International Center for Theoretical Physics, Trieste, Italy
Fuggle-Fonda School on Synchrotron Radiation and Applications

LECTURES FOR 16 APRIL THROUGH 18 APRIL, 2008

SURFACE, INTERFACE, AND MATERIALS STUDIES USING PHOTOELECTRON SPECTROSCOPY, DIFFRACTION, AND HOLOGRAPHY

Lecturers:

Chuck Fadley, Department of Physics, University of California, Davis &
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http://www.physics.ucdavis.edu/fadleygroup/
*Introduction to surface and interface science, vuv/soft x-ray spectroscopies,
photoelectron spectroscopy/diffraction/holography*

Andrea Goldoni, Elettra, Trieste, Italy
*Valence bands, dispersion, and Fermi surface mapping by photoemission,
angle-resolved photoemission, many-body effects,
complex materials, spin-resolved studies*

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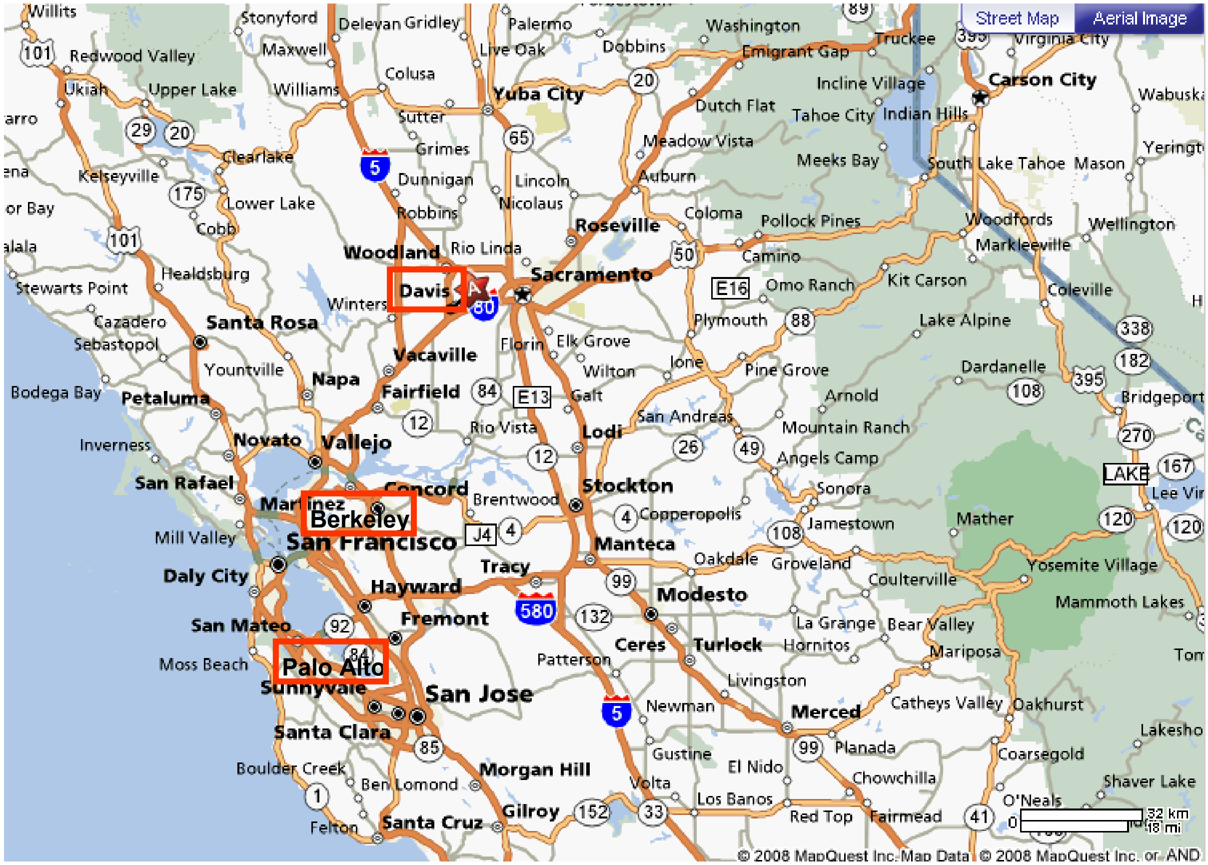
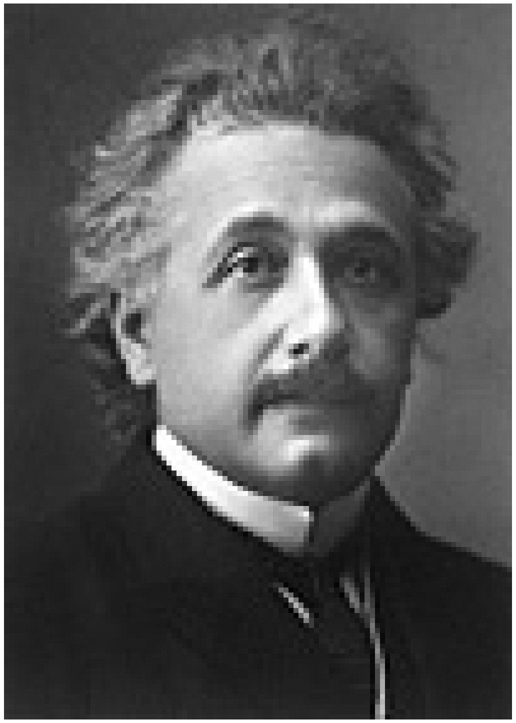
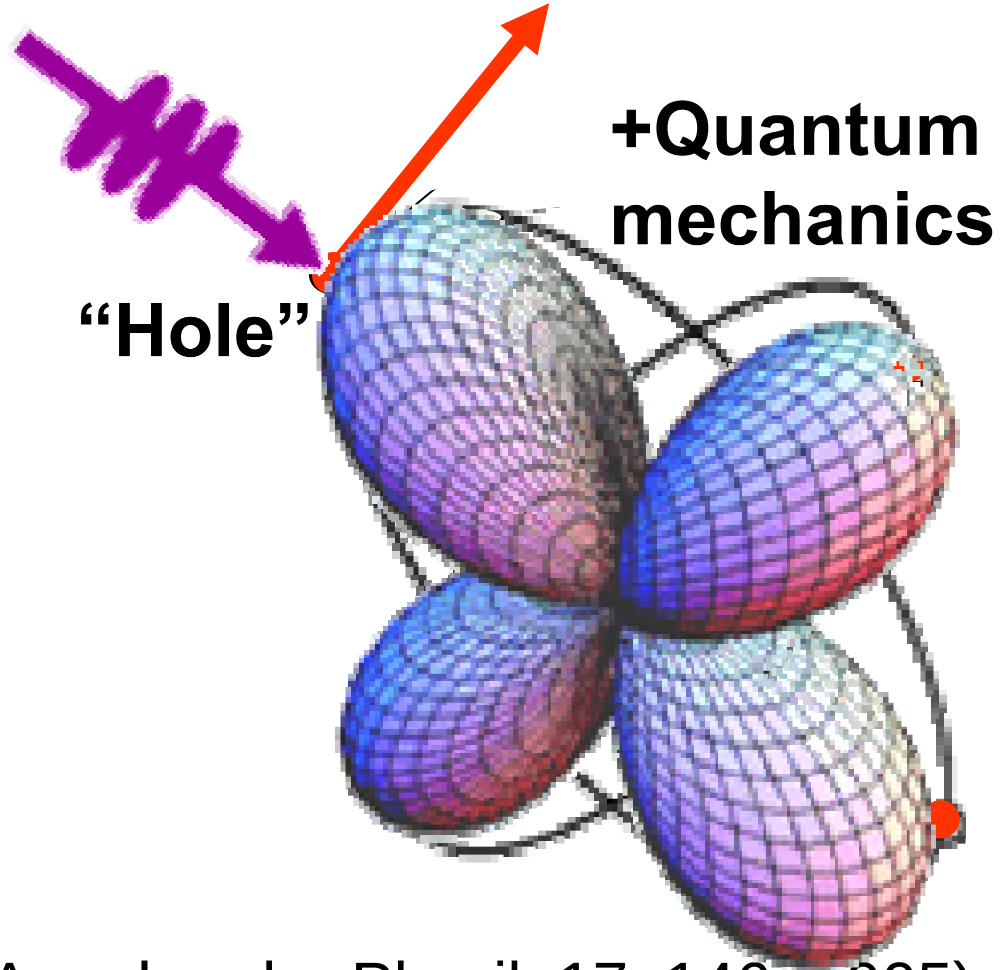


Fuggle-Fonda School on Synchrotron Radiation and Applications
International Center for Theoretical Physics
April, 2008

With acknowledgments to:





+Quantum mechanics

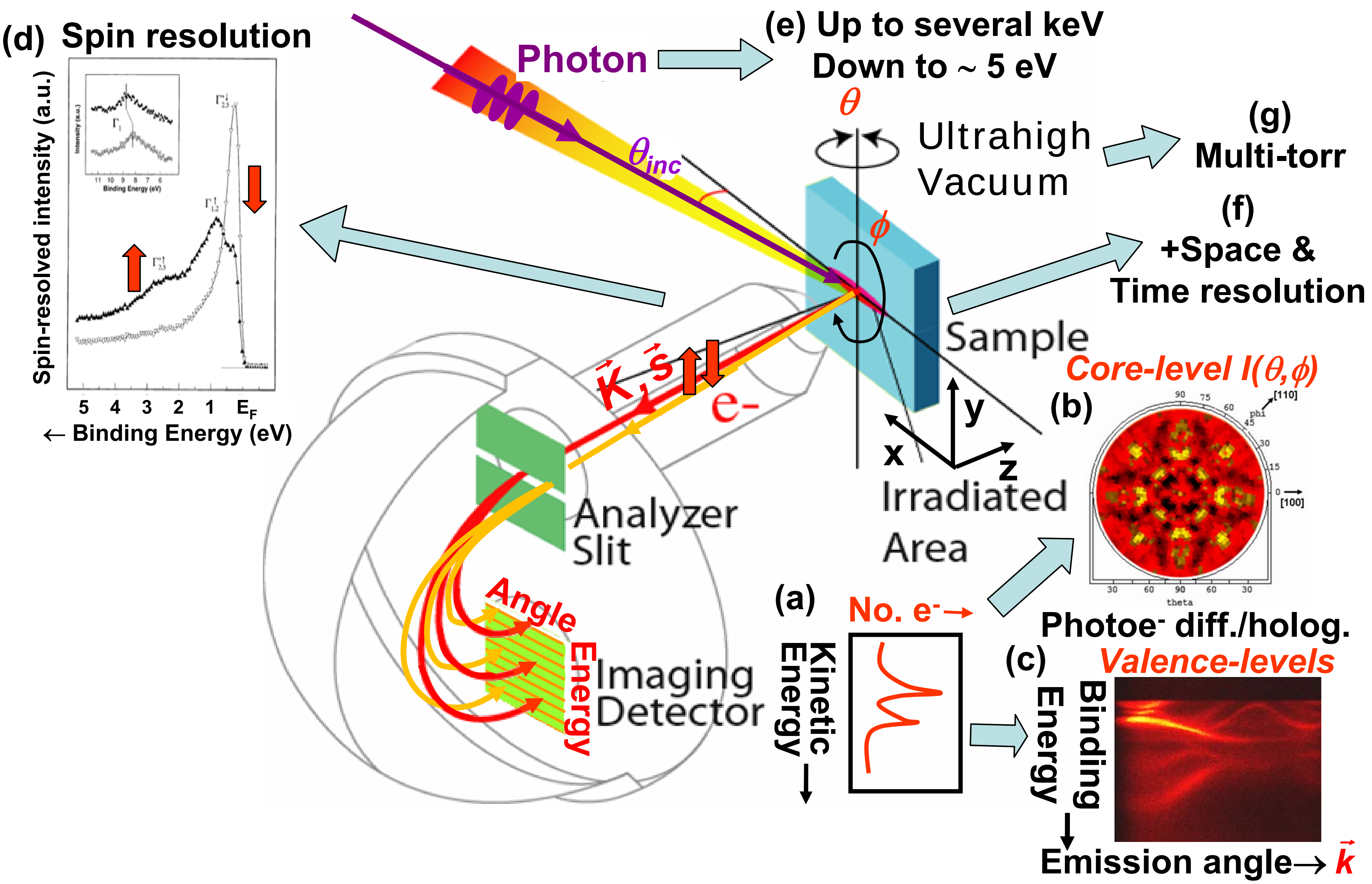
“Hole”

The photoelectric effect: Annalen der Physik 17, 146 (1905)

$$h\nu = E_{initial} - E_{final} = E_{binding} + E_{kinetic}$$

(Nobel Prize for it in1921– But no mention of it in his Nobel lecture)

Some possible photoemission measurements



Outline

Surface, interface, and nanoscience—short introduction

Some surface/interface concepts and techniques

Experimental aspects:
intro. to laboratory-based and SR-based

Electronic structure—a brief review

The basic synchrotron radiation techniques:
more experimental and theoretical details

Core-level photoemission

Valence-level photoemission

SURFACE, INTERFACE, AND MATERIALS STUDIES USING PHOTOELECTRON SPECTROSCOPY, DIFFRACTION, HOLOGRAPHY, AND MICROSCOPY; (X-RAY FLUORESCENCE HOLOGRAPHY)

Chuck Fadley
Department of Physics, University of California-Davis, Davis, CA, &
Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA

---OUTLINE OF FADLEY LECTURES FOR 16 APRIL THROUGH 18 APRIL, 2008---
(With complementary coverage of related/additional material by Andrea Goldoni, Elettra)

References below are to papers handed out as in format: Paper [No.], section no. or page nos, or to other lectures in this School as appropriate. See also original literature references referred to directly on many slides.

Slide Set 1

- ***INTRODUCTION:***
  - **--Surface and interface phenomena*: ("Modern Techniques of Surface Science", D.P. Woodruff and T.A. Delchar, (Cambridge Univ. Press, 1994), 2nd Edition,; "Surface Physics", A. Zangwill (Cambridge Univ. Press, 1990))***
    - **What are they? Why study them?**
    - **Applications in technology: semiconductor ICs, spintronics, et al.**
    - **Nanoscience/nanotechnology**
    - **Ultrahigh vacuum**
    - **Some basic concepts and characterization techniques: TEM, LEED and STM**
    - **Electron escape and surface sensitivity**
    - **Typical experimental systems**
  - **--Synchrotron radiation experiments: *(Other lectures in this School)***
    - **Basic considerations—brief review**
    - **X-ray emission and nomenclature**
    - **Synchrotron radiation**
    - **X-ray interactions with matter and basic techniques**
    - **Photoelectron spectroscopy = photoemission(PS, PES)**
    - **X-ray absorption spectroscopy (XAS, NEXAFS(=XANES) + EXAFS = XAFS *(Other lectures in this School)***
    - **X-ray emission/x-ray fluorescence spectroscopy (XES, XFS) and resonant inelastic x-ray scattering (RIXS)**
    - **X-ray scattering and diffraction (XRD, *other lectures in this School*)**
    - **X-ray optical measurements (refraction, reflection and penetration depth, Standing waves,…)**

- ***ELECTRONIC STRUCTURE:*** ***(Zangwill book, Paper [1], Chap.III):***

Basics of electronic structure and bonding
Hartree Fock Method, Koopmans Theorem and
corrections to it
The exchange interaction and magnetism
Atomic orbitals, spin-orbit splitting
Molecular orbitals
Electrons in solids, bands

Slide Set 2

- ***THE BASIC SR SPECTROSCOPIES—MORE EXPERIMENTAL AND THEORETICAL DETAILS:*** ***(Paper [1], Chaps.I and III, Paper [15])***

Photoelectron spectroscopy (PES, PS, XPS)
Auger electron spectroscopy (AES)
X-ray absorption spectroscopy (XAS, NEXAFS, XANES)
X-ray emission and resonant inelastic scattering (XES, RIXS)
Instrumentation for PES

Spectrometers and detectors
Electron spin detection
Measuring electron kinetic and binding energies:
Work function, inner potential
Sample charging

Slide Set 3

(Cont'd.)

•*CORE-LEVEL SPECTROSCOPY (PART 1):*

- --Core intensities (the 3-step model) and quantitative surface analysis: *(Papers [1], Chap. VI, Paper [2],1-4, Paper [15])*
  - Quantitative formulas for surface analysis
  - Surface sensitivity enhancement at grazing emission
- --Differential photoelectric cross sections and selection rules
  - Basic forms and tabulations
  - Cooper minima
  - Resonant photoemission:
    - Intraatomic single atom resonant photoemission (RPE, SARPE)--
      Well known
    - Interatomic multi-atom resonant photoemission (MARPE)--
      a new effect in molecules, solids *(Paper [8])*
  - Non-dipole effects at higher energies
- --Inelastic attenuation length tabulations and estimates
- --Elastic scattering effects in surface analysis
- --Electron refraction in escape from surface

Slide Set 3

(Cont'd.)

Slide Set 3

(Cont'd.)

- ***PHOTOELECTRON DIFFRACTION (CORE LEVELS):***

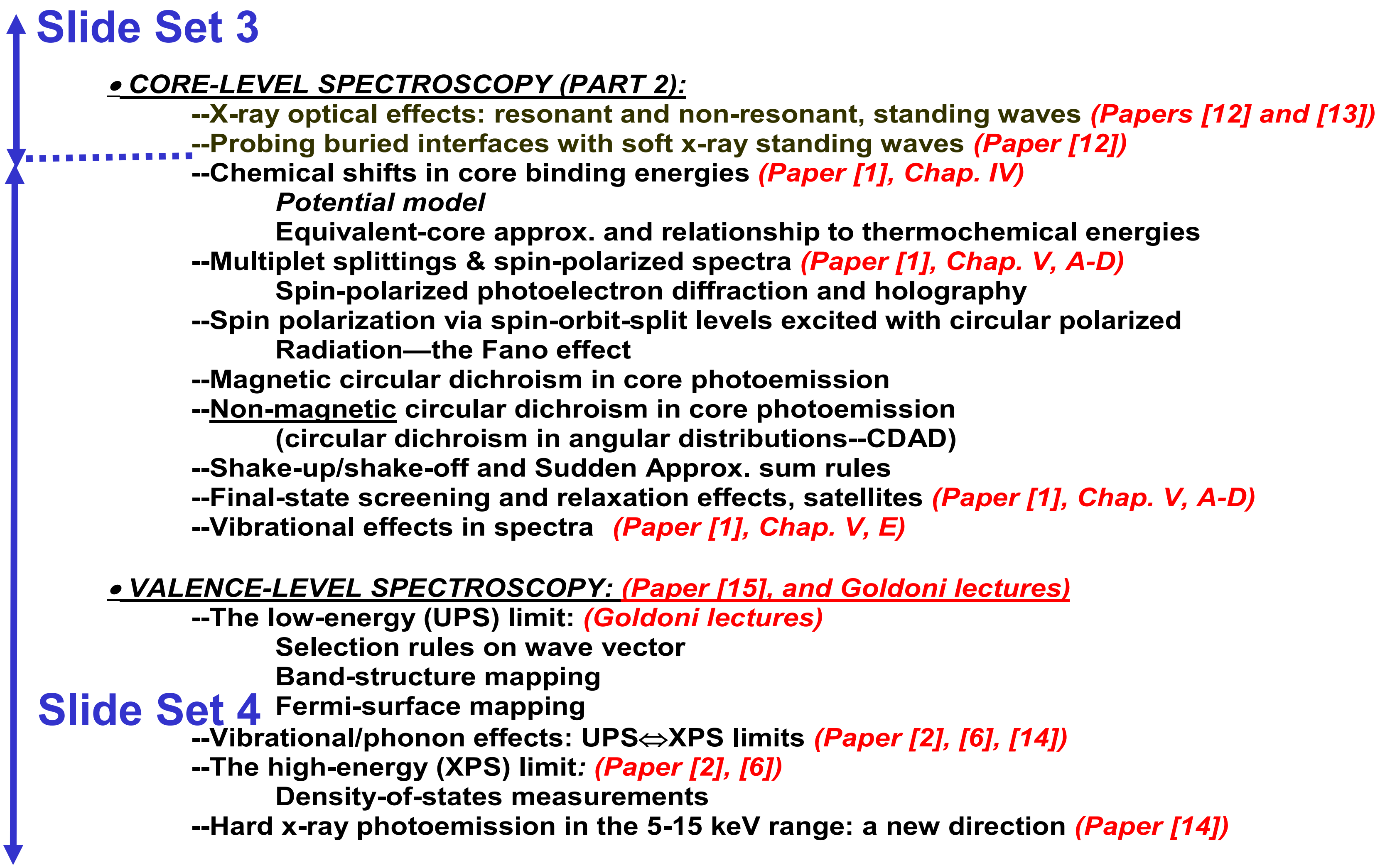
  (Papers [1], D; [2], 5; [3]-[5], and [15])

  --Basic diffraction and measurement process: scanned-angle and scanned-energy
  --Energy dependence of scattering:
    Forward-dominated at high energies
    Back and forward at low energies
  --Basic theory:
    Scattering factors: plane-wave and spherical-wave
    Vibrational effects and Debye-Waller factors
  --Determination of structures from:
    Forward scattering peaks—adsorbed molecules
    More complex diffraction patterns
      (incl. full-solid -angle data and R-factor analysis)
    Analysis via single-scattering and multiple scattering theory--review of theoretical approaches and computer exercises for those interested *(Paper [9] plus program EDAC discussed in lecture and exercises)*
  --Fingerprint diffraction patterns
  --Some example applications: adsorbates, clean surface core-level shifts, epitaxial overlayers, Moiré structures, time-dependent surface reactions
  --Fourier transforms of scanned-energy data: path-length differences

- ***PHOTOELECTRON (AND X-RAY FLUORESCENCE) HOLOGRAPHY:***

  (Papers [3], 5.4; [4], 5.3; [5]; [6]; [7];[11]; [15])

  --Basic process of hologram formation and image reconstruction:
    ~a Fourier-like transform of several types
  --Applications in single-energy and multiple-energy form to adsorbates and multilayer substrates
  --Comparison of methods, including new approaches



Slide Set 3

• CORE-LEVEL SPECTROSCOPY (PART 2):

--X-ray optical effects: resonant and non-resonant, standing waves *(Papers [12] and [13])*
--Probing buried interfaces with soft x-ray standing waves *(Paper [12])*
--Chemical shifts in core binding energies *(Paper [1], Chap. IV)*
    Potential model
    Equivalent-core approx. and relationship to thermochemical energies
--Multiplet splittings & spin-polarized spectra *(Paper [1], Chap. V, A-D)*
    Spin-polarized photoelectron diffraction and holography
--Spin polarization via spin-orbit-split levels excited with circular polarized
    Radiation—the Fano effect
--Magnetic circular dichroism in core photoemission
--Non-magnetic circular dichroism in core photoemission
    (circular dichroism in angular distributions--CDAD)
--Shake-up/shake-off and Sudden Approx. sum rules
--Final-state screening and relaxation effects, satellites *(Paper [1], Chap. V, A-D)*
--Vibrational effects in spectra *(Paper [1], Chap. V, E)*

• VALENCE-LEVEL SPECTROSCOPY: *(Paper [15], and Goldoni lectures)*

--The low-energy (UPS) limit: *(Goldoni lectures)*
    Selection rules on wave vector
    Band-structure mapping

Slide Set 4

    Fermi-surface mapping
--Vibrational/phonon effects: UPS⇔XPS limits *(Paper [2], [6], [14])*
--The high-energy (XPS) limit*: (Paper [2], [6])*
    Density-of-states measurements
--Hard x-ray photoemission in the 5-15 keV range: a new direction *(Paper [14])*

General references on various aspects of photoelectron spectroscopy, diffraction, holography (available at website):

Paper [1] "Basic Concepts of X-ray Photoelectron Spectroscopy", C.S.F, in Electron Spectroscopy, Theory, Techniques, and Applications, Brundle and Baker, Eds. (Pergamon Press, 1978) Vol. II, Ch. 1.

Paper [2] "Angle-Resolved X-ray Photoelectron Spectroscopy", C.S.F., Progress in Surface Science 16, 275 (1984).

Paper [3] "The Study of Surface Structures by Photoelectron Diffraction and Auger Electron Diffraction", C.S.F., in Synchrotron Radiation Research: Advances in Surface and Interface Science, Bachrach, Ed. (Plenum,1992)

Paper [4] "Photoelectron Diffraction: New Dimensions in Space, Time, and Spin", C.S. Fadley, M.A. Van Hove, Z. Hussain, and A.P. Kaduwela, J. Electron Spectrosc. 75, 273, (1995).

Paper [5] "Diffraction and Holography with Photoelectrons and Fluorescent X-Rays", C. S. Fadley et al., Progress in Surface Science 54, 341 (1997).

Paper [6] "Atomic Holography with Electrons and X-rays", P.M. Len, C.S. Fadley, and G. Materlik, invited paper appearing in X-ray and Inner-Shell Processes: 17th International Conference, R.L. Johnson, H. Schmidt-Böcking, and B.F. Sonntag, Eds., American Institute of Physics Conference Proceedings, No. 389 (AIP, New York, 1997) pp. 295-319.

Paper [7] "Theoretical Aspects of Electron Emission Holography", L. Fonda, Phys. Stat. Sol. (b) 188, 599 (1995). (Theoretical study by founder of this school.)

Paper [8] "Multi-Atom Resonant Photoemission", A.W. Kay, F.J. Garcia de Abajo, S.-H. Yang, E. Arenholz, B.S. Mun, N. Mannella, Z. Hussain, M.A. Van Hove, and C.S. Fadley, Physical Review B 63, 115119 (2001).

Paper [9] "Multiple Scattering of Electrons in Solids and Molecules: a Novel Cluster-Model Approach", F. J. Garcia de Abajo, C.S. Fadley, and M.A. Van Hove, Physical Review B63, 075404 (2001). (Paper describing the new "EDAC" multiple scattering program available for online usage at http://electron.lbl.gov/~edac/ in course tutorials and for anyone wishing to try it at home. See also downloadable "MSCD" program at http://electron.lbl.gov/~mscd/.)

Paper [10] "Fermi Surface Mapping by Angle-Resolved Photoemission", J. Osterwalder, Surface Review and Letters 4, 391 (1997). (Covered in greater detail in Osterwalder lectures.)

Paper [11] "Photoelectron and X-ray Holography by Contrast: Enhancing Image Quality and Dimensionality", C.S. Fadley, M.A. Van Hove, A. Kaduwela, S. Omori, L. Zhao, and S. Marchesini, J. Phys. Cond. Mat. 13, 10517 (2001).

Paper [12] "Probing Buried Interfaces with Soft X-ray Standing Wave Spectroscopy: Application to the Fe/Cr Interface", S.-H. Yang, B.S. Mun, N. Mannella, S.-K. Kim, J.B. Kortright, J. Underwood, F. Salmassi, E. Arenholz, A. Young, Z. Hussain, M.A. Van Hove, and C.S. Fadley, J. Phys. Cond. Matt. 14, L406 (2002).

Paper [13] "X-ray Optics, Standing Waves, and Interatomic Effects in Photoemission and X-ray Emission", C. S. Fadley, S.-H. Yang, B. S. Mun, J. Garcia de Abajo, invited Chapter in the book "Solid-State Photoemission and Related Methods: Theory and Experiment", W. Schattke and M.A. Van Hove, Editors, (Wiley-VCH Verlag, Berlin GmbH, 2003), ISBN: 3527403345, 38 pp., 17 figs.

Paper [14] "X-Ray Photoelectron Spectroscopy and Diffraction in The Hard X-Ray Regime: Fundamental Considerations and Future Possibilities", C. S. Fadley, Nuclear Instruments and Methods A 547, 24-41 (2005), special issue edited by J. Zegenhagen and C. Kunz.

Paper [15] "Atomic-Level Characterization of Materials with Core- and Valence-Level Photoemission: Basic Phenomena and Future Directions", C.S. Fadley, to appear in Surface and Interface Analysis (2008).

Key Reference [16] "X-ray Data Booklet", Center for X-Ray Optics and the Advanced Light Source, LBNL, January, 2001, available online at: http://xdb.lbl.gov/

Additional websites of use:

X-ray optical calculations: reflectivities, penetration depths for a variety of mirror/surface geometries—

http://www-cxro.lbl.gov/optical_constants/

General properties of the elements and their compounds: http://www.webelements.com

Calculation of photoelectron diffraction with program EDAC:
http://csic.sw.ehu.es/jga/software/edac/a.html

[15]

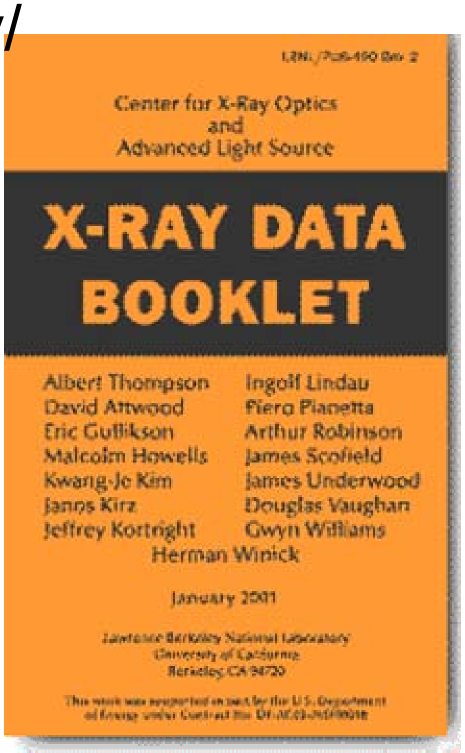
X-RAY DATA BOOKLET

Center for X-ray Optics and Advanced Light Source

Lawrence Berkeley National Laboratory

http://xdb.lbl.gov/

- Introduction
- X-Ray Properties of Elements
- Electron Binding Energies
- X-Ray Energy Emission Energies
- Fluorescence Yields for K and L Shells
- Principal Auger Electron Energies
- Subshell Photoionization Cross-Sections
- Mass Absorption Coefficients
- Atomic Scattering Factors
- Energy Levels of Few Electron Ions
- Periodic Table of X-Ray Properties
- Synchrotron Radiation
- Characteristics of Synchrotron Radiation
- History of X-rays and Synchrotron Radiation
- Synchrotron Facilities
- Scattering Processes
- Scattering of X-rays from Electrons and Atoms
- Low-Energy Electron Ranges in Matter
- Optics and Detectors
- Crystal and Multilayer Elements
- Specular Reflectivities for Grazing-Incidence Mirrors
- Gratings and Monochromators
- Zone Plates
- X-Ray Detectors
- Miscellaneous
- Physical Constants
- Physical Properties of the Elements
- Electromagnetic Relations
- Radioactivity and Radiation Protection
- Useful Formulas



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X-RAY DATA
BOOKLET

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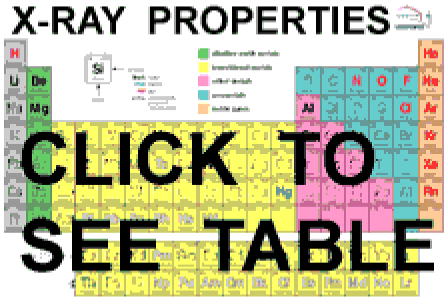


Periodic Table, with the Outer Electron Configurations of Neutral Atoms in Their Ground States

The notation used to describe the electronic configuration of atoms and ions is discussed in all textbooks of introductory atomic physics. The letters s, p, d, . . . signify electrons having orbital angular momentum 0, 1, 2, . . . in units $\hbar$; the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.

H^{1} $1s$																	**He**^{2} $1s^{2}$
Li^{3} $2s$	**Be**^{4} $2s^{2}$											**B**^{5} $2s^{2}2p$	**C**^{6} $2s^{2}2p^{2}$	**N**^{7} $2s^{2}2p^{3}$	**O**^{8} $2s^{2}2p^{4}$	**F**^{9} $2s^{2}2p^{5}$	**Ne**^{10} $2s^{2}2p^{6}$
Na^{11} $3s$	**Mg**^{12} $3s^{2}$											**Al**^{13} $3s^{2}3p$	**Si**^{14} $3s^{2}3p^{2}$	**P**^{15} $3s^{2}3p^{3}$	**S**^{16} $3s^{2}3p^{4}$	**Cl**^{17} $3s^{2}3p^{5}$	**Ar**^{18} $3s^{2}3p^{6}$
K^{19} $4s$	**Ca**^{20} $4s^{2}$	**Sc**^{21} $3d$ $4s^{2}$	**Ti**^{22} $3d^{2}$ $4s^{2}$	**V**^{23} $3d^{3}$ $4s^{2}$	**Cr**^{24} $3d^{5}$ $4s$	**Mn**^{25} $3d^{5}$ $4s^{2}$	**Fe**^{26} $3d^{6}$ $4s^{2}$	**Co**^{27} $3d^{7}$ $4s^{2}$	**Ni**^{28} $3d^{8}$ $4s^{2}$	**Cu**^{29} $3d^{10}$ $4s$	**Zn**^{30} $3d^{10}$ $4s^{2}$	**Ga**^{31} $4s^{2}4p$	**Ge**^{32} $4s^{2}4p^{2}$	**As**^{33} $4s^{2}4p^{3}$	**Se**^{34} $4s^{2}4p^{4}$	**Br**^{35} $4s^{2}4p^{5}$	**Kr**^{36} $4s^{2}4p^{6}$
Rb^{37} $5s$	**Sr**^{38} $5s^{2}$	**Y**^{39} $4d$ $5s^{2}$	**Zr**^{40} $4d^{2}$ $5s^{2}$	**Nb**^{41} $4d^{4}$ $5s$	**Mo**^{42} $4d^{5}$ $5s$	**Tc**^{43} $4d^{6}$ $5s$	**Ru**^{44} $4d^{7}$ $5s$	**Rh**^{45} $4d^{8}$ $5s$	**Pd**^{46} $4d^{10}$ –	**Ag**^{47} $4d^{10}$ $5s$	**Cd**^{48} $4d^{10}$ $5s^{2}$	**In**^{49} $5s^{2}5p$	**Sn**^{50} $5s^{2}5p^{2}$	**Sb**^{51} $5s^{2}5p^{3}$	**Te**^{52} $5s^{2}5p^{4}$	**I**^{53} $5s^{2}5p^{5}$	**Xe**^{54} $5s^{2}5p^{6}$
Cs^{55} $6s$	**Ba**^{56} $6s^{2}$	**La**^{57} $5d$ $6s^{2}$	**Hf**^{72} $4f^{14}$ $5d^{2}$ $6s^{2}$	**Ta**^{73} $5d^{3}$ $6s^{2}$	**W**^{74} $5d^{4}$ $6s^{2}$	**Re**^{75} $5d^{5}$ $6s^{2}$	**Os**^{76} $5d^{6}$ $6s^{2}$	**Ir**^{77} $5d^{9}$ –	**Pt**^{78} $5d^{9}$ $6s$	**Au**^{79} $5d^{10}$ $6s$	**Hg**^{80} $5d^{10}$ $6s^{2}$	**Tl**^{81} $6s^{2}6p$	**Pb**^{82} $6s^{2}6p^{2}$	**Bi**^{83} $6s^{2}6p^{3}$	**Po**^{84} $6s^{2}6p^{4}$	**At**^{85} $6s^{2}6p^{5}$	**Rn**^{86} $6s^{2}6p^{6}$
Fr^{87} $7s$	**Ra**^{88} $7s^{2}$	**Ac**^{89} $6d$ $7s^{2}$															
			Ce^{58} $4f^{2}$ $6s^{2}$	**Pr**^{59} $4f^{3}$ $6s^{2}$	**Nd**^{60} $4f^{4}$ $6s^{2}$	**Pm**^{61} $4f^{5}$ $6s^{2}$	**Sm**^{62} $4f^{6}$ $6s^{2}$	**Eu**^{63} $4f^{7}$ $6s^{2}$	**Gd**^{64} $4f^{7}$ $5d$ $6s^{2}$	**Tb**^{65} $4f^{8}$ $5d$ $6s^{2}$	**Dy**^{66} $4f^{10}$ $6s^{2}$	**Ho**^{67} $4f^{11}$ $6s^{2}$	**Er**^{68} $4f^{12}$ $6s^{2}$	**Tm**^{69} $4f^{13}$ $6s^{2}$	**Yb**^{70} $4f^{14}$ $6s^{2}$	**Lu**^{71} $4f^{14}$ $5d$ $6s^{2}$	
			Th^{90} – $6d^{2}$ $7s^{2}$	**Pa**^{91} $5f^{2}$ $6d$ $7s^{2}$	**U**^{92} $5f^{3}$ $6d$ $7s^{2}$	**Np**^{93} $5f^{5}$ $7s^{2}$	**Pu**^{94} $5f^{6}$ $7s^{2}$	**Am**^{95} $5f^{7}$ $7s^{2}$	**Cm**^{96} $5f^{7}$ $6d$ $7s^{2}$	**Bk**^{97}	**Cf**^{98}	**Es**^{99}	**Fm**^{100}	**Md**^{101}	**No**^{102}	**Lr**^{103}	

Table 3 Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there.

