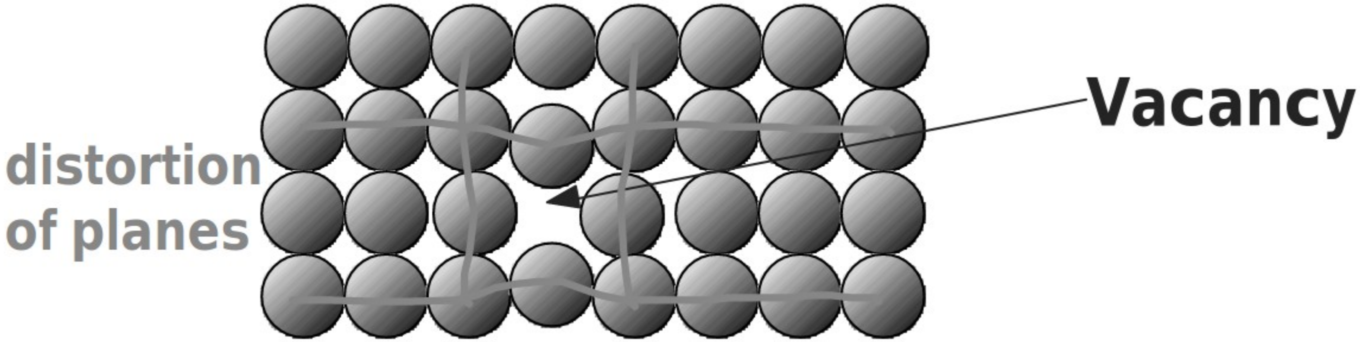
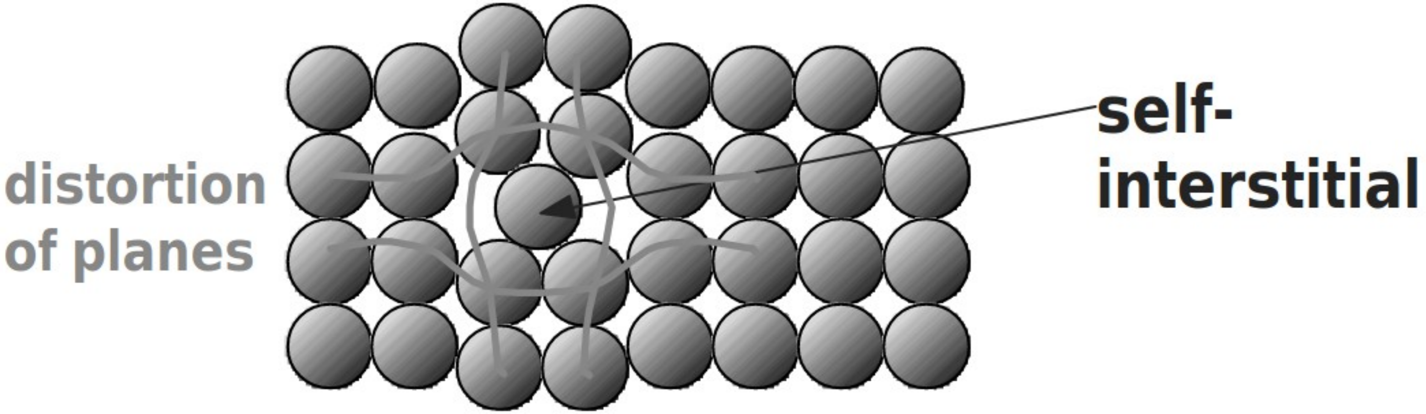


Figure 4.2 Two-dimensional schematic representations of substitutional and interstitial impurity atoms. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 77. Copyright © 1964 by John Wiley & Sons, New York, NY. Reprinted by permission of John Wiley & Sons, Inc.)

