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SCHOOL ON SYNCHROTRON RADIATION

6 November – 8 December 2000

Miramare - Trieste, Italy

Supported in part by the Italian Ministry of Foreign Affairs in connection with the SESEME project

Co-sponsors: Sincrotrone Trieste, Società Italiana di Luce di Sincrotrone (SILS) and the Arab Fund for Economic and Social Development

Photoemission, x-ray emission, x-ray absorption in surface, interface, nanostructure, and materials studies

Chuck Fadley
Lawrence Berkeley Laboratory
Berkeley, United States of America

LECTURES FOR 29 NOVEMBER--4 DECEMBER, 2000

PHOTOEMISSION, X-RAY EMISSION, X-RAY ABSORPTION IN SURFACE, INTERFACE, NANOSTRUCTURE, AND MATERIALS STUDIES

Lecturers:

Professor 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/microscopy, x-ray fluorescence holography

Professor Anders Nilsson, Institute of Physics, Uppsala University, Sweden &
Stanford Synchrotron Radiation Laboratory, Stanford, USA
Photoelectron spectroscopy, x-ray emission spectroscopy, x-ray inelastic scattering, and x-ray absorption spectroscopy applied to molecules and surfaces

Professor 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

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 LECTURES, 29 NOVEMBER-4 DECEMBER, 2000---

(With complementary coverage of related/additional material
by Anders Nilsson, Uppsala, and Juerg Osterwalder, Zürich)

- ***INTRODUCTION:***
  - --Surface and interface phenomena: Why study them? Nanotechnology
    Some instrumentation considerations
  - --The basic vuv/x-ray techniques: Photoelectron spectroscopy = photoemission(PS, PES)
    X-ray absorption spectroscopy (XAS, NEXAFS(=XANES) + EXAFS = XAFS
    X-ray emission/x-ray fluorescence spectroscopy (XES, XFS)
    X-ray scattering and diffraction (XRD, prior lectures)
    X-ray optical measurements (refraction, reflection, standing waves, Kerr, Faraday rotations,...)
  - --The photoemission process: Energy conservation
    Hartree Fock, Koopmans Theorem and corrections to it
    Electron escape and surface sensitivity
  - --Instrumentation:
    Laboratory-based: e.g., PS, STM, LEED combined
    At third-generation synchrotron radiation sources: e.g. the Advanced Light Source or Elettra
    Prospects for time-dependent spectroscopy & detector development
    Spin detection

- *CORE-LEVEL SPECTROSCOPY:*
  - --Basic cross sections and selection rules
  - --The dipole approximation and beyond
  - --The Sudden Approximation and its sum rules
  - --Photoelectric cross sections
    - 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
  - --Core intensities and quantitative surface analysis:
    - Surface sensitivity enhancement at grazing emission
    - Quantitative formulas for surface analysis
  - --Chemical shifts in core binding energies
  - --Final-state screening and relaxation effects, satellites
  - --Vibrational effects in spectra
  - --Multiplet splittings & spin-polarized spectra
  - --Spin polarization via spin-orbit-split levels excited with circular polarized radiation
  - --Probing surfaces and buried interfaces with soft x-ray standing waves

- *VALENCE-LEVEL SPECTROSCOPY:*
  - --The low-energy (UPS) limit:
    - Selection rules on wave vector
    - Band-structure mapping
    - Fermi-surface mapping
  - --Vibrational/phonon effects: UPS⇔XPS limits
  - --The high-energy (XPS) limit:
    - Density-of-states
    - Surface band narrowing

- *PHOTOELECTRON DIFFRACTION (CORE LEVELS):*
  - --Basic diffraction and measurement process
  - --Energy dependence of scattering:
    - Forward-dominated at high energies
    - Back and forward at low energies
  - --Determination of structures from:
    - Forward scattering peaks
    - More complex diffraction patterns
      - (incl. full-solid -angle data)
    - Analysis via single-scattering and multiple scattering theory--review of theoretical approaches and computer exercises for those interested
  - --Some example applications: adsorbates, epitaxial overlayers, Moiré structures, surface phase transitions, time-dependent surface reactions
  - --Fourier transforms of data: path-length differences
  - --Comparison to extended x-ray absorption fine structure (EXAFS)

•*CIRCULAR DICHROISM IN CORE-LEVEL EMISSION:*

--Non-magnetic systems: adsorbates, semiconductors, metals

--Magnetic systems: metals

•*SPIN-POLARIZED PHOTOELECTRON DIFFRACTION:*

--Multiplets or excitation of spin-orbit-split levels with variable-polarization radiation

--Surface magnetic phase transitions

•*PHOTOELECTRON HOLOGRAPHY:*

--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 differential holography approach

--Spin-polarized holography and direct imaging of magnetic order?

•*X-RAY FLUORESCENCE HOLOGRAPHY:*

--Two basic types:

Single energy (direct) x-ray fluorescence holography (XFH)

Multi-energy (inverse) holography (MEXH or $[XFH]^{-1}$)

--Applications in single-energy and multi-energy form to bulk crystals of oxides and metals, quasicrystals

--Comparison to classical x-ray crystallography

•PHOTOELECTRON MICROSCOPY, "SPECTROMICROSCOPY":

--Methods of image formation, ultimate resolutions

--Some example results: semiconductor structures

magnetic bit structures

magnetic domains in ferromagnets and antiferromagnets

polymeric microstructures

Handouts as general references on angle-resolved photoelectron spectroscopy, diffraction, holography:

[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.

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

[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)

[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). (Not numbered in handout.)

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

[6] "Atomic Holography with Electrons and X-rays", P.M. Len, C.S. Fadley, and G. Materlik, paper appearing in the Proceedings of the X-96 Conference, AIP Proceedings, 1997, pp. 295-319.

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

[8] "Multi-Atom Resonant Photoemission Revisited", 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, to appear.

[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 B, to appear. (Paper describing the new "EDAC" multiple scattering program available for limited online usage at http://electron.lbl.gov/~edac/ for those wishing to try it.)

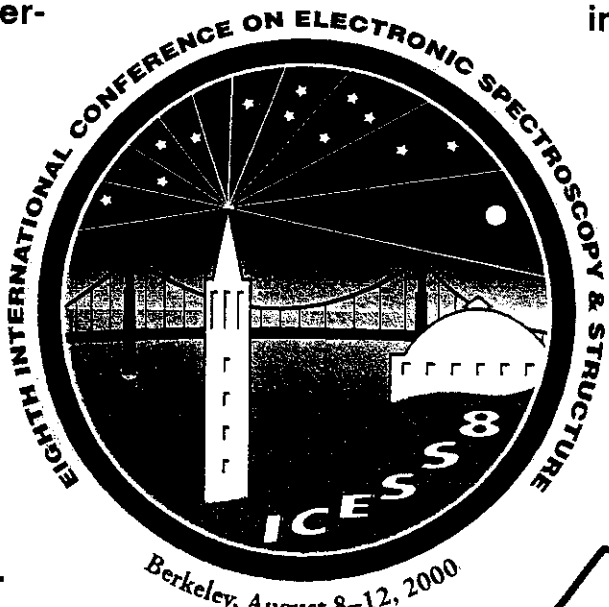
[10] "Fermi Surface Mapping by Angle-Resolved Photoemission", J. Osterwalder, Surface Review and Letters 4, 391 (1997). (Covered in greater detail in Osterwalder lectures.)

Plus, in mid-2000, the Proceedings of the Eighth International Conference on Electronic Spectroscopy and Structure will appear in the *Journal of Electron Spectroscopy and Related Phenomena*. These proceedings and the overall Conference program (also available at http://www-als.lbl.gov/icess/) cover the present status of all of the topics considered during this week's lectures.

ICESS8

An international conference on all aspects of electronic spectroscopy and electronic structure, including electron and photon excitation, various types of spectromicroscopies, new experimental methods, and novel theoretical methods. Scientific applications areas include atomic and molecular physics, solid state physics, materials science, surface and interface science, environmental/geological science, and biology. Conference program, participants, and photos are at http://www-als.lbl.gov/icess.

Full program



Location
Clark Kerr Campus, UC Berkeley

Honorary Chairperson
David A. Shirley, UC Berkeley (ret.)

Co-Chairpersons
Charles S. Fadley, UC Davis Physics and LBNL Materials Sciences Division
Louis J. Terminello, LLNL Chemistry and Materials Science Division

Sponsors
Department of Physics, UC Davis
Advanced Light Source, LBNL
Seaborg Institute, LLNL
Stanford Synchrotron Radiation Laboratory
Canadian Light Source

Some Statistics
408 participants from 33 countries (largest in series)
Oral presentations: Plenary--10, Invited--43, Contributed--50
Poster presentations: approximately 330

Out ~ May, 2000

Proceedings
To appear in The Journal of Electron Spectroscopy and Related Phenomena
Editors: Adam P. Hitchcock and K.Tong Leung

SURFACES, INTERFACES, AND NANOSTRUCTURES IN NEXT-GENERATION TECHNOLOGIES

● HIGHER-DENSITY, HIGHER-SPEED INTEGRATED CIRCUITS

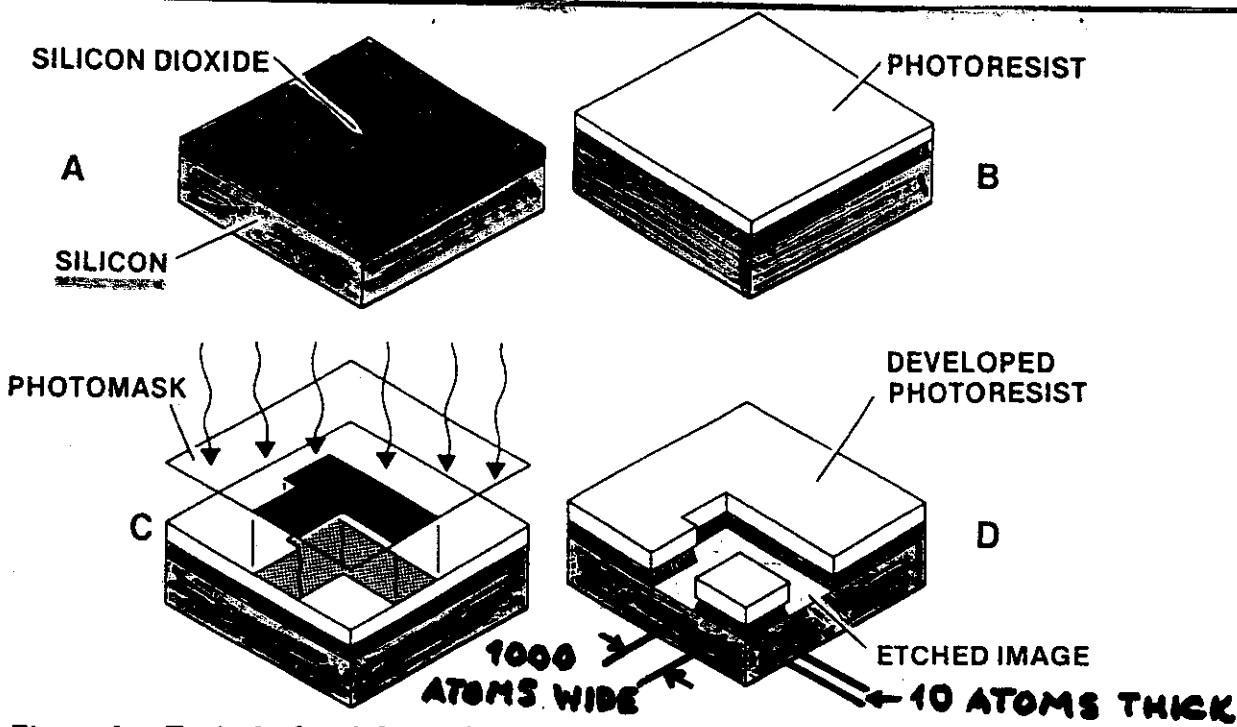
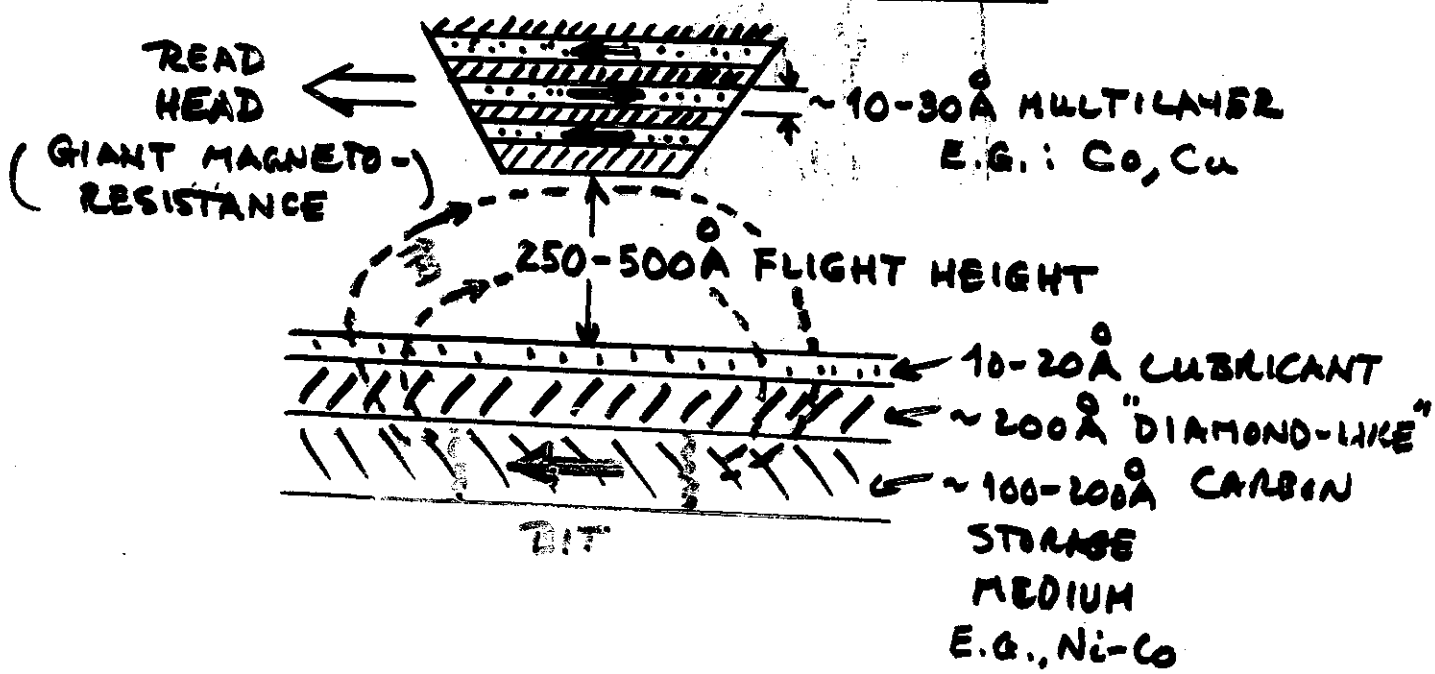


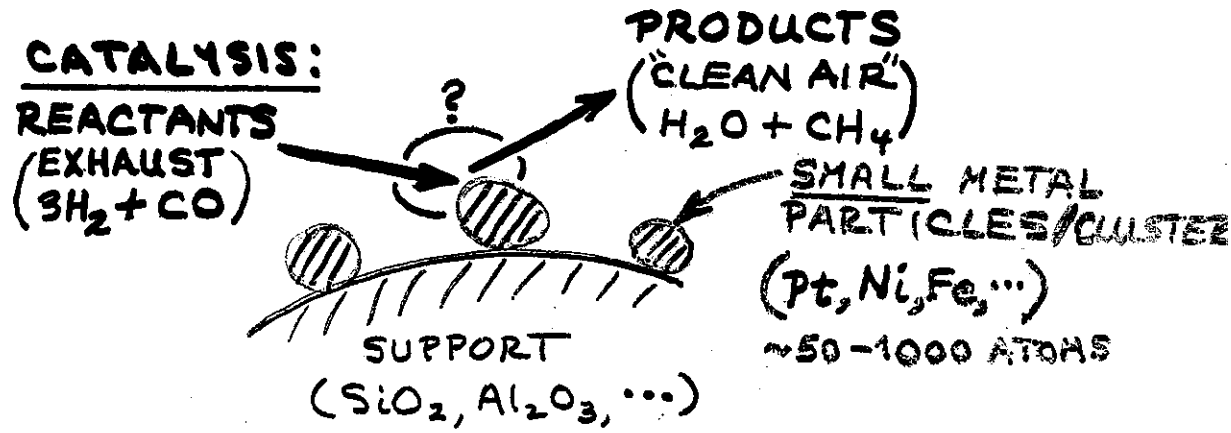
Figure 1. Typical photolithographic processing steps necessary to pattern SiO_2 layer on a Si substrate. Key: A, thermal oxidation; B, photoresist deposition; C, resist exposure through photomask; and D, develop photoresist.

● HIGHER-DENSITY MAGNETIC STORAGE:

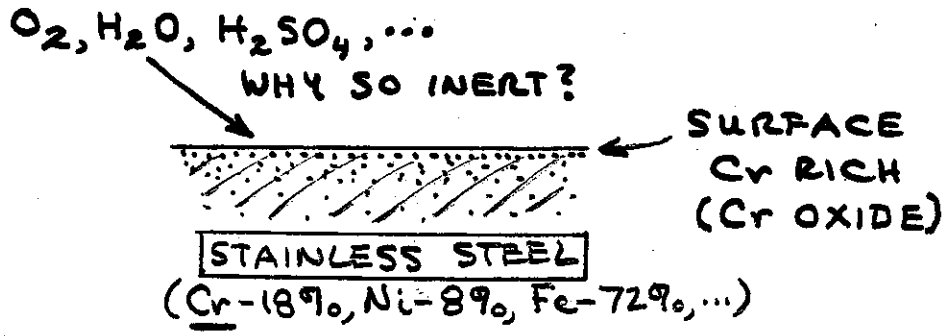


SOME AREAS OF APPLICATION:

① CATALYSIS:

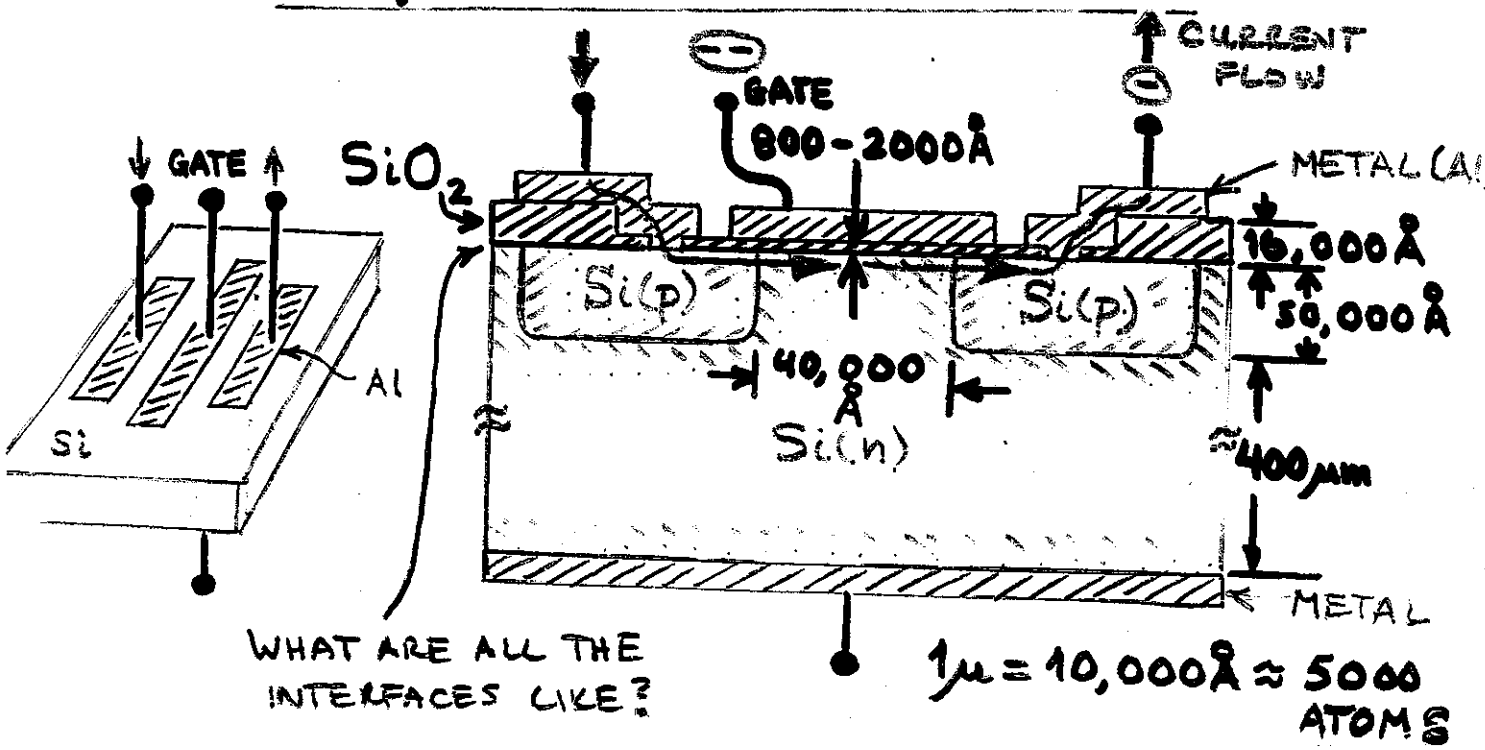


② CORROSION:

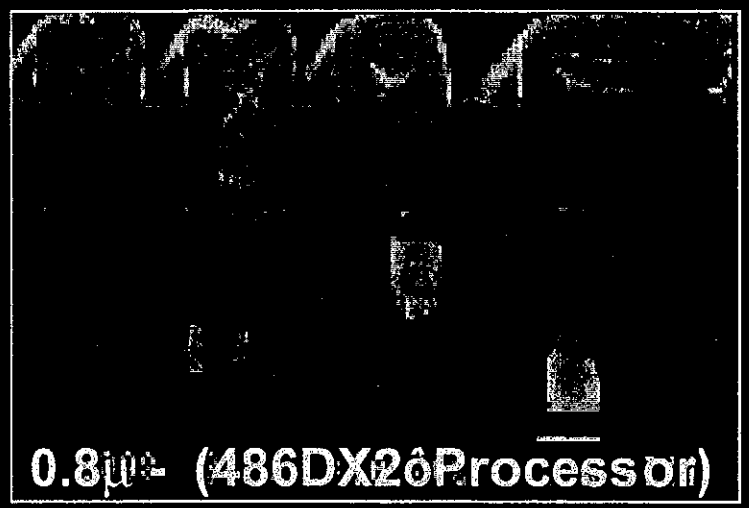


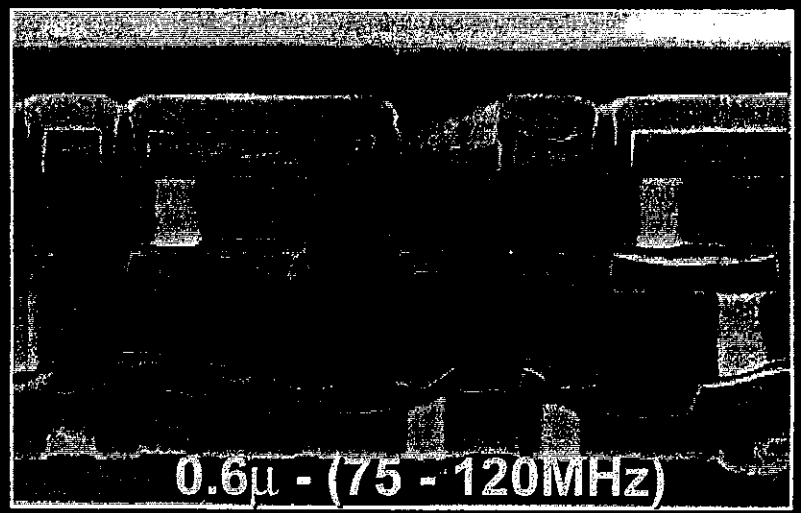
③ SOLID-STATE MICROCIRCUITS:

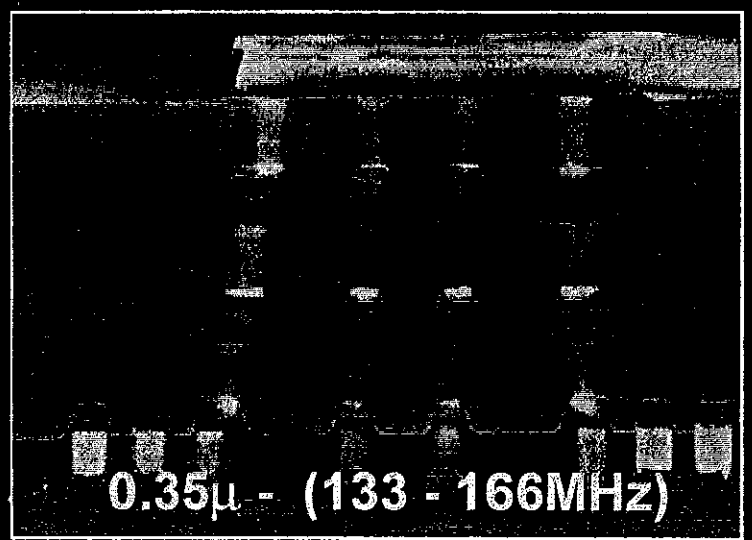
E.G., THE FIELD-EFFECT TRANSISTOR-

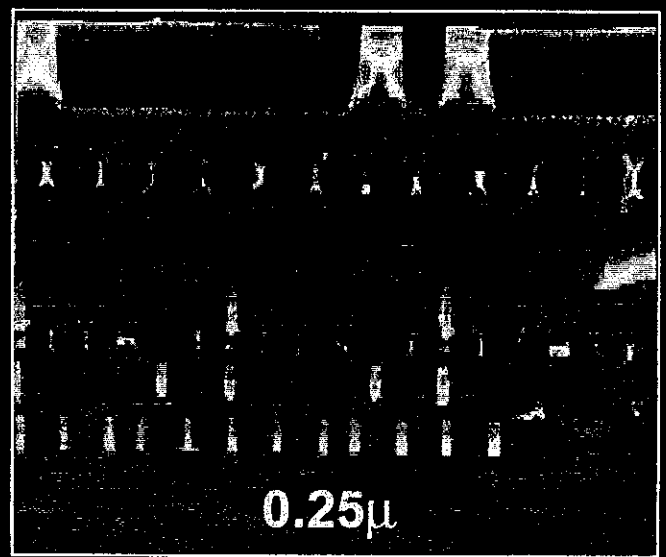


Intel Process





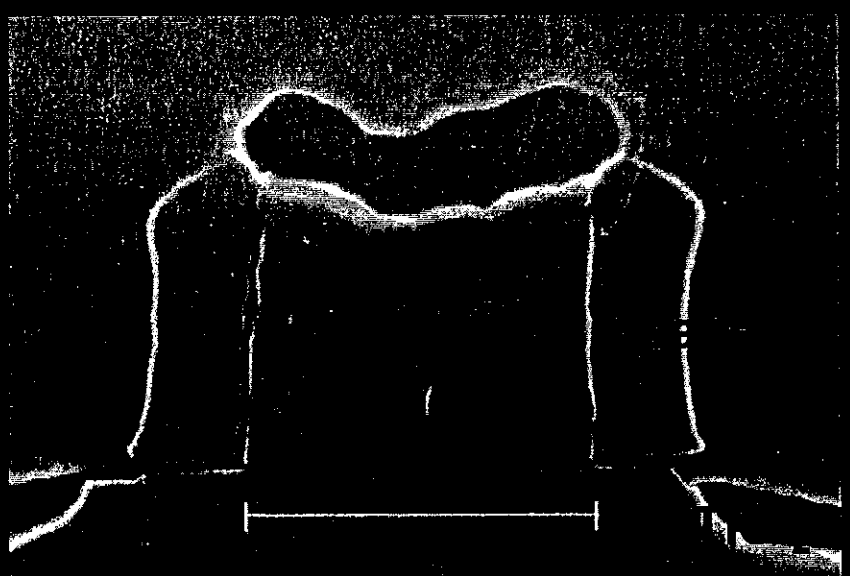




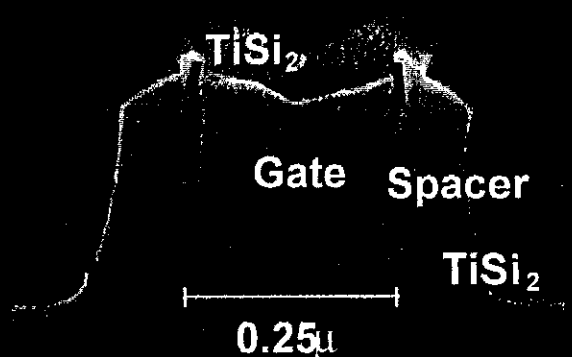
intel

And the Shrink Goes On...

.35μ Process Technology



.25μ Process Technology

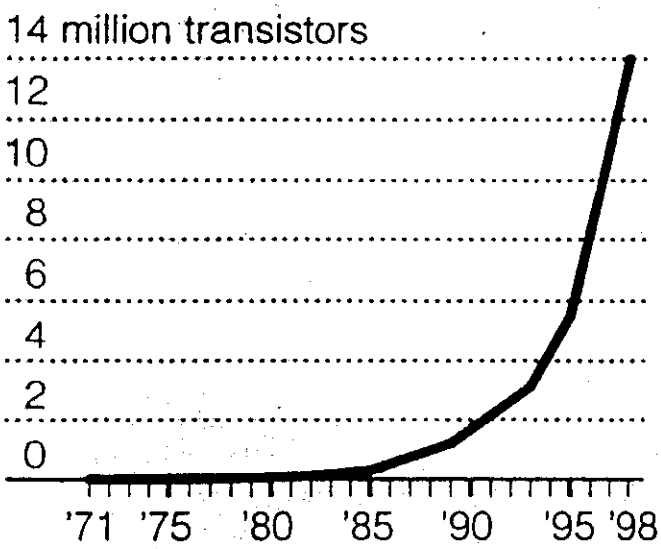


intel

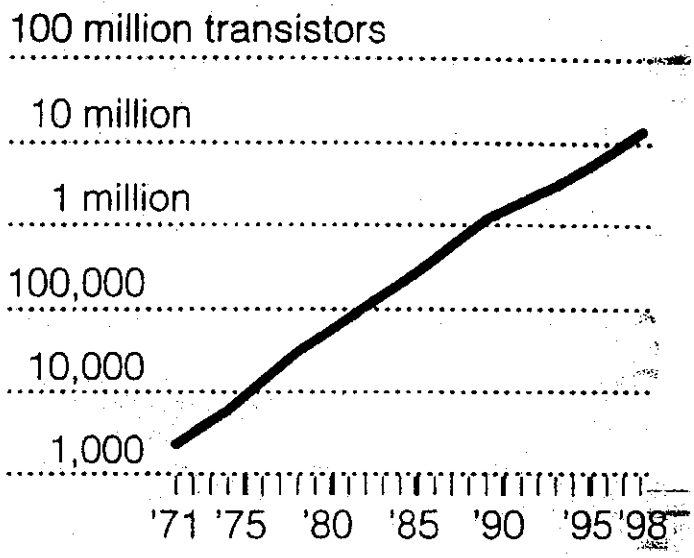
Moore's Law

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

The New York Times

The New York Times

SATURDAY, OCTOBER 9, 1999

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.