← Crystal structure →
← *a* lattice parameter, in Å →
← *c* lattice parameter, in Å →

H^1 4K hcp 3.75 6.12																	**He^4** 2K hcp 3.57 5.83
Li 78K bcc 3.491	**Be** hcp 2.27 3.59											**B** rhomb.	**C** diamond 3.567	**N** 20K cubic 5.66 (N$_2$)	**O** complex (O$_2$)	**F**	**Ne** 4K fcc 4.46
Na 5K bcc 4.225	**Mg** hcp 3.21 5.21											**Al** fcc 4.05	**Si** diamond 5.430	**P** complex	**S** complex	**Cl** complex (Cl$_2$)	**Ar** 4K fcc 5.31
K 5K bcc 5.225	**Ca** fcc 5.58	**Sc** hcp 3.31 5.27	**Ti** hcp 2.95 4.68	**V** bcc 3.03	**Cr** bcc 2.88	**Mn** cubic complex	**Fe** bcc 2.87	**Co** hcp 2.51 4.07	**Ni** fcc 3.52	**Cu** fcc 3.61	**Zn** hcp 2.66 4.95	**Ga** complex	**Ge** diamond 5.658	**As** rhomb.	**Se** hex. chains	**Br** complex (Br$_2$)	**Kr** 4K fcc 5.64
Rb 5K bcc 5.585	**Sr** fcc 6.08	**Y** hcp 3.65 5.73	**Zr** hcp 3.23 5.15	**Nb** bcc 3.30	**Mo** bcc 3.15	**Tc** hcp 2.74 4.40	**Ru** hcp 2.71 4.28	**Rh** fcc 3.80	**Pd** fcc 3.89	**Ag** fcc 4.09	**Cd** hcp 2.98 5.62	**In** tetr. 3.25 4.95	**Sn** (α) diamond 6.49	**Sb** rhomb.	**Te** hex. chains	**I** complex (I$_2$)	**Xe** 4K fcc 6.13
Cs 5K bcc 6.045	**Ba** bcc 5.02	**La** hex. 3.77 *ABAC*	**Hf** hcp 3.19 5.05	**Ta** bcc 3.30	**W** bcc 3.16	**Re** hcp 2.76 4.46	**Os** hcp 2.74 4.32	**Ir** fcc 3.84	**Pt** fcc 3.92	**Au** fcc 4.08	**Hg** rhomb.	**Tl** hcp 3.46 5.52	**Pb** fcc 4.95	**Bi** rhomb.	**Po** sc 3.34	**At** —	**Rn** —
Fr —	**Ra** —	**Ac** fcc 5.31															

Ce fcc 5.16	**Pr** hex. 3.67 *ABAC*	**Nd** hex. 3.66	**Pm** —	**Sm** complex	**Eu** bcc 4.58	**Gd** hcp 3.63 5.78	**Tb** hcp 3.60 5.70	**Dy** hcp 3.59 5.65	**Ho** hcp 3.58 5.62	**Er** hcp 3.56 5.59	**Tm** hcp 3.54 5.56	**Yb** fcc 5.48	**Lu** hcp 3.50 5.55
Th fcc 5.08	**Pa** tetr. 3.92 3.24	**U** complex	**Np** complex	**Pu** complex	**Am** hex. 3.64 *ABAC*	**Cm** —	**Bk** —	**Cf** —	**Es** —	**Fm** —	**Md** —	**No** —	**Lr** —

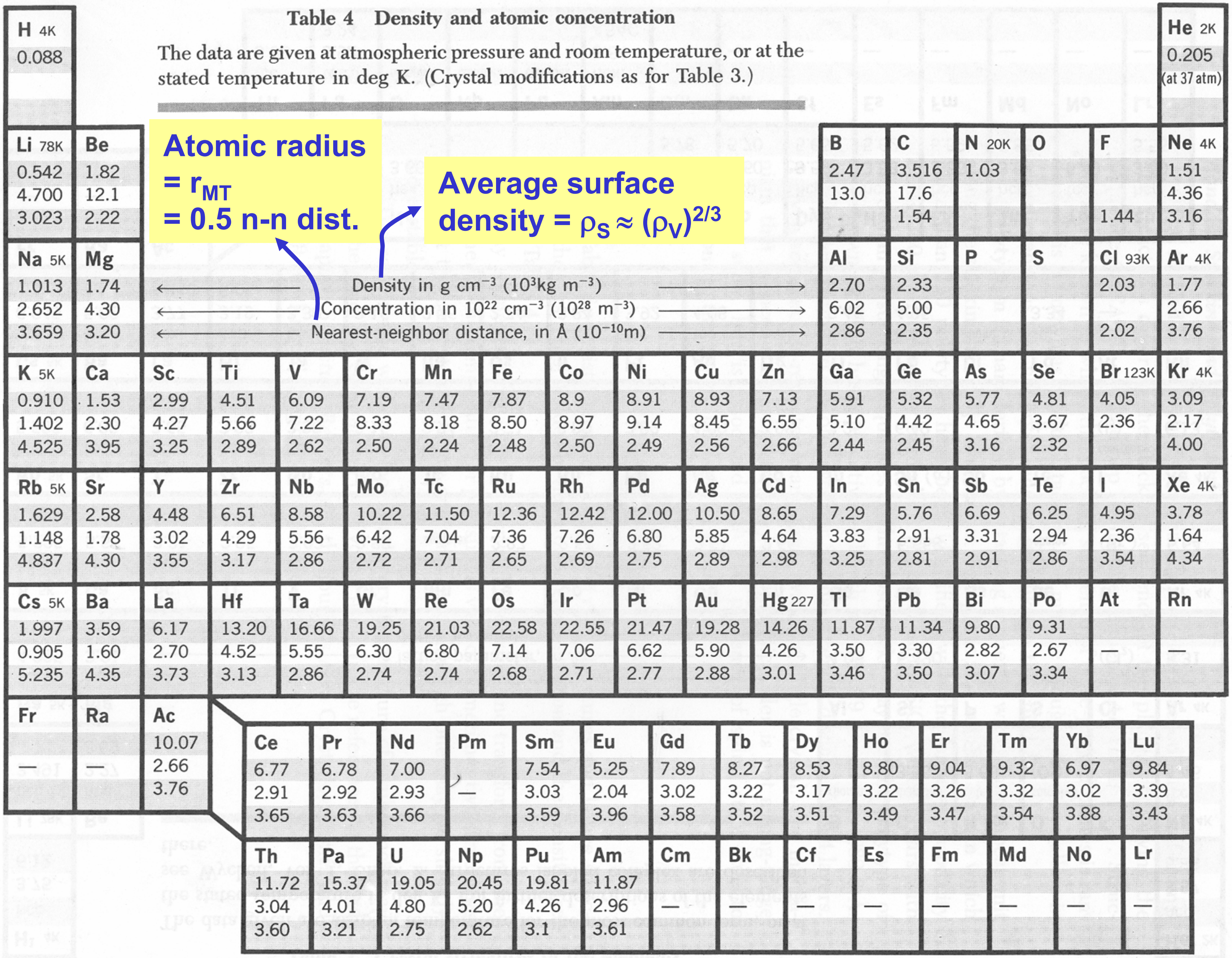


Table 4 Density and atomic concentration

The data are given at atmospheric pressure and room temperature, or at the stated temperature in deg K. (Crystal modifications as for Table 3.)

Atomic radius = r_{MT} = 0.5 n-n dist.

Average surface density = $\rho_S \approx (\rho_V)^{2/3}$

← Density in g cm^{-3} (10^3kg m^{-3}) →

← Concentration in 10^{22} cm^{-3} (10^{28} m^{-3}) →

← Nearest-neighbor distance, in Å (10^{-10}m) →

H 4K 0.088																	**He** 2K 0.205 (at 37 atm)
Li 78K 0.542 4.700 3.023	**Be** 1.82 12.1 2.22											**B** 2.47 13.0	**C** 3.516 17.6 1.54	**N** 20K 1.03	**O**	**F** 1.44	**Ne** 4K 1.51 4.36 3.16
Na 5K 1.013 2.652 3.659	**Mg** 1.74 4.30 3.20											**Al** 2.70 6.02 2.86	**Si** 2.33 5.00 2.35	**P**	**S**	**Cl** 93K 2.03 2.02	**Ar** 4K 1.77 2.66 3.76
K 5K 0.910 1.402 4.525	**Ca** 1.53 2.30 3.95	**Sc** 2.99 4.27 3.25	**Ti** 4.51 5.66 2.89	**V** 6.09 7.22 2.62	**Cr** 7.19 8.33 2.50	**Mn** 7.47 8.18 2.24	**Fe** 7.87 8.50 2.48	**Co** 8.9 8.97 2.50	**Ni** 8.91 9.14 2.49	**Cu** 8.93 8.45 2.56	**Zn** 7.13 6.55 2.66	**Ga** 5.91 5.10 2.44	**Ge** 5.32 4.42 2.45	**As** 5.77 4.65 3.16	**Se** 4.81 3.67 2.32	**Br** 123K 4.05 2.36	**Kr** 4K 3.09 2.17 4.00
Rb 5K 1.629 1.148 4.837	**Sr** 2.58 1.78 4.30	**Y** 4.48 3.02 3.55	**Zr** 6.51 4.29 3.17	**Nb** 8.58 5.56 2.86	**Mo** 10.22 6.42 2.72	**Tc** 11.50 7.04 2.71	**Ru** 12.36 7.36 2.65	**Rh** 12.42 7.26 2.69	**Pd** 12.00 6.80 2.75	**Ag** 10.50 5.85 2.89	**Cd** 8.65 4.64 2.98	**In** 7.29 3.83 3.25	**Sn** 5.76 2.91 2.81	**Sb** 6.69 3.31 2.91	**Te** 6.25 2.94 2.86	**I** 4.95 2.36 3.54	**Xe** 4K 3.78 1.64 4.34
Cs 5K 1.997 0.905 5.235	**Ba** 3.59 1.60 4.35	**La** 6.17 2.70 3.73	**Hf** 13.20 4.52 3.13	**Ta** 16.66 5.55 2.86	**W** 19.25 6.30 2.74	**Re** 21.03 6.80 2.74	**Os** 22.58 7.14 2.68	**Ir** 22.55 7.06 2.71	**Pt** 21.47 6.62 2.77	**Au** 19.28 5.90 2.88	**Hg** 227 14.26 4.26 3.01	**Tl** 11.87 3.50 3.46	**Pb** 11.34 3.30 3.50	**Bi** 9.80 2.82 3.07	**Po** 9.31 2.67 3.34	**At** —	**Rn** —
Fr —	**Ra** —	**Ac** 10.07 2.66 3.76															

Ce 6.77 2.91 3.65	**Pr** 6.78 2.92 3.63	**Nd** 7.00 2.93 3.66	**Pm** —	**Sm** 7.54 3.03 3.59	**Eu** 5.25 2.04 3.96	**Gd** 7.89 3.02 3.58	**Tb** 8.27 3.22 3.52	**Dy** 8.53 3.17 3.51	**Ho** 8.80 3.22 3.49	**Er** 9.04 3.26 3.47	**Tm** 9.32 3.32 3.54	**Yb** 6.97 3.02 3.88	**Lu** 9.84 3.39 3.43
Th 11.72 3.04 3.60	**Pa** 15.37 4.01 3.21	**U** 19.05 4.80 2.75	**Np** 20.45 5.20 2.62	**Pu** 19.81 4.26 3.1	**Am** 11.87 2.96 3.61	**Cm** —	**Bk** —	**Cf** —	**Es** —	**Fm** —	**Md** —	**No** —	**Lr** —

Table 1 Debye temperature and thermal conductivity[a]

Low temperature limit of θ, in Kelvin

Thermal conductivity at 300 K, in W $cm^{-1}K^{-1}$

Li	**Be**											**B**	**C**	**N**	**O**	**F**	**Ne**
344	1440												2230				75
0.85	2.00											0.27	1.29				
Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
158	400											428	645				92
1.41	1.56											2.37	1.48				
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
91	230	360.	420	380	630	410	470	445	450	343	327	320	374	282	90		72
1.02		0.16	0.22	0.31	0.94	0.08	0.80	1.00	0.91	4.01	1.16	0.41	0.60	0.50	0.02		
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn** *w*	**Sb**	**Te**	**I**	**Xe**
56	147	280	291	275	450		600	480	274	225	209	108	200	211	153		64
0.58		0.17	0.23	0.54	1.38	0.51	1.17	1.50	0.72	4.29	0.97	0.82	0.67	0.24	0.02		
Cs	**Ba**	**La** β	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
38	110	142	252	240	400	430	500	420	240	165	71.9	78.5	105	119			
0.36		0.14	0.23	0.58	1.74	0.48	0.88	1.47	0.72	3.17		0.46	0.35	0.08			
Fr	**Ra**	**Ac**															

Ce	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
						200		210				120	210
0.11	0.12	0.16		0.13		0.11	0.11	0.11	0.16	0.14	0.17	0.35	0.16
Th	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**
163		207											
0.54		0.28	0.06	0.07									

---

[a] Most of the θ values were supplied by N. Pearlman; references are given the *A.I.P. Handbook*, 3rd ed; the thermal conductivity values are from R. W. Powell and Y. S. Touloukian, Science **181**, 999 (1973).

Outline

➡ Surface, interface, and nanoscience—short introduction

Some surface concepts and techniques

Experimental aspects: laboratory-based and SR-based

Electronic structure—a brief review

The basic synchrotron radiation techniques

Core-level photoemission

Valence-level photoemission

Microscopy with photoemission

- *Why surfaces, interfaces, structures at the nanometer scale?*

  1 nm = 10 Å = 0.001 micron

  Cube of 1 nm sides has 75% of its atoms on the surface

  Many areas of science/technology

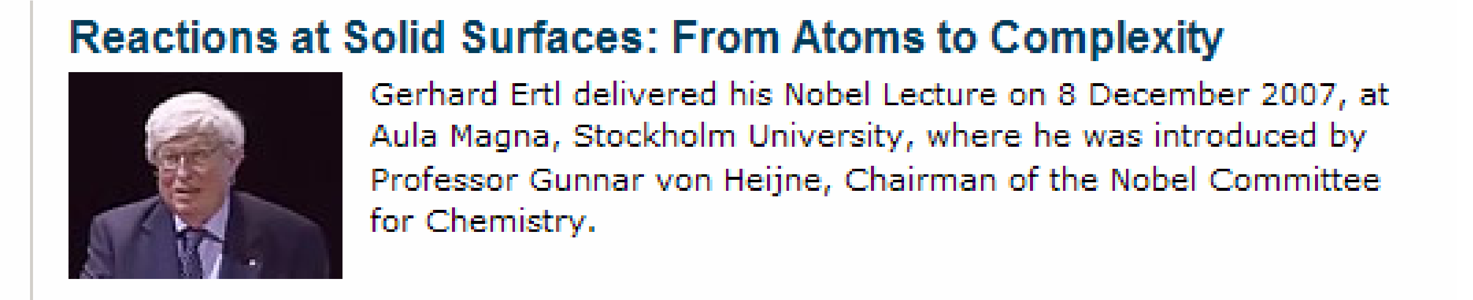
Nobel Prizes in Physics and Chemistry--2007

From Spinwaves to Giant Magnetoresistance (GMR) and Beyond

Peter Grünberg held his Nobel Lecture on 8 December 2007, at Aula Magna, Stockholm University. He was introduced by Professor Per Carlson, Chairman of the Nobel Committee for Physics.

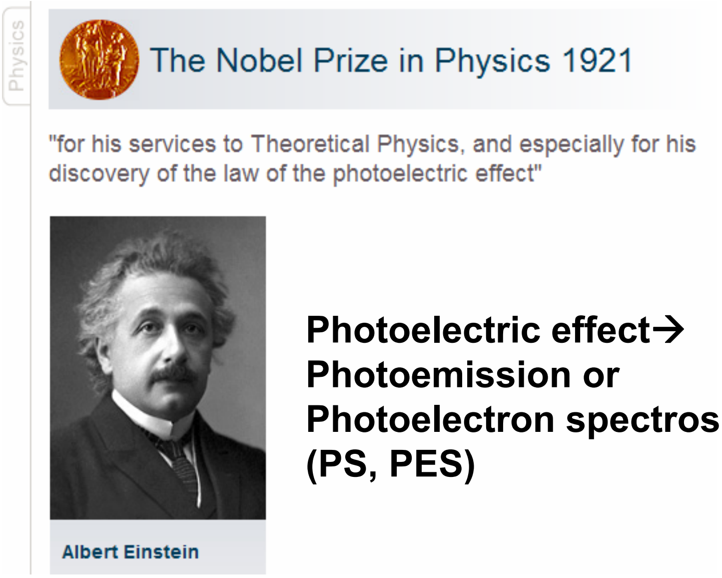
The Origin, the Development and the Future of Spintronics

Albert Fert delivered his Nobel Lecture on 8 December 2007, at Aula Magna, Stockholm University. He was introduced by Professor Per Carlson, Chairman of the Nobel Committee for Physics.



Reactions at Solid Surfaces: From Atoms to Complexity

Gerhard Ertl delivered his Nobel Lecture on 8 December 2007, at Aula Magna, Stockholm University, where he was introduced by Professor Gunnar von Heijne, Chairman of the Nobel Committee for Chemistry.

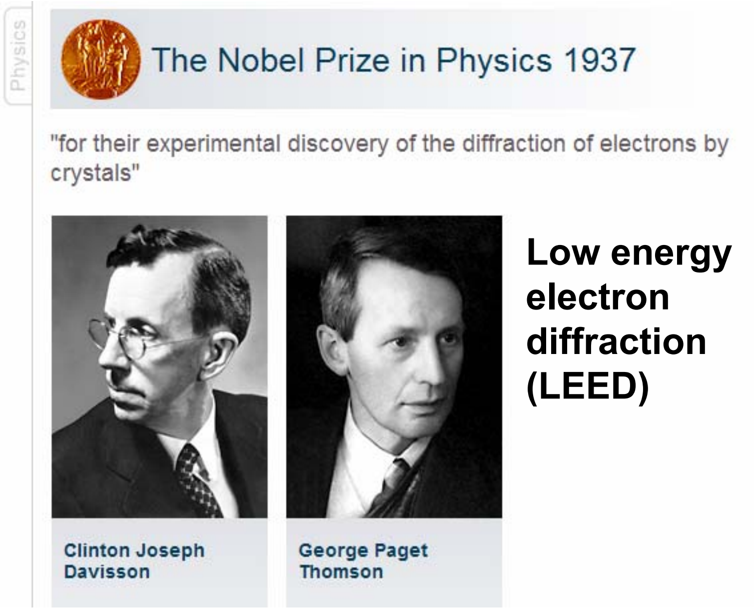


The Nobel Prize in Physics 1921

"for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect"

Albert Einstein

Photoelectric effect→
Photoemission or
Photoelectron spectroscopy
(PS, PES)



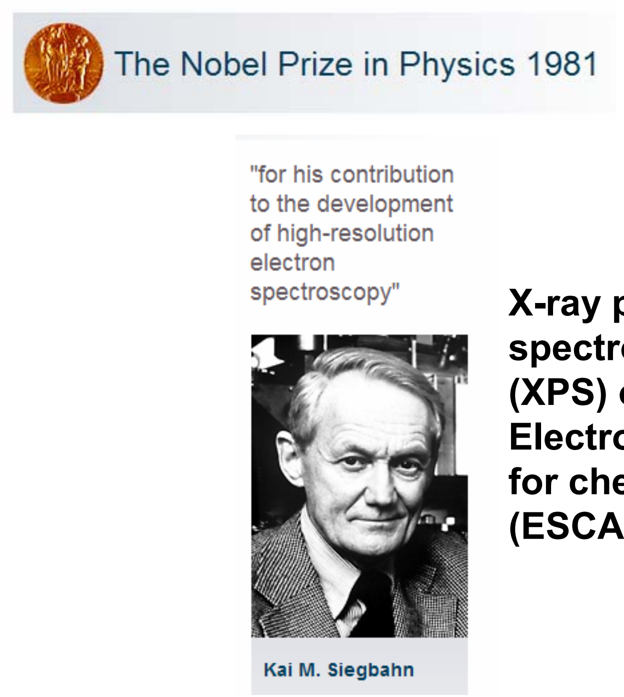
The Nobel Prize in Physics 1937

"for their experimental discovery of the diffraction of electrons by crystals"

Clinton Joseph Davisson

George Paget Thomson

Low energy
electron
diffraction
(LEED)

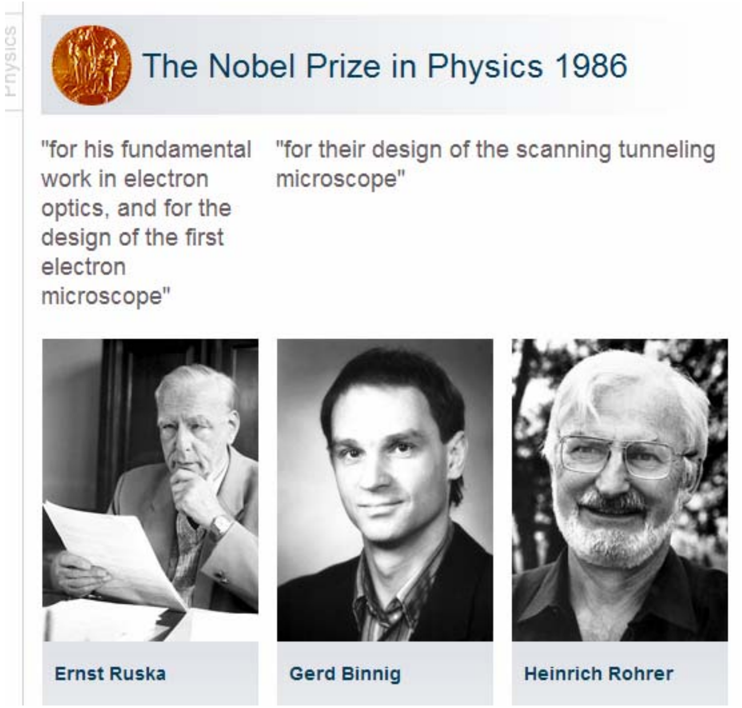


The Nobel Prize in Physics 1981

"for his contribution to the development of high-resolution electron spectroscopy"

Kai M. Siegbahn

X-ray photoelectron
spectroscopy
(XPS) or
Electron spectroscopy
for chemical analysis
(ESCA)



The Nobel Prize in Physics 1986

"for his fundamental work in electron optics, and for the design of the first electron microscope"

"for their design of the scanning tunneling microscope"

Ernst Ruska

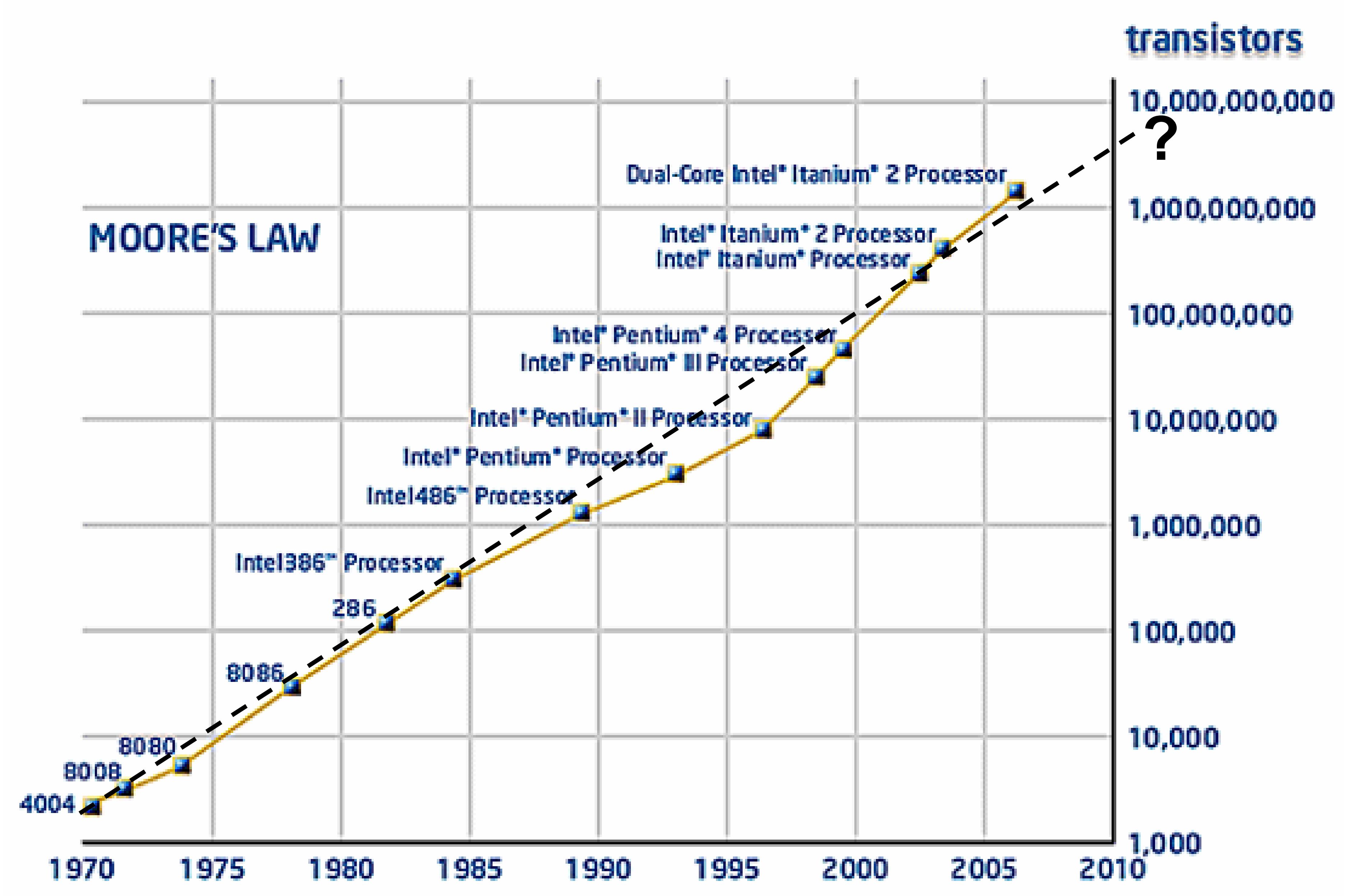
Gerd Binnig

Heinrich Rohrer

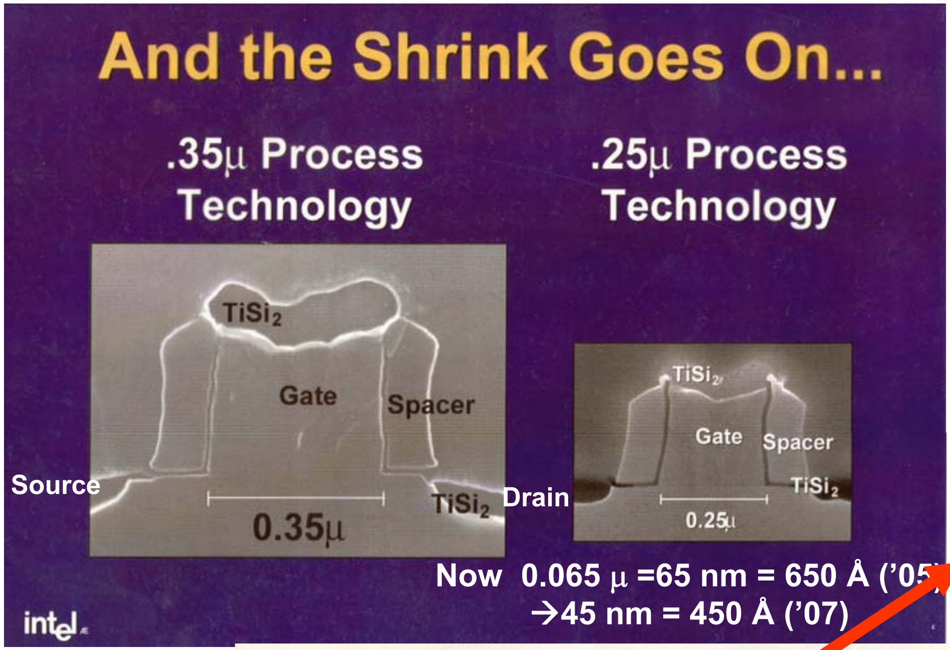
Scanning tunneling microscopy (STM)

Scientific and technological areas involving surface/interface/nano science:

- **Integrated circuits—higher speed, higher density**



http://www.intel.com/technology/mooreslaw/index.htm

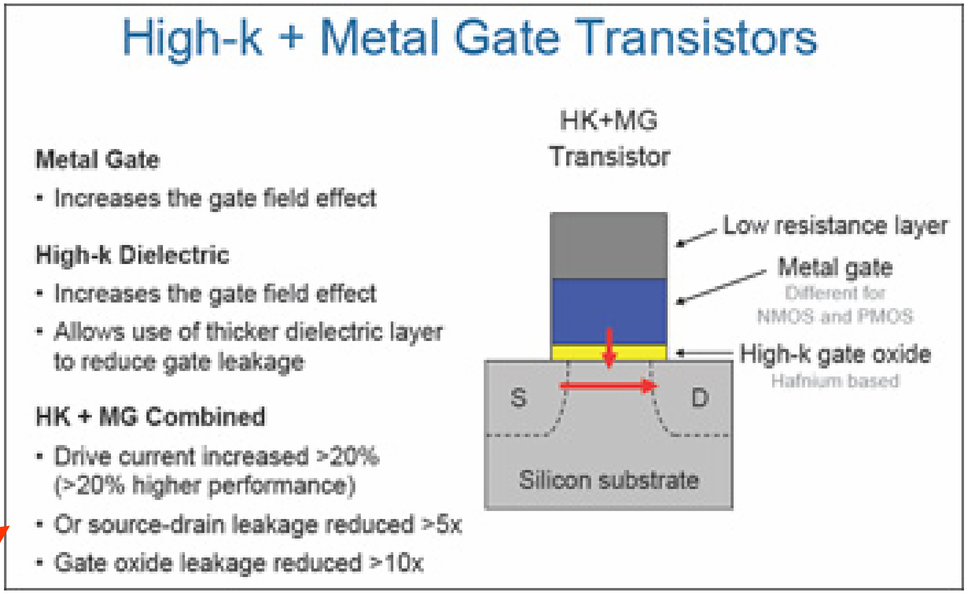


And the Shrink Goes On...

.35µ Process Technology

.25µ Process Technology

Now 0.065 µ =65 nm = 650 Å ('05)
→45 nm = 450 Å ('07)

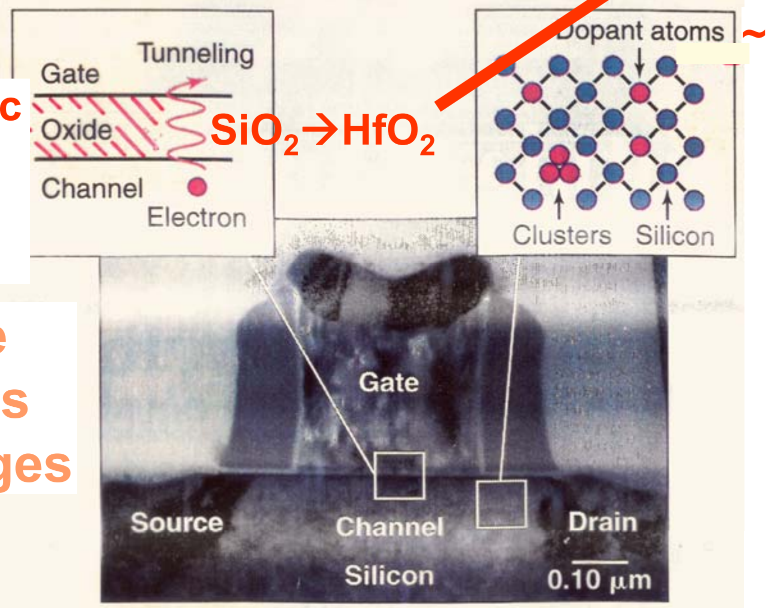


High-k + Metal Gate Transistors

Metal Gate
- Increases the gate field effect

High-k Dielectric
- Increases the gate field effect
- Allows use of thicker dielectric layer to reduce gate leakage

HK + MG Combined
- Drive current increased >20% (>20% higher performance)
- Or source-drain leakage reduced >5x
- Gate oxide leakage reduced >10x



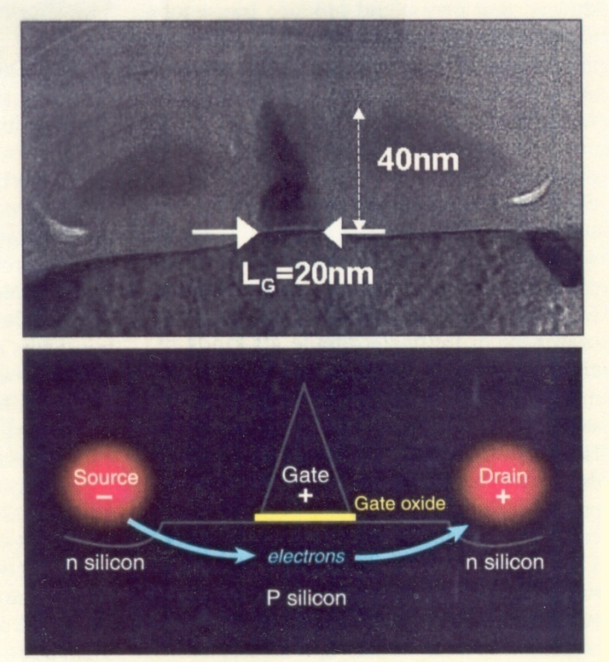
~few atomic layers—currently 15 Å SiO_2

$SiO_2 \rightarrow HfO_2$

~1 %

Cross section of a MOS transistor. Electron tunneling through the gate oxide (**left inset**) and high-concentration dopant interactions (**right inset**) are posing fundamental limitations to continuing historical transistor scaling trends.

