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"Structural characterization of interfaces with x-ray photoelectron diffraction"

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Transparency Notes on

Structural characterization of interfaces with X-Ray Photoelectron Diffraction (XPD)

by

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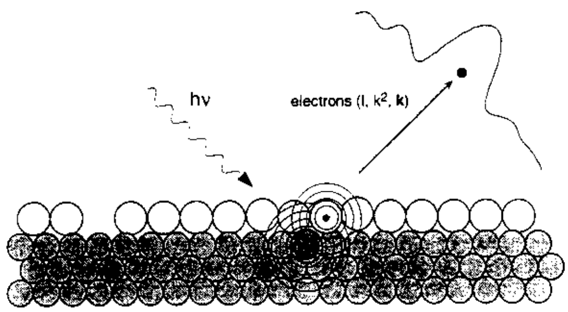

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Principles of X-ray photoelectron diffraction (XPD)

First observations of anisotropies in angular resolved X-ray Photoemission spectroscopy (XPS) date back to 1970 [1].

In combination with all features of XPS the large anisotropies and structural sensitivity promised this kind of experiments to become a versatile tool for the structural investigation of surfaces and interfaces. Later this method where the emission angle from the surface is scanned was named X-ray Photoelectron Diffraction (XPD). Today XPD has matured to a standard technique in surface science and a number of excellent reviews on the topic exist[2][3][4]. In particular it has to be mentioned, that the two-dimensional display of XPD data that cover all emission angles into the hemisphere above the surface pushed us to new insights in respect with interpretation of such data. [5]

One very appealing feature of XPD is the direct interpretation of the data. The underlying physical principle for this is forward scattering. Forward scattering manifests itself as a strong intensity enhancement along the axis between the emitter and the nearest neighbor atoms. It is a direct consequence of the attractive potential of the ion cores in the solid that focus the electrons along the axis between the emitter and the scatterer. It should be noted that this feature can be understood in a classical picture. In Transparency 1 the XPD Process is sketched in this view:

(i) An x-ray photon excites a particular core electron off the emitter atom. The angular distribution of the initial emission (source wave) is given by the selection rules of the photoemission process.

(ii) The photoelectron starts to propagate in the solid. As soon as the photoelectron starts to cross a neighbor atom it starts to feel the attractive Coulomb force of the positive ion core and gets deviated (focused) towards the emitter-scatterer axis.

From the solid angle that ion cores typically cover for an emitter and the strength of the Coulomb potential anisotropies i.e. intensity enhancements with respect to isotropic emission of a factor of two can be readily rationalized.

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[1]Siegbahn et al. Phys. Lett.A 32, 221 (1970)
[2]C.F. Fadley, in Synchrotron Radiation Research: Advances in Surf, Sci. ed. R. Z. Barach, Plenum New York (1990) Chap. 9.
[3]W.F. Egelhoff, Crit. Rev. in Sol. State & Mat. Sci. **16**, 213 (1990)
[4] S. A. Chambers, Surf. Sci. Rep. **16**, 261 (1992)
[5]Osterwalder et al. PRB, **41**, 12495 (1991)

Of course, a complete picture of the scattering process involves a fully quantum mechanical description of the photoelectron on all paths to the detector. A correct description of the scattering process was fist given by Liebsch [6]. Today multiple scattering codes may be downloaded from the World Wide Web [7].

The scattering of electrons thus involves as well backscattering and true, i.e. non zero order diffraction. Transparency 2 shows the scattering of an electron plane wave on an atom. The wave function (that is a solution of the Schrödinger equation) is the superposition of the incoming wave and the scattered wave. The scattered wave is modulated by the complex scattering amplitude f(θ). In the top part of Transparency 2 it is seen that the scattering amplitude is strongly peaked along the forward scattering direction f(θ=0). It can be seen that f(θ) depends on the kind of atom on which an electron plane wave is scattered. Furthermore interference effects as backscattering (θ=180°) and angular modulations in the scattering amplitude (that reflect the size of the atom) can be seen. These latter effects will however decrease in importance if the electron energies are increased.

