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

LECTURES FOR 18 MAY THROUGH 22 MAY, 2006

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

Lecturers:

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

Introduction to surface and interface science, vuv/soft x-ray spectroscopies, photoelectron spectroscopy/diffraction/holography

Jürg Osterwalder, Institute of Physics, Univ. of Zürich, Switzerland

Valence band studies and Fermi surface mapping by photoemission, magnetic studies, core-level photoelectron diffraction and holography

Chuck Fadley
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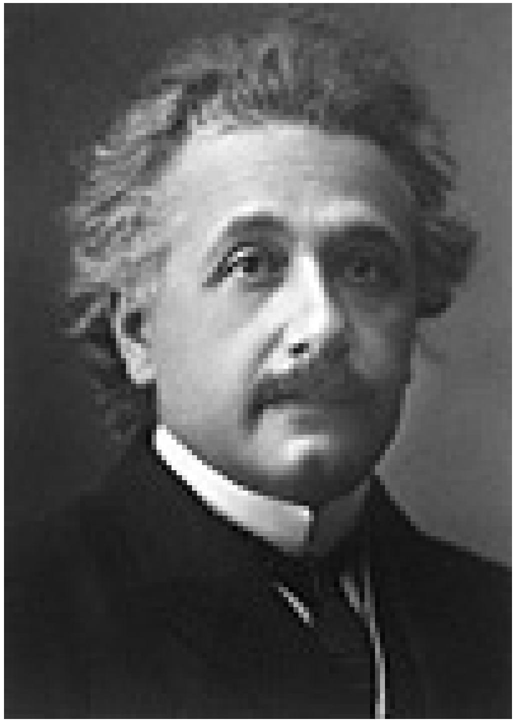
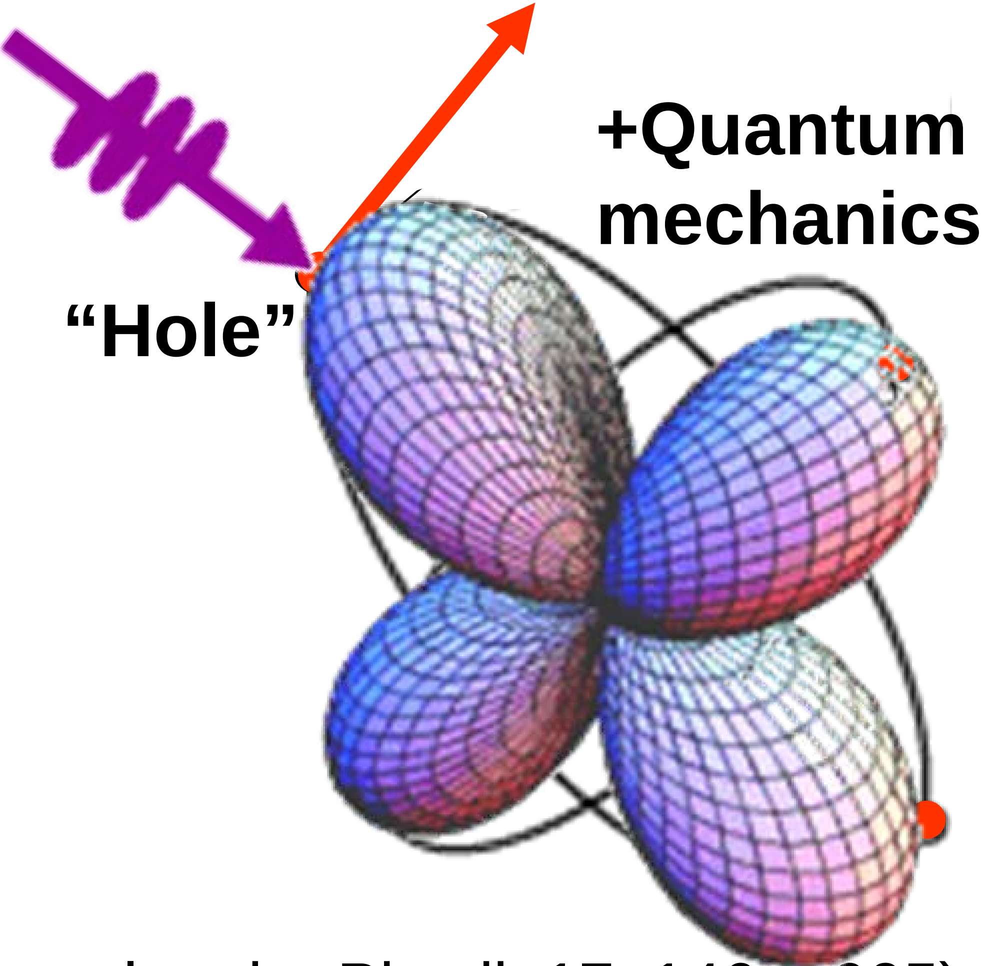
Berkeley, California

Fuggle-Fonda School on Synchrotron Radiation and Applications
International Center for Theoretical Physics
May, 2006

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)

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)

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Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA

---OUTLINE OF FADLEY LECTURES FOR 18 MAY THROUGH 22 MAY, 2006---
(With complementary coverage of related/additional material by Juerg Osterwalder, Zürich)
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.

• *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,…)

Slide Set 1

- ***ELECTRONIC STRUCTURE: (Altarelli lectures, 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)***

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:

(Paper [1], Chap. VI, Paper [2],1-4)

- **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.)

• PHOTOELECTRON DIFFRACTION (CORE LEVELS):

(Papers [1], D; [2], 5; [3]-[5], plus Osterwalder lectures)

--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)

Slide Set 3

--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])

--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

(Cont’d.)

--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:***
  - --The low-energy (UPS) limit: (Osterwalder Paper [10], plus Osterwalder lectures)
    - Selection rules on wave vector

Slide Set 4

    - Band-structure mapping
    - 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

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.

Key Reference [15] "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

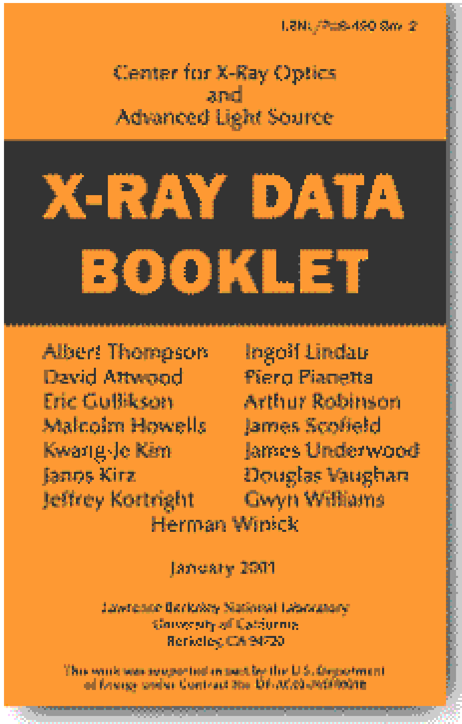
X-RAY DATA BOOKLET

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



Center for X-Ray Optics
and
Advanced Light Source

X-RAY DATA BOOKLET

Albert Thompson
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James Underwood
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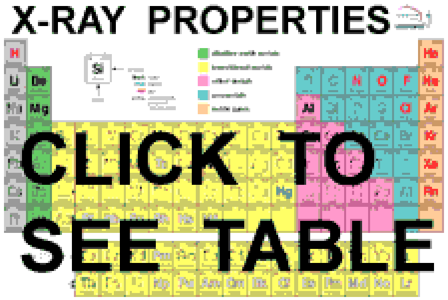
January 2001



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 ℏ; 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** —

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

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

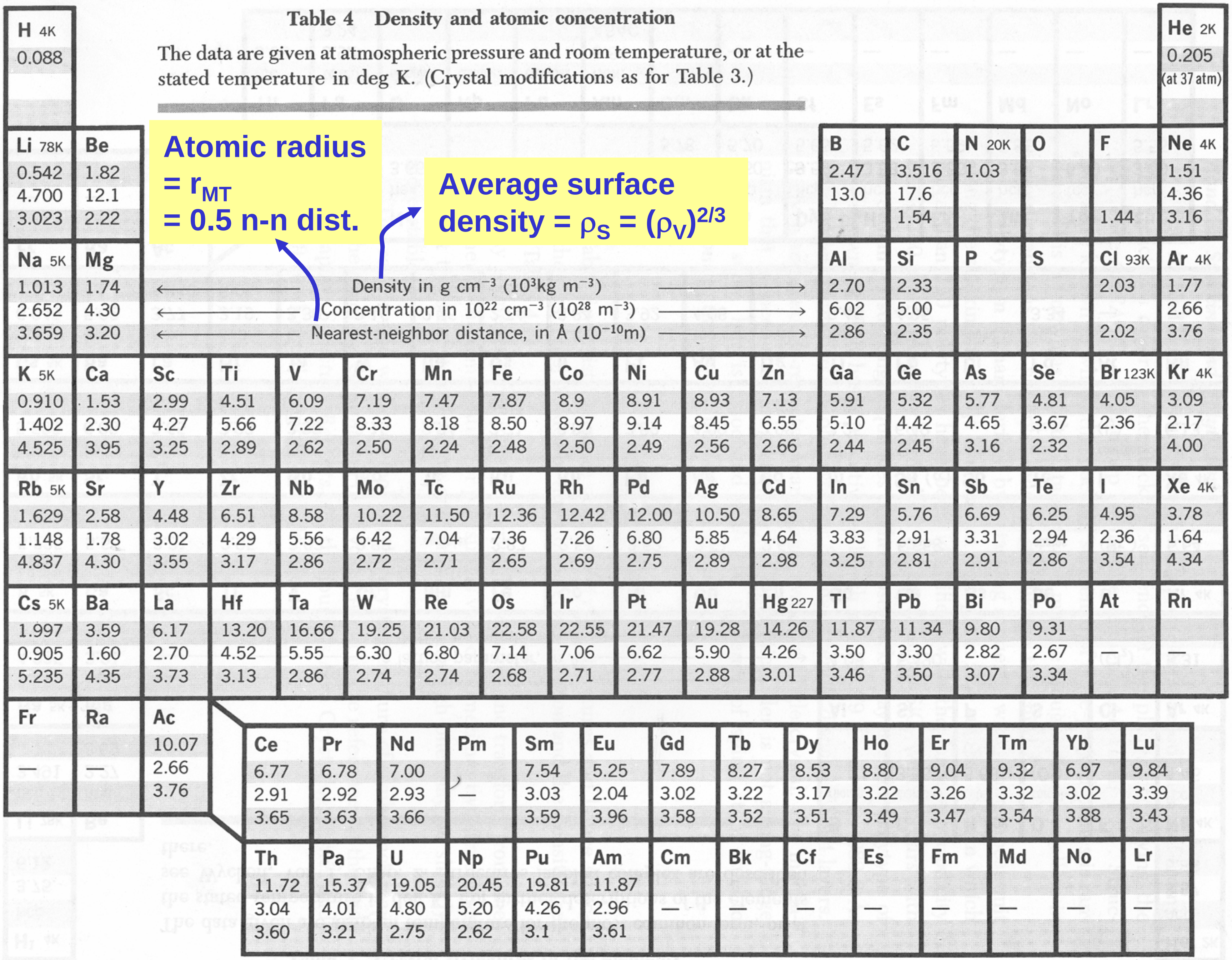


Table 4 Density and atomic concentration

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} (10^3kg 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 $\mathrm{cm^{-1}K^{-1}}$

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

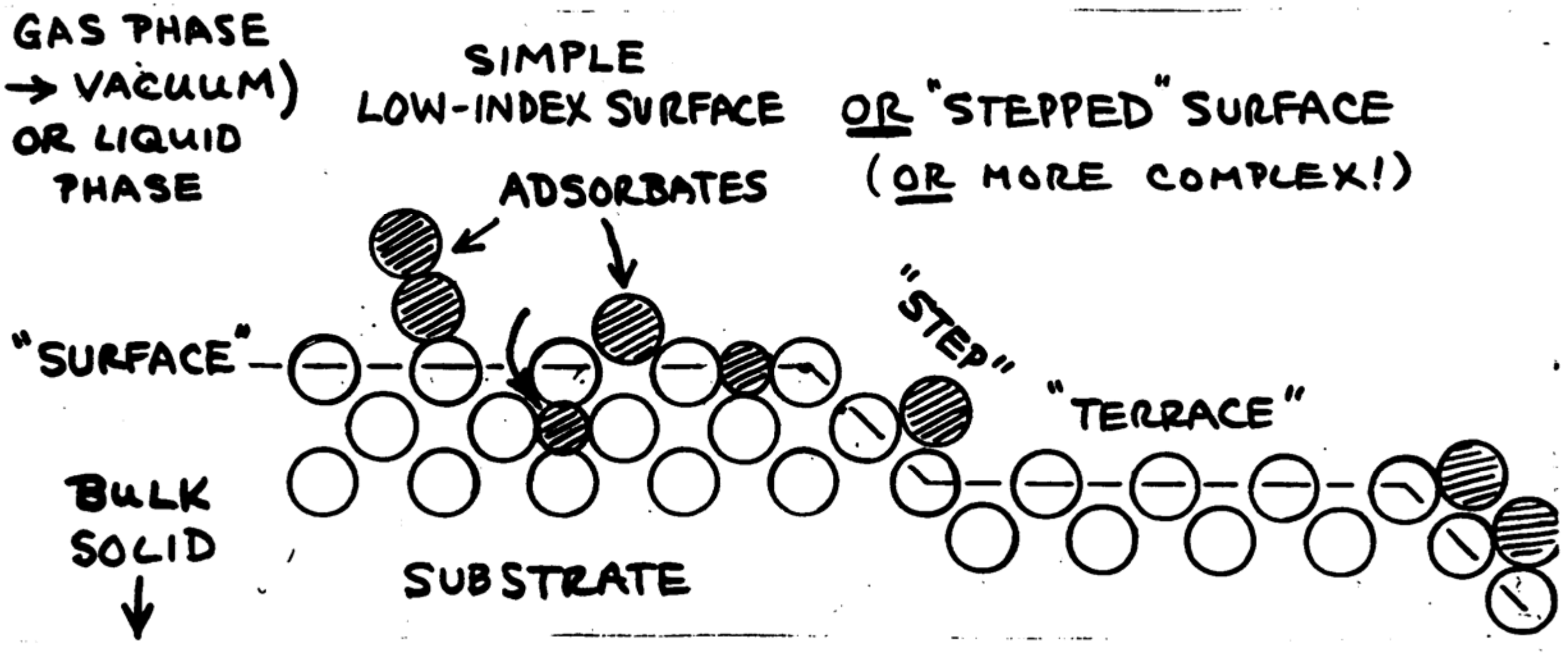
The basic synchrotron radiation techniques

Core-level photoemission

Valence-level photoemission

Microscopy with photoemission

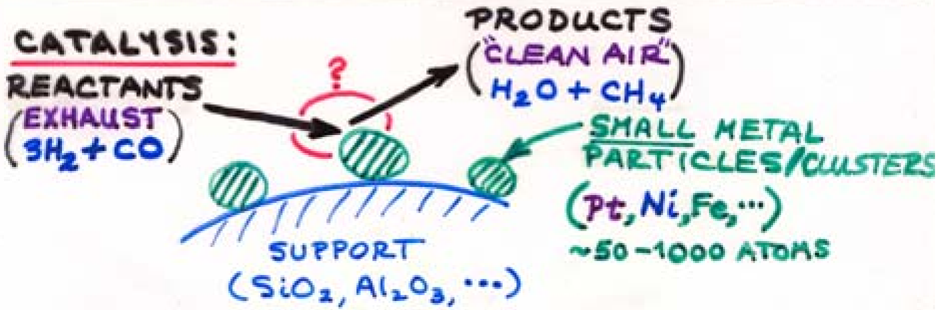
What is a surface?



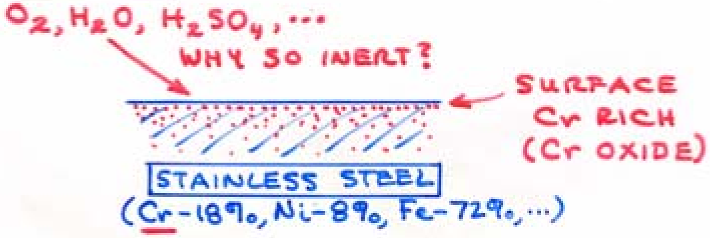
…as well as buried interfaces between two different solids: more and more important!

SOME AREAS OF APPLICATION: SURFACE SCIENCE

① CATALYSIS:

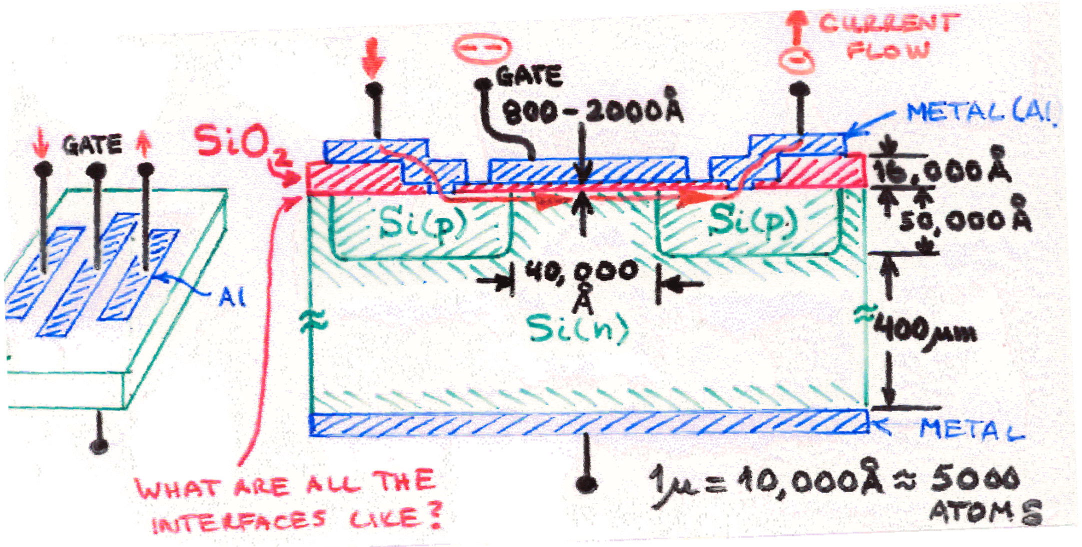


② CORROSION:



③ SOLID-STATE MICROCIRCUITS:

E.G., THE FIELD-EFFECT TRANSISTOR -



SURFACES, INTERFACES, AND NANOSTRUCTURES IN NEXT-GENERATION TECHNOLOGIES

- HIGHER-DENSITY, HIGHER-SPEED INTEGRATED CIRCUITS:

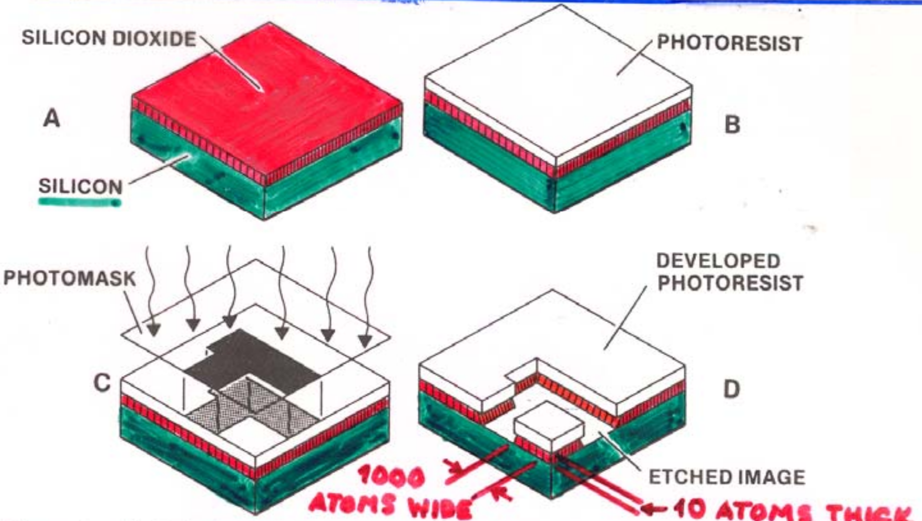
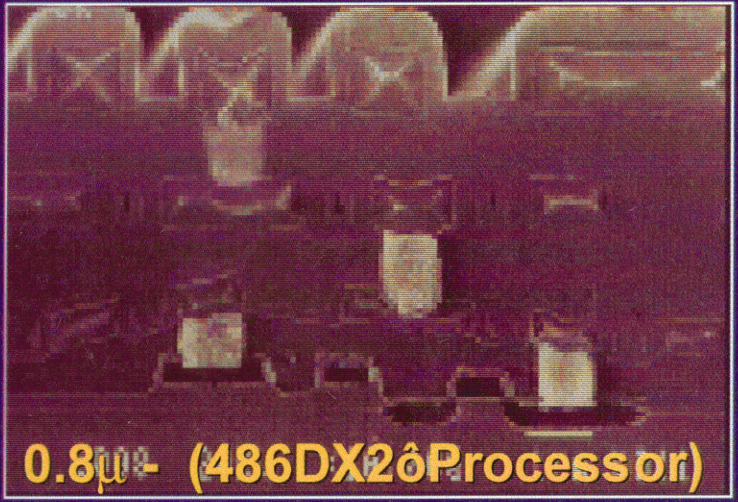
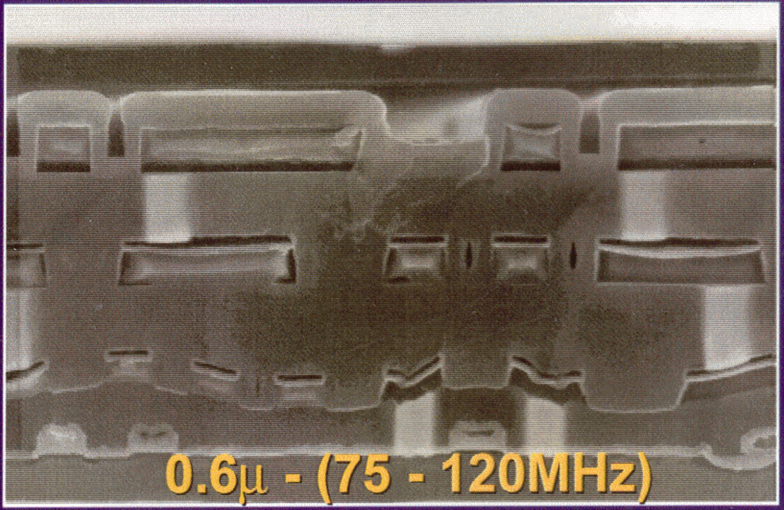


Figure 1. Typical photolithographic processing steps necessary to pattern SiO_2 layer on a Si substrate. Key: A, thermal oxidation; B, photoresist deposition; C, resist exposure through photomask; and D, develop photoresist.

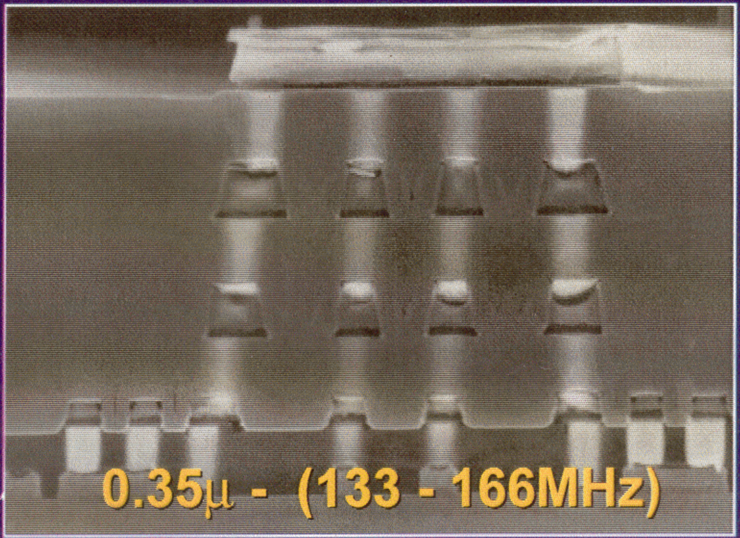
Intel Process



0.8μ - (486DX2ôProcessor)



0.6μ - (75 - 120MHz)



0.35μ - (133 - 166MHz)

0.25μ

The New York Times

SATURDAY, OCTOBER 9, 1999

Printec

Chip Progress Forecast to Hit A Big Barrier

Scientists Seeing Limits to Miniaturization

By JOHN MARKOFF

SAN FRANCISCO, Oct. 8 — For more than three decades, it has been an unshakable principle of the computer industry: every 18 months, the number of transistors that will fit on a silicon chip doubles.

The phenomenon, known as Moore's Law for the semiconductor pioneer who first observed it, has been the basic force underlying the computer revolution and the rise of the Internet. As transistors have been scaled ever smaller, computing performance has risen exponentially while the cost of that power has been driven down. And it has been assumed in the industry that the rate of progress would hold for at least another 10 to 15 years.

But now a researcher at Intel, the world's leading chip company, has reported glimpsing a potentially insurmountable barrier to the advance of Moore's Law much closer at hand, perhaps early in the coming decade.

In an article in the journal Science, the Intel scientist, Paul A. Packan, says it is not clear whether the most common type of silicon transistor can be scaled down beyond the generation of chips that will begin to appear next year, because semiconductor engineers have not found ways around basic physical limits.

"These fundamental issues have not previously limited the scaling of transistors," he wrote in the Sept. 24 issue. "There are currently no known solutions to these problems," he added, calling it "the most difficult challenge the semiconductor industry has ever faced."

Dennis Allison, a Silicon Valley physicist and computer designer, said: "The fact that this warning comes from Intel's process group is really significant. This says that they see actual limits."

The report by the Intel scientist will be echoed by researchers from the University of Glasgow in a paper to be presented in December at a conference in Washington.

Without further advances in the miniaturization of silicon-based transistors, hopes for continued progress would have to be based on technol-

Continued on Page B14

Chip Progress May Soon Be Hitting Barrier

Continued From Page A1

ogies that are promising but unproved: new materials, new transistor designs and advances like molecular computing, in which single molecules act as digital on-off switches.

To be sure, such dire warnings have been made periodically in the past — an article in Scientific American in 1987 said Moore's Law was unlikely to be maintained through the 1990's — and each time semiconductor designers have shown remarkable ingenuity to surmount seemingly impossible barriers.

Indeed, Moore's Law — first stated in 1965 by Gordon Moore, an Intel co-founder — proved to be understated; Moore had to revise his initial prediction of 24 months for each doubling of chip capacity. And while it is not an actual physical law, his observation has taken on an almost mystical quality as the clearest expression of the power of human science and engineering and many industry executives have come to see it as a self-fulfilling prophecy.

In the last decade the advances described by Moore's Law have had an accelerating impact on the personal computer industry, driving the cost of desktop machines down from $3,000 to as low as $500 while increasing their power.

The inventors of the original semiconductor design technology are for the most part still bullish about extending that progress, whatever the immediate hurdles.

"Historically the economic incentives to find new methods for device improvement have regularly overcome the predicted scaling limits," said John Moussouris, a physicist and semiconductor designer. "The physical challenges may be getting harder, but the people and financial resources to surmount them are also growing each year."

But for the first time the global semiconductor industry is grappling with transistors so small that the placement of individual atoms will soon become crucial.

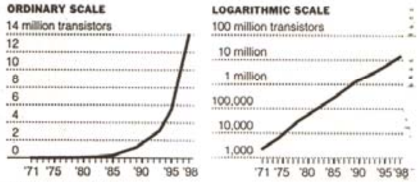
For example, in the current generation of semiconductors, the wires that interconnect transistors are etched as fine as 0.18 micron — one five-hundredth the width of a human hair — and the individual insulating layers that are inside a transistor may be only four or five atoms thick.

Semiconductor factories in Japan plan to begin mass production of chips based on widths of 0.13 micron early next year, and such chips should be in widespread use within two years. But beyond that generation, the industry's leading researchers acknowledge there remain far more questions than answers.

The next step would be widths of 0.10 micron, a milestone that in the Moore's Law progression would be expected three to five years from now. But at that scale, Mr. Packan writes, transistors will be composed of fewer than 100 atoms, and statistical variations in this Lilliputian world are beyond the ability of semiconductor engineers to control.

Moore's Law

Gordon Moore, a co-founder of the Intel Corporation, has observed that the capacity of computer chips should double every 18 months. Up to now, that has largely been true. Here are the capacities of top-of-the-line Intel chips charted on an ordinary scale and on a logarithmic scale, which depicts comparable rates of change similarly.



Source: VLSI Technology

The New York Times

Mr. Packan said he had written the Science article to challenge the industry and academia to focus on areas where breakthroughs are needed. "For the last 30 years we've been engineering the device, and now what's required is fundamental science," he said in a telephone interview today.

Intel executives cautioned against reading too much gloom into their technical papers, saying that while they did not yet have precise engineering solutions for breaking the 0.10 micron barrier, they were confident that answers would be found.

> *Transistor size may soon be an issue of great concern. Then again, maybe not.*

They suggested that part of the reason for Intel's recent pessimism might have more to do with the need for corporate secrecy than the arrival of fundamental technical limits.

"We face serious challenges," said Mark Bohr, an Intel technology development director and the co-author of an internal Intel technical paper that enumerates the company's unsolved problems. "We all have ideas to address some of these problems and admittedly they are iffy and not fully developed, and you don't want to tip your cards too soon."

And Carver Mead, a physicist and a pioneer in semiconductor design, says he still adheres to what has been the conventional industry wisdom, suggesting that Moore's Law will continue to account for the pace of silicon technology advances until at least 2014. "There are still some open issues," he said. "and so the Chicken Little sky-is-falling articles are a recurring theme."

But James Heath, a chemistry professor at the University of California at Los Angeles who is a co-inventor of the carbon 60 molecule known as the Buckyball, said the industry might be overly optimistic because it had such a vast investment in today's silicon technology.

With researchers at Hewlett-Packard, Mr. Heath has developed a prototype memory cell the size of a single molecule that operates on different principles from today's semiconductors.