Some serious challenges



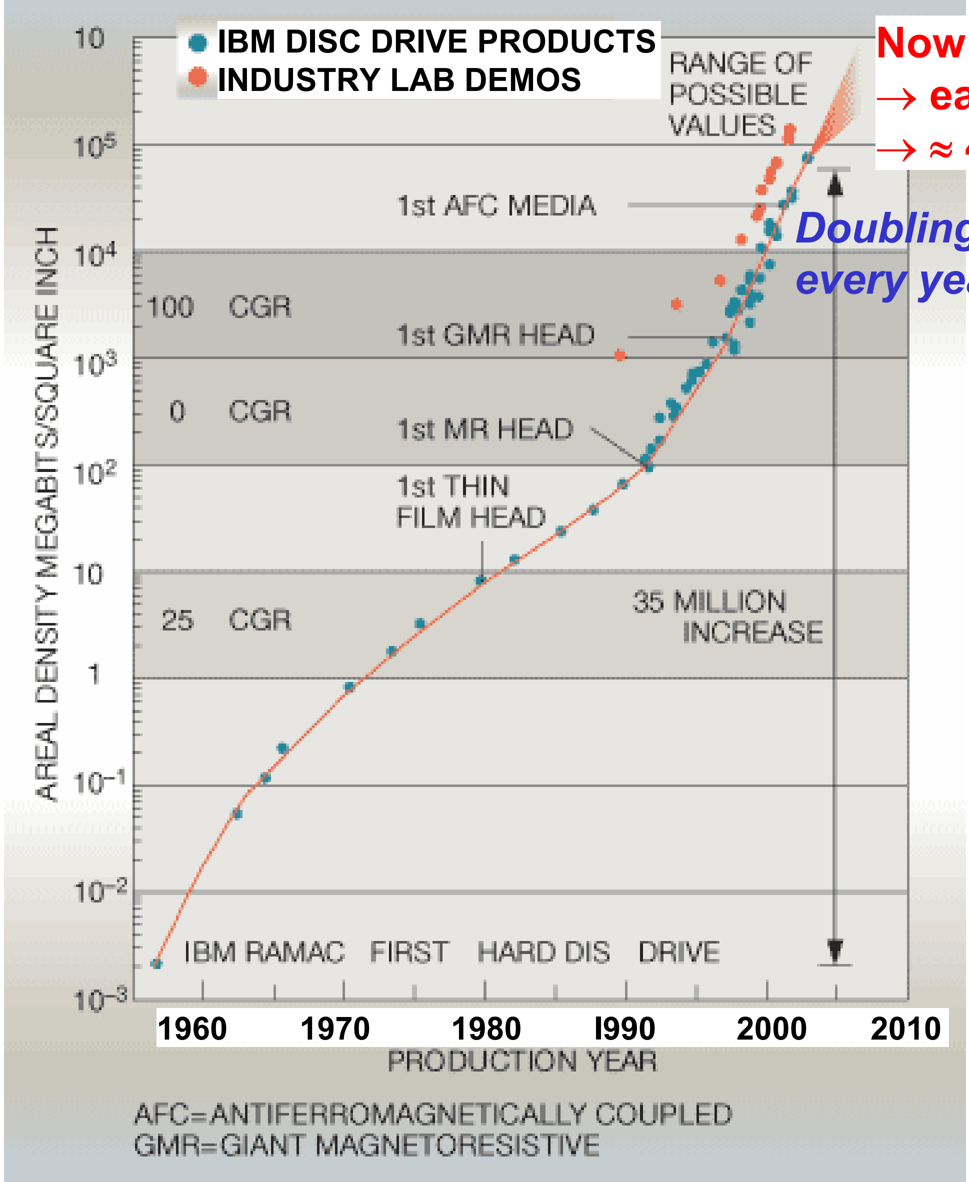
World's Smallest Transistor

IBM Science 2001

Scientific and technological areas related to surface/interface/nano science:

- **Integrated circuits—higher speed, higher density**
- **Magnetic storage and circuits—higher density, magnetic logic**

“Moore’s Law” for magnetic storage



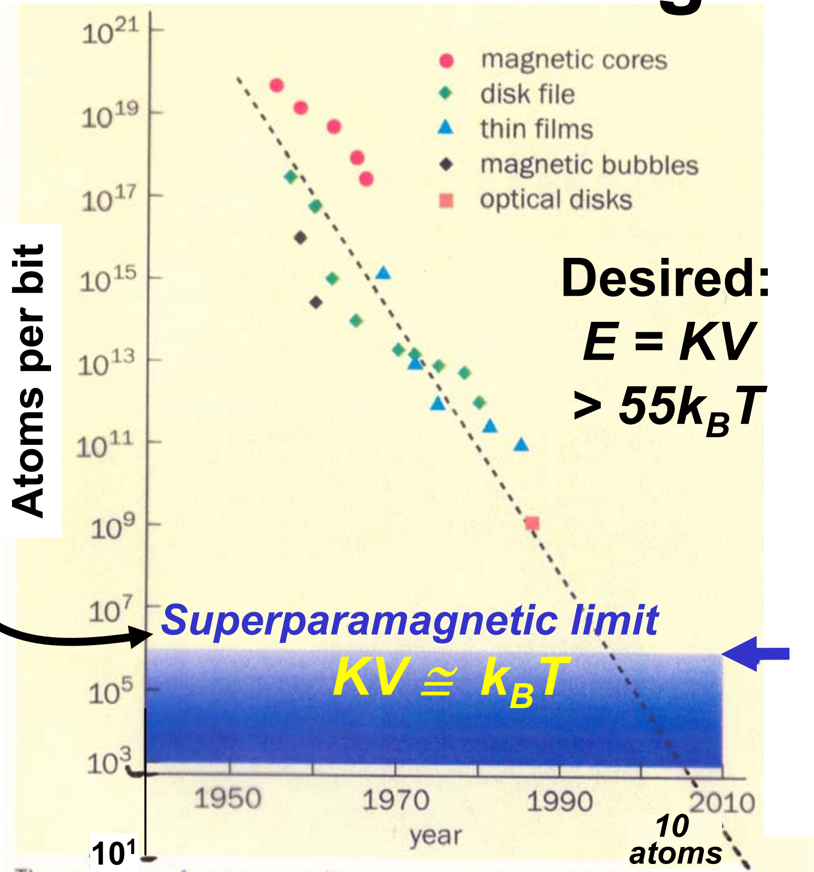
Doubling every year!

Now 170 Gbits/in^2 = 20 Gbytes/in^2

→ each bit ~14 nm x 30 nm x 210 nm

→ ≈ <u>4,000,000</u> atoms, read at GHz rates

How for can we go?



Superparamagnetic limit

$KV \cong k_BT$

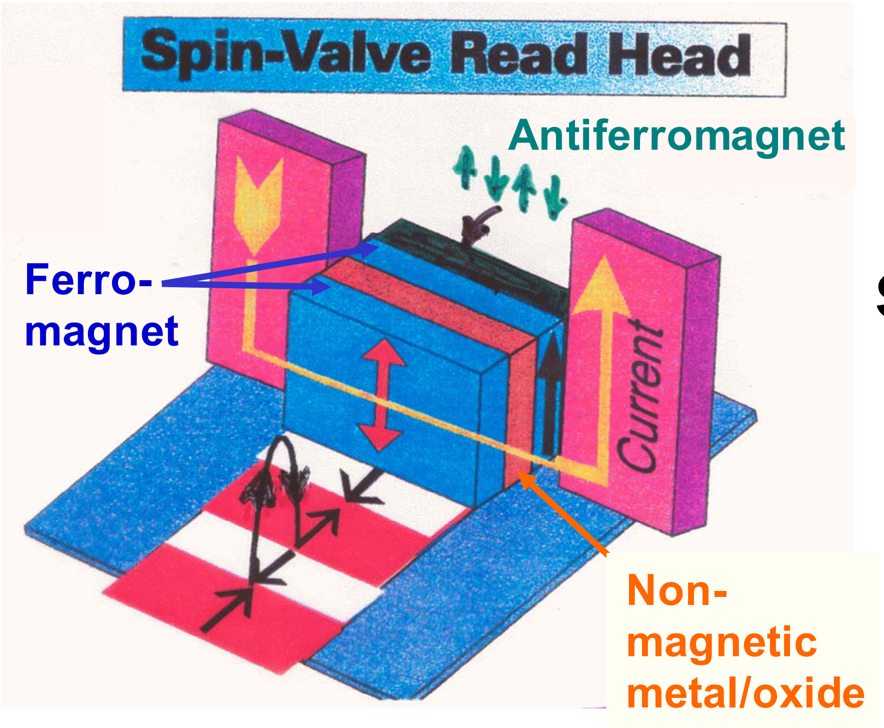
Desired:
$E = KV$
$> 55k_BT$

The number of atoms used to store one bit of information with different forms of magnetic or optical storage has reduced over the years. The blue region indicates the superparamagnetic regime, below which thermal fluctuations at room temperature could alter the orientation of magnetic bits.

http://www.research.ibm.com/journal/sj/422/grochowski.html

Harris, Awschalom
Physics World,
Jan. ‘99

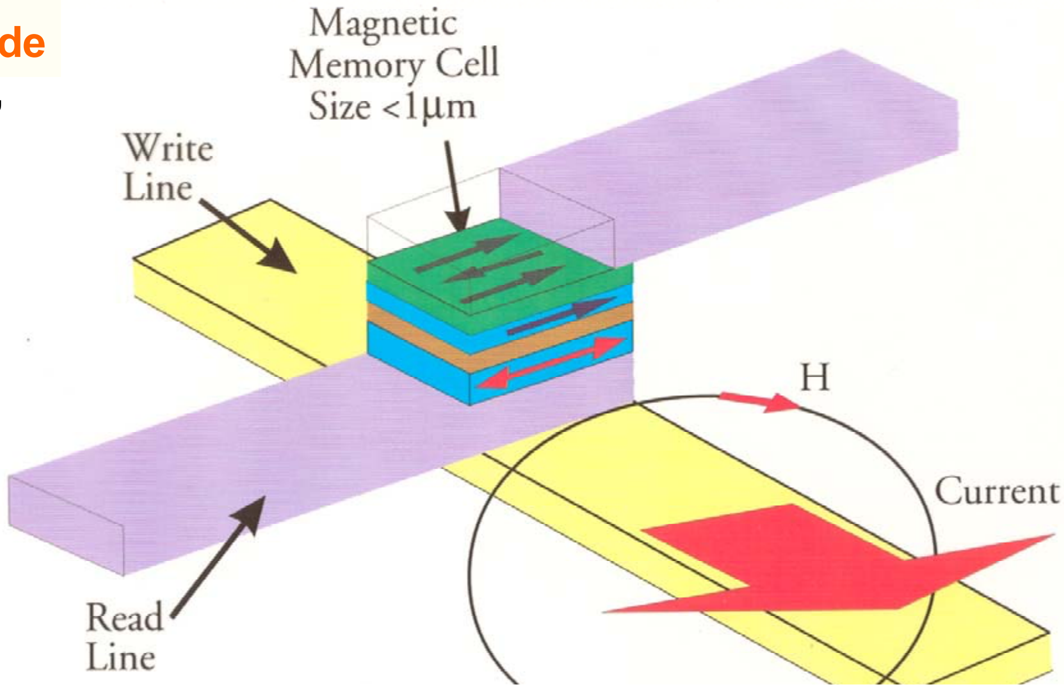
Some new directions with magnetic nanolayer structures--”spintronics”



Uses “giant magnetoresistance (GMR)” and “exchange bias” --in every high-speed read head now

Crucial surfaces & buried interfaces everywhere, as well as complex materials (e.g. colossal magnetoresistance (CMR))

Magnetic Random Access Memory (MRAM-Non Volatile)



Up to 100 Mbit devices in R&D: applications to e.g. cell phone use

Scientific and technological areas related to surface/interface/nano science:

- Integrated circuits—higher speed, higher density
- Magnetic storage—higher density, magnetic logic
- Catalysis—auto catalytic converter, petrochemical processing
- Corrosion—major annual economic cost
- Polymer surface modification—promote adhesion, fire resistance,…
- Batteries, fuel cells—the hydrogen economy?
- Lubrication (tribology)—nanometer-scale layers
- Atmospheric particulates—ice, carbonaceous,…
- Nuclear reactors and waste storage—how long-lasting?
- Environmental science—retention of contaminants in soil
- Biomaterials—compatibility through surface interactions
- Sensors—surface reactions→change in voltage, resistance

Outline

Surface, interface, and nanoscience—short introduction

➡ Some surface techniques and concepts

Experimental aspects: laboratory-based and SR-based

Electronic structure—a brief review

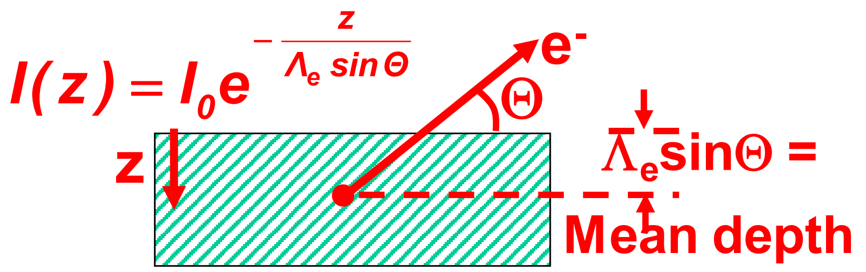
The basic synchrotron radiation techniques

Core-level photoemission

Valence-level photoemission

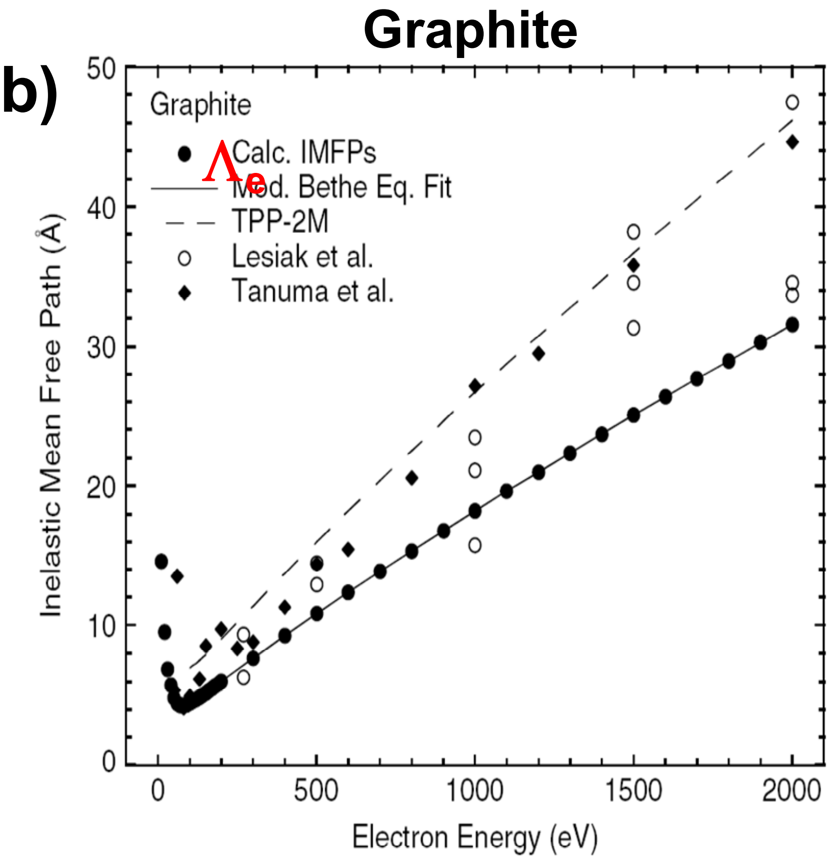
Electrons as surface probes: the electron inelastic mean free paths in solids

(a)

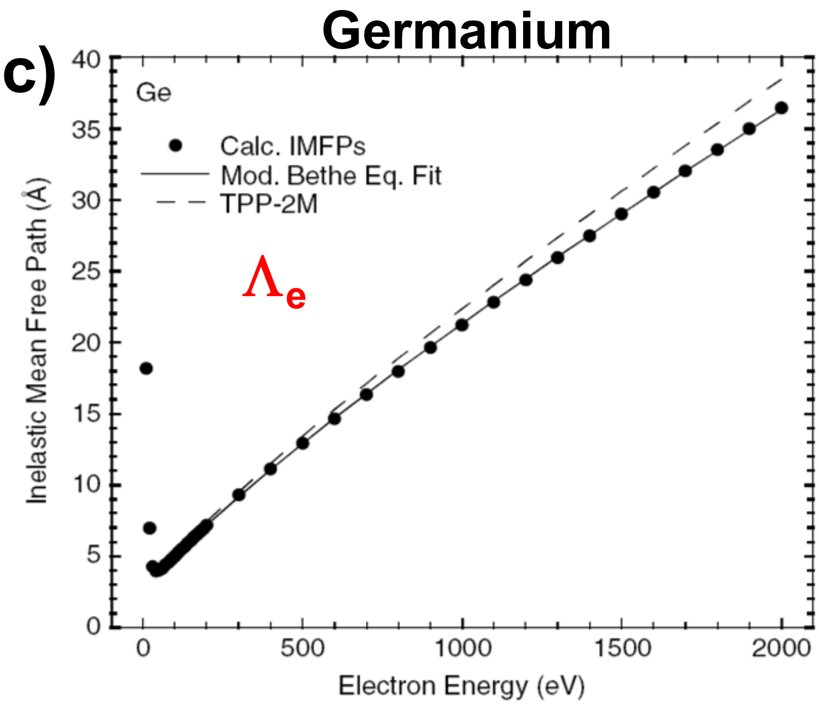


$$I(z) = I_0 e^{-\frac{z}{\Lambda_e \sin\Theta}}$$

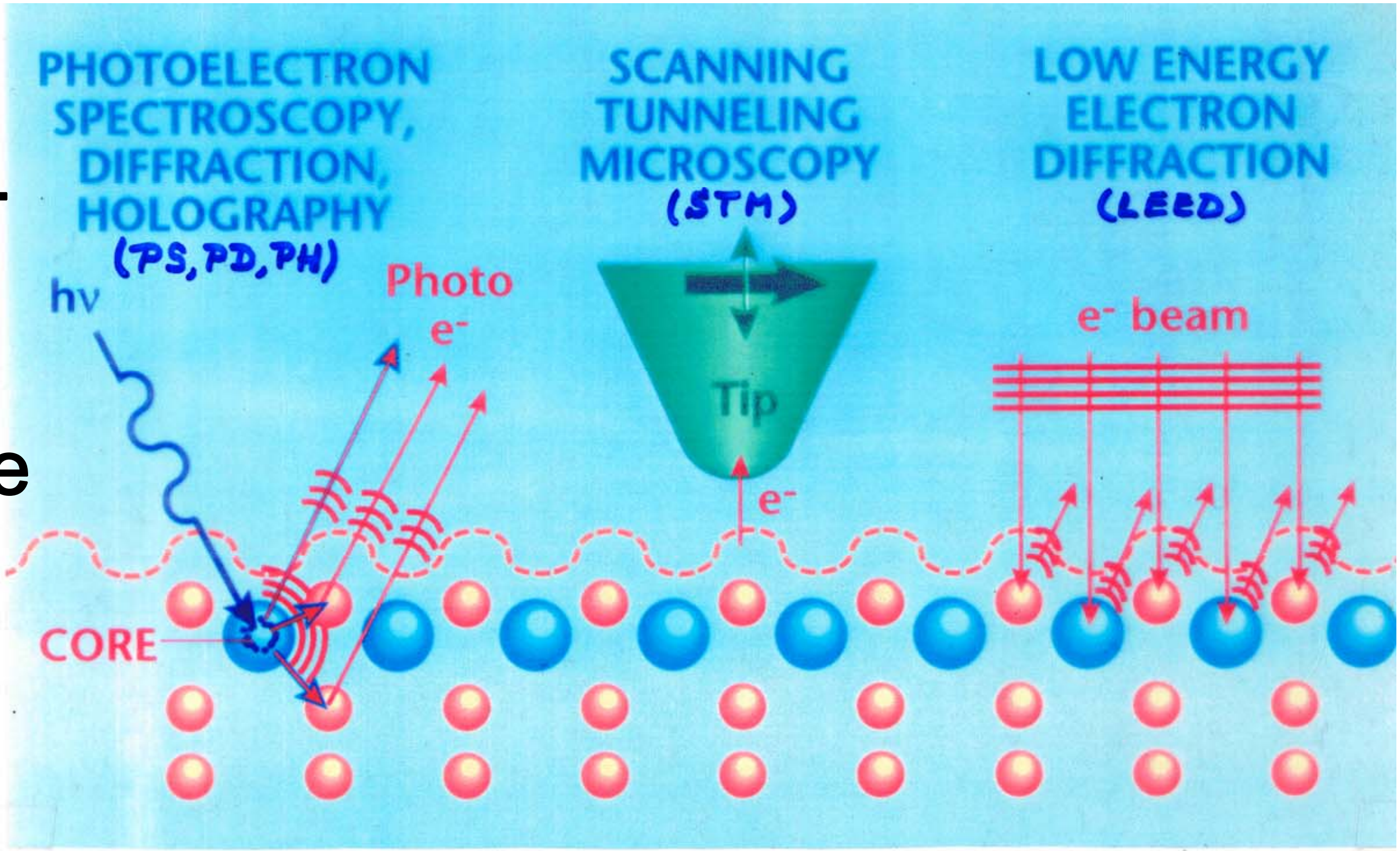
(b)



(c)

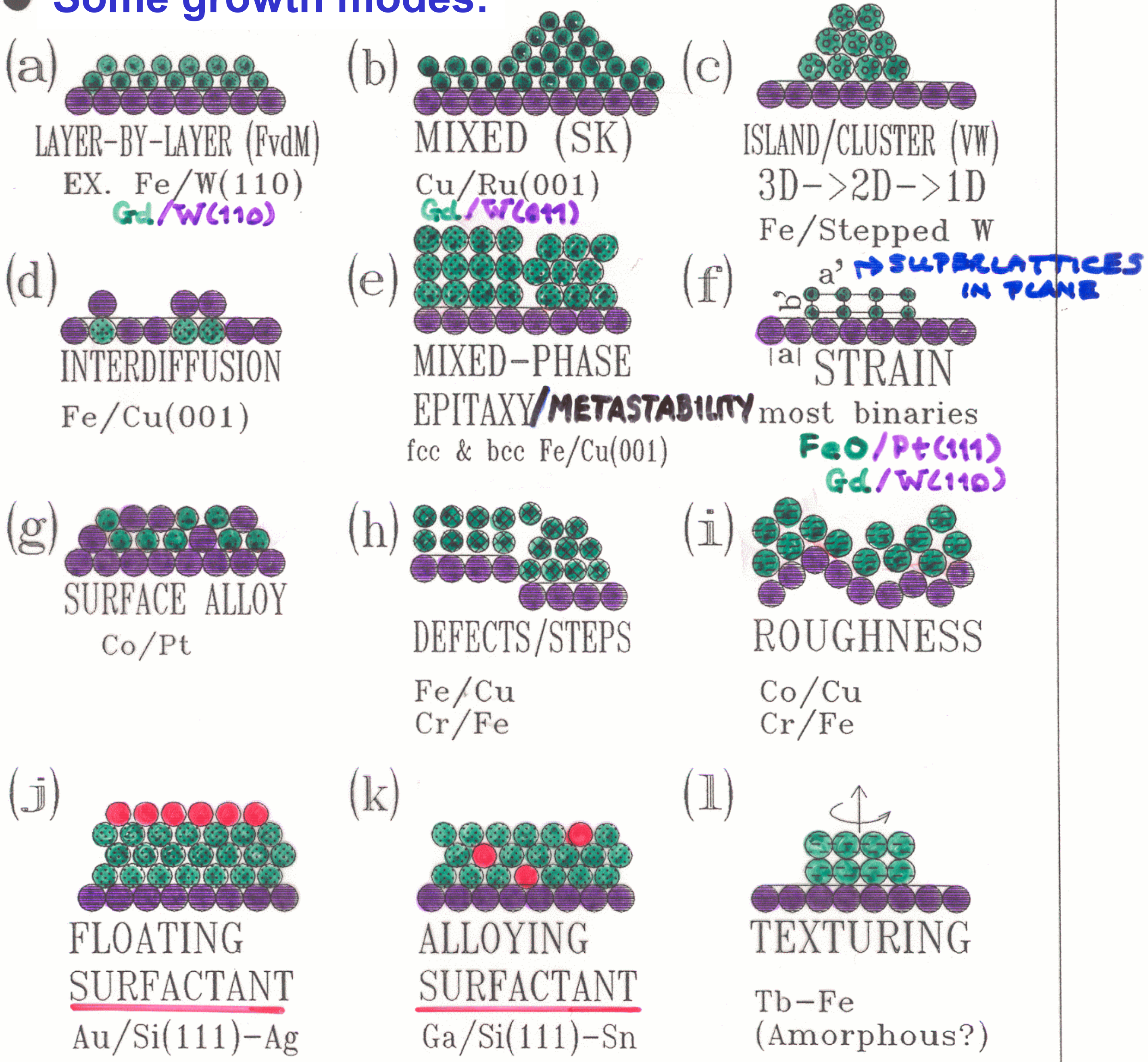


Some Complementary Surface Structure Probes

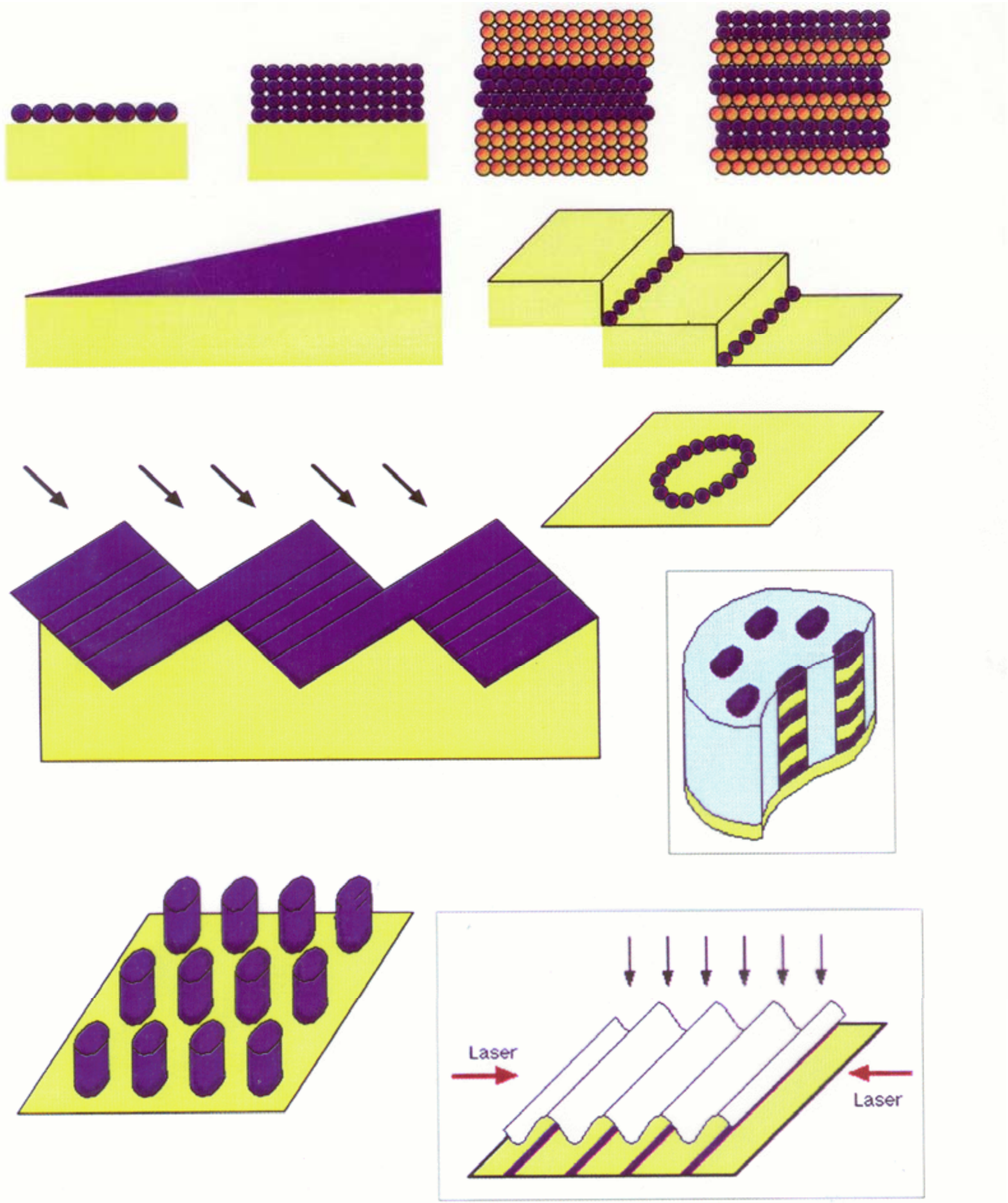


-Type of order:	Short (< 10Å)	Short, long and disorder	Long (> 100Å)
-Atom & site specific:	Yes	No	No
-Sensing depth:	5-40Å	Mostly surface D.O.S.	5-20Å
-Lateral resolution:	1 mm^2 to (300Å)^2	Single atom	1 mm^2 to 1 micron^2

- **Some growth modes:**

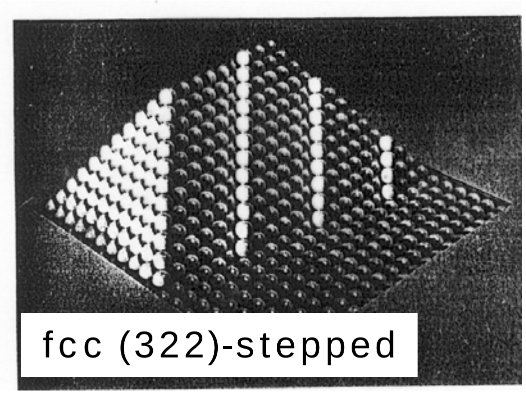


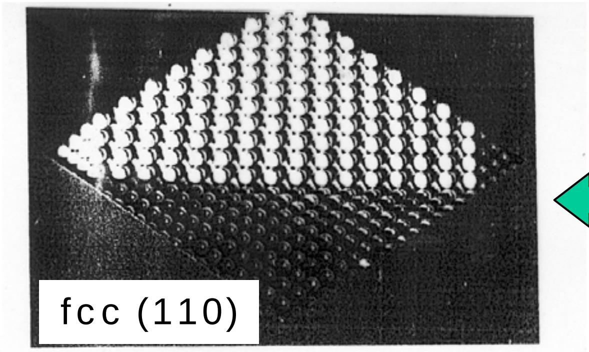
Some important structures in nanoscience/nanotechnology



KORTRIGHT
ET AL., J.M.M.
207, 44('99')

WHAT DO SURFACES LOOK LIKE?
SOME fcc AND bcc SURFACES


fcc (322)-stepped


fcc (110)

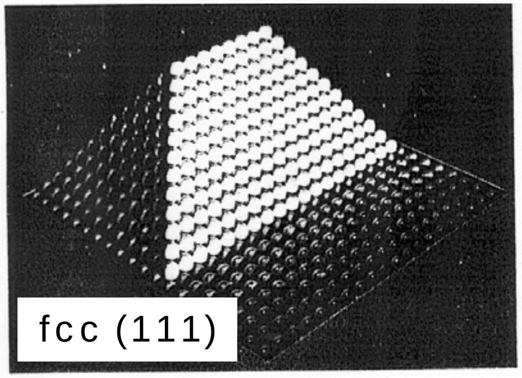
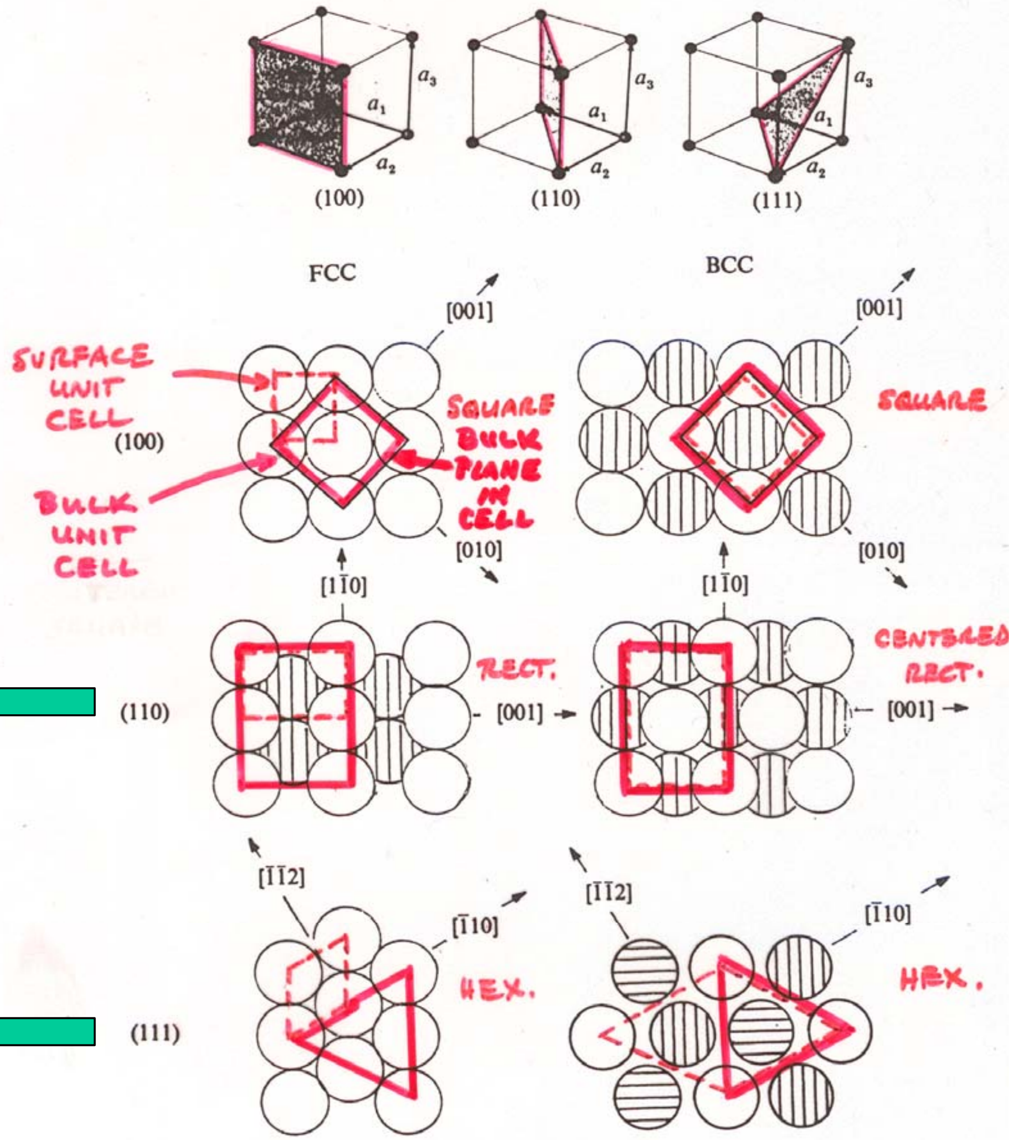
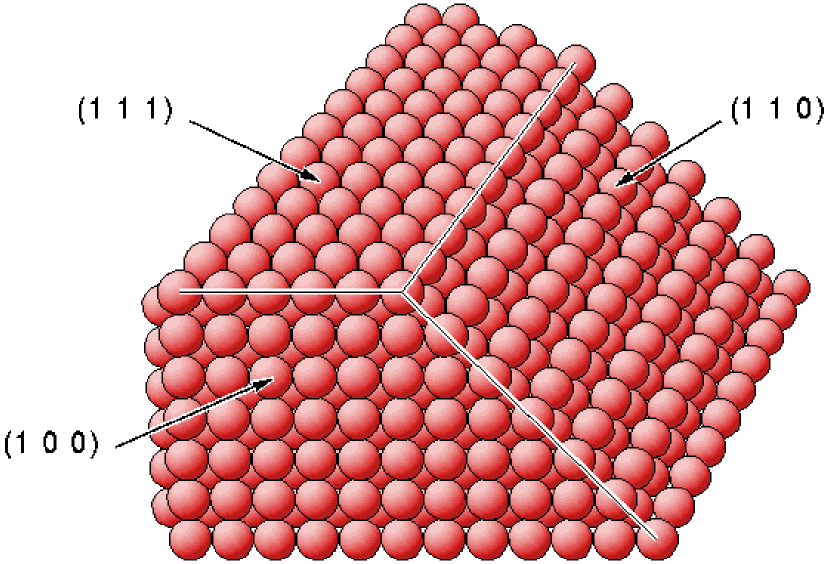

fcc (111)

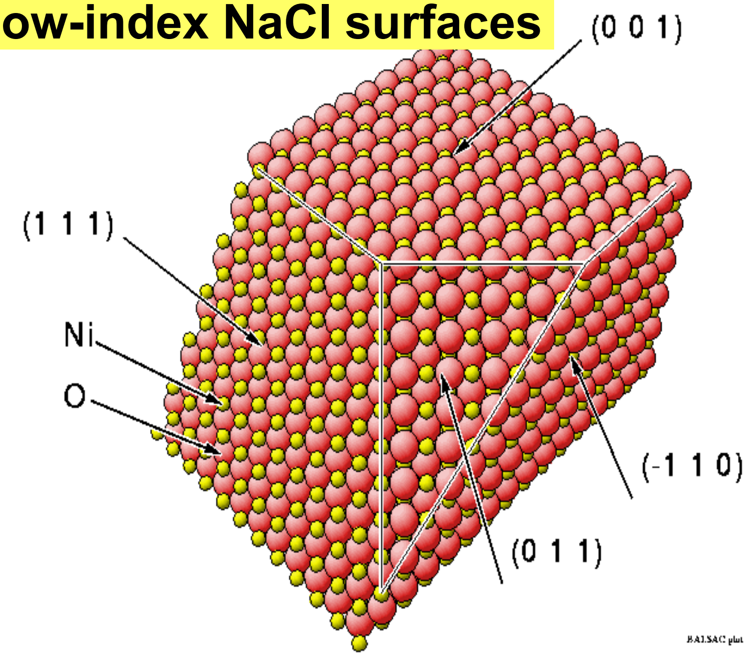
Fig. 3.2. Low-index ideal surfaces of a hard-sphere cubic crystal. Vertical and horizontal markings indicate the second and third atom layers, respectively. Cube face is indicated for (100) to set the scale (Nicholas, 1965).