In Transparency 3 all basic features of electron scattering from atoms in the energy regime between 0.1 and 2 keV are summarized. The data are taken from the Fink Tables [8].

In a) the trend of the elastic scattering cross section (as determined from the optical theorem) is given as a function of the atomic number Z. It is roughly proportional to Z.

In b) It is shown that the forward scattering amplitude f(θ=0) depends on the atomic number (see a)) but is increasing only weakly with energy.

In c) it is shown that the Backward scattering depends stronger on Z than the elastic scattering cross section shown in a).

In d) the energy dependence of the backscattering is shown. For large energies compared to a reference energy that describes the Z dependent ion core the backscattering amplitude is proportional to E^{-1} as expected from the reflection at a potential step. (see inset).

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[6] A. Liebsch, Phys. Rev. Lett. 32, 1203 (1974)

[7] http://electron.lbl.gov/mscdpack.html

[8] Fink et al. At. Data and Nuc Tables 4 129 (1972), At. Data and Nuc Tables 14 39 (1974)

Experiment

XPD Experiments can be performed in any standard XPS experiment. The sample has to have some cristallinity in order to provide XPD information. In addition to that a sample 2π manipulator has to be provided in order to rotate the emission angle in polar and azimuthal angle in front of the surface. Transparency 4 sketches the procedure of data acquisition in a typical XPD experiment.

Examples:

1) Forward Scattering: Co/Cu(111)

Transparency 5 shows the evolution of the Co/Cu(111) interface by means of XPD 2π scans.
In a) the clean Cu(111) substrate is shown. From the substrate diffraction features the absolute azimuthal orientation of the sample is given.
In the following 2π scans of the Co 2p signal are displayed.
At 0.5 ML Co deposition already clear forward scattering peaks for Co emission can be seen. It indicates a surface alloy formation with Co atoms in the 2nd layer. Between 5 and 10 monolayers(ML) of Co the three- fold symmetry of the fcc (111) substrate disappeared and the hcp like Co is found.

2) Interference with more than one Scatterer: h-BN on Ni(111)

Transparency 6 shows the XPD data from one single monolayer of h-BN grown on Ni(111).[9] From the three fold symmetry of the N1s and the B1s pattern it can be inferred that the h-BN layer formation is influenced as well by the second Ni layer i.e. that the system discriminates fcc from hcp adsorption sites.
The forward scattering peaks in the B1s emission and its absence in the N1s emission indicate that the h-BN layer is corrugated and that nitrogen terminates the surface.
In Transparency 7 the N1s diffraction pattern is shown once more: Due to the lack of forward scattering features the ring like first order diffraction

[9] Auwärter et al. Surf. Sci. in press (1999)

cones can clearly be seen. From their size and position the structural model can be derived.
It is worth mentioning that the diffraction intensity at an intersection point between two such constructive interference fringes does not sum up linearly. This nonlinear pile up of diffraction intensity is given due to the fact that the diffraction amplitudes get summed up at these intersections. This is a clear indication that two different scatterers can be involved in a coherent diffraction process.
Although the azimuthal orientation of the h-BN layer is determined, the data in Transparency 6 and 7 do not allow a statement on the absolute alignment of the h-BN layer with respect to the Ni(111) substrate. This is caused by the lack of visible backscattering features from the substrate. In the next example we will encounter the first observation of such backscattering features at an electron kinetic energy above 700 eV.