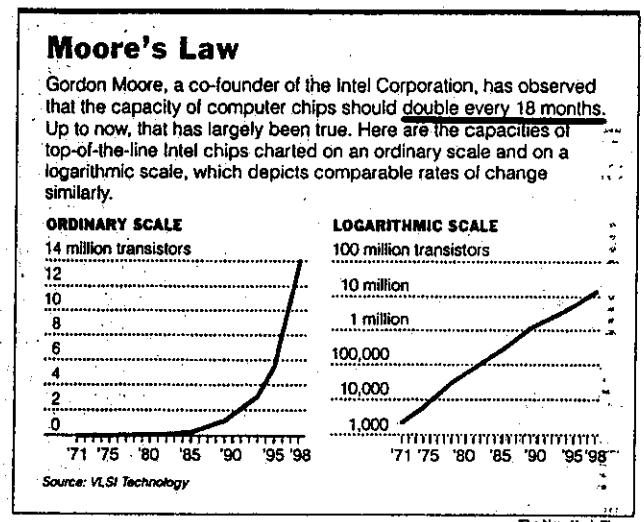
"Historically the economic incentives to find new methods for device improvement have regularly overcome the predicted scaling limits," said John Moussouris, a physicist and semiconductor designer. "The physical challenges may be getting harder, but the people and financial resources to surmount them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



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

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

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.

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.

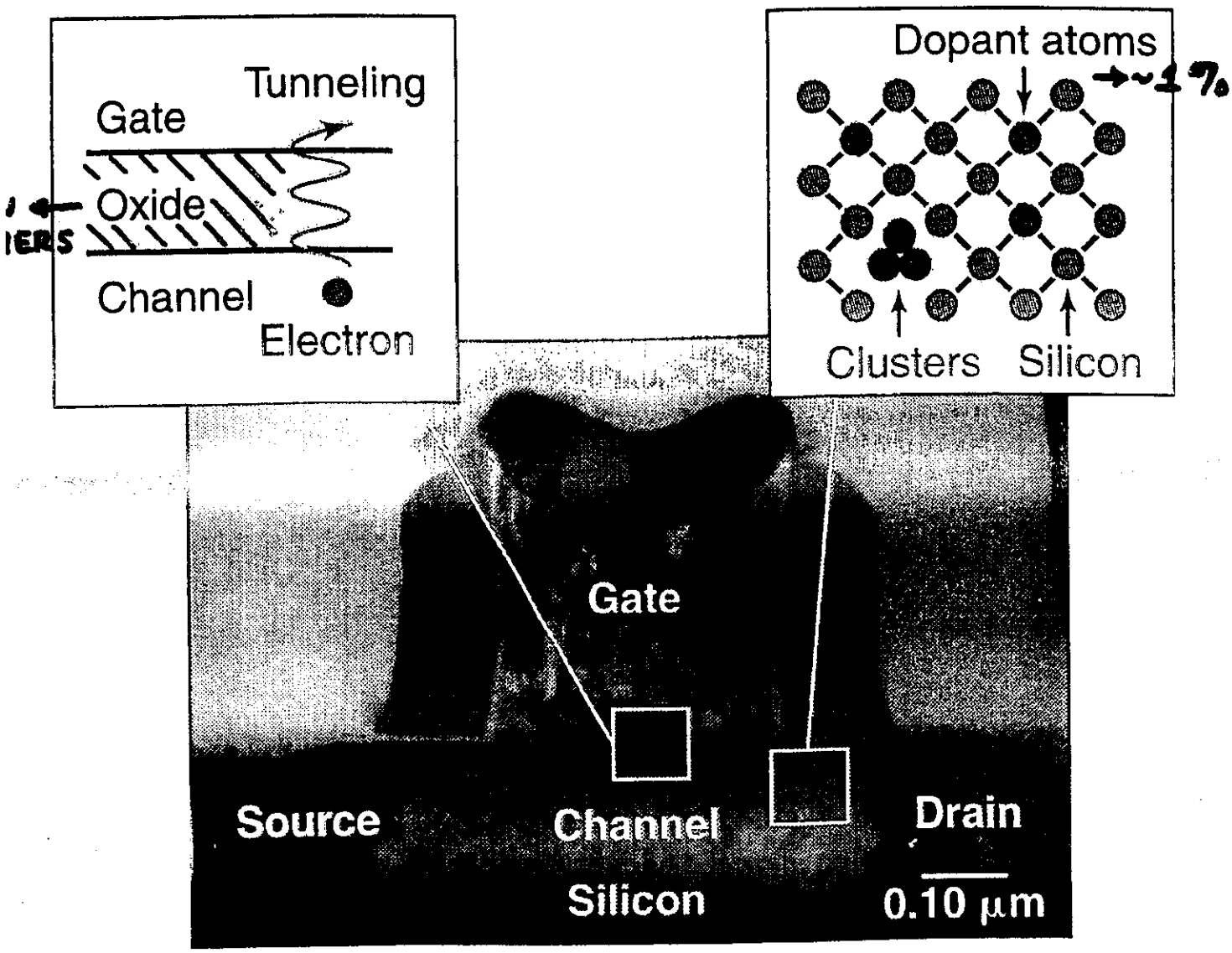
With researchers at Hewlett-Packard, Mr. Heath has developed a prototype memory cell the size of a single molecule that operates on different principles from today's semiconductors.

"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."

SOME FUTURE CHALLENGES:



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.

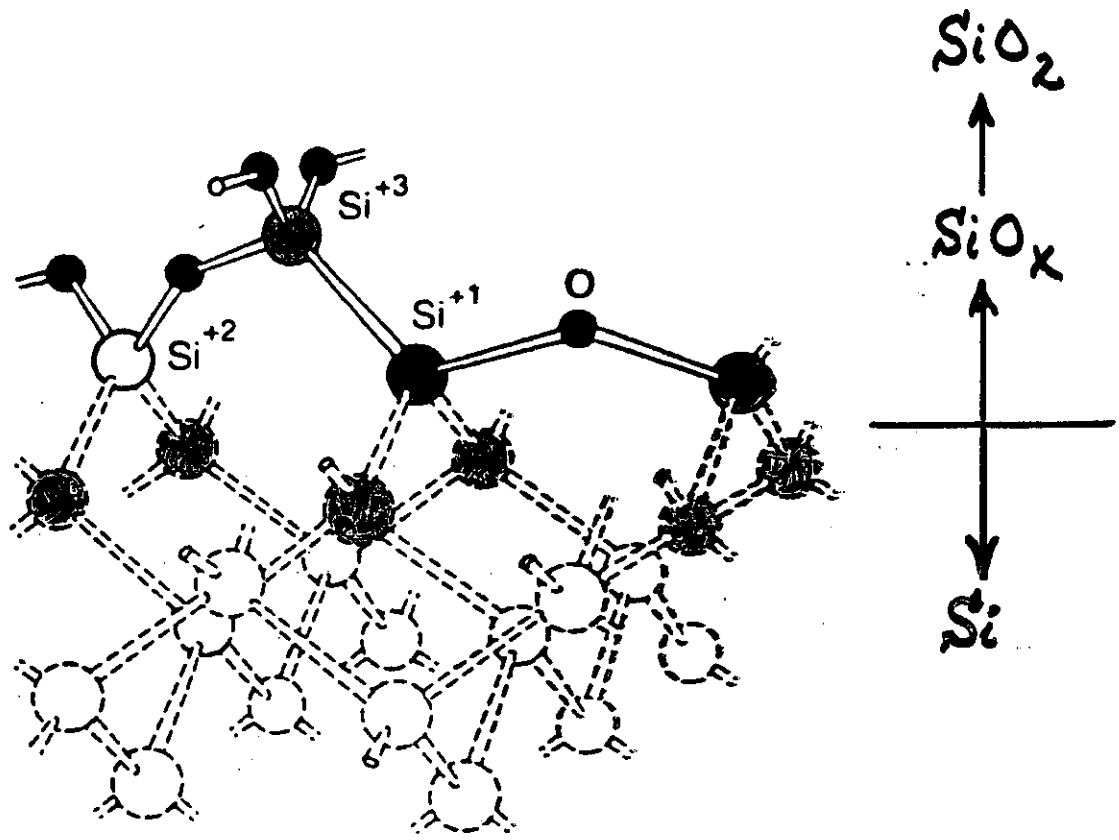


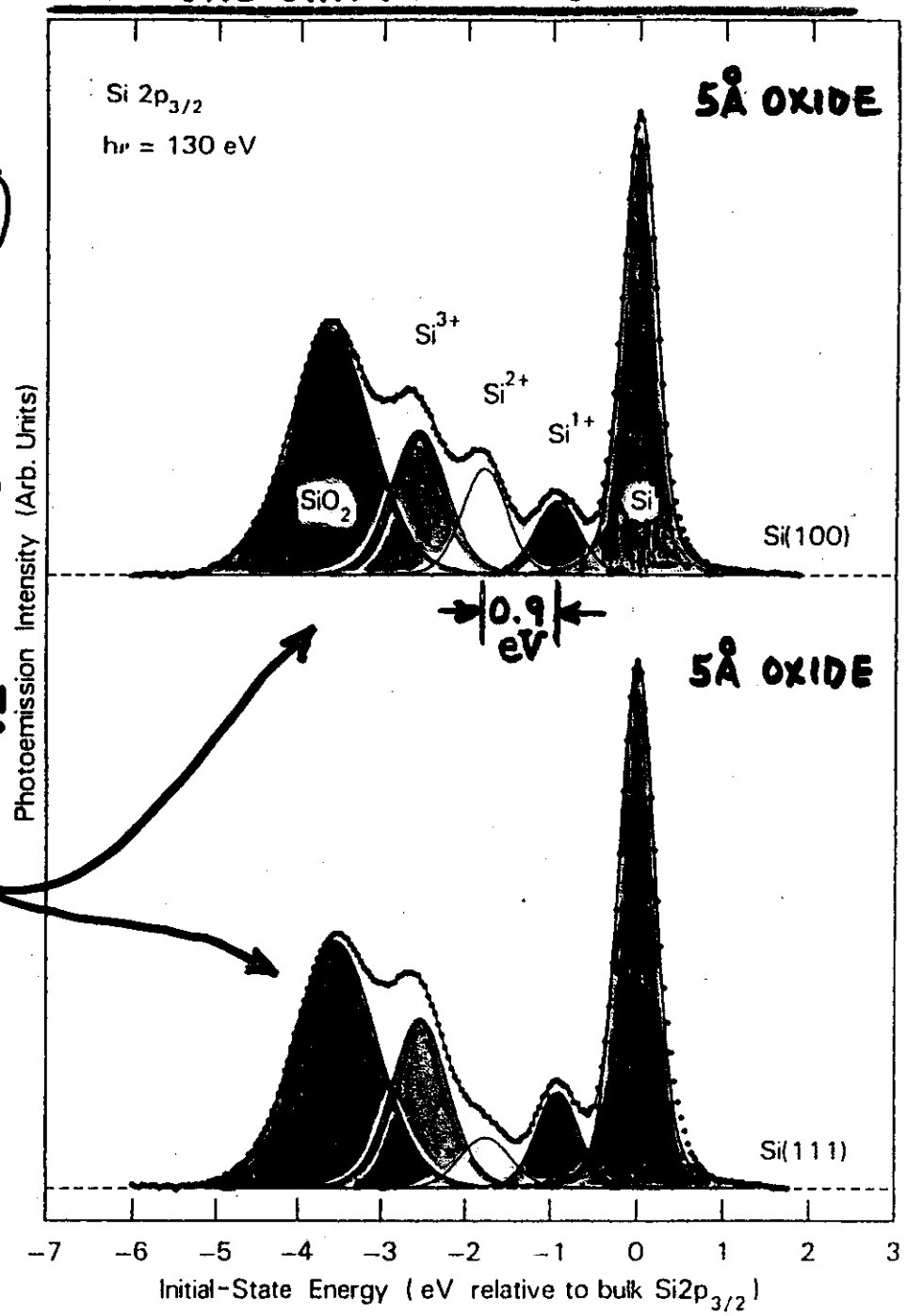
FIG. 2. Topological structure of various silicon suboxides at the SiO_2/Si (100) interface. The structure is based on the plastic ball and spoke model proposed by Ohdomari *et al.*[9]

PHOTOELECTRON SPECTRA

OXIDIZED SILICON

CHEMICAL SHIFTS OF CORE LEVELS

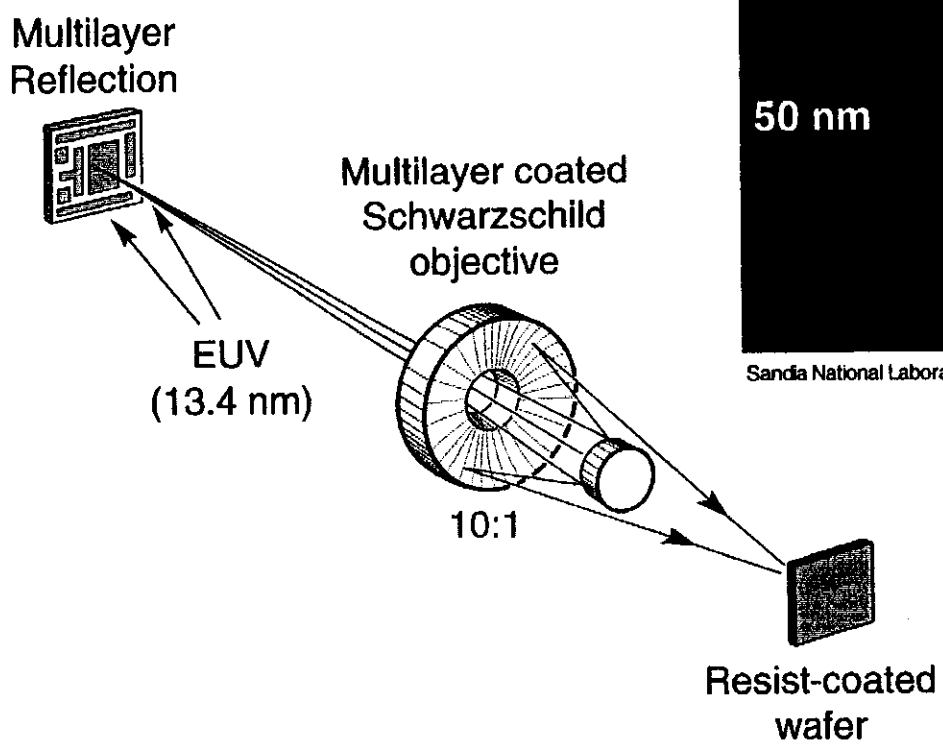
EXACTLY WHAT IS STRUCTURE OF INTERFACE? NEED STATE-SPECIFIC STRUCTURAL INFORMATION!

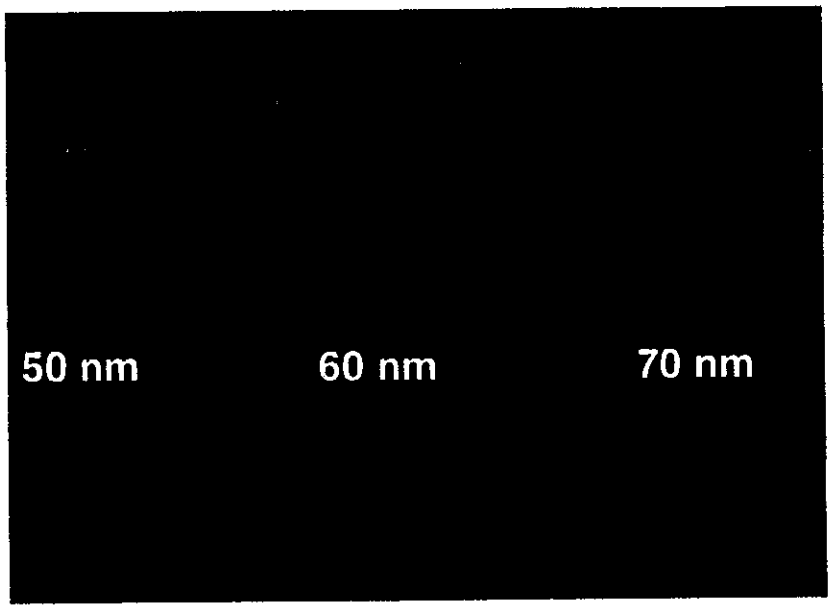


HIMPSEL ET AL., PHYS. REV. B, 38, 6084('90)

EUV Lithography for Sub-100 nm Feature Sizes

100 nm = 1000 Å = 0.1 micron



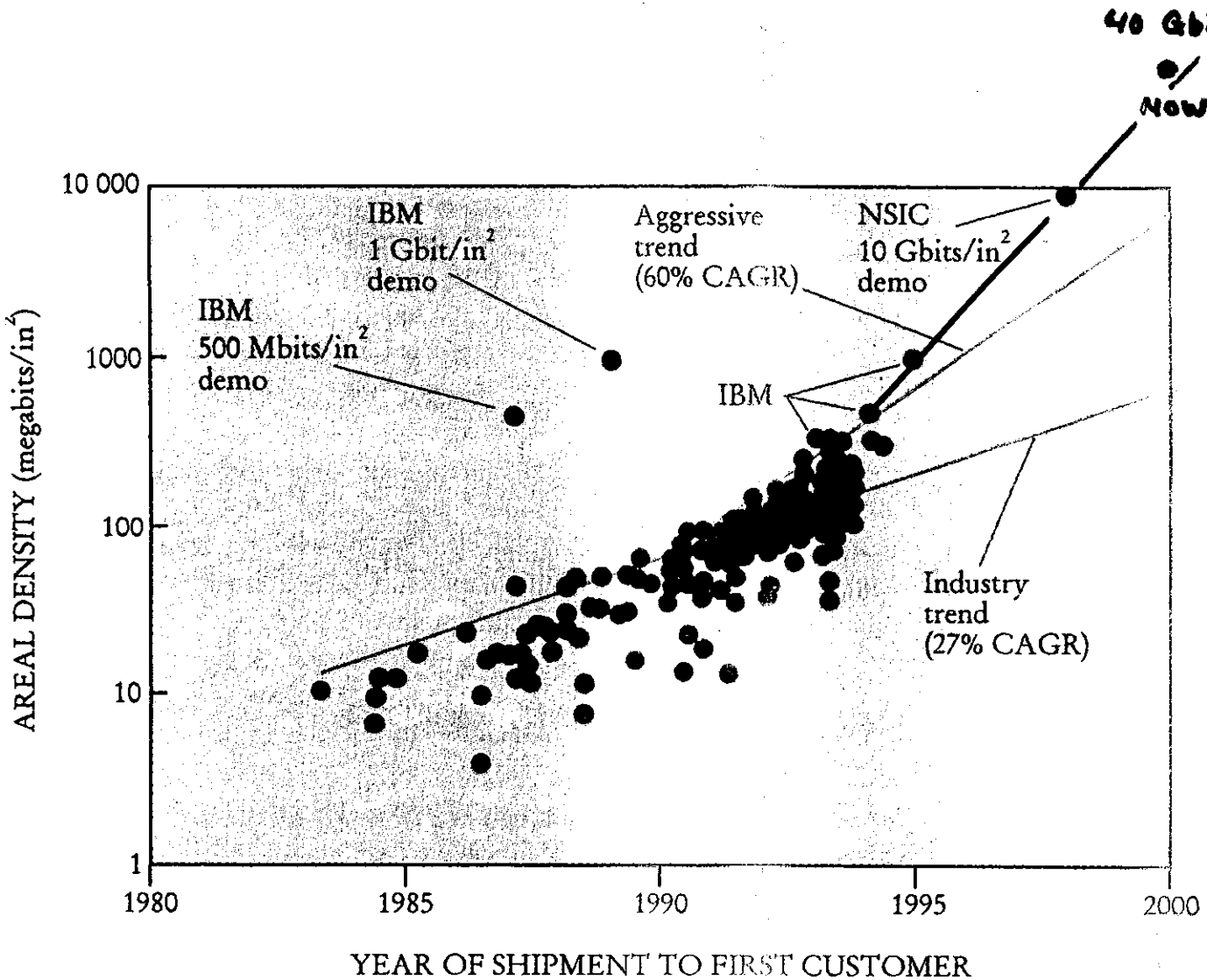


Sandia National Laboratories

PROMISING FOR NEXT-GENERATION TECHNOLOGY

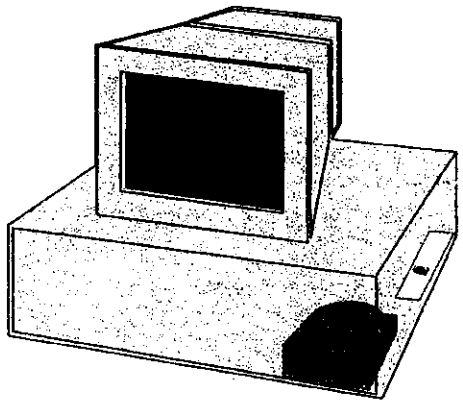
(Sandia, Lawrence Livermore, Lawrence Berkeley)

(Intel, Motorola, Adv. Micro Devices)

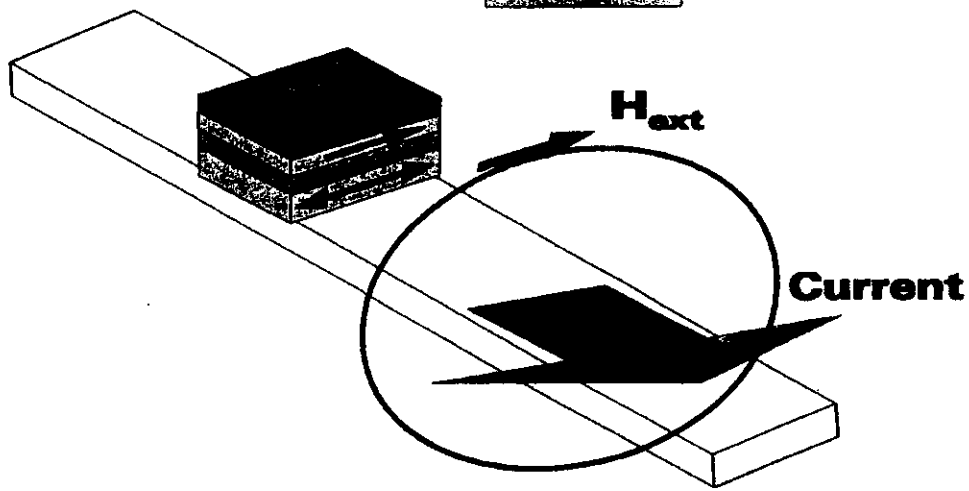


AREAL DENSITIES of commercial disk drives over the past decade. A 27% compound annual growth rate represents a doubling roughly every three years. The inch (one inch equals 2.54 centimeters) is the traditional unit of length in this industry. (Courtesy of NBT Consulting, Minneapolis, Minn.)
FIGURE 3

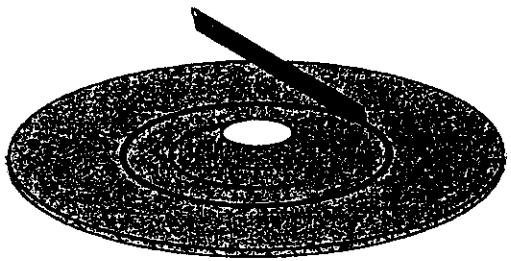
Use of Magnetic Multilayers in Technology

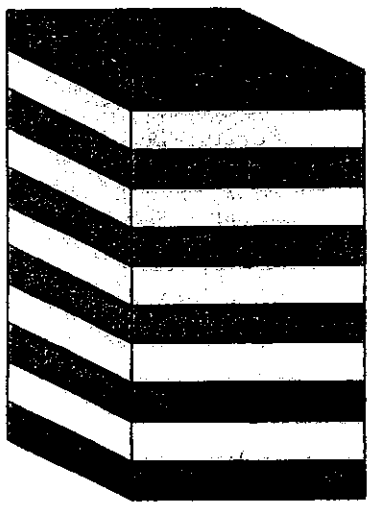


MRAM



Magneto-optical Disk





Spin-Valve Read Head

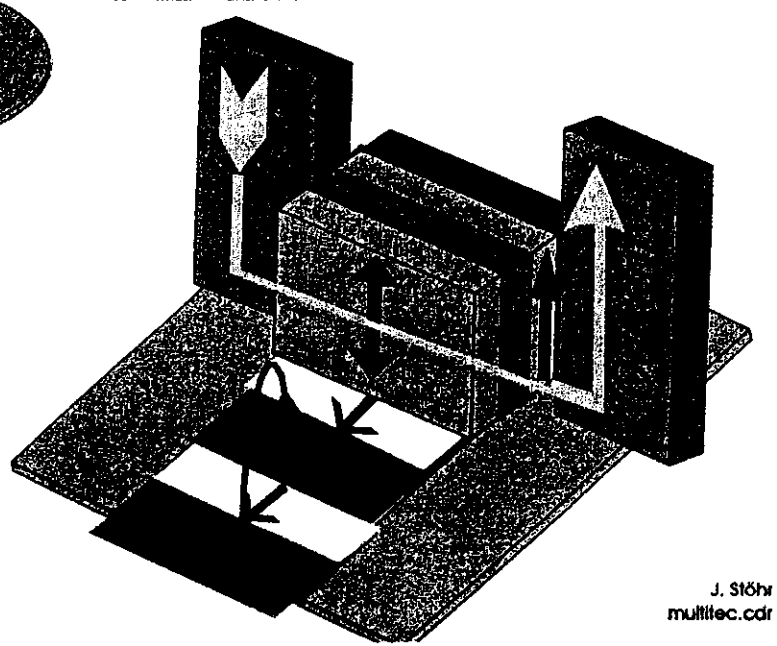
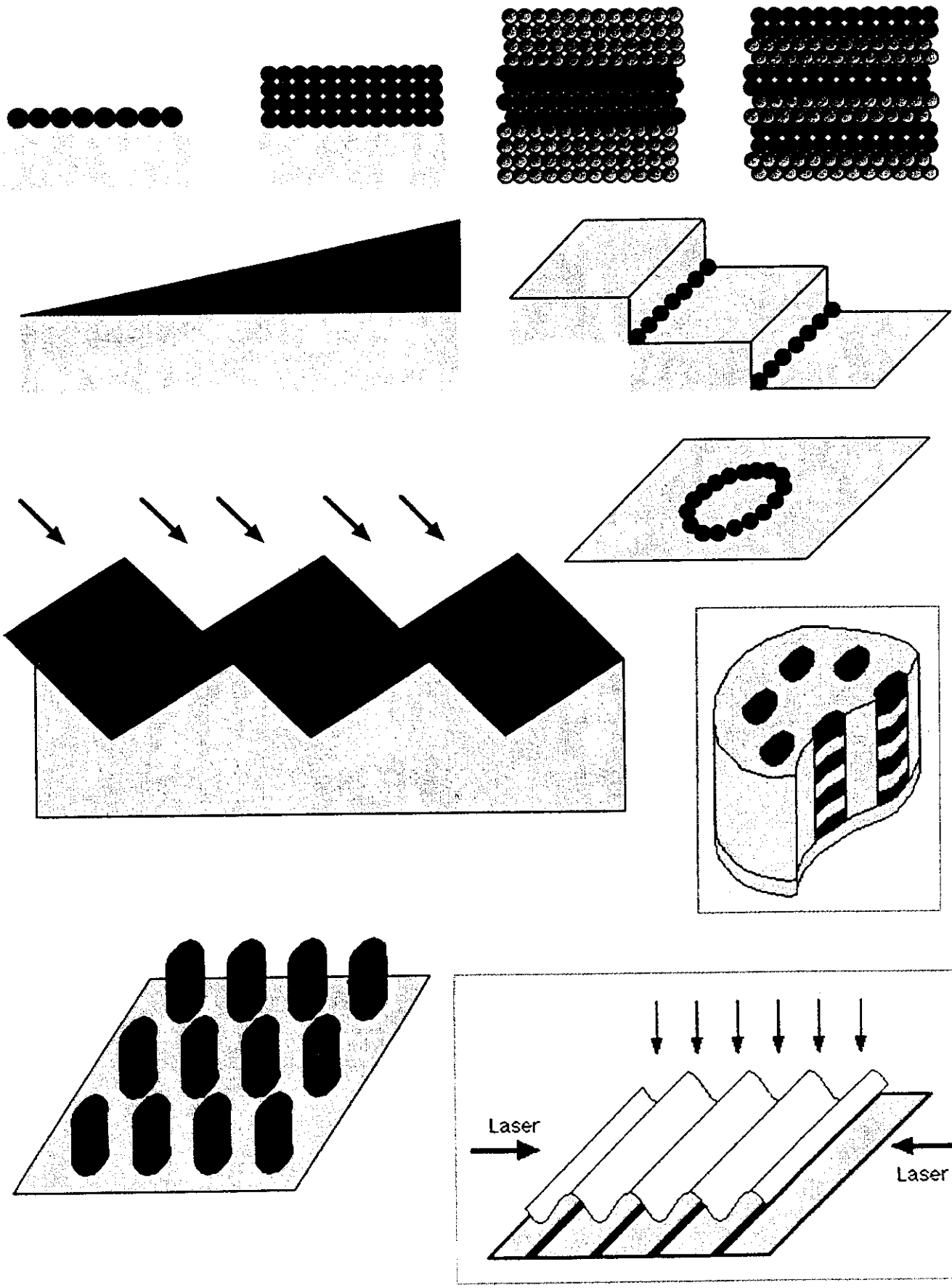


Figure 1

J. Stöhr
multitec.cdr

J. STöHR

SOME IMPORTANT STRUCTURES IN MAGNETISM + ... :

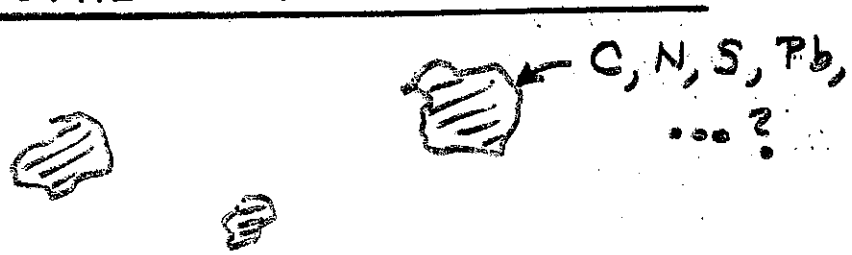


S. BADER

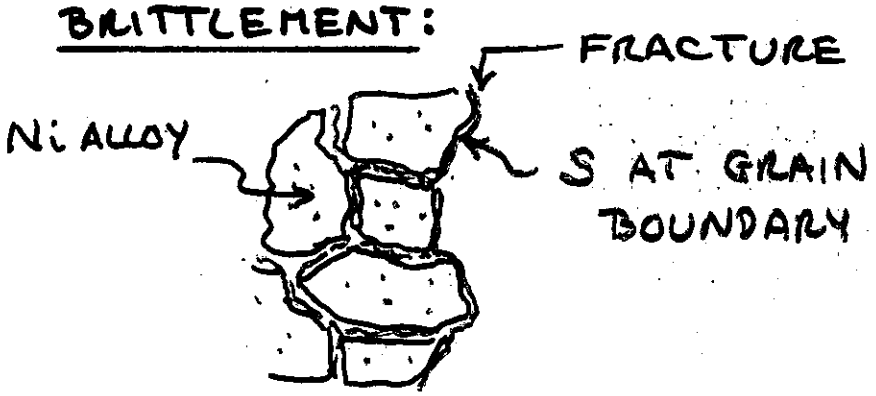
(4) POLYMER SURFACE MODIFICATION: E.G., TO REDUCE FRICTION OR PROMOTE ADHESIVE PROPERTIES OR REDUCE FLAMMABILITY.