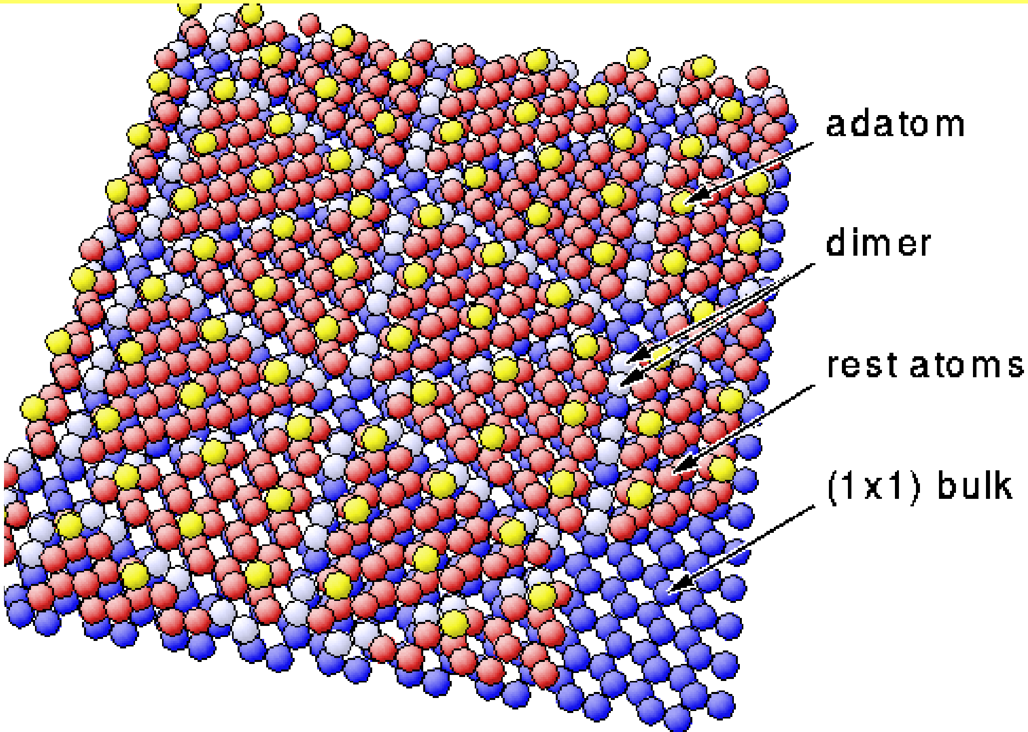
Low-index fcc metal surfaces



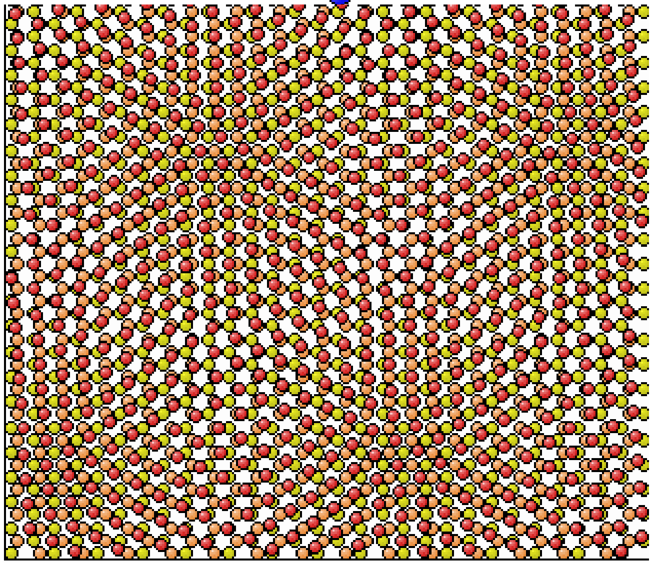
Low-index NaCl surfaces



Si(111)-(7x7)—Dimer-adatom-stacking fault model

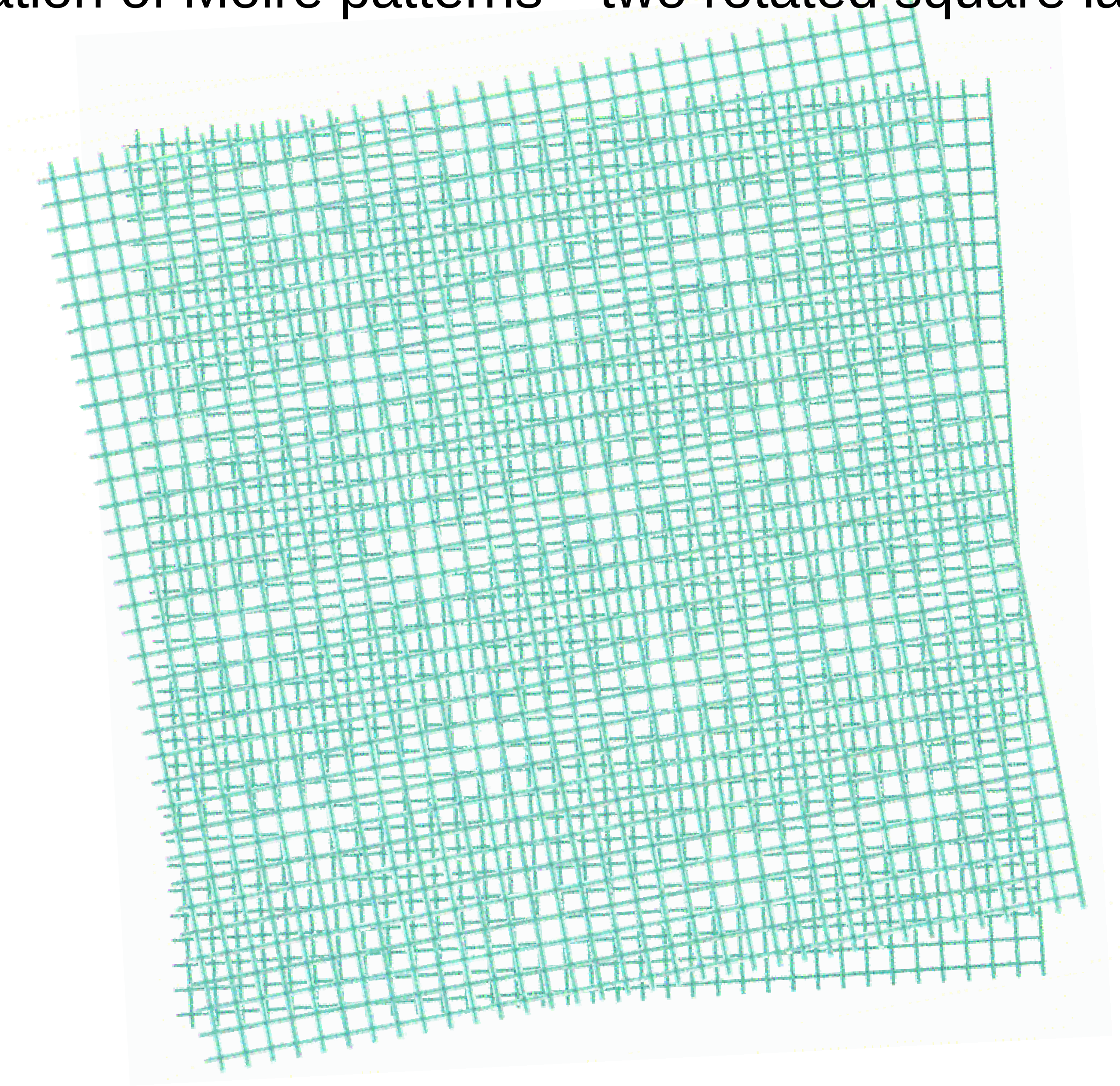


Fcc(111) super-lattice = a Moiré pattern: 4 degree rot'n.

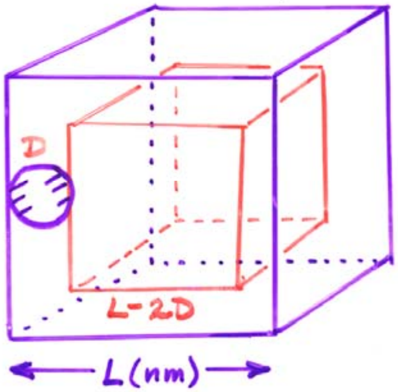


http://www.fhi-berlin.mpg.de/th/personal/hermann/pictures.html

Formation of Moire patterns—two rotated square lattices



FRACTION OF ATOMS ON THE SURFACE OF A CUBE: D = ATOMIC DIAM. ≈ 0.2 nm = 2 Å



$$\text{SURFACE FRACTION} = \frac{L^3-(L-2D)^3}{L^3}$$

L	FRACTION
1 μm = 1000 nm	0.001 = 0.1%
0.1 μm = 100 nm	0.012 ≈ 1.2%
0.01 μm = 10 nm	0.115 = 11.5%
0.001 μm = 1 nm	0.784 = 78.4%

Nanoscience is surface science

SOME UNITS:

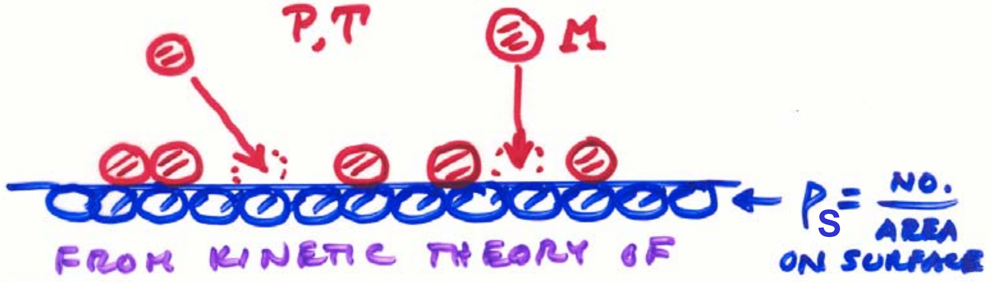
1 HAIR ≈ 50 microns

1 micron = 10^{-6} m = 1,000 nm = 10,000 Å
≈ 5,000 atoms

0.001 micron = 10^{-9} m = 1 nanometer = 1 nm = 10 Å
≈ 5 atoms

WHY IS ULTRAHIGH VACUUM IMPORTANT?

TIME TO BUILD UP A SINGLE ATOMIC/MOLECULAR LAYER = 1 MONOLAYER ≡ 1 ML IF EACH ATOM/MOLECULE FROM GAS PHASE HITTING SURFACE STICKS: τ_1



FROM KINETIC THEORY OF GASES:

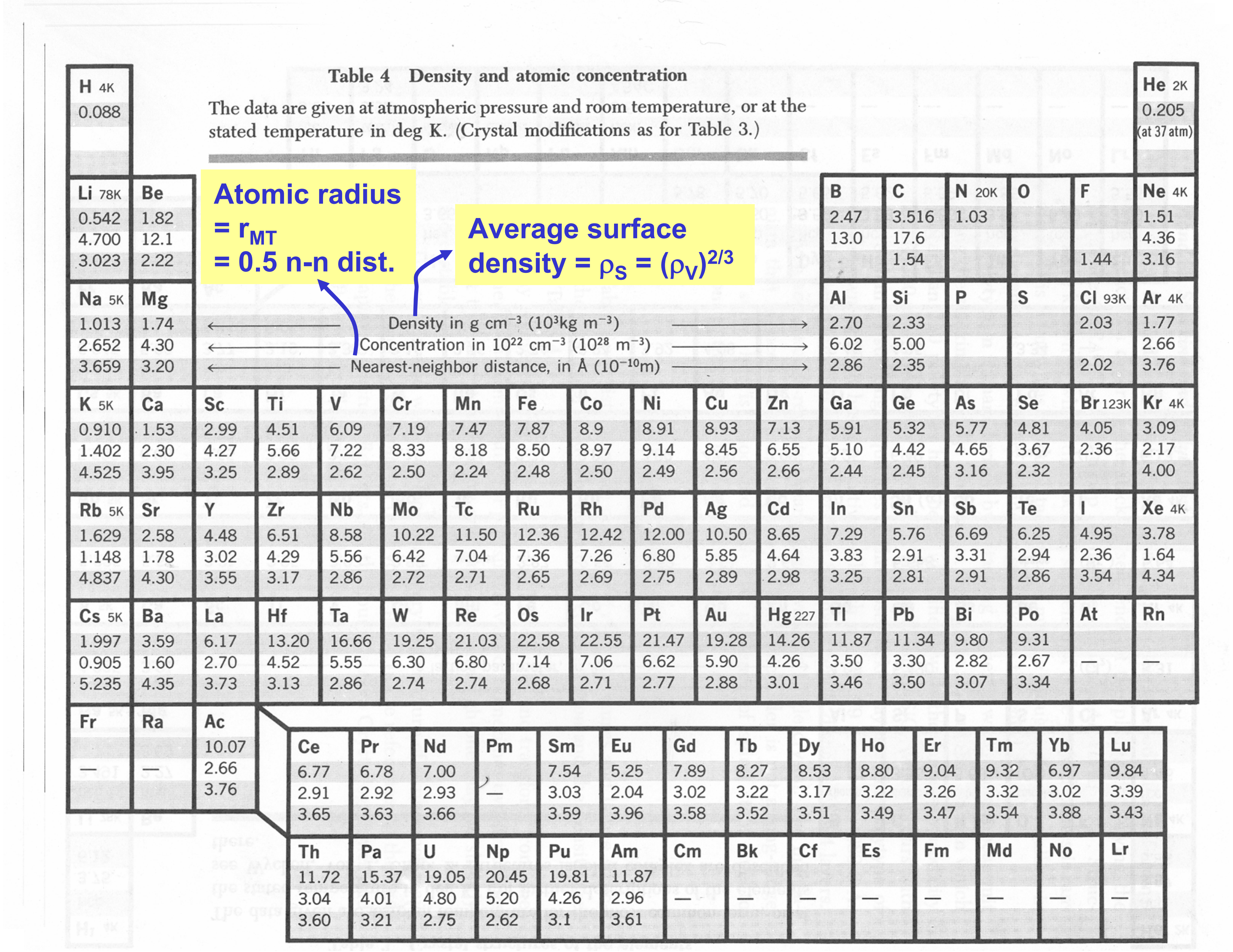
$$\tau_1\,(\text{sec}) = 2.84 \times 10^{-23}[T(K)M]^{1/2}\rho_S(\text{cm}^{-2})/P(\text{torr})$$

N_2, CO O_2
↓ ↓

WITH TYPICAL NOS. FOR $M = 28, 32$
$T = 298K$
$\rho_S = 1-2 \times 10^{15}\ \text{cm}^{-2}$
↑
METALS, SEMICOND.

	τ_1	P
	1 s	10^{-6} torr
	100 s ~2 min	10^{-8} "
	~15 min	10^{-9} "
TYPICAL [	~2.8 hr	10^{-10} "
	~27.8 hr	10^{-11} "

→ **Need to work at ~10^{-10}-10^{-11} torr**



Atomic radius = r_{MT} = 0.5 n-n dist.

Average surface density = $\rho_S = (\rho_V)^{2/3}$

Table 4 Density and atomic concentration

The data are given at atmospheric pressure and room temperature, or at the stated temperature in deg K. (Crystal modifications as for Table 3.)

← Density in g cm^{-3} (10^3 kg m^{-3}) →

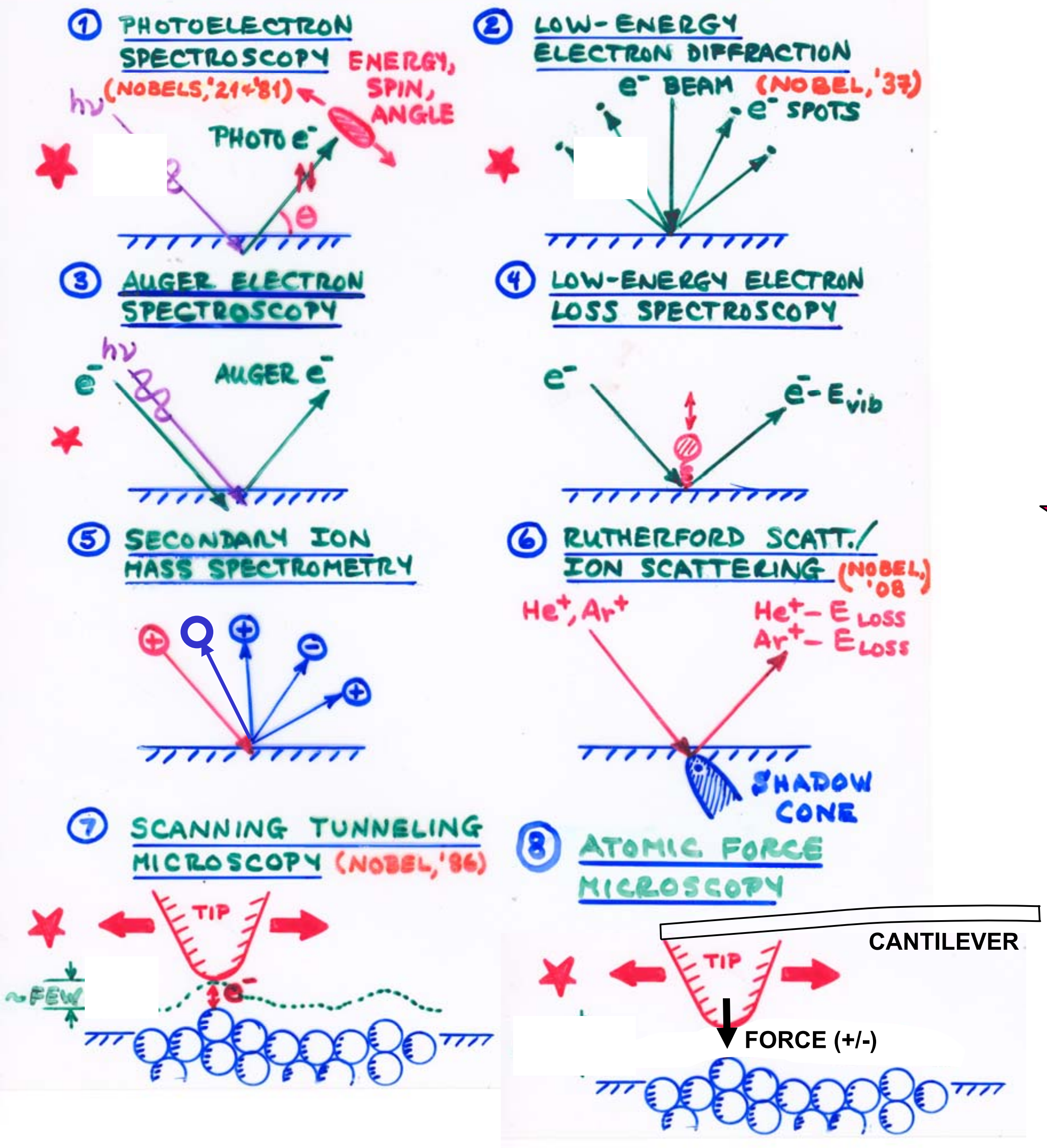
← Concentration in 10^{22} cm^{-3} (10^{28} m^{-3}) →

← Nearest-neighbor distance, in Å (10^{-10}m) →

H 4K																	He 2K
0.088																	0.205
																	(at 37 atm)
Li 78K	Be											B	C	N 20K	O	F	Ne 4K
0.542	1.82											2.47	3.516	1.03			1.51
4.700	12.1											13.0	17.6				4.36
3.023	2.22												1.54			1.44	3.16
Na 5K	Mg											Al	Si	P	S	Cl 93K	Ar 4K
1.013	1.74											2.70	2.33			2.03	1.77
2.652	4.30											6.02	5.00				2.66
3.659	3.20											2.86	2.35			2.02	3.76
K 5K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br 123K	Kr 4K
0.910	1.53	2.99	4.51	6.09	7.19	7.47	7.87	8.9	8.91	8.93	7.13	5.91	5.32	5.77	4.81	4.05	3.09
1.402	2.30	4.27	5.66	7.22	8.33	8.18	8.50	8.97	9.14	8.45	6.55	5.10	4.42	4.65	3.67	2.36	2.17
4.525	3.95	3.25	2.89	2.62	2.50	2.24	2.48	2.50	2.49	2.56	2.66	2.44	2.45	3.16	2.32		4.00
Rb 5K	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe 4K
1.629	2.58	4.48	6.51	8.58	10.22	11.50	12.36	12.42	12.00	10.50	8.65	7.29	5.76	6.69	6.25	4.95	3.78
1.148	1.78	3.02	4.29	5.56	6.42	7.04	7.36	7.26	6.80	5.85	4.64	3.83	2.91	3.31	2.94	2.36	1.64
4.837	4.30	3.55	3.17	2.86	2.72	2.71	2.65	2.69	2.75	2.89	2.98	3.25	2.81	2.91	2.86	3.54	4.34
Cs 5K	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg 227	Tl	Pb	Bi	Po	At	Rn
1.997	3.59	6.17	13.20	16.66	19.25	21.03	22.58	22.55	21.47	19.28	14.26	11.87	11.34	9.80	9.31		
0.905	1.60	2.70	4.52	5.55	6.30	6.80	7.14	7.06	6.62	5.90	4.26	3.50	3.30	2.82	2.67	—	—
5.235	4.35	3.73	3.13	2.86	2.74	2.74	2.68	2.71	2.77	2.88	3.01	3.46	3.50	3.07	3.34		
Fr	Ra	Ac															
		10.07															
—	—	2.66															
		3.76															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
6.77	6.78	7.00		7.54	5.25	7.89	8.27	8.53	8.80	9.04	9.32	6.97	9.84
2.91	2.92	2.93	—	3.03	2.04	3.02	3.22	3.17	3.22	3.26	3.32	3.02	3.39
3.65	3.63	3.66		3.59	3.96	3.58	3.52	3.51	3.49	3.47	3.54	3.88	3.43
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
11.72	15.37	19.05	20.45	19.81	11.87								
3.04	4.01	4.80	5.20	4.26	2.96	—	—	—	—	—	—	—	—
3.60	3.21	2.75	2.62	3.1	3.61								

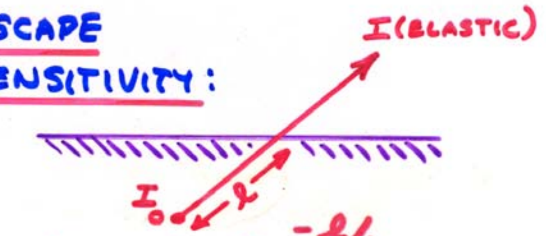
SOME SURFACE-ANALYTICAL TECHNIQUES



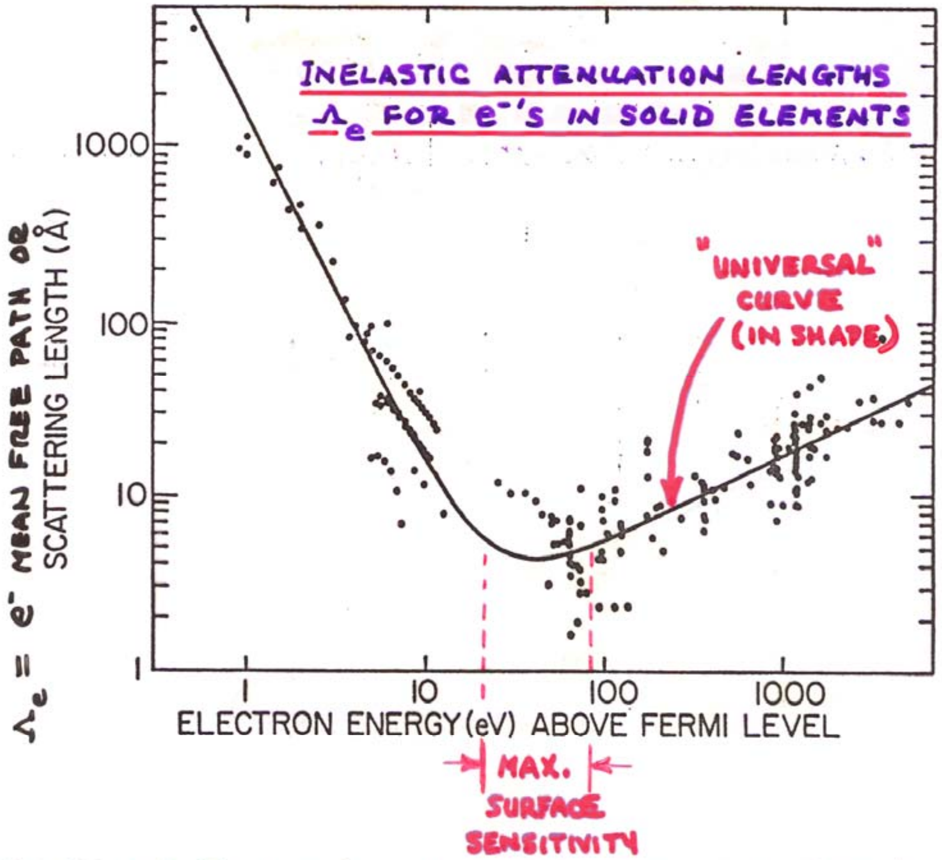
★ = AT UC DAVIS

Why are electrons so useful as probes of surfaces?

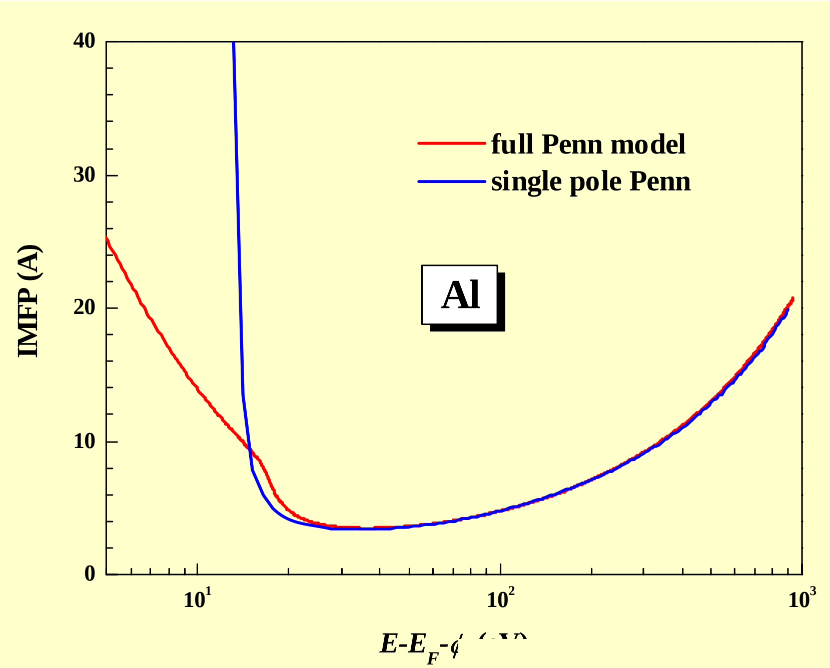
ELECTRON ESCAPE + SURFACE SENSITIVITY:

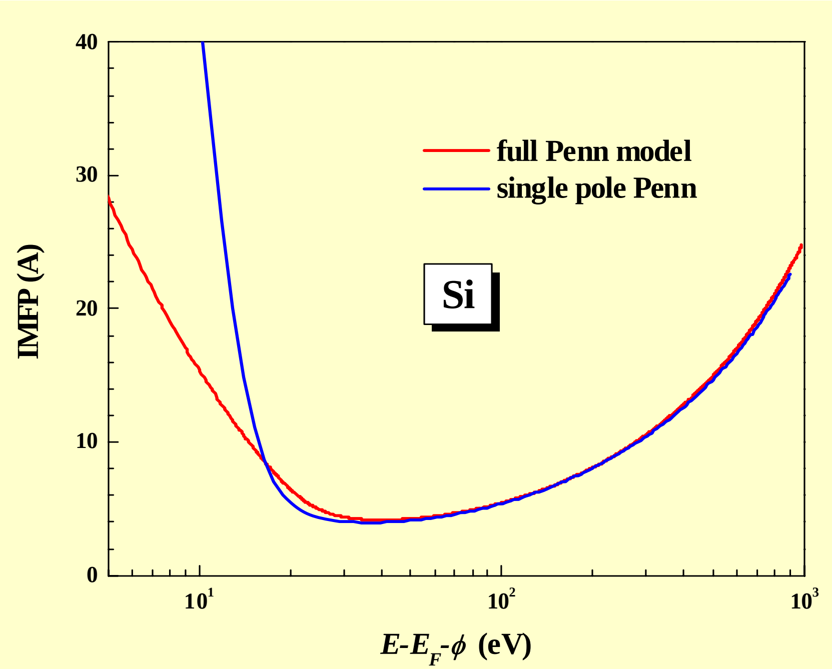


$$I(\text{ELASTIC}) = I_0 e^{-\ell/\Lambda_e}$$

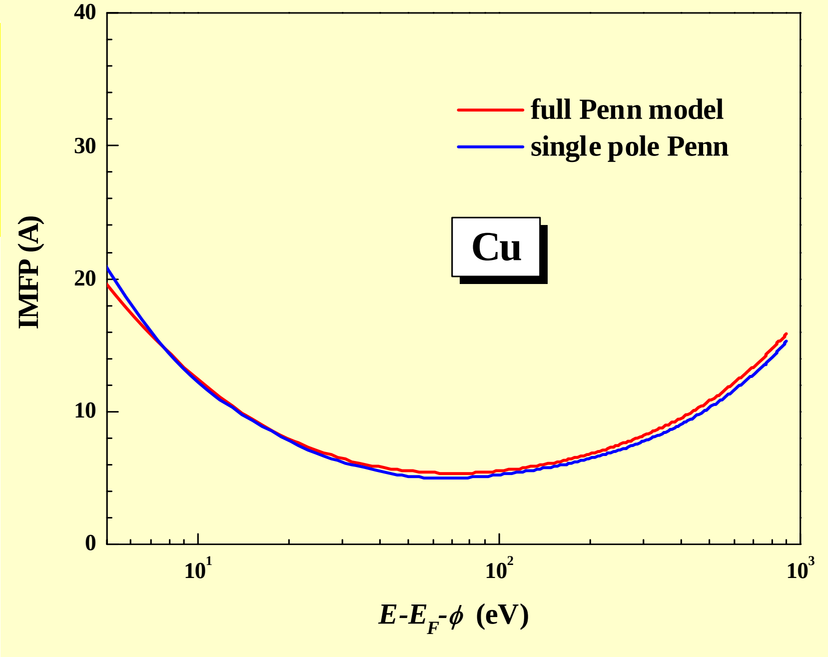


COMPILATIONS: Seah + Dench, Surf. Int. Anal. 1, 2 (1979)
Tanuma, Powell, + Penn, Surf. Int. Anal.
17, 911 + 927 (1991); 21, 165 (1994)
Powell + Jablonski, J. Phys. Chem. Ref.
Data 28, 19 (1999); Surf. Int. Anal.
29, 108 (2000)





More realistic look at low-energy inelastic mean free paths--theory

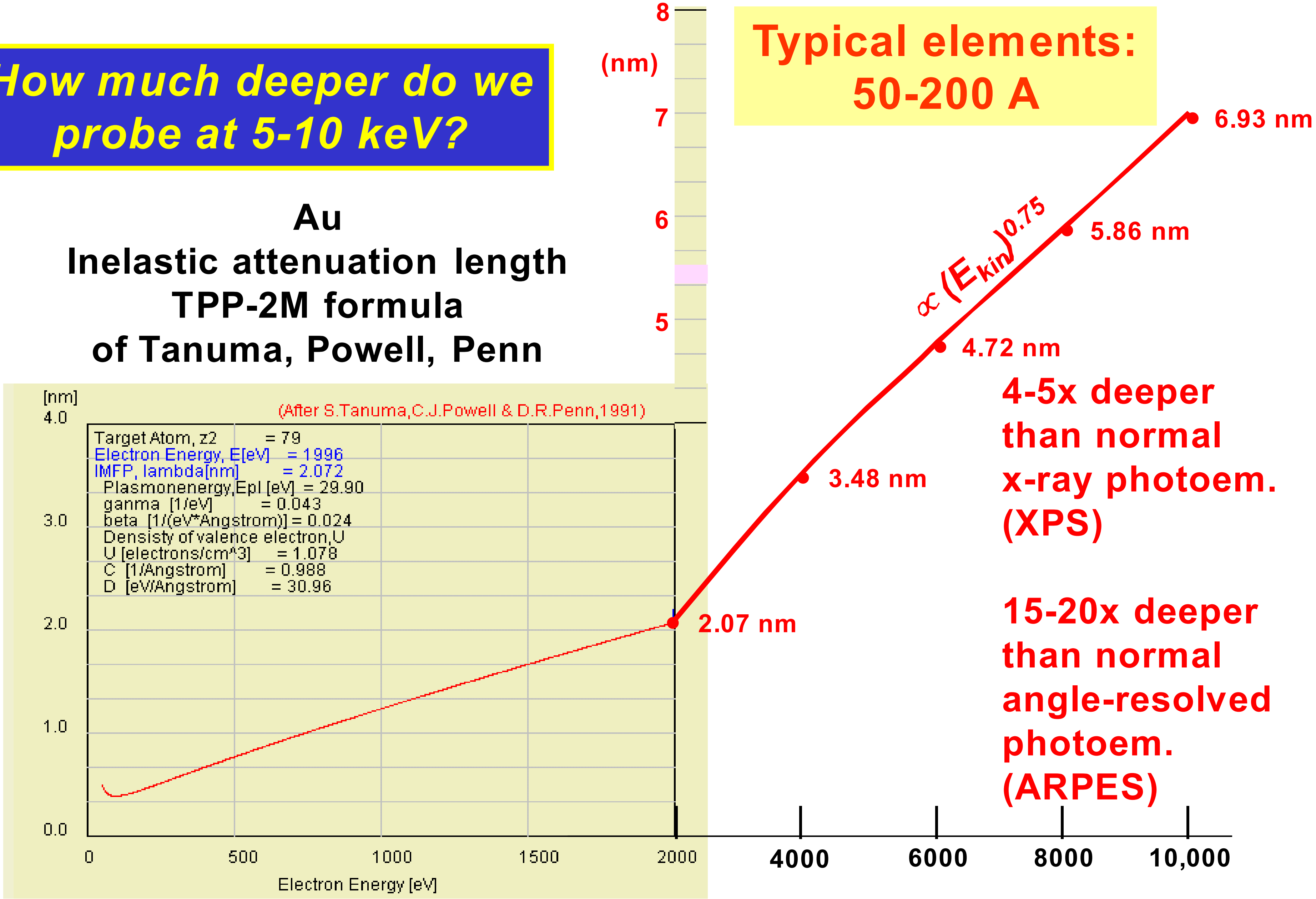


IMFPs do not necessarily go up drastically at lower energy

S.F. Mao and Z.J. Ding, Hefei (TBP)

How much deeper do we probe at 5-10 keV?