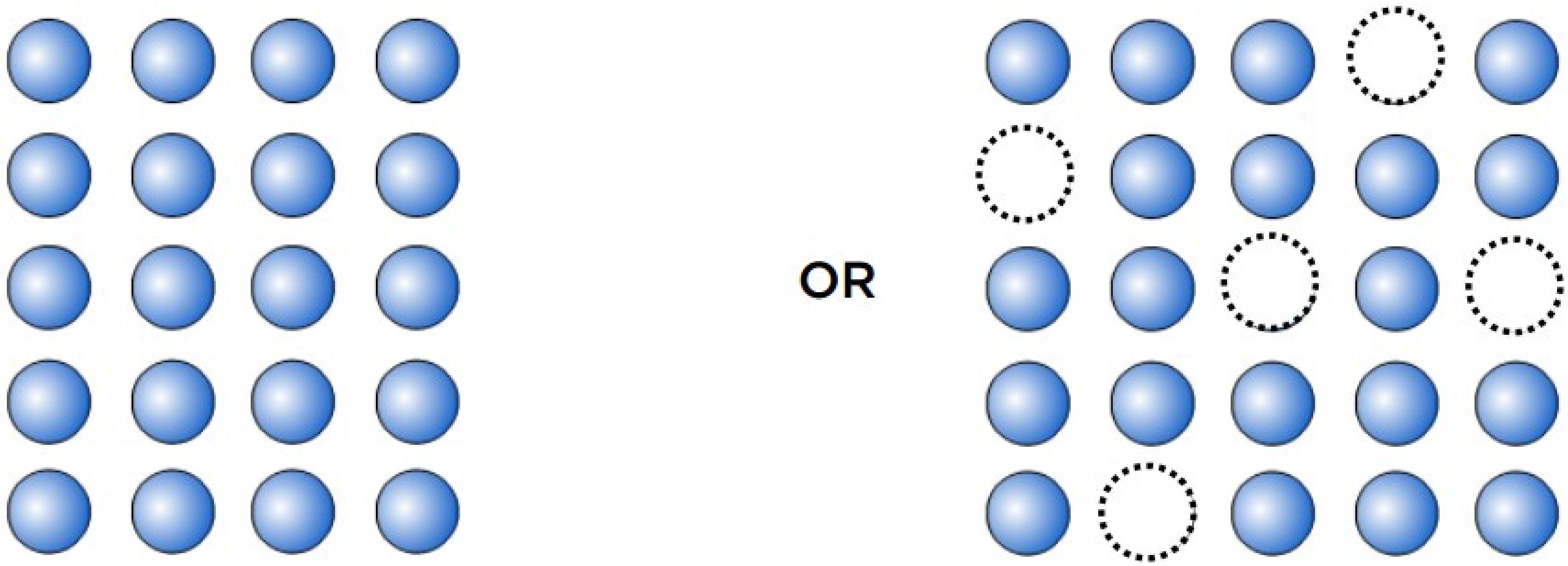
Lattice Strain from point defects





Equilibrium concentration of (point) defects

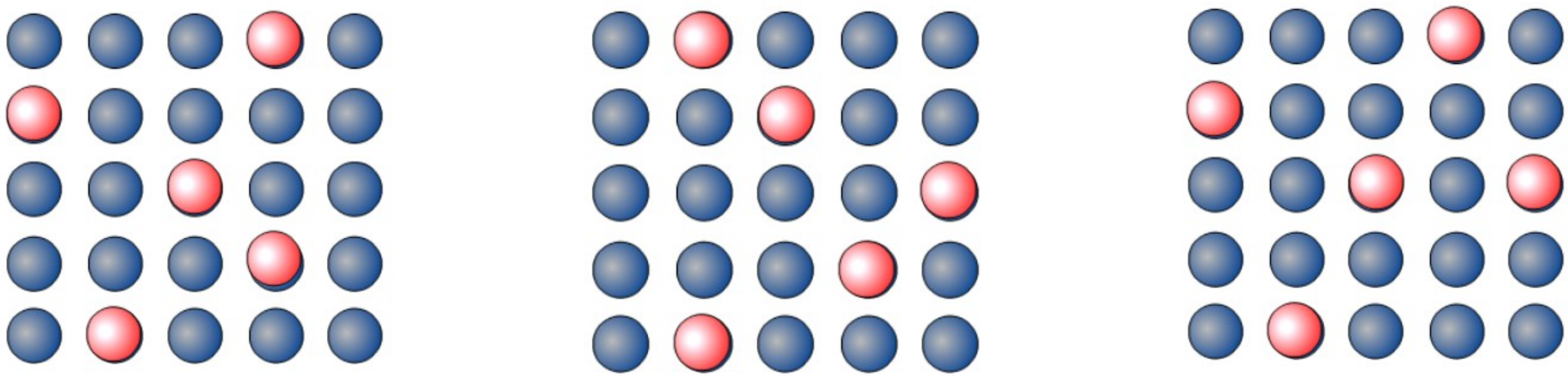
Thermodynamically, there will be some finite concentration of defects



Equilibrium concentration of (point) defects

Equilibrium concentration of (point) defects: Microstates

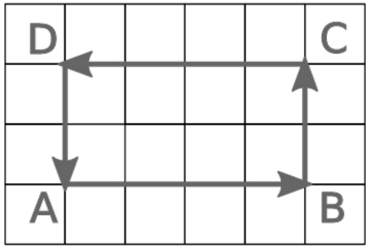
Configurational Entropy: How many microstates are there for a given macrostate?



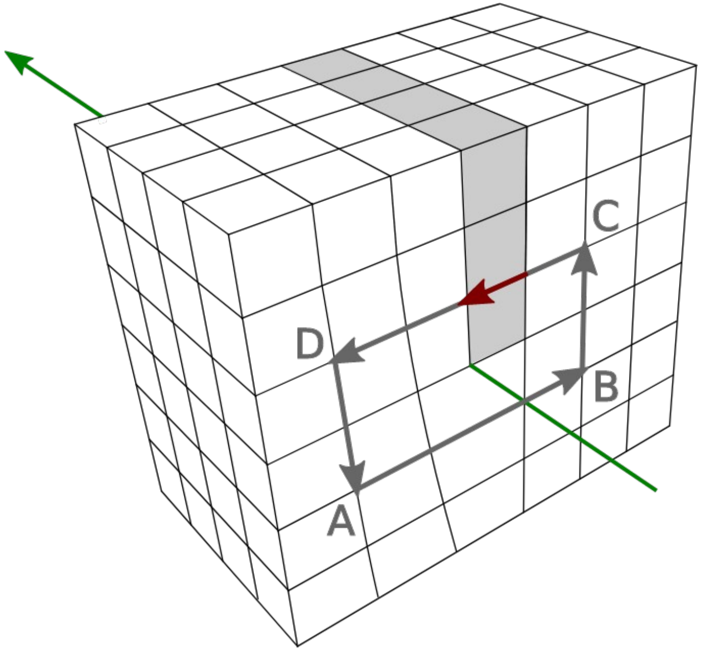
Equilibrium concentration of (point) defects: Derivation