3) Backward Scattering: O on Rh(111)

Only recently the backward scattering features of oxygen that adsorbed on top of the a Rh(111) surface were found [10]. We assign this unexpected observation to the high Z of the substrate and to the low temperatures (and thus low Debye-Waller like loss of coherence that is most severe in the backscattering geometry) at which the experiment was conducted.
Transparency 8 shows the Rh(111) substrate and the O1s XPD pattern after different Oxygen dosages. The three ring like features in the oxygen diffraction pattern indicate backscattering cones of 11th diffraction order. These highest order diffraction features are most sensitive to the bond length of adsorbates and the accuracy of bond length determination may compete with other structural methods as LEED.
In the last 2π scan of Transparency 8 additional forward scattering features that stem from subsurface oxygen may be observed [11].

4) Holography: Suppression of Forward Scattering

As already implicit in the theory of Liebsch[6] photoelectron diffraction can be viewed as the recording of a hologram. (Transparency 9).

[10]Greber et al, PRL, **81**, 1654 (1998)
[11]Wider et al. Surf. Sci. 417, 301 (1998)

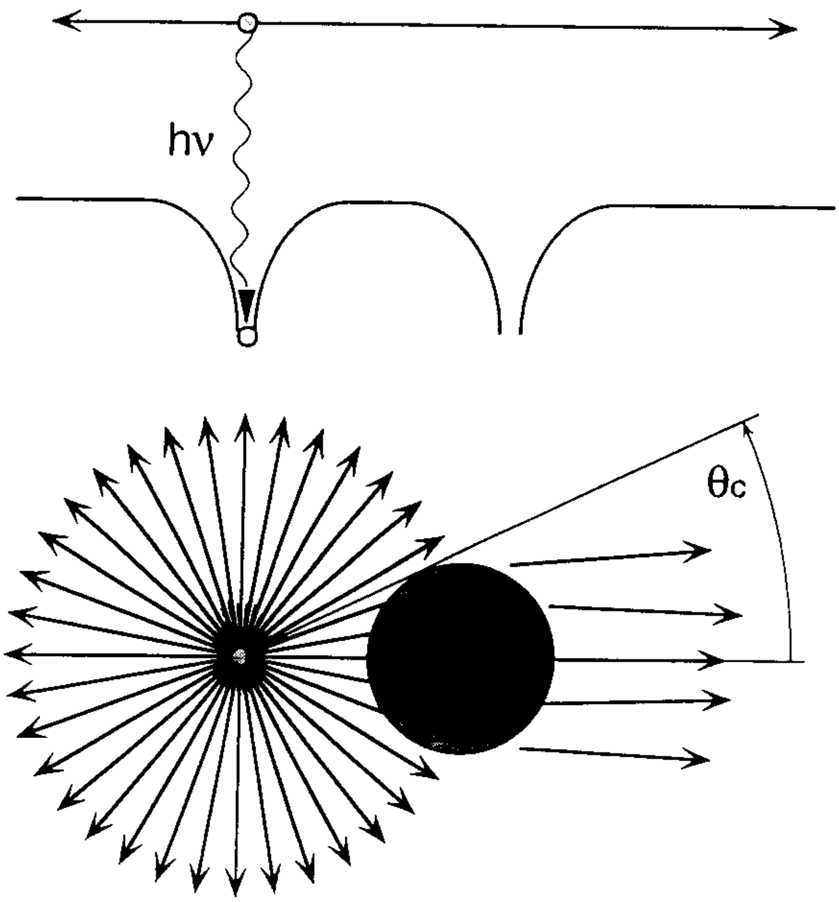
However photoelectron holography suffers from the strong forward scattering that contains no holographic information since it is a zero order diffraction feature. Only recently it was shown theoretically that if forward scattering is suppressed - by exploitation of the selection rules - holographic reconstruction from XPD-data of the real space should become feasible[12]. Transparency 10 shows experimental evidence of suppression of forward scattering. The data taken this month on the ALOISA beam line at ELETTRA indicate that for Al 2s emission in Al(111) the forward scattering along the [110] direction gets strongly suppressed if the electrons are measured near the node of the outgoing electron wave. This indicates that Gabor's idea of a new microscopic principle might be realized as well for small structures at surfaces by means of XPD.