Au
Inelastic attenuation length
TPP-2M formula
of Tanuma, Powell, Penn



(After S.Tanuma,C.J.Powell & D.R.Penn,1991)

```
Target Atom, z2         = 79
Electron Energy, E[eV]   = 1996
IMFP, lambda[nm]        = 2.072
  Plasmonenergy,Epl [eV]  = 29.90
  ganma  [1/eV]        = 0.043
  beta  [1/(eV*Angstrom)] = 0.024
  Densisty of valence electron,U
  U [electrons/cm^3]     = 1.078
  C  [1/Angstrom]        = 0.988
  D  [eV/Angstrom]        = 30.96
```

Typical elements:
50-200 A

4-5x deeper than normal x-ray photoem. (XPS)

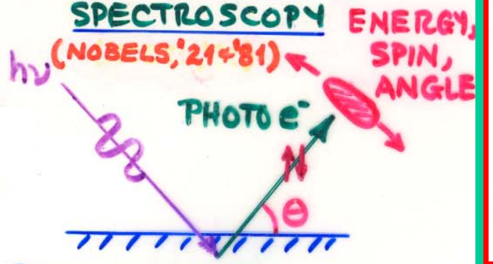
15-20x deeper than normal angle-resolved photoem. (ARPES)

http://www.ss.teen.setsunan.ac.jp/e-imfp.html

SOME SURFACE-ANALYTICAL TECHNIQUES

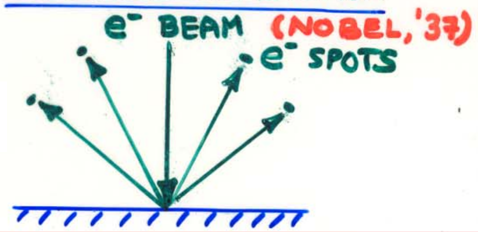
① PHOTOELECTRON SPECTROSCOPY

(NOBELS,'21+'81)

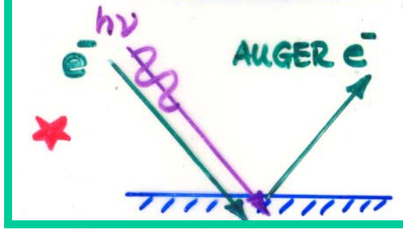


② LOW-ENERGY ELECTRON DIFFRACTION

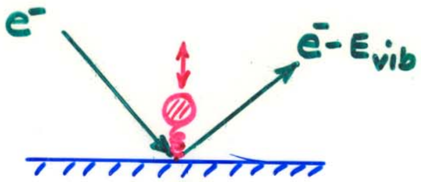
(NOBEL,'37)



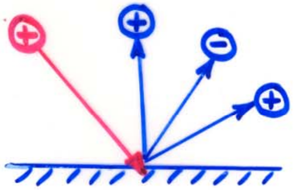
③ AUGER ELECTRON SPECTROSCOPY



④ LOW-ENERGY ELECTRON LOSS SPECTROSCOPY

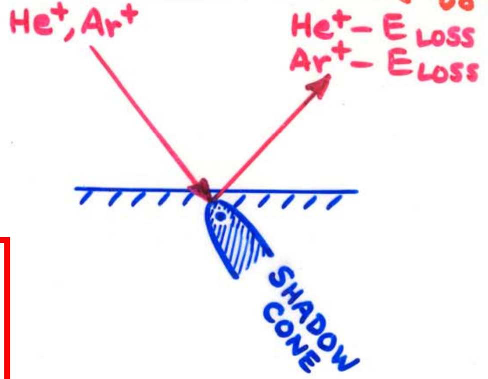


⑤ SECONDARY ION MASS SPECTROMETRY



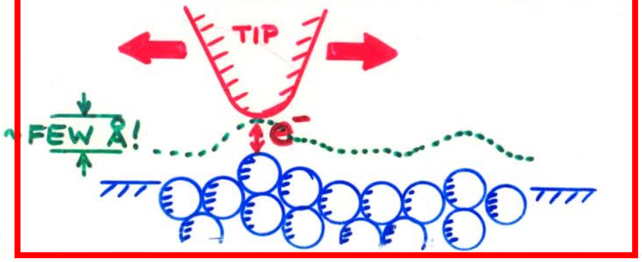
⑥ RUTHERFORD SCATT./ ION SCATTERING

(NOBEL,'08)



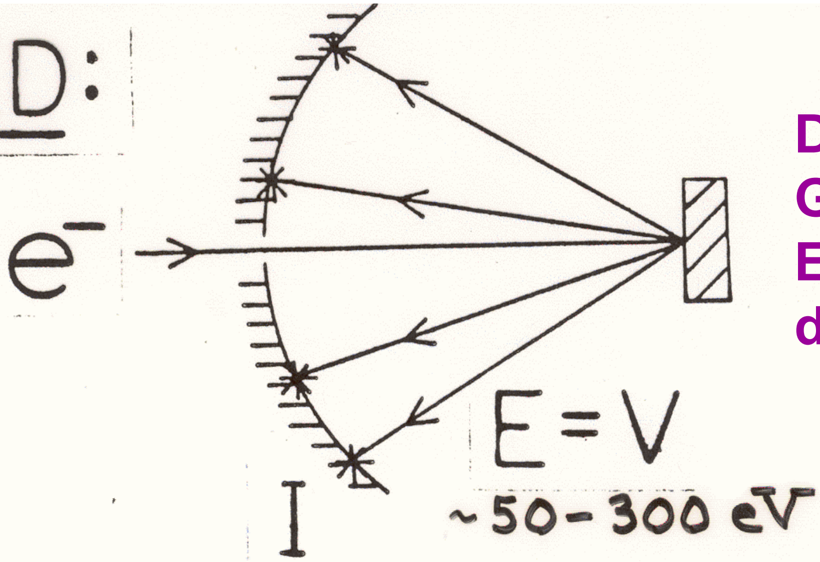
⑦ SCANNING TUNNELING MICROSCOPY

(NOBEL,'86)



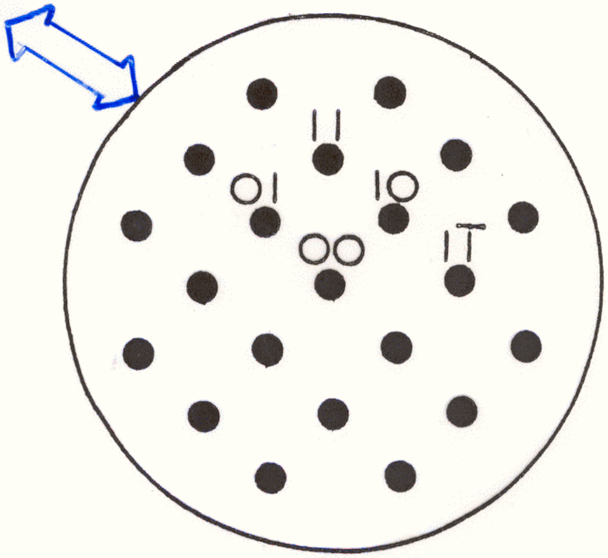
LOW ENERGY ELECTRON DIFFRACTION

LEED:



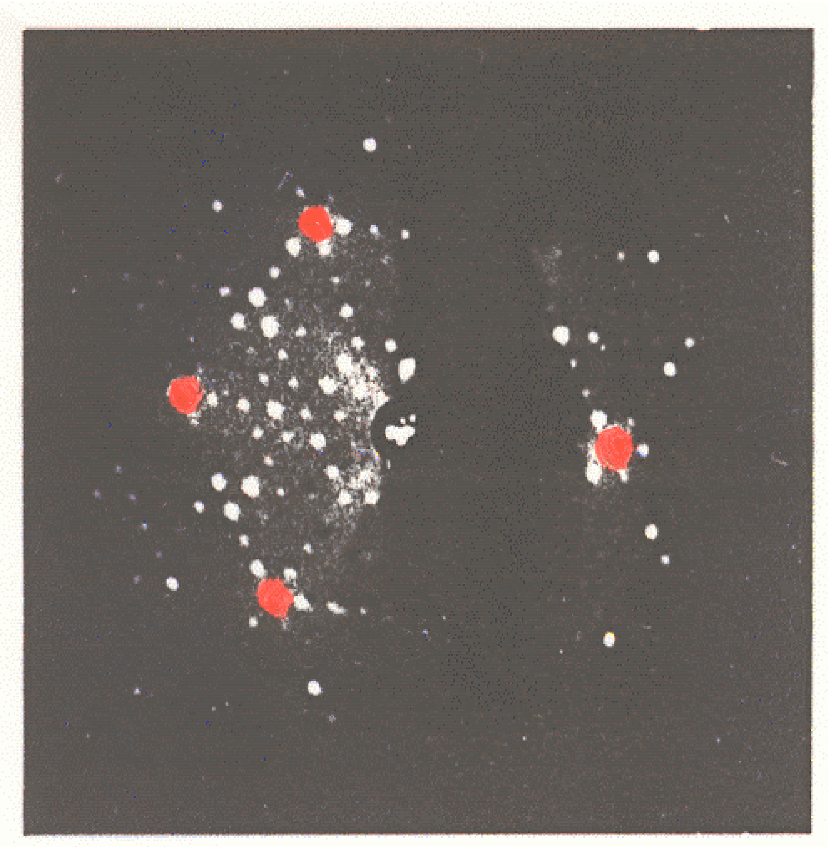
Davisson & Germer (1927): Electrons are de Broglie waves

TWO-DIMENSIONAL SURFACE RECIPROCAL LATTICE

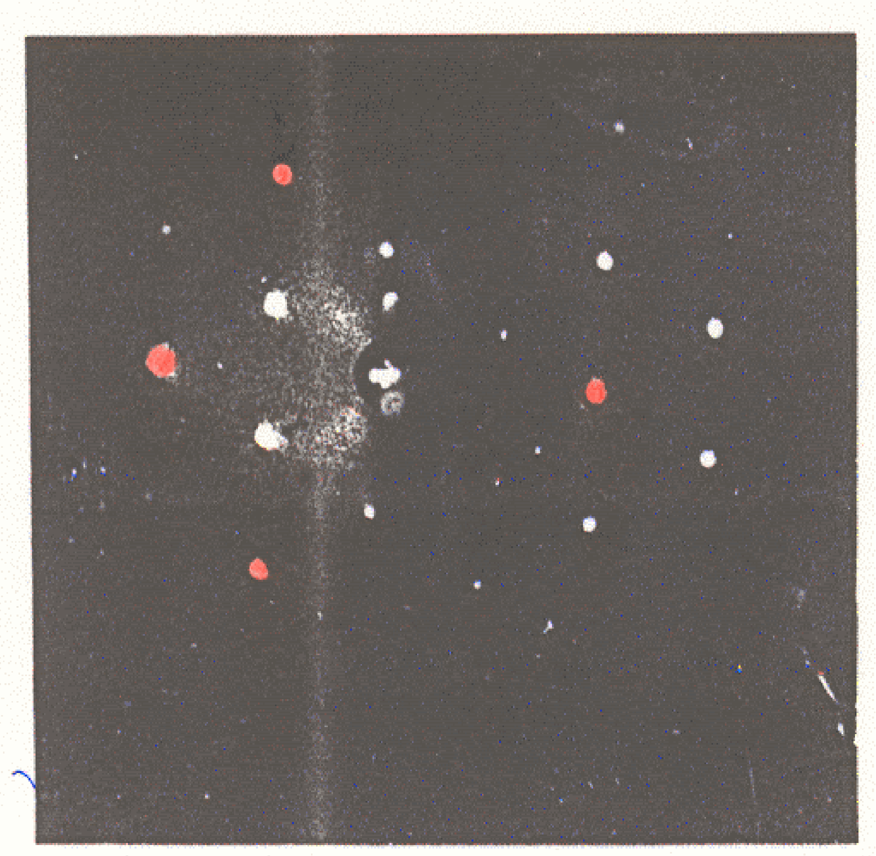


LONG-RANGE ORDER REQUIRED OVER ≳100Å.

SOME TYPICAL LEED PATTERNS:



Si(111)-(7x7)

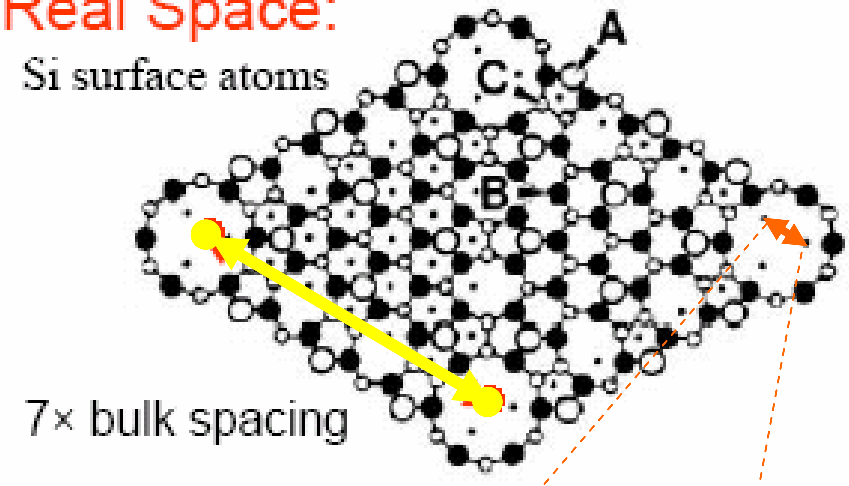


(√3 x √3)R30° Ag/Si(111)

● = spots seen without any reconstruction or adsorption of simple Si(111) surface

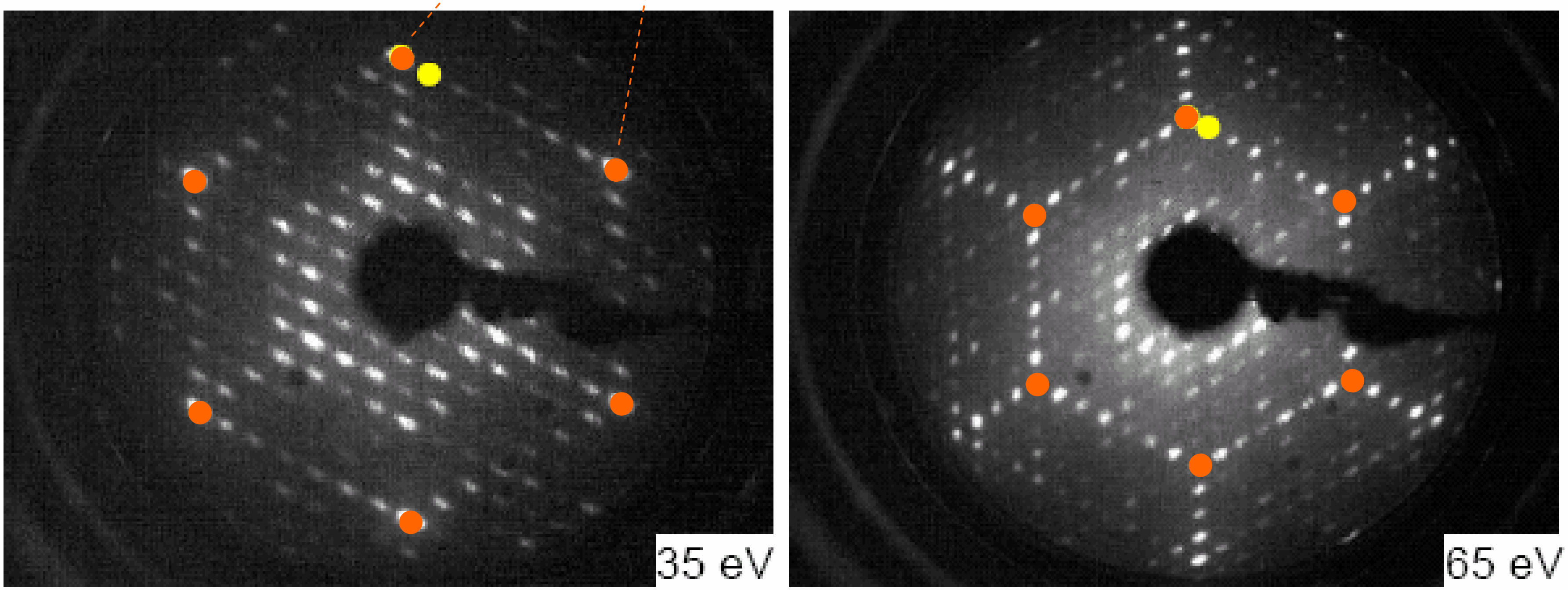
LEED: Si(111)7x7

Real Space:



- Longer periodicities in real space give closer spots in k-space.
- Higher energy LEED images show spots closer together.

K-Space



SCANNING TUNNELING MICROSCOPY

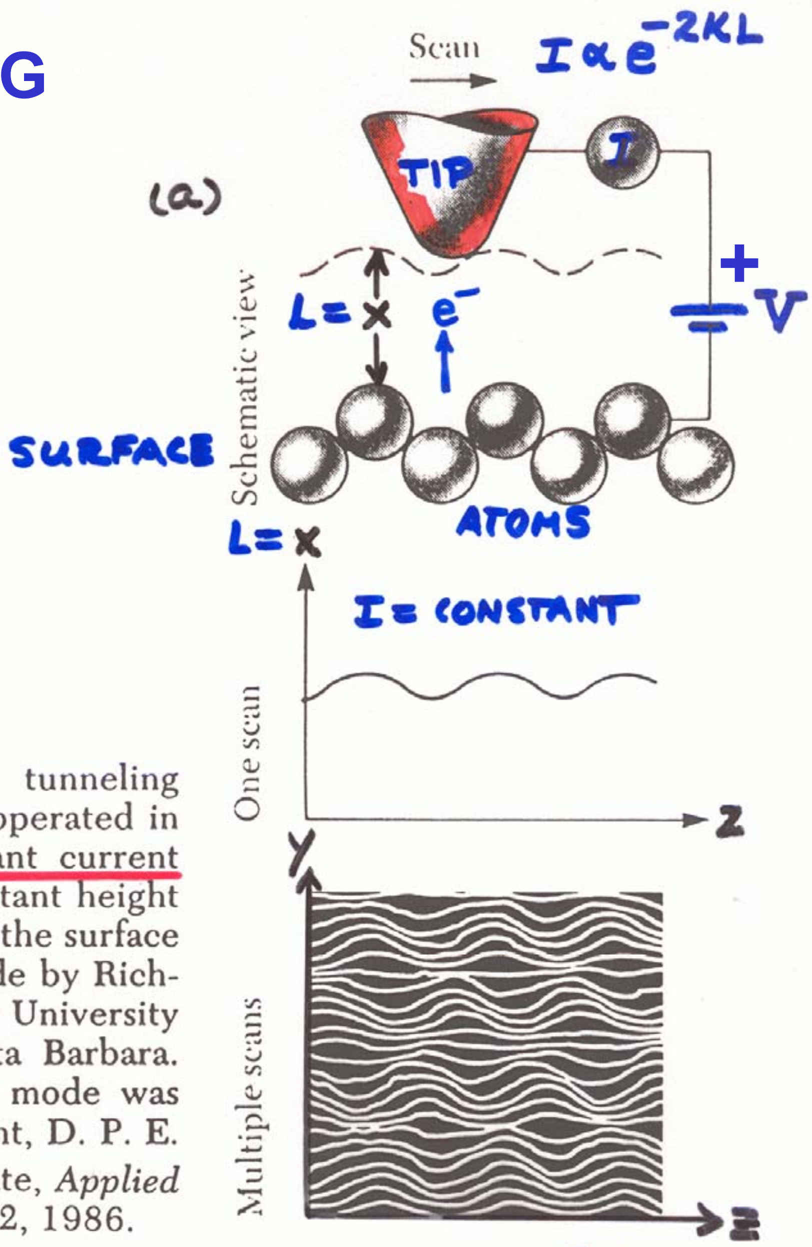
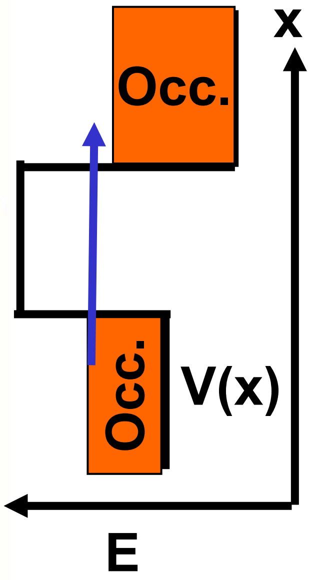


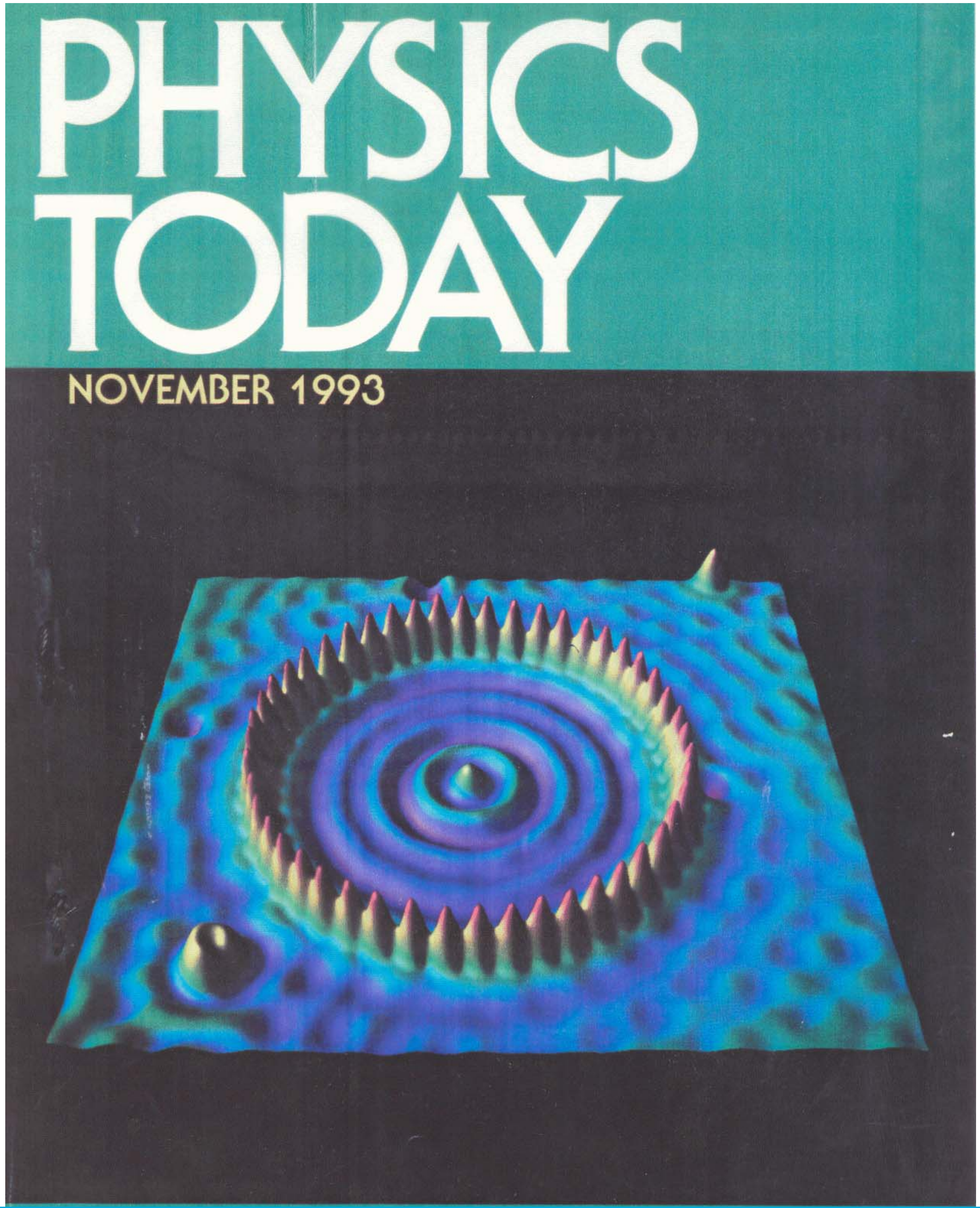
Figure 4 Scanning tunneling microscopes can be operated in either (a) the constant current mode or (b) the constant height mode. The images of the surface of graphite were made by Richard Sonnenfeld at the University of California at Santa Barbara. The constant height mode was first used by A. Bryant, D. P. E. Smith, and C. F. Quate, *Applied Physics Letters* 48: 832, 1986.

$\Delta x = \Delta L \approx 0.01 \text{Å}!$

$\Delta y = \Delta z \approx 0.3\text{-}0.4 \text{Å}$

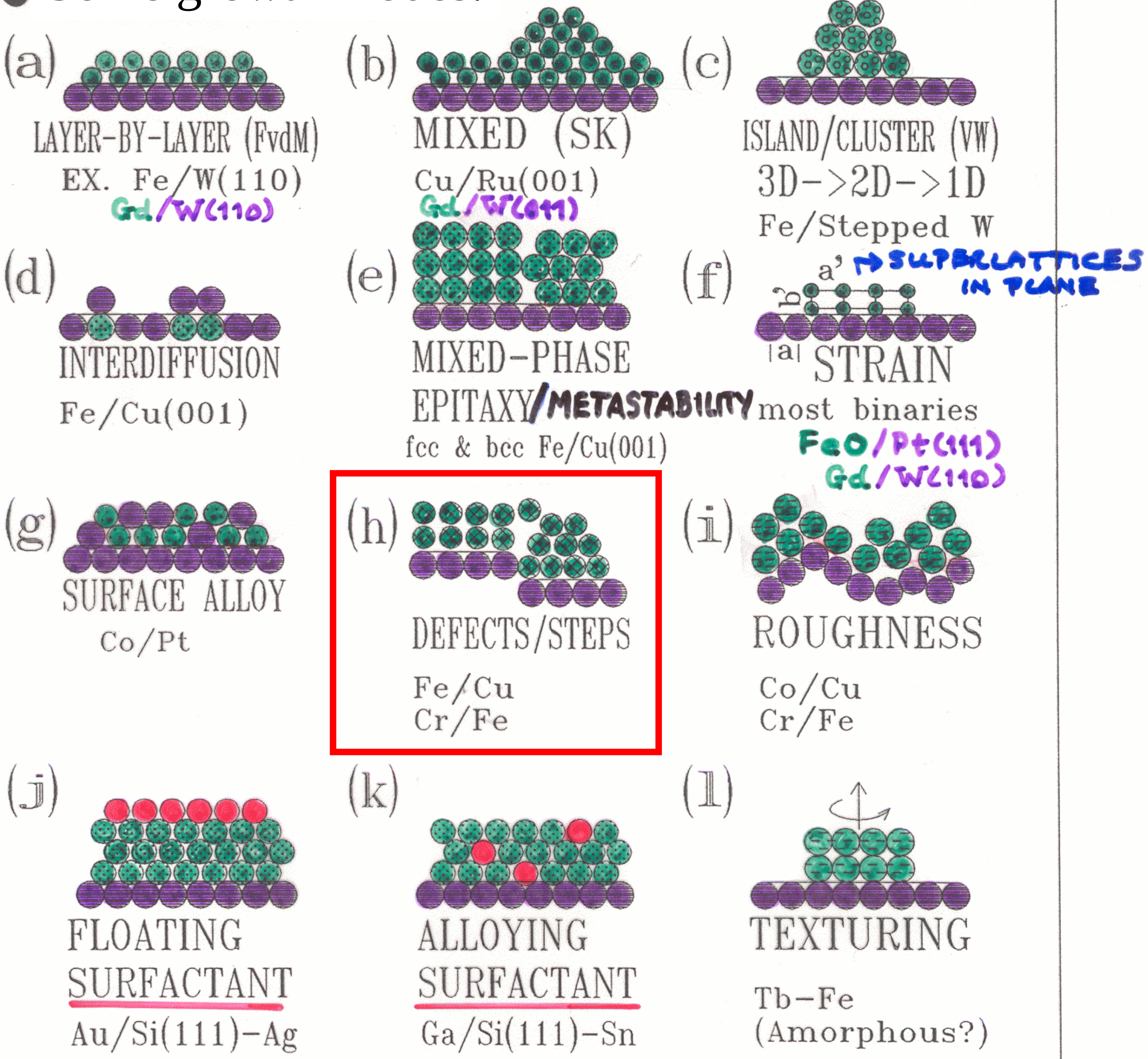


IMAGING, AND MANIPULATING, ATOMS AT SURFACES WITH THE STM



48 iron atoms on a Cu(111) surface—a “quantum corral”

- Some growth modes:



Scanning tunneling microscopy: stepped Si(111) surface

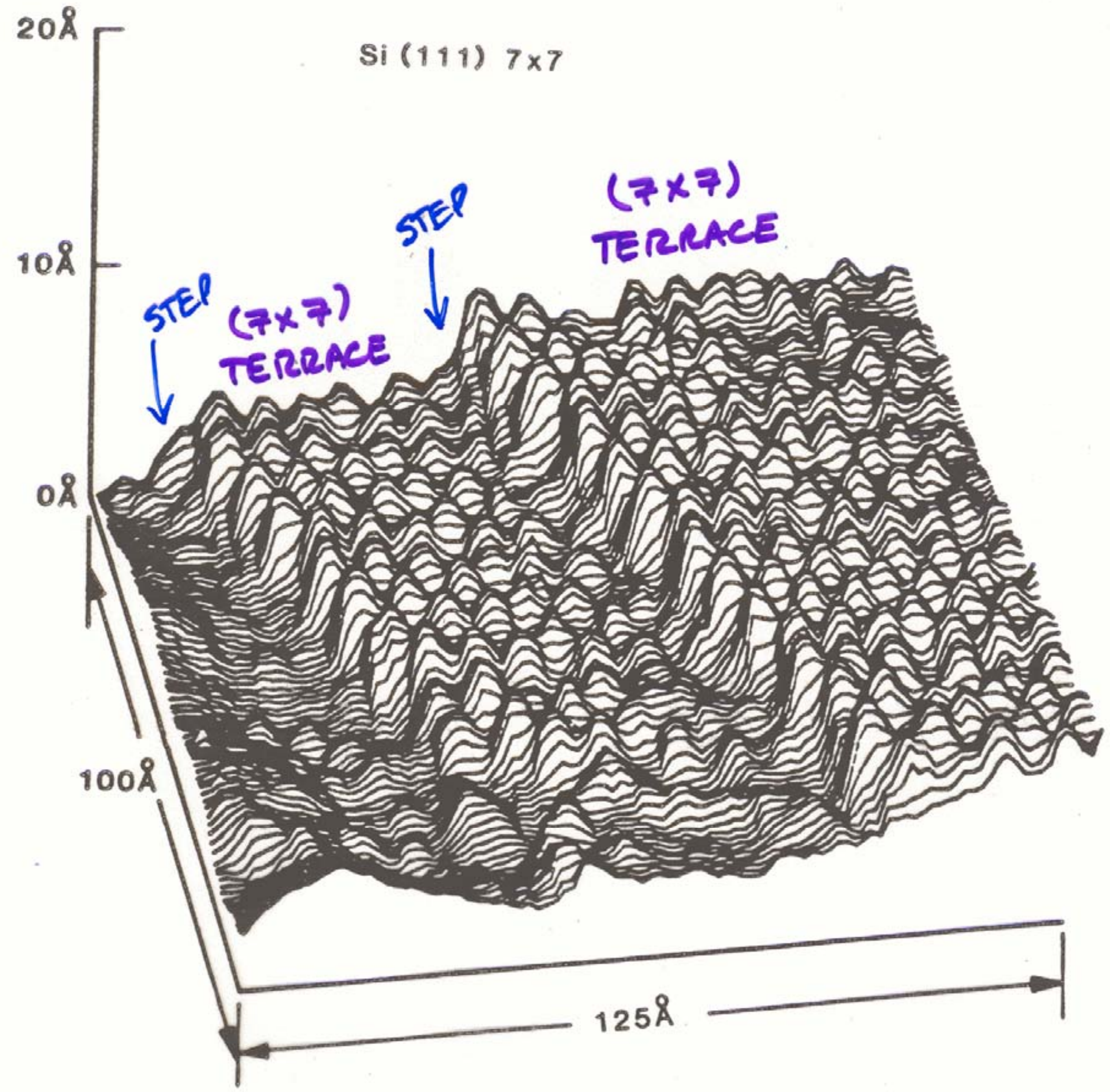
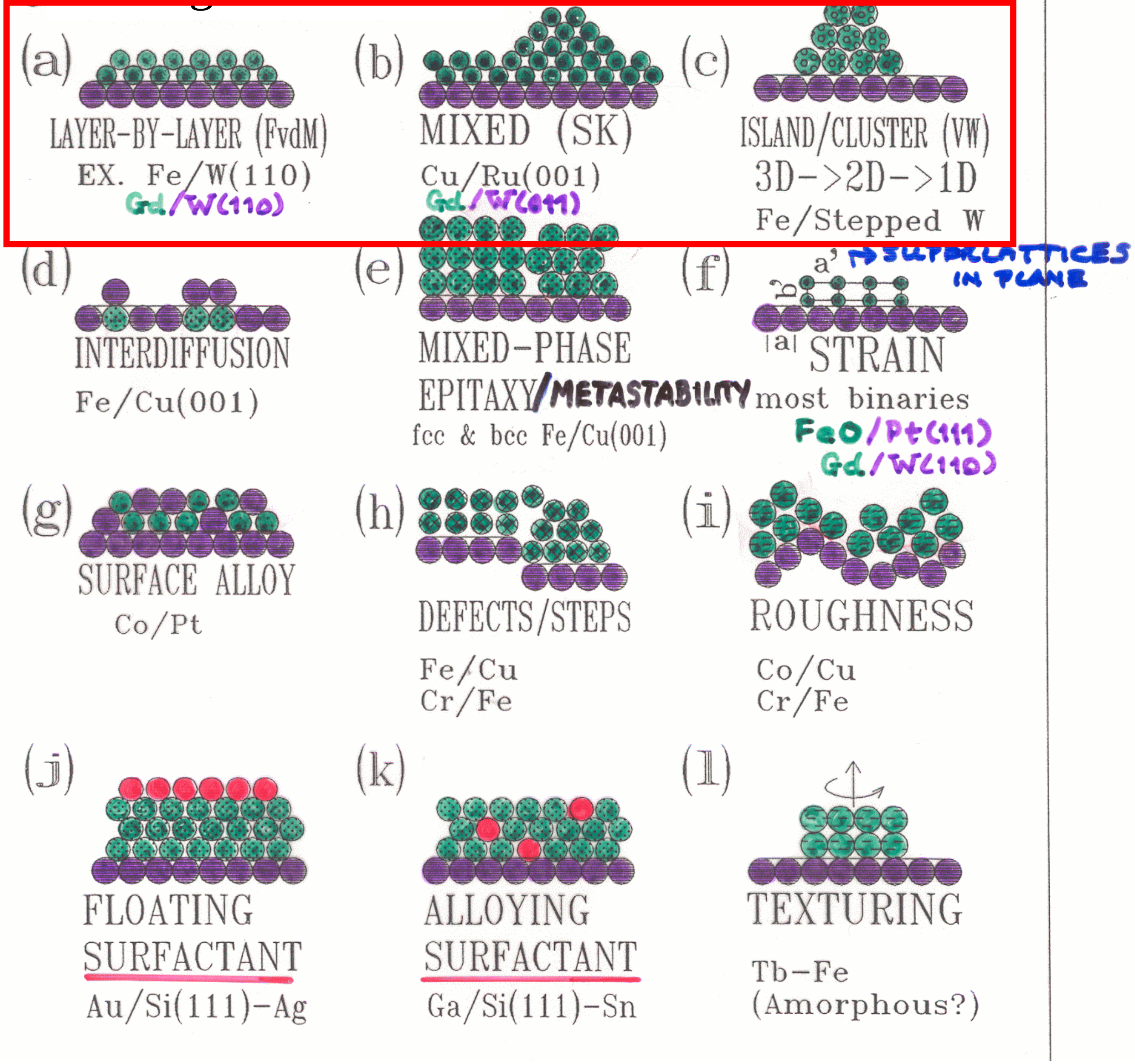


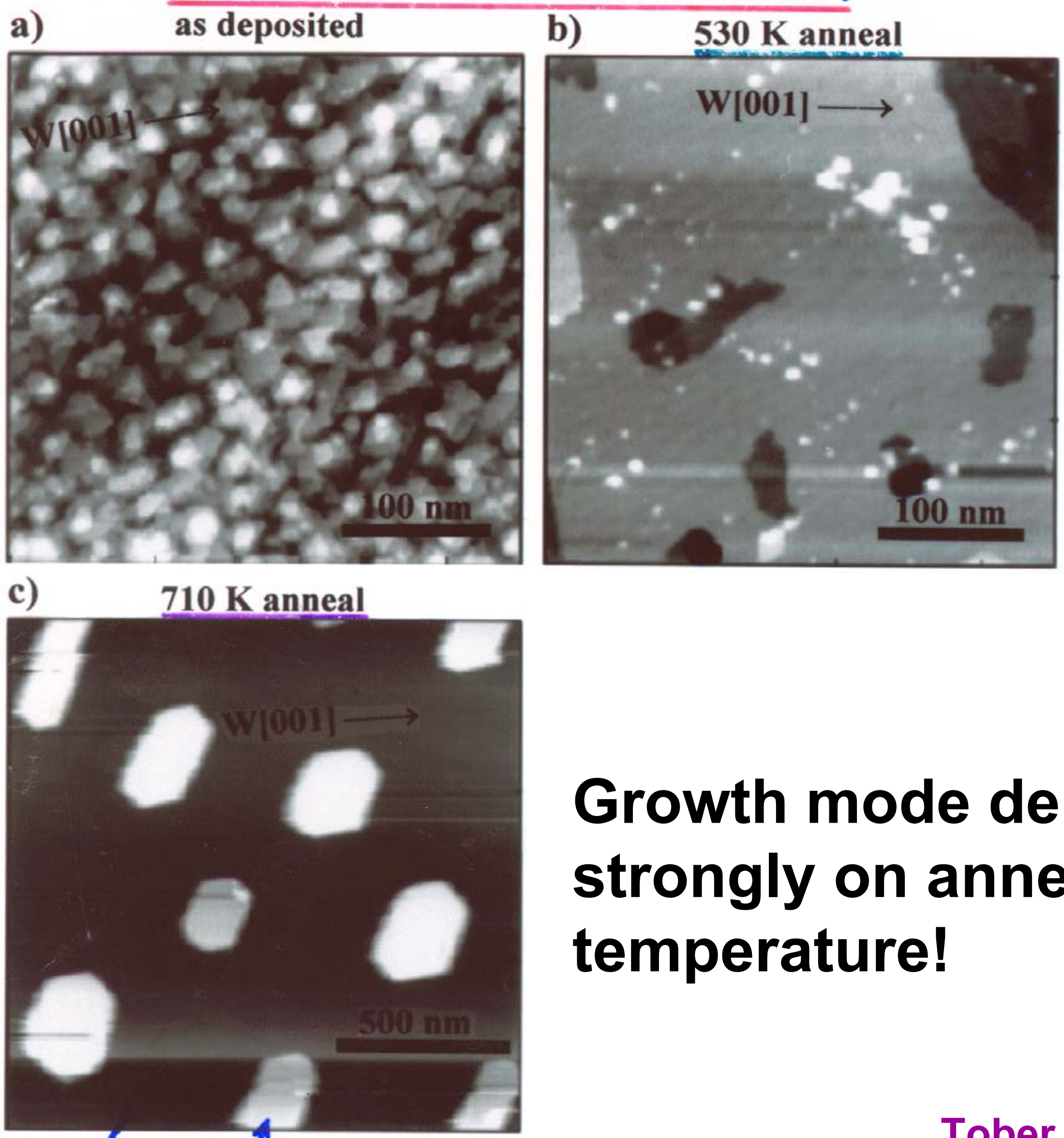
Fig. 2. Tunneling image of silicon (111) surface that shows the 7×7 atomic reconstruction on terraces separated by atomic steps.

- Some growth modes:



Scanning tunneling microscopy: metal-on-metal epitaxial growth

GROWTH OF 11 ML Gd ON W(110)



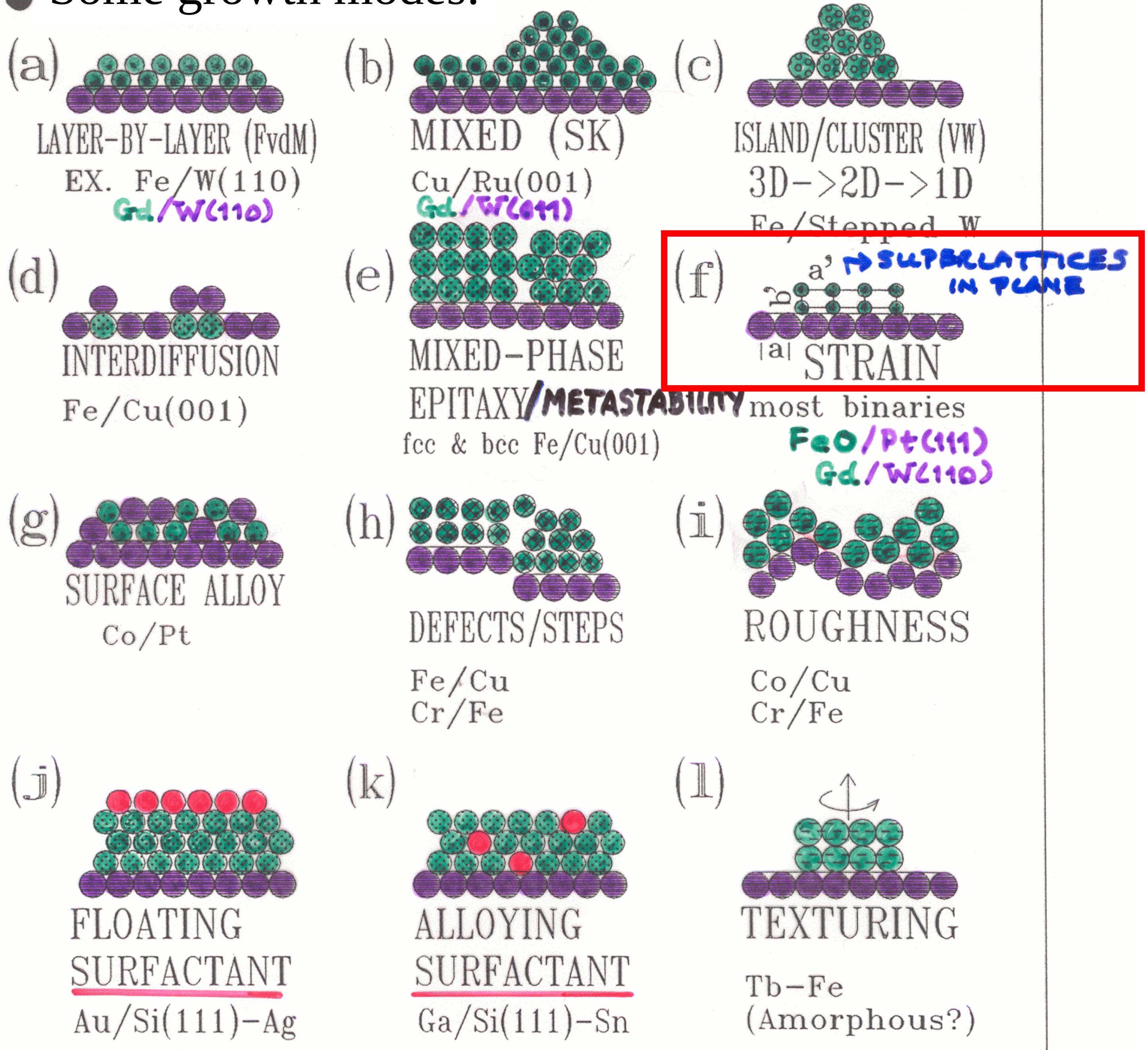
WETTING SINGLE LAYER

ISLANDS: ~ 10 nm (~35 ML) THICK (= t) × ~ 310 nm IN DIAMETER (= d)

Growth mode depends strongly on anneal temperature!

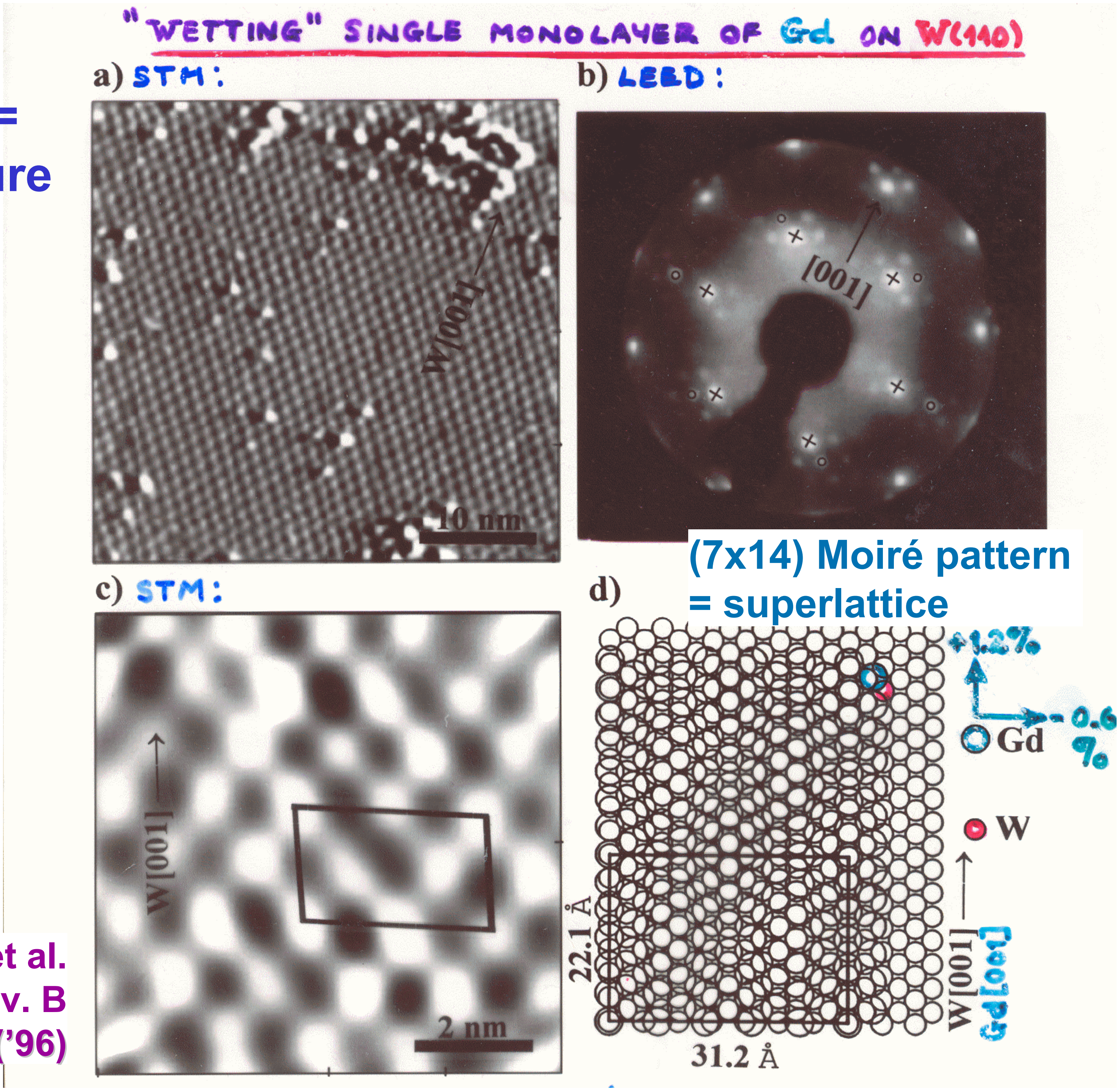
Tober et al. Phys. Rev. B 53, 5444 (1996).

- Some growth modes:



Superlattice = Moiré structure in metal-on-metal epitaxial growth

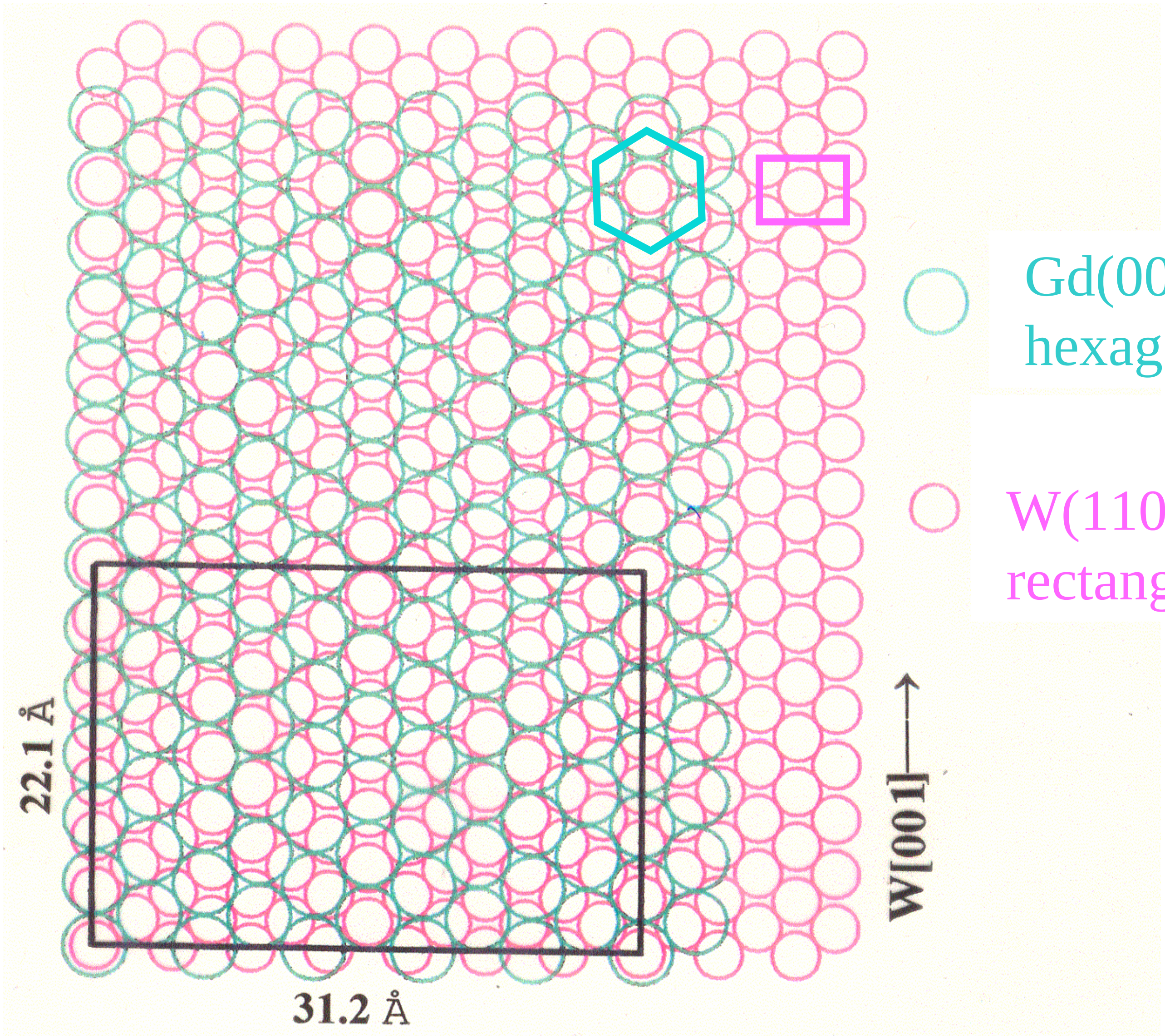
"WETTING" SINGLE MONOLAYER OF Gd ON W(110)



(7x14) Moiré pattern = superlattice

E. Tober et al.
Phys. Rev. B
53, 544 ('96)

A Moiré pattern—Monolayer Gd on W(110)

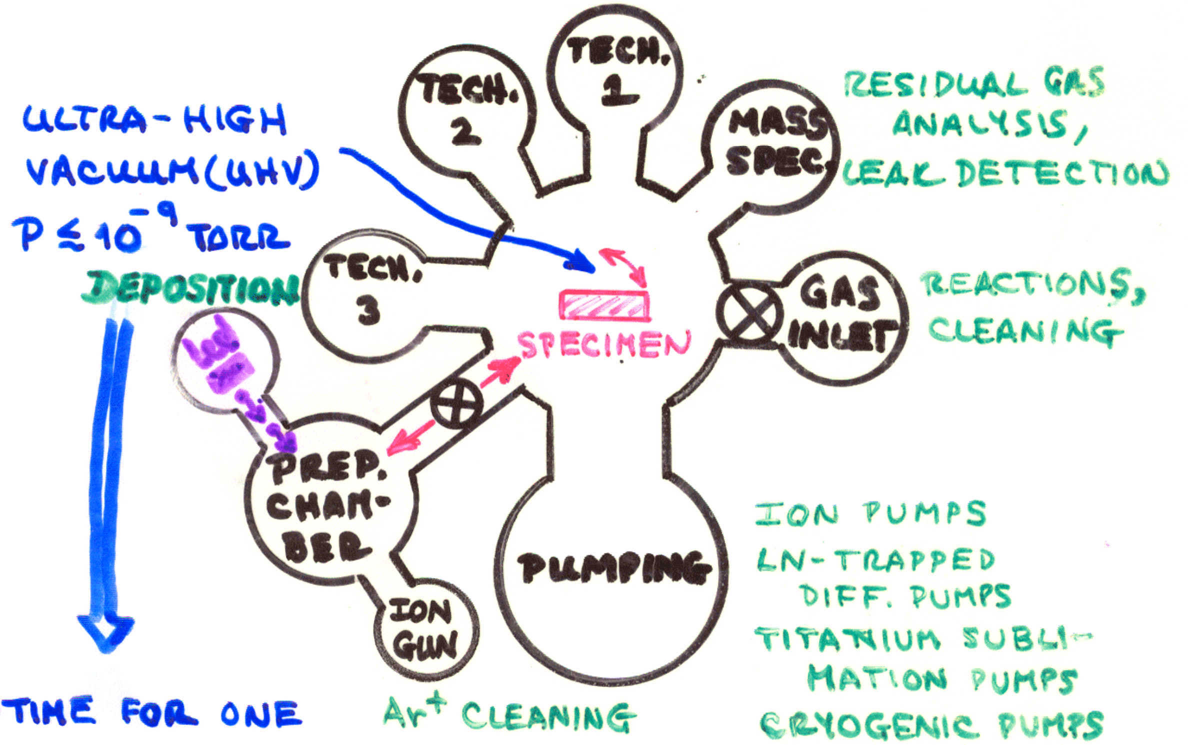


○ Gd(0001)—
hexagonal

○ W(110)—
rectangular

A typical surface science research system

≥ 1 TECHNIQUE: SURFACE SENSITIVE (e^-, IONS, ATOMS AS PROBES)
NON-DESTRUCTIVE



ULTRA-HIGH VACUUM (UHV)
$P \leq 10^{-9}$ TORR

DEPOSITION

RESIDUAL GAS ANALYSIS, LEAK DETECTION

REACTIONS, CLEANING

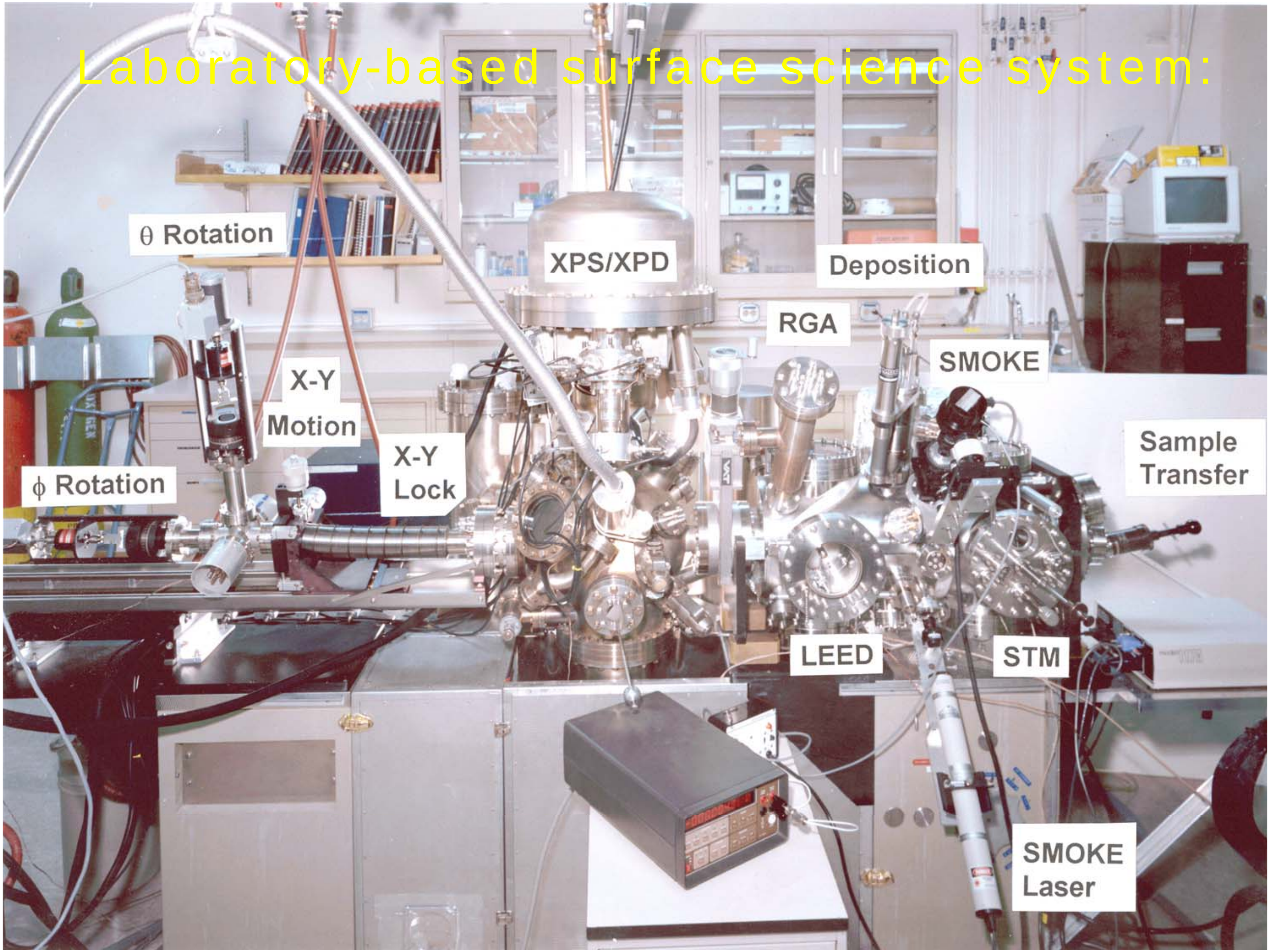
ION PUMPS
LN-TRAPPED DIFF. PUMPS
TITANIUM SUBLIMATION PUMPS
CRYOGENIC PUMPS

Ar^+ CLEANING

~TIME FOR ONE MONOLAYER:

t	P(torr)
10^{-9} sec	1 atm = 760
25 sec	10^{-7}
40 min	10^{-9}
2.8 days	10^{-11}

Laboratory-based surface science system:



Outline

Surface, interface, and nanoscience—short introduction

Some surface concepts and techniques→photoemission

➡ Synchrotron radiation: introductory experimental aspects

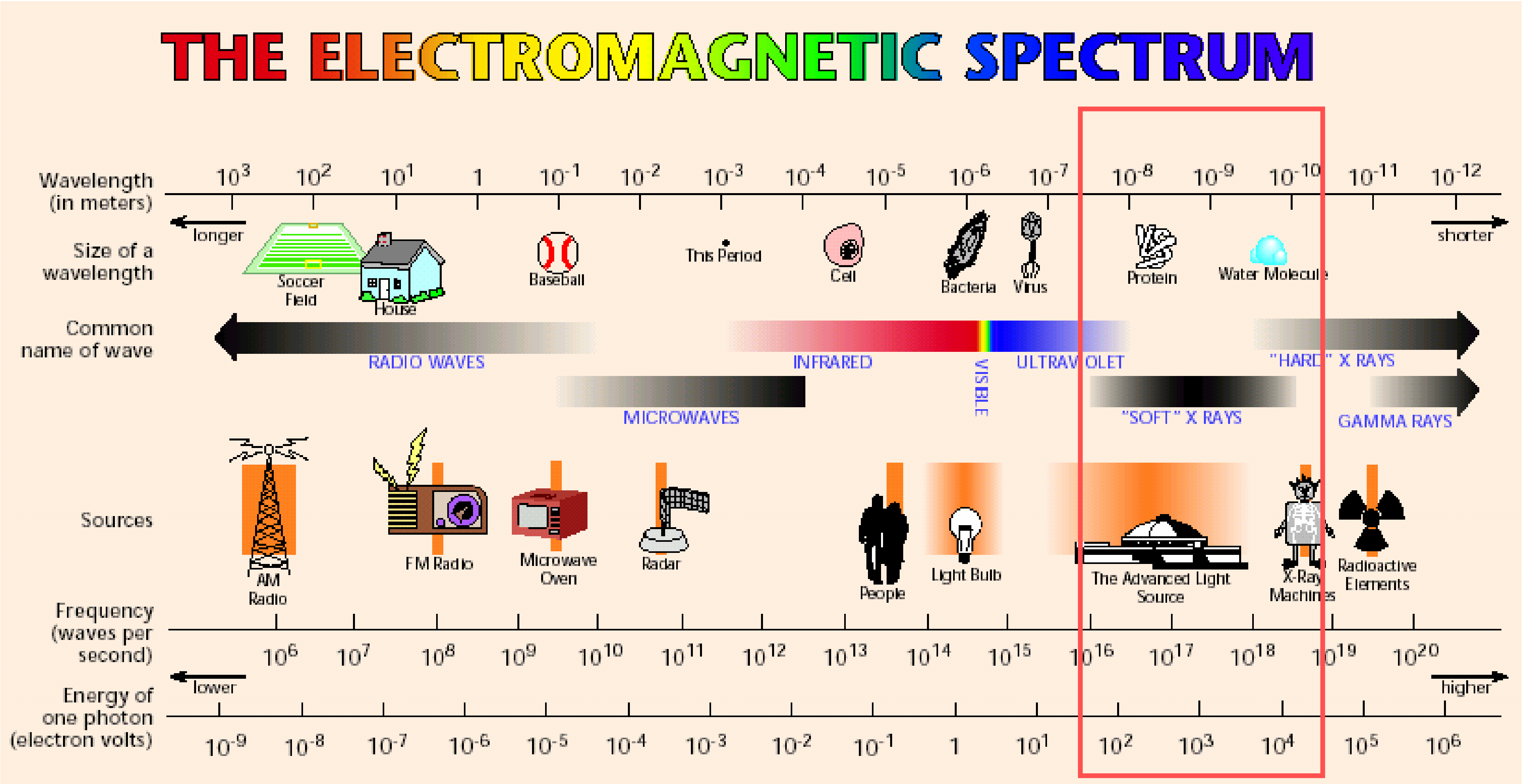
Electronic structure—a brief review

The basic synchrotron radiation techniques:
more experimental and theoretical details

Core-level photoemission

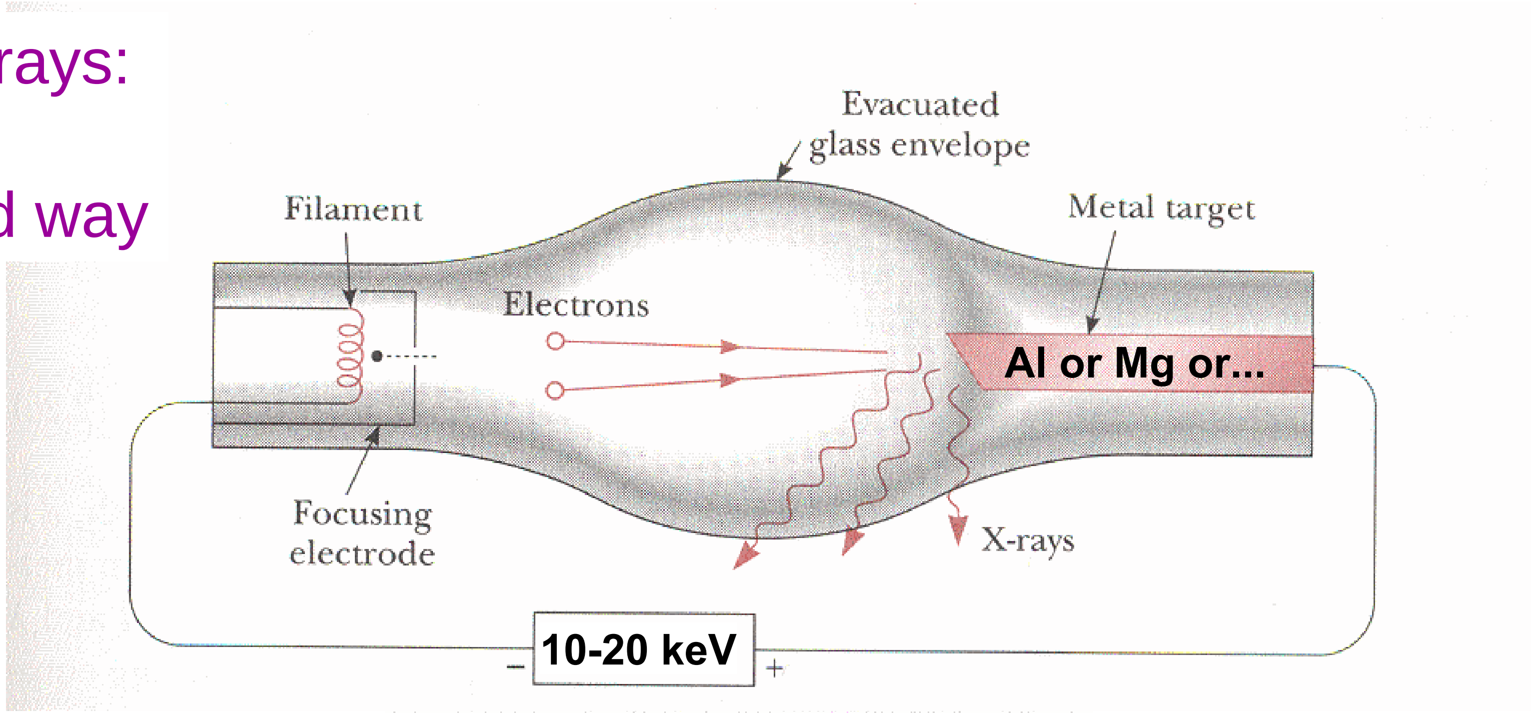
Valence-level photoemission

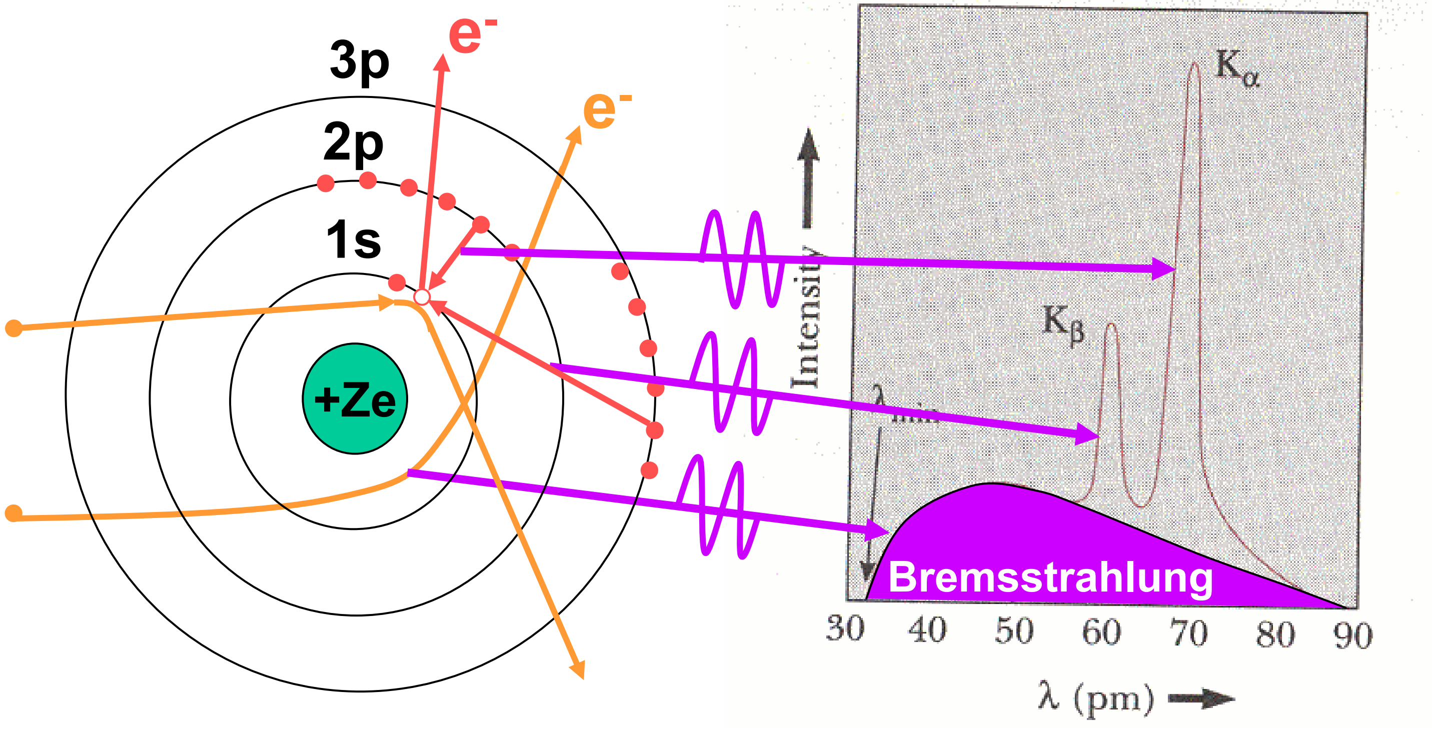
Microscopy with photoemission



Typical surface/materials science expts.