Equilibrium concentration of (point) defects: Derivation

Edge Dislocation



Burgers Vector $\vec{b}$
Dislocation Line Vector $\vec{L}$



$\vec{b}$

$\vec{L}$

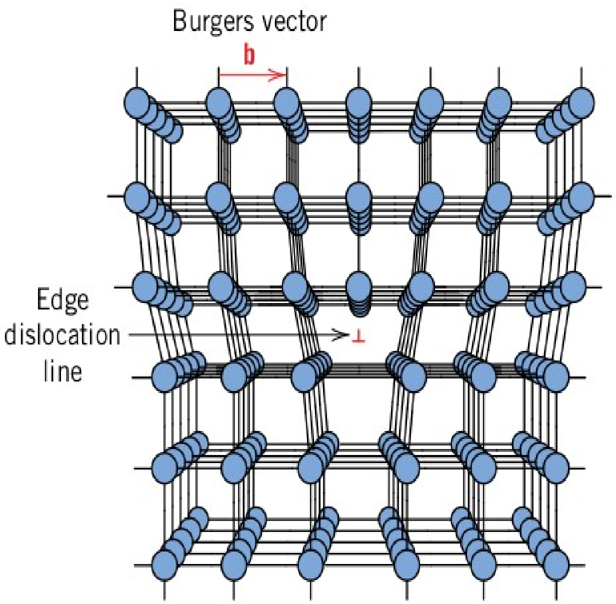
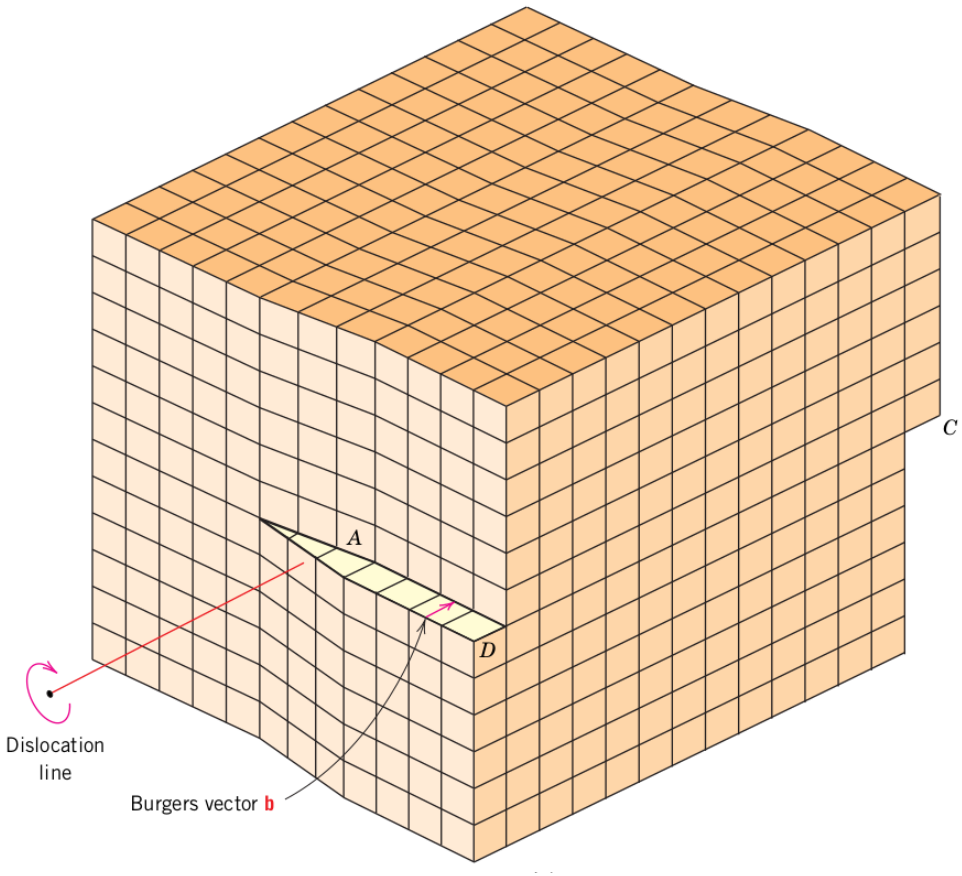


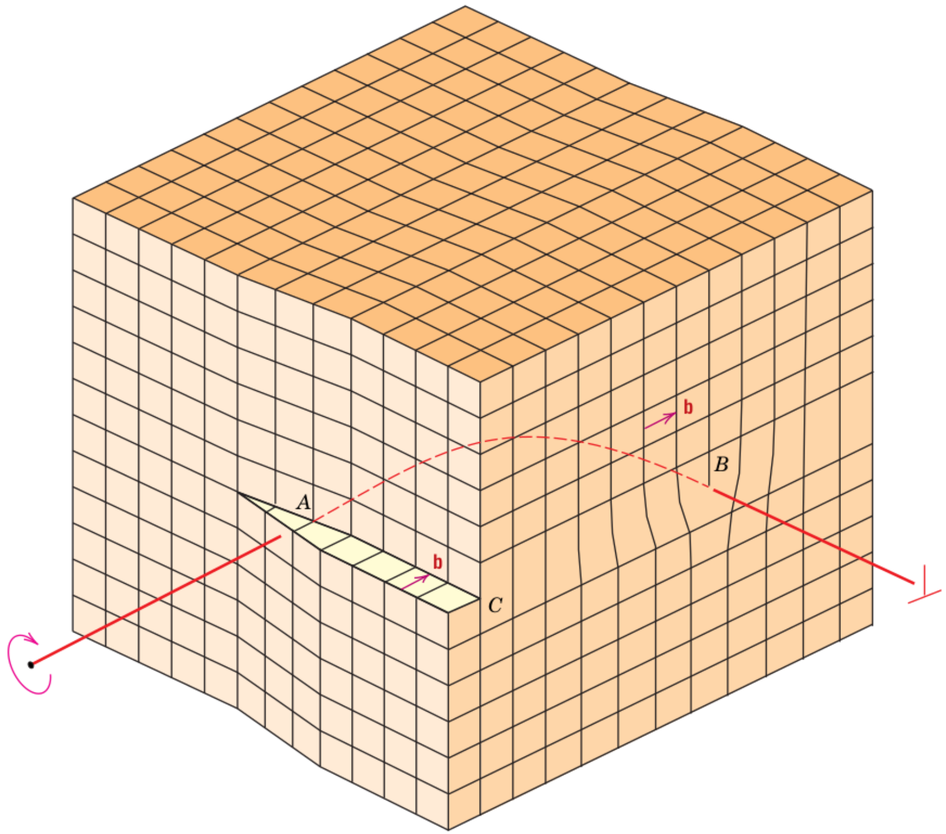
Figure 4.
edge dislc
shown in
(Adapted f
Science, M
NY, 1976,

Screw Dislocation

Figure 4.5 (*a*) A screw dislocation within a crystal. (*b*) The screw dislocation in (*a*) as viewed from above. The dislocation line extends along line *AB*. Atom positions above the slip plane are designated by open circles, those below by solid circles.
[Figure (*b*) from W. T. Read, Jr., *Dislocations in Crystals,* McGraw-Hill Book Company, New York, NY, 1953.]