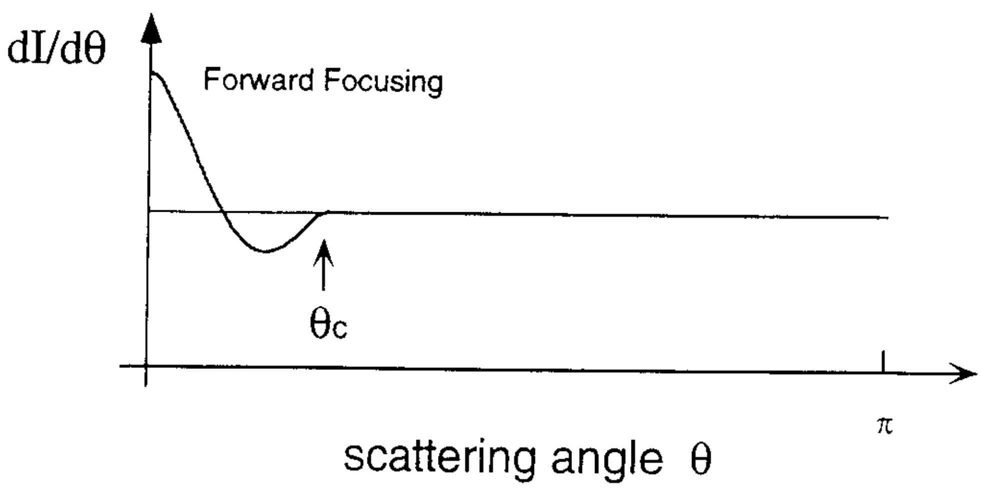
Conclusions

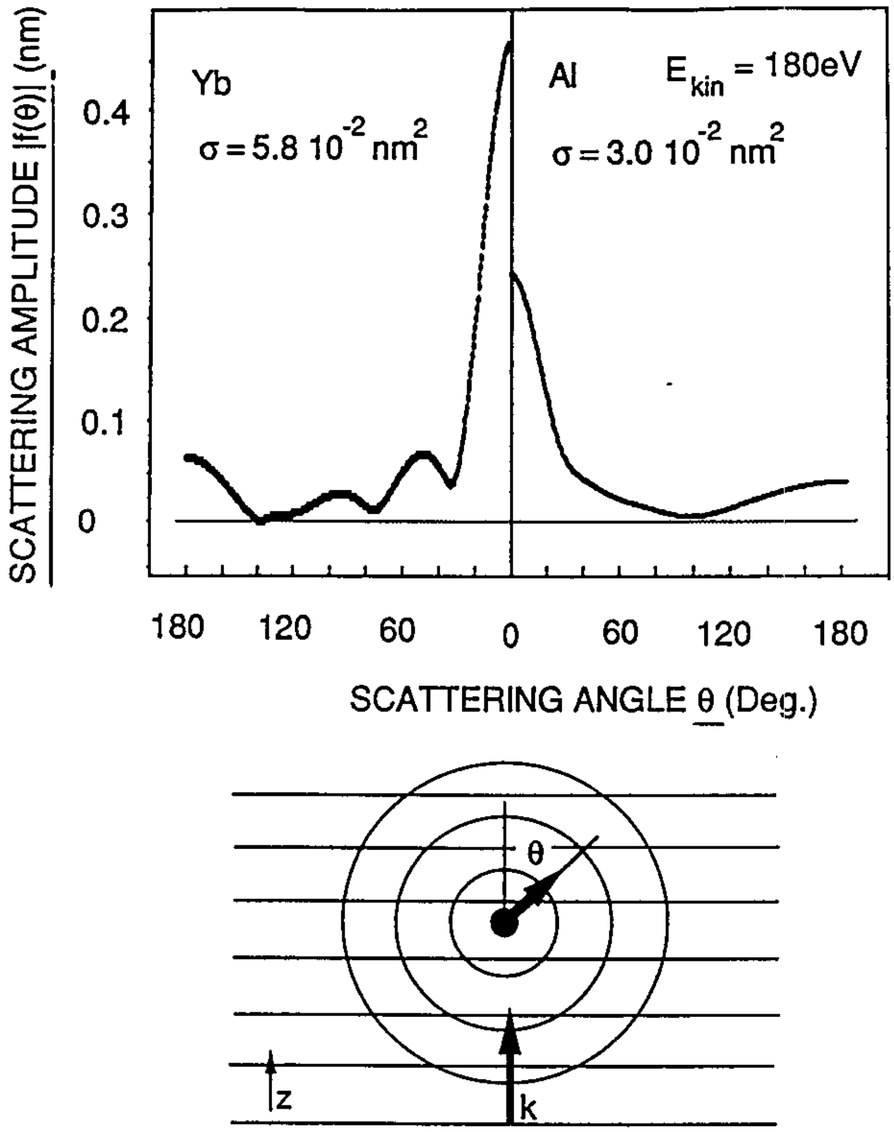
XPD has matured in a strong tool for structure determination of surfaces and interfaces. Forward scattering may be exploited for the search of minute amounts of subsurface species. Backward scattering on the other hand can give direct identification of adsorption sites of atoms or molecules.
If forward scattering is suppressed as it is if s-photoelectrons are measured near their node, holographic interpretation of such data should become feasible.