(5) ELECTRODE SURFACES IN ELECTROCHEMICAL CELLS, FUEL CELLS, BATTERIES, SENSORS:

(6) ATMOSPHERIC PARTICULATES:



(7) FRACTURE SURFACES DUE TO EMBRITTLEMENT:



(8) WALL MATERIALS IN NUCLEAR REACTORS, FUSION REACTORS:

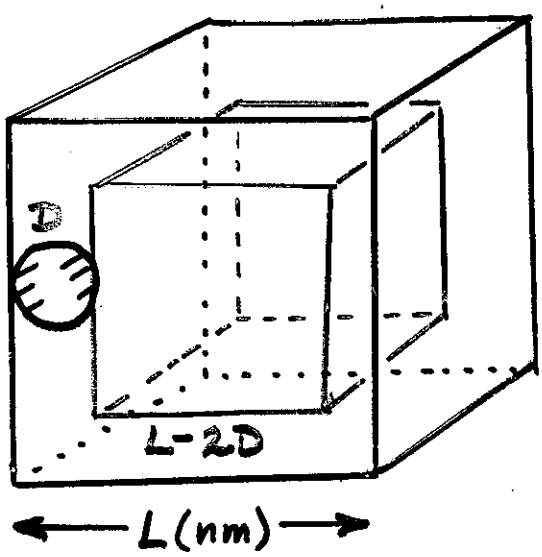
(9) LUBRICATION (TRIBOLOGY):

(10) ENVIRONMENTAL / GEOLOGICAL SCIENCE: UPTAKE OF METALS, POLLUTANTS ON SOIL SURFACES

(11) BIOMATERIALS: COMPATIBILITY THROUGH SURFACE INTERACTIONS... METALS, POLYMERS, CERAMICS, ...

(12) ANY SORT OF NANOTECHNOLOGY! HIGH FRACTION OF SURFACE/INTERFACE ATOMS

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%

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

SURFACE SCIENCE: WHY DO IT?

--Ubiquitous in modern technology, esp. with increasing emphasis on nanometer-scale objects: semiconductor devices, magnetic storage devices, sensors, corrosion, catalysis, environmental processes,.bulk material grain boundaries,...

--Novel physics and chemistry: electronic, magnetic, and chemical states; phase transitions, reactivity

--Interplay of complex systems with lateral/vertical inhomogeneity (multilayers, quantum dots) and model systems (single crystals, well-controlled deposition and reaction): both essential for complete microscopic understanding

WHY VUV/SOFT X-RAY EXCITATION?

--Many surface techniques, but vuv/soft x-rays permit probing core and valence levels of surfaces and shallow interfaces via angle-resolved photoemission and core spectroscopy/diffraction/holography; deeper structures and bulk properties via various types of x-ray absorption/x-ray optical measurements

WHY PHOTOELECTRONS OUT?

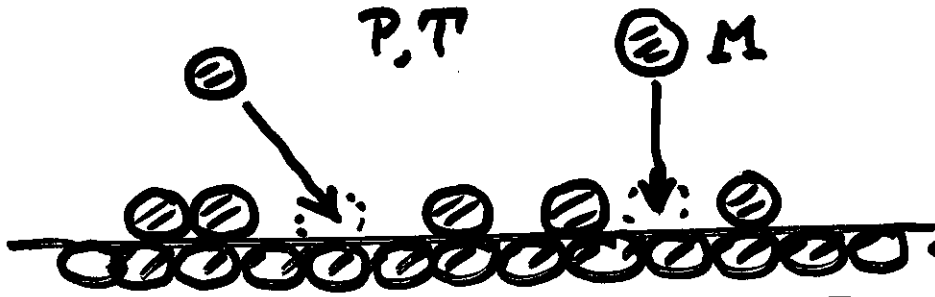
--Method of choice for measurement of valence band structures, also a method of choice for surface analysis and core studies of atomic and magnetic structure: photoelectrons everywhere in surface science

--Plus future photoelectron-out experiments with:

- -Faster detectors--time resolved deposition/reaction studies
- -Much easier variation of light polarization and measurement of spin polarization with third-generation sources
- -Use of total reflection and standing waves to enhance interface sensitivity
- -Lateral resolution of complex surfaces with resolution down to ~100 Å: spectromicroscopy
- -Differentially-pumped sample cells with ≥torr-level ambient pressures--deposition and reaction studies at closer to real-world conditions
- -Better charge neutralization with ion+electron flux--higher resolution studies of oxides, polymers, other insulators
- -Studies of cleaved, fractured, or delaminated surfaces--direct view of buried interfaces

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:

$$\tau_1 = C \sqrt{\frac{M}{kT} \cdot \frac{\rho}{P}}$$

N_2, CO O_2

WITH TYPICAL NOS. FOR $M = 28, 32$

$T = 298\,K$

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

↑ METALS, SEMICOND.

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

Some Structural Issues in Surface/Interface Growth:

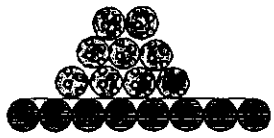
- Growth Modes:

(a) 

LAYER-BY-LAYER (FvdM)
EX. Fe/W(110)
Gd/W(110)

(b) 

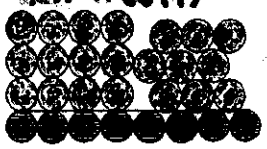
MIXED (SK)
Cu/Ru(001)
Gd/W(211)

(c) 

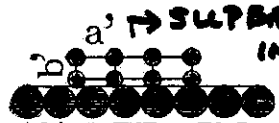
ISLAND/CLUSTER (VW)
3D->2D->1D
Fe/Stepped W

(d) 

INTERDIFFUSION
Fe/Cu(001)

(e) 

MIXED-PHASE EPITAXY/METASTABILITY
fcc & bcc Fe/Cu(001)

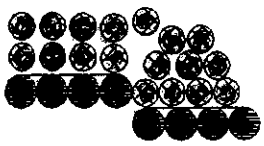
(f) 

⇒ SUPERLATTICES IN PLANE

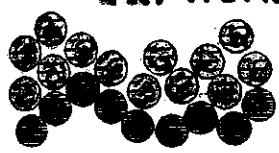
[a] STRAIN
most binaries
FeO/Pt(111)
Gd/W(110)

(g) 

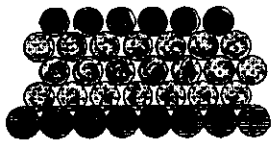
SURFACE ALLOY
Co/Pt

(h) 

DEFECTS/STEPS
Fe/Cu
Cr/Fe

(i) 

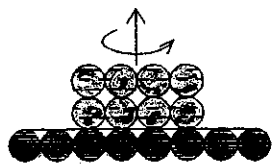
ROUGHNESS
Co/Cu
Cr/Fe

(j) 

FLOATING SURFACTANT
Au/Si(111)-Ag

(k) 

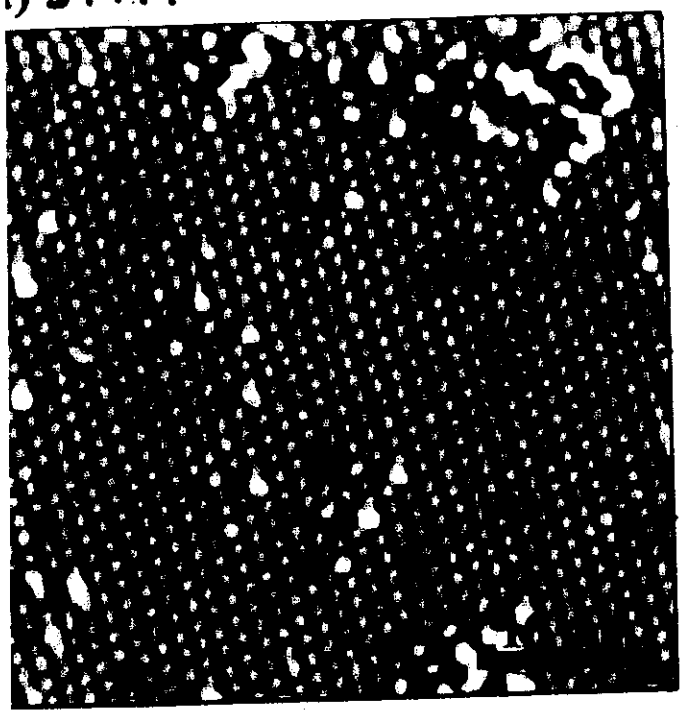
ALLOYING SURFACTANT
Ga/Si(111)-Sn

(l) 

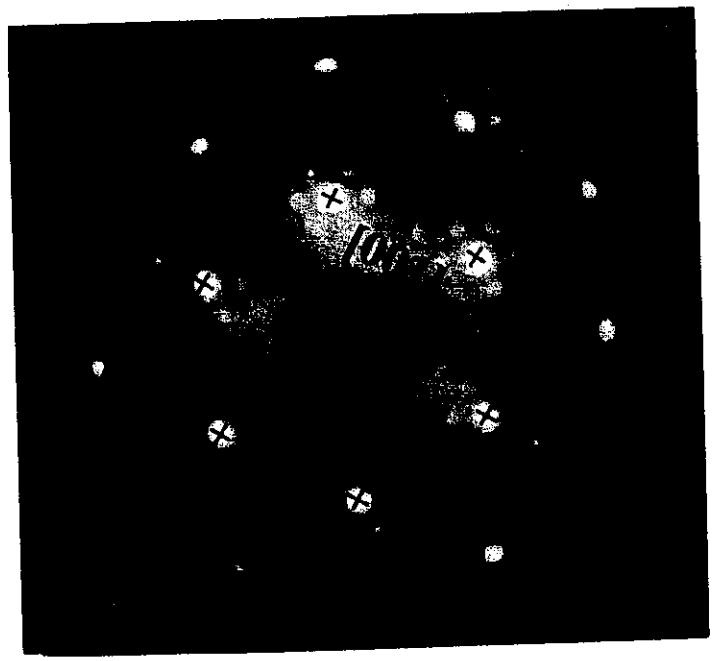
TEXTURING
Tb-Fe
(Amorphous?)

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

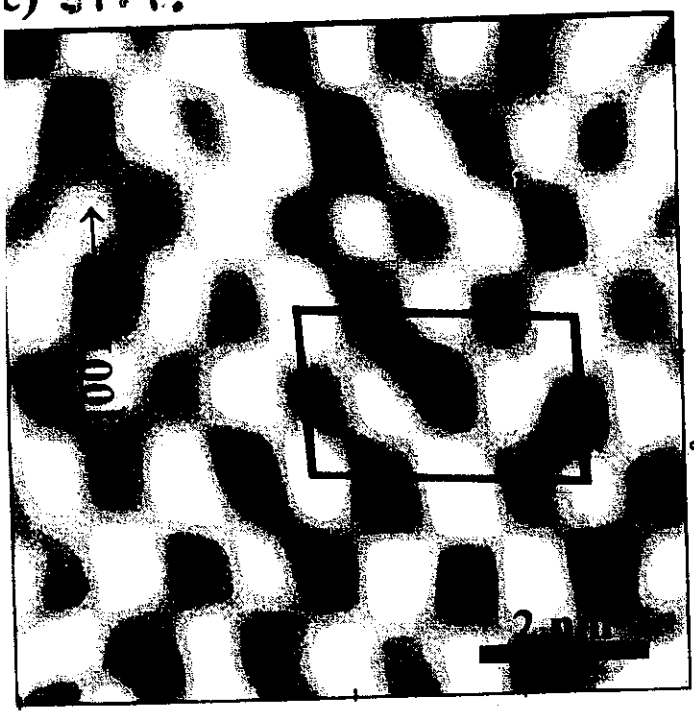
a) STM:



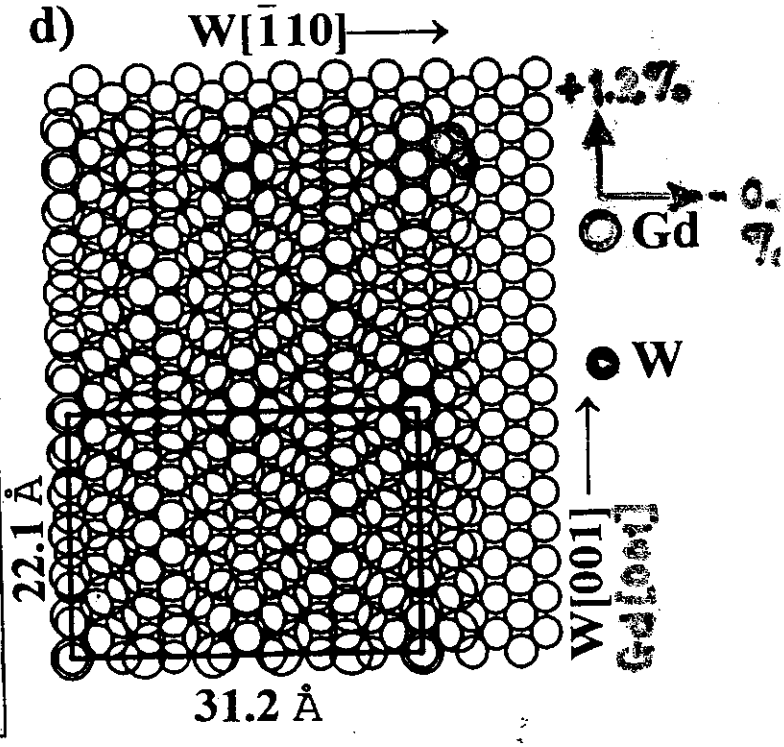
b) LEED:



c) STM:



d)



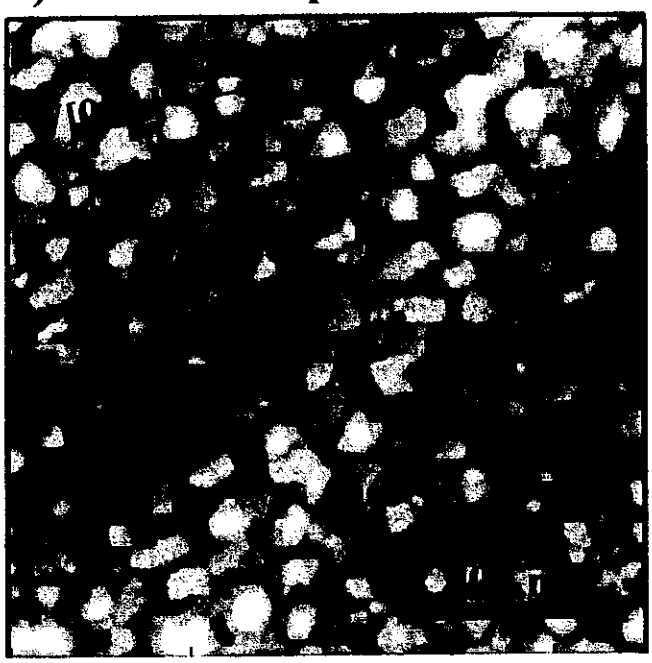
(7x14) SUPERLATTICE
ALSO ~(7x7)

E. TOBER ET AL.
P.R.B 53, 5444 ('96)

A MOIRÉ PATTERN

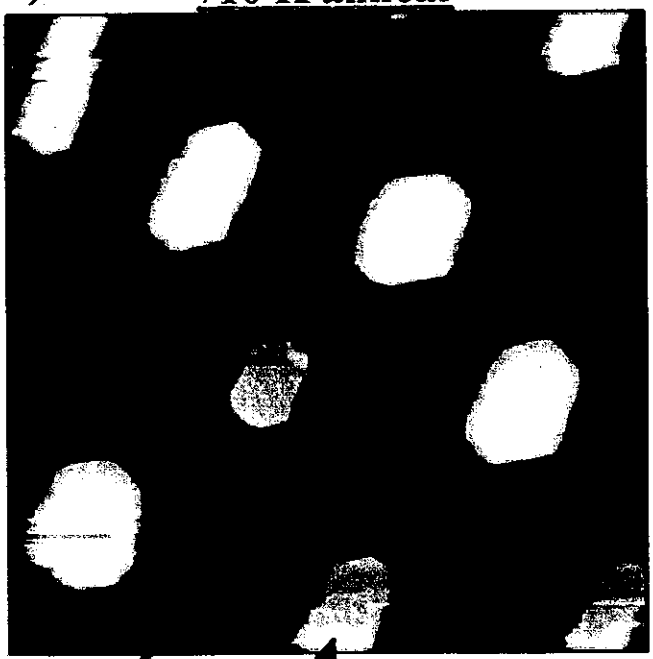
GROWTH OF 11 ML Gd ON W(110)

a) as deposited

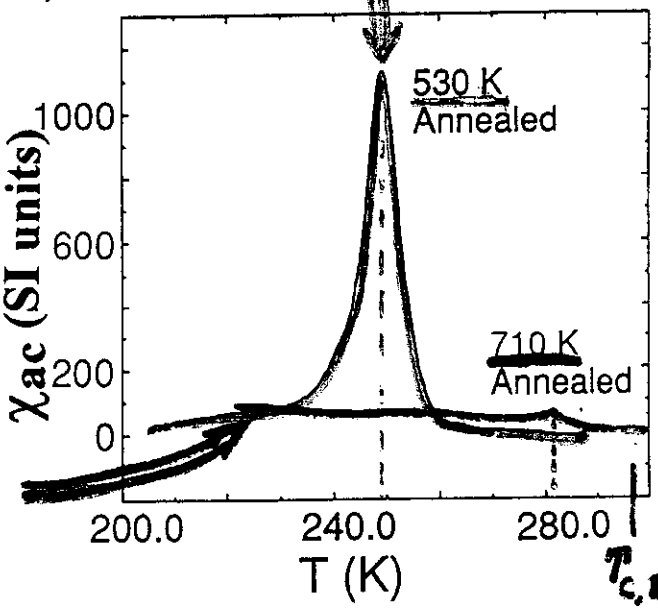


b) 530 K anneal

c) 710 K anneal



d) AC MAGNETIC SUSCEPTIBILITY†



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

WETTING SINGLE LAYER

TOBER ET AL.

$$\chi_{ac} = \frac{\chi_{INT}}{[1 + N\chi_{INT}]}$$

$$N = \frac{\pi \frac{t}{d}}{4} - \left(\frac{t}{d}\right)^2$$

† APPELMEIER ET AL., J.M.M.M. 132, 22 (1994)

SOME THINGS WE WOULD LIKE TO KNOW

What atomic species are present? How are they distributed at surfaces and interfaces, including buried interfaces, and in alloys. E.g is there compositional clustering/segregation?

What is the atomic structure around each species?

What are the chemical states, magnetic states, bonding of these species?

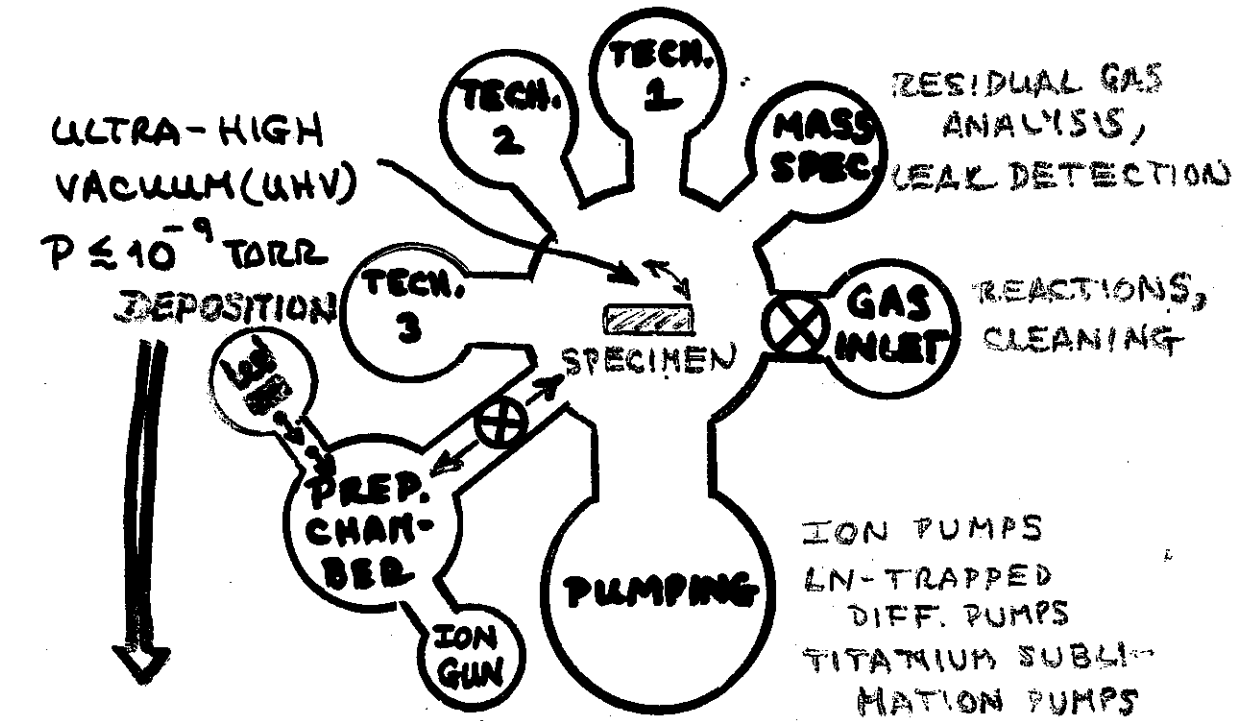
How do magnetic moments and transition temperatures vary with species and nanostructure, e.g. heading for the paramagnetic limit?

Can the above be measured as well with lateral inhomogeneity on the nanometer scale?

Can the above be measured on time scales of relevant to switching times of 20 psec or less?

A TYPICAL SYSTEM:

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



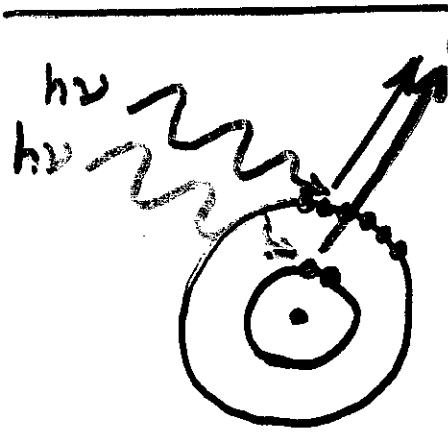
~TIME FOR ONE MONOLAYER:

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

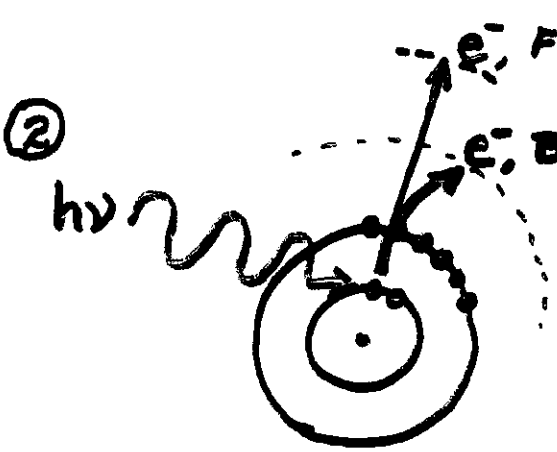
ALL FOR ONLY
~ $100k - $500k ! - THEN
↳ ~ $400k - $2M - NOW

SOME KEY TYPES OF EXPERIMENTS WITH X-RAYS, UV

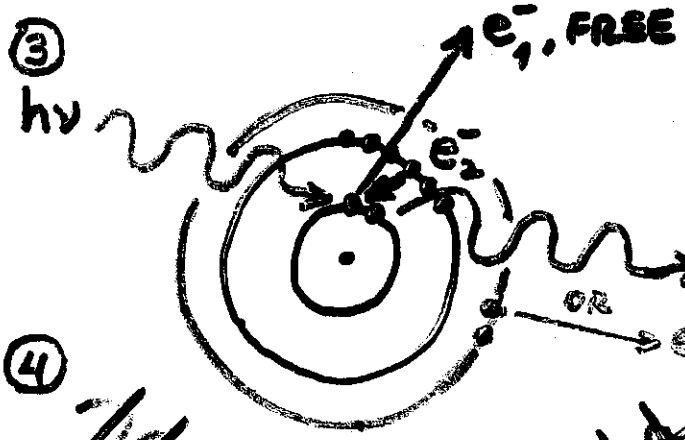
↓
SYNCHROTRON RADIATION

① 

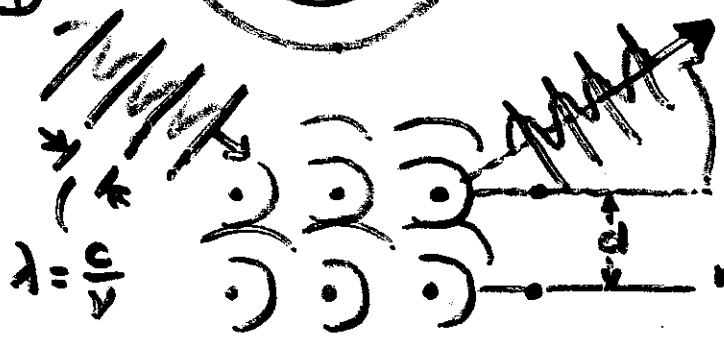
PHOTOELECTRON SPECTROSCOPY
+ DIFFRACTION
+ HOLOGRAPHY
+ MICROSCOPY

② 

X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY
*NEAR-EDGE -- NEXAFS, XANES
†EXTENDED -- EXAFS

③ 

X-RAY EMISSION (FLUORESCENCE SPECTROSCOPY, OR AUGER ELECTRON SPECTROSCOPY

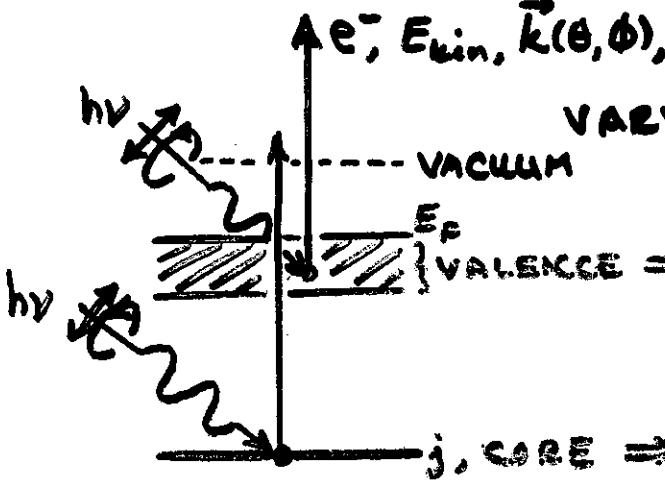
④ 

$n\lambda = 2d \sin\theta_B$

X-RAY BRAGG DIFFRACTION, SURFACE X-RAY SCATTERING, STANDING WAVES

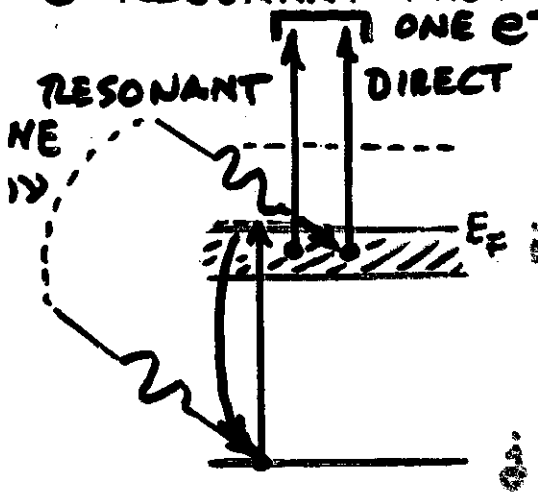
THE BASIC VUV/SOFT X-RAY EXPERIMENTS:

- PHOTOELECTRON SPECTROSCOPY (PS):



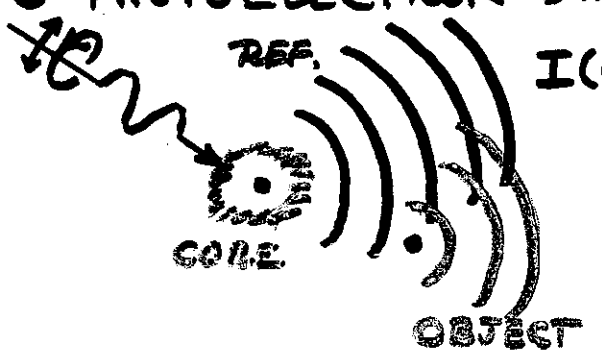
BONDING TYPE / BANDS
⇒ QUANTUM-WELL STATES
SPIN-RESOLVED BANDS / LEVELS
ELEMENT-SPECIFIC
⇒ CHEMICAL/SITE SHIFTS
→ BONDING SITE
MULTIPLETS → SPIN STATE, SPIN POLARIZATION
CIRC. POLAR. + SPIN-ORBIT →

- RESONANT PHOTOELECTRON EMISSION:



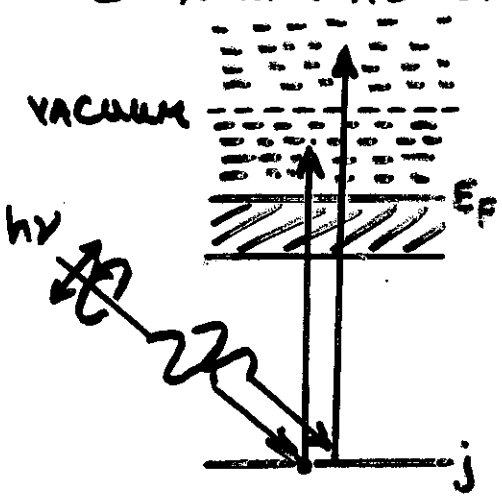
⇒ ENHANCED INTENSITY
+ SPIN POLARIZATION
⇒ INTERATOMIC: NEAR-NEIGHBOR ATOMIC NO./BONDING

- PHOTOELECTRON DIFFRACTION/HOLOGRAPHY (PD/PH)



$I(\theta,\phi,h\nu)$
⇒ SHORT-RANGE ATOMIC STRUCT.
SHORT-RANGE MAGNETIC ORDER

- X-RAY ABSORPTION SPECTROSCOPIES (XAS):
  EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS)



} NEAR-EDGE X-RAY ABSORP. FINE STRUCTURE (NEXAFS)

WITH CIRCULAR POLARISATION A/O $\vec{M}$ VARIATION:
X-RAY MAGNETIC CIRCULAR DICHROISM (XMCD)

EXAFS ⇒ SHORT-RANGE ATOMIC STRUCTURE

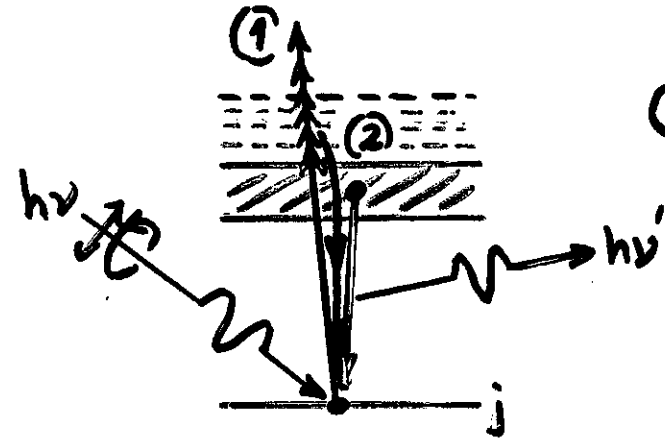
SPIN-POLARIZED EXAFS ⇒ SHORT-RANGE MAGNETIC ORDER
(CIRCUL. POLAR.)