Mixed Dislocations



Plastic deformation through motion of dislocations

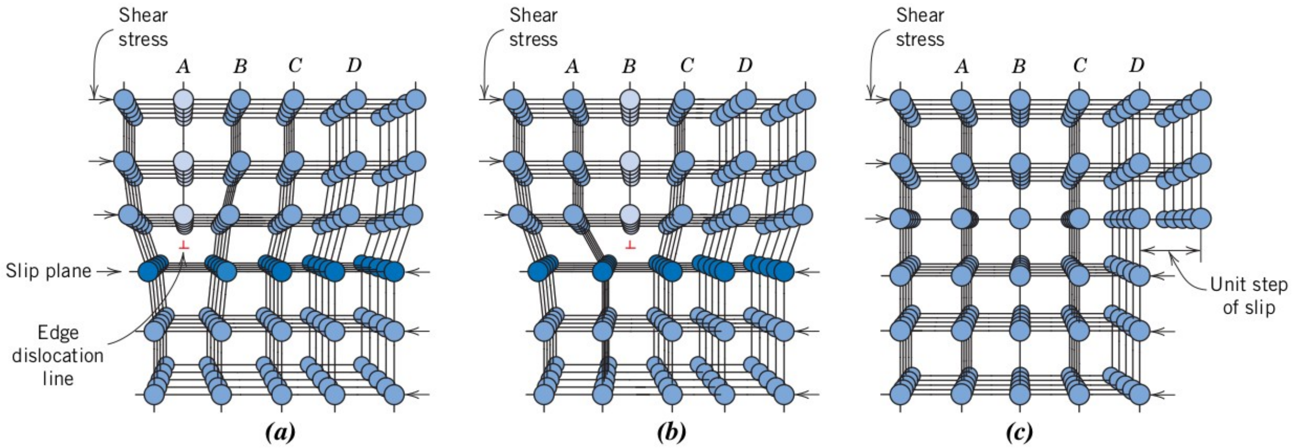


Figure 7.1 Atomic rearrangements that accompany the motion of an edge dislocation as it moves in response to an applied shear stress. (*a*) The extra half-plane of atoms is labeled *A*. (*b*) The dislocation moves one atomic distance to the right as *A* links up to the lower portion of plane *B*; in the process, the upper portion of *B* becomes the extra half-plane. (*c*) A step forms on the surface of the crystal as the extra half-plane exits.
(Adapted from A. G. Guy, *Essentials of Materials Science,* McGraw-Hill Book Company, New York, 1976, p. 153.)

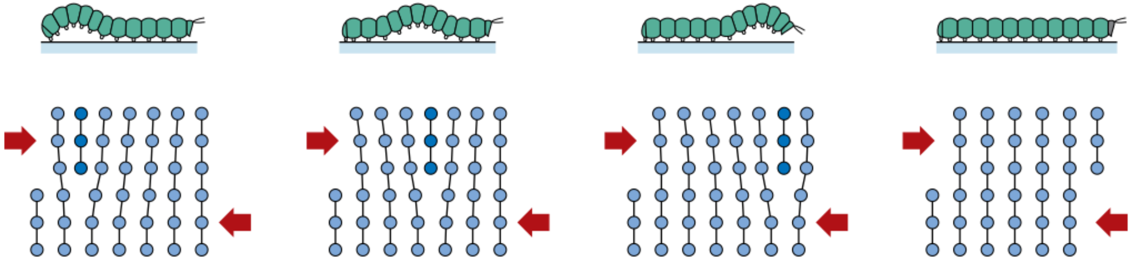


Figure 7.3 The analogy between caterpillar and dislocation motion.

Grain Boundaries

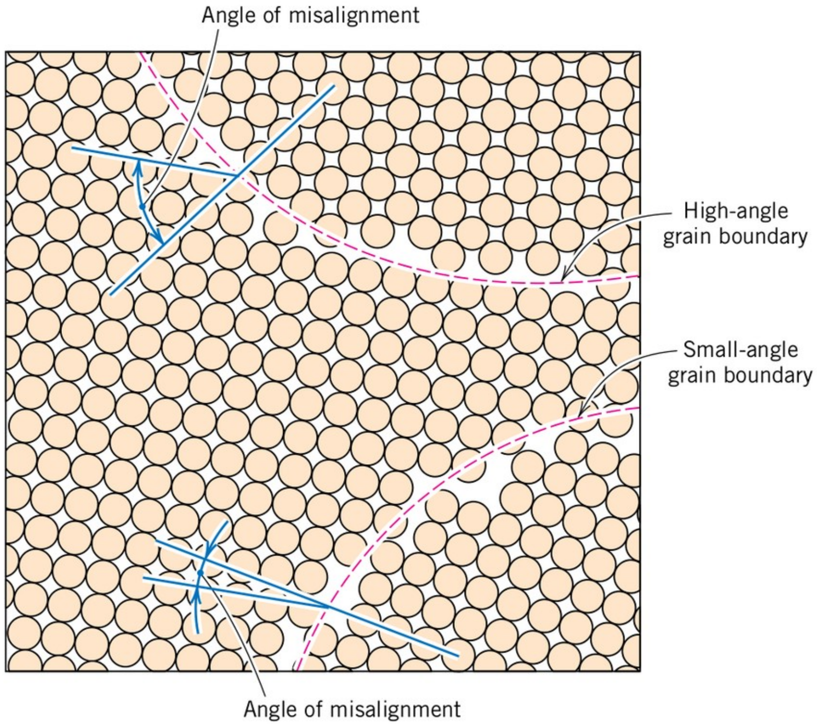


Figure 4.8 Schematic diagram showing small- and high-angle grain boundaries and the adjacent atom positions.