[12] Greber and Osterwalder, CPL, 256, 653 (1996); Prog in Surf. Sci. 53, 163 (1996)

Forward Focusing

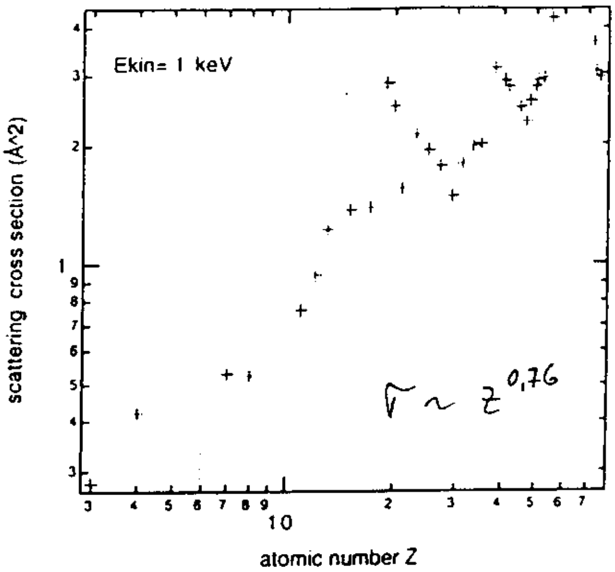




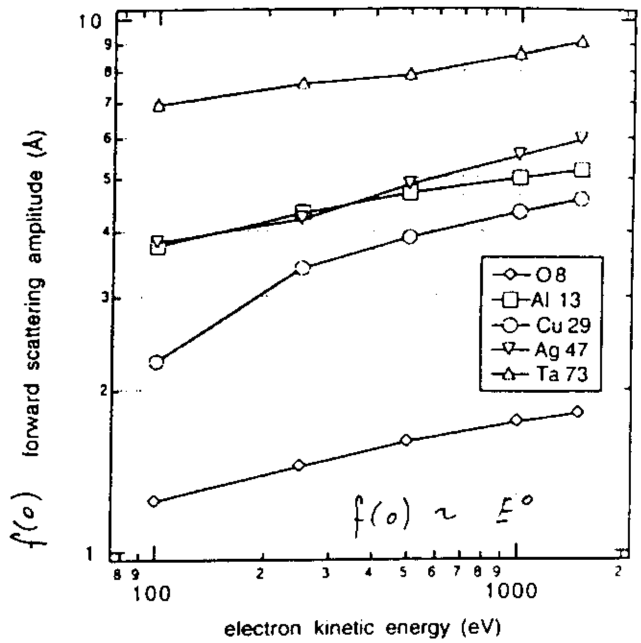


$$\Psi(r) \sim e^{ikz} + f(\theta)\,\frac{e^{ikr}}{r}$$

elastic scattering cross sections



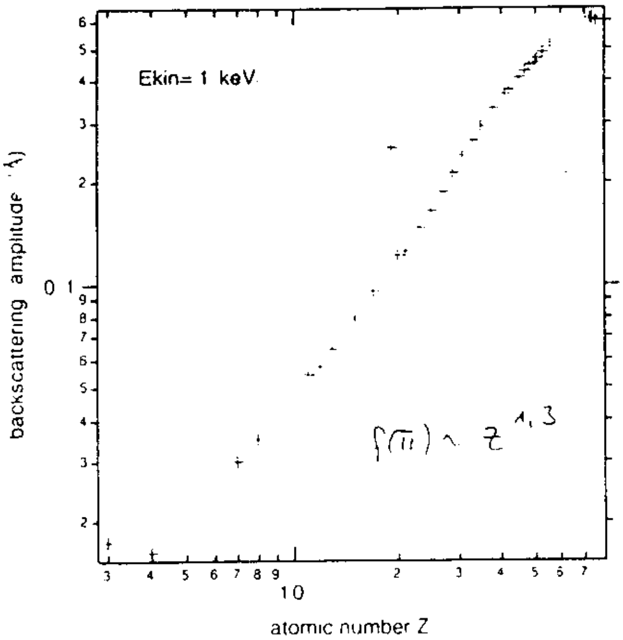
forward scattering

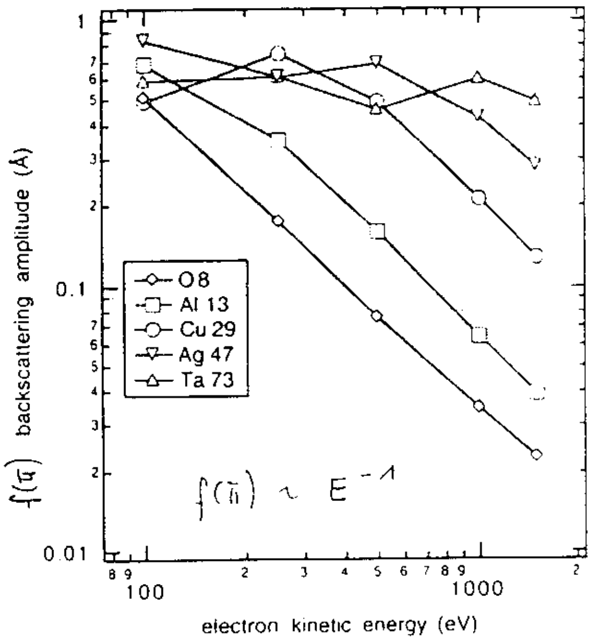


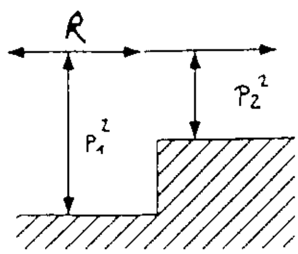
optical theorem:

$$\sigma = \frac{4\pi}{k} \, \mathrm{Im}\left(f(\theta=0)\right)$$

backward scattering:







$$R = \left(\frac{p_1 - p_2}{p_1 + p_2}\right)^2$$

Fink tables
At Data and Nuc Tables 4, 129 (1972)
At Data and Nuc Tables 14, 39 (1974)

XPD EXPERIMENT

$$A = \frac{I - I_{min}}{I + I_{min}}$$

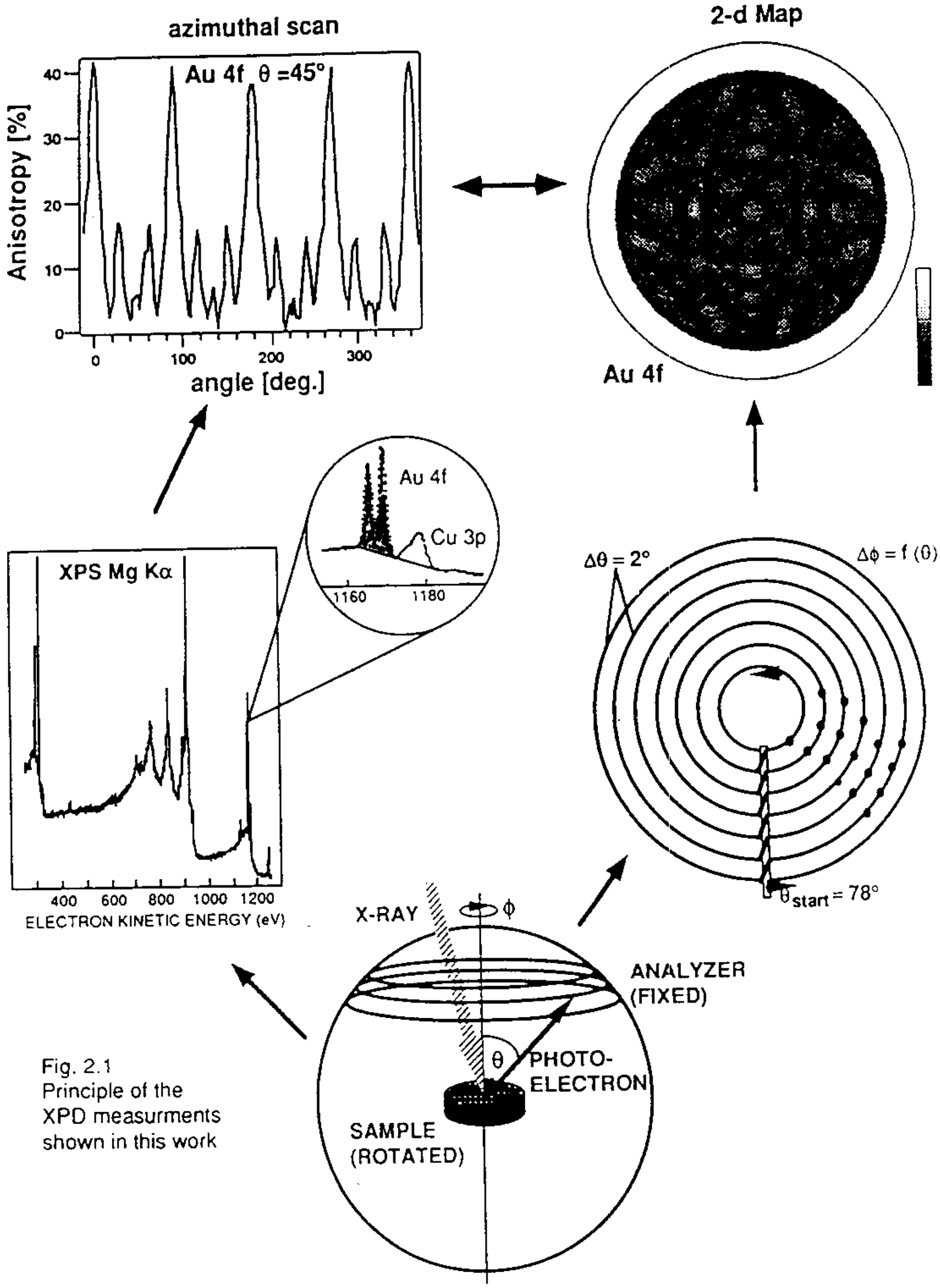