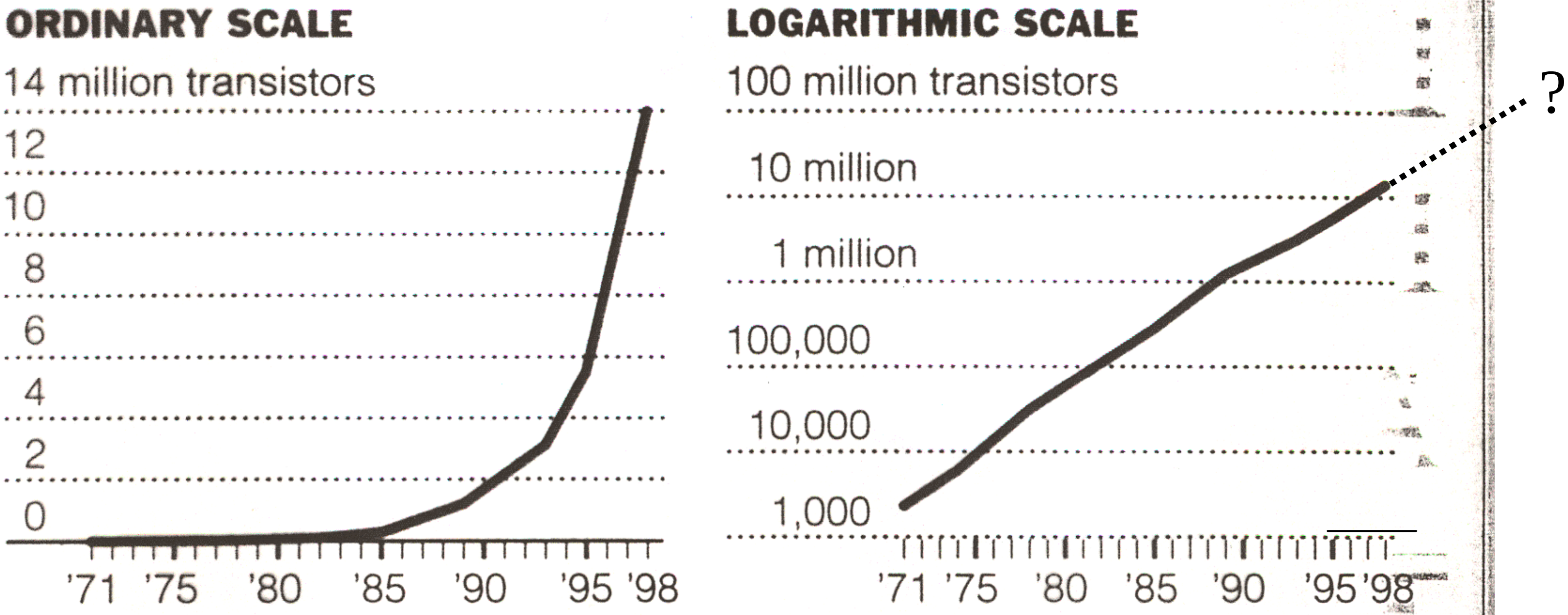
"I think their optimism for being able to continue until 2014 is not very realistic," he said. "When you get to very, very small sizes, you are limited by relying on only a handful of electrons to describe the difference between on and off."

Executives at I.B.M., which along with Intel and Motorola is one of the nation's dominant chip makers, acknowledged that it might be accurate to warn of an impending limit to the shrinking of today's dominant chips, known as C.M.O.'s, or complimentary metal oxide semiconductors. But they said they believed they had found an alternative approach, known as silicon-on-insulator, that held great promise at dimensions of 0.10 micron and smaller.

"This paper is quite consistent with work we've published," said Randall Isaac, vice president for systems technology and science at I.B.M.'s Watson Laboratory in Yorktown Heights, N.Y. "But when a given technology saturates, it is usually replaced by a new one."

Moore's Law

Gordon Moore, a co-founder of the Intel Corporation, has observed that the capacity of computer chips should double every 18 months. Up to now, that has largely been true. Here are the capacities of top-of-the-line Intel chips charted on an ordinary scale and on a logarithmic scale, which depicts comparable rates of change similarly.



ORDINARY SCALE

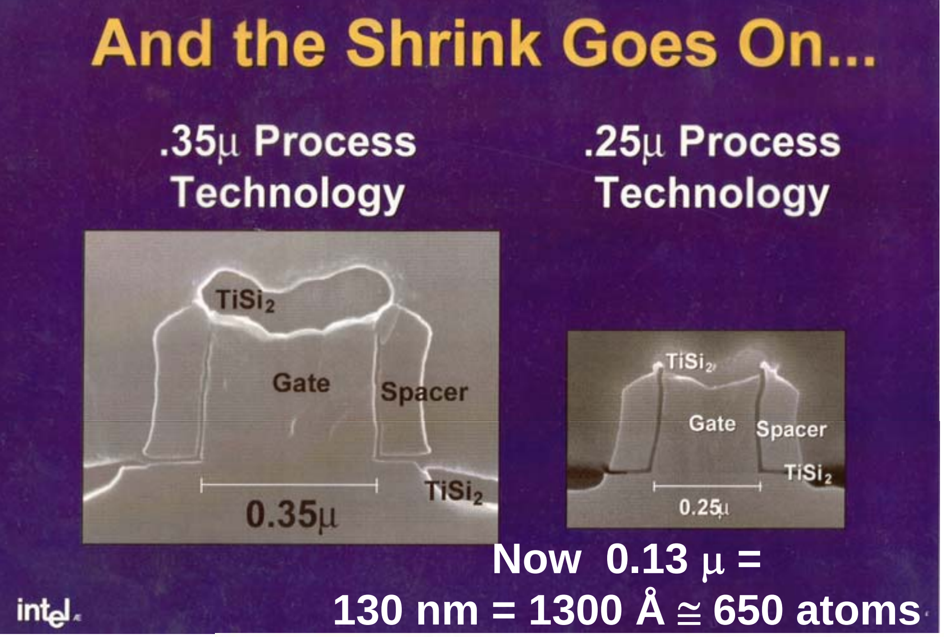
LOGARITHMIC SCALE

Source: VLSI Technology

Oct. 9, 1999

The New York Times

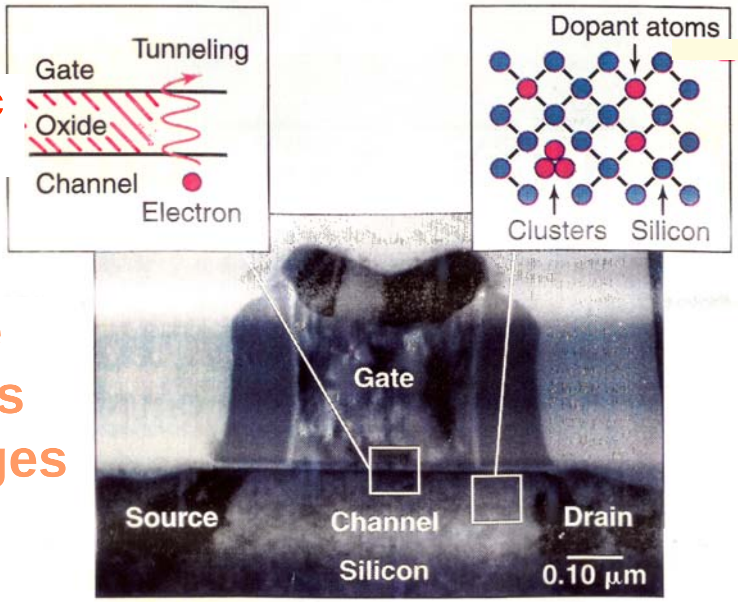
And the Shrink Goes On...



Now 0.13 µ =
130 nm = 1300 Å ≅ 650 atoms

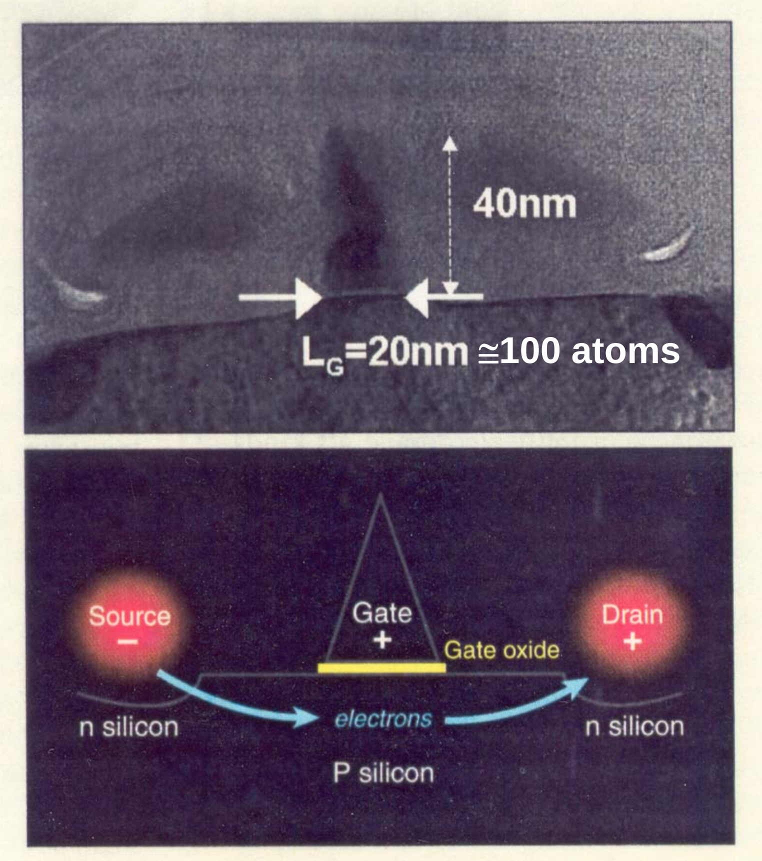
~10 atomic layers

~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

What does the interface look like? How thick is it?

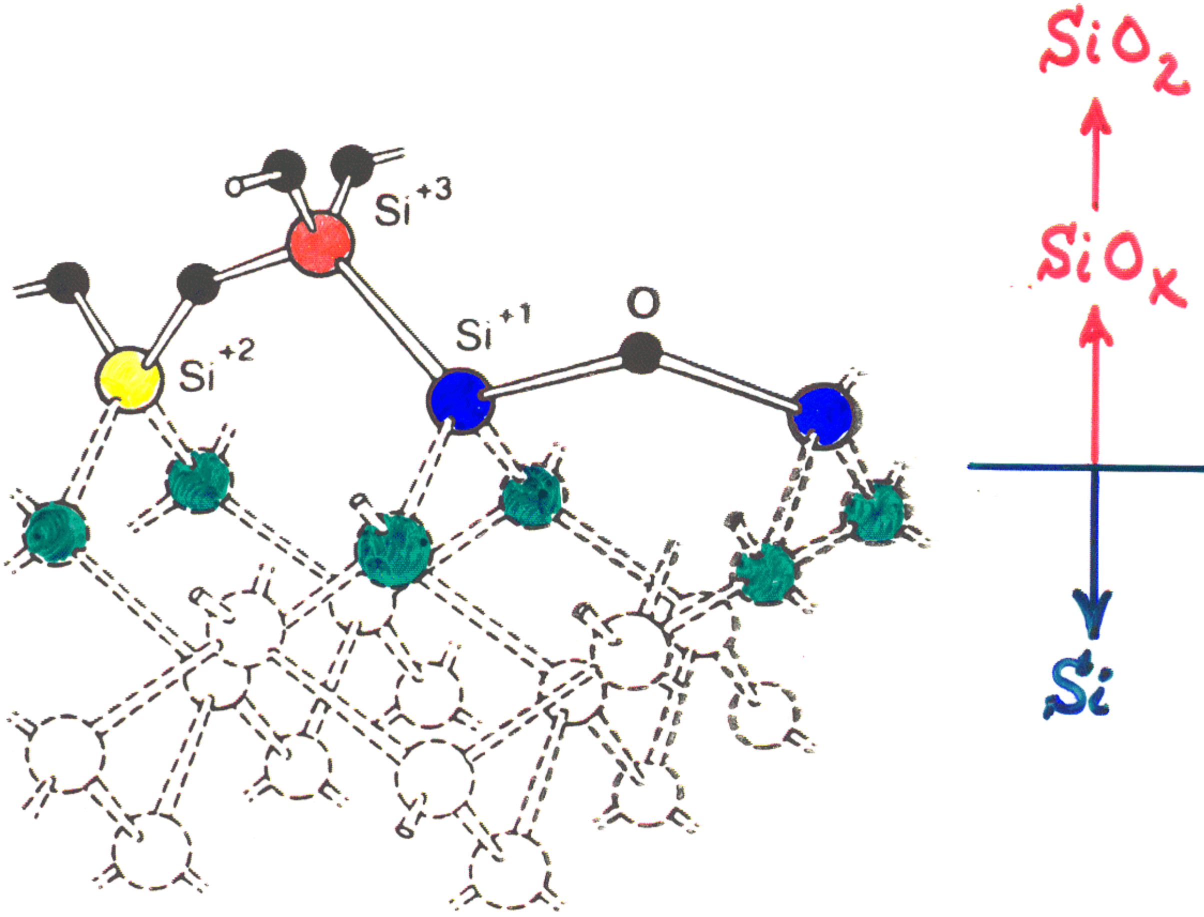
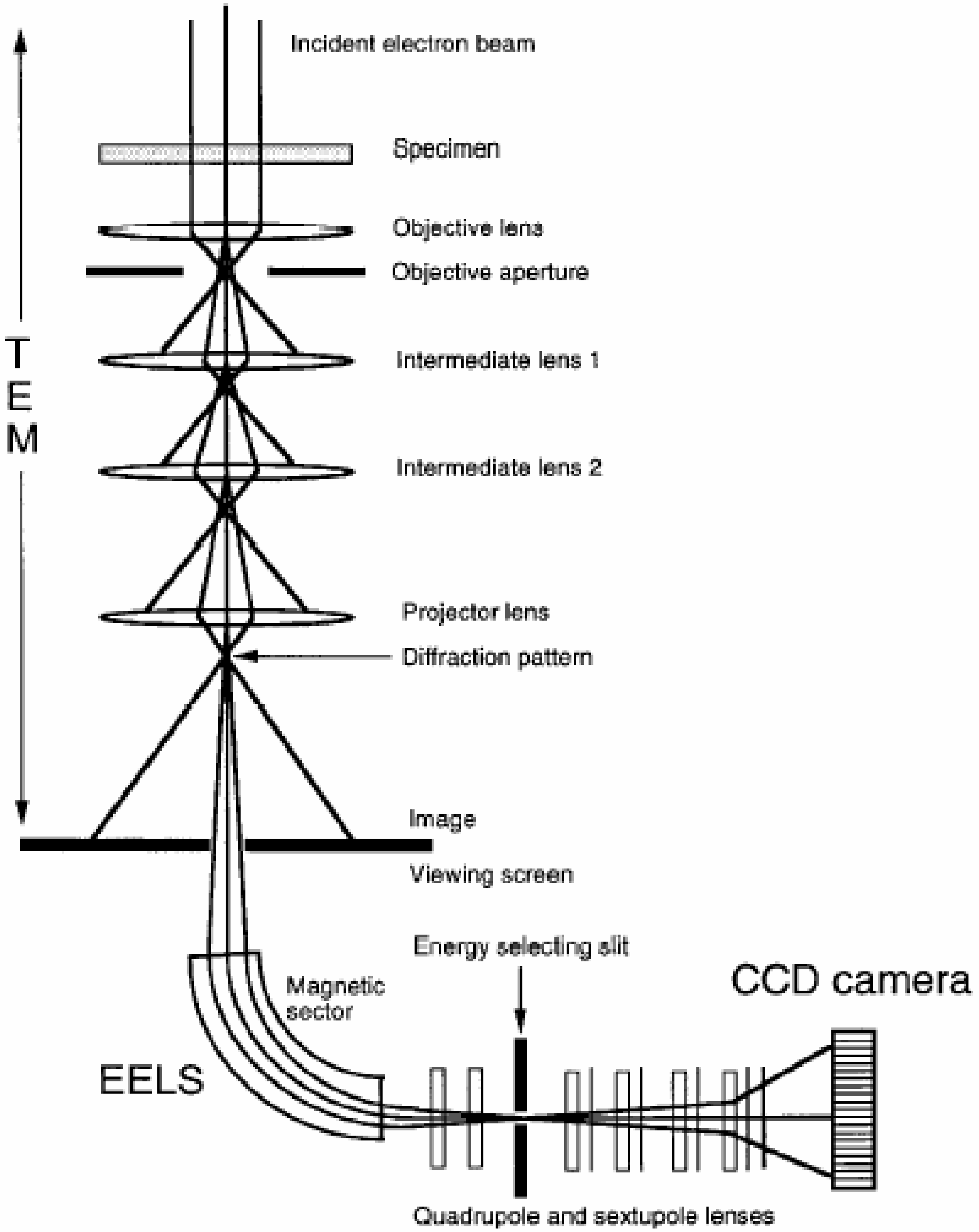


FIG. 2. Topological structure of various silicon suboxides at the SiO_2/Si (100) interface. The structure is based on the plastic ball and spoke model proposed by Ohdomari *et al.*[9]

Probing buried interfaces: Transmission Electron Microscope with Electron Energy Loss Spectroscopy (not SR)



J. Res. Nat. Inst. Stds. & Tech.
Volume 102, Number 1,
January–February 1997

HIGH-RESOLUTION TRANSMISSION e^- MICROSCOPY OF SiO_2/Si INTERFACES

(GOODNICK ET AL., PHYS. REV. B 32, 8171 ('85))

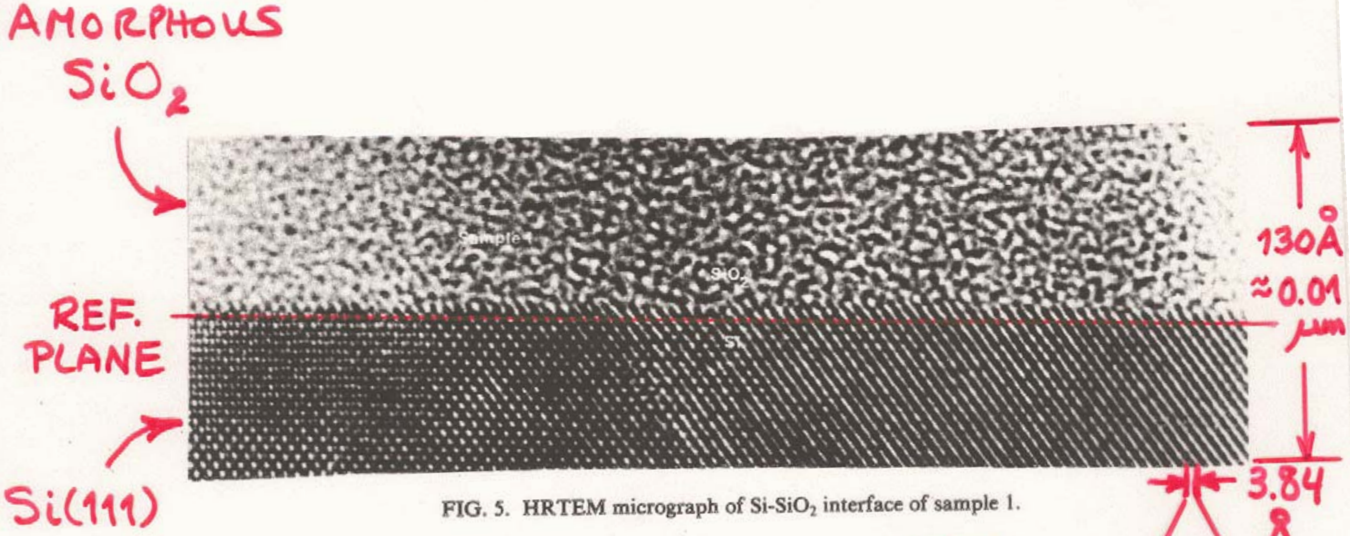


FIG. 5. HRTEM micrograph of Si-SiO_2 interface of sample 1.

1000°C, O_2 ONLY

SMOOTH INTERFACE

●,● = Si

IN TETRAHEDRAL "DIAMOND" STRUCTURE

⟹ 6-MEMBER RING

SCANNING TRANSMISSION e^- µSCOPY WITH EELS :

Si 2p excitations— like x-ray absorption spectra

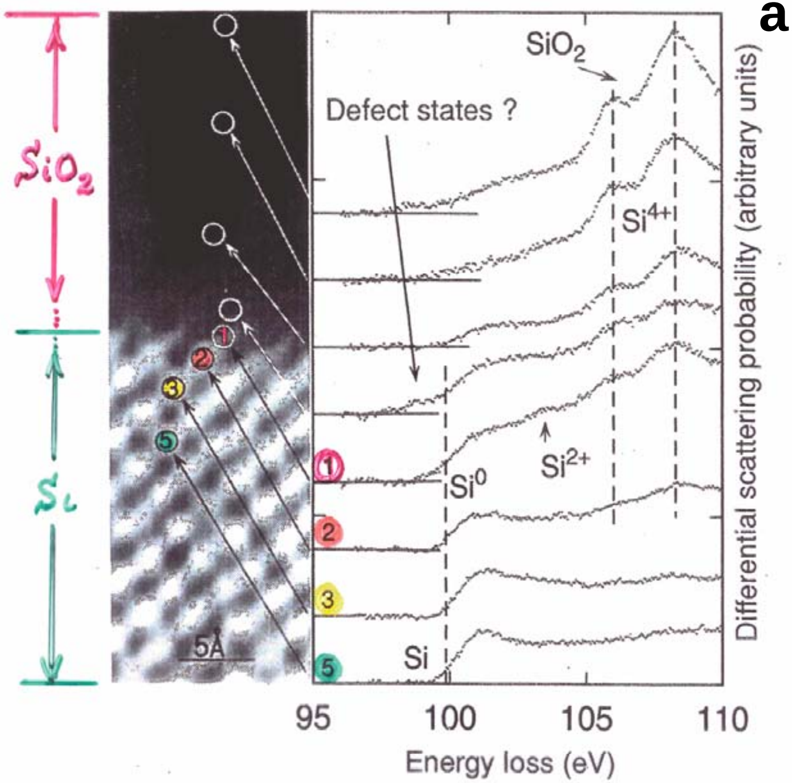
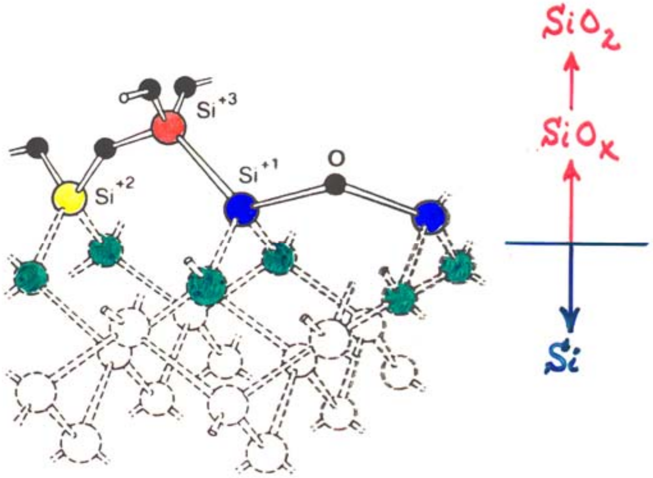


FIG. 1 Left, Incoherent dark-field image of the Si–SiO$_2$ interface for a steam-formed oxide. The elongated bright structures coincide with chains of Si atom pairs, oriented along the ⟨110⟩ directions. Right, EELS spectra obtained at eight locations indicated by the circles at the left. The bulk Si onset (Si^0) is near 100 eV. The SiO$_2$ (Si^{4+}) structure lies between 105 and 108 eV. At the interface, a fairly strong Si^{2+} signal is seen for the first time in the bulk. Some structure corresponding to electronic defect states in the silicon gap also appears to be present.

$\Delta E \approx 0.1$ eV
$\Delta x, \Delta y \approx 0.2$ nm



P. E. BATSON,
NATURE, 366,
727 (1993)

PHOTOELECTRON SPECTROSCOPY

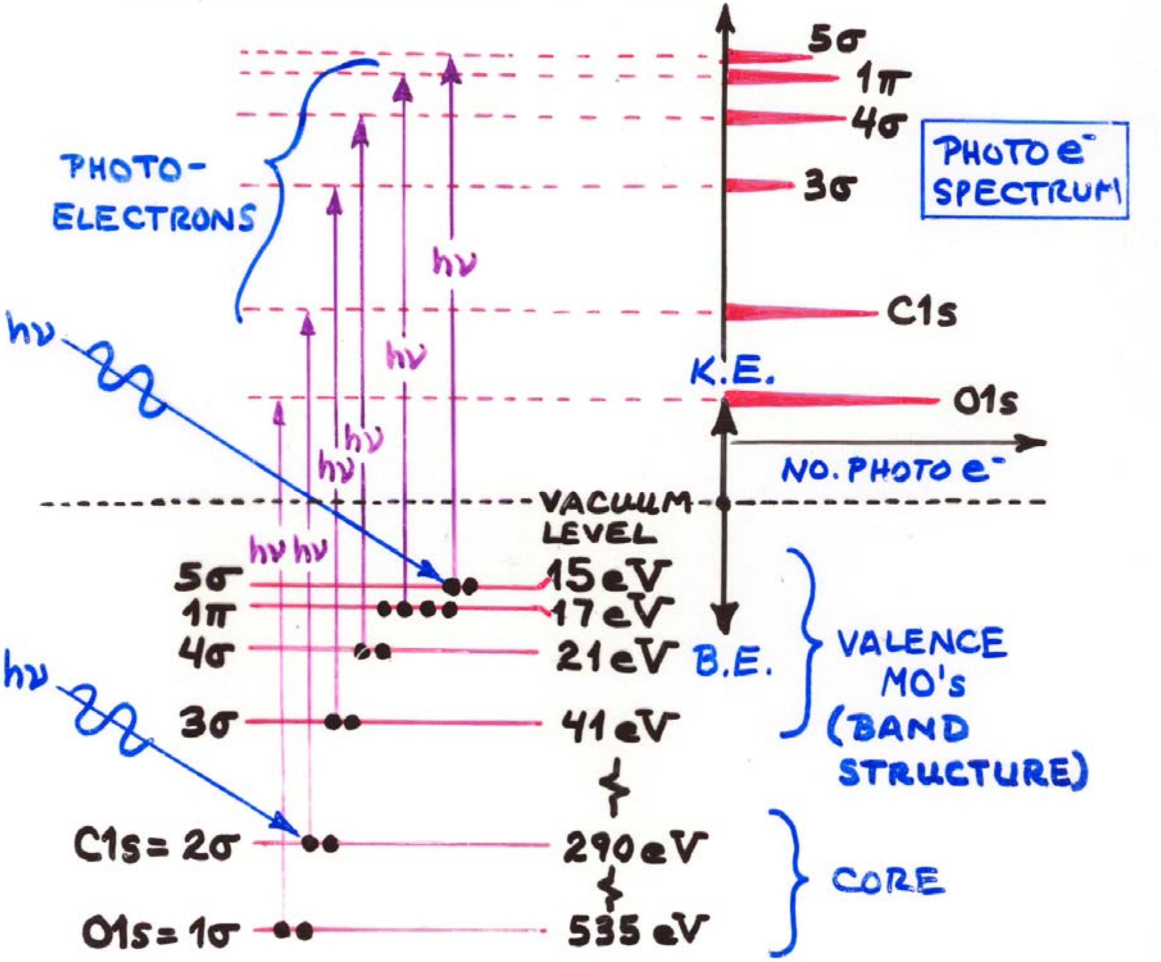
THE PHOTOELECTRIC EFFECT (EINSTEIN, 1905):

(PHOTON ENERGY) = (e^- BINDING ENERGY IN SYSTEM) + (PHOTOELECTRON KINETIC ENERGY)

(ABSORBED) (EMITTED)

= B.E. + K.E.

EXAMPLE – CO MOLECULE:

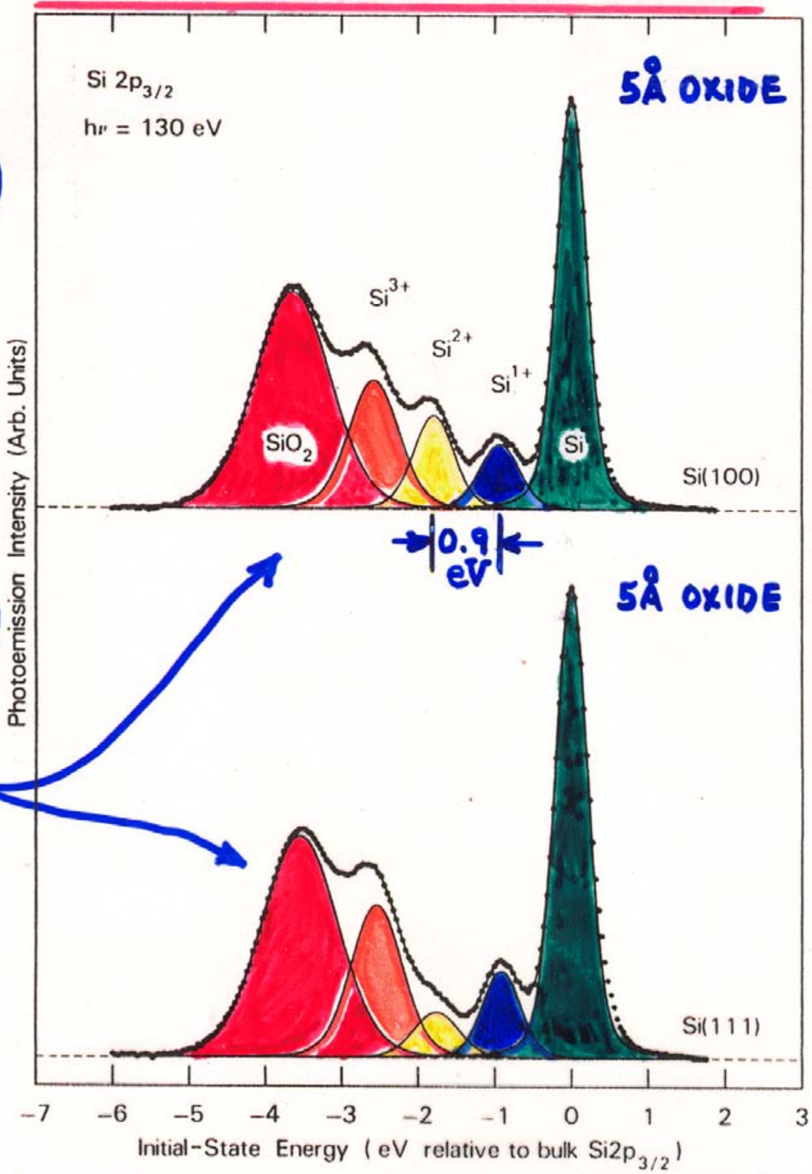


PHOTOELECTRON SPECTRA

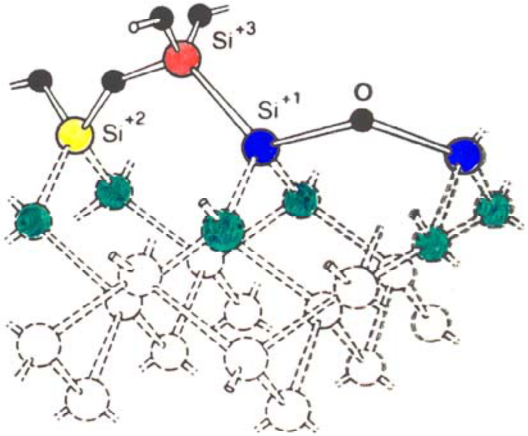
OXIDIZED SILICON

CHEMICAL SHIFTS OF CORE LEVELS

EXACTLY WHAT IS STRUCTURE OF INTERFACE? NEED STATE-SPECIFIC STRUCTURAL INFORMATION!