Grain Boundaries

S.E. Merzlikin et al. Practical Metallography. 48, 365-375 (2011)

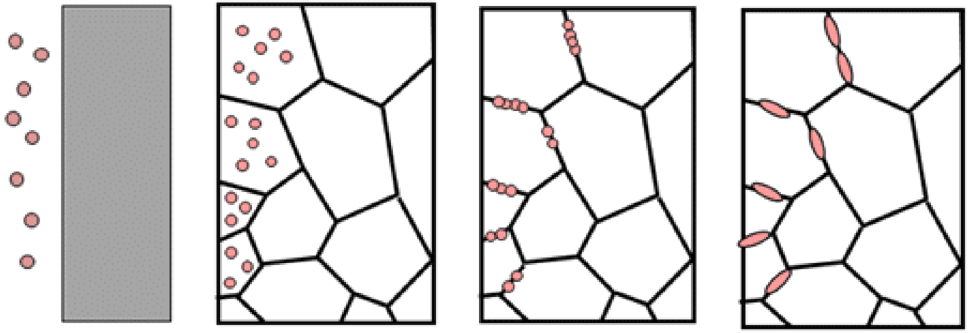


Image from Industrial Metallurgists, LLC

Bubble Raft Videos

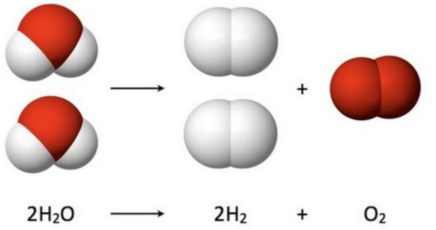
From The Royal Institution archives

Used to understand defects in metals using a 2D HCP model

Narrated by Sir William Lawrence Bragg

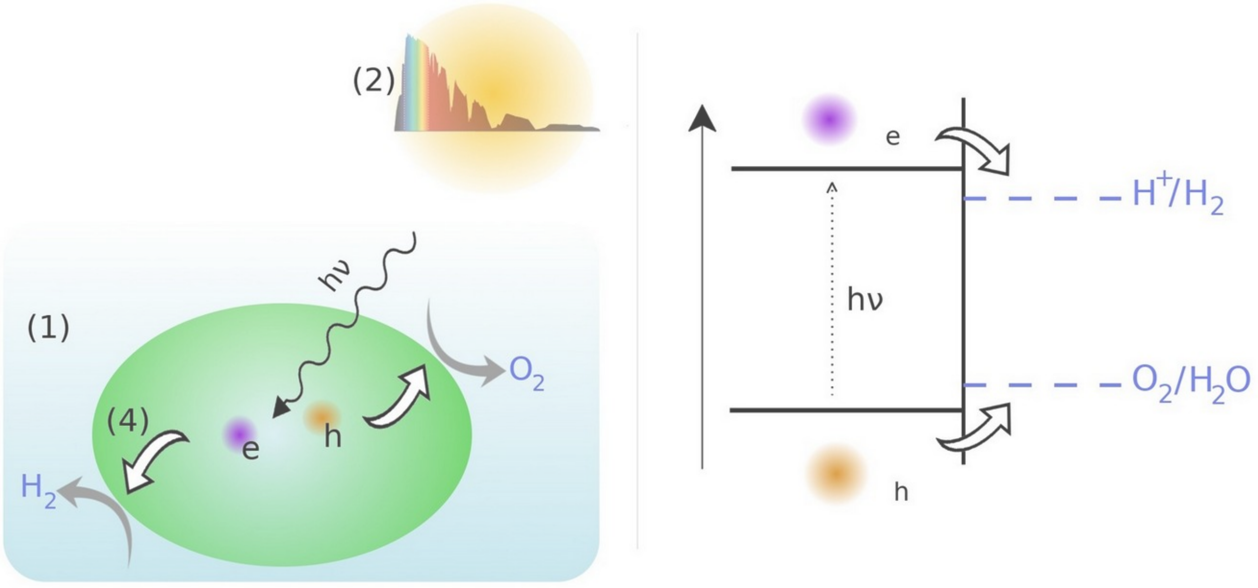
Water Splitting for Clean Fuel (with oxides)

Materials for photoelectrodes in **water splitting** offer a sustainable way of producing **clean fuels**



Wikipedi

An ideal material:



(Minimum) Materials Criteria:

(1) **Stability** in aqueous environment

(2) **Band gap** in visible

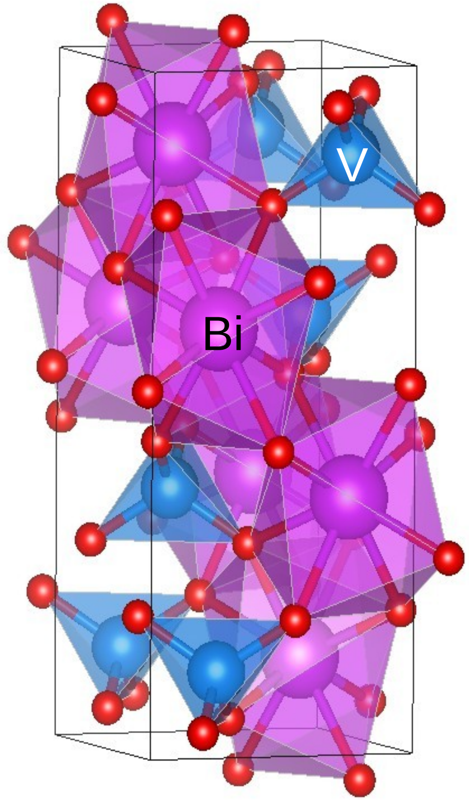
(3) **Band edges** near reaction potentials

(4) Sufficient hole and electron **mobilities** *

Our materials system of choice is bismuth vanadate ($BiVO_4$)

*W. Wang, et al. "The role of surface oxygen vacancies in $BiVO_4$." Chemistry of Materials. 32, 2899-2909 (2020).