NEXAFS ⇒ ELEMENT-SPECIFIC BONDING TYPE

XMCD ⇒ NO. d HOLES,
SPIN & ORBITAL MOMENTS,
... FROM SUM RULES

XMLD ⇒

- X-RAY EMISSION/FLUORESCENCE SPECTROSCOPY (XES, XFS)

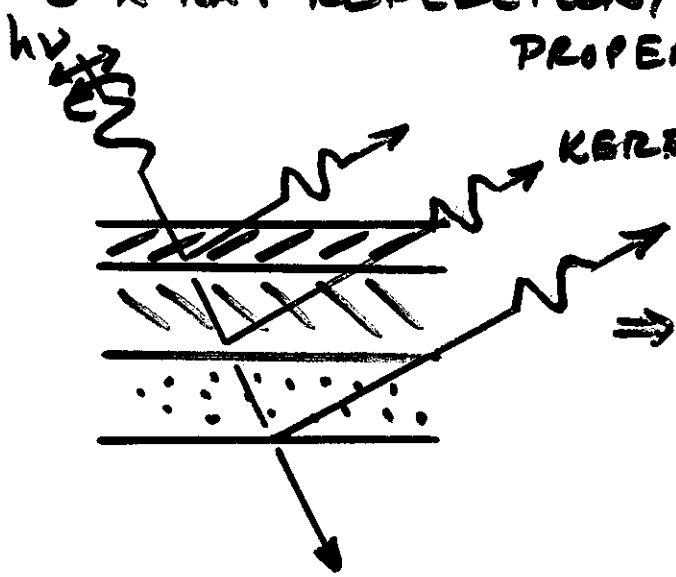


② PARTICIPATOR VS SPECTATOR DECAY

⇒ ELEMENT-SPECIFIC BONDING, MAGNETISM

⇒ RAMAN SCATTERING, RES. INELASTIC X-RAY SCATTERING

- X-RAY REFLECTION/TRANSMISSION/OPTICAL PROPERTIES:



BRAGG REFLECTION-MULTILAYERS, STANDING WAVES IN SINGLE LAYER AND

⇒ MULTILAYER PHASE RETARDERS: LINEAR → CIRCULAR

KERR, FARADAY IN X-RAY REGIME:

hν ≈ CORE RESONANCES

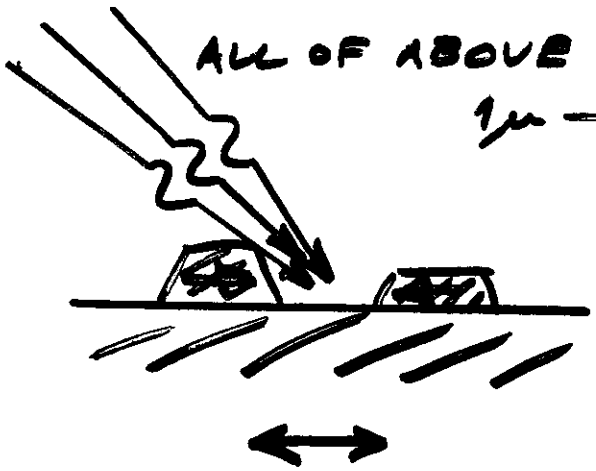
ELEMENT-SPECIFIC HYSTERESIS

INTERFACE CHEMICAL & MAGNETIC ROUGHNESS

- SPECTROMICROSCOPY & MICROSPECTROSCOPY:

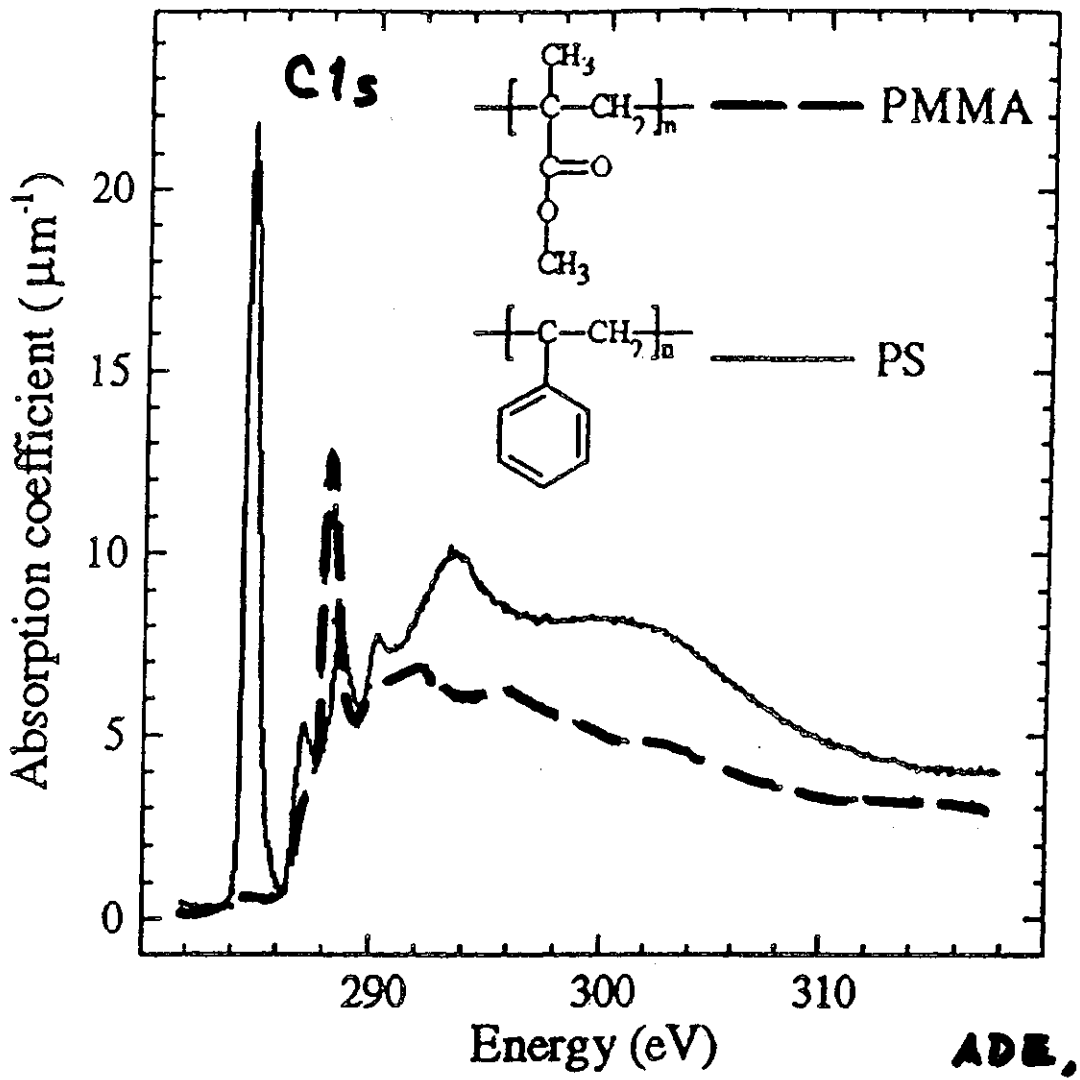
ALL OF ABOVE WITH LATERAL RESOLUTION-

1μ ⟶ ~20 nm (FUTURE)

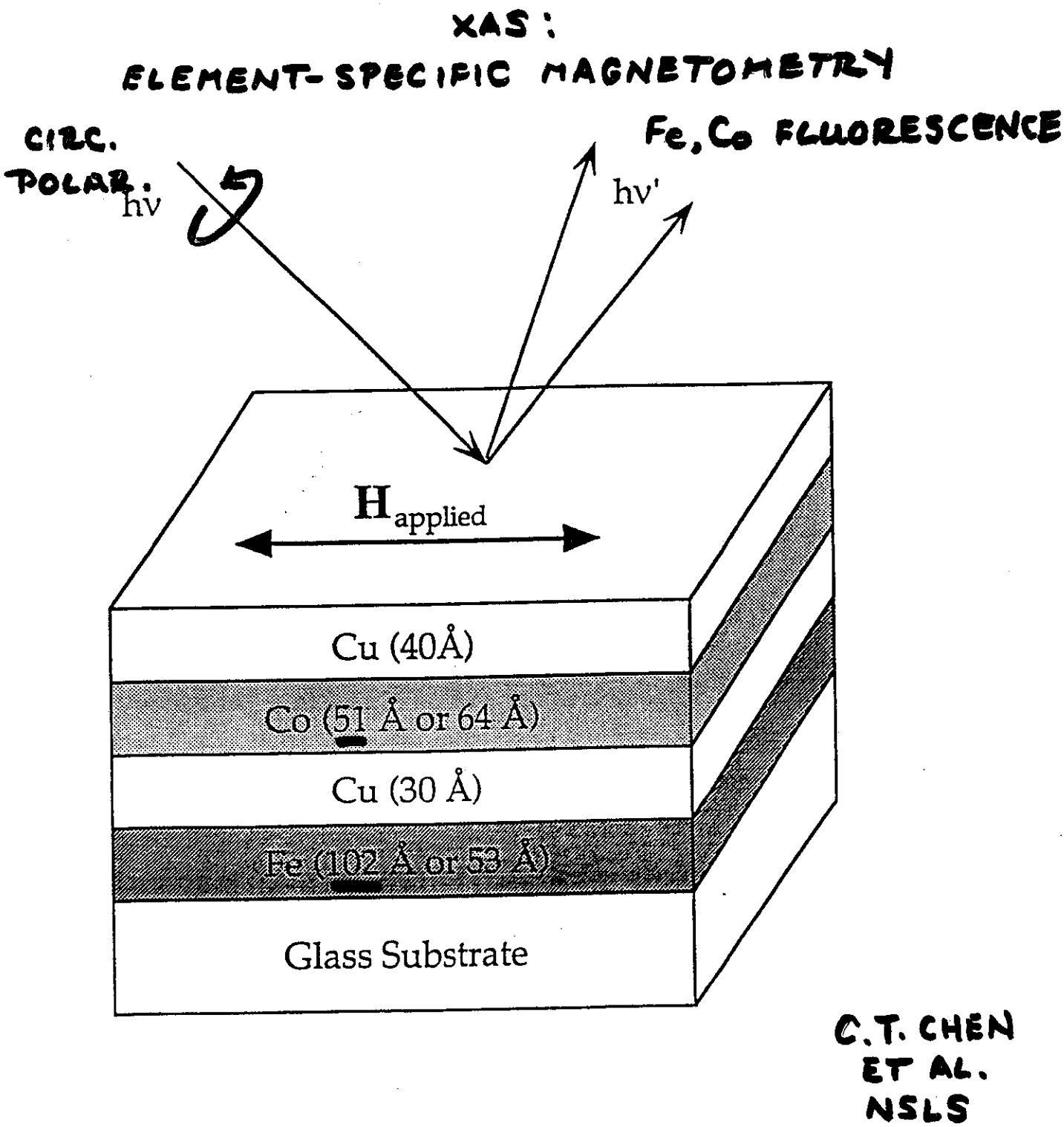


⇒ DIRECT IMAGING OF NANOSTRUCTURE & MAGNETIC DOMAINS

NEXAFS OF POLYMERS

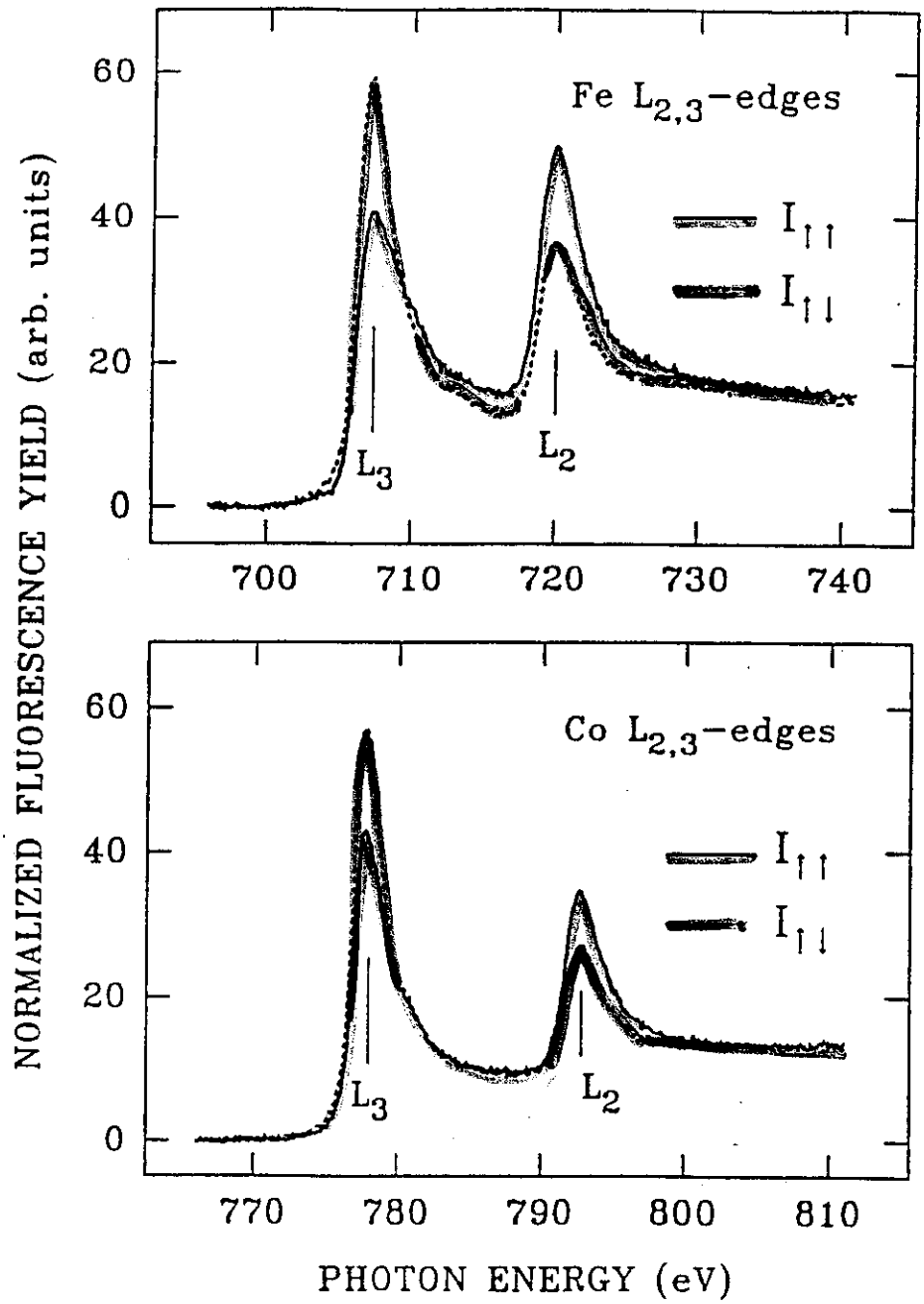


ADE, URQUART



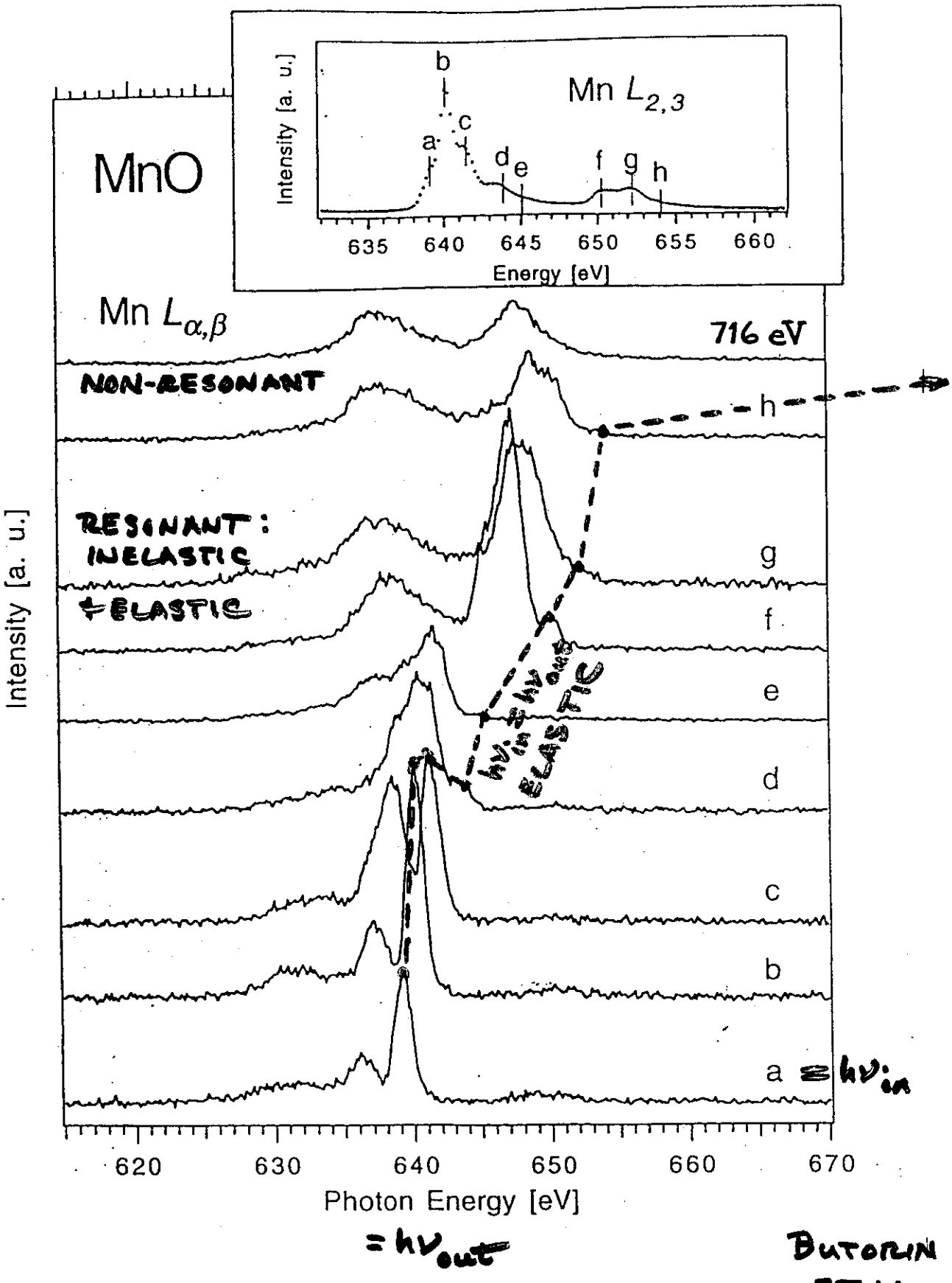
Chen *et al.*, Fig. 1

XMCD = X-RAY MAGNETIC CIRC. DICHROISM



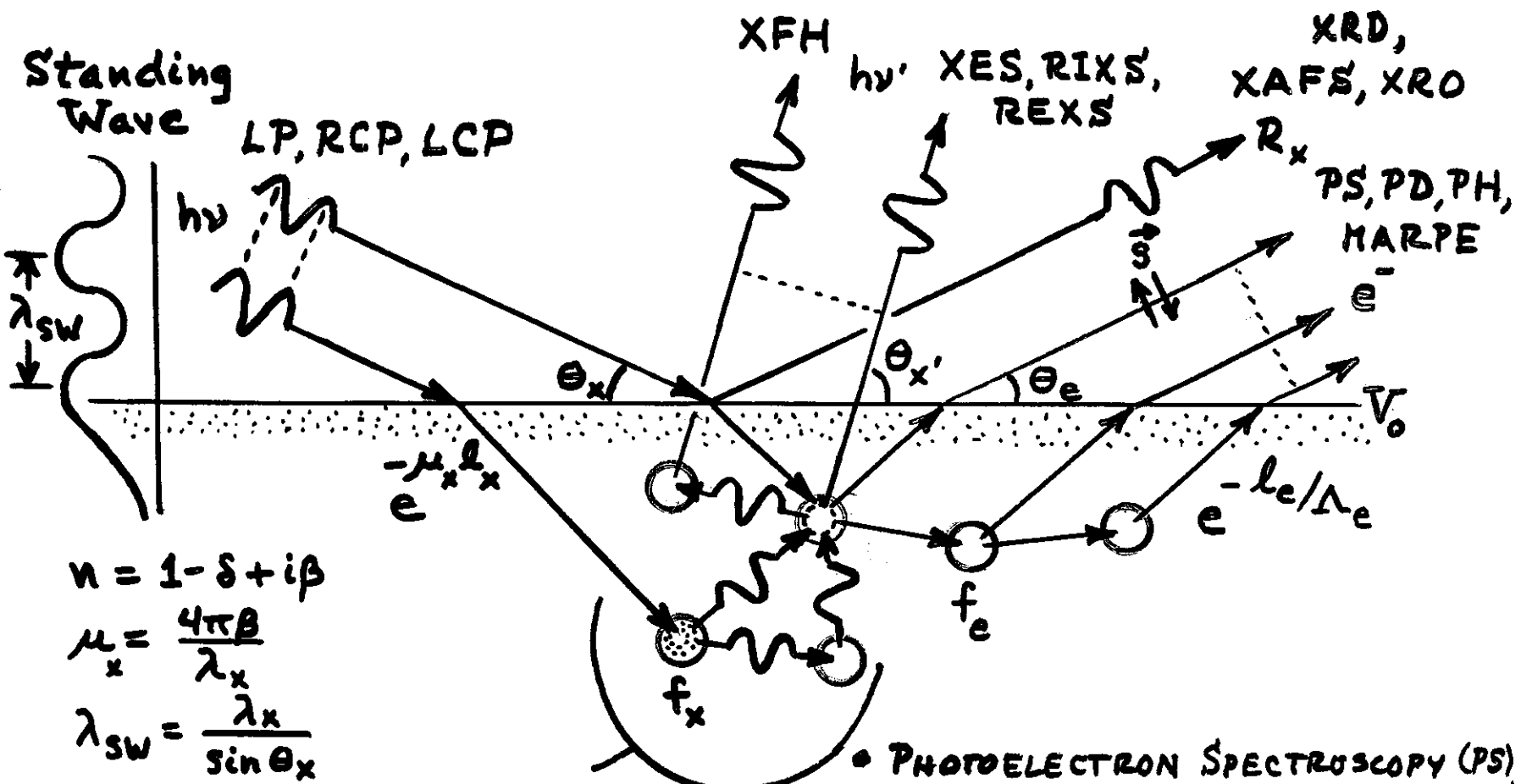
Chen *et al.*, Fig. 2

X-RAY EMISSION SPECTROSCOPY

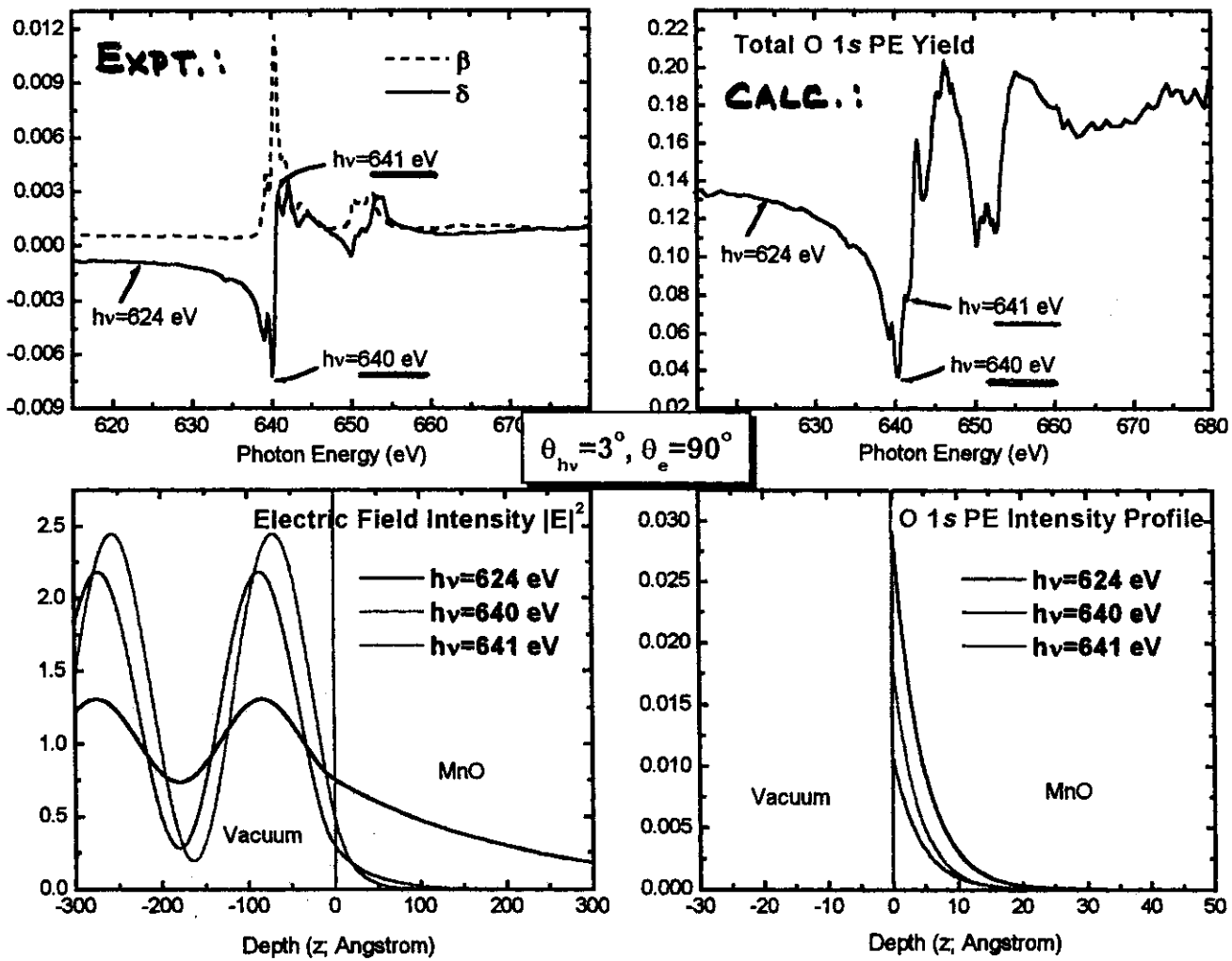


BUTORIN ET AL.