HIMPSEL ET AL., PHYS. REV. B, 38, 6084('90)



SURFACES, INTERFACES, AND NANOSTRUCTURES IN NEXT-GENERATION TECHNOLOGIES

③ HIGHER-DENSITY, HIGHER-SPEED INTEGRATED CIRCUITS:

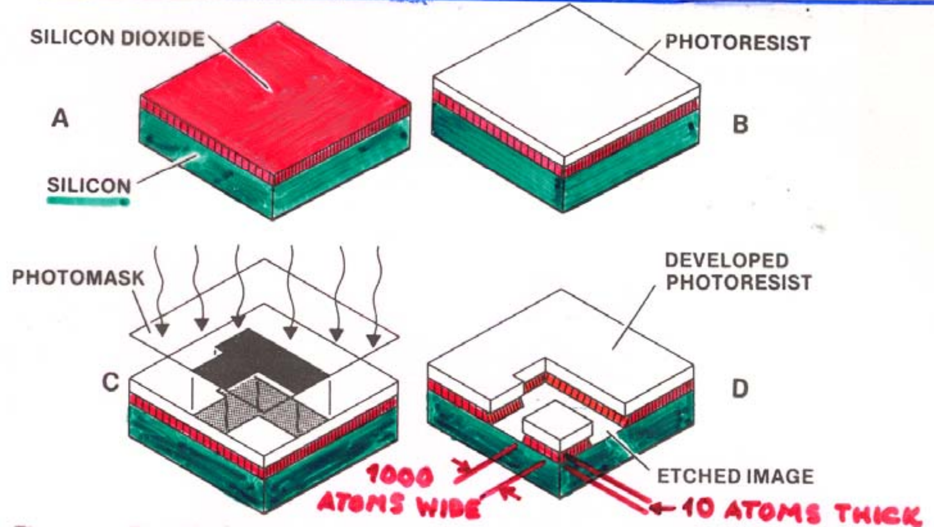
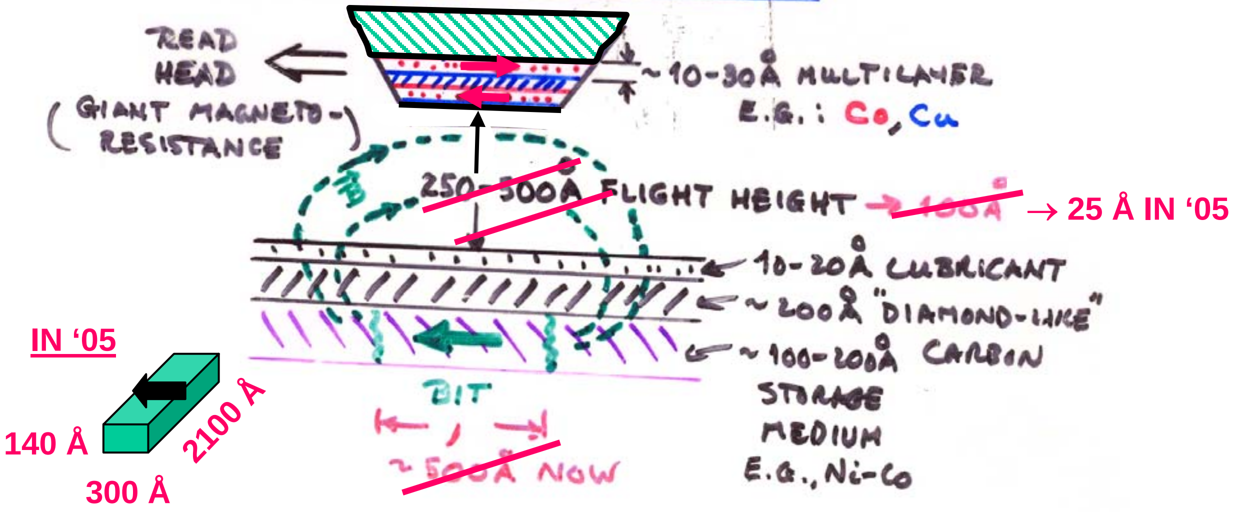
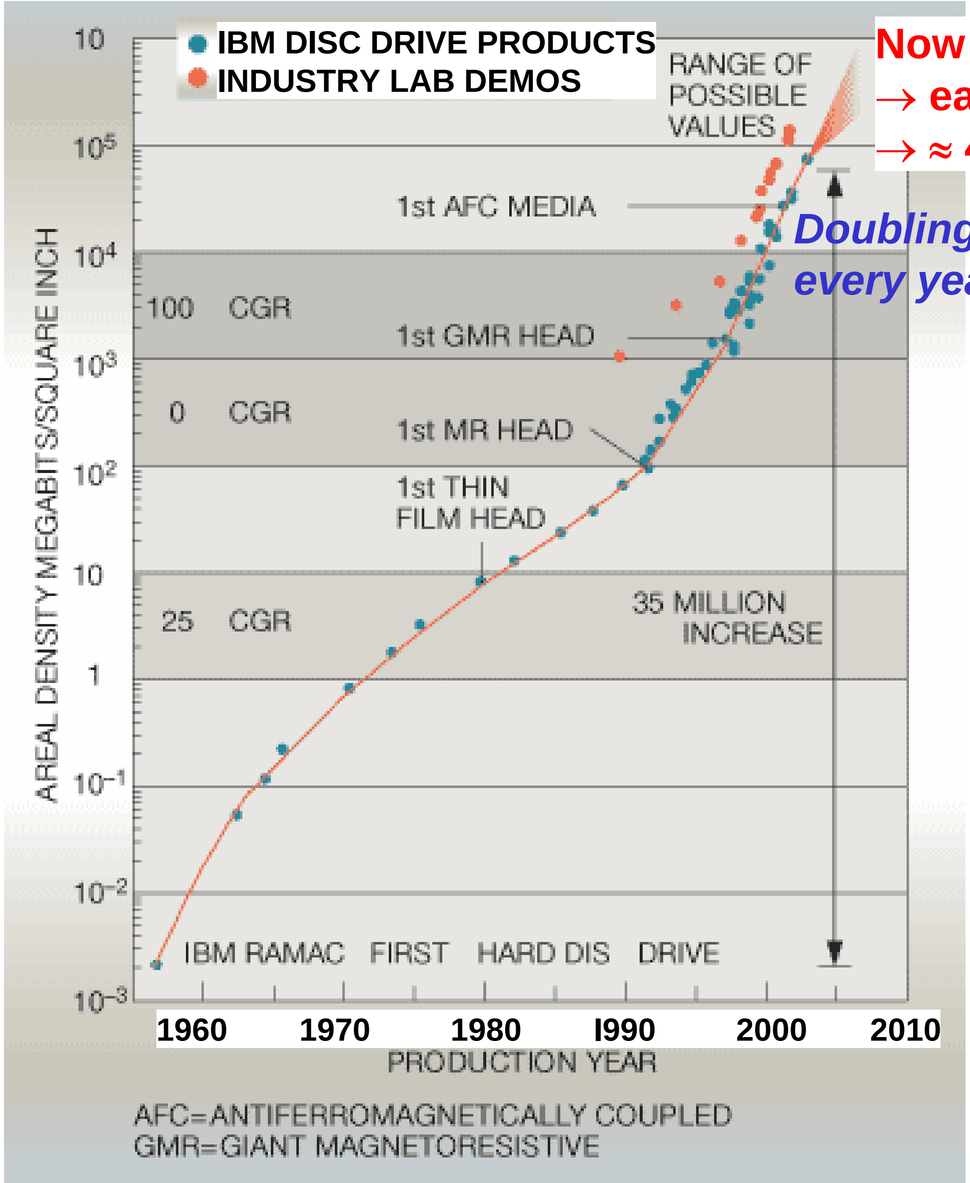


Figure 1. Typical photolithographic processing steps necessary to pattern SiO_2 layer on a Si substrate. Key: A, thermal oxidation; B, photoresist deposition; C, resist exposure through photomask; and D, develop photoresist.

④ HIGHER-DENSITY MAGNETIC STORAGE:



“Moore’s Law” for magnetic storage



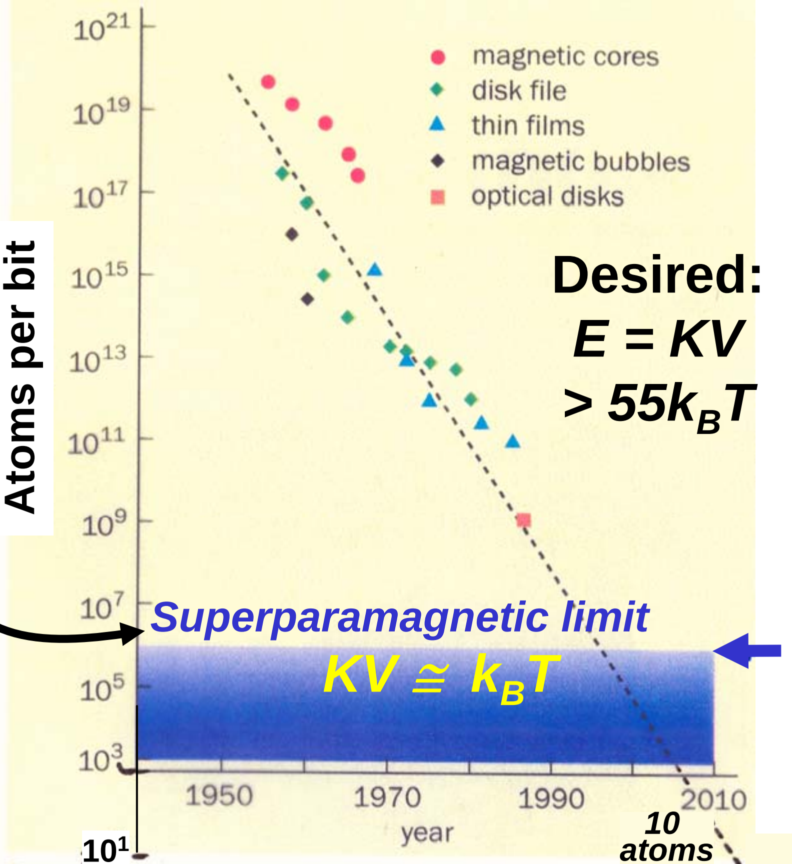
Doubling every year!

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

→ each bit ~14 nm x 30 nm x 210 nm

→ ≈ 4,000,000 atoms, read at GHz rates

How for can we go?



Atoms per bit

Superparamagnetic limit

$KV \cong k_B T$

Desired:

$E = KV$

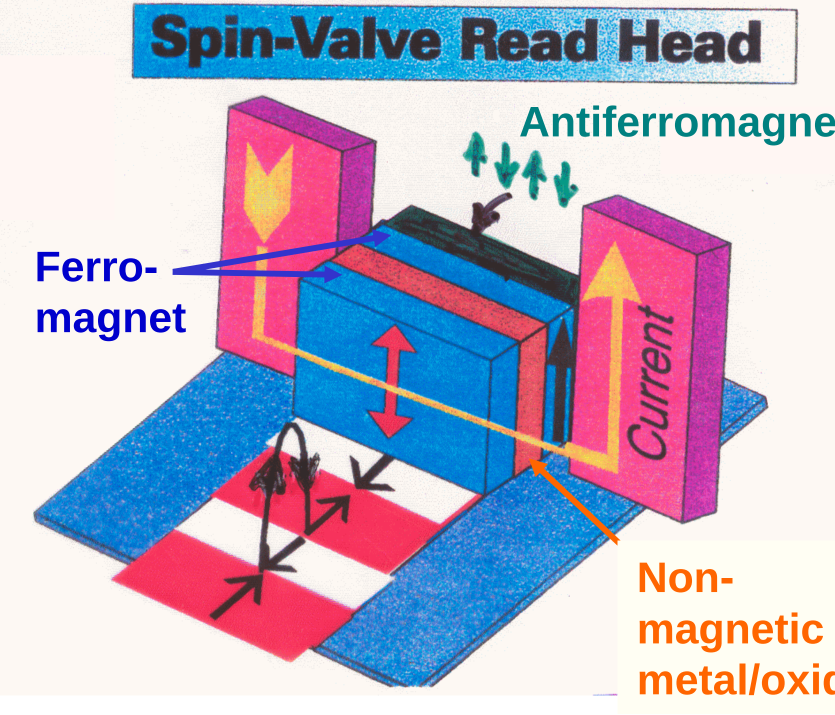
$> 55 k_B T$

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”



Antiferromagnet

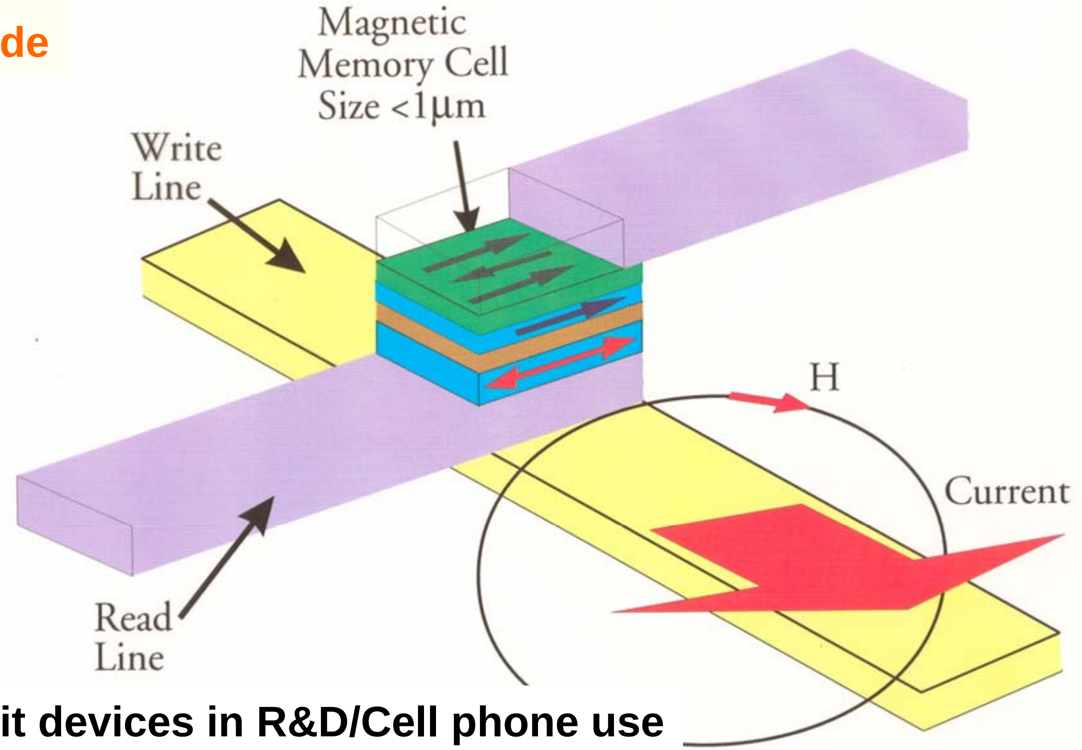
Ferro-magnet

Non-magnetic metal/oxide

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

Crucial surfaces/buried interfaces everywhere!

Magnetic Random Access Memory (MRAM-Non Volatile)



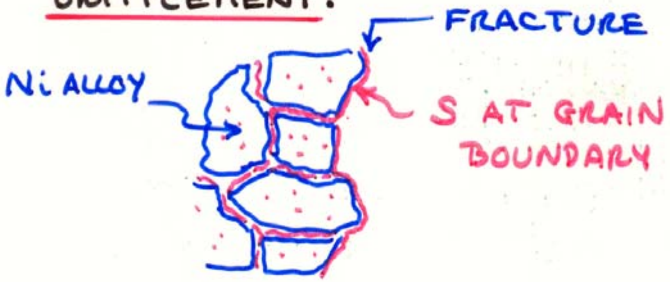
Up to 100 Mbit devices in R&D/Cell phone use

⑤ POLYMER SURFACE MODIFICATION: E.G., TO REDUCE FRICTION OR PROMOTE ADHESIVE PROPERTIES OR REDUCE FLAMMABILITY.

⑥ ELECTRODE SURFACES IN ELECTROCHEMICAL CELLS, FUEL CELLS, BATTERIES, SENSORS:

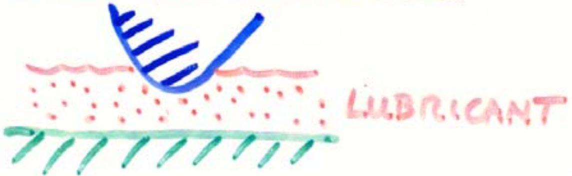
⑦ ATMOSPHERIC PARTICULATES:

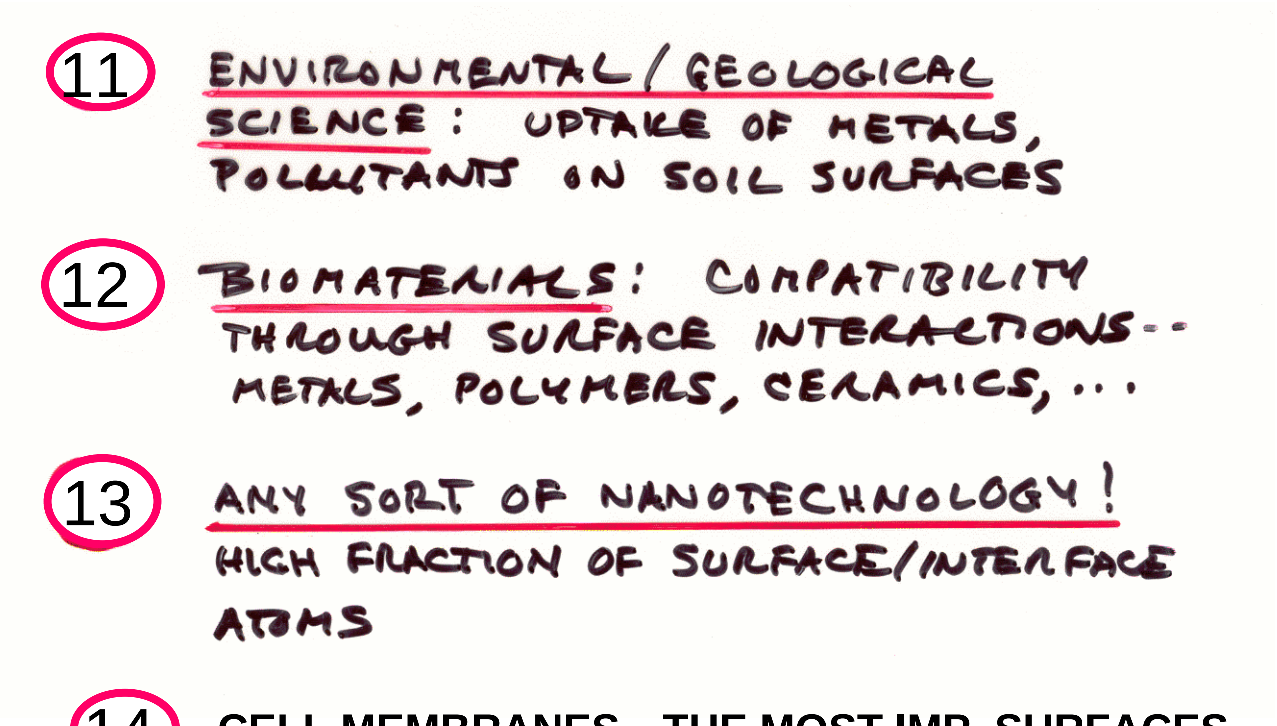
⑧ FRACTURE SURFACES DUE TO EMBRITTLEMENT:



⑨ WALL MATERIALS IN NUCLEAR REACTORS, FUSION REACTORS:

⑩ LUBRICATION (TRIBOLOGY):





11 ENVIRONMENTAL / GEOLOGICAL SCIENCE: UPTAKE OF METALS, POLLUTANTS ON SOIL SURFACES

12 BIOMATERIALS: COMPATIBILITY THROUGH SURFACE INTERACTIONS -- METALS, POLYMERS, CERAMICS, ...

13 ANY SORT OF NANOTECHNOLOGY! HIGH FRACTION OF SURFACE/INTERFACE ATOMS

14 **CELL MEMBRANES—THE MOST IMP. SURFACES**

15 **AND PROBABLY OTHERS**

Outline

Surface, interface, and nanoscience—short introduction

➡ Some surface concepts and techniques

Experimental aspects: laboratory-based and SR-based

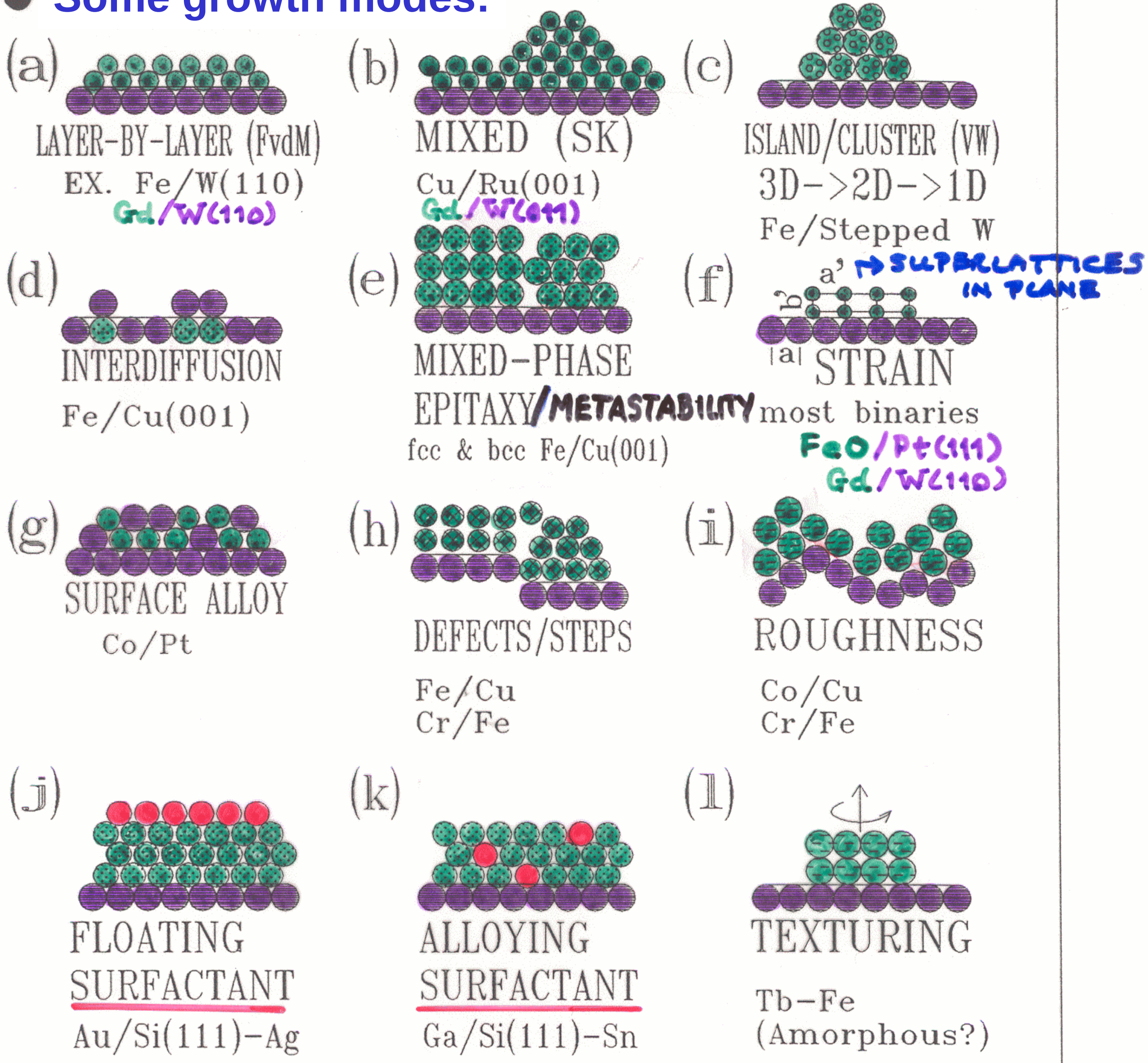
Electronic structure—a brief review

The basic synchrotron radiation techniques

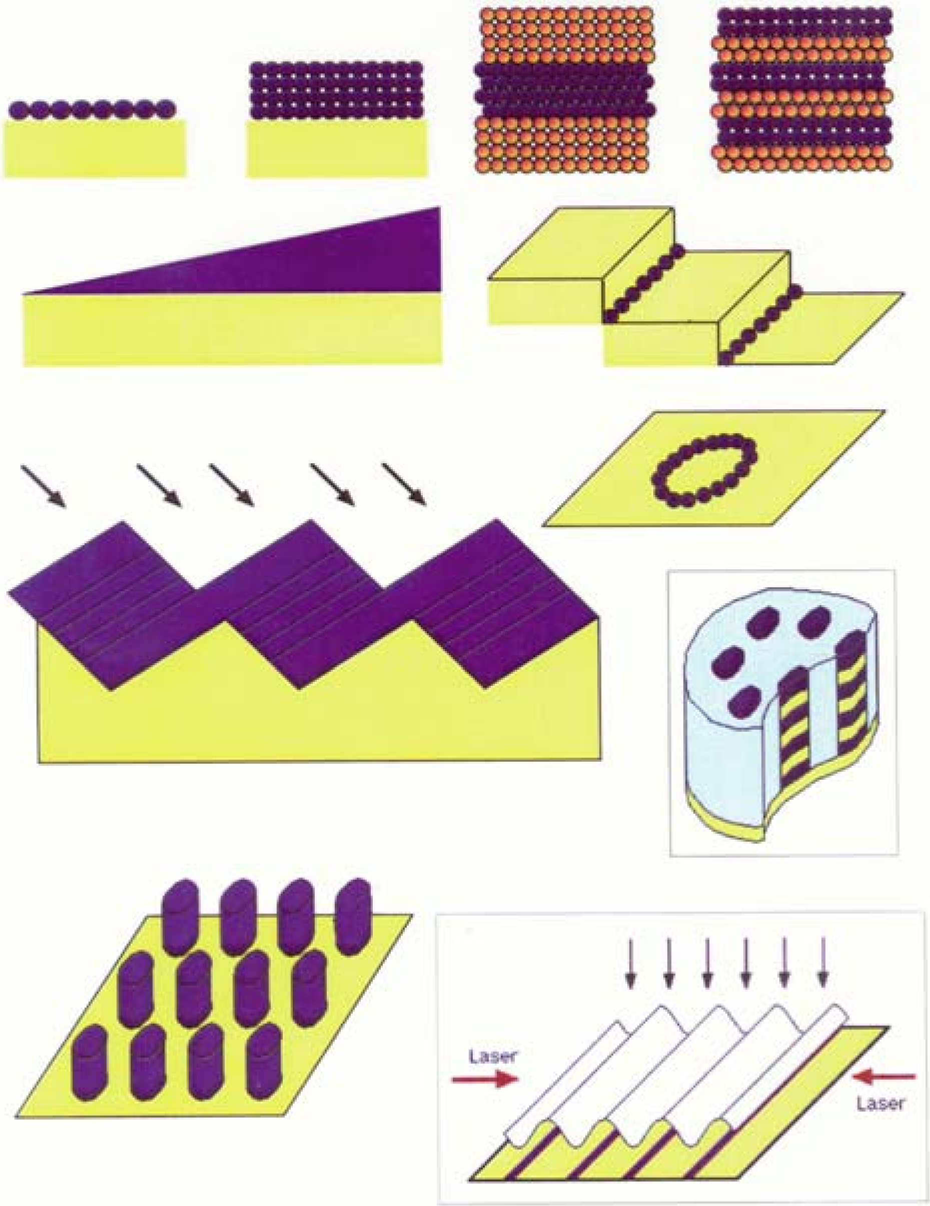
Core-level photoemission

Valence-level photoemission

- **Some growth modes:**

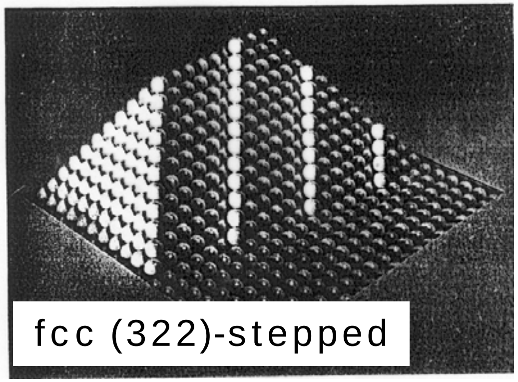


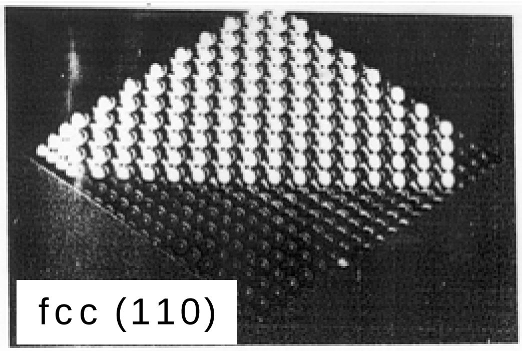
Some important structures in nanoscience/nanotechnology



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

WHAT DO SURFACES LOOK LIKE?
SOME fcc AND bcc SURFACES


fcc (322)-stepped


fcc (110)