Why $BiVO_4$?



$BiVO_4$ is an attractive photoanode for oxygen evolution

Stable	**against corrosion[1,2]**
Band gap	2.4 – 2.6 eV [3,4,5,6]
Band alignment	**Favorable w/ H_2 [3,7]**
Synthesis	**Many and varied; not $$[1]**
e^--h^+ yields	**High, >70%[4]**
OER kinetics	Slow (requires co-catalyst)
Recombination	In bulk & surface (?)

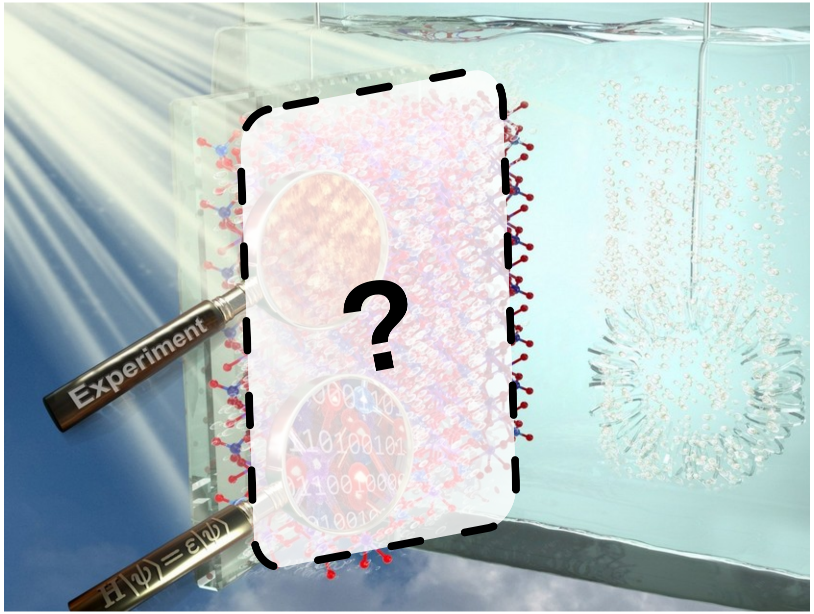
Interfacial phenomena

1) Y. Park, … K.S. Choi. *Chem. Soc. Rev.* **42**, 2321 (2013).
2) T.W. Kim and K.S. Choi. *Science*, **343**, 990 (2014).
3) M. Favaro, … R. van de Krol, D. Starr. *J. Phys. Chem. C*, **123**, 8347 (2019).
4) T.W. Kim,… G. Galli, K.S. Choi. *Nat. Comm.*, **6**, 8769 (2015).
5) D.J. Payne, … L.F.J Piper. *App. Phys. Lett.*, **98**, 212110 (2011)
6) M.V. Malashchonak, …A.V. Mazanik. *Mat. Chem & Phys.*, **201**, 183 (2017)
7) J.K. Cooper, … I.D. Sharp. *Chem. Mater.* **26**, 5365 (2014).

Motivations: Interface- & Surface-driven phenomena

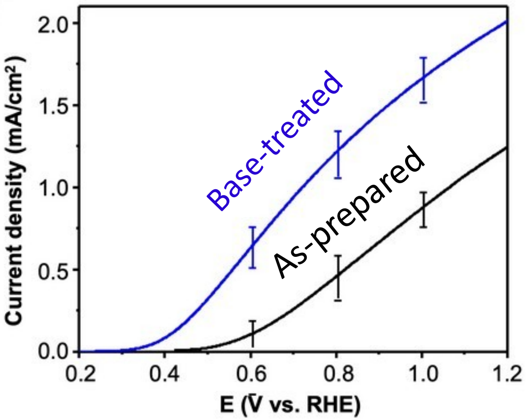
What is the structure of the surface?

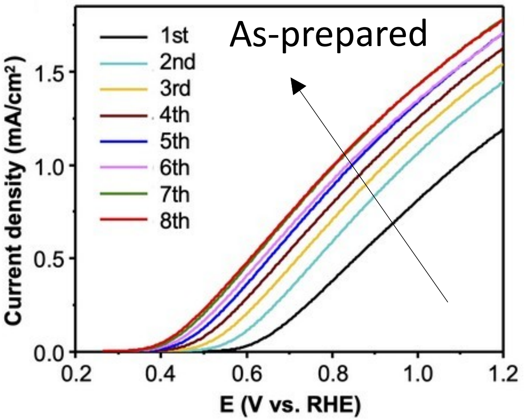
How does surface/interface influence photoelectrochemical activity?

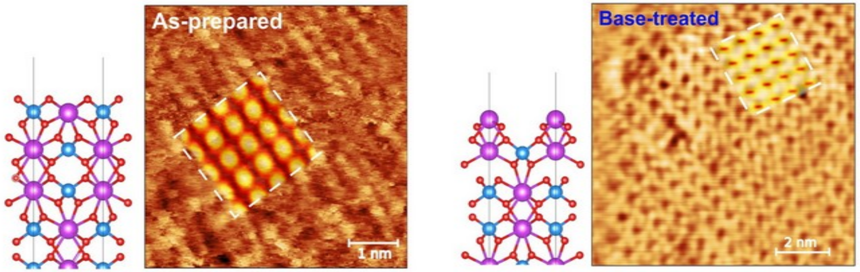


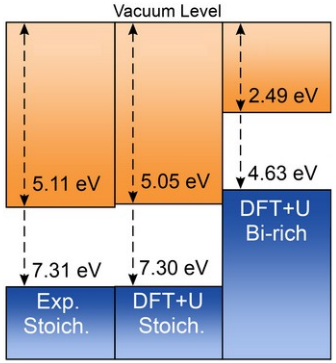
Correlating PEC performance and surface composition