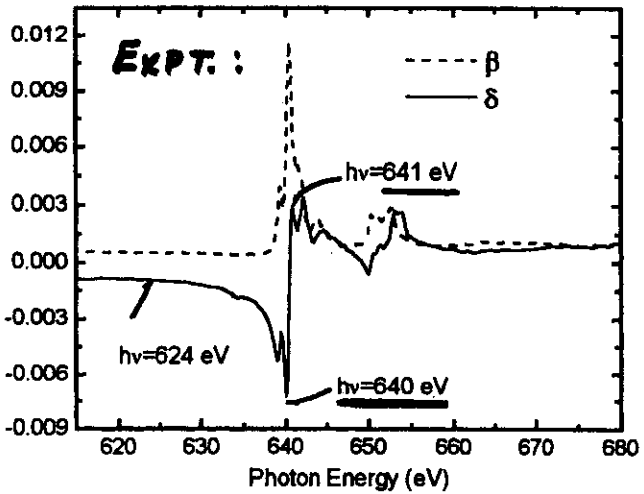
THE BASIC PHENOMENA

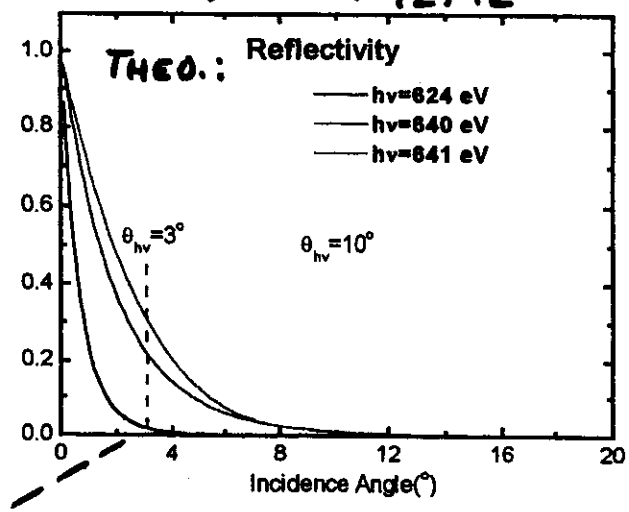


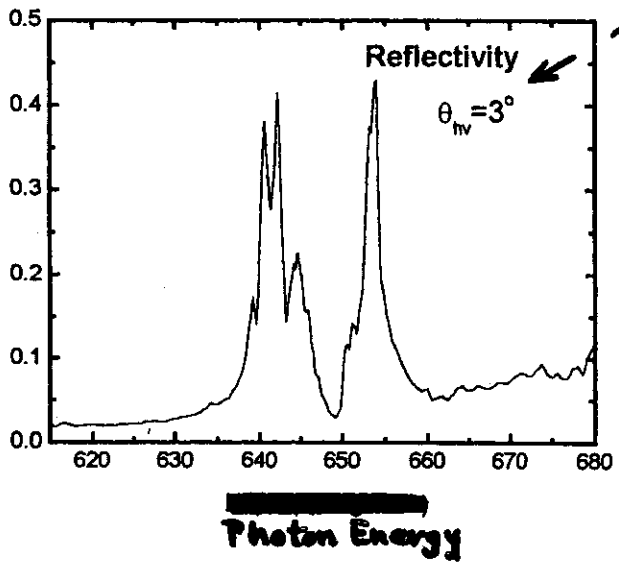
- MULTI-ATOM RESONANT PHOTO-EMISSION (MARPE)
- PHOTOELECTRON SPECTROSCOPY (PS) DIFFRACTION (PD), HOLOGRAPHY (PH)
- X-RAY ABSORPTION FINE STRUCTURE (XAFS), X-RAY OPTICS (XRO)
- X-RAY EMISSION SPECTROSCOPY (XES), RESONANT INELASTIC/ELASTIC X-RAY SCATTERING (RIXS, REXS)
- X-RAY FLUORESCENCE HOLOGRAPHY (XFH)

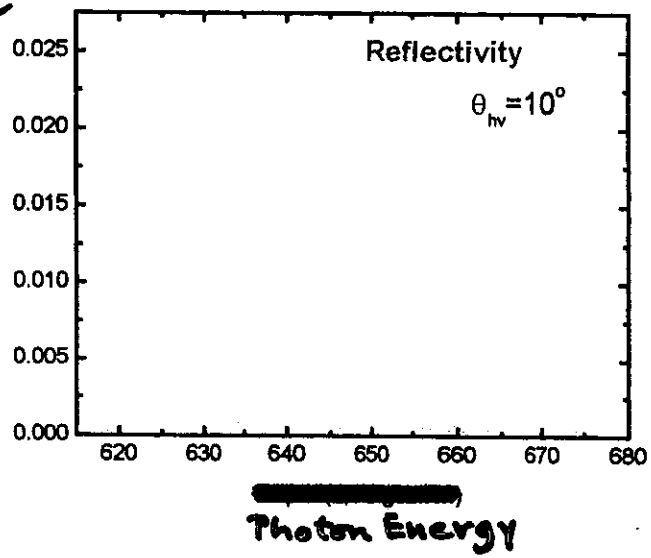

EXPT.:
β
δ
hν=641 eV
hν=624 eV
hν=640 eV
Photon Energy (eV)
Total O 1s PE Yield
CALC.:
hν=624 eV
hν=641 eV
hν=640 eV
Photon Energy (eV)
θhν=3°, θe=90°
Electric Field Intensity |E|2
hν=624 eV
hν=640 eV
hν=641 eV
Vacuum
MnO
Depth (z; Angstrom)
O 1s PE Intensity Profile
hν=624 eV
hν=640 eV
hν=641 eV
Vacuum
MnO
Depth (z; Angstrom)

RESONANT X-RAY OPTICS : MnO, Mn2p3/2, 1/2



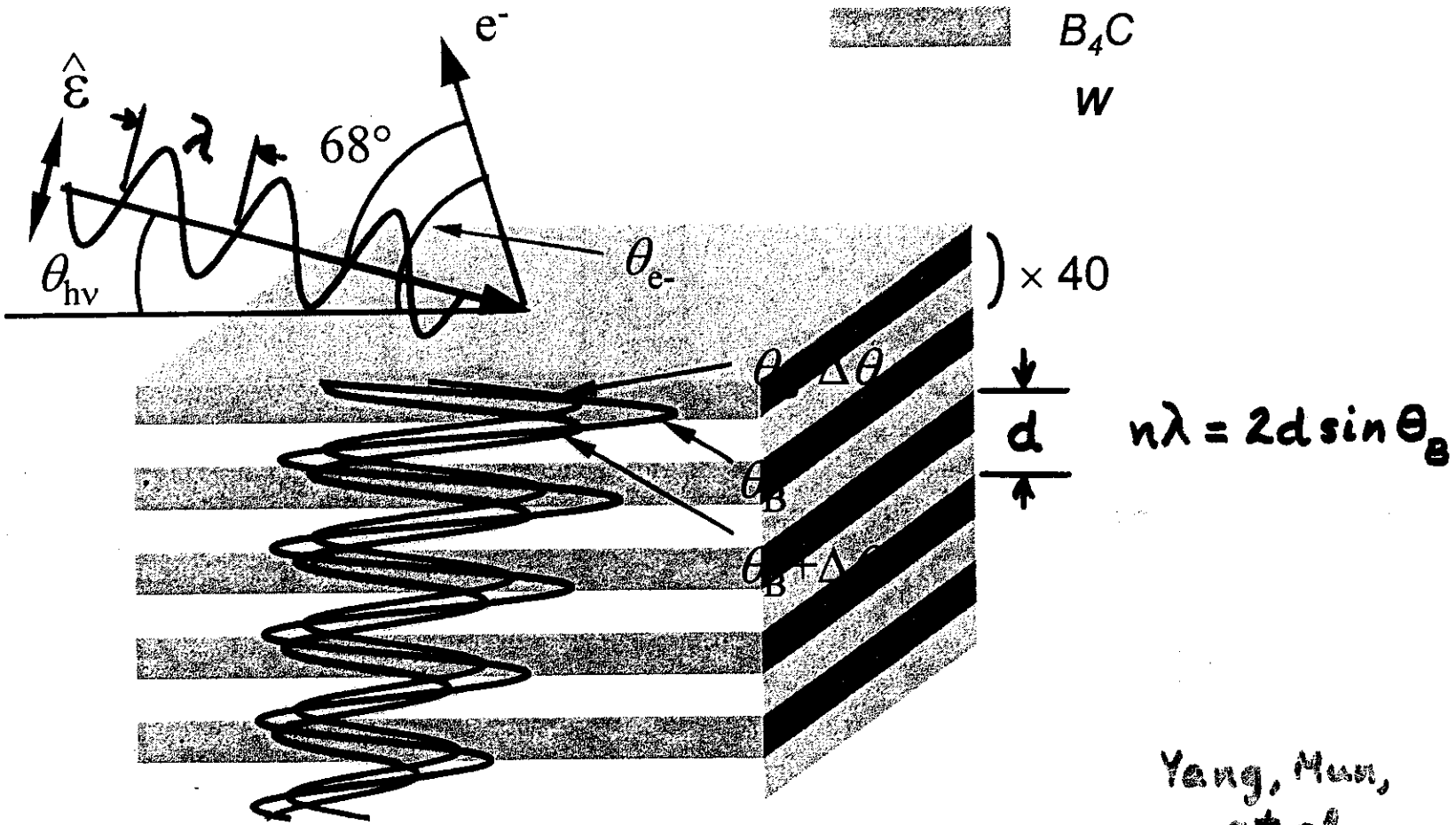






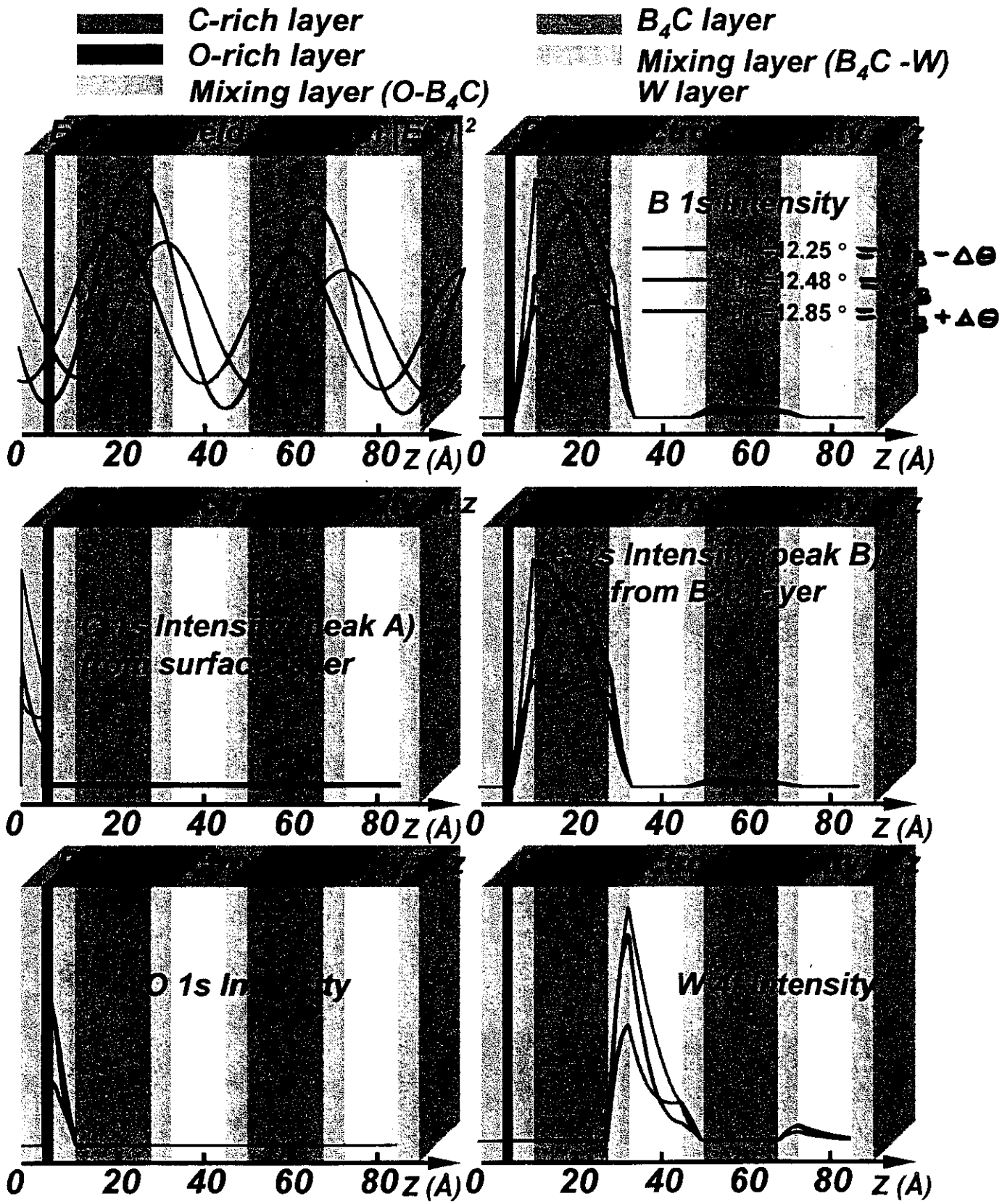
S.-H. Yang

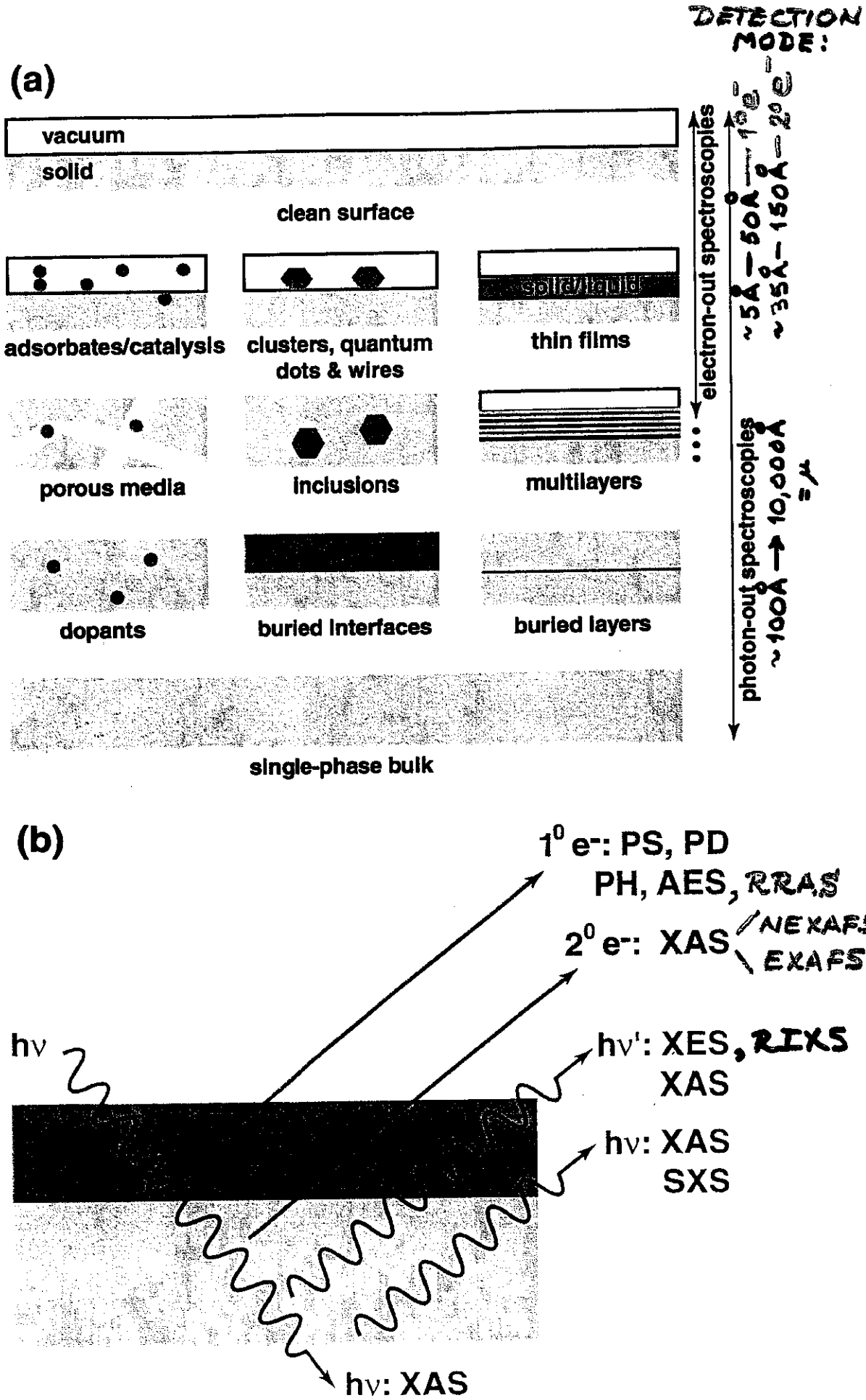
Depth-Resolved Spectroscopy with Standing Waves



Yang, Mun, et al.,

Surf. Sci. Lett. 461, L557-L564 ('00)


C-rich layer
O-rich layer
Mixing layer (O-B4C)
B4C layer
Mixing layer (B4C -W)
W layer
B 1s Intensity
12.25 °
12.48 °
12.85 °
-Δθ
+Δθ
0 20 40 60 80 Z (Å)
Intens peak A)
surfac er
Intens peak B)
from B yer
O 1s In ty
W tensity


DETECTION MODE:
(a)
vacuum
solid
clean surface
adsorbates/catalysis
clusters, quantum dots & wires
solid/liquid
thin films
porous media
inclusions
multilayers
dopants
buried interfaces
buried layers
single-phase bulk
electron-out spectroscopies
~5Å – 50Å → 1°
~35Å – 150Å → 2°
photon-out spectroscopies
~100Å → 10,000Å
= μ
(b)
1⁰ e⁻: PS, PD
PH, AES, RRAS
2⁰ e⁻: XAS / NEXAFS \ EXAFS
hν
hν': XES, RIXS
XAS
hν: XAS
SXS
hν: XAS

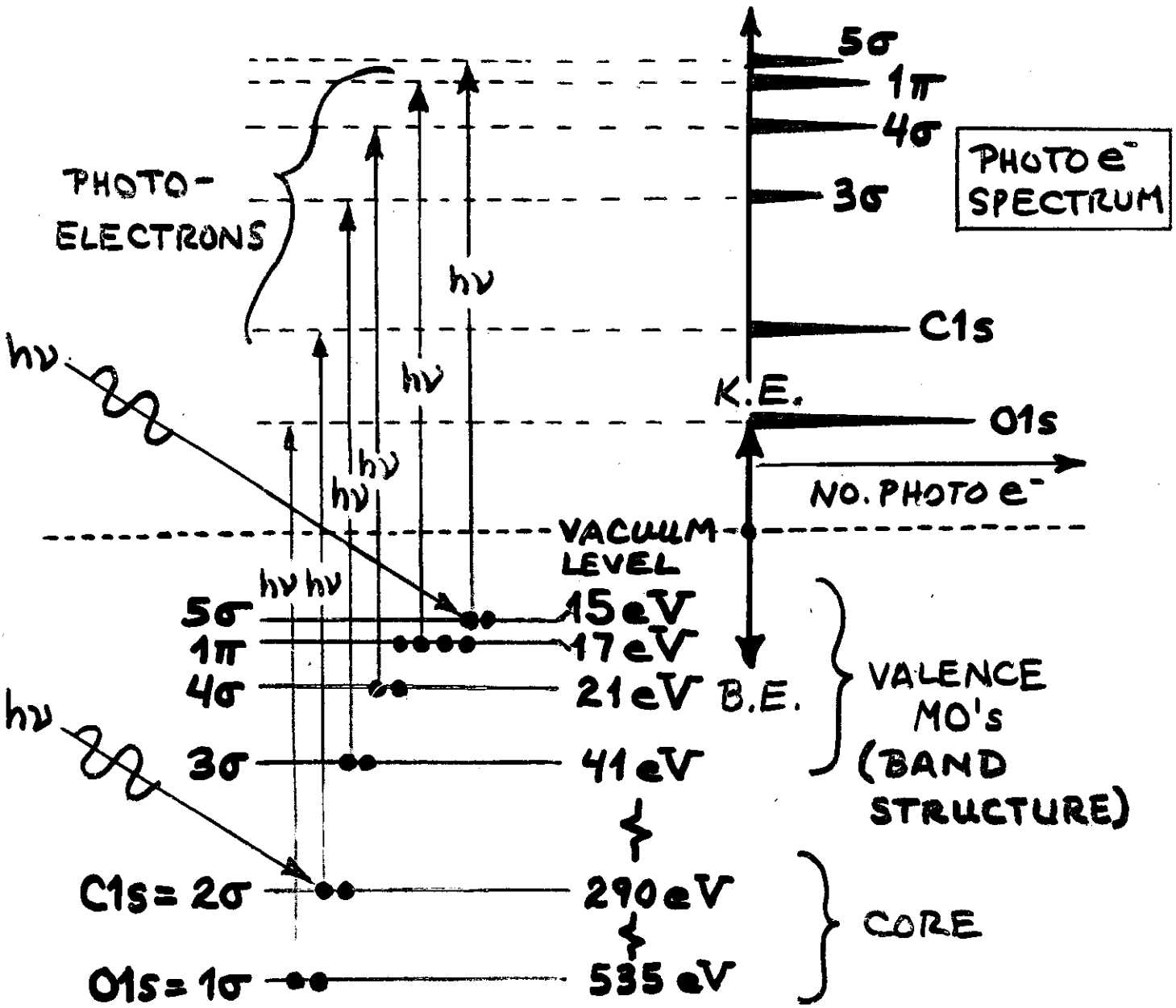
PHOTOELECTRON SPECTROSCOPY

THE PHOTOELECTRIC EFFECT (EINSTEIN, 1905):

(PHOTON ENERGY) (ABSORBED) = (e⁻ BINDING ENERGY IN SYSTEM) + (PHOTOELECTRON KINETIC ENERGY) (EMITTED)

= B.E. + K.E.

EXAMPLE – CO MOLECULE:



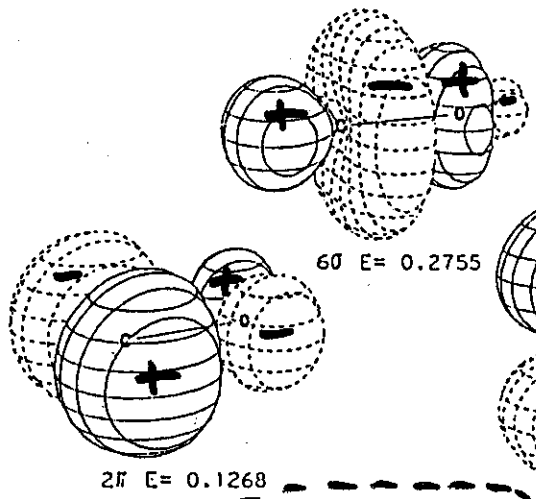
THE ELECTRONS IN CARBON MONOXIDE:

15. Carbon Monoxide — Symmetry: $C_{\infty v}$

ε_k = + NO.

↑

UNBOUND + UNOCCUPIED

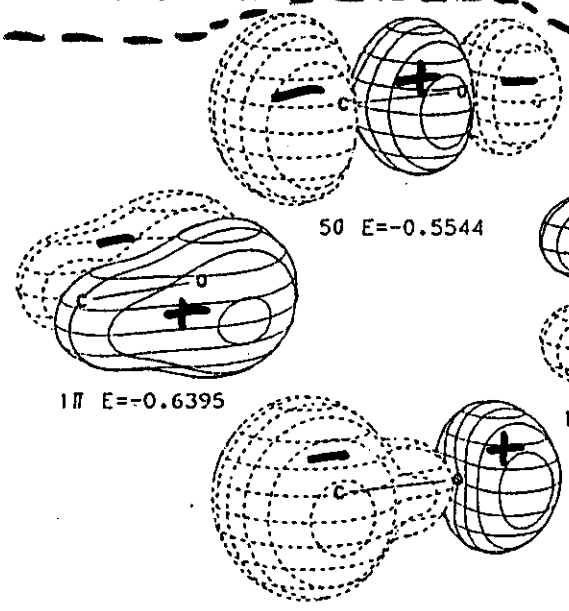


ANTI-BONDING 2π (8, 9)

BOUND + OCCUPIED

↓

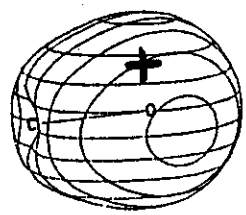
ε_k = − NO.



BONDING 5σ (7)

BONDING 1π (×2) (5, 6)

NON/WEAKLY BONDING 4σ (4)



BONDING 3σ

O: $(O1s)^2(C1s)^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$

↑ 3e⁻ — 14e⁻

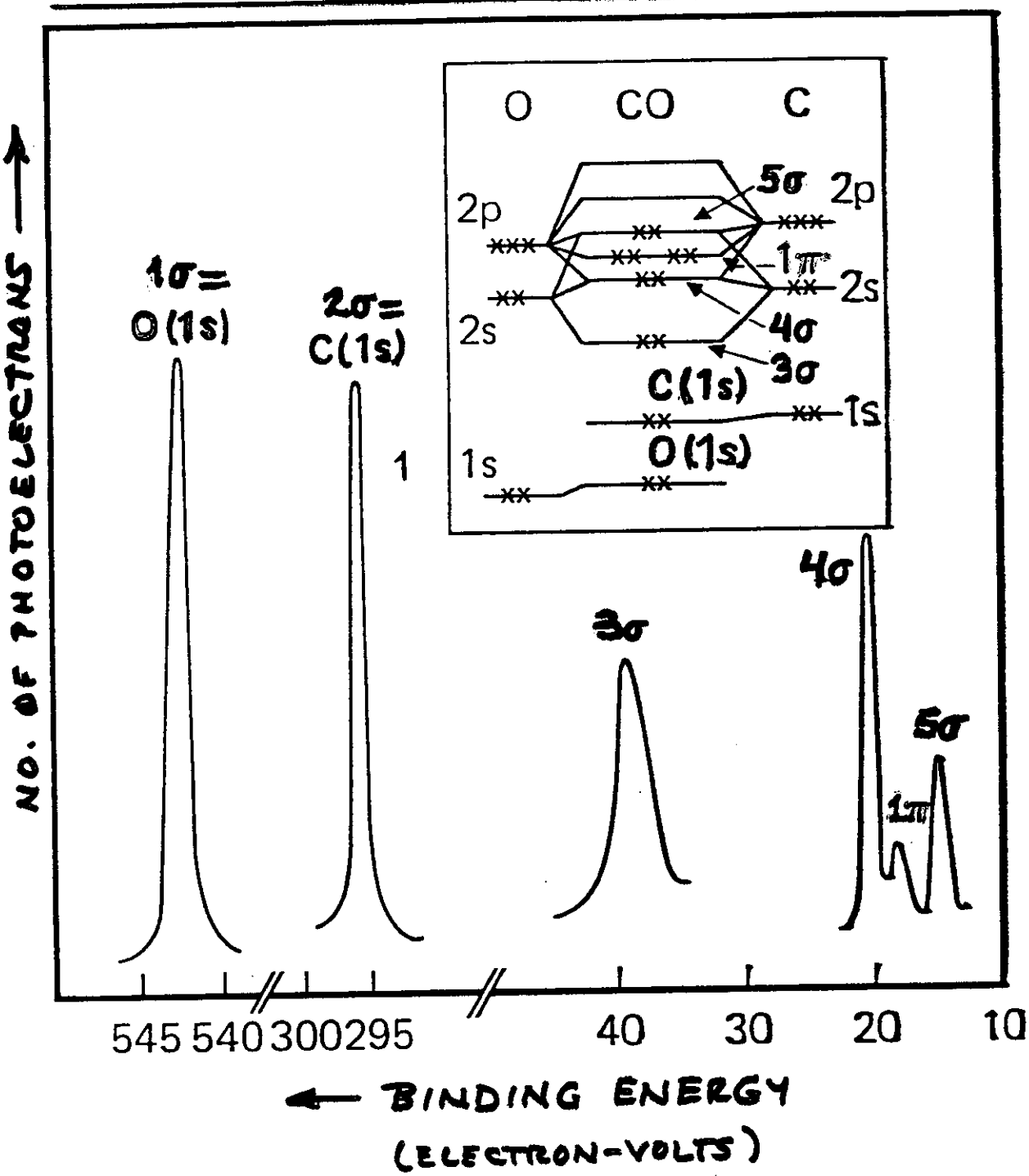
O C1s CORE

2σ E = −10.88

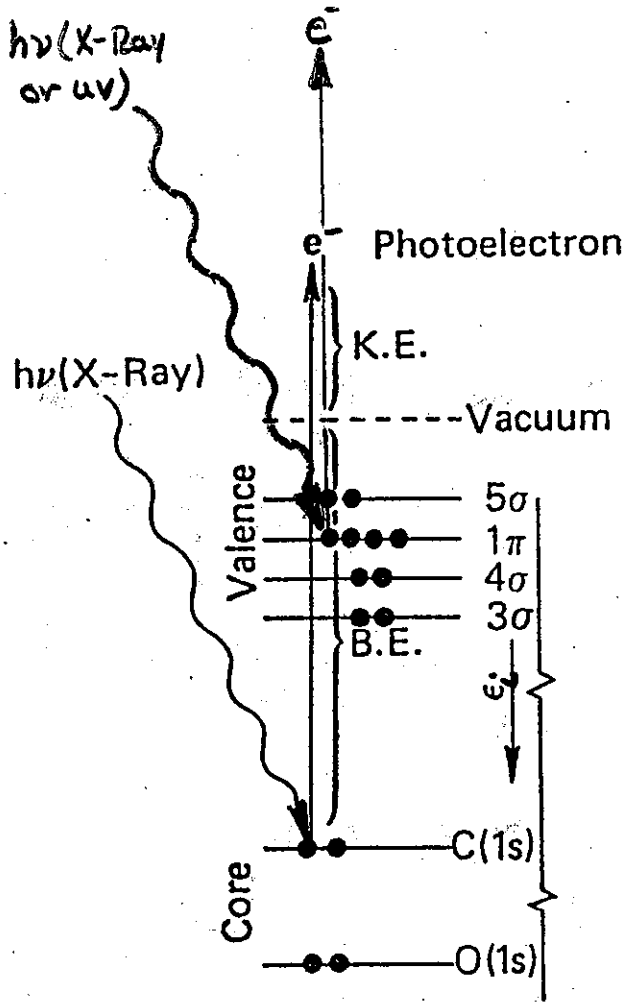
O 1s CORE

1σ E = − 20.00 a.u. (1 a.u. = 27.2eV)

PHOTOELECTRON SPECTRUM OF CO

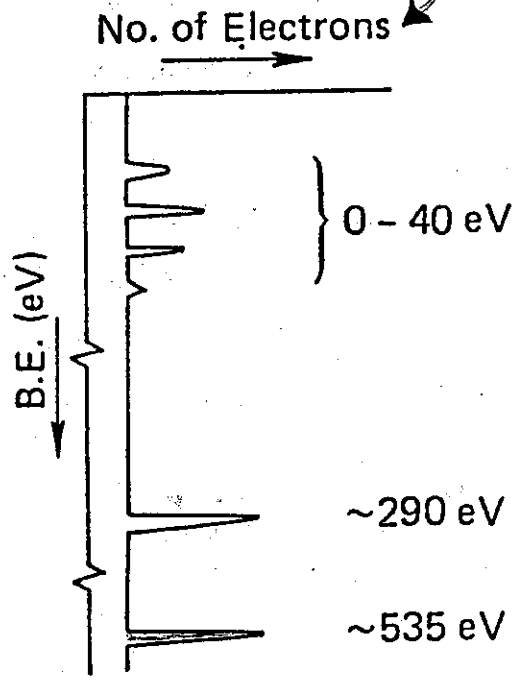


THE PHOTOELECTRON EMISSION PROCESS



Molecular Orbital, energy, ϵ

ONE-STEP PROCESS
ONE-HOLE FINAL STATE
STRONG DIPOLE RULES
SIMPLER SPECTRA



Schematic of XPS Spectrum (UPS)

$$K.E._i = h\nu - B.E._i \sim h\nu - \epsilon_i$$

$= \epsilon_i$ = HARTREE-FOCK ONE-ELECTRON EIGENVALUE:

$\hat{H}\varphi_i = \epsilon_i \varphi_i$

(KOOPMANS' THEOREM)

THE AUGER PROCESS

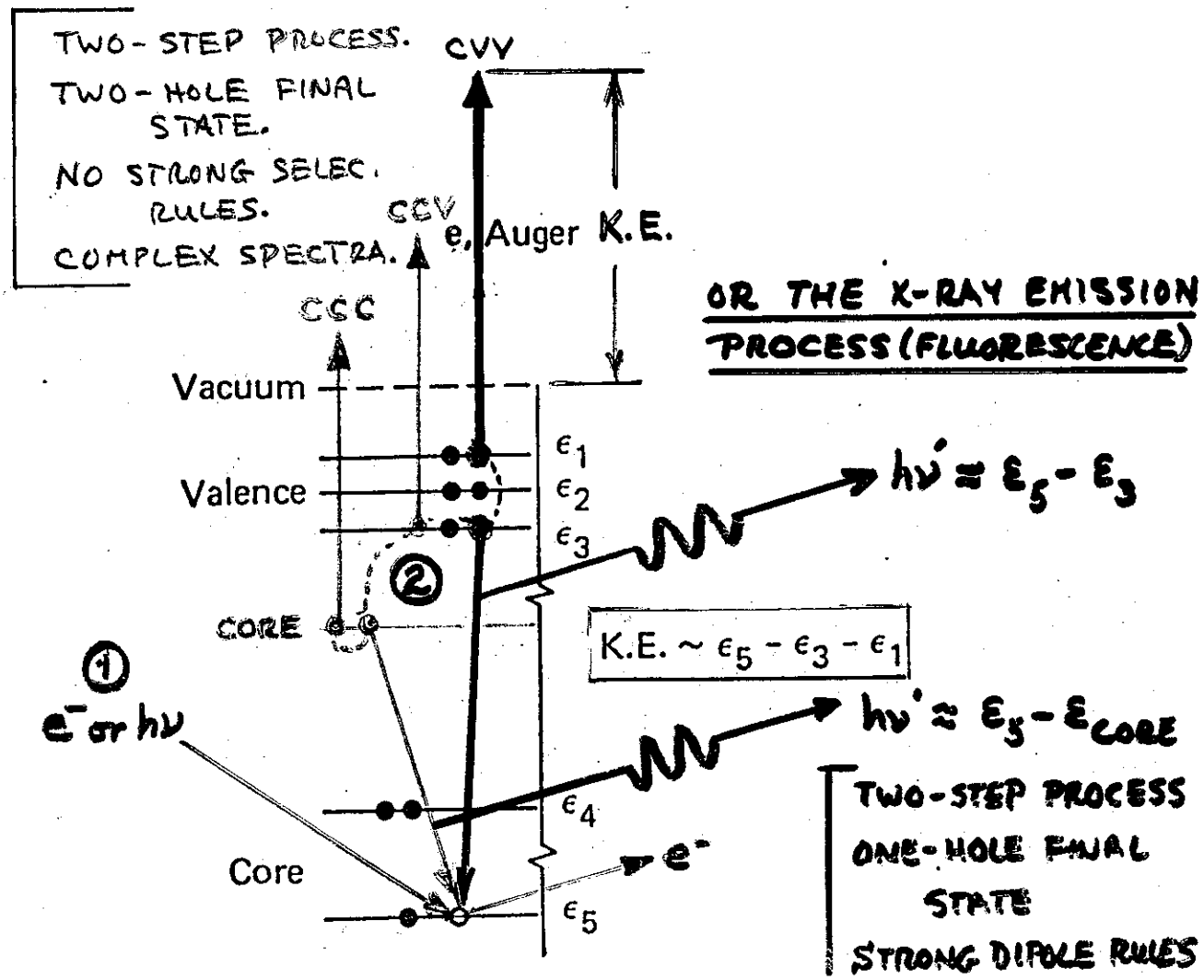
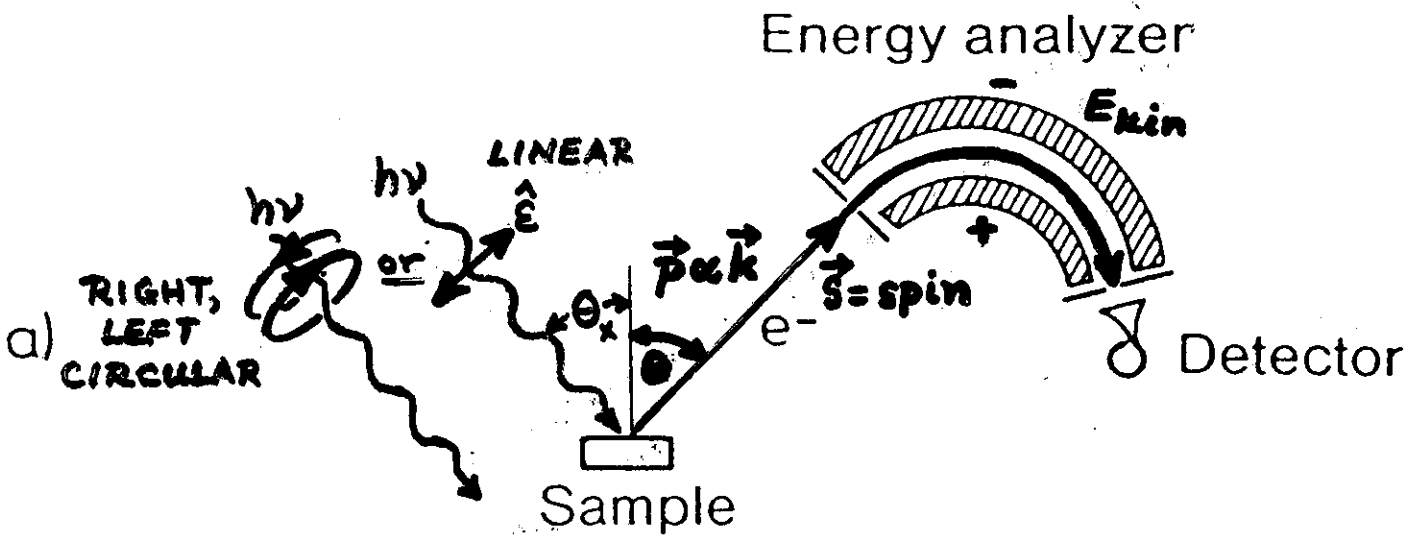
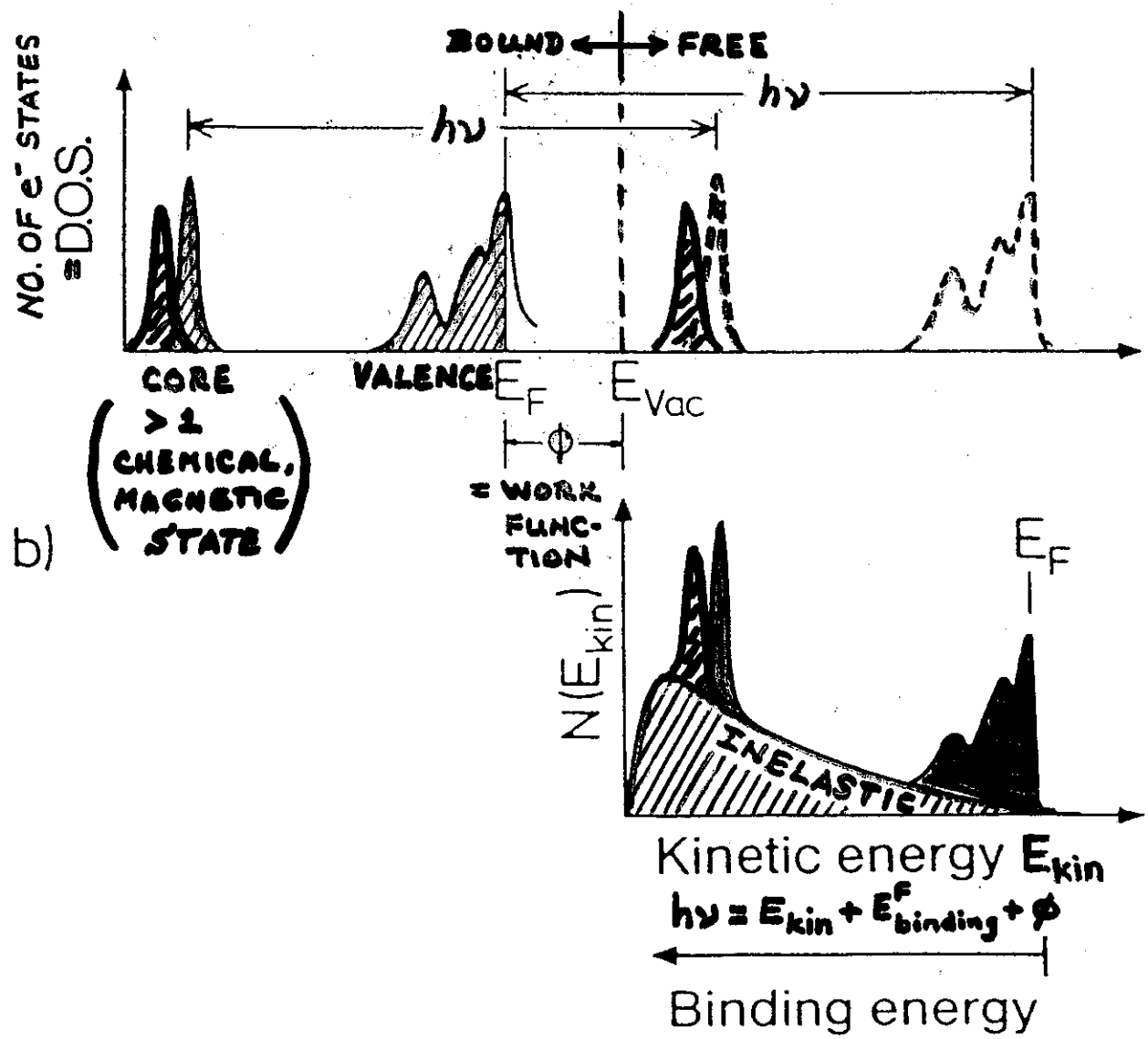


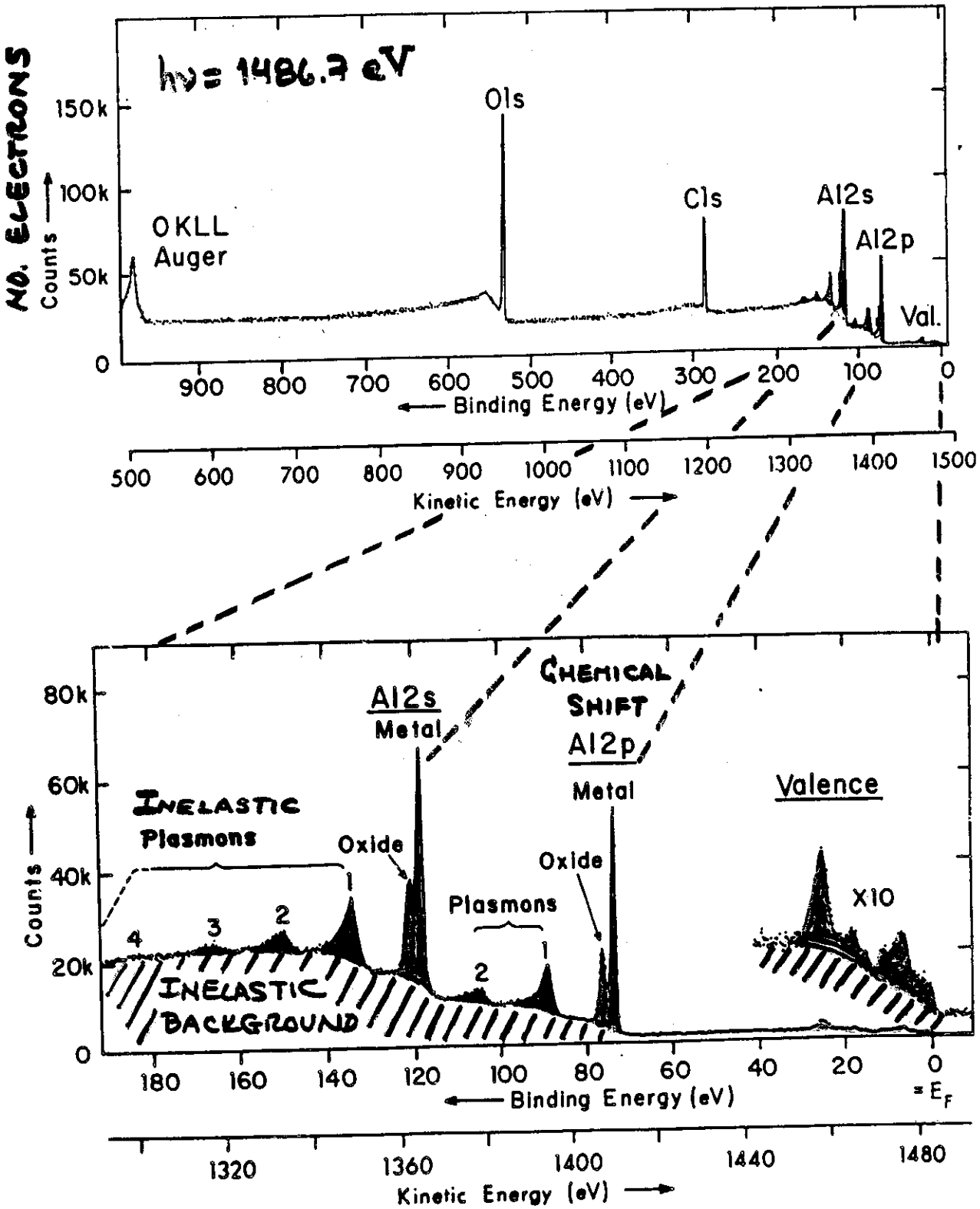
Figure 2. Scheme of the Auger process. A valence-level involved Auger emission is illustrated here, but the two electrons involved also could have come from core level, ϵ_4, provided $\epsilon_5 - 2\epsilon_4 > 0$.

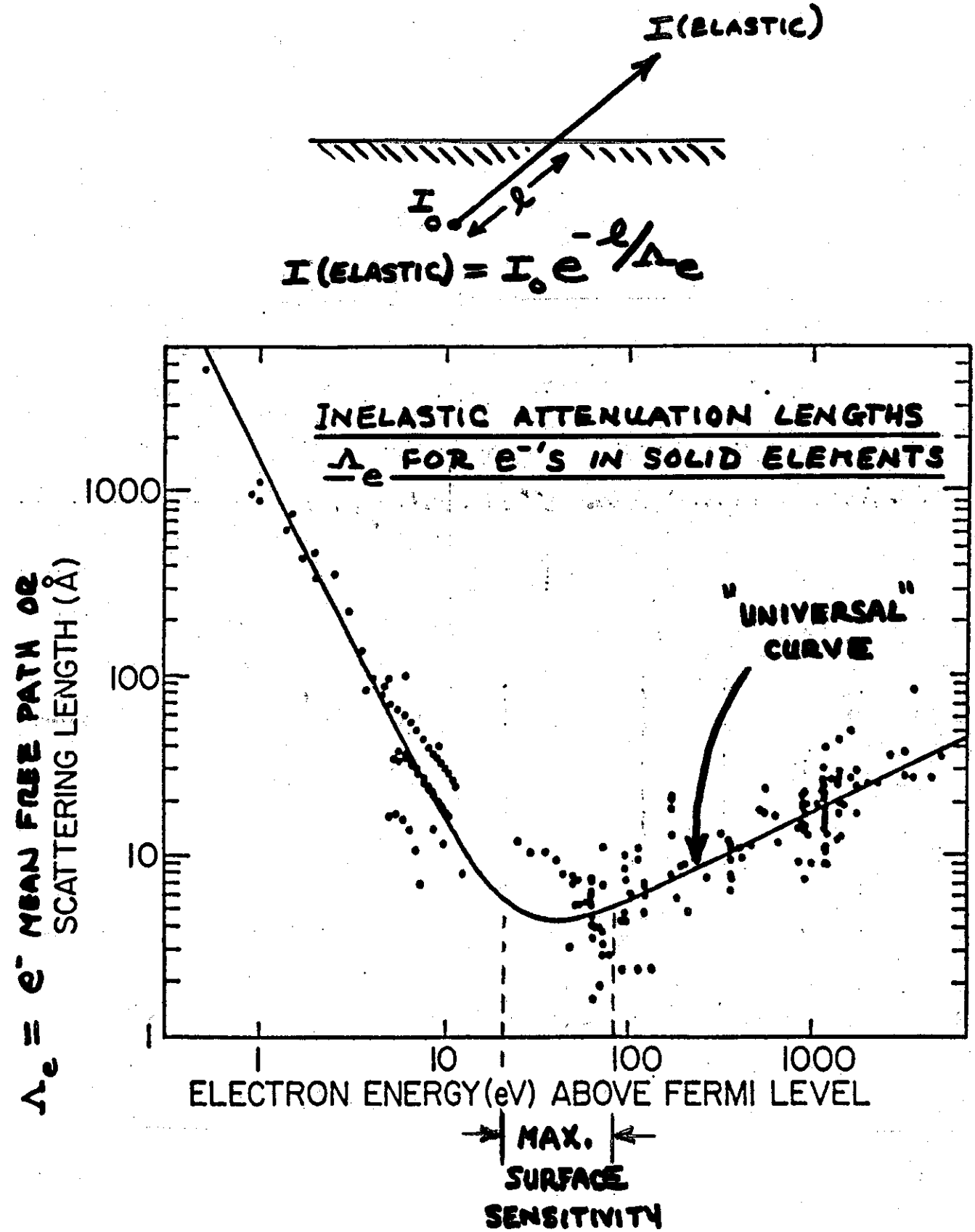
PHOTOELECTRON SPECTROSCOPY





TYPICAL PHOTOELECTRON SPECTRA: OXIDIZED ALUMINUM





COMPILATIONS: Seah + Dench, Surf. Int. Anal. 1, 2 (1979)
Tanuma, Powell, + Penn, Surf. Int. Anal. 17, 911 + 927 (1991) + more recent

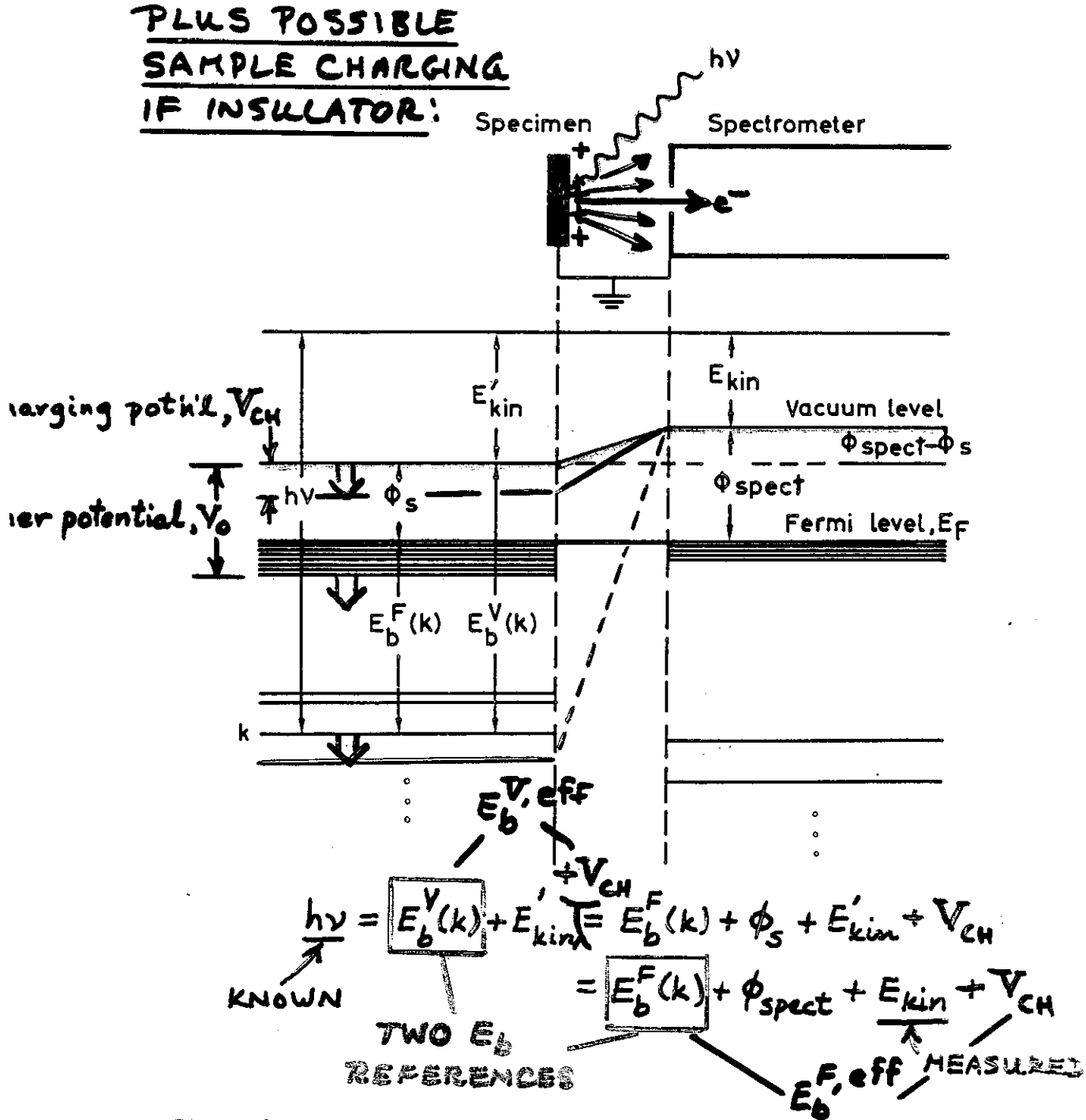


Figure 3 -- Energy level diagram for a metallic specimen in electrical equilibrium with an electron spectrometer. The closely spaced levels near the Fermi level E_F represent the filled portions of the valence bands in specimen and spectrometer. The deeper levels are core levels. An analogous diagram also applies to semiconducting or insulating specimens, with the only difference being that E_F lies somewhere between the filled valence bands and the empty conduction bands above.

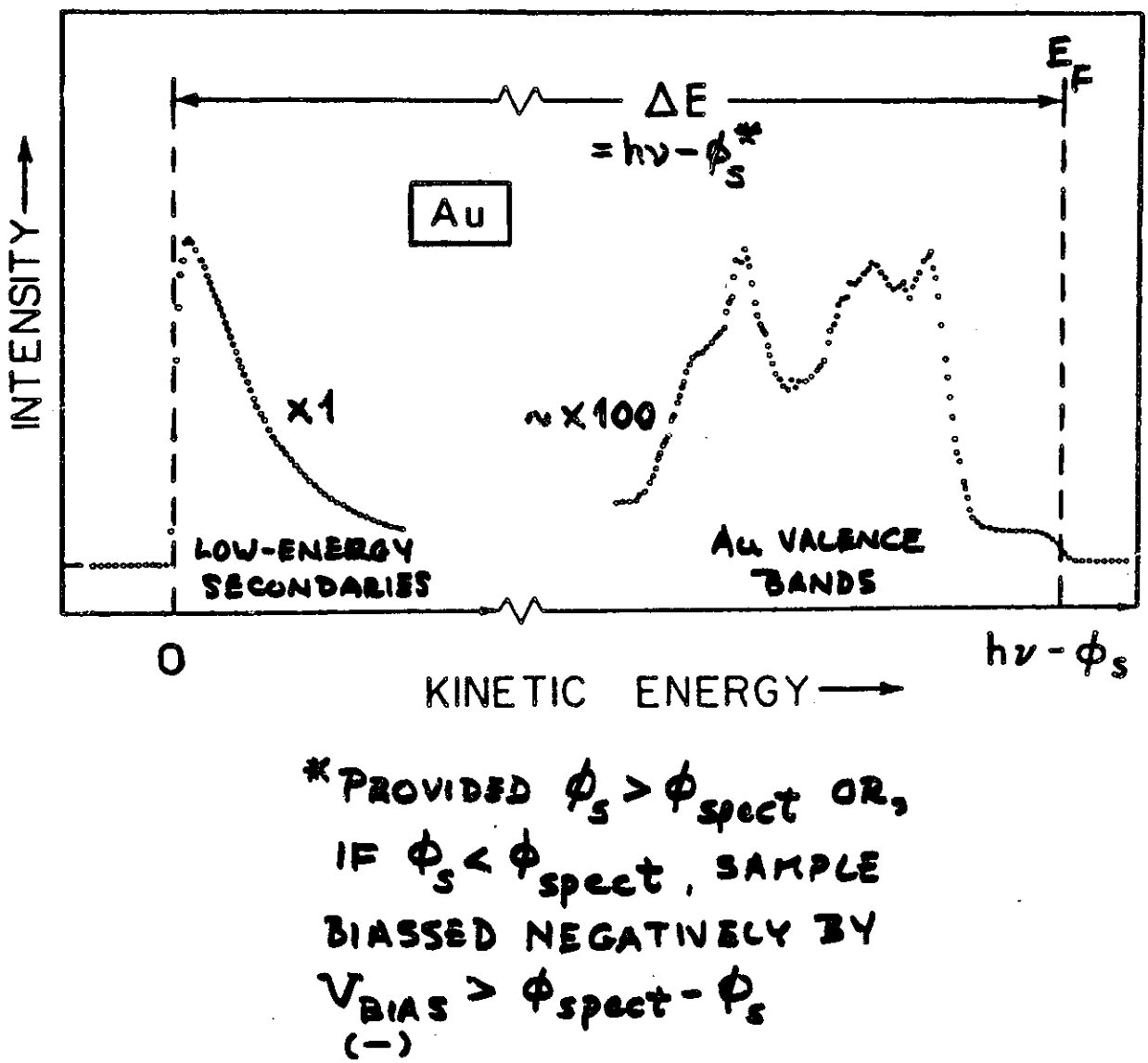
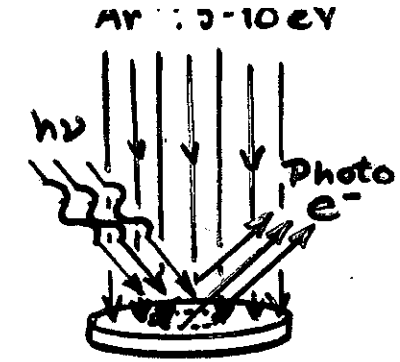
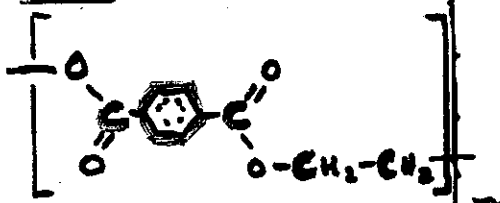


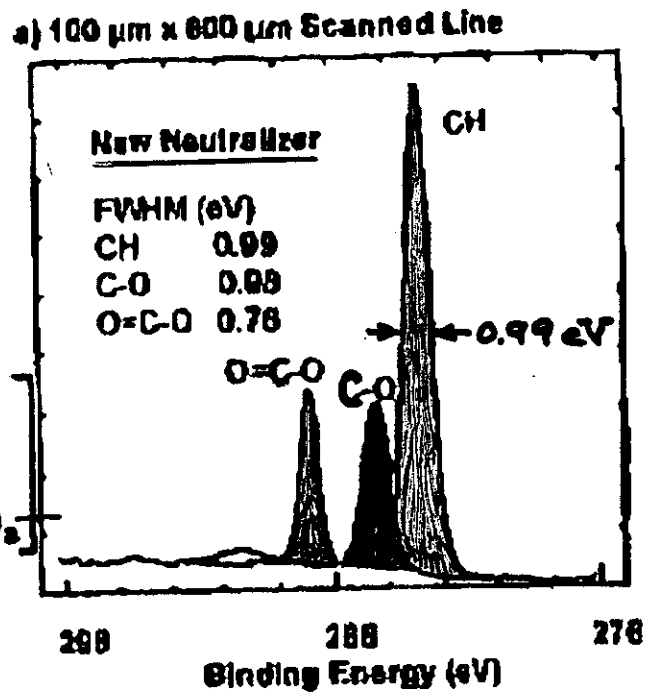
Figure 4 -- Full XPS spectral scan for a polycrystalline Au specimen, showing both the cutoff of the secondary electron peak at zero kinetic energy and the high-energy cutoff for emission from levels at the metal Fermi level. The measureable distance ΔE thus equals $h\nu-\phi_s$, provided that suitable specimen biasing has been utilized. For this case, $h\nu$ was 1253.6 eV and ϕ_s was 5.1 eV. (From Baer, reference 56).

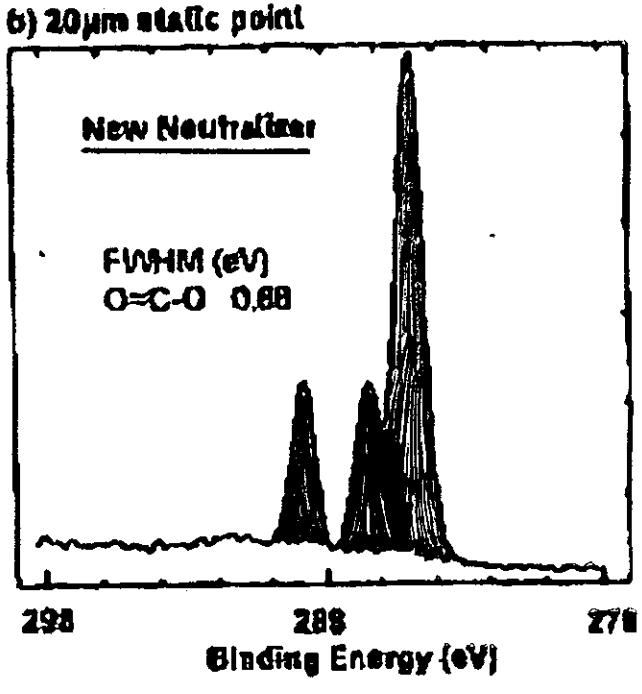
CHARGE NEUTRALIZATION IN INSULATORS

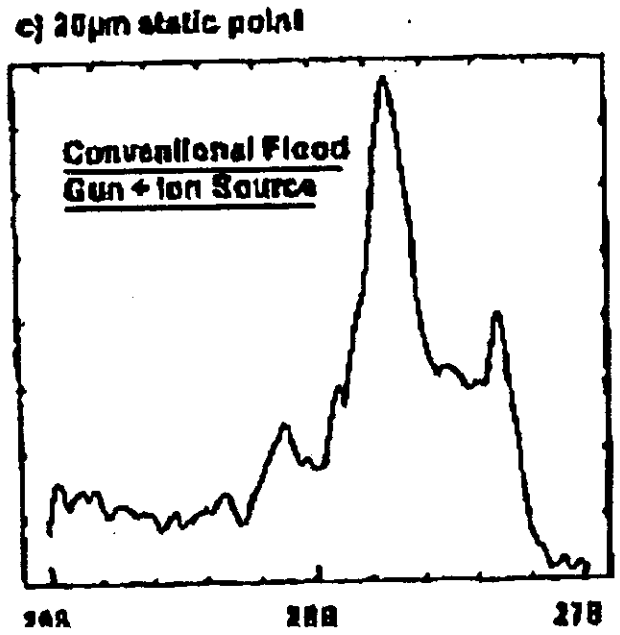


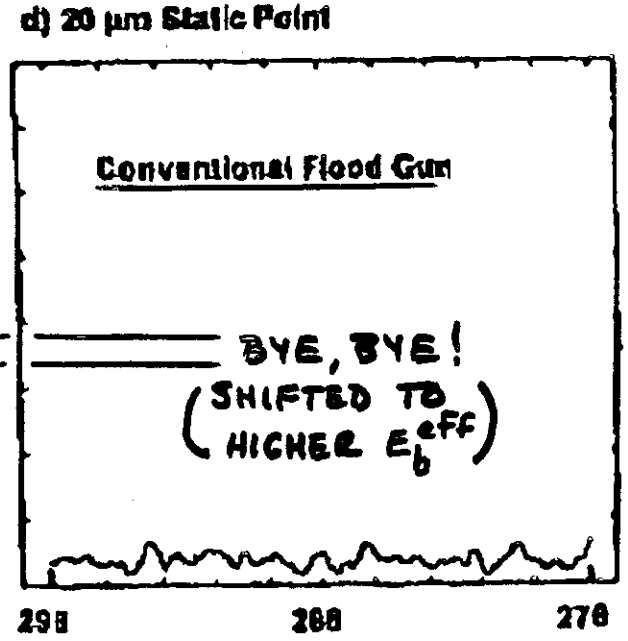
PET :



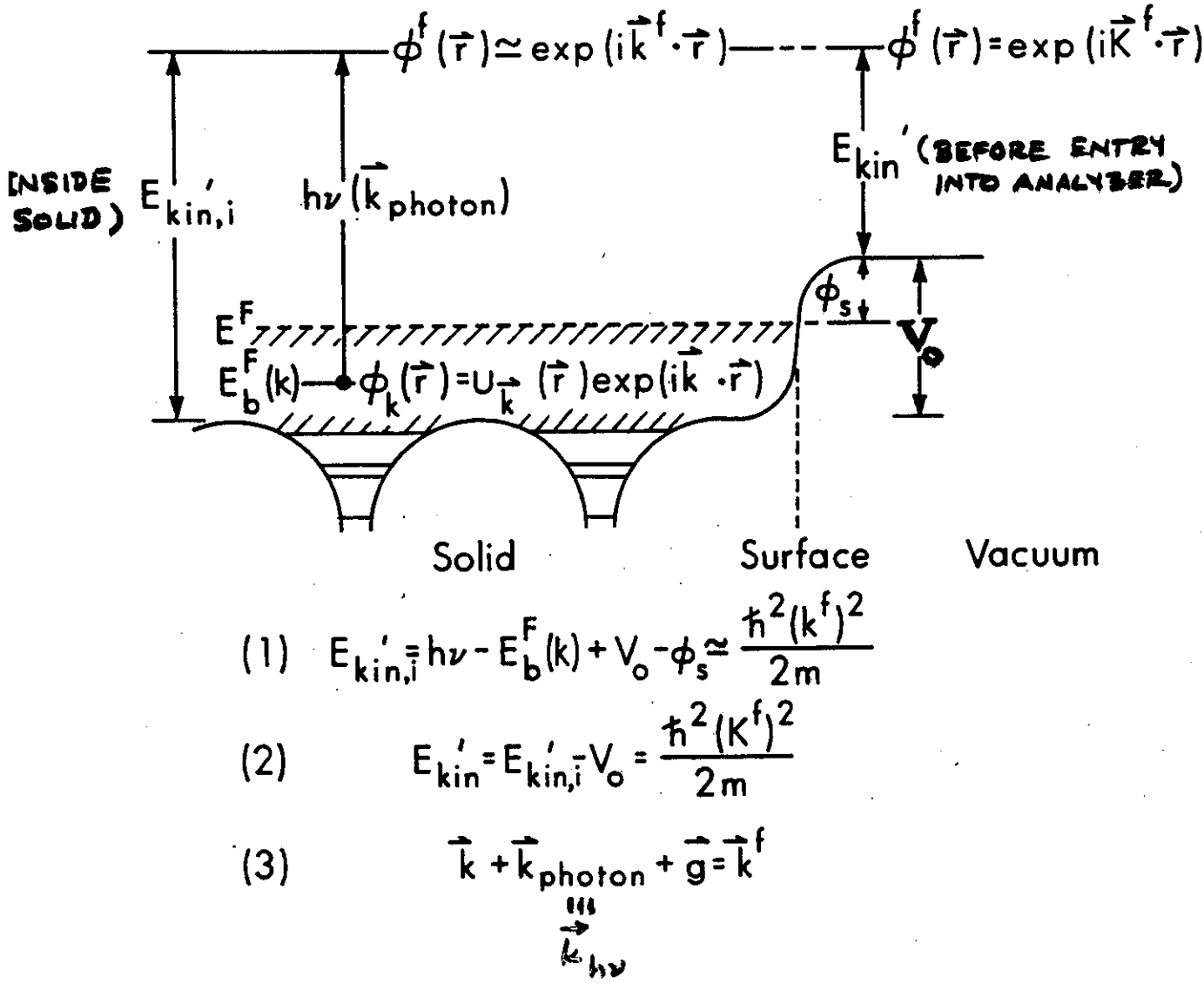








P. LARSON, M. KELLY, J. VAC. SCI. TECH. 16, 3483



$$(1)\quad E'_{kin,i} \equiv h\nu - E_b^F(k) + V_o - \phi_s \simeq \frac{\hbar^2 (k^f)^2}{2m}$$

$$(2)\quad E'_{kin} = E'_{kin,i} - V_o = \frac{\hbar^2 (K^f)^2}{2m}$$

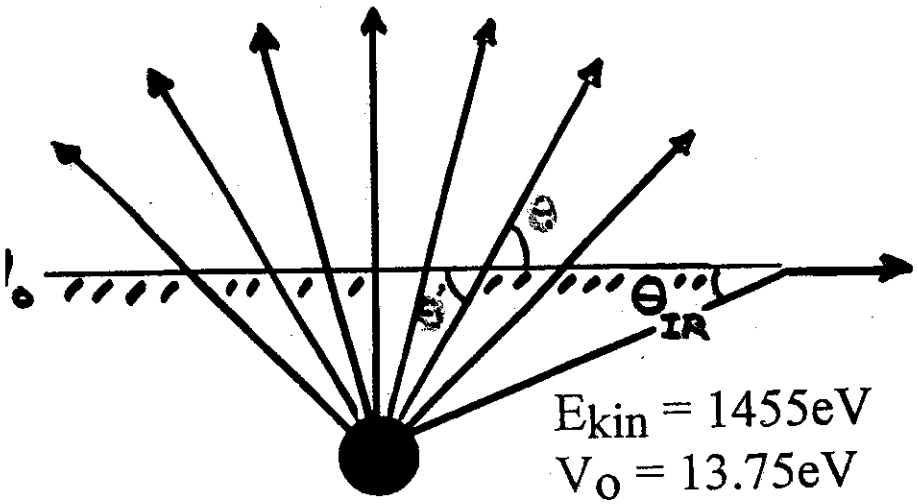
$$(3)\quad \vec{k} + \vec{k}_{photon} + \vec{g} = \vec{k}^f$$

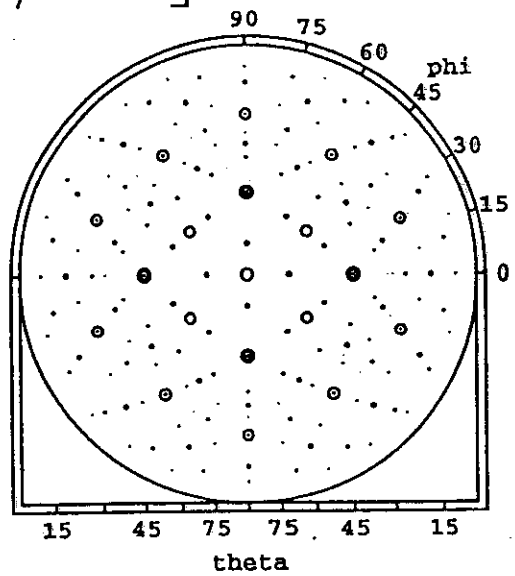
$\vec{k}_{h\nu}$

Figure 12 -- One-electron model of photoemission in a metallic solid, shown as an energy-level diagram superimposed on the one-electron potential energy curve near the surface. The initial and final states inside the solid are assumed to have Bloch-wave character. Applicable conservation relations on energy and wave vector are also shown.

Effects of Electron Refraction

$$\theta = \tan^{-1}\left[\sqrt{\sin^2\theta' - \frac{V_o}{E_{kin}}} \Big/ \cos\theta'\right]$$

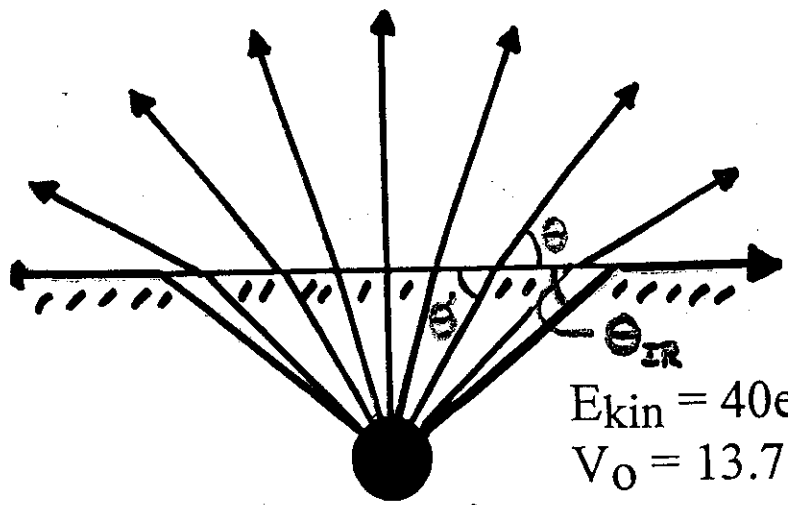


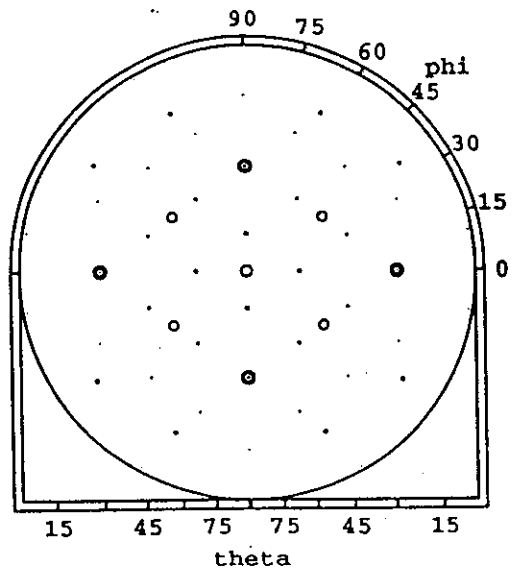


$E_{kin} = 1455eV$

$V_o = 13.75eV$

$\theta'_{min} = \theta_{IR} \approx 6°$



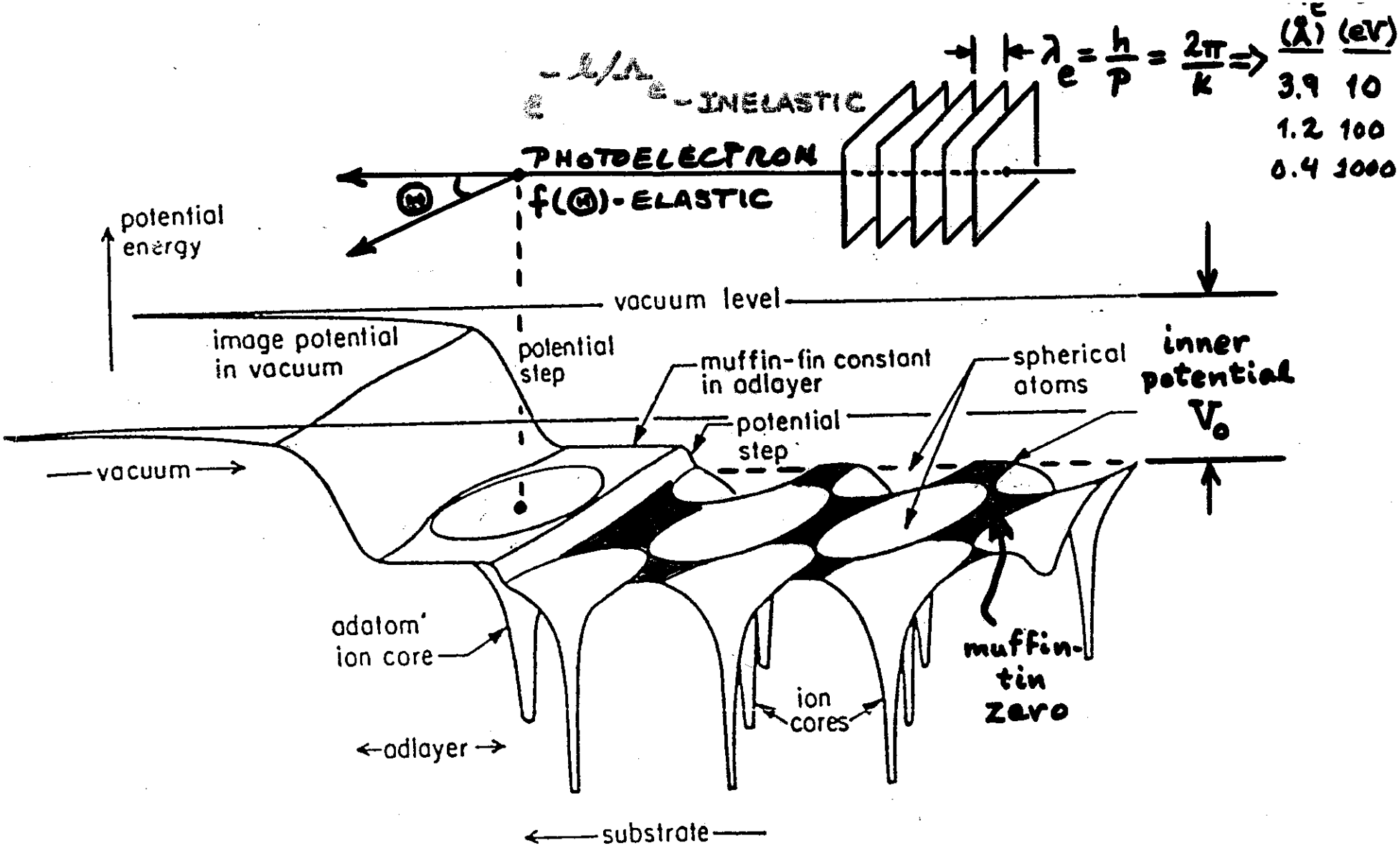


$E_{kin} = 40eV$

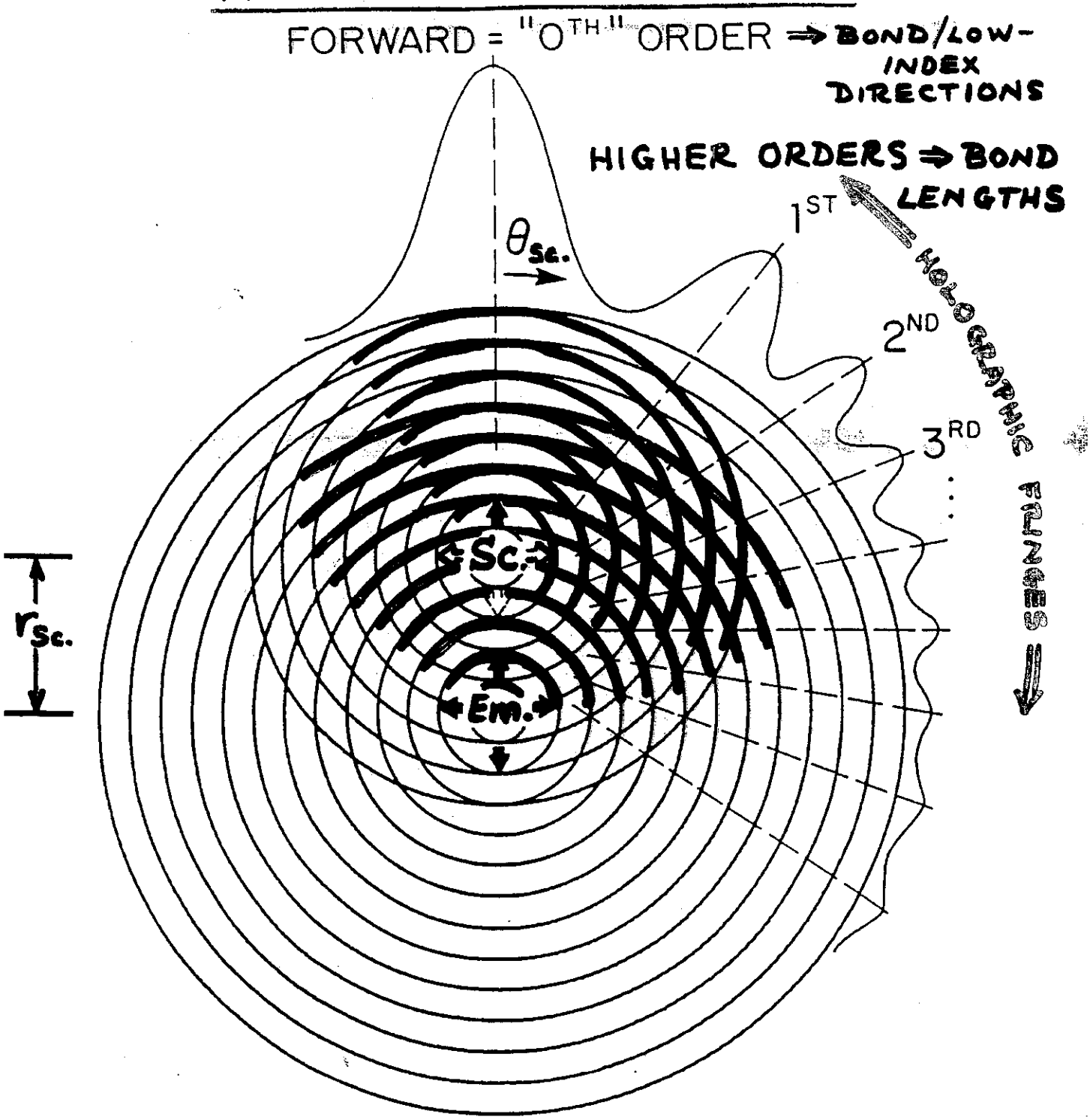
$V_o = 13.75eV$

$\theta'_{min} = \theta_{IR} \approx 39°$

C.S. Fadley, Progress in Solid State Chem., Vol. 11, 1976


$\lambda_e = \frac{h}{p} = \frac{2\pi}{k} \Rightarrow$
(Å) (eV)
3.9 10
1.2 100
0.4 1000
e^{-l/Λ_e} - INELASTIC
PHOTOELECTRON
f(Θ)-ELASTIC
Θ
potential energy
vacuum level
image potential in vacuum
potential step
muffin-tin constant in adlayer
spherical atoms
inner potential V_o
potential step
vacuum
adatom' ion core
ion cores
muffin-tin zero
adlayer
substrate

PHOTOELECTRON DIFFRACTION



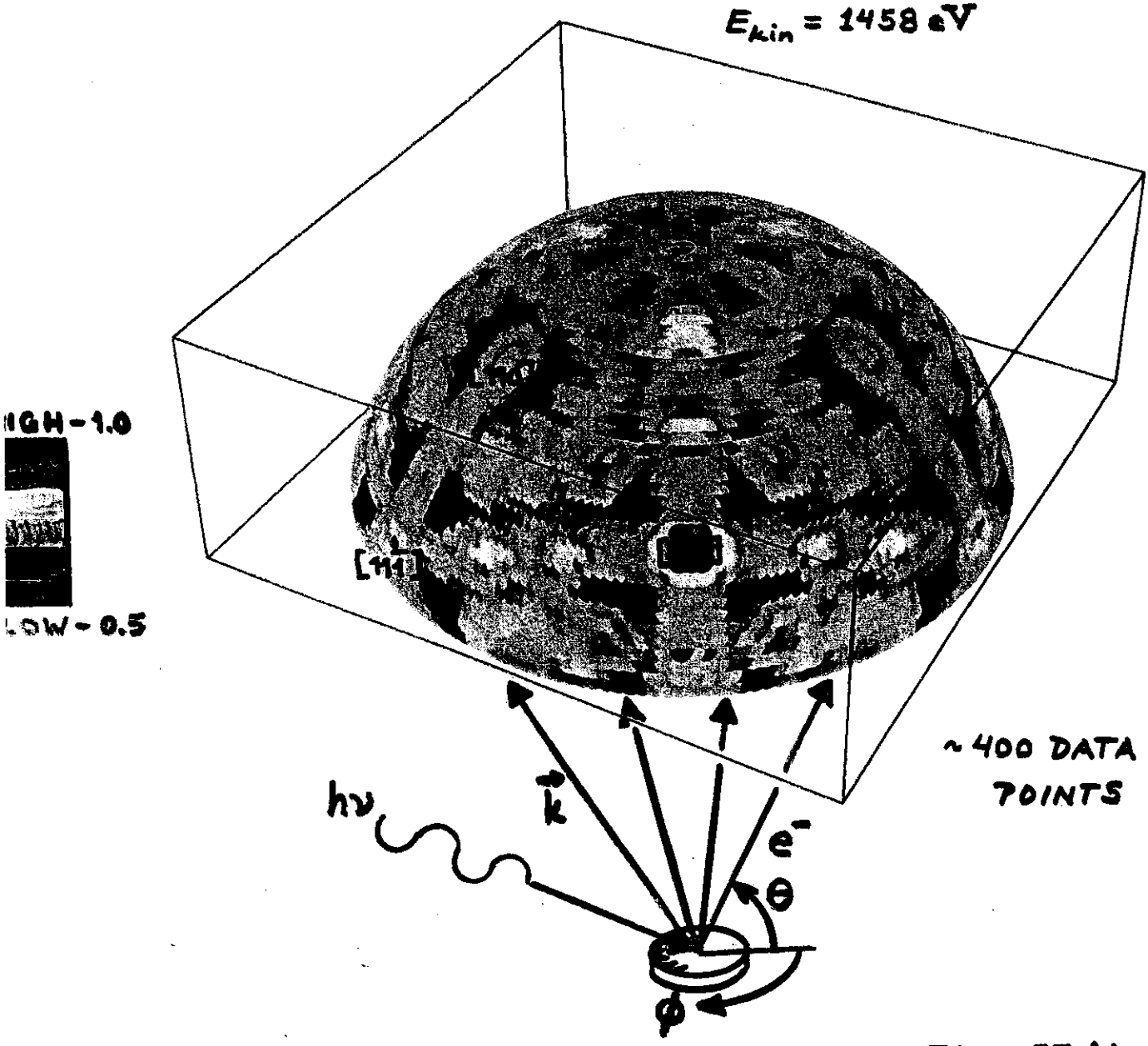
IN REAL CASE, ORDERS (FRINGES) FROM:

$$2\pi n = \underbrace{k r_{Sc.}(1-\cos\theta_{Sc.})}_{\text{PATH LENGTH DIFFERENCE}} + \underbrace{\psi_{Sc.}(\theta_{Sc.})}_{\text{SCATTERING PHASE}}$$

SCANNED-ANGLE PHOTOELECTRON DIFFRACTION

Example:

Ge(111) - Ge3d Photoelectron Hologram



~400 DATA POINTS

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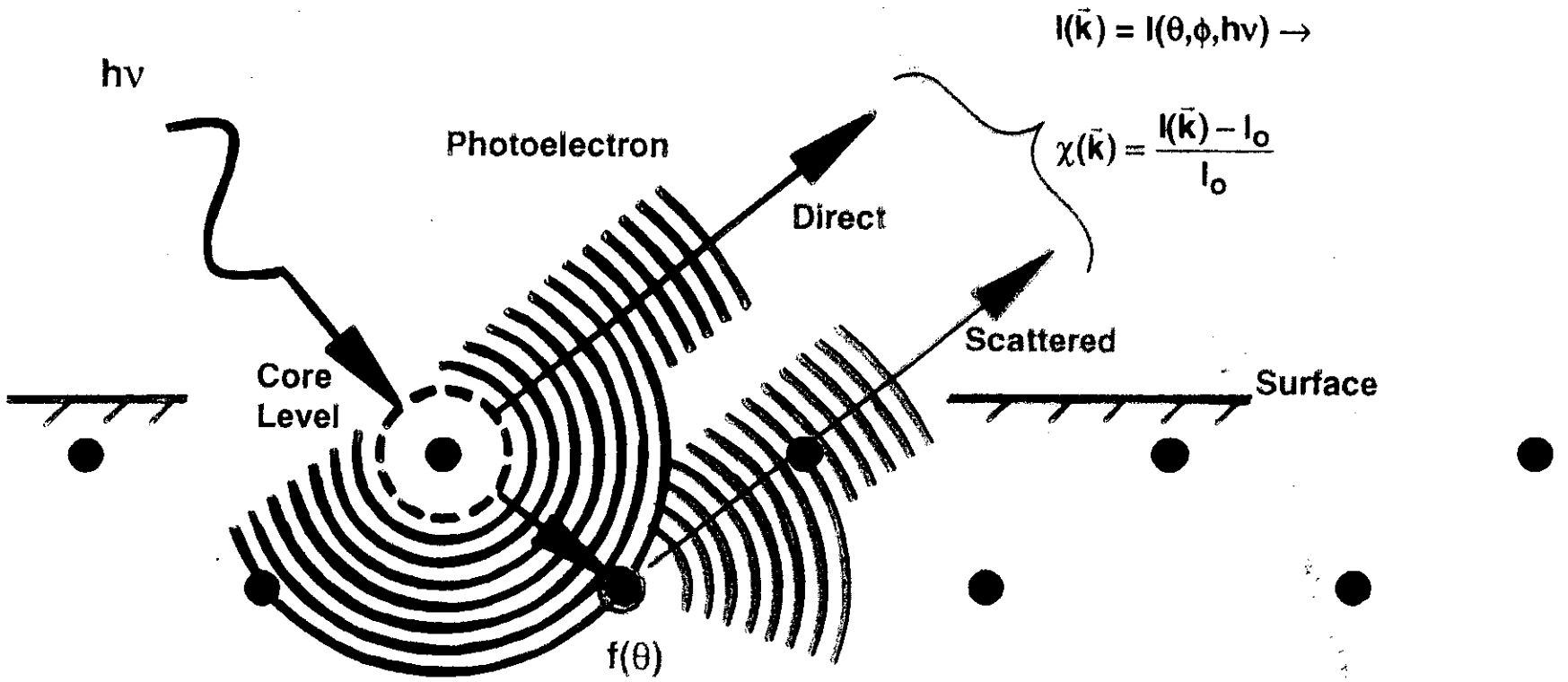
PHOTOELECTRON DIFFRACTION



- *Element-specific and chemical state- or site- specific* atomic structure
- Probes *local or short-range order*: long-range order not necessary (unlike LEED)
- *Time-resolved measurements* of surface reactions possible: → except in substrate
  ~10-20 s/spectrum now→~0.1-1.0 s/spectrum with new detector and undulator
- *Direct derivation of structural parameters* from forward scattering and
  Fourier a/o holographic transforms of data and fingerprint features (e.g. fringes)
- *Accurate structures (≤0.05Å)* : expt. vs. multiple scattering theory with R-factors
- *Variation of spin and light polarization* for magnetic studies possible:
  element-specific structure and magnetometry

SUR-FACE

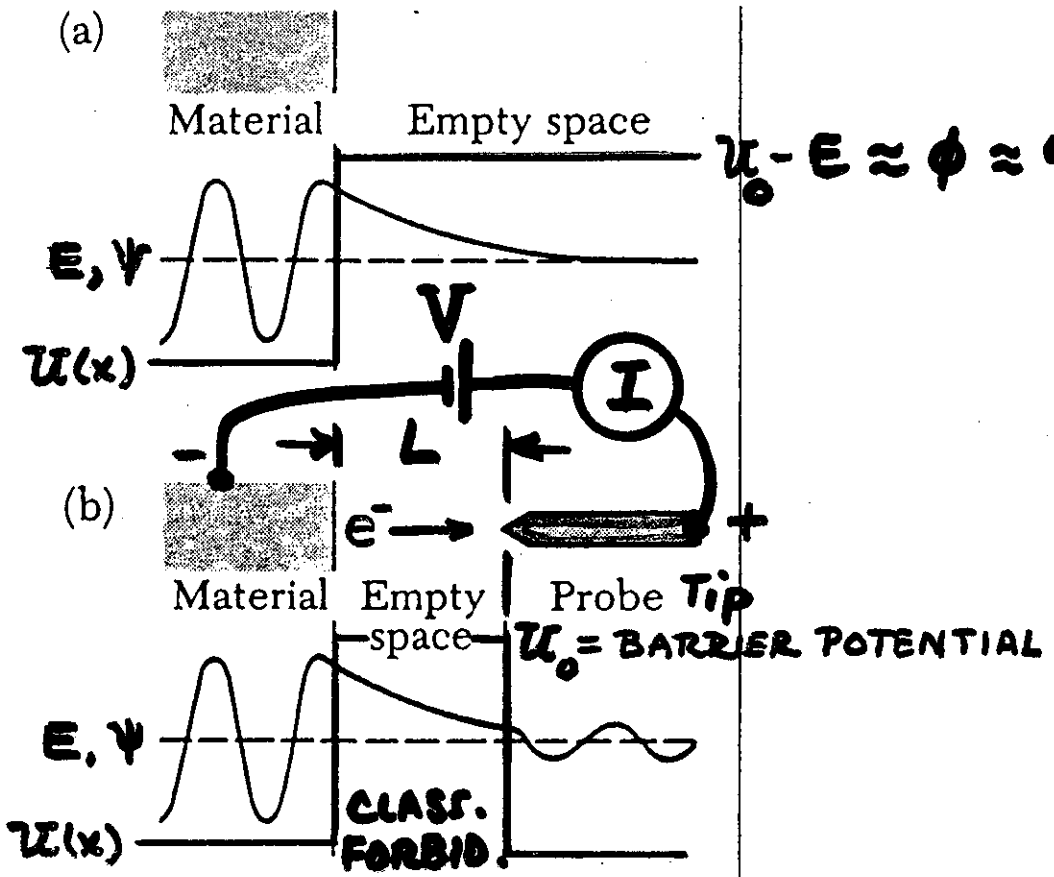


Figure 3 (a) The wavefunction of an electron in the surface of the material to be studied. The wavefunction extends beyond the surface into the empty region. (b) The sharp tip of a conducting probe is brought close to the surface. The wavefunction of a surface electron penetrates into the tip, so that the electron can "tunnel" from surface to tip. Compare this figure to Figure 6.7b.

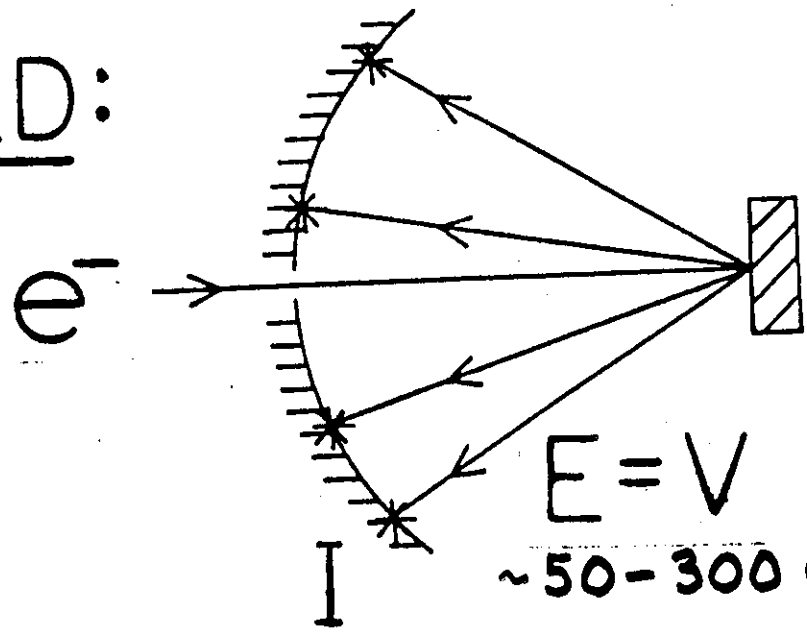
THE CANNING UNNELING GROSCOPE:

j = CURRENT/UNIT AREA

$$\approx \frac{e^2 V}{4\pi^2 L S \hbar} e^{-2L/\delta} \propto e^{-2\kappa L}$$

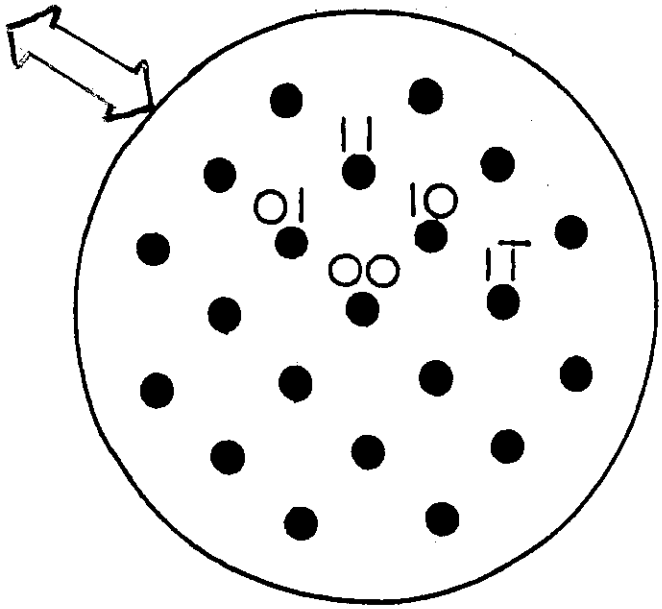
$$\delta = \frac{1}{\kappa} = \sqrt{\frac{\hbar^2}{2m(U_0 - E)}} \approx 1.0\,\text{Å}$$

LEED:



a)

TWO-DIMENSIONAL SURFACE RECIPROCAL LATTICE



b)

LONG-RANGE ORDER REQUIRED OVER $\gtrsim 100$ Å.

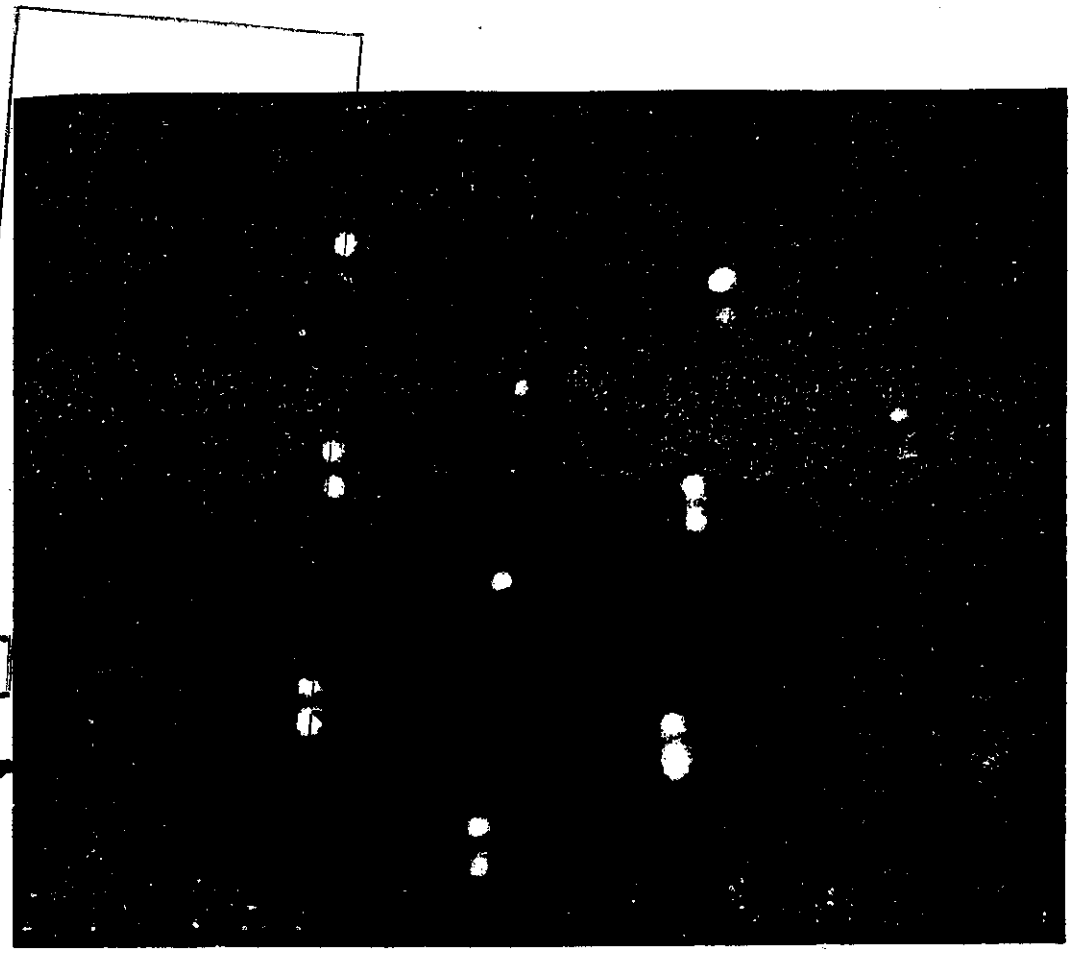


Figure 1.36. *Diffraction pattern of a platinum crystal face that was cut 6°27′ with respect to the (111) crystal face in the direction of the (110) face. Note the doubling of the diffraction spots.*

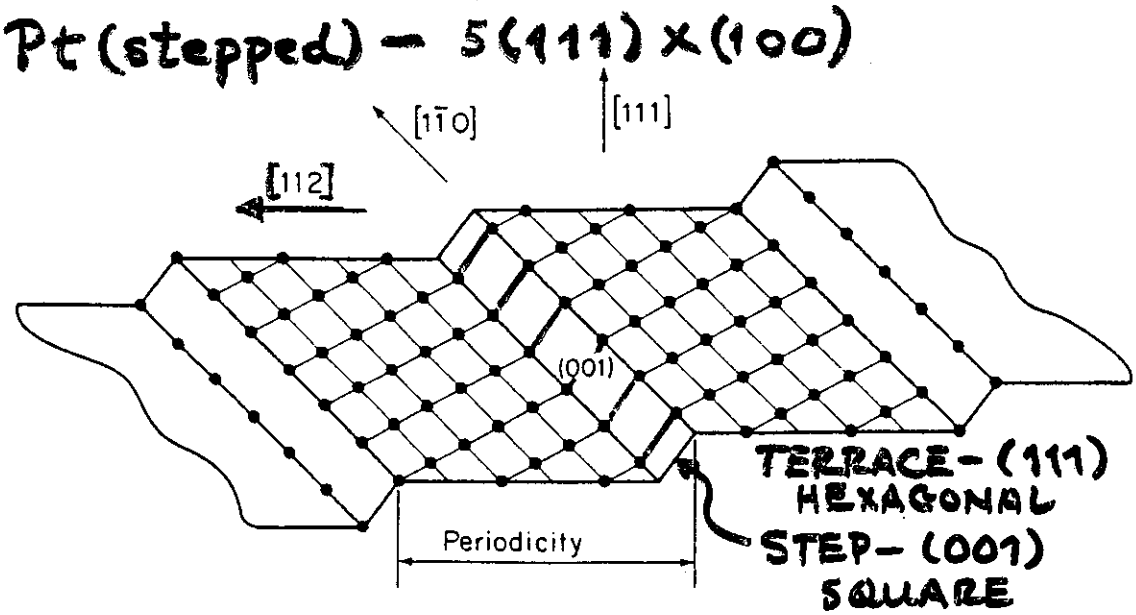
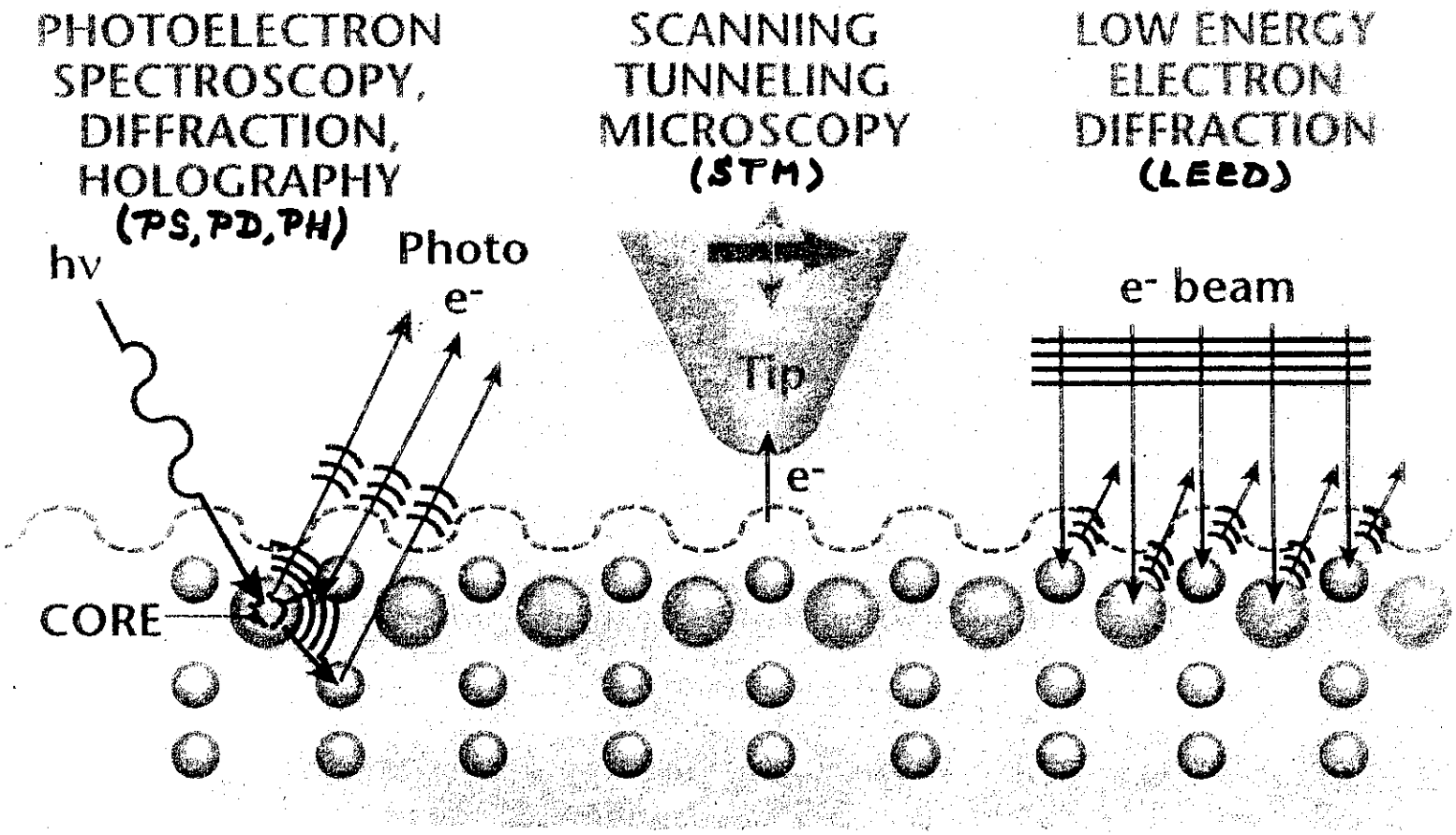
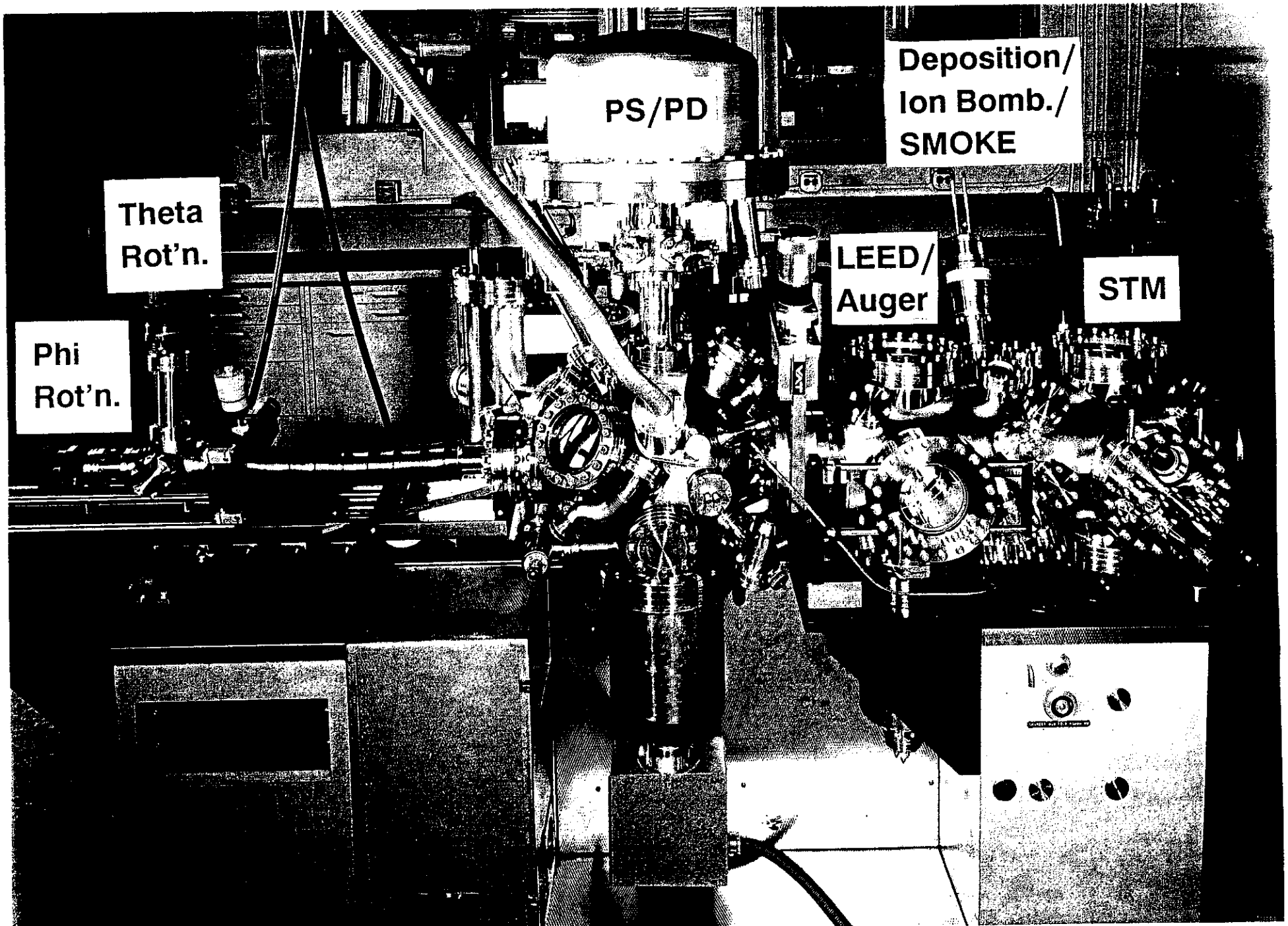


Figure 1.37. *Schematic representation of the platinum surface that exhibits ordered atomic steps.*

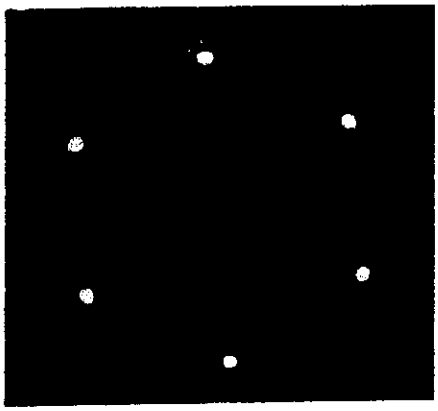


	PHOTOELECTRON SPECTROSCOPY, DIFFRACTION, HOLOGRAPHY (PS, PD, PH)	SCANNING TUNNELING MICROSCOPY (STM)	LOW ENERGY ELECTRON DIFFRACTION (LEED)
-Type of order:	Short (< 10Å)	Short, long and disorder	Long (> 100Å)
-Atom & site specific:	Yes	No	No
-Sensing depth:	5-40Å	Mostly surface D.O.S.	5-20Å
-Lateral resolution:	1 mm^2 to $(300Å)^2$ ↳ "SPECTROMICROSCOPY"	Single atom	1 mm^2 to 1 $micron^2$

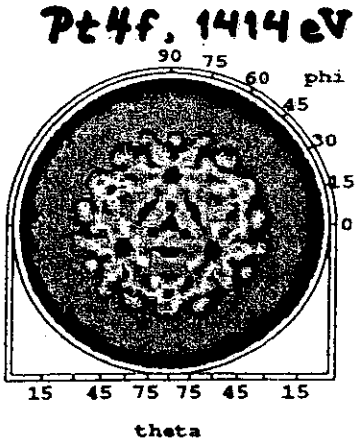

PS/PD
Deposition/
Ion Bomb./
SMOKE
Theta
Rot'n.
LEED/
Auger
STM
Phi
Rot'n.

GROWTH OF A MAGNETIC OXIDE (FeO) ON A METAL (Pt): Complementary data from three techniques

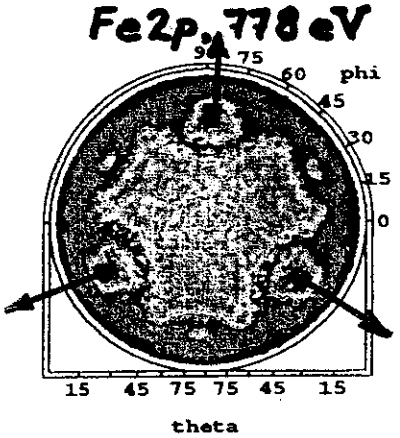
Low energy electron diffraction-->
surface long-range order



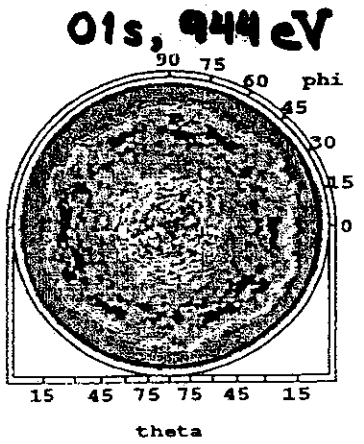
Photoelectron diffraction-->
atom-specific internal
atomic and magnetic structure



1 ML FeO



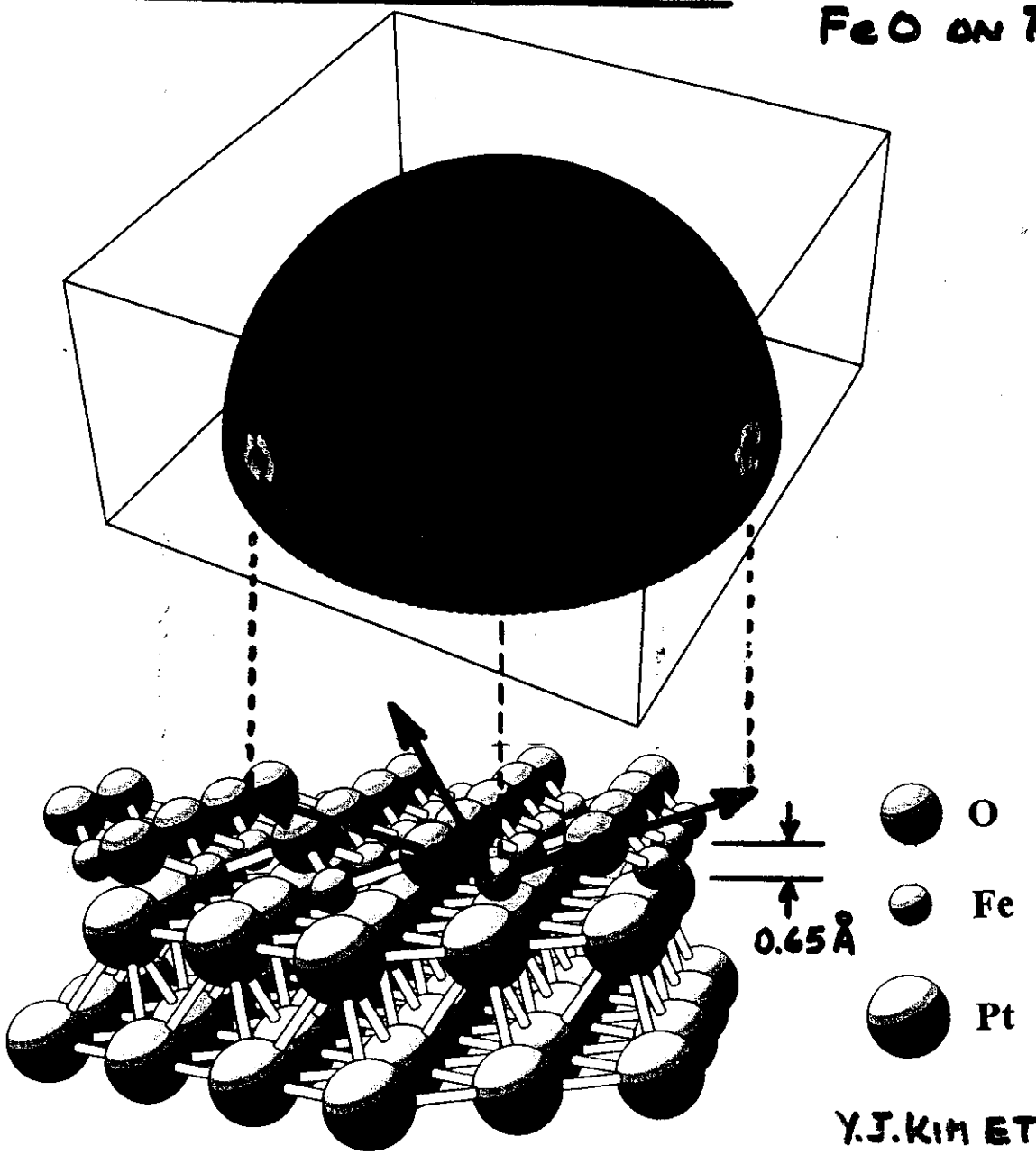
Scanning tunneling microscopy-->
surface topography,
short- and long- range order



Somorjai and Salmeron Groups
UCB & LBL-MSD
Galloway

Fadley Group
UCD & LBL-MSD
Kim, Westphal, Xiao, Ynzunza...

PHOTOELECTRON DIFFRACTION : Fe2p FROM FeO ON Pt(111)



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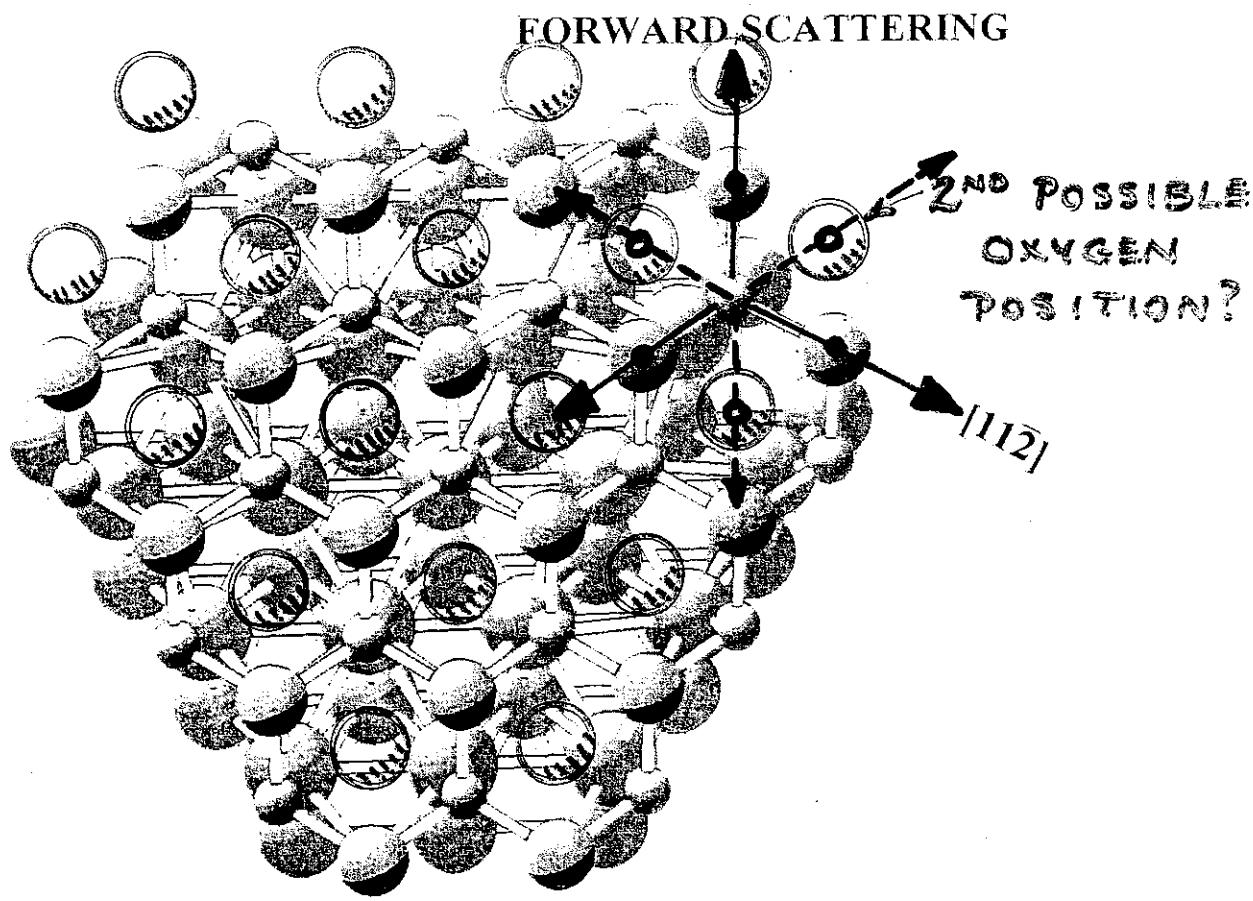
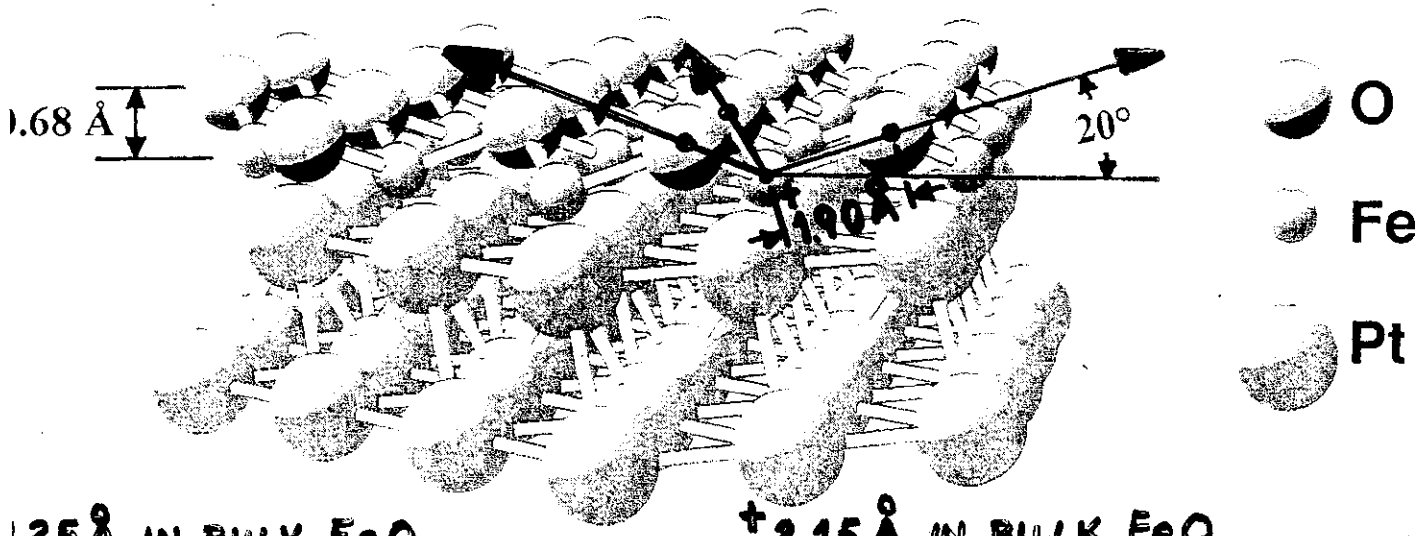
FeO/Pt(111)

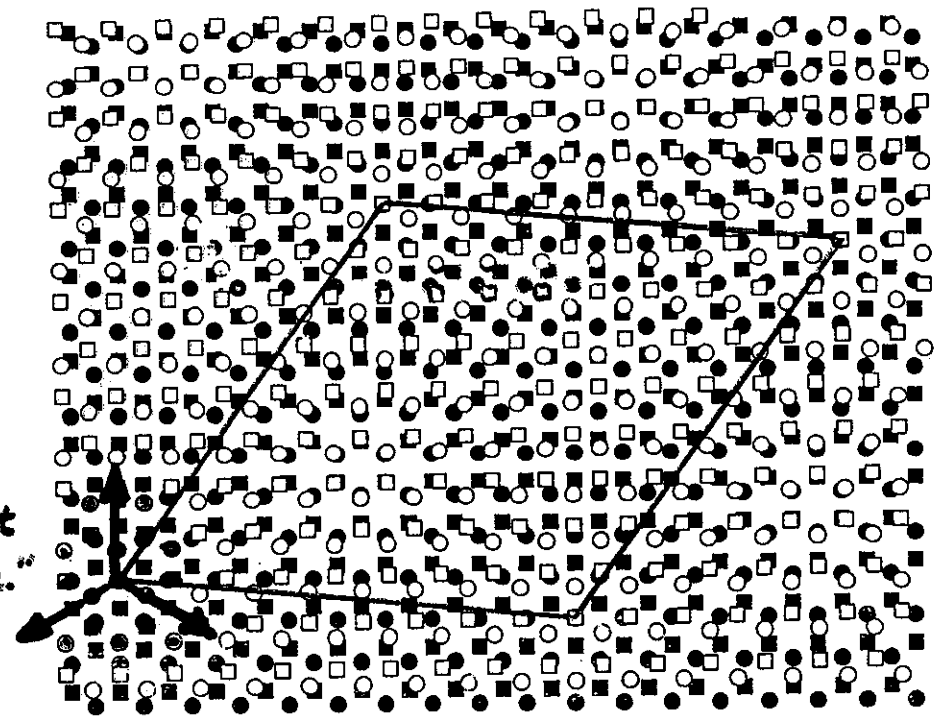




.25Å IN BULK FeO

+2.15 Å IN BULK FeO
1.88 Å IN BULK Fe_3O_4

FeO/Pt(111) - Favored



FeO/Pt(111) - Unfavored