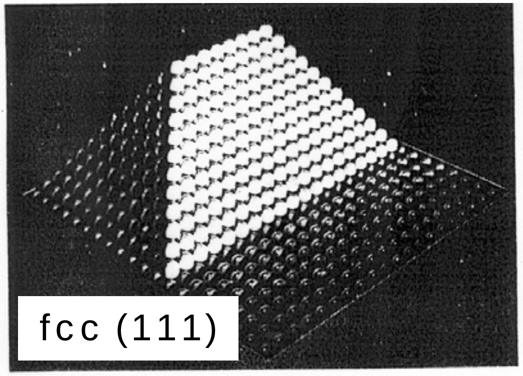
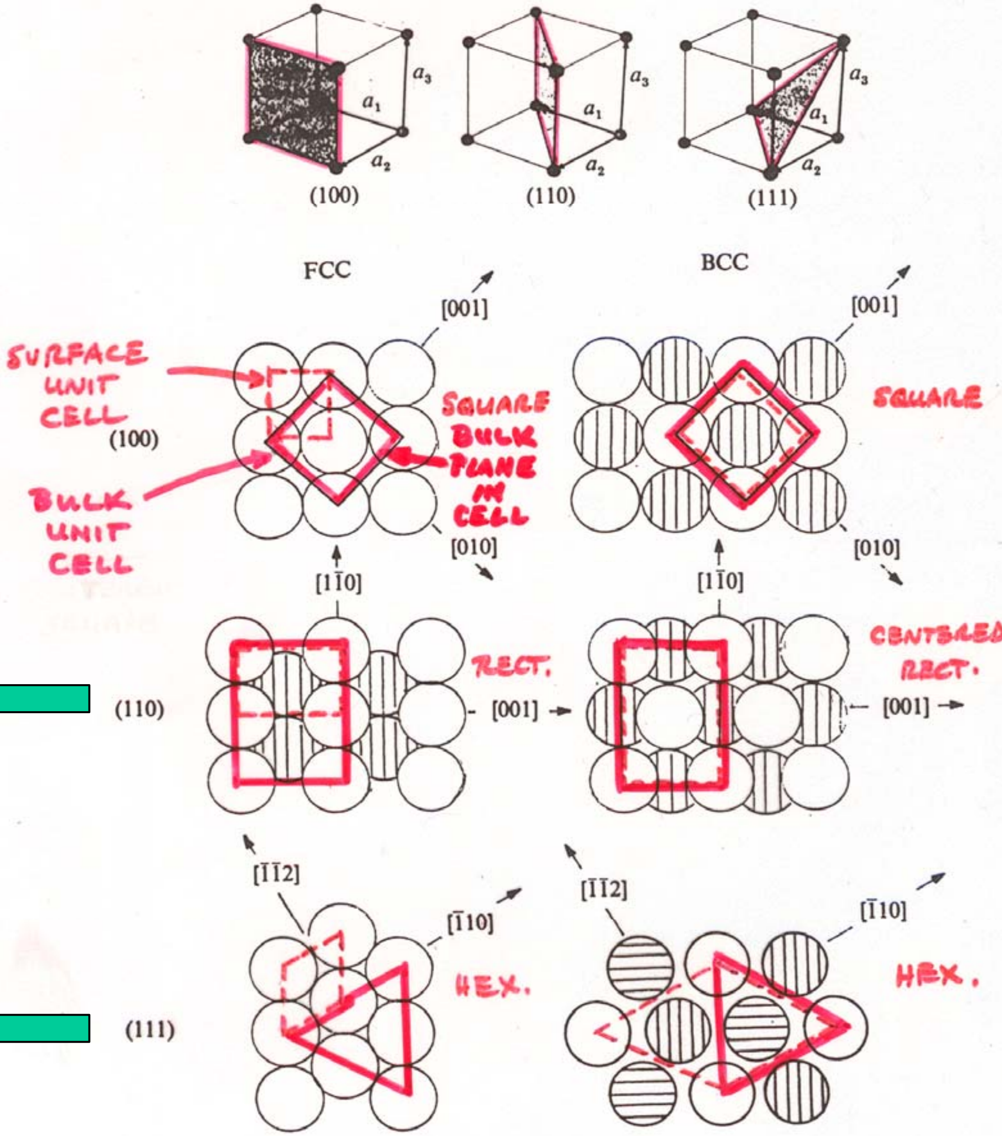
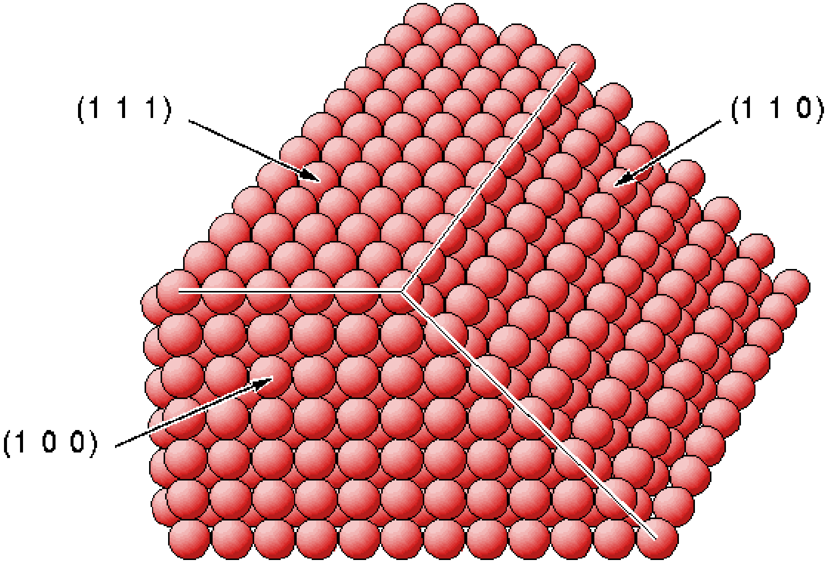

fcc (111)

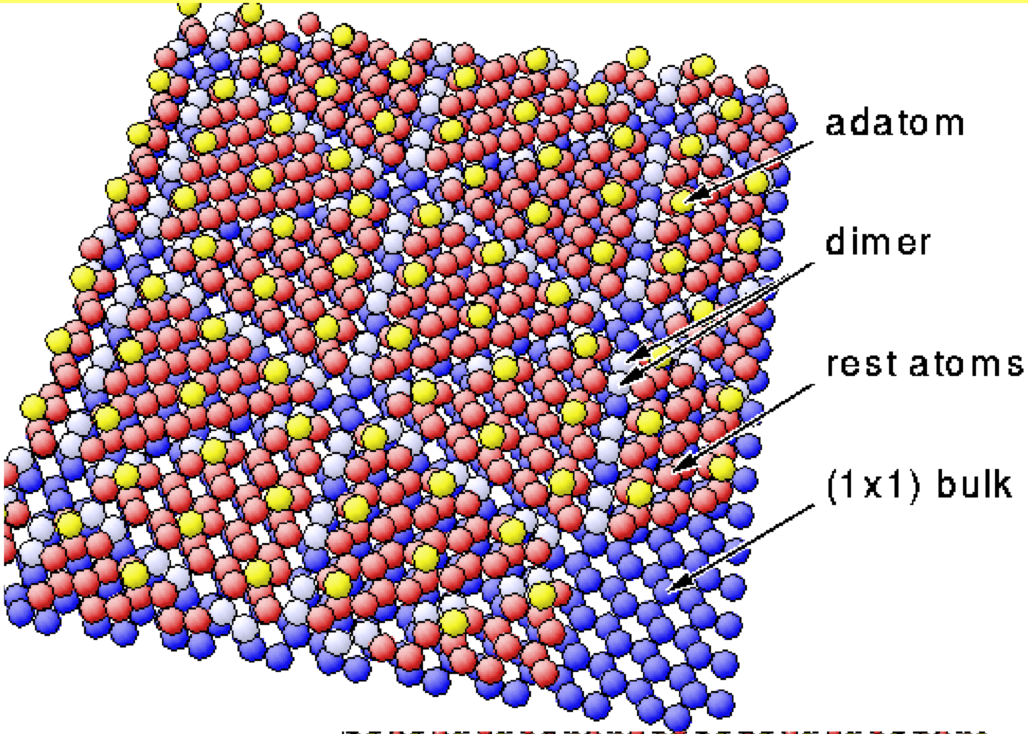
Fig. 3.2. Low-index ideal surfaces of a hard-sphere cubic crystal. Vertical and horizontal markings indicate the second and third atom layers, respectively. Cube face is indicated for (100) to set the scale (Nicholas, 1965).



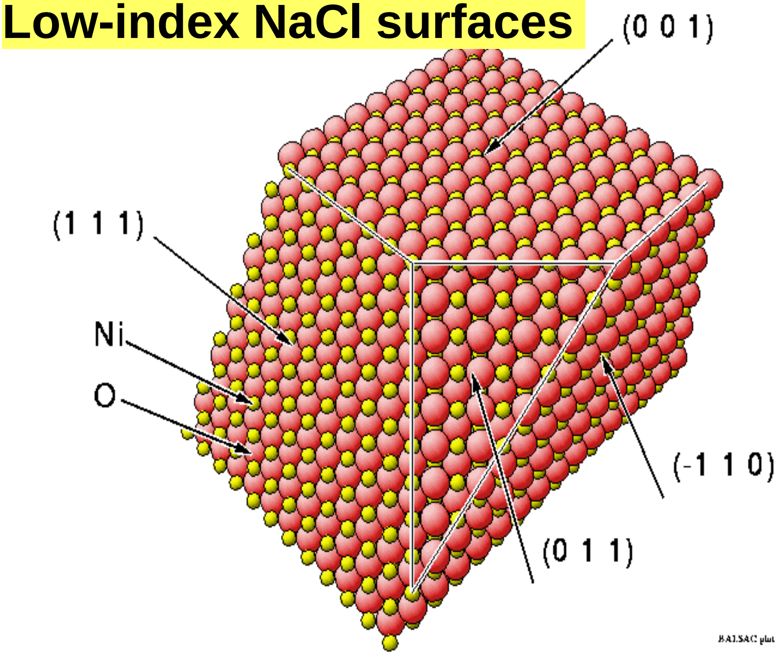
Low-index fcc metal surfaces



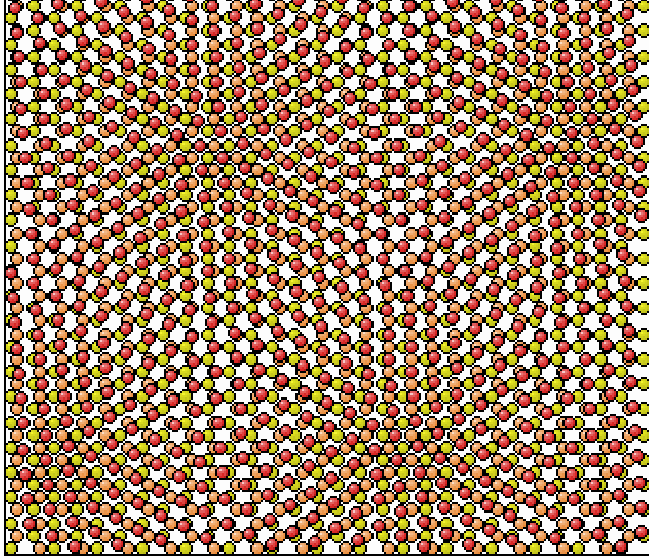
Si(111)-(7x7)—Dimer-adatom-stacking fault model



Low-index NaCl surfaces

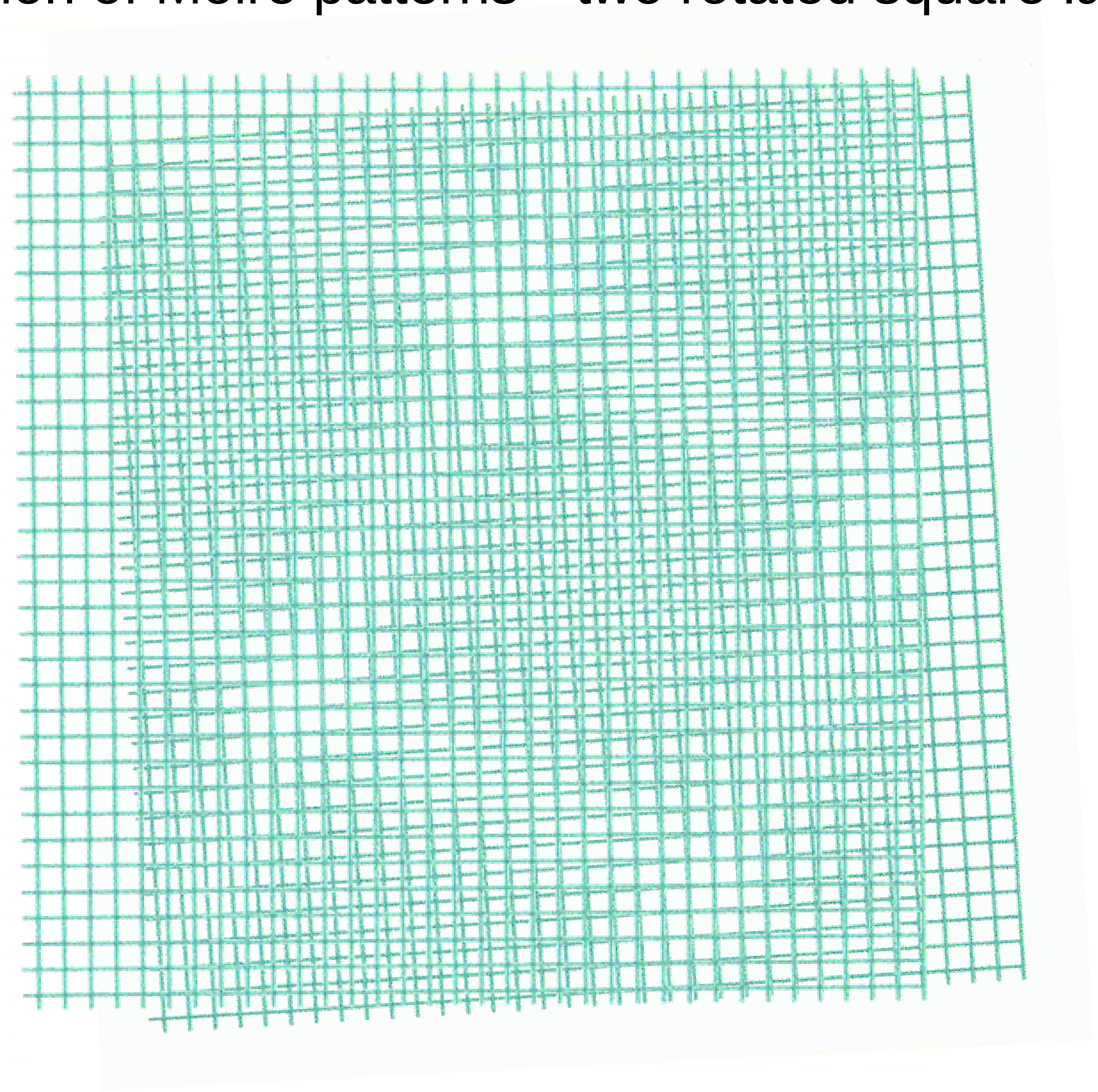


Fcc(111) super-lattice = a Moiré pattern: 4 degree rot'n.

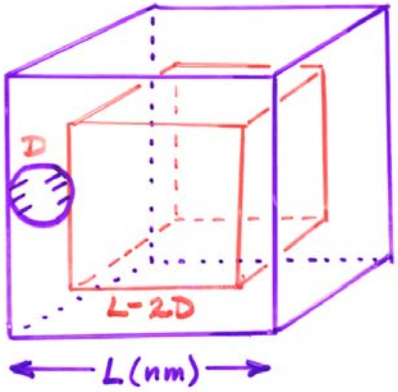


http://www.fhi-berlin.mpg.de/th/personal/hermann/pictures.html

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



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

L	FRACTION
$1\mu m$ = 1000 nm	0.001 ≈ 0.1%
$0.1\mu m$ = 100 nm	0.012 ≈ 1.2%
$0.01\mu m$ = 10 nm	0.115 ≈ 11.5%
$0.001\mu m$ = 1 nm	0.784 = 78.4%

Nanoscience is surface science

SOME UNITS :

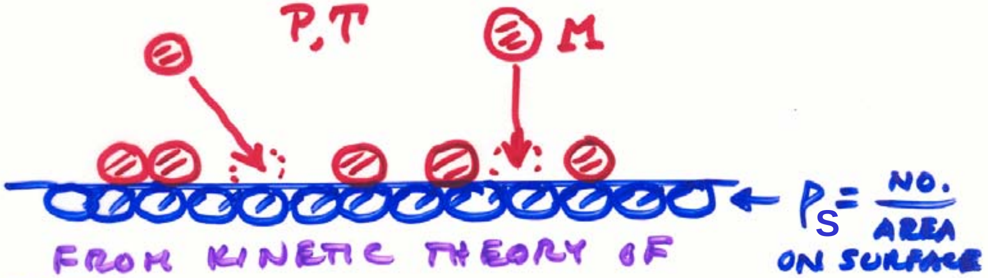
1 HAIR ≈ 50 microns

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 $M = 28, 32$

$T = 298K$

$\rho = 1\text{-}2 \times 10^{15}\ \text{cm}^{-2}$ ↑ 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} ..

work

0-10^{-11} torr

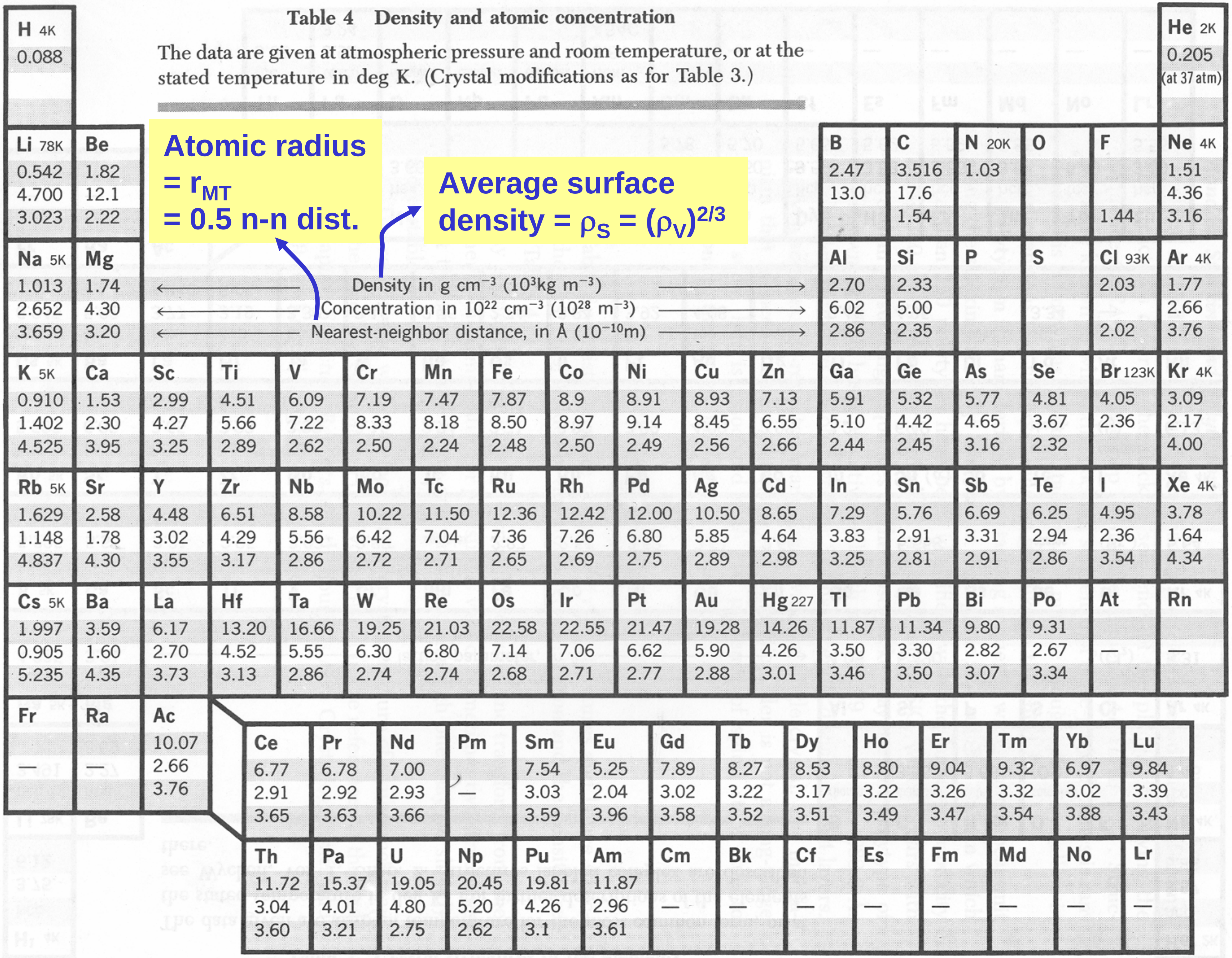


Table 4 Density and atomic concentration

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.

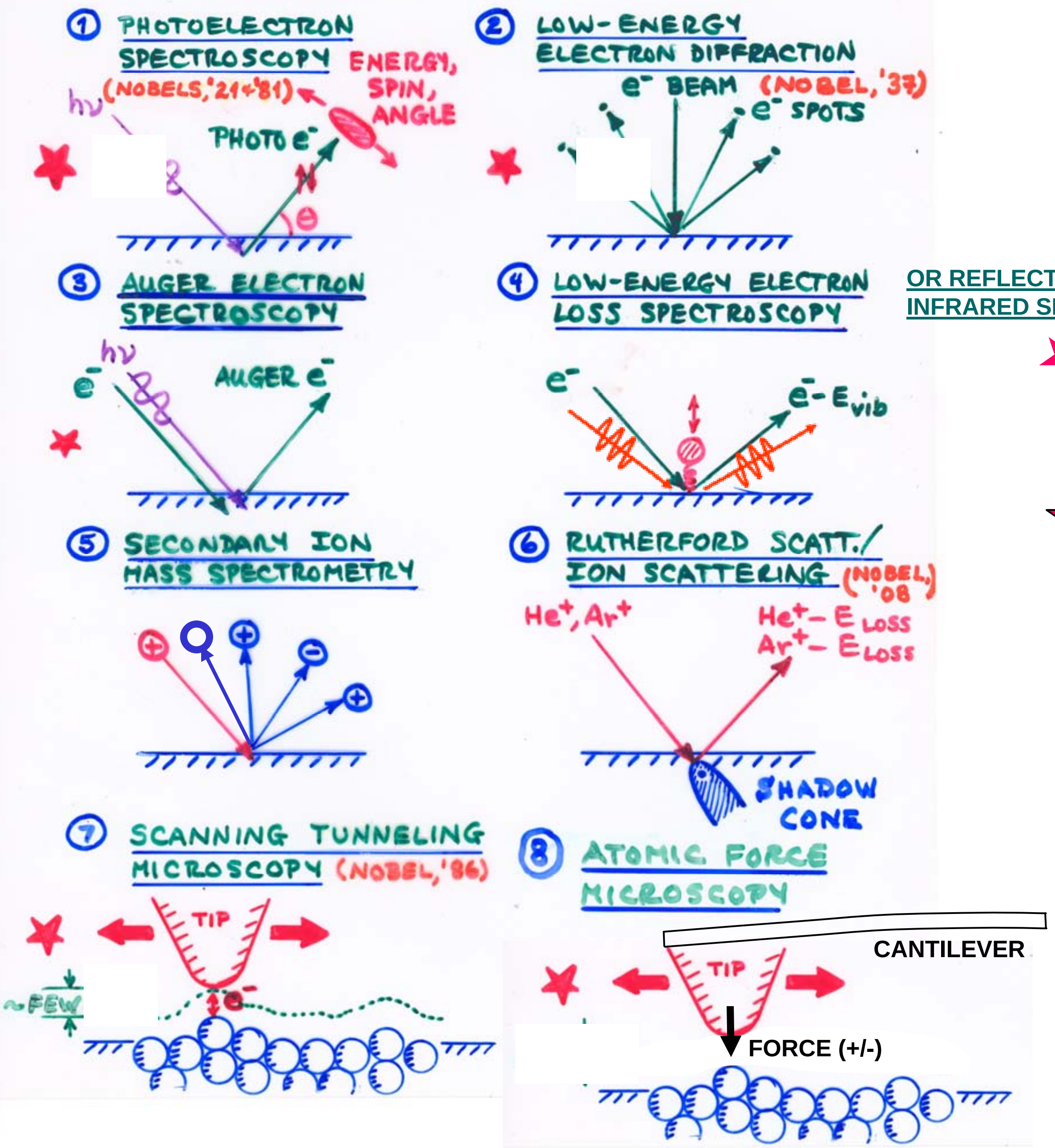
Average surface density = $\rho_S = (\rho_V)^{2/3}$

← Density in g cm⁻³ (10³kg m⁻³) →
← Concentration in 10²² cm⁻³ (10²⁸ m⁻³) →
← Nearest-neighbor distance, in Å (10⁻¹⁰m) →

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** —

SOME SURFACE-ANALYTICAL TECHNIQUES

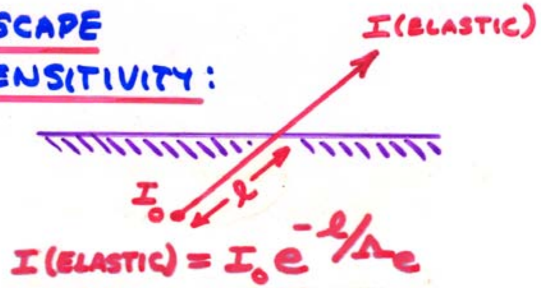


OR REFLECTION/ABSORPTION INFRARED SPECTROSCOPY ★

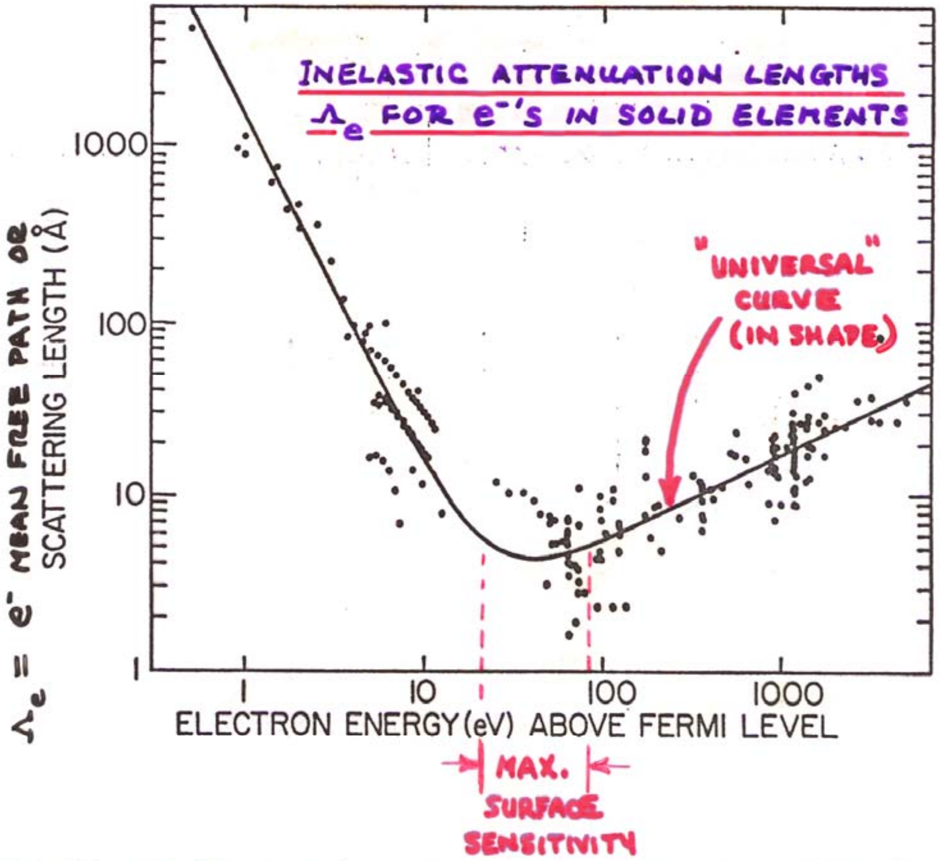
★ = AT UC DAVIS

Why are electrons so useful as probes of surfaces?

ELECTRON ESCAPE & SURFACE SENSITIVITY:



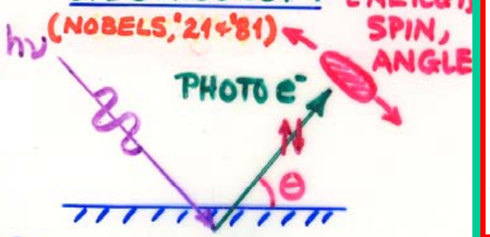
$$I(\text{ELASTIC}) = I_0 e^{-\ell/\Lambda_e}$$



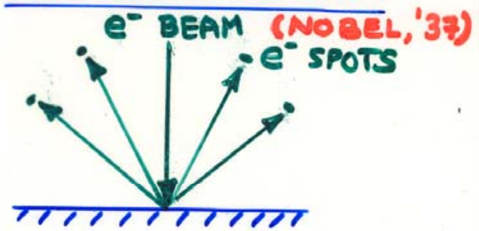
COMPILATIONS: Seah & Dench, Surf. Int. Anal. 1, 2 (1979)
Tanuma, Powell, & Penn, Surf. Int. Anal. 17, 911 & 927 (1991); 21, 165 (1994)
Powell & Jablonski, J. Phys. Chem. Ref. Data 28, 19 (1999); Surf. Int. Anal. 29, 108 (2000)

SOME SURFACE-ANALYTICAL TECHNIQUES

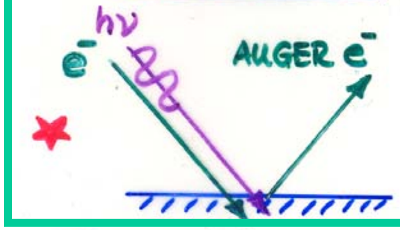
① PHOTOELECTRON SPECTROSCOPY



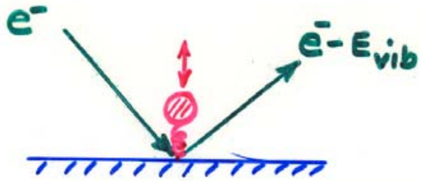
② LOW-ENERGY ELECTRON DIFFRACTION



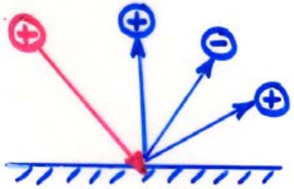
③ AUGER ELECTRON SPECTROSCOPY



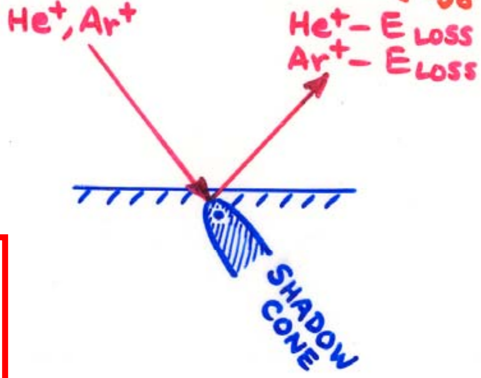
④ LOW-ENERGY ELECTRON LOSS SPECTROSCOPY



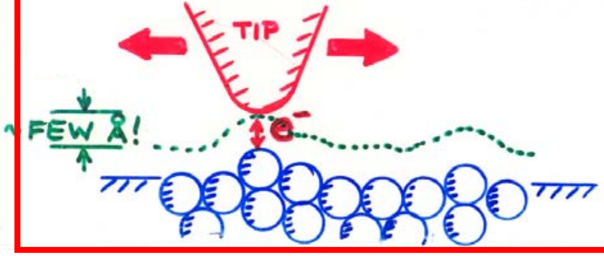
⑤ SECONDARY ION MASS SPECTROMETRY



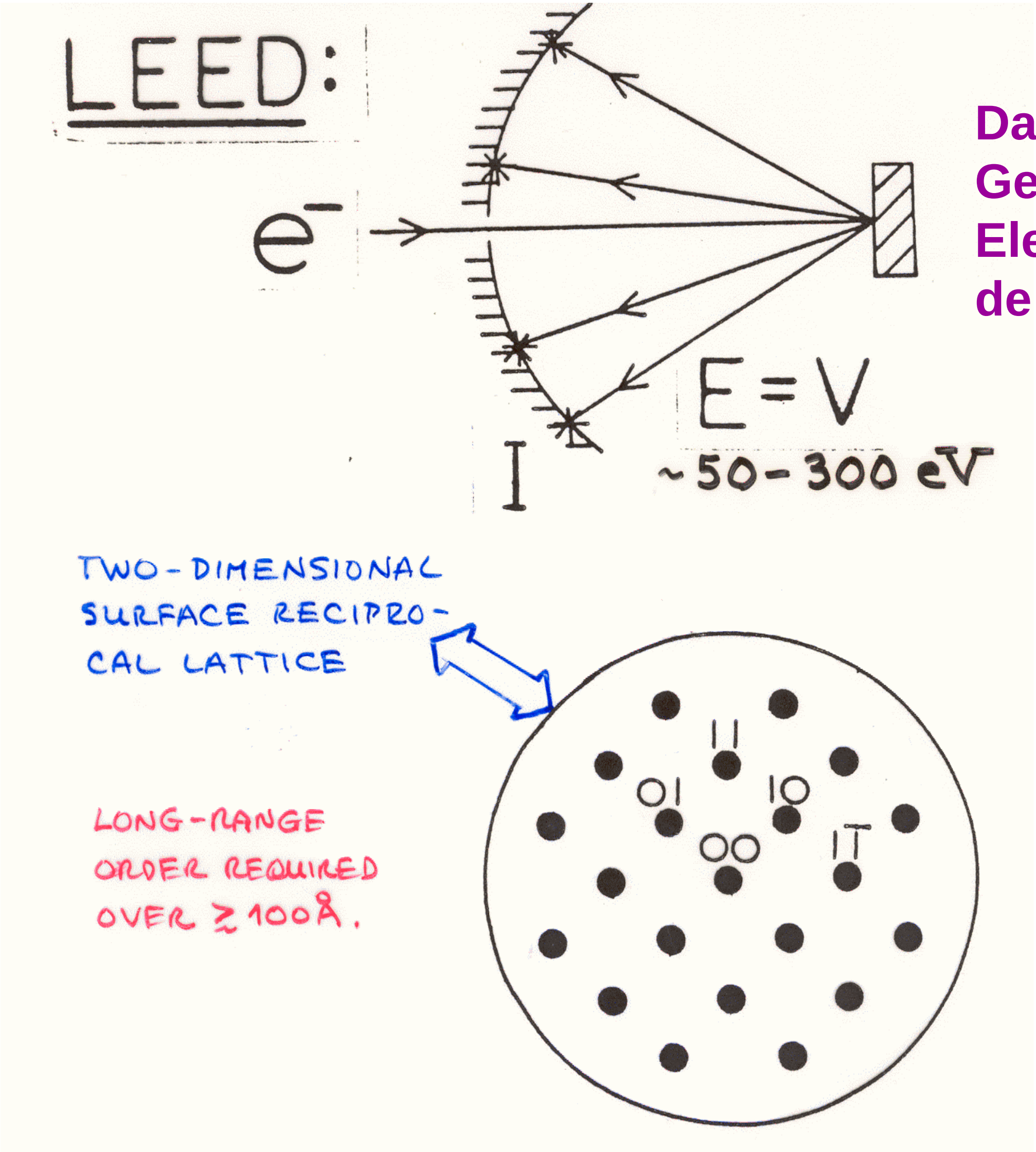
⑥ RUTHERFORD SCATT./ ION SCATTERING (NOBEL,'08)