Surface composition changes with each J-V cycle







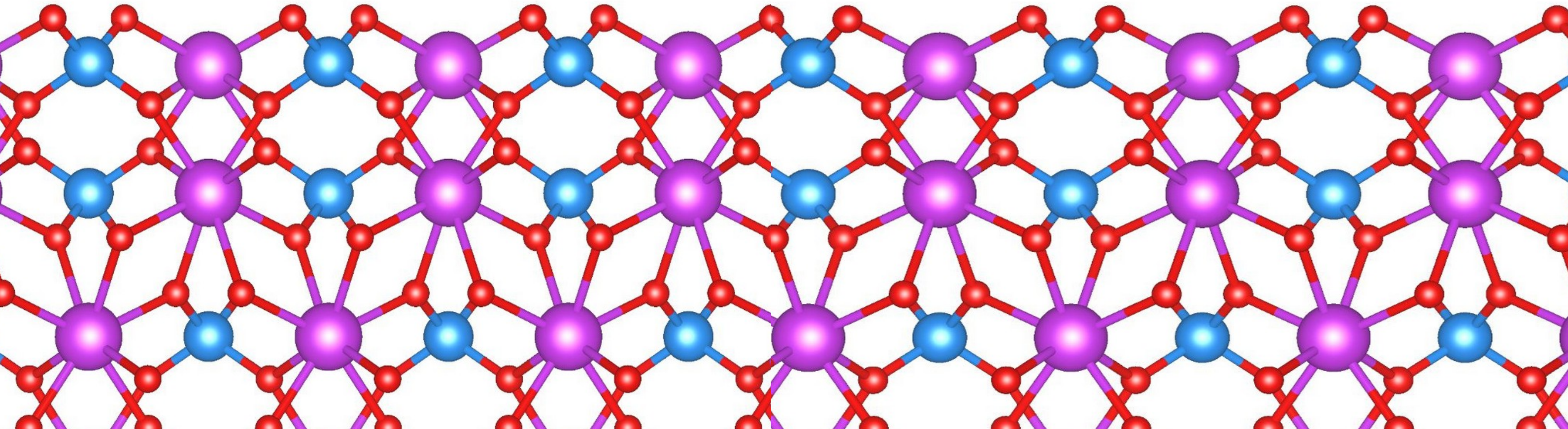


As-prepared	Before J-V	After 1 J-V	After 8 J-Vs
Bi:V ratio	43:57	79:21	84:16
φ (eV)	4.80	4.59	4.36
VBM (eV)	6.38	6.29	6.10

Demonstrate atomic-level understanding of the surface composition directly affecting photoelectrochemical properties, enabled by coupled experiment and theory efforts

What is the nature of interaction between the $BiVO_4$ surface and water?

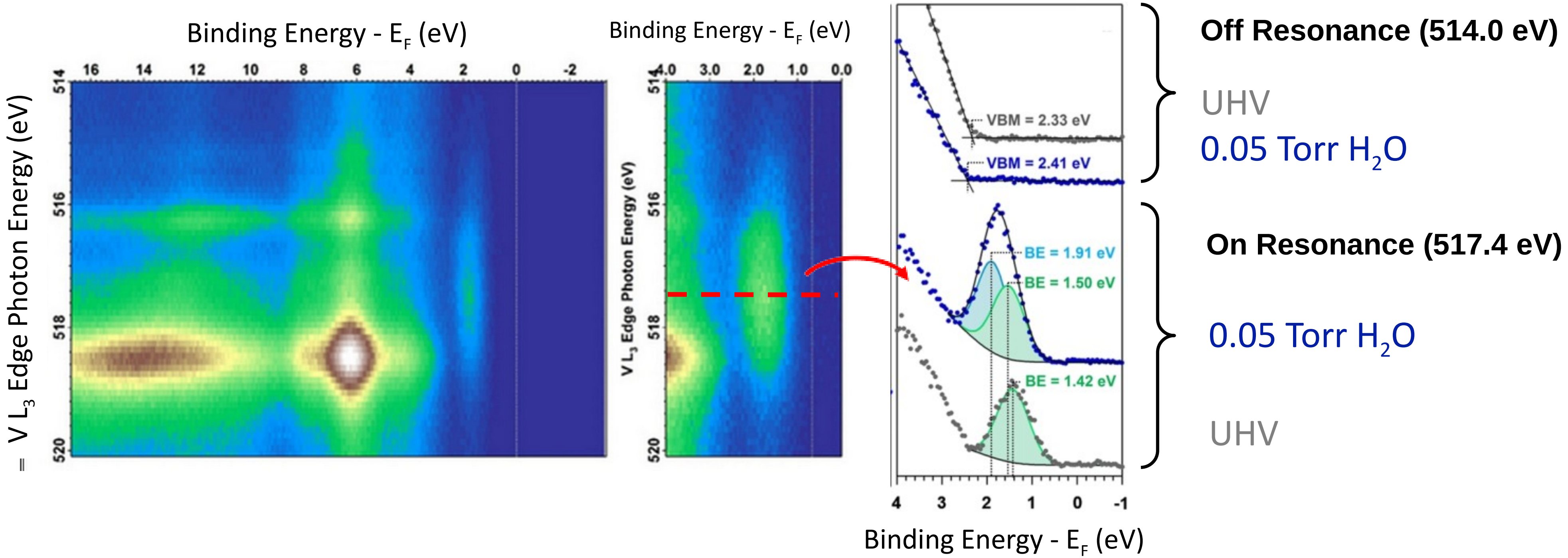
How does this manifest in the electronic structure?



Hydroxylation of the $BiVO_4$ surface

What is the nature of interaction between the $BiVO_4$ surface and water?