Producing x-rays: the good old-fashioned way





See Section 1.2 in "X-Ray Data Booklet"

X-Ray Nomenclature (from “X-Ray Data Booklet”)

In general:

$$nl \longrightarrow \text{Spin-orbit} \begin{cases} nl_{j=l+1/2} \\ nl_{j=l-1/2} \end{cases}$$

1-14

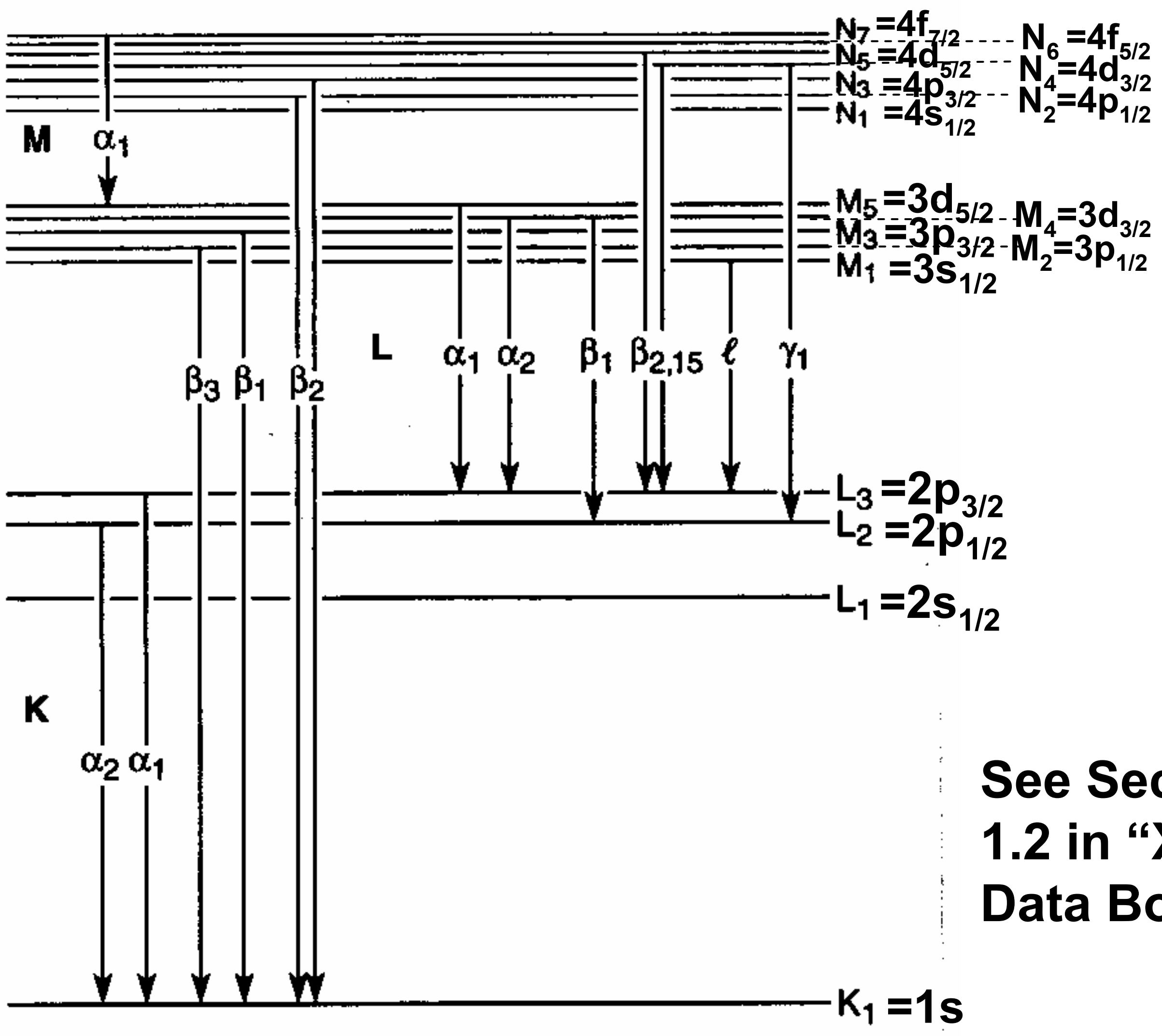


Fig. 1-1. Transitions that give rise to the emission lines in Table 1-3.

See Section 1.2 in “X-Ray Data Booklet”

X-Ray energies from the "X-Ray Data Booklet"

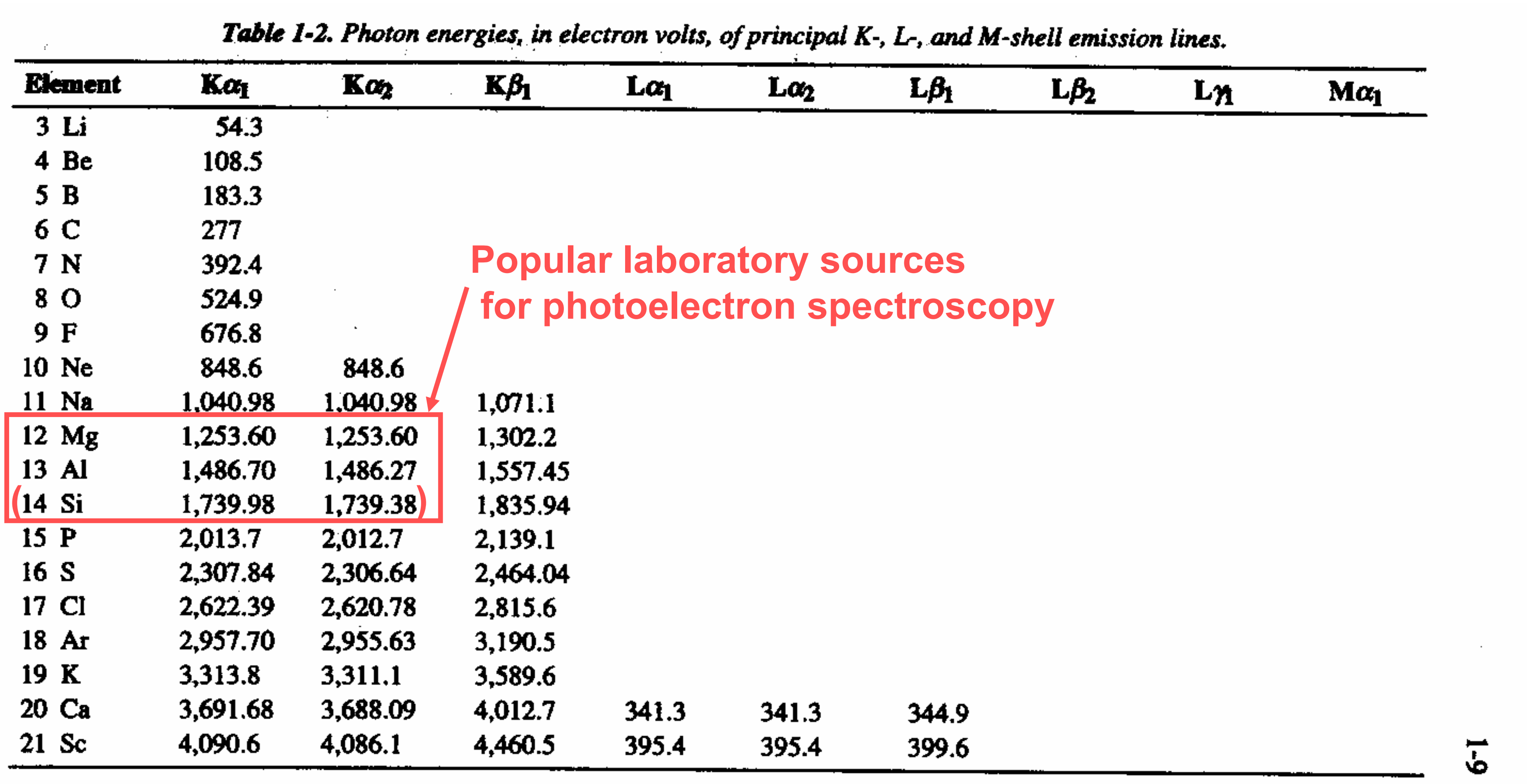


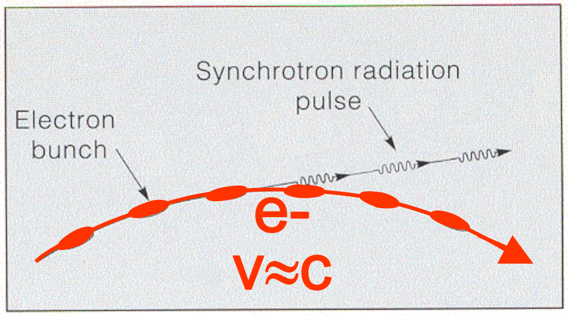
Table 1-2. Photon energies, in electron volts, of principal K-, L-, and M-shell emission lines.

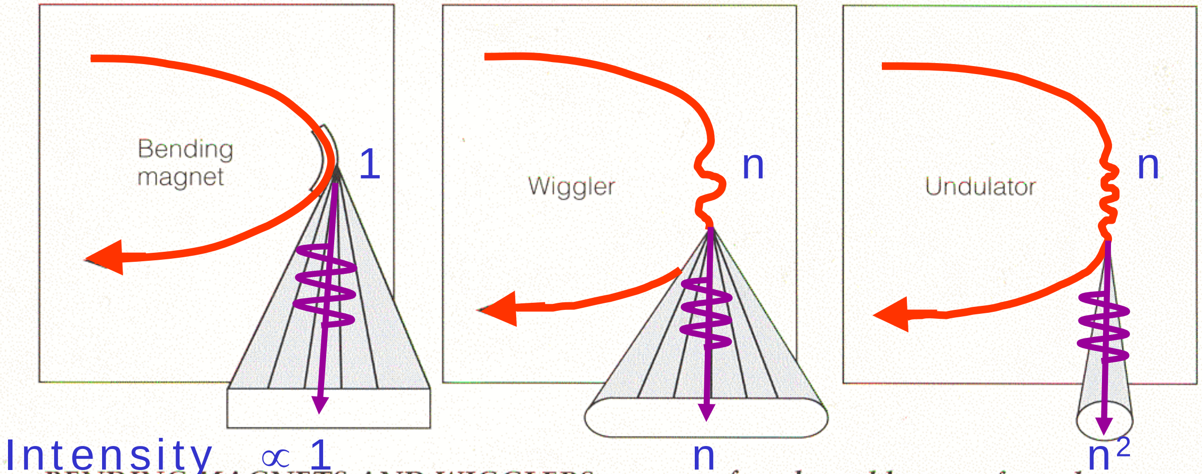
Element	$K\alpha_1$	$K\alpha_2$	$K\beta_1$	$L\alpha_1$	$L\alpha_2$	$L\beta_1$	$L\beta_2$	$L\gamma_1$	$M\alpha_1$
3 Li	54.3								
4 Be	108.5								
5 B	183.3								
6 C	277								
7 N	392.4								
8 O	524.9								
9 F	676.8								
10 Ne	848.6	848.6							
11 Na	1,040.98	1,040.98	1,071.1						
12 Mg	1,253.60	1,253.60	1,302.2						
13 Al	1,486.70	1,486.27	1,557.45						
14 Si	1,739.98	1,739.38	1,835.94						
15 P	2,013.7	2,012.7	2,139.1						
16 S	2,307.84	2,306.64	2,464.04						
17 Cl	2,622.39	2,620.78	2,815.6						
18 Ar	2,957.70	2,955.63	3,190.5						
19 K	3,313.8	3,311.1	3,589.6						
20 Ca	3,691.68	3,688.09	4,012.7	341.3	341.3	344.9			
21 Sc	4,090.6	4,086.1	4,460.5	395.4	395.4	399.6			

1-9

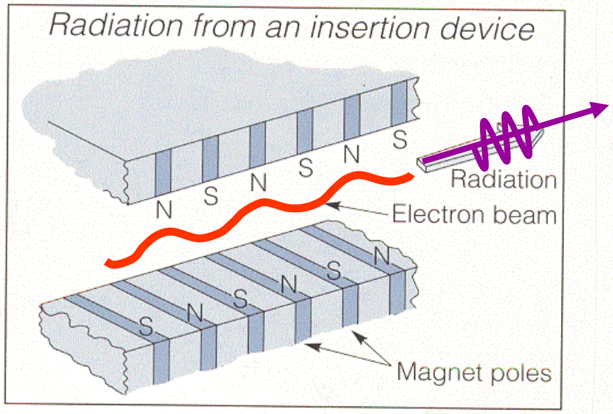
Popular laboratory sources
for photoelectron spectroscopy

Synchrotron Radiation Sources:

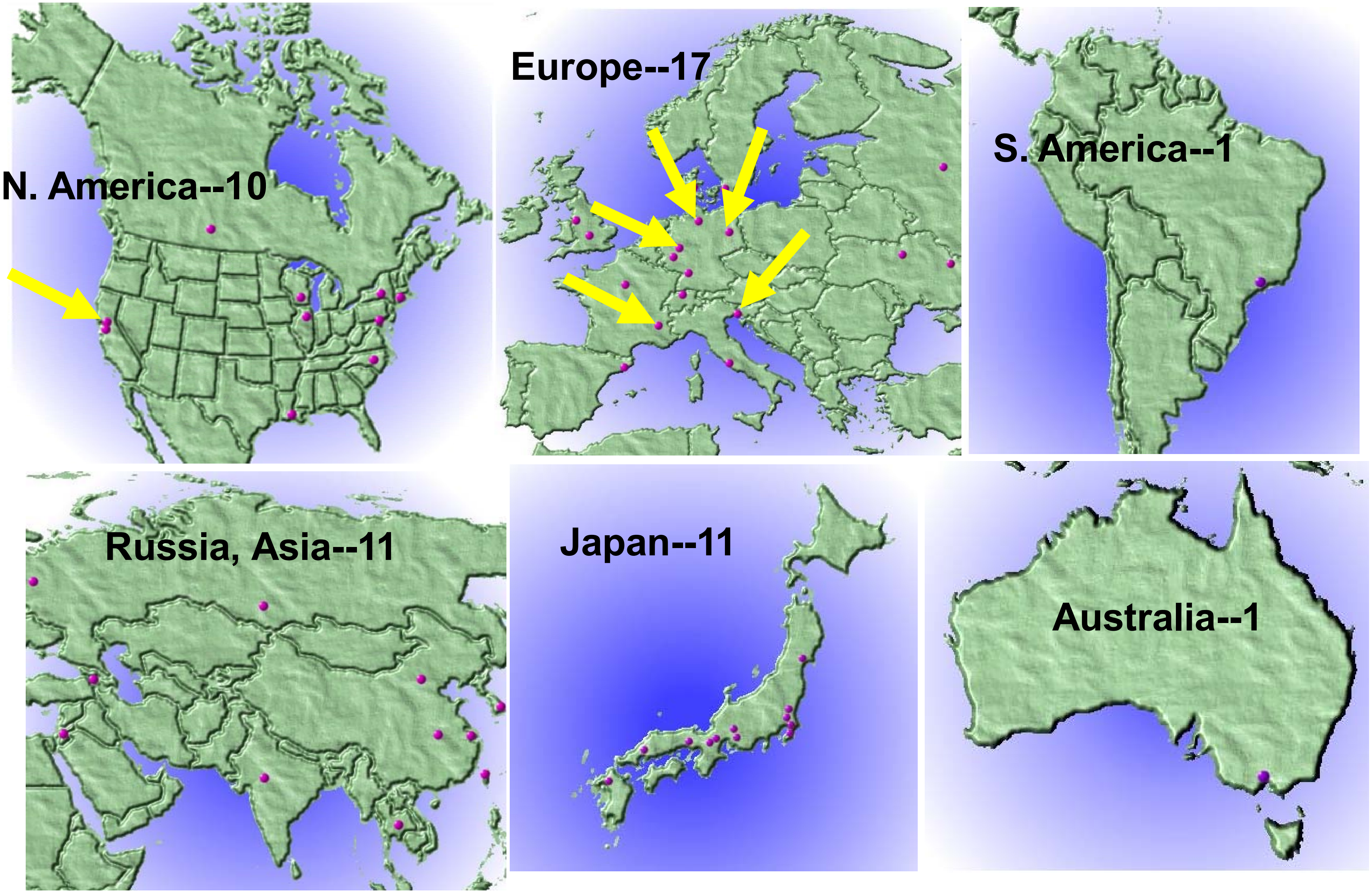




BENDING MAGNETS AND WIGGLERS generate fan-shaped beams of synchrotron radiation, whereas undulators emit pencil-thin beams.



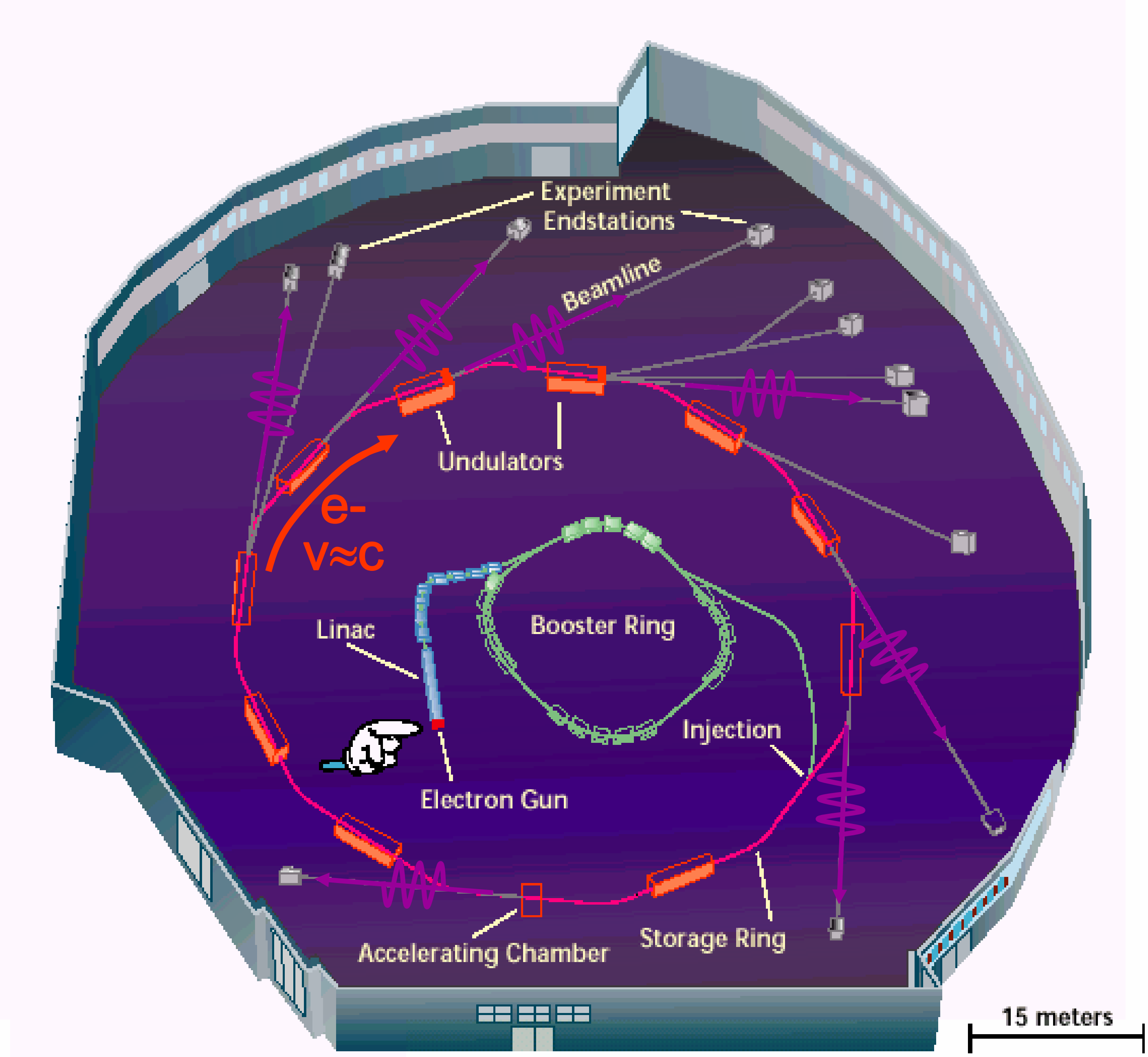
Synchtron Radiation Sources of the World: ~ 40 operating, 10 planned



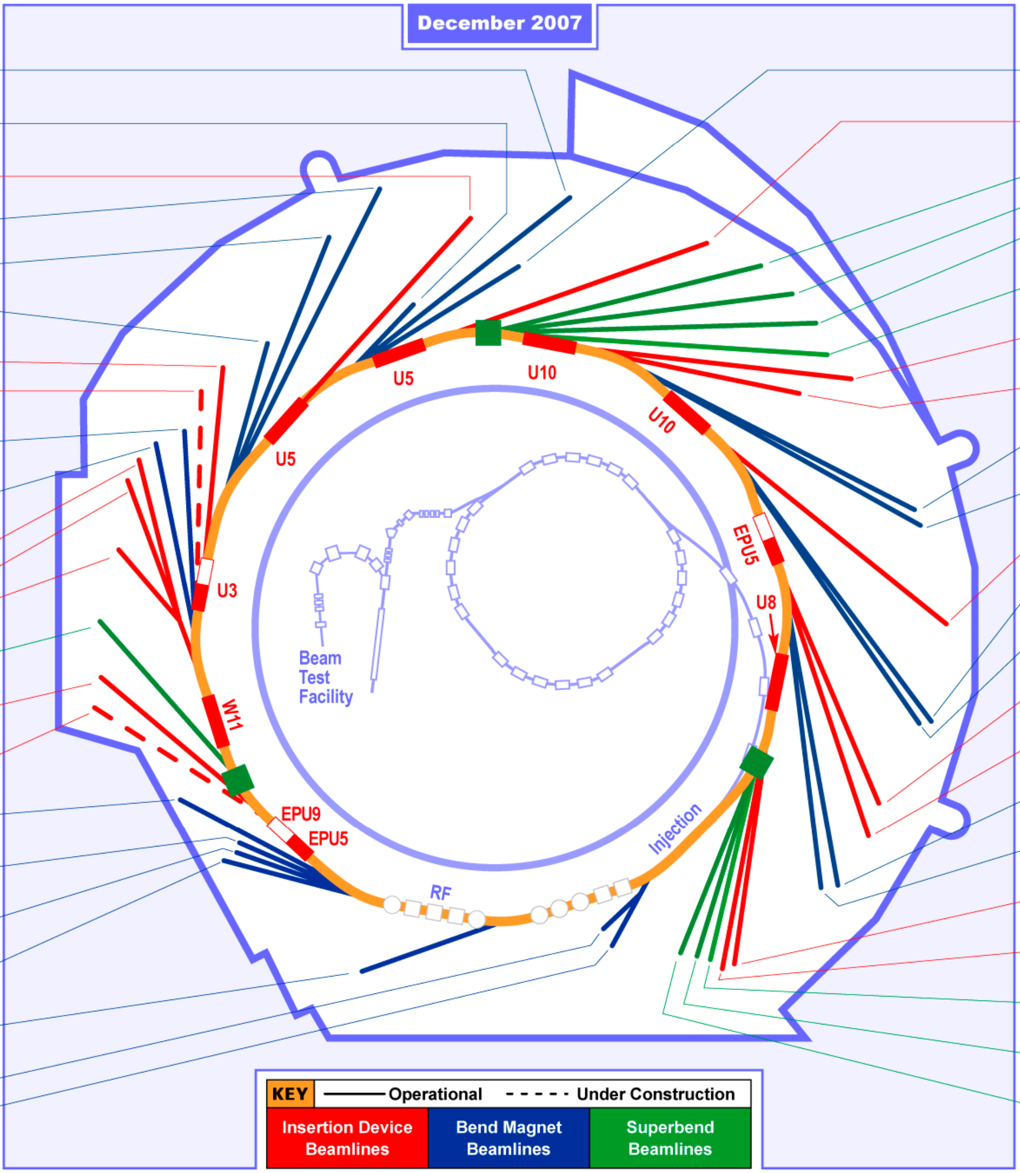
http://www.srs.ac.uk/srs/SRworldwide/


San Francisco
Marin County
UC Berkeley
Advanced Light Source
Group offices & lab.

Layout of the ALS



Beamlines at the ALS 2007



December 2007

PEEM2, MicroXPS	7.3.1
Diagnostic Beamline	7.2
Surface, Materials Science	7.0.1
Magnetic Spectroscopy, Materials Science	6.3.1
Calibration, Optics Testing, Spectroscopy	6.3.2
X-Ray Microscopy	6.1.2
Femtosecond Phenomena	6.0.2 6.0.1
Polymer STXM	5.3.2
Femtosecond Phenomena	5.3.1
Protein Crystallography	5.0.3 5.0.2 5.0.1
Protein Crystallography	4.2.2
Magnetic Spectroscopy	4.0.2
MERLIN	4.0.3
LIGA	3.3.2
LIGA	3.3.1
Commercial LIGA	3.2.1
Diagnostic Beamline	3.1
National Center for X-Ray Tomography	2.1
IR Spectromicroscopy	1.4.4 1.4.3

7.3.3	SAXS/WAXS
8.0.1	Surface, Materials Science
8.2.1 8.2.2 8.3.1	Protein Crystallography
8.3.2	Tomography
9.0.2	Chemical Dynamics
9.0.1	Coherent Optics/Scattering Experiments
9.3.1	AMO, Materials Science
9.3.2	Chemical, Materials Science
10.0.1	Correlated Materials, AMO
10.3.1	X-Ray Fluorescence Microprobe
10.3.2	MicroXAS
11.0.1	PEEM3
11.0.2	Molecular Environmental Science
11.3.1	Small-Molecule Crystallography
11.3.2	EUV Lithography Mask Inspection
12.0.1	EUV Interferometry, Photoemission
12.0.2	Coherent Soft X-Ray Science
12.2.2	High Pressure
12.3.1	Protein Crystallography
12.3.2	X-Ray Microdiffraction

KEY ——— Operational - - - - Under Construction

🟥	🟦	🟩
Insertion Device Beamlines	Bend Magnet Beamlines	Superbend Beamlines

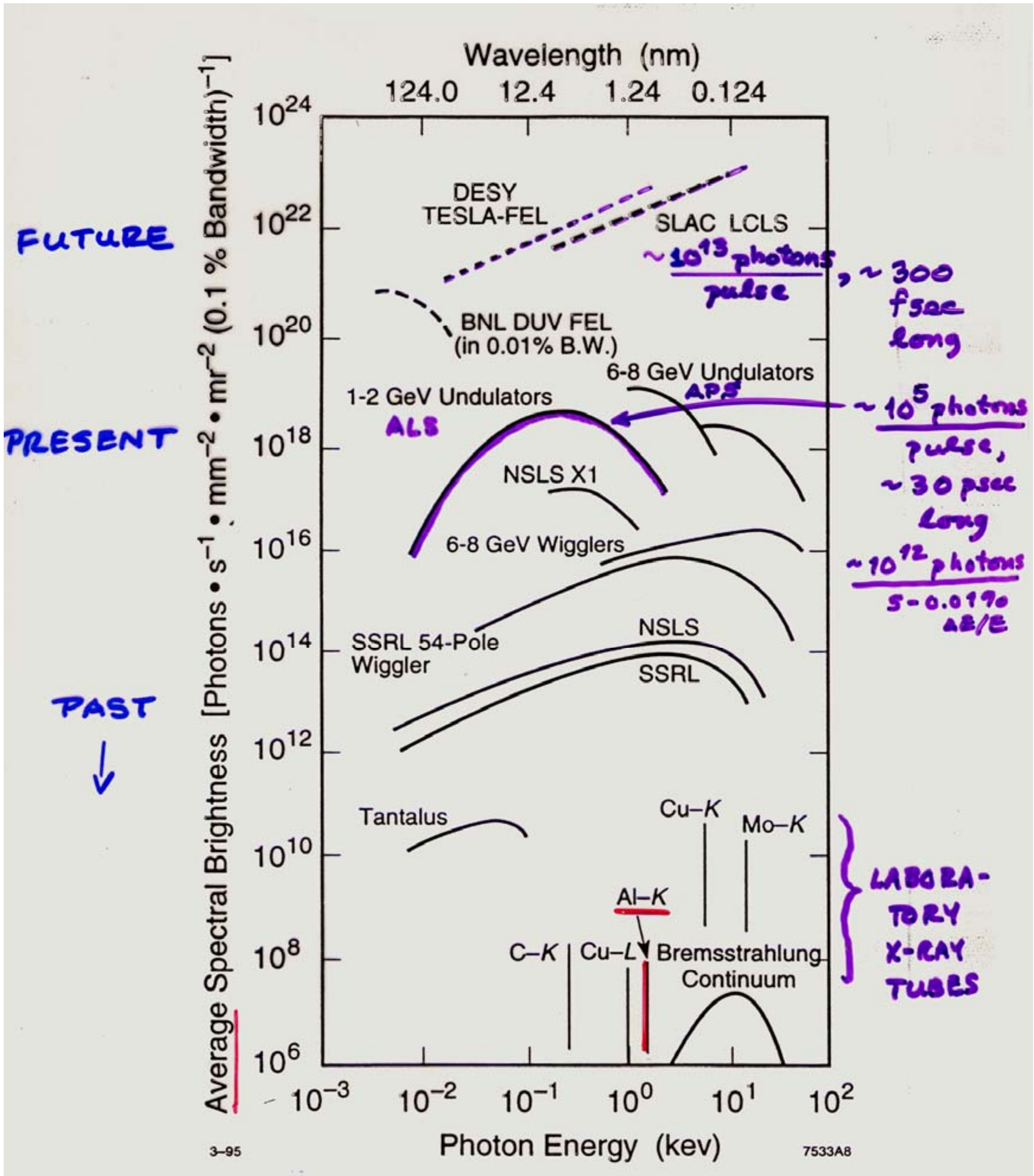
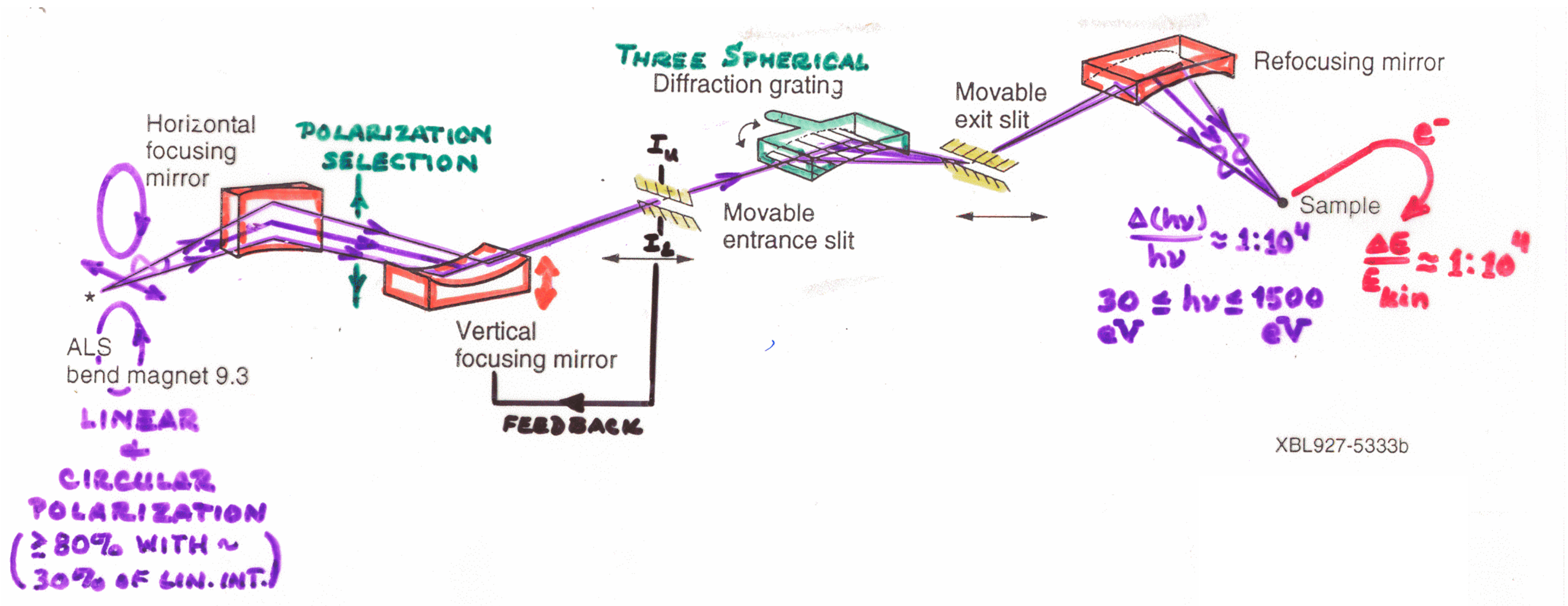


Fig. 2. Average brightness comparisons of the LCLS and other light sources, including proposed FELs at Brookhaven [14] and DESY [15].