⑦ SCANNING TUNNELING MICROSCOPY (NOBEL,'86)

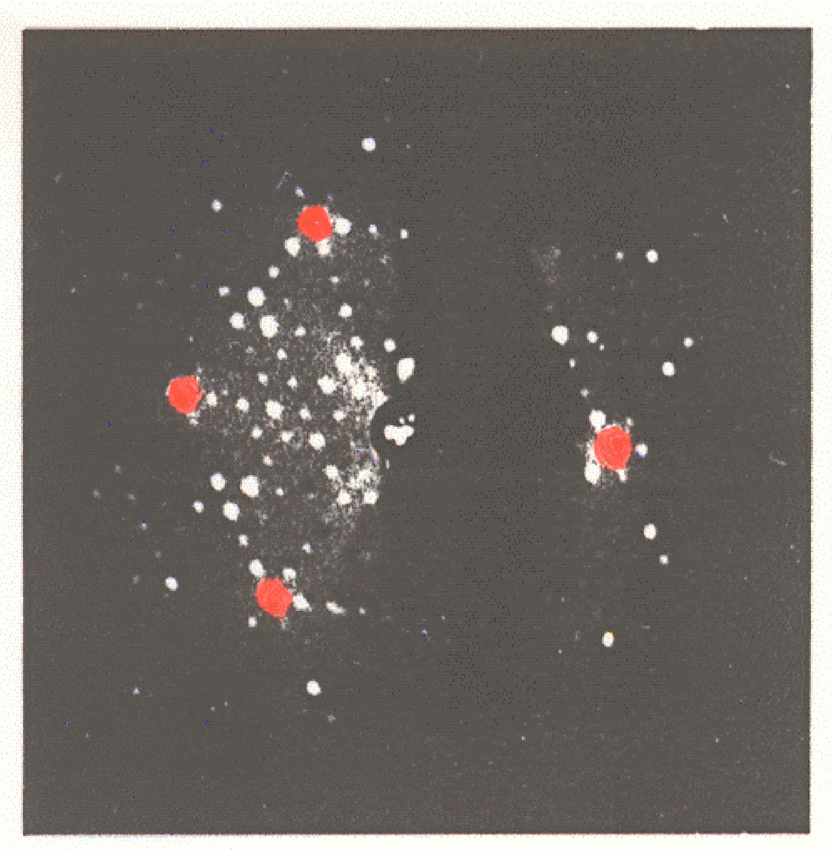


LOW ENERGY ELECTRON DIFFRACTION

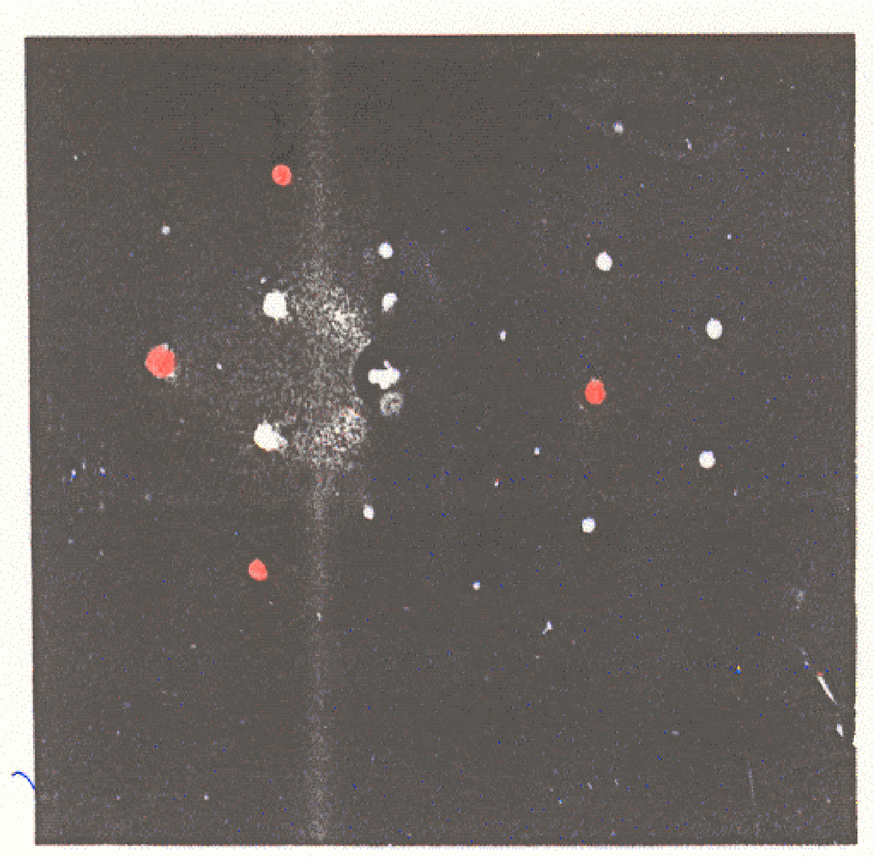


Davisson & Germer (1927): Electrons are de Broglie waves

SOME TYPICAL LEED PATTERNS:



Si(111)-(7x7)



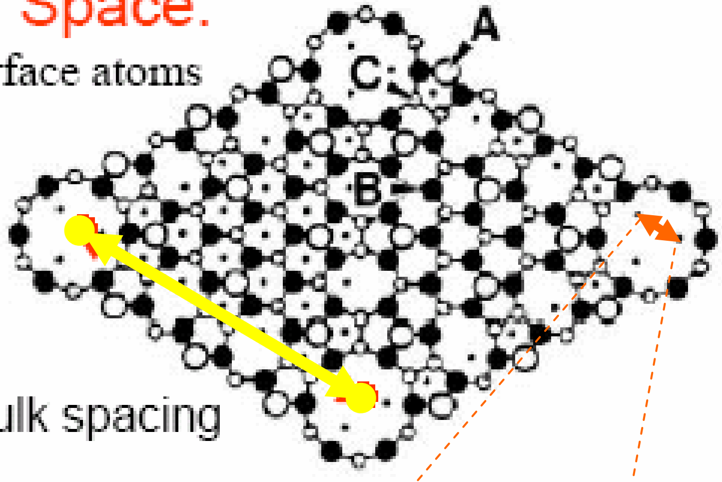
(√3 x √3)R30° Ag/Si(111)

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

LEED: Si(111)7x7

Real Space:

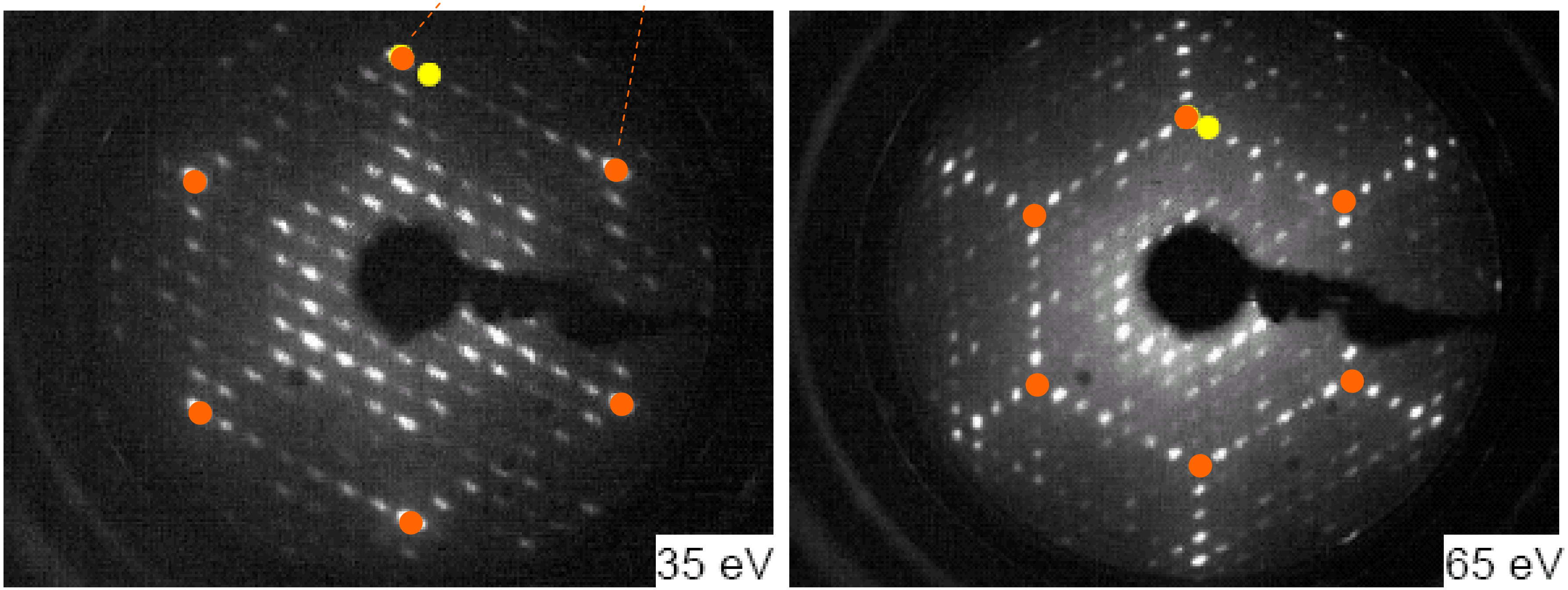
Si surface atoms



7× bulk spacing

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

K-Space



SCANNING TUNNELING MICROSCOPY

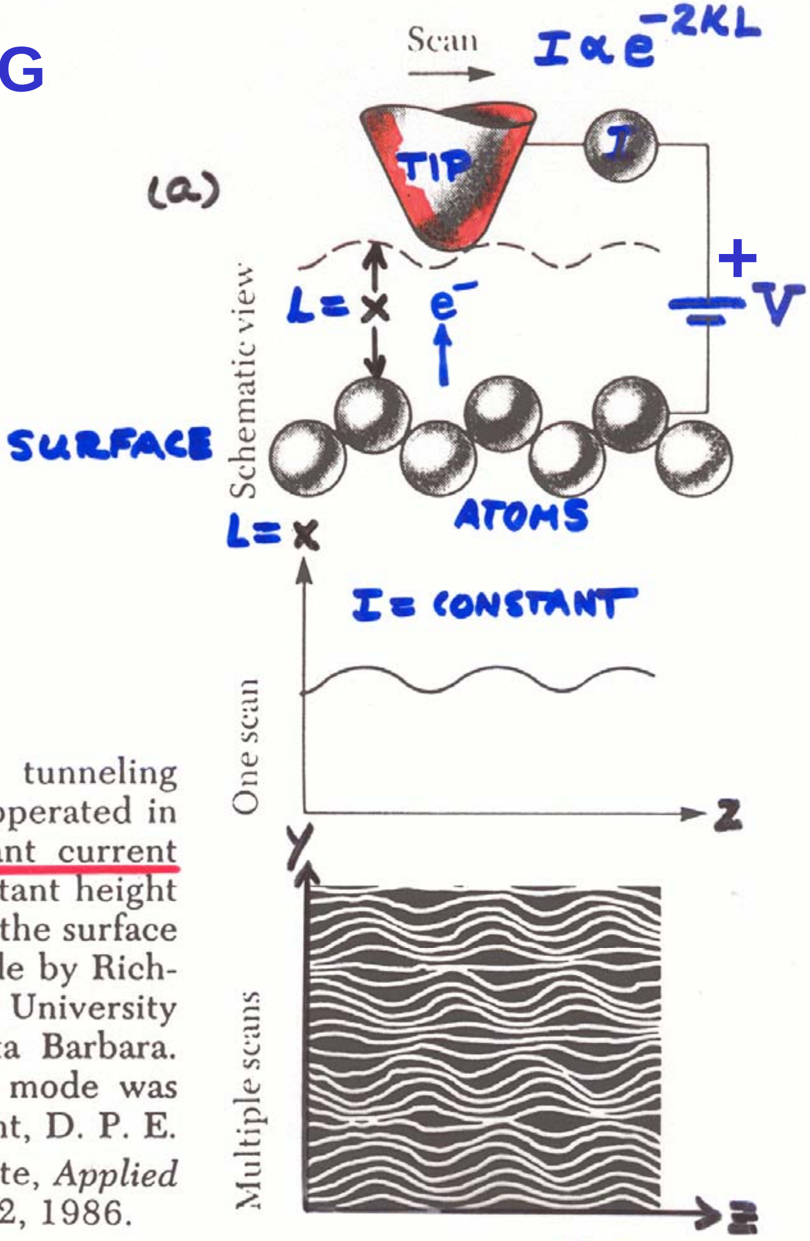
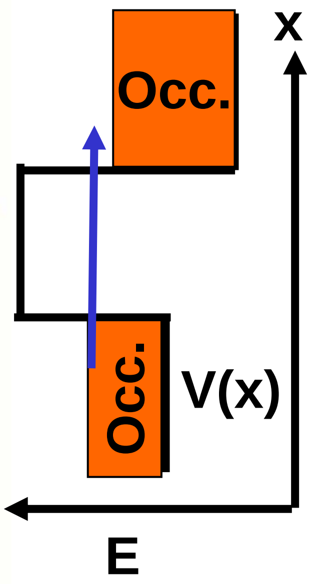


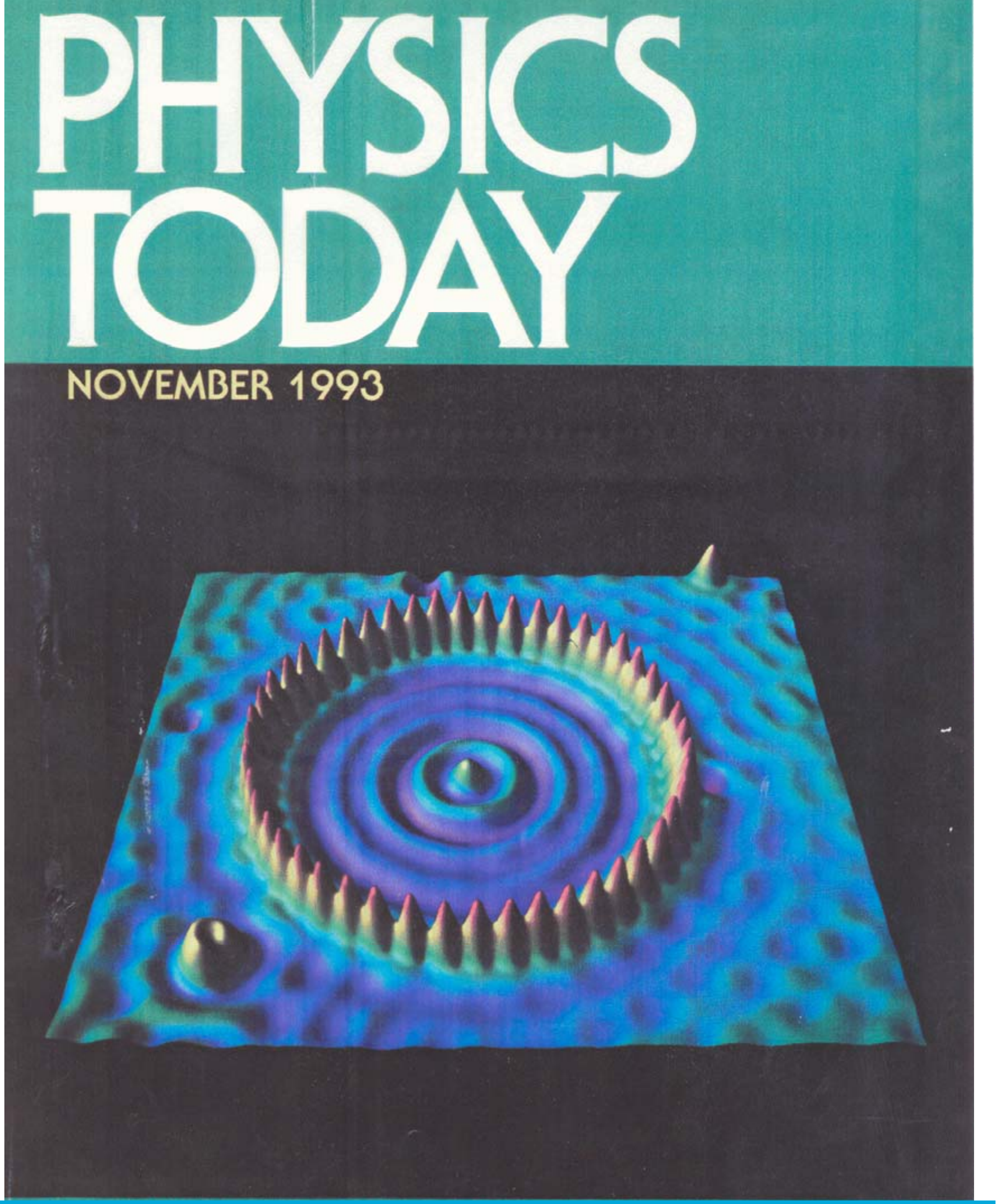
Figure 4 Scanning tunneling microscopes can be operated in either (a) the constant current mode or (b) the constant height mode. The images of the surface of graphite were made by Richard Sonnenfeld at the University of California at Santa Barbara. The constant height mode was first used by A. Bryant,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

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

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

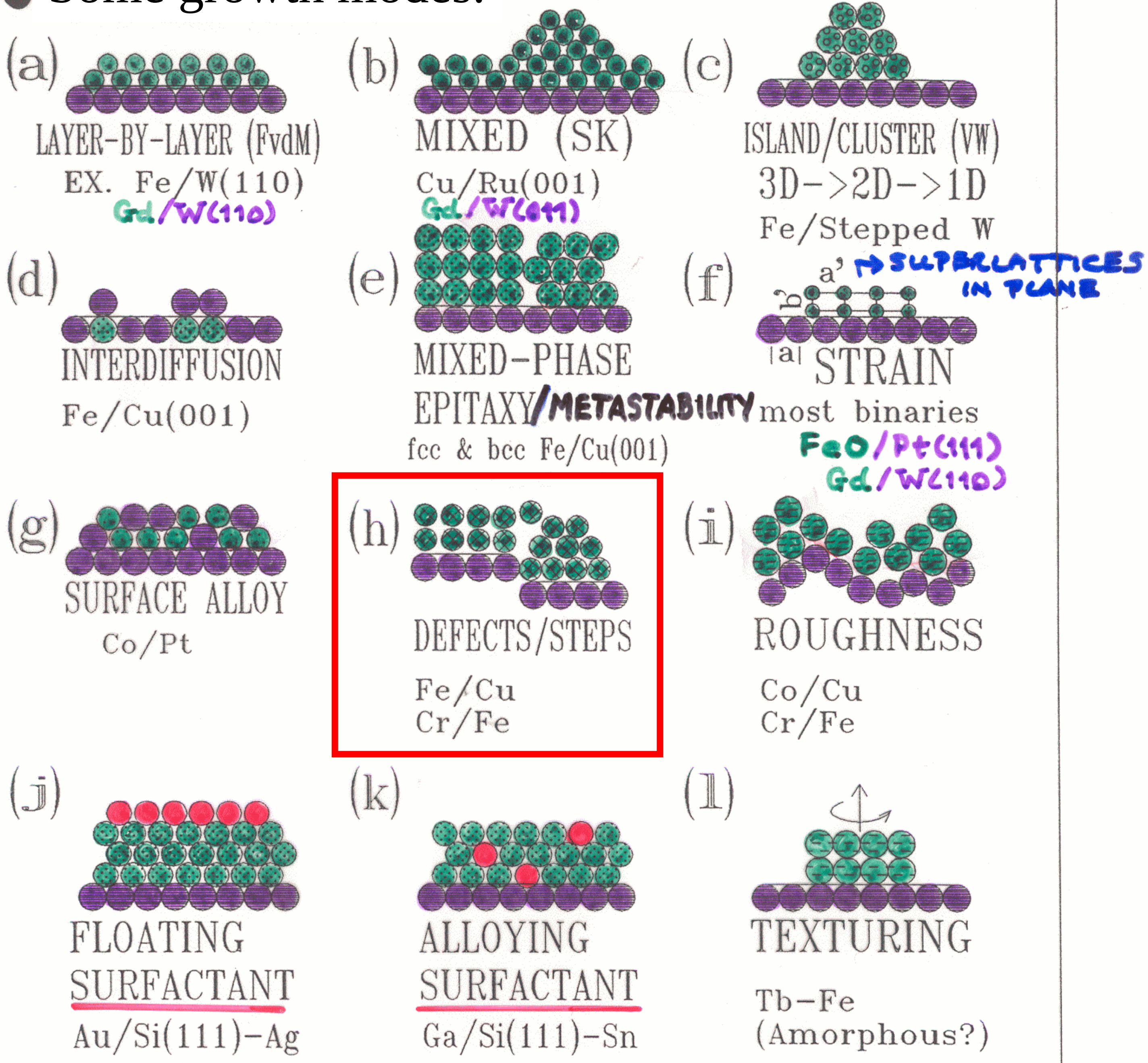


IMAGING, AND MANIPULATING, ATOMS AT SURFACES WITH THE STM



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

- Some growth modes:



Scanning tunneling microscopy: stepped Si(111) surface

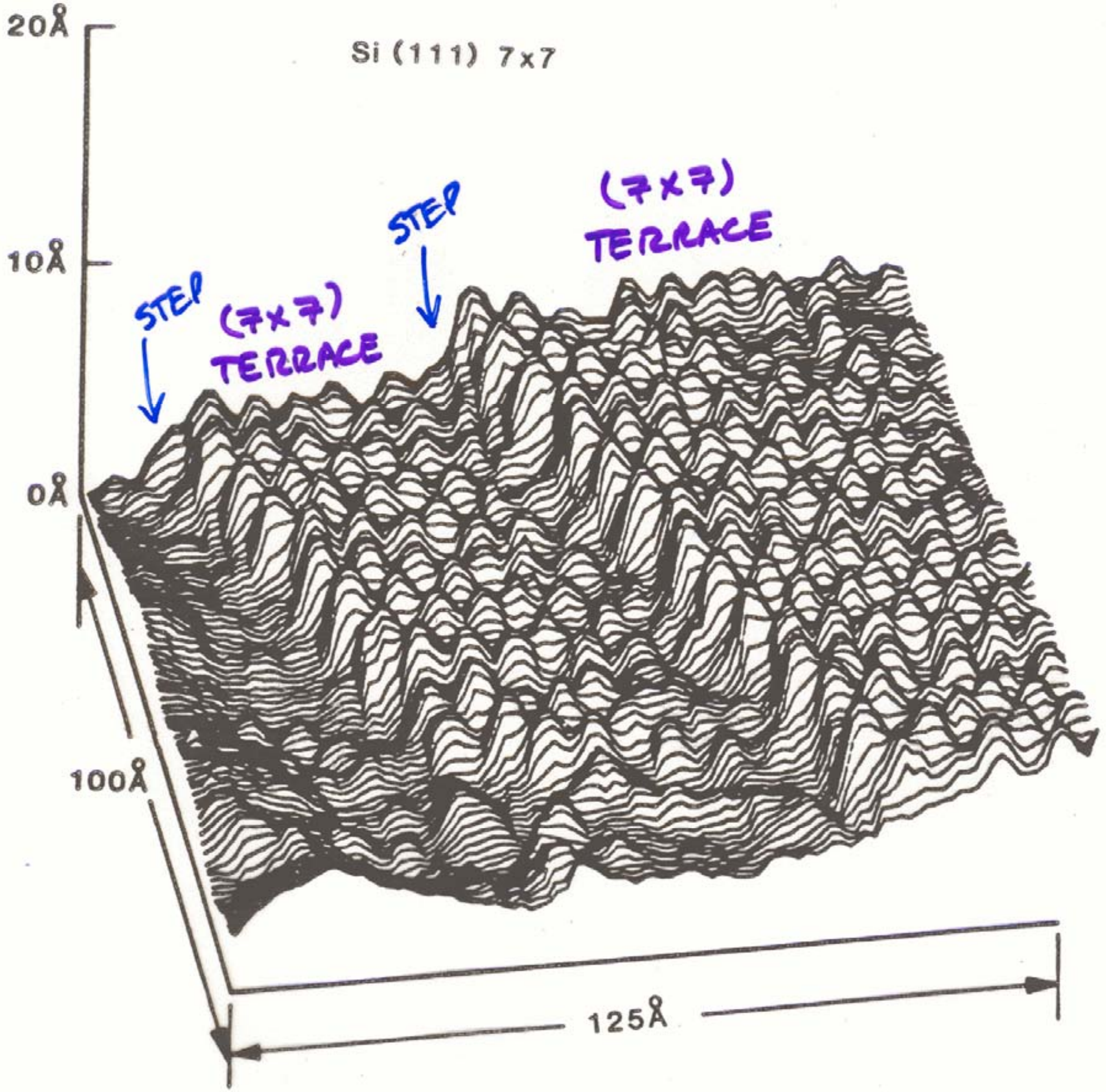
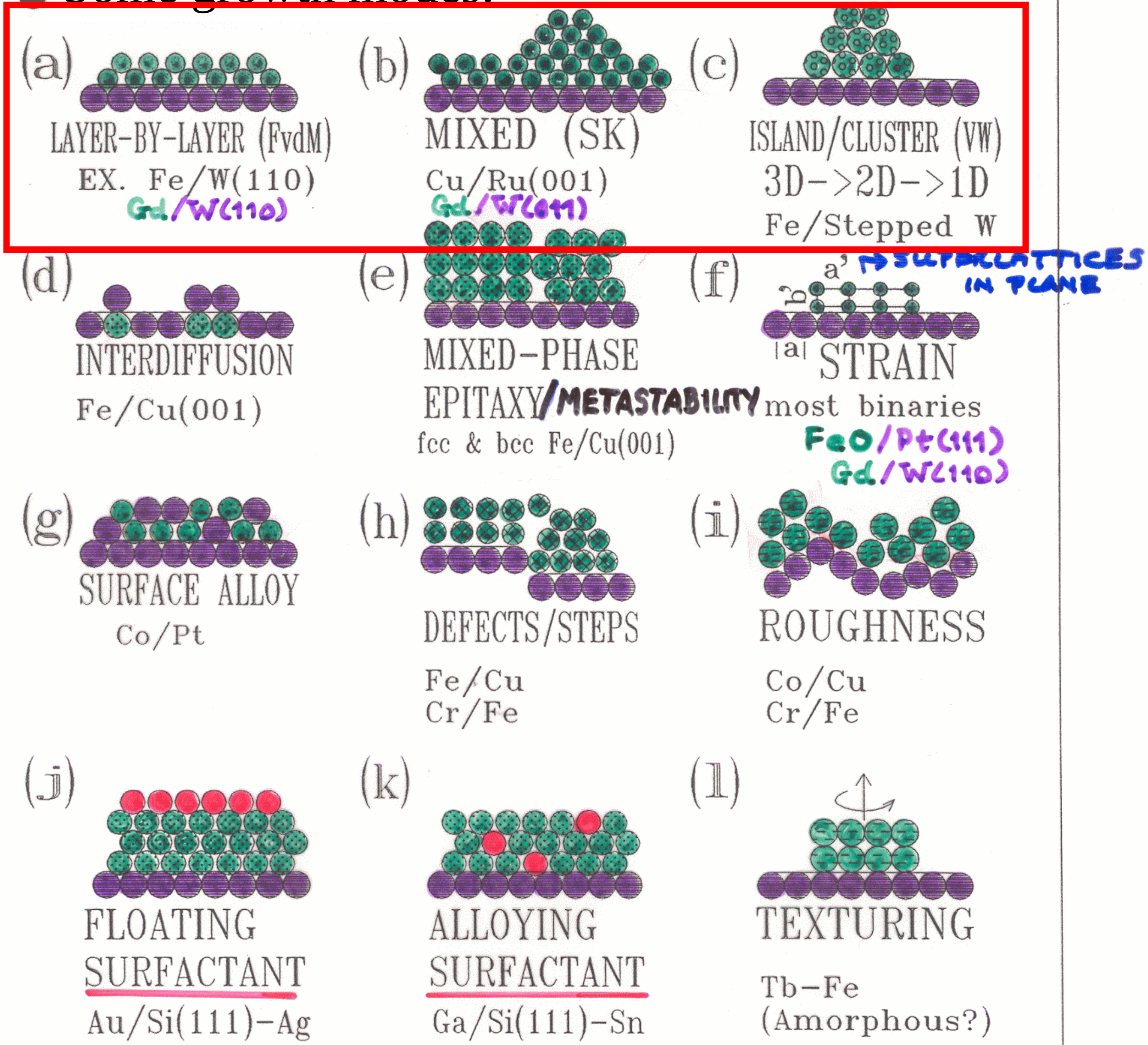


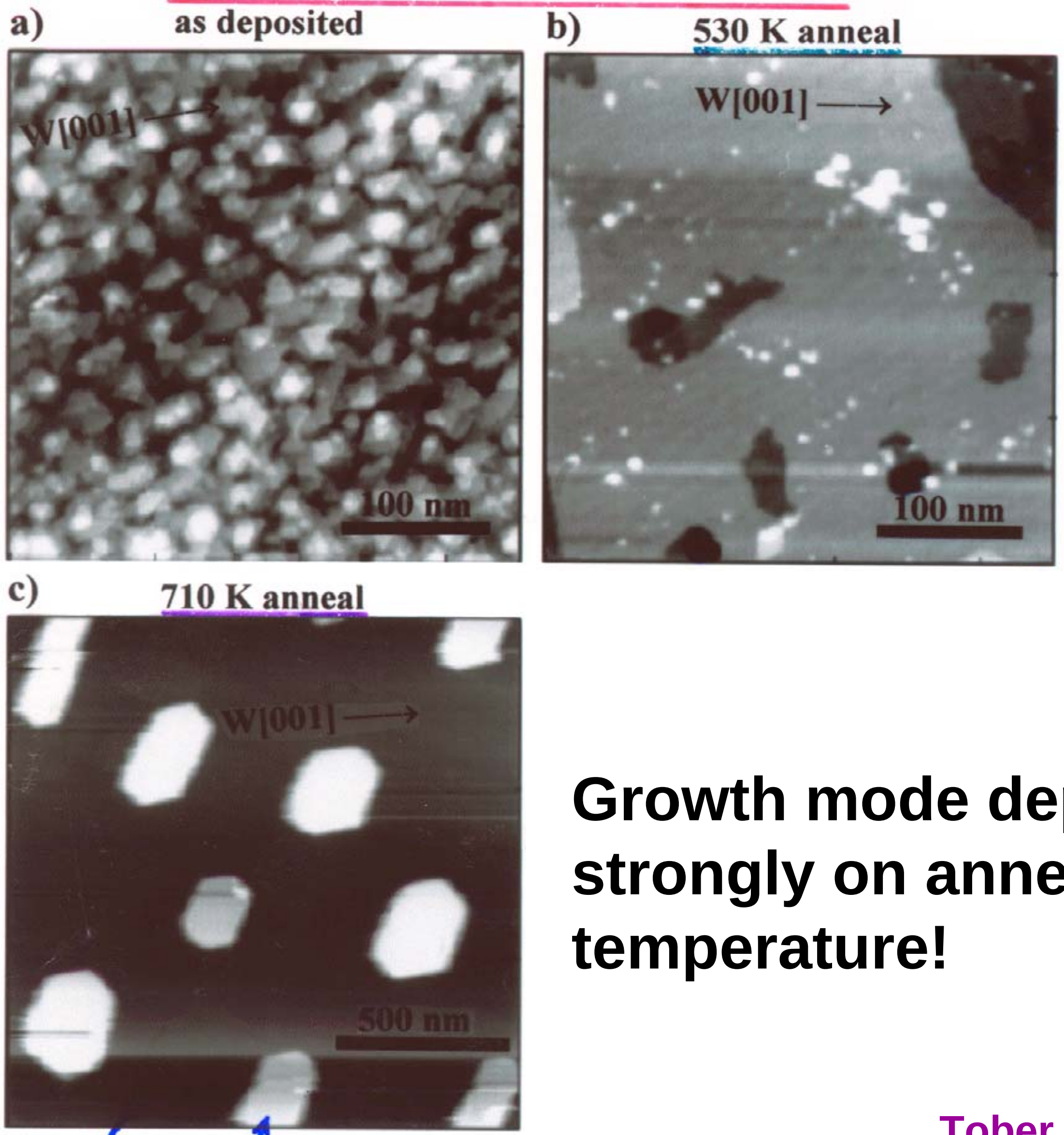
Fig. 2. Tunneling image of silicon (111) surface that shows the 7×7 atomic reconstruction on terraces separated by atomic steps.

- Some growth modes:



Scanning tunneling microscopy: metal-on-metal epitaxial growth

GROWTH OF 11 ML Gd ON W(110)



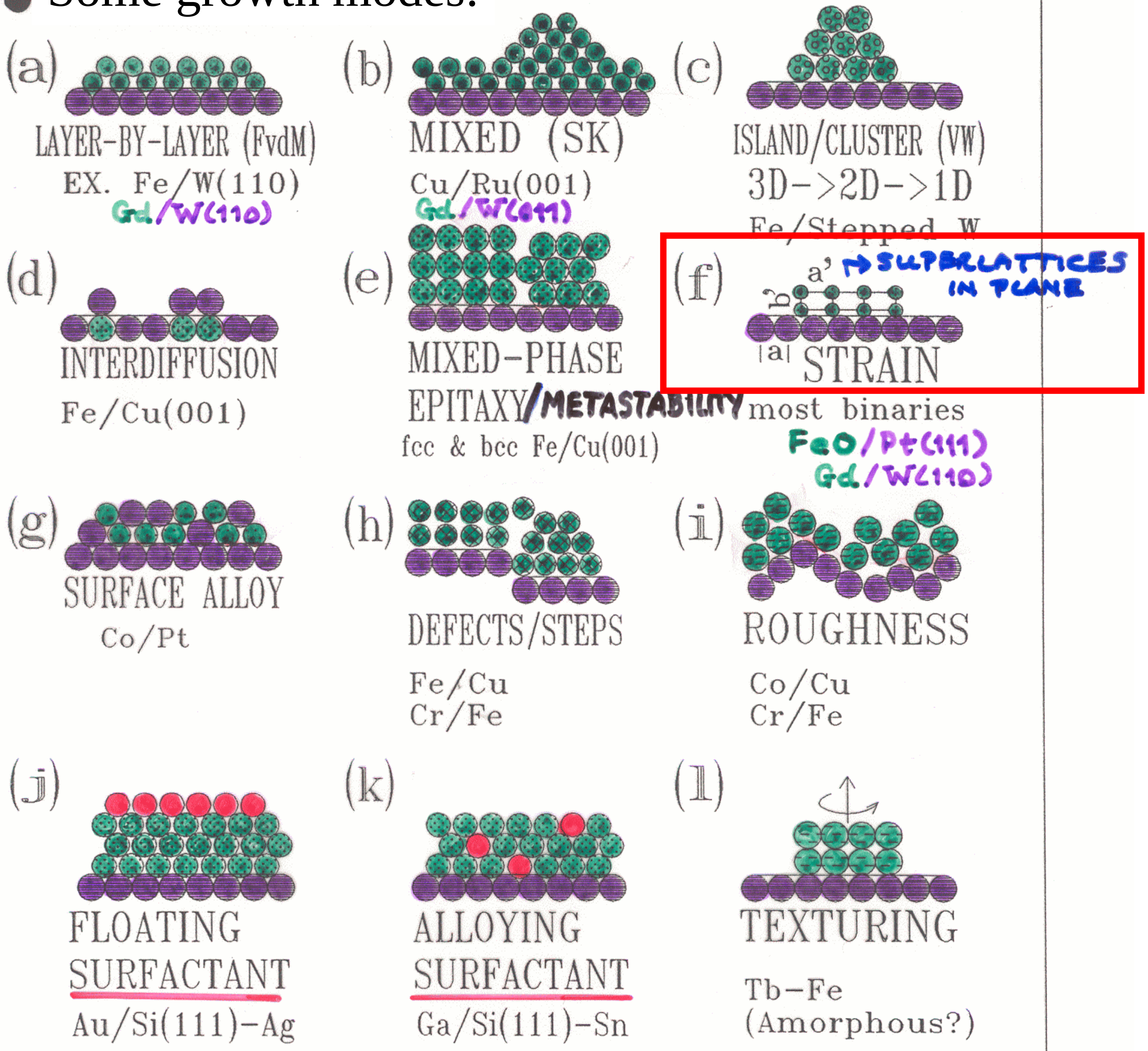
WETTING SINGLE LAYER

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

Growth mode depends strongly on anneal temperature!

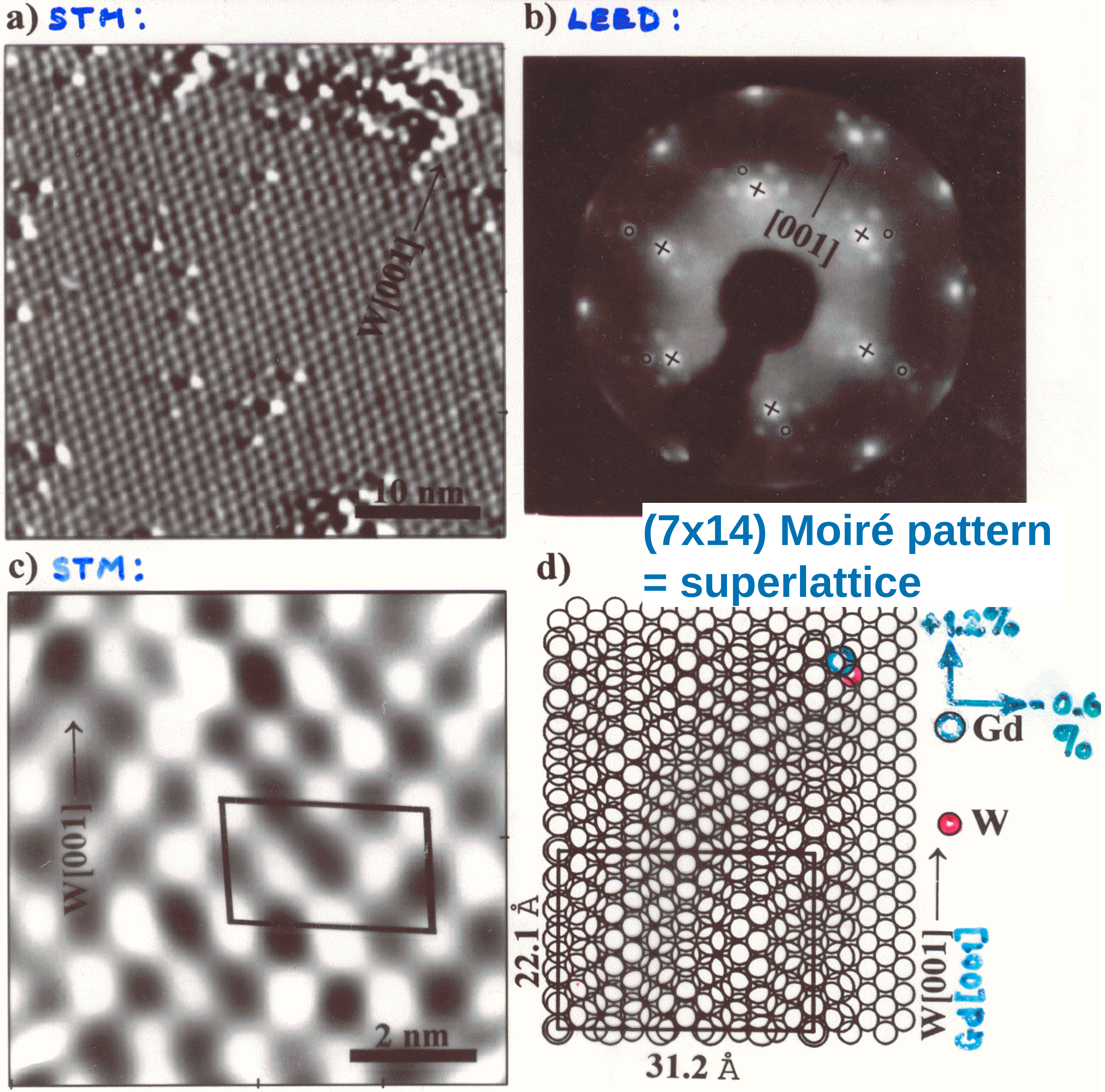
Tober et al.
Phys. Rev. B
53, 5444 (1996).

- Some growth modes:



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

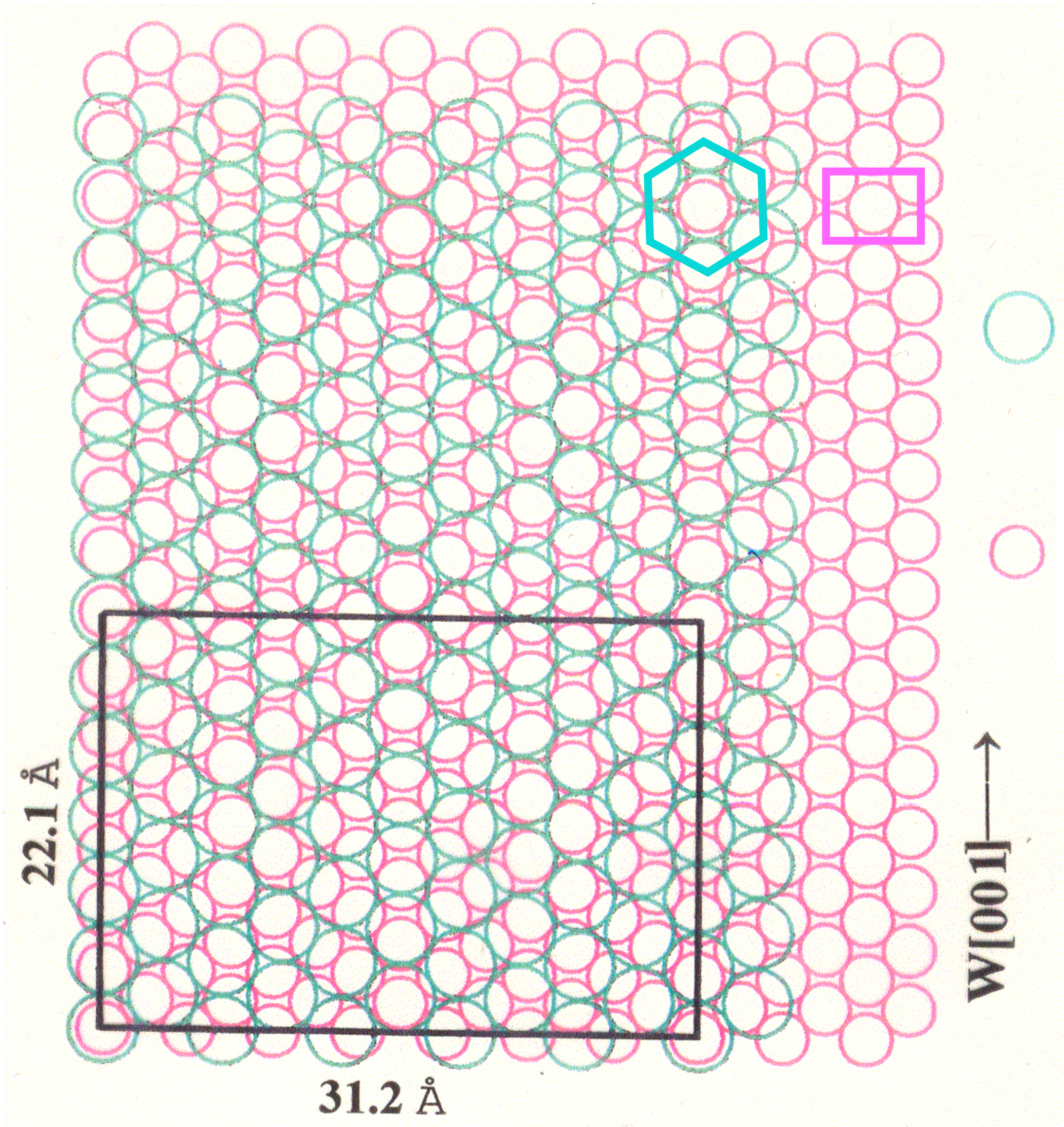
Superlattice = Moiré structure in metal-on-metal epitaxial growth



(7x14) Moiré pattern = superlattice

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

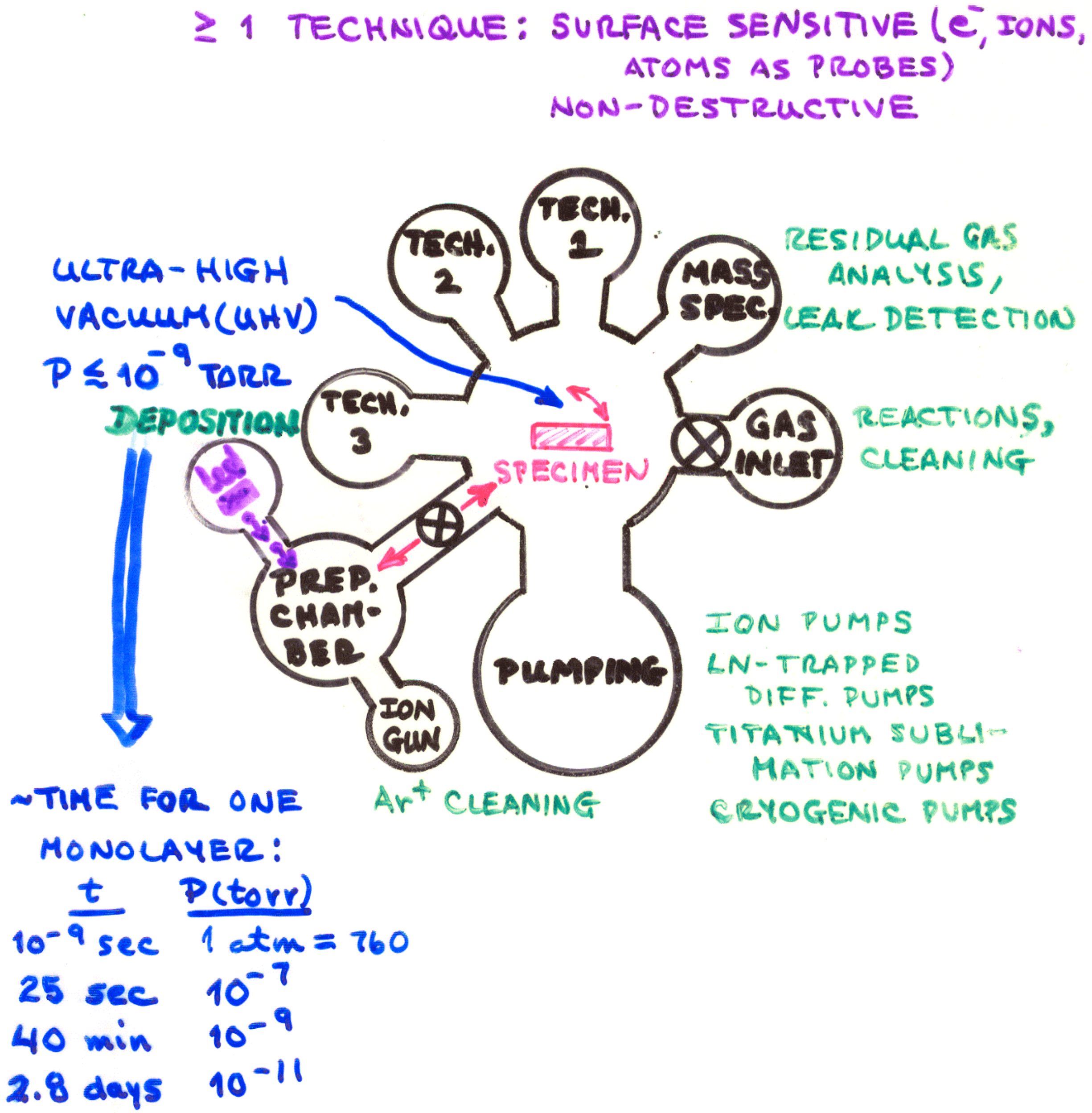
A Moiré pattern—Monolayer Gd on W(110)



Gd(0001)—hexagonal

W(110)—rectangular

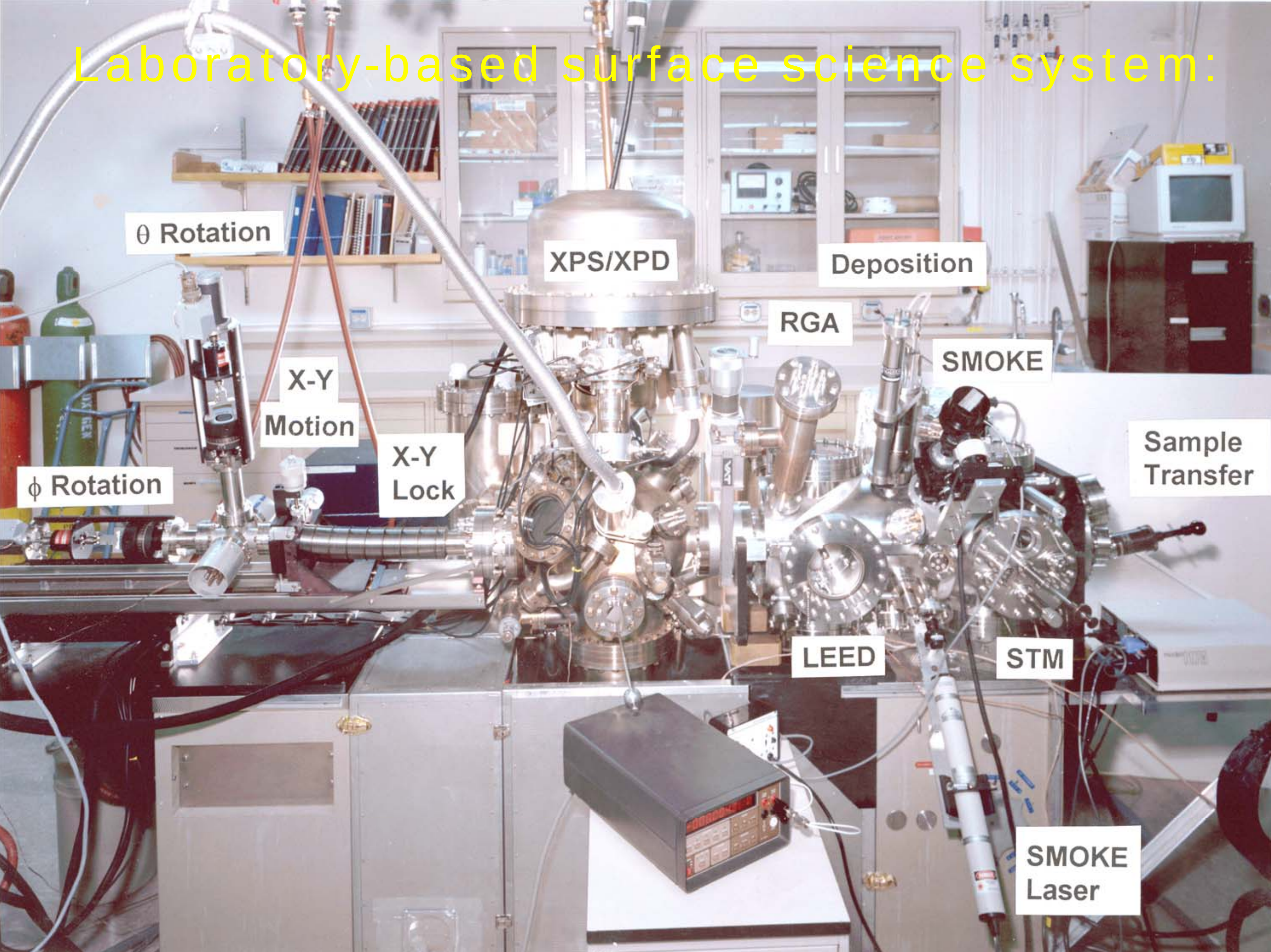
A typical surface science research system



~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

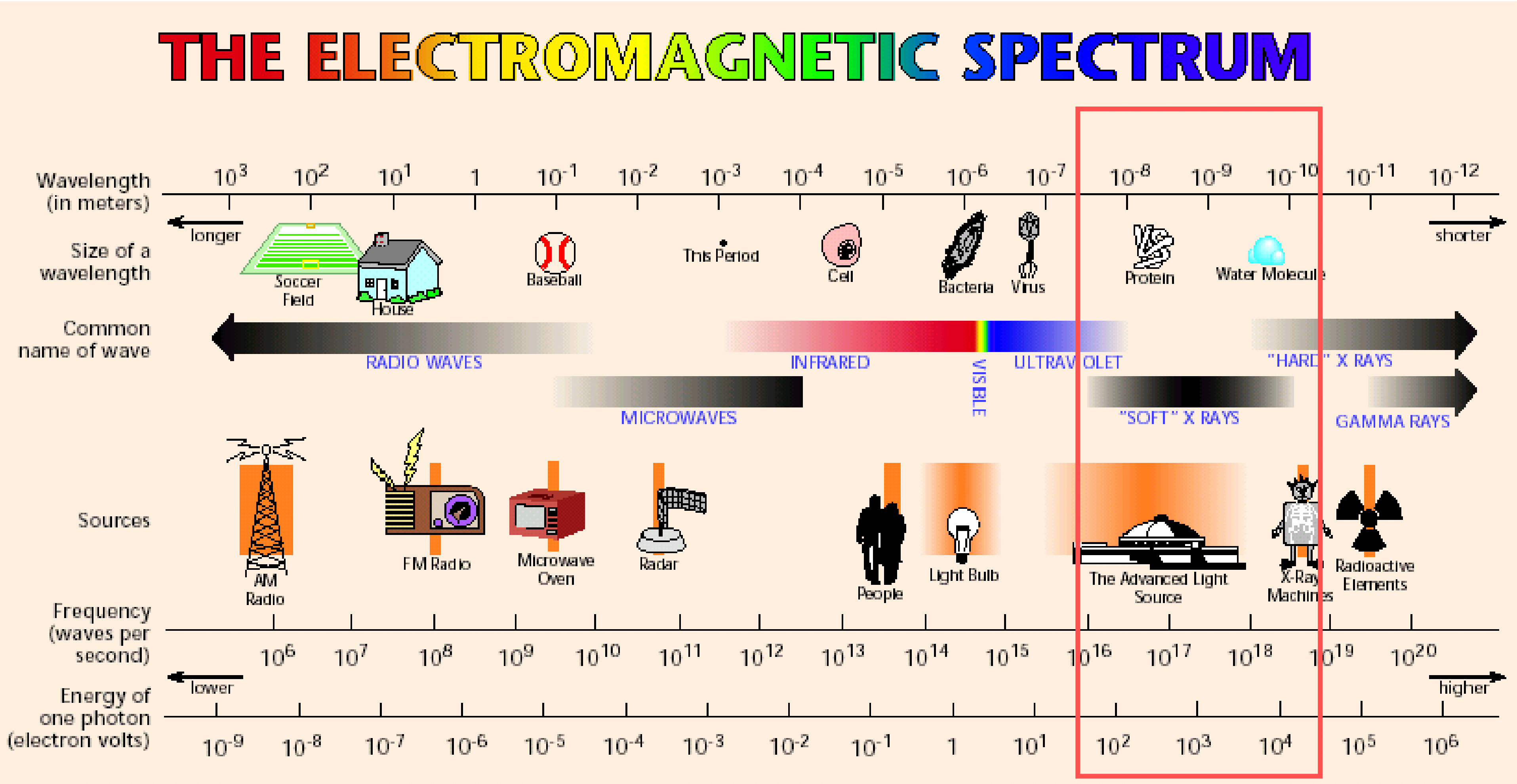
Electronic structure—a brief review

The basic synchrotron radiation techniques:
more experimental and theoretical details

Core-level photoemission

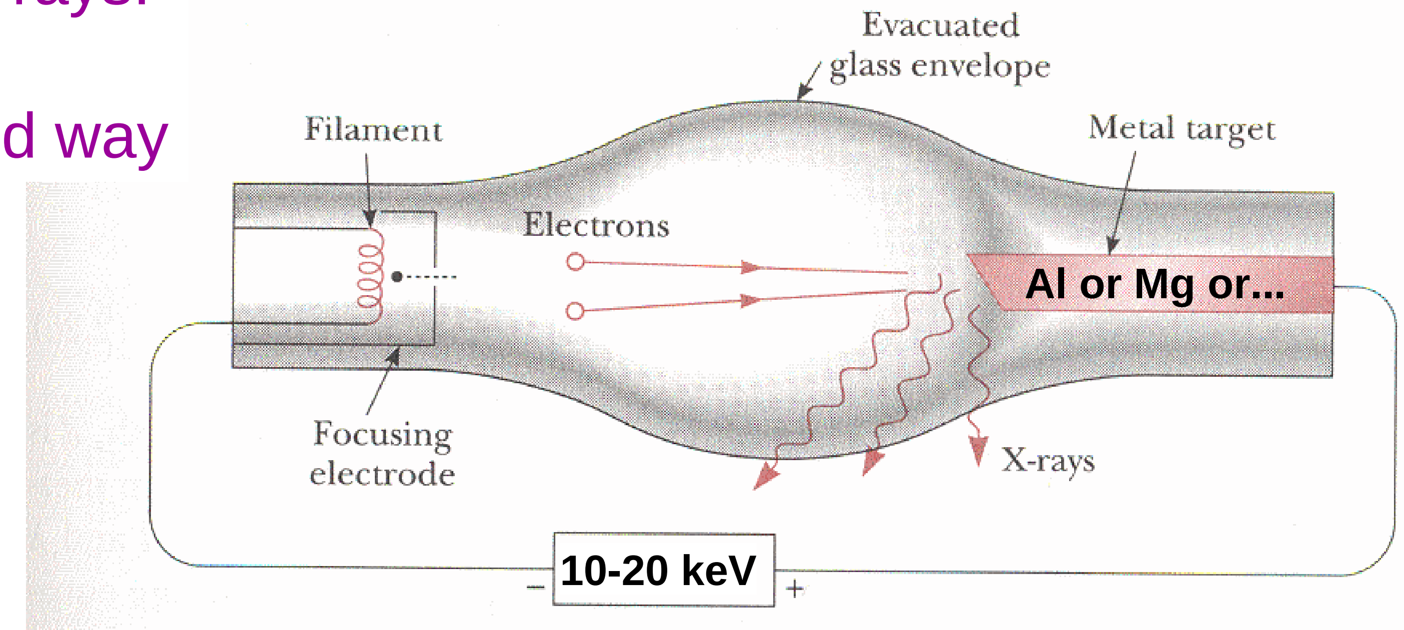
Valence-level photoemission

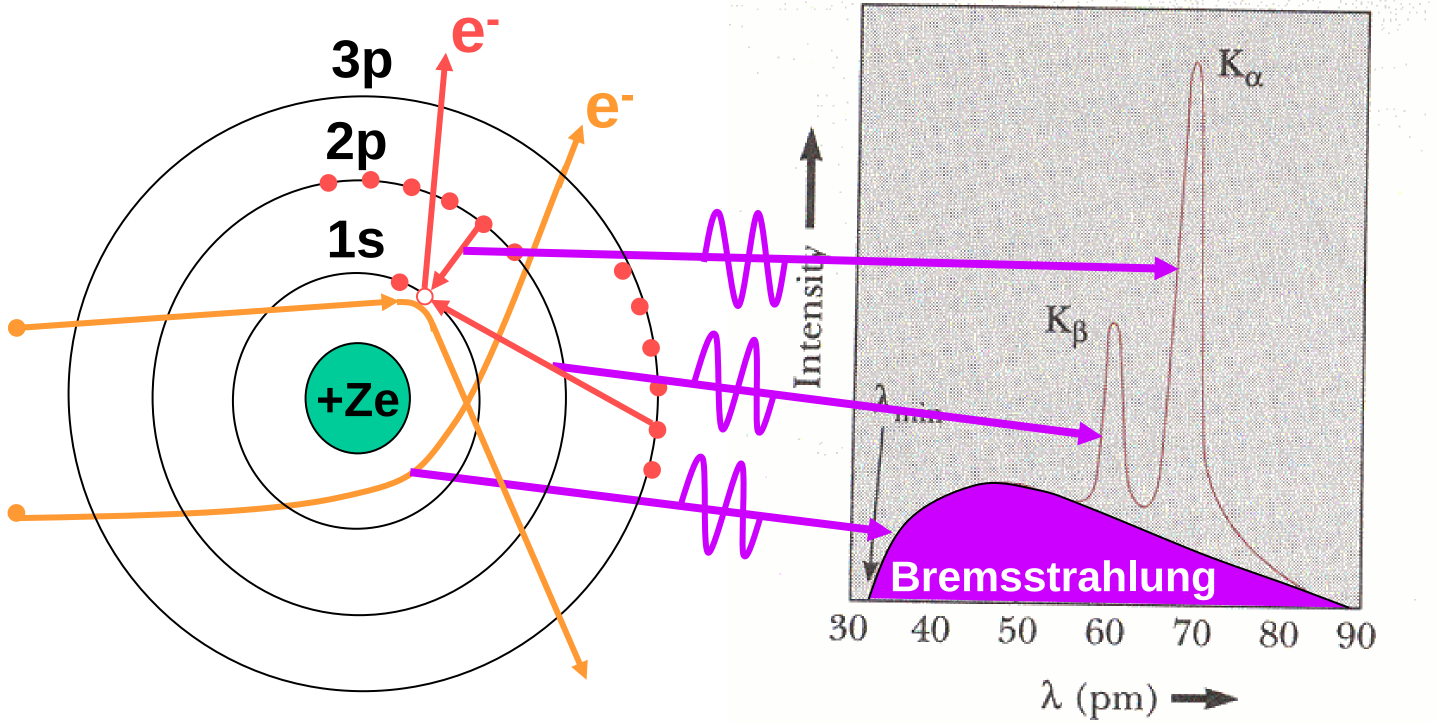
Microscopy with photoemission



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:

1-14

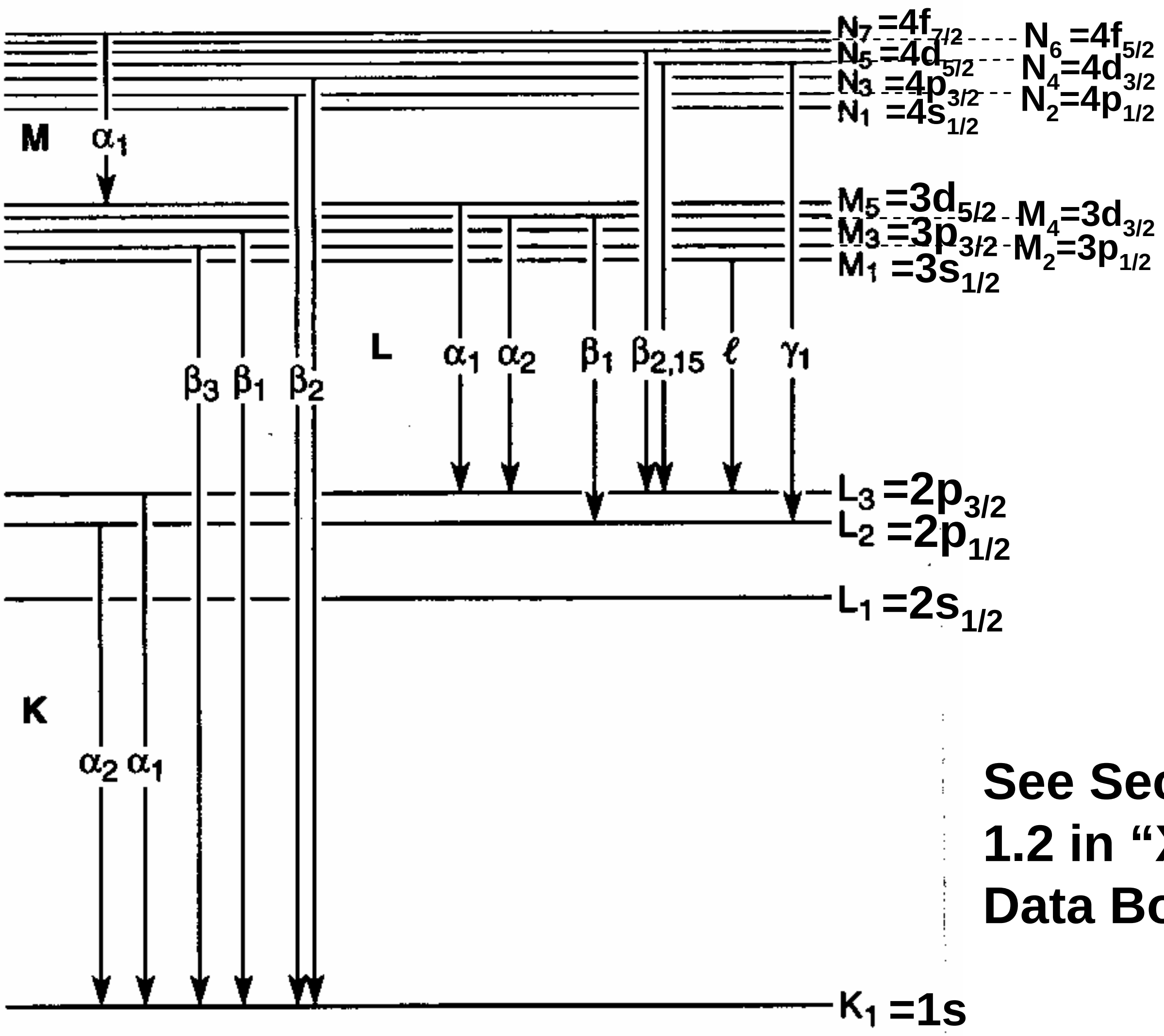


Fig. 1-1. *Transitions that give rise to the emission lines in Table 1-3.*

See Section 1.2 in “X-Ray Data Booklet”

X-Ray energies from the “X-Ray Data Booklet”

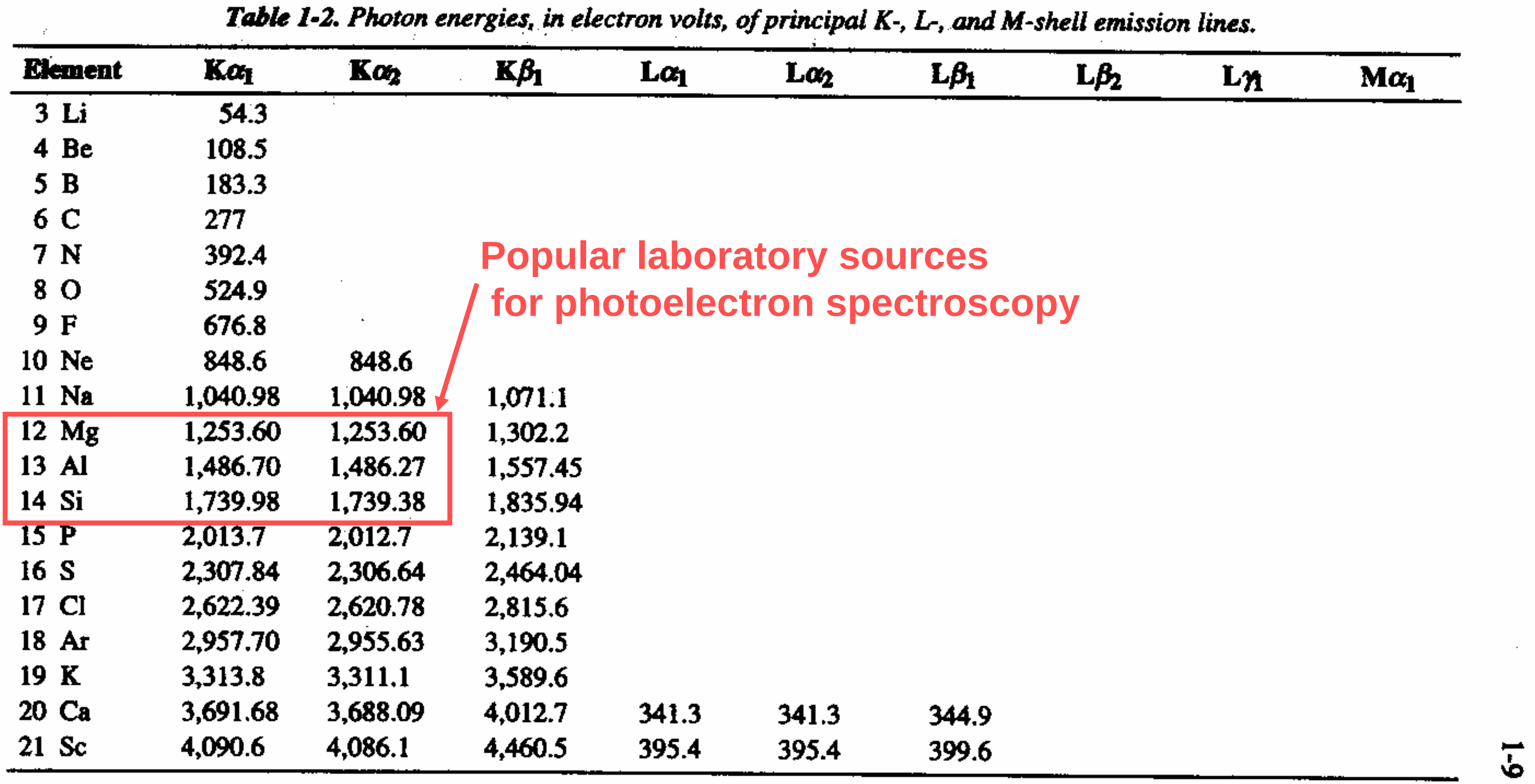
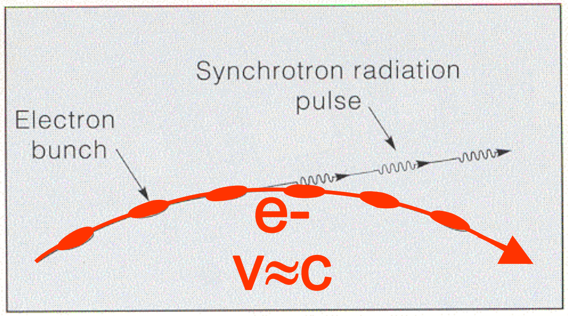


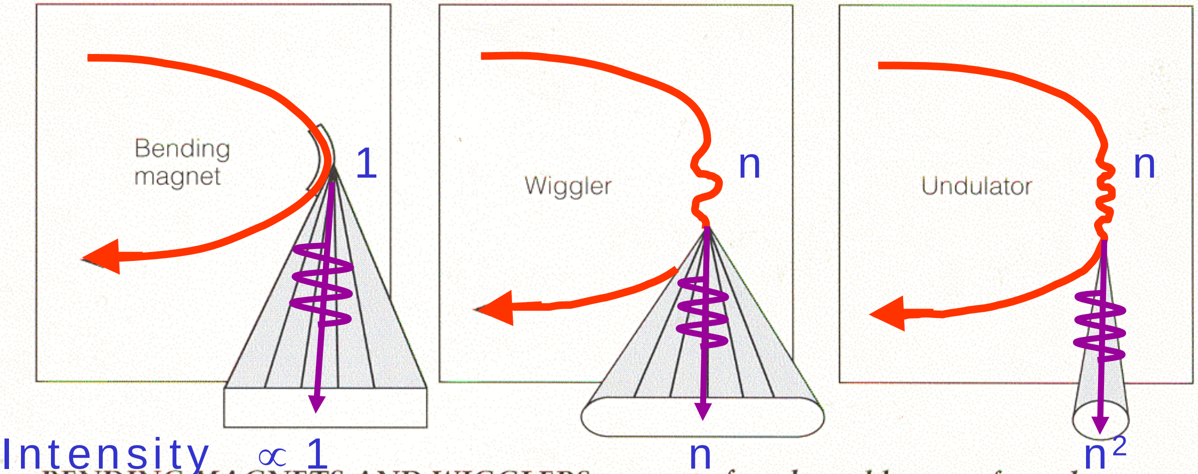
Table 1-2. Photon energies, in electron volts, of principal K-, L-, and M-shell emission lines.

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			

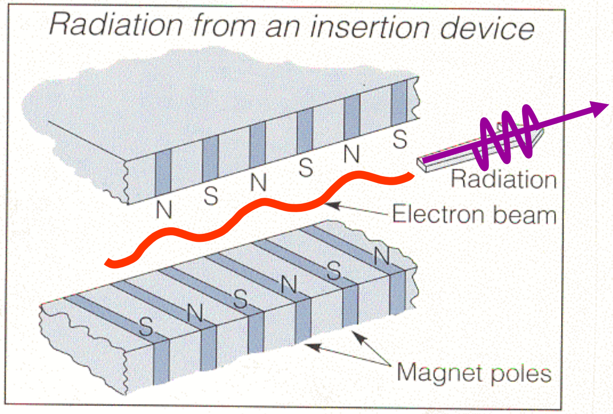
Popular laboratory sources
for photoelectron spectroscopy

Synchrotron Radiation Sources:





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

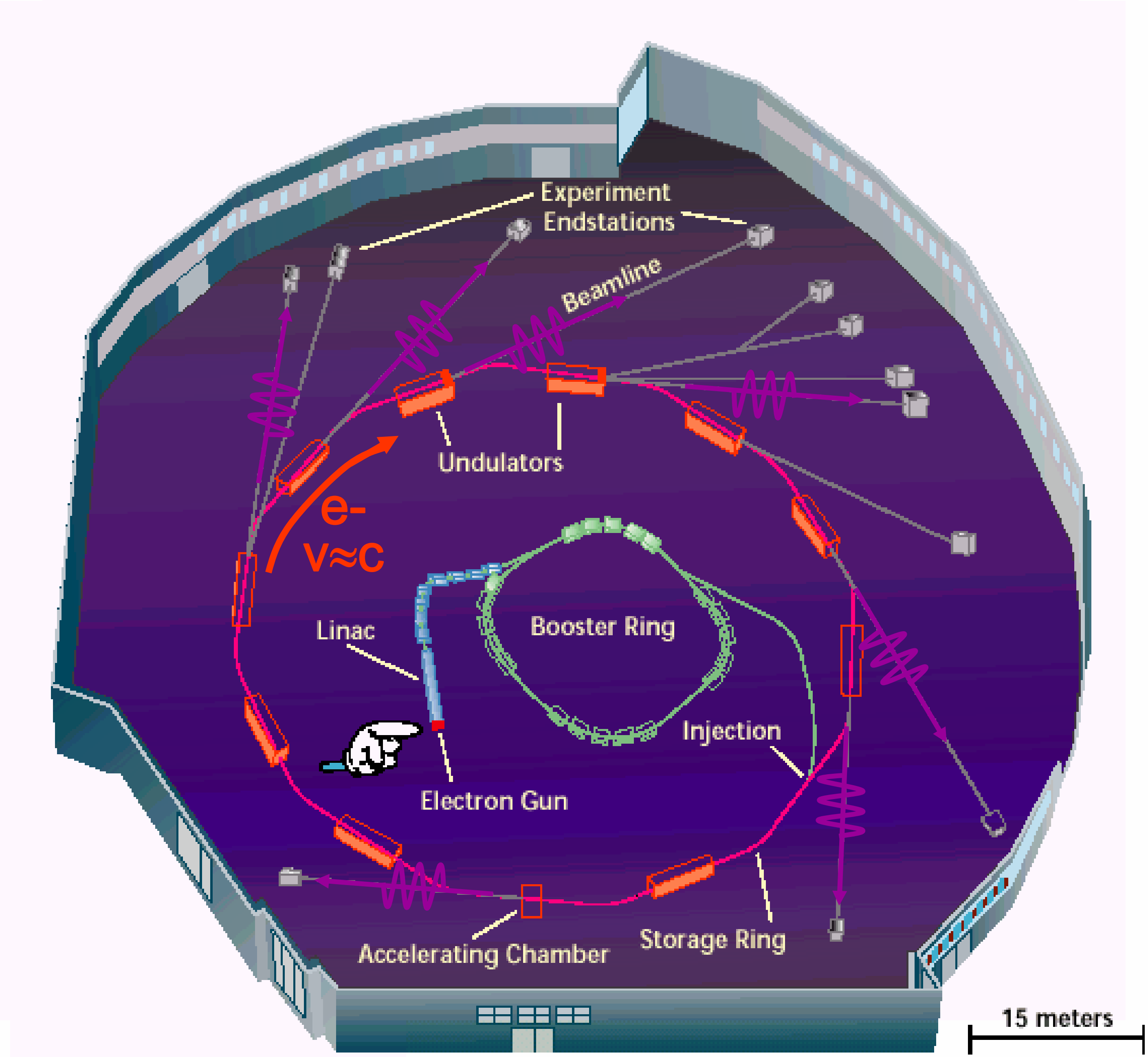


Synchtron Radiation Sources of the World

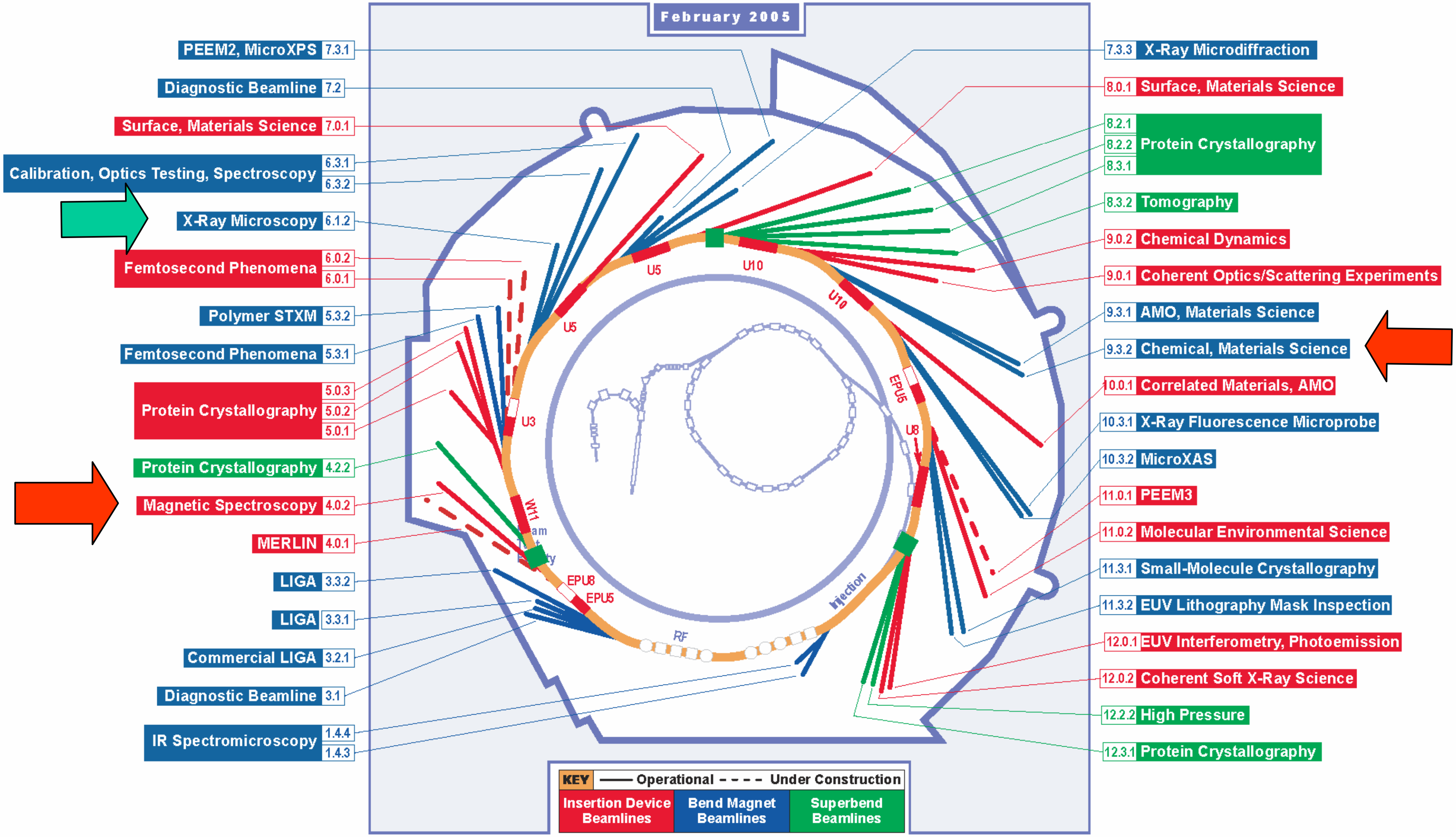
See also www.lightsources.org


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

Layout of the ALS



Beamlines at the ALS 2005



February 2005

PEEM2, MicroXPS	7.3.1
Diagnostic Beamline	7.2
Surface, Materials Science	7.0.1
Calibration, Optics Testing, Spectroscopy	6.3.1 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	4.0.1
LIGA	3.3.2
LIGA	3.3.1
Commercial LIGA	3.2.1
Diagnostic Beamline	3.1
IR Spectromicroscopy	1.4.4 1.4.3

7.3.3	X-Ray Microdiffraction
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

KEY —— Operational - - - - Under Construction

Insertion Device Beamlines	Bend Magnet Beamlines	Superbend Beamlines

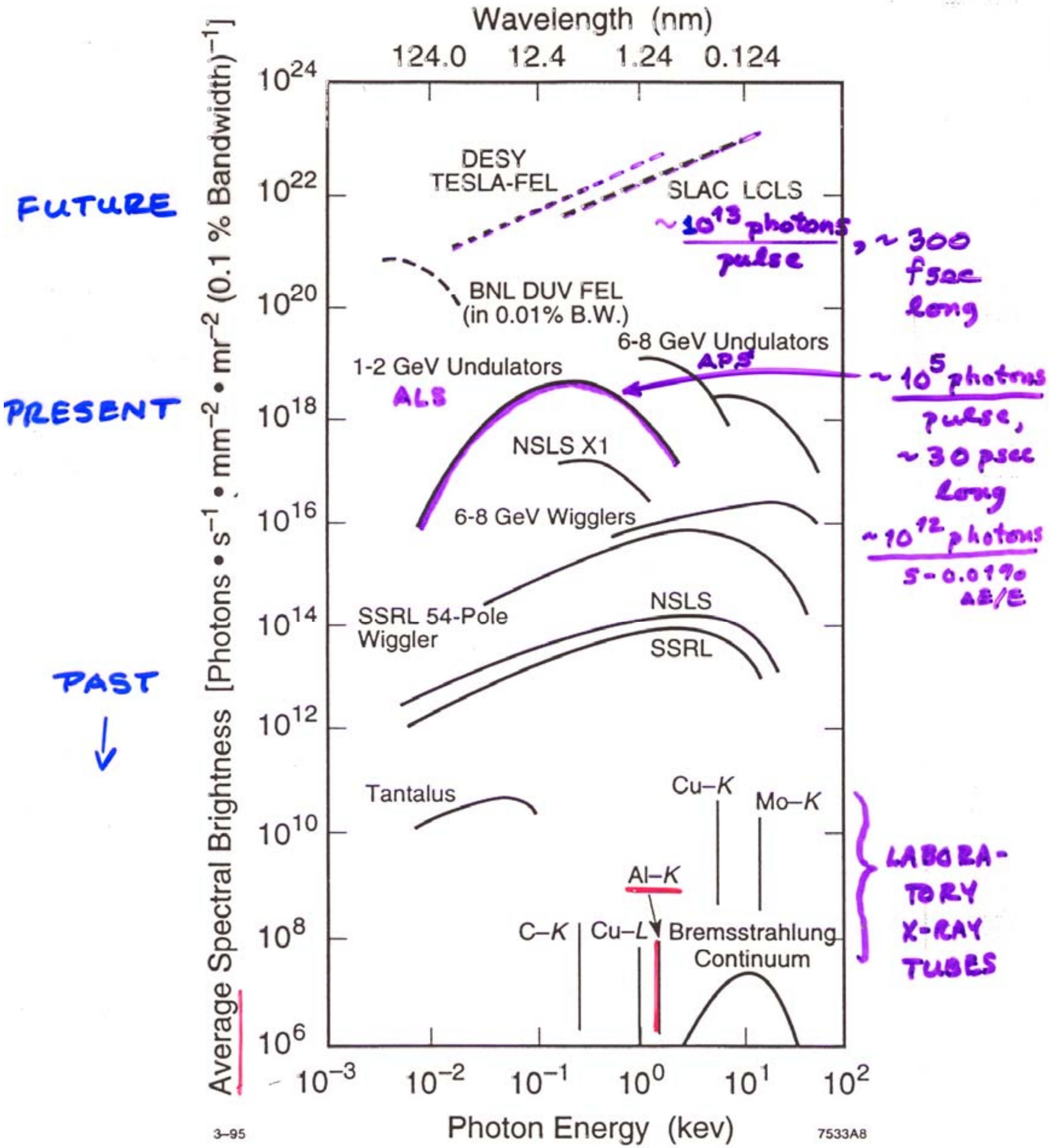
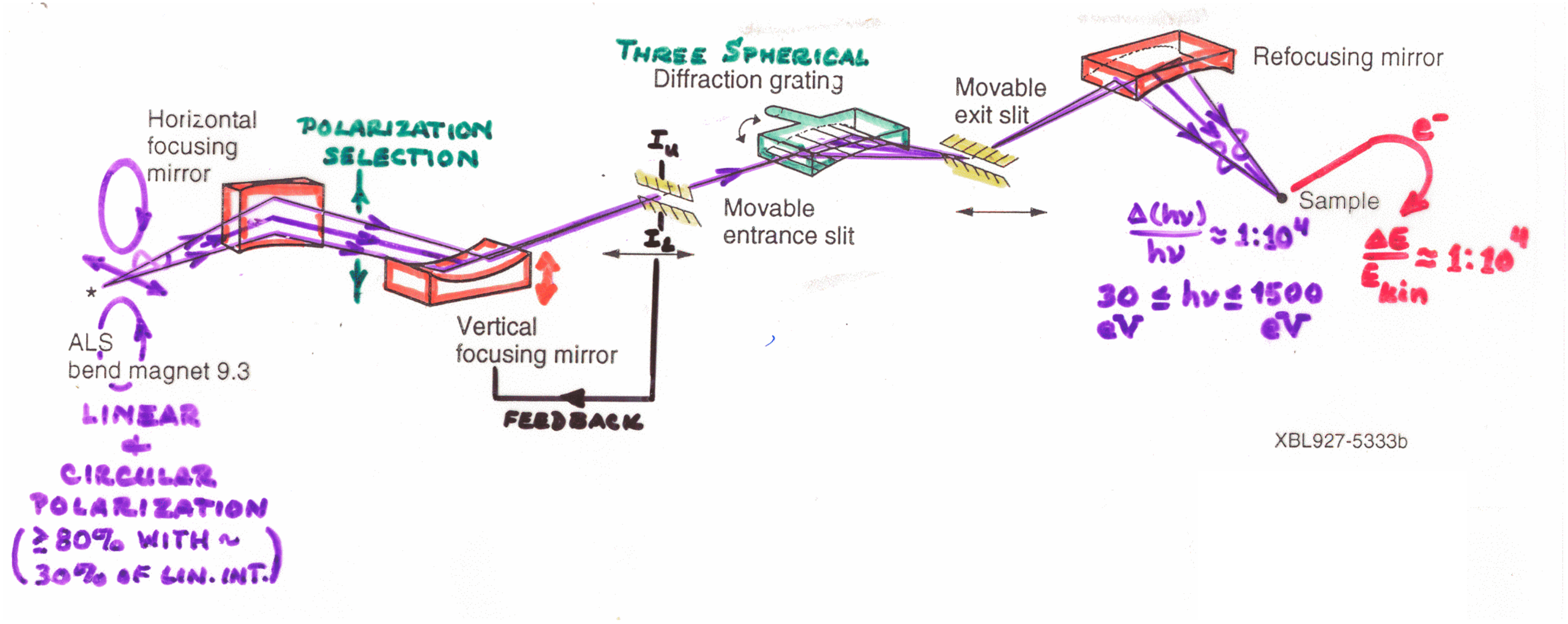


Fig. 2. Average brightness comparisons of the LCLS and other light sources, including proposed FELs at Brookhaven [14] and DESY [15].

"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:

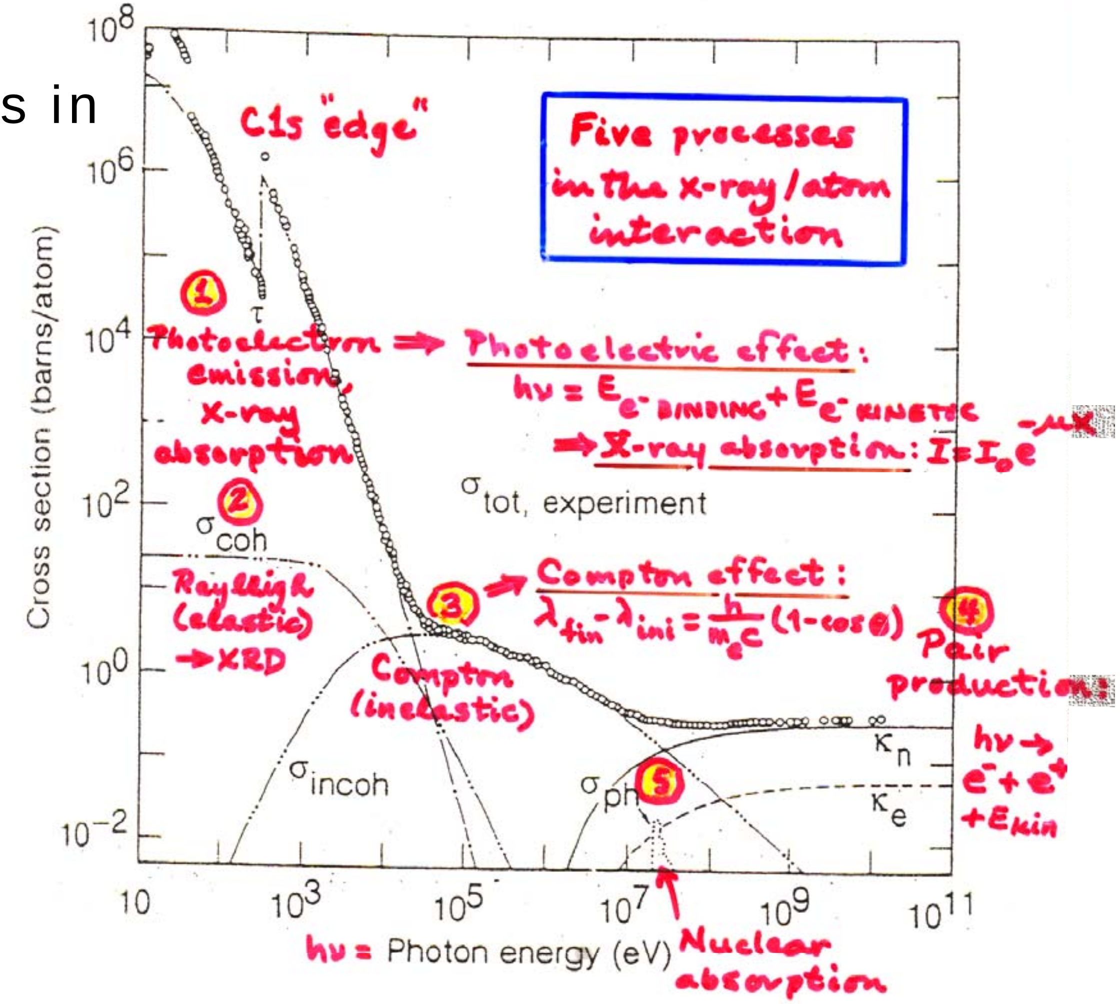
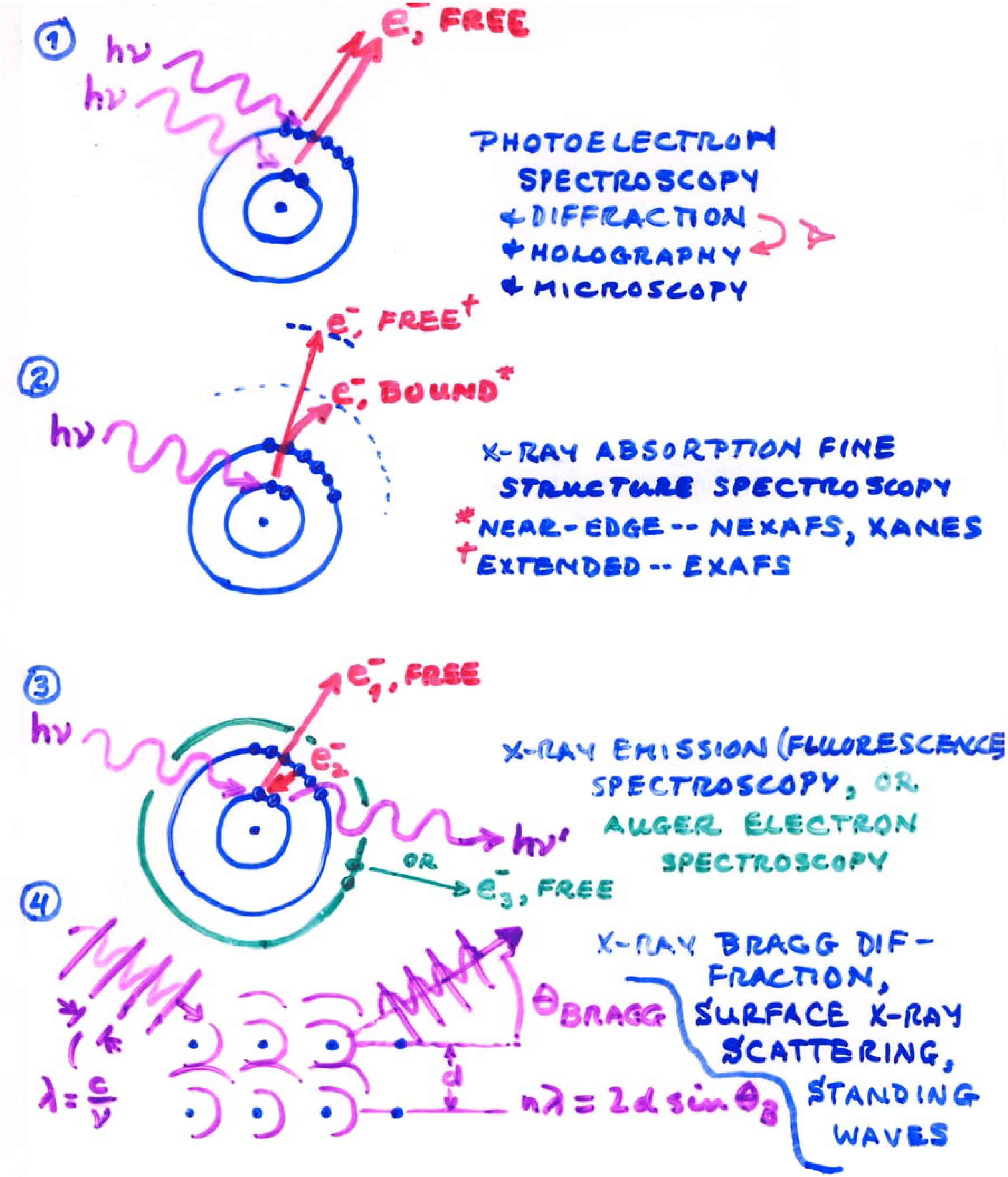


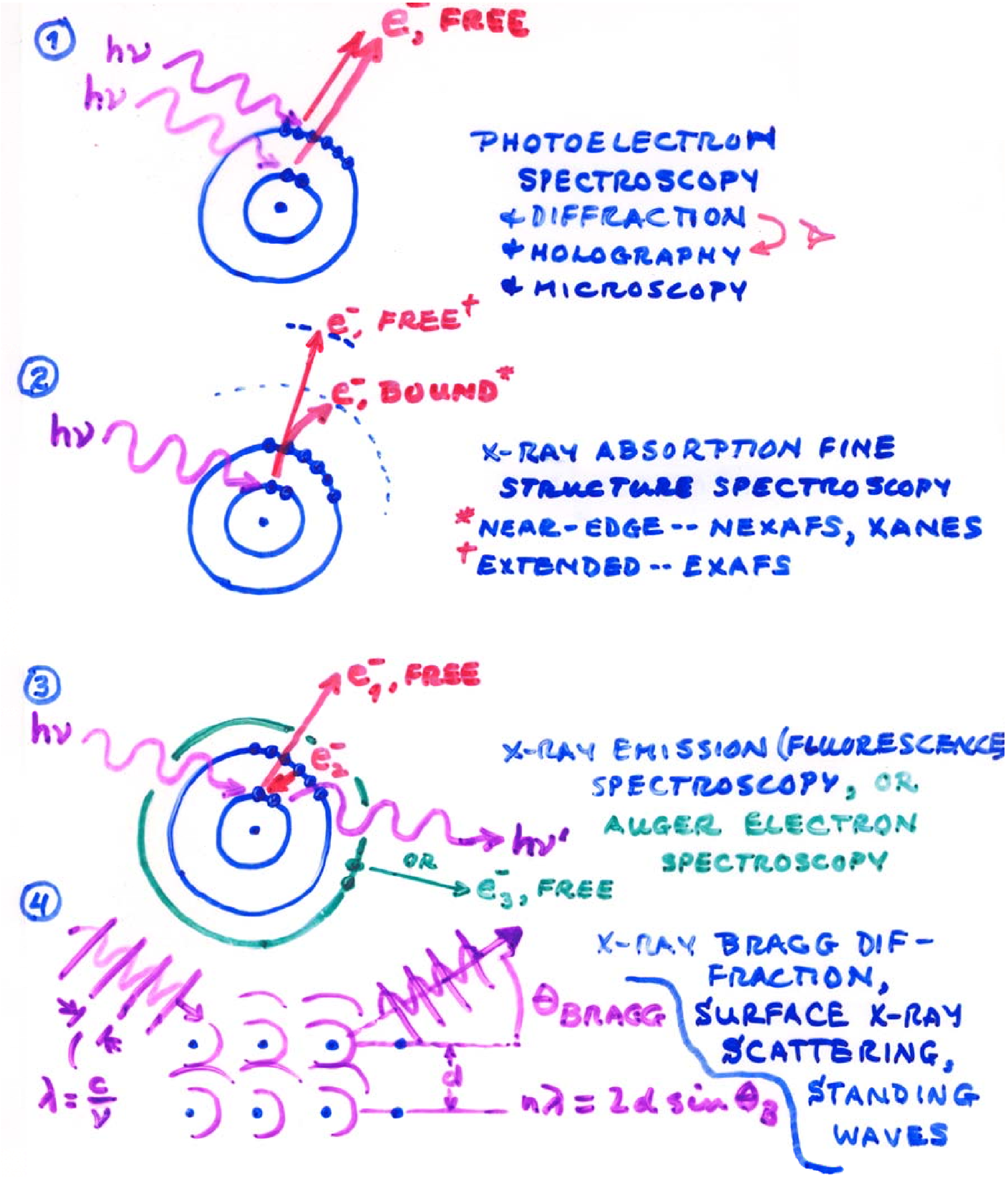
Fig. 3-1. *Total photon cross section σ_{tot} in carbon, as a function of energy, showing the contributions of different processes: τ, atomic photo-effect (electron ejection, photon absorption); σ_{coh}, coherent scattering (Rayleigh scattering—atom neither ionized nor excited); σ_{incoh}, incoherent 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. [illegible]; figure courtesy of J. H. Hubbell.)*

"X-Ray Data Booklet"
Section 3.1

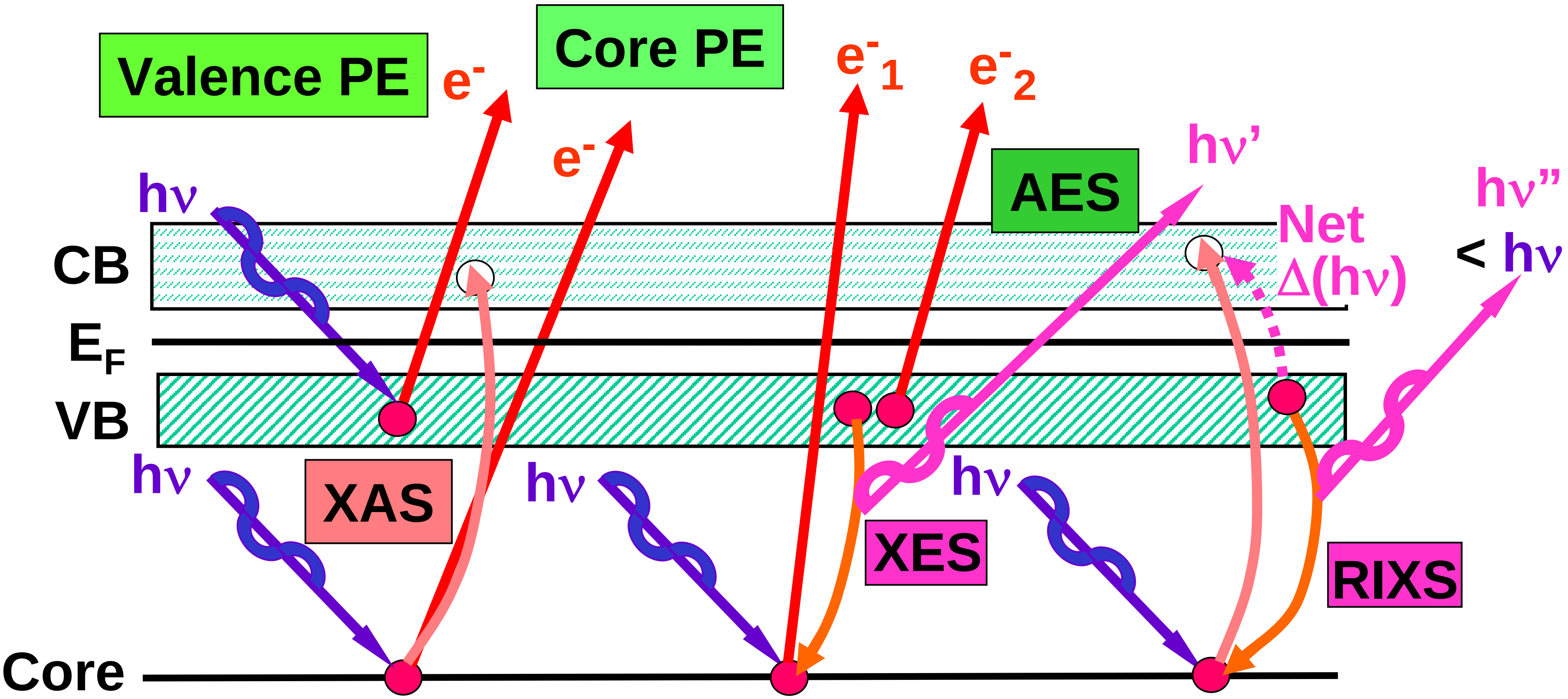
The ultraviolet, soft x-ray, hard x-ray measurements:



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

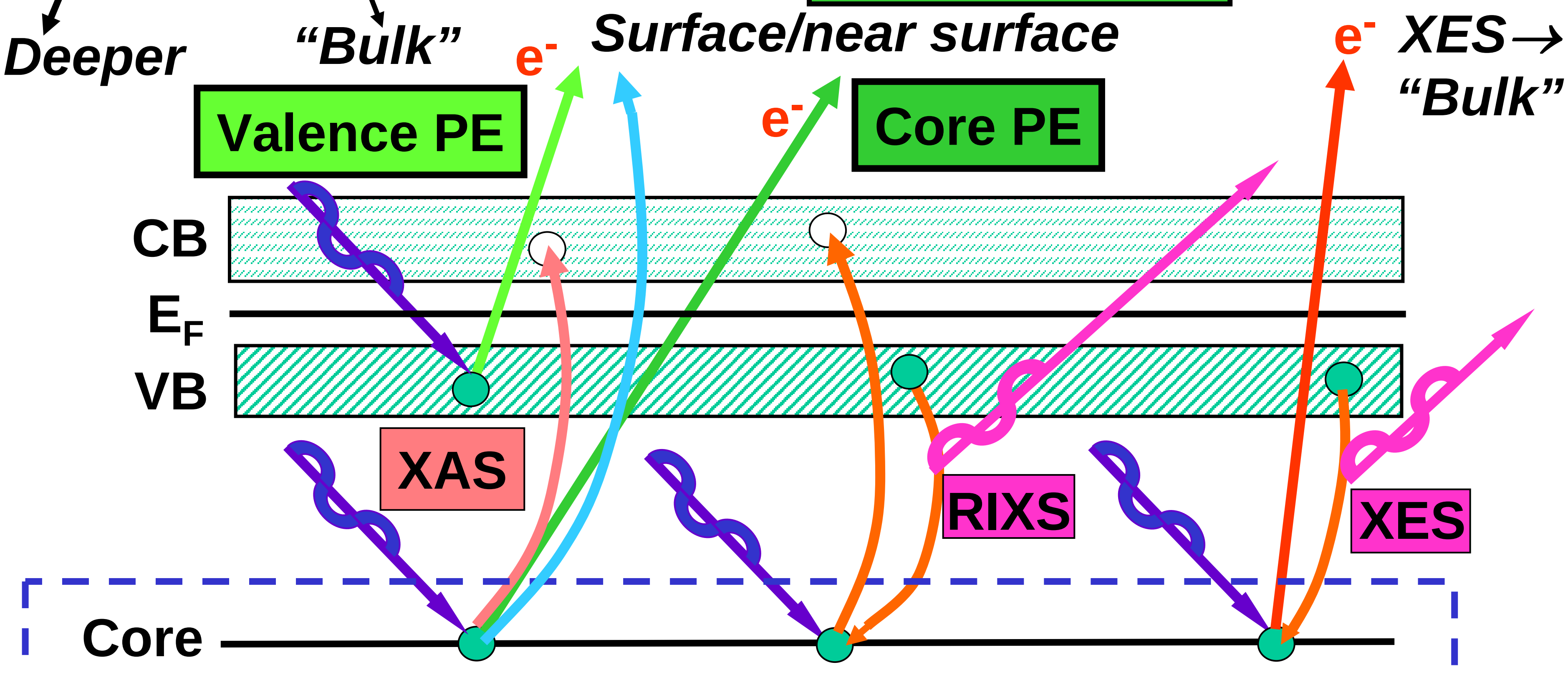
EXAFS
Atomic structure

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

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

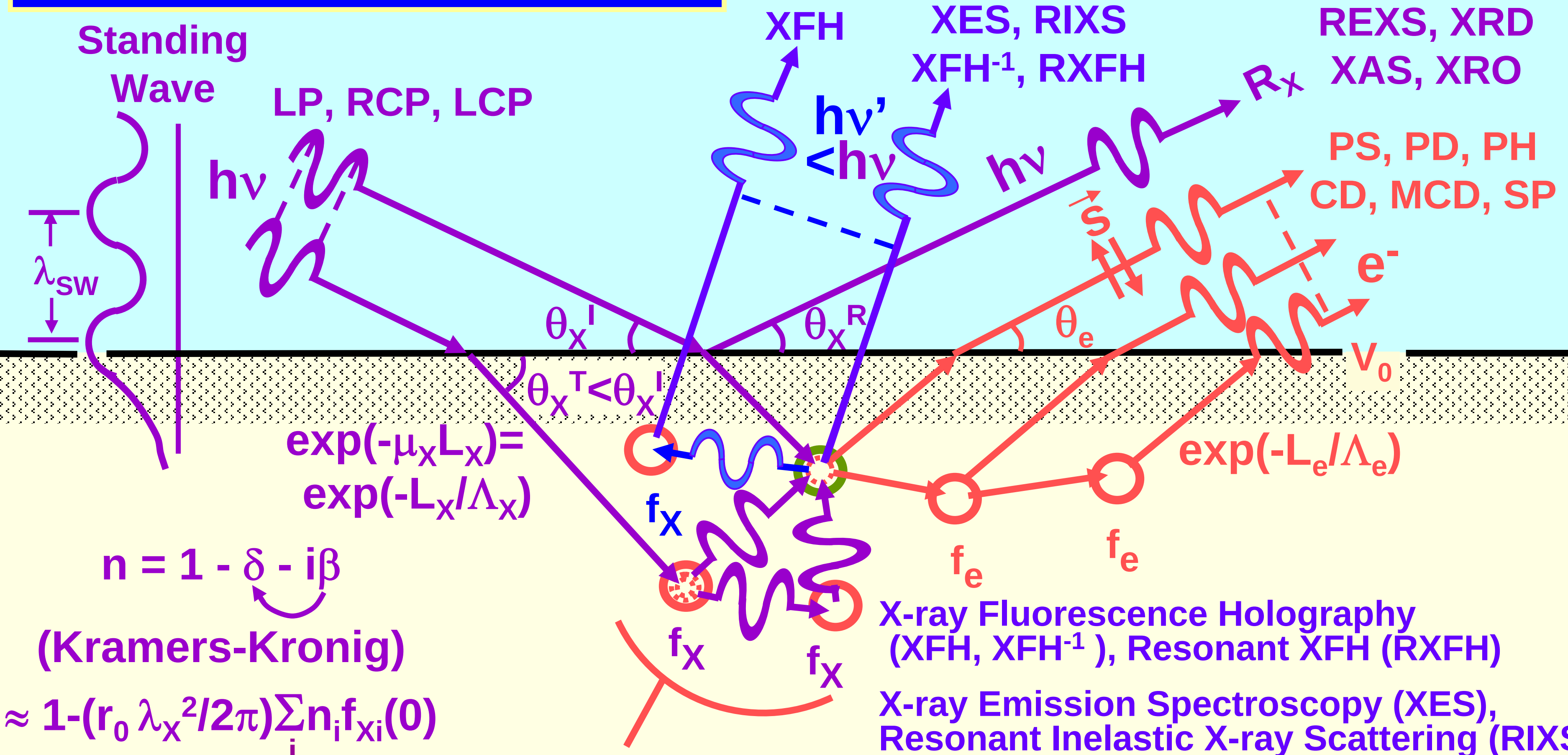
Core PE -
stoichiometry
BE shifts
splittings, MCD
spin polarization
diffraction

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



Core levels→ Element-specific methods

Some basic measurements:



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

(Kramers-Kronig)

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

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

$\theta_X^R = \theta_X^I$

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

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

Multi-atom resonant photoemission (MARPE)

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)

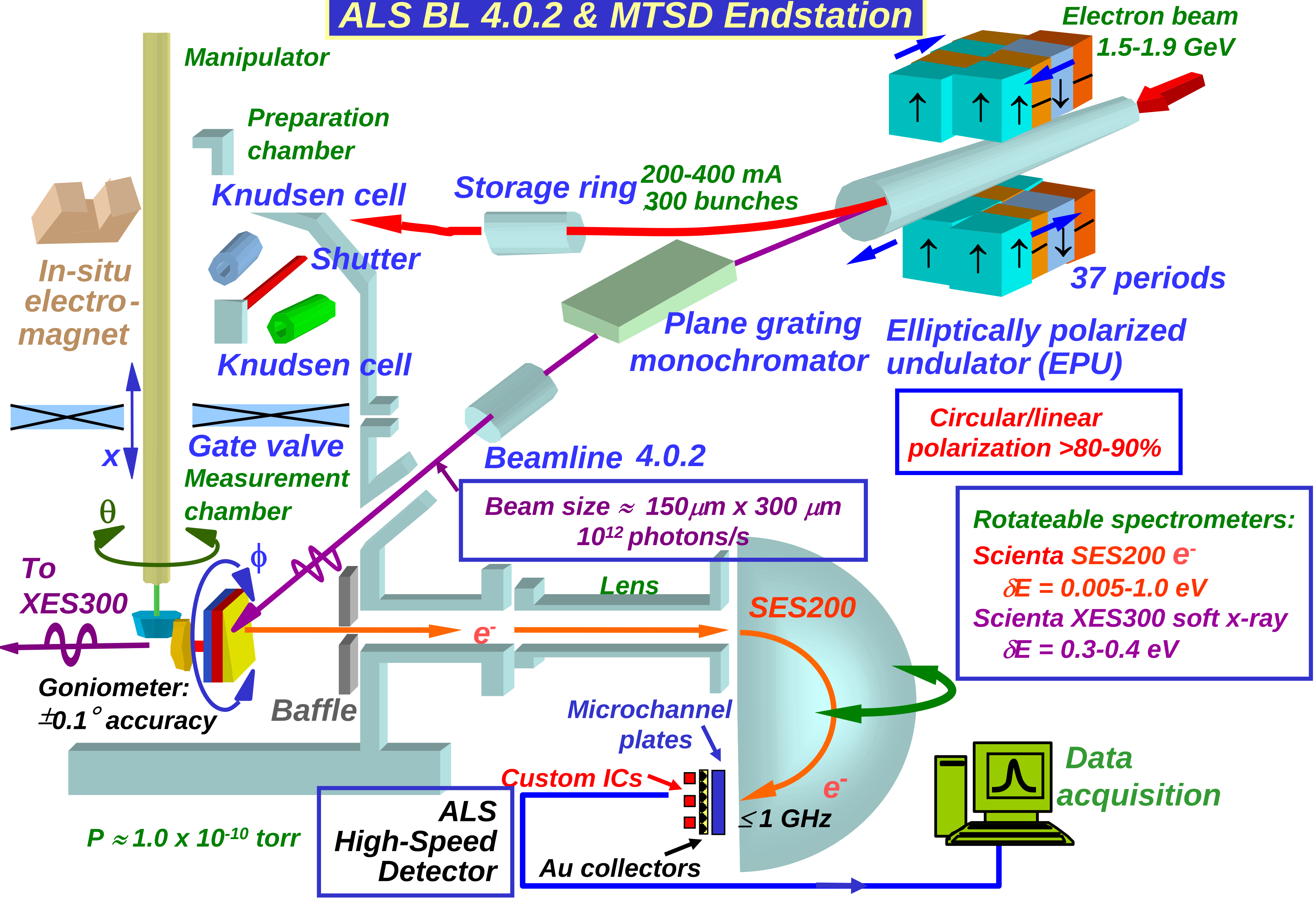
X-Ray Diffraction (XRD)

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)

Experimental system
ALS BL 4.0.2 & MTSD Endstation



Electron beam 1.5-1.9 GeV

Manipulator

Preparation chamber

Knudsen cell

Storage ring

200-400 mA
300 bunches

In-situ electro-magnet

Shutter

37 periods

Knudsen cell

Plane grating monochromator

Elliptically polarized undulator (EPU)

Circular/linear polarization >80-90%

x

Gate valve

Measurement chamber

Beamline 4.0.2

Beam size ≈ 150 μm x 300 μm
10^{12} photons/s

θ

ϕ

Rotateable spectrometers:

Scienta SES200 e^-
$\delta E = 0.005\text{-}1.0$ eV

Scienta XES300 soft x-ray
$\delta E = 0.3\text{-}0.4$ eV

To XES300

Lens

SES200

e^-

Goniometer:
±0.1° accuracy

Baffle

Microchannel plates

Custom ICs

e^-

Data acquisition

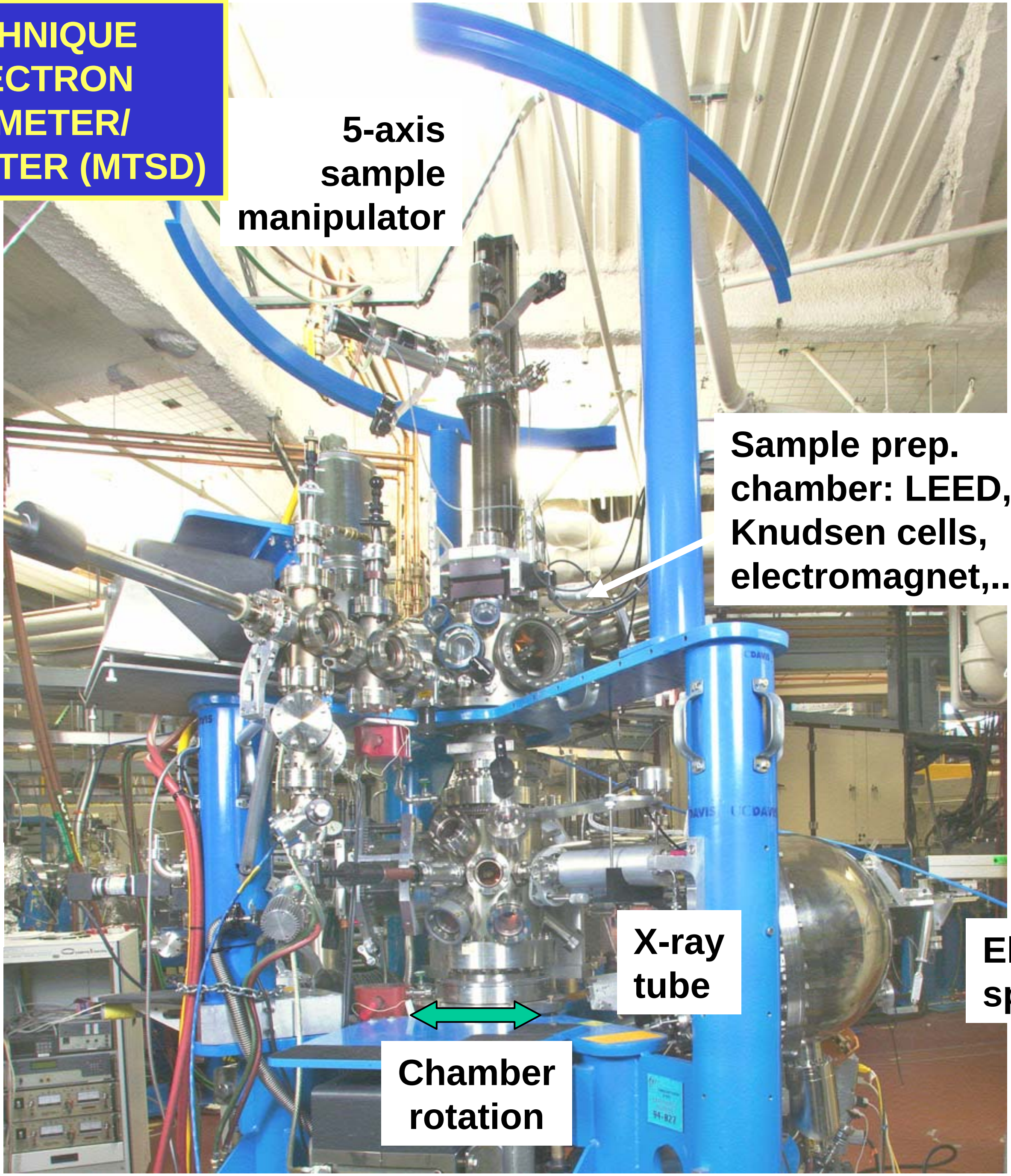
ALS
High-Speed
Detector

≤ 1 GHz

$P \approx 1.0 \times 10^{-10}$ torr

Au collectors

MULTI-TECHNIQUE PHOTOELECTRON SPECTROMETER/ DIFFRACTOMETER (MTSD)



5-axis sample manipulator

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

Loadlock for sample introduction

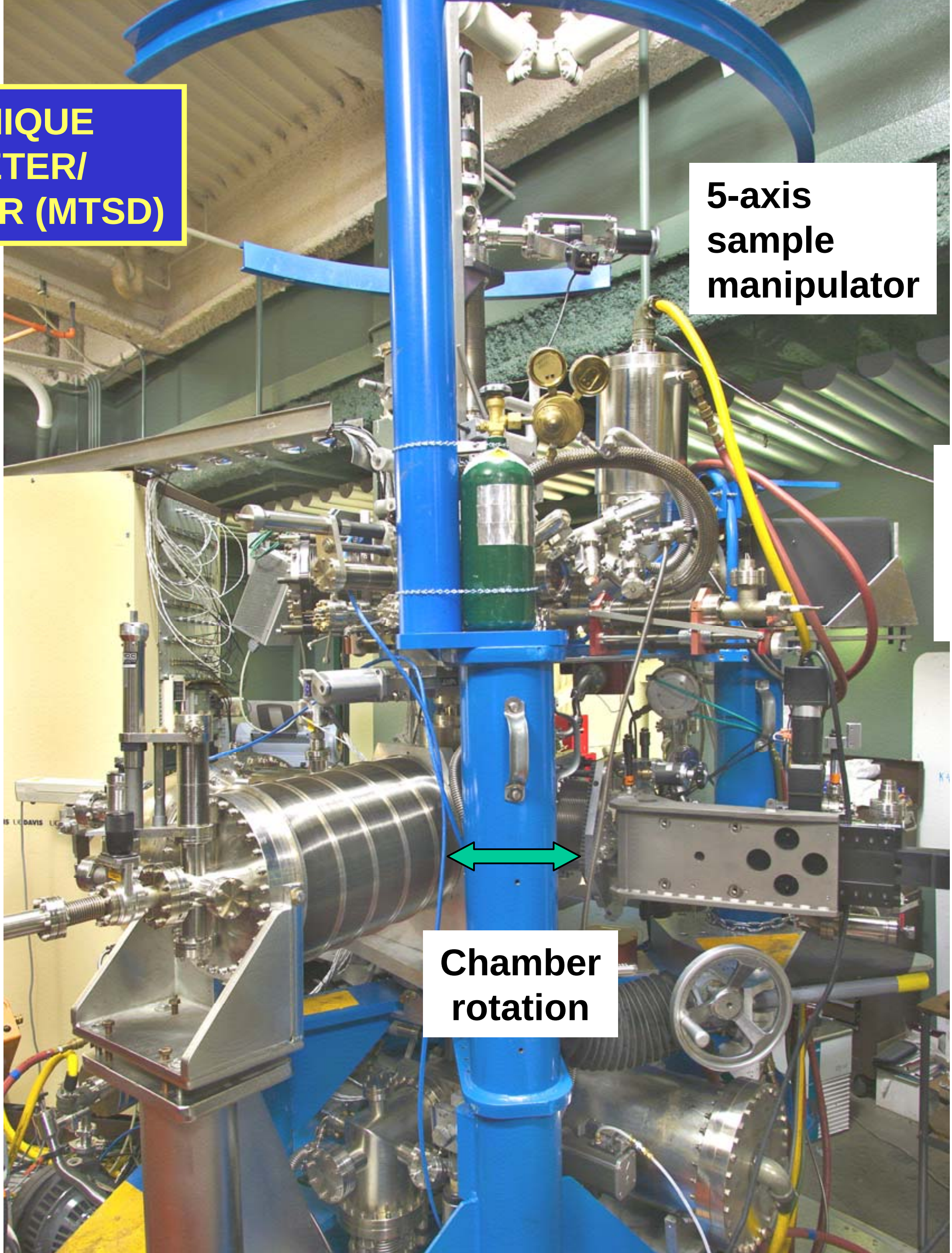
Soft x-ray spectrometer

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