Vanadium L_3 edge, Resonant Photoemission in 0.05 Torr H_2O of "Stoichiometric" Surface with single-crystalline Mo-$BiVO_4$

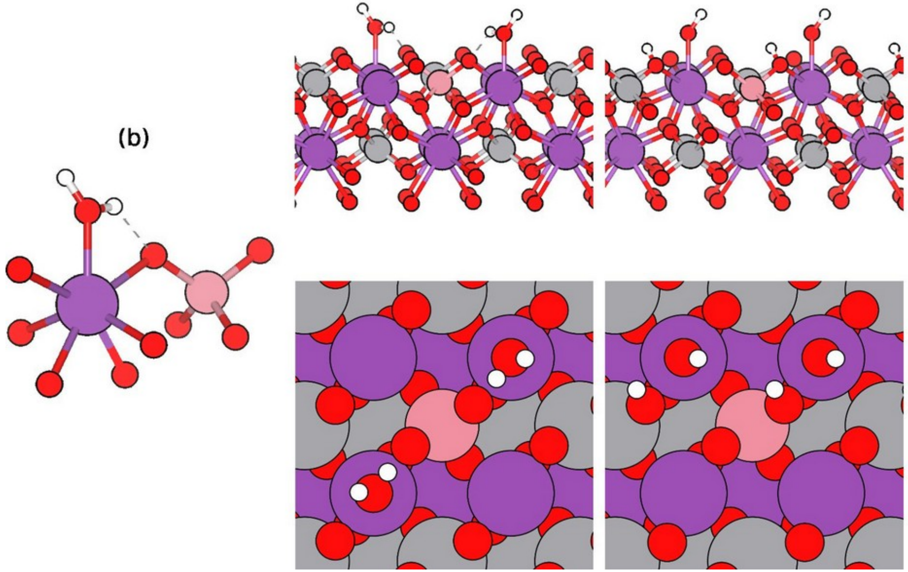


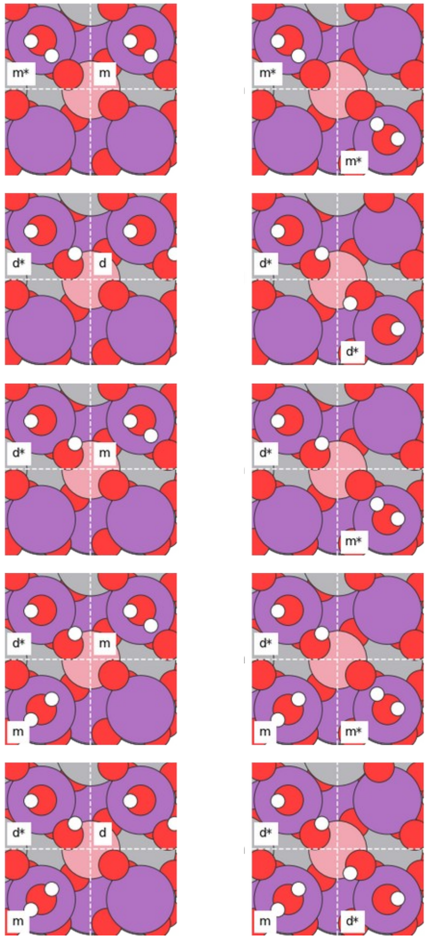
W. Wang, et al. J. Am. Chem. Soc. 2022, 144 (37), 17173–17185. https://doi.org/10.1021/jacs.2c07501.

Hydroxylation of the $BiVO_4$ surface

Configurational search of adsorbed water species on "stoichiometric" $BiVO_4$ surface:

- single- v double-hydroxylation
- molecular v dissociated water
- with & without excess charge or Mo-dopant

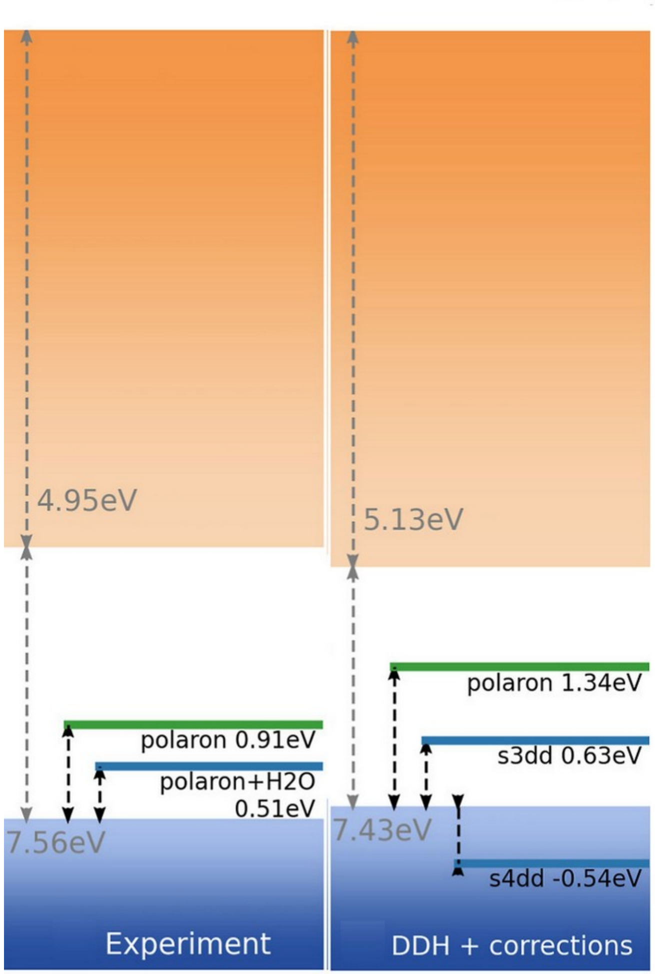




using DFT+U and hybrid functionals

and so on...

Hydroxylation of the $BiVO_4$ surface



- Molecular water can adsorb,

but in the *absence* of excess surface charge

Dissociated water adsorbs and is further stabilized in the *presence* of excess surface charge
→ formation of V^{4+} polaron
→ peak enhancement in ResPES

Excess surface charge from

- Mo doping
- Oxygen vacancies

(Surface) defects play a critical role in the hydroxylation of oxide surfaces