"X-Ray Data Booklet" See Fig. 2.9

Advanced Light Source--
Typical Spectroscopy Beamline Layout



The five ways in which x-rays Interact with Matter:

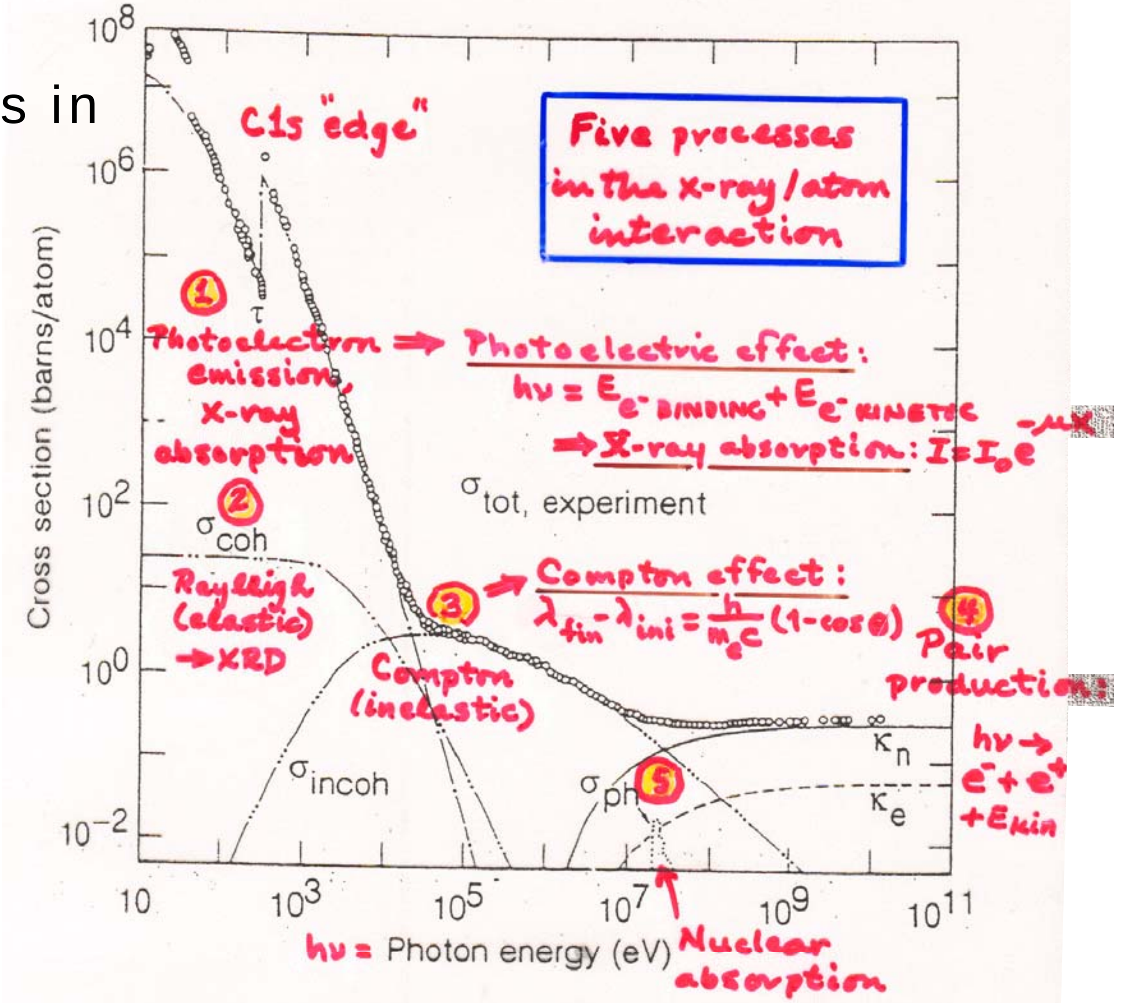
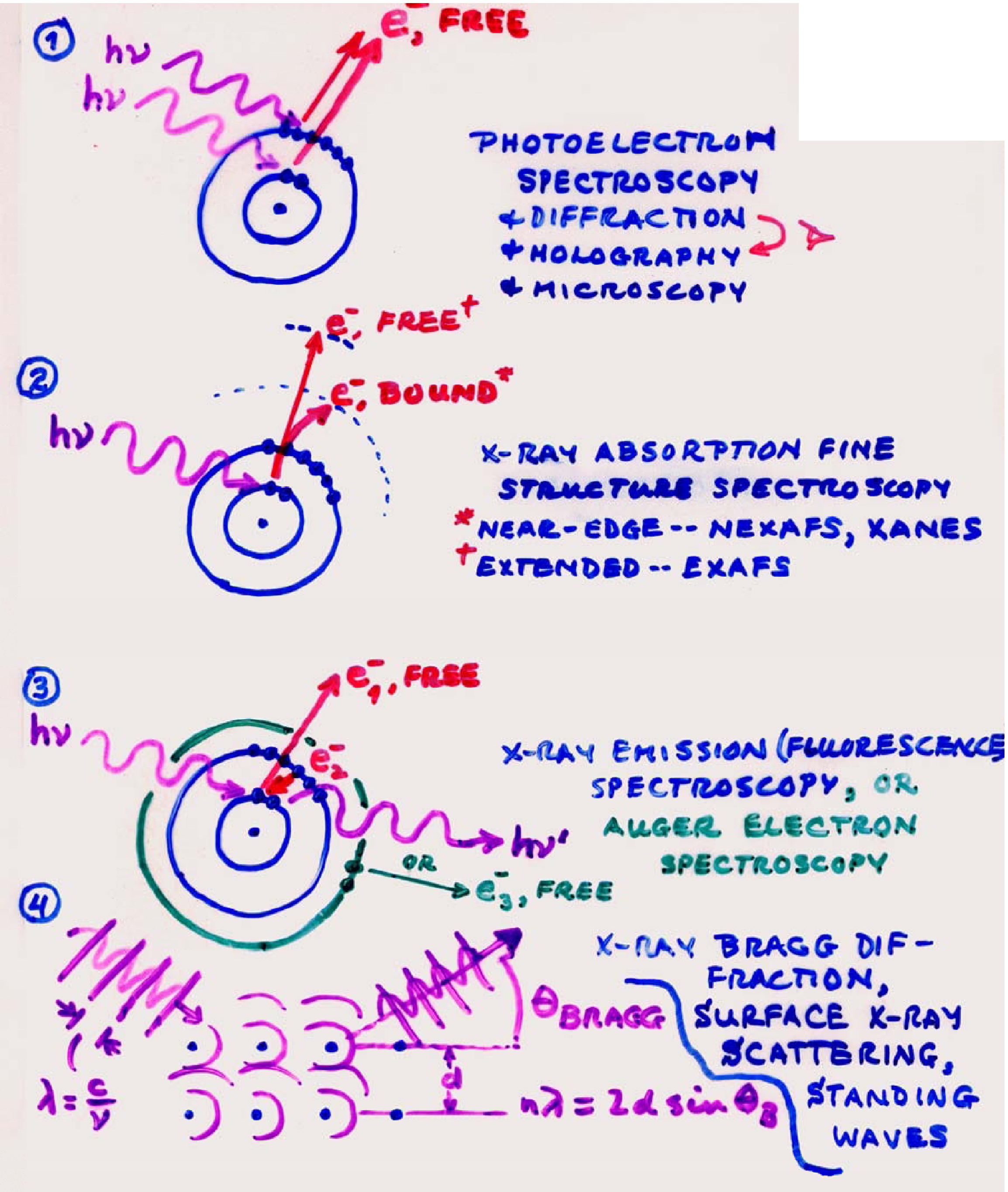


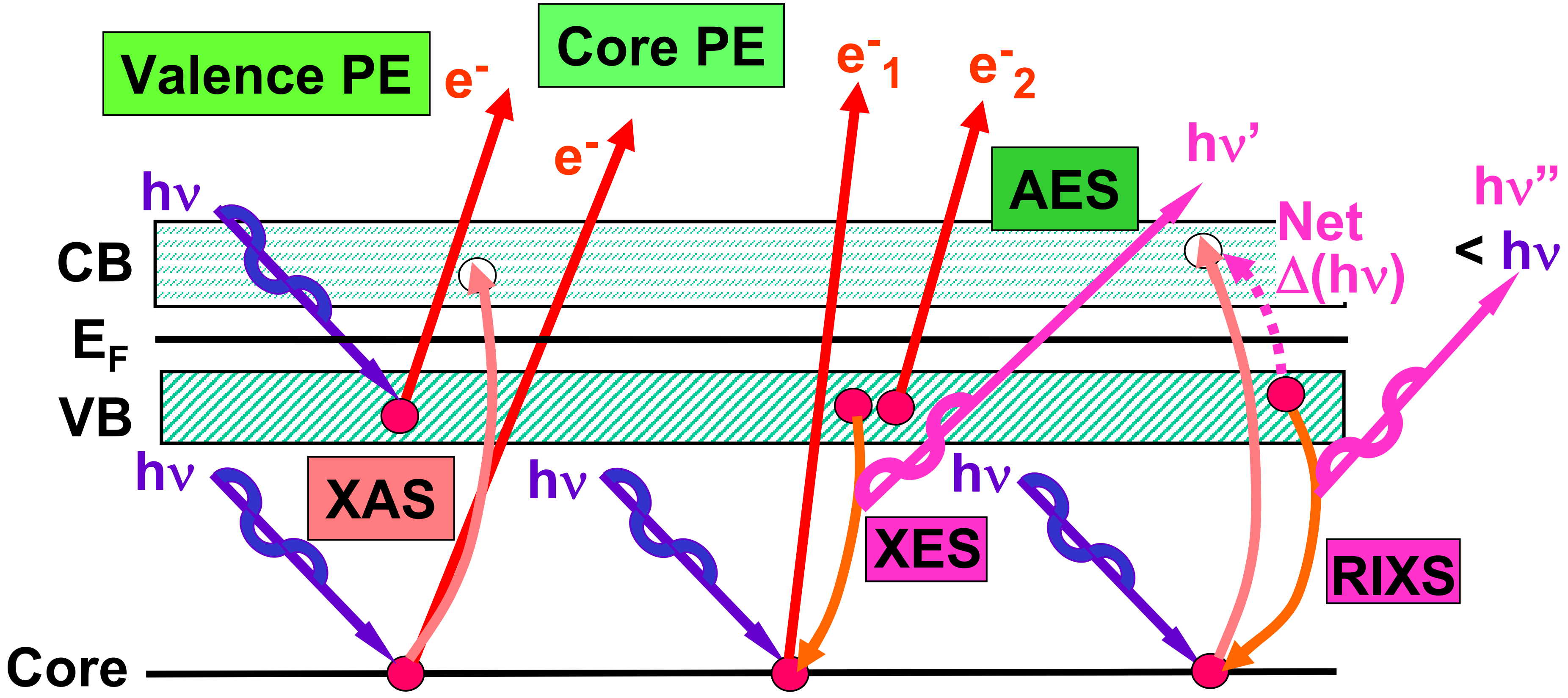
Fig. 3-1. *Total photon cross section σ_{tot} in carbon, as a function of energy, showing the contributions of different processes: τ, atomic photo-effect (electron ejection, photon absorption); σ_{coh}, coherent scattering (Rayleigh scattering—atom neither ionized nor excited); σ_{incoh}, incoherent scattering (Compton scattering off an electron) κ_n, pair production, nuclear field; κ_e, pair production, electron field; σ_{ph}, photonuclear absorption (nuclear absorption, usually followed by emission of a neutron or other particle). (From Ref. 3; figure courtesy of J. H. Hubbell.)*

"X-Ray Data Booklet"
Section 3.1

The ultraviolet, soft x-ray, hard x-ray measurements:



The Soft X-Ray Spectroscopies



PE = photoemission = photoelectron spectroscopy
XAS = x-ray absorption spectroscopy
AES = Auger electron spectroscopy
XES = x-ray emission spectroscopy
RIXS = resonant inelastic x-ray scattering / x-ray Raman scatt.

The Soft and Hard X-Ray Spectroscopies

EXAFS
Atomic structure

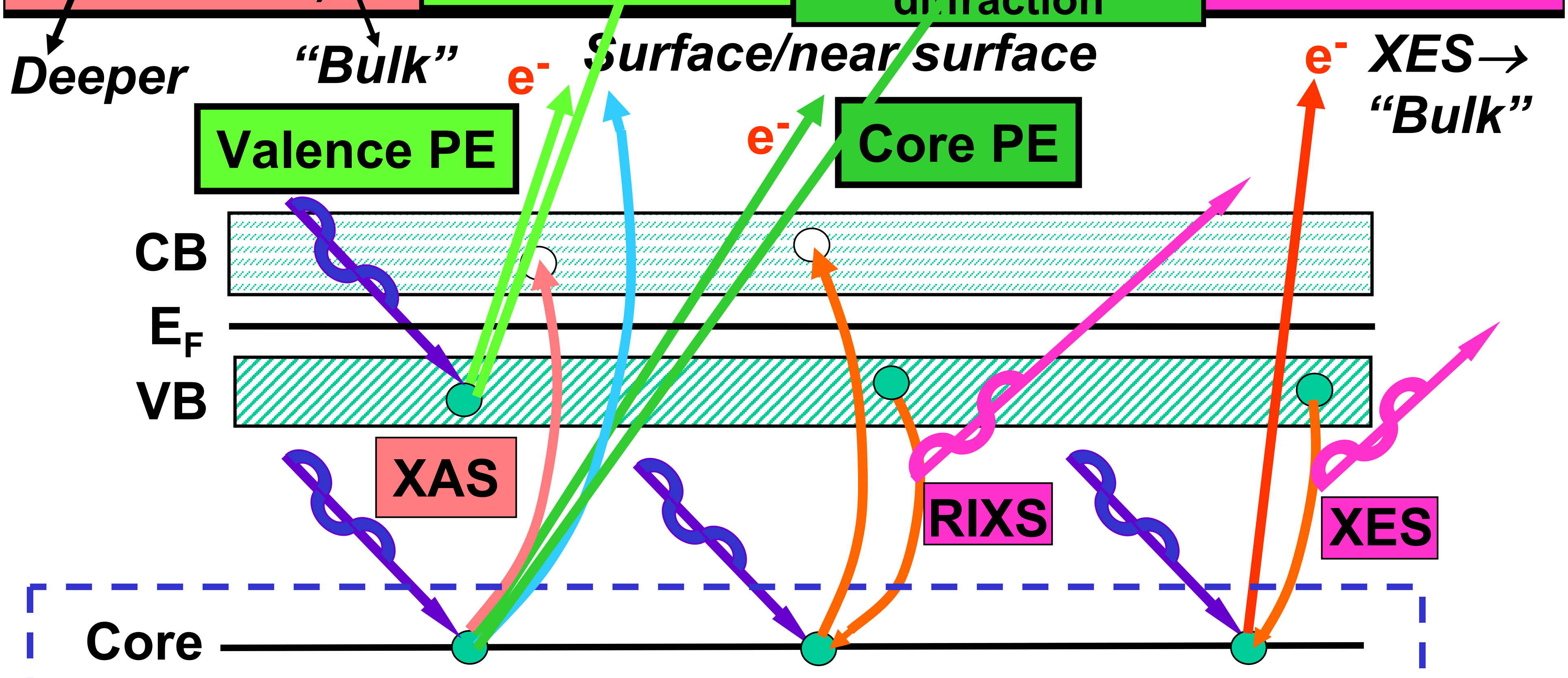
HXPS/ HAXPES

XAS
unoccupied DOS
(2° e- and hν Detection)

Valence PE -
band struct.,
quasipart. exc.,
DOS, spin pol.

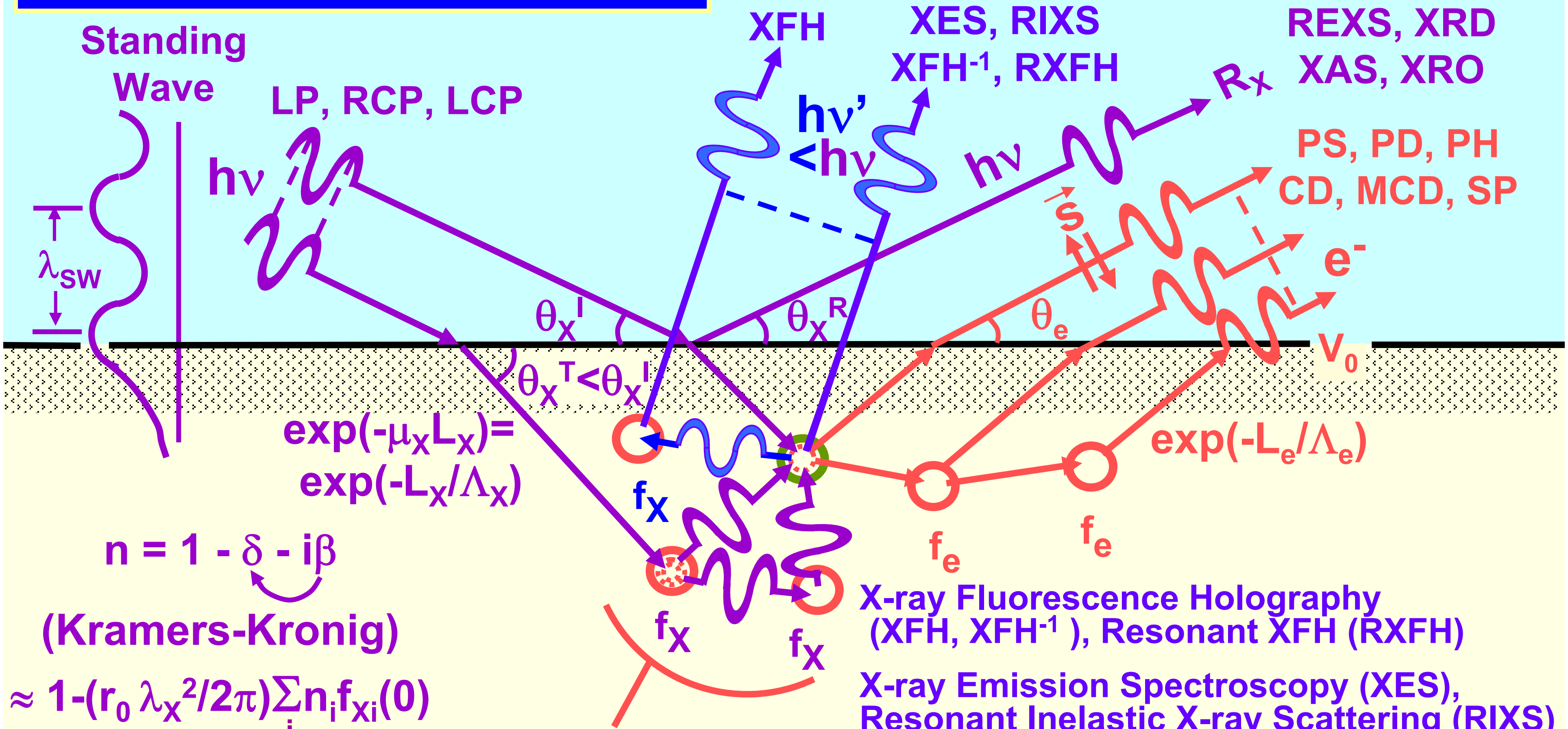
Core PE -
stoichiometry
BE shifts
splittings, MCD
spin polarization
diffraction

XES, RIXS –
band structure,
partial DOS,
d-d excitations



Core levels→ Element-specific methods

Some basic measurements:



$$n = 1 - \delta - i\beta$$

(Kramers-Kronig)

$$\approx 1-(r_0\,\lambda_X^2/2\pi)\sum_i n_i f_{Xi}(0)$$

$$\mu_X = 4\pi\beta/\lambda_X$$

$$\theta_X^R = \theta_X^I$$

$$\lambda_{SW} = \lambda_X/(2\sin\theta_X^I)$$

$$\theta_{CRIT}^I = (2\delta)^{1/2}$$

X-ray Fluorescence Holography (XFH, XFH^{-1}), Resonant XFH (RXFH)

X-ray Emission Spectroscopy (XES), Resonant Inelastic X-ray Scattering (RIXS)

Resonant Elastic X-ray Scattering (REXS)

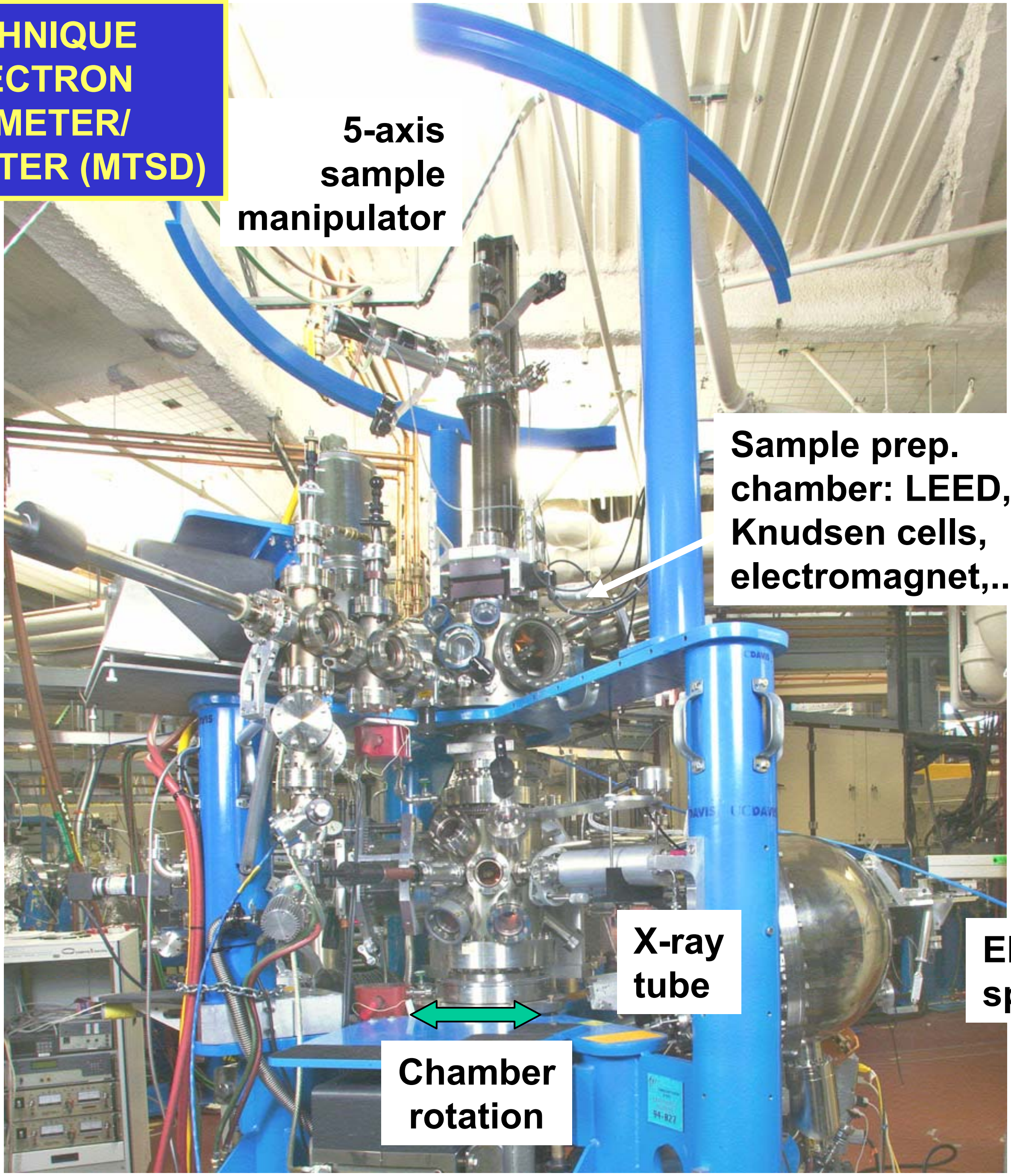
X-Ray Diffraction (XRD)

X-ray Absorption Spectroscopy (XAS)

X-Ray Optical measurements (XRO)

Photoelectron Spectroscopy (PS), Diffraction (PD), Holography (PH)
+ Circular Dichroism (CD),
Magnetic CD (MCD),
Spin Polarization (SP)

MULTI-TECHNIQUE PHOTOELECTRON SPECTROMETER/ DIFFRACTOMETER (MTSD)



5-axis sample manipulator

Sample prep. chamber: LEED, Knudsen cells, electromagnet,...

Loadlock for sample introduction

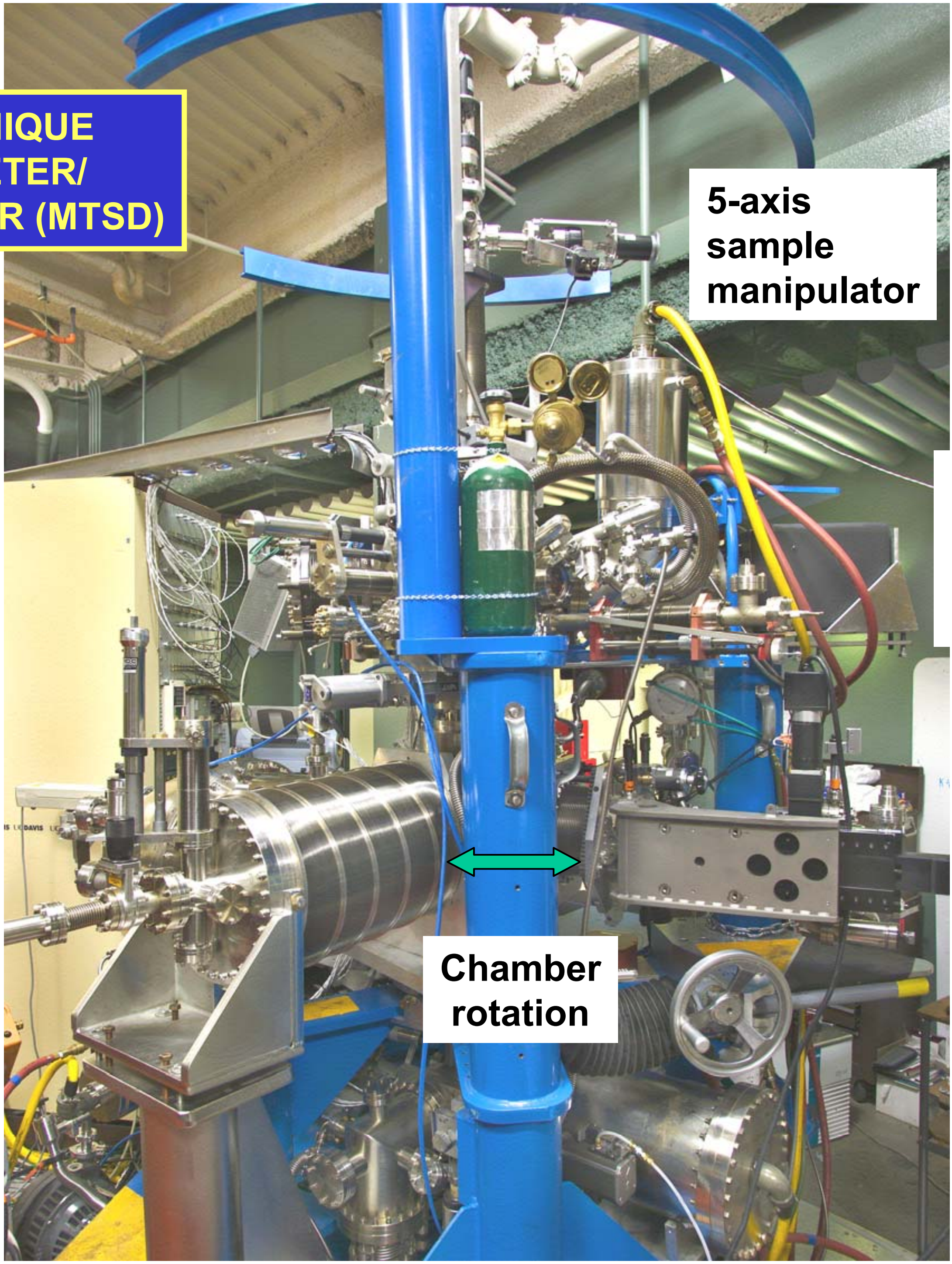
Soft x-ray spectrometer

X-ray tube

Electron spectrometer

Chamber rotation

MULTI-TECHNIQUE SPECTROMETER/ DIFFRACTOMETER (MTSD)



5-axis sample manipulator

Sample prep. chamber: LEED, Knudsen cells, electromagnet,...

Soft x-ray spectrometer

Chamber rotation

ALS

hν

Some possible photoemission measurements

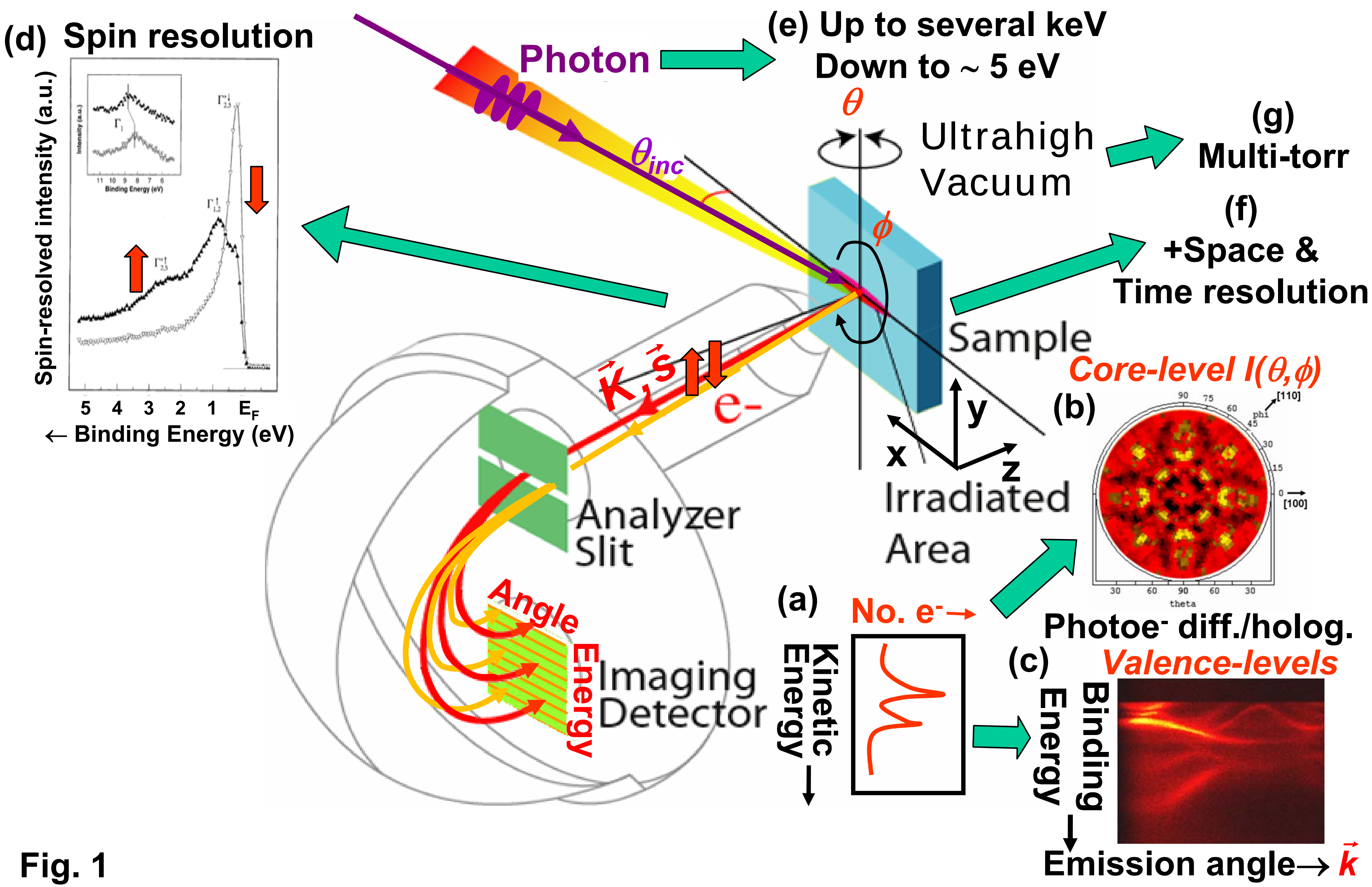


Fig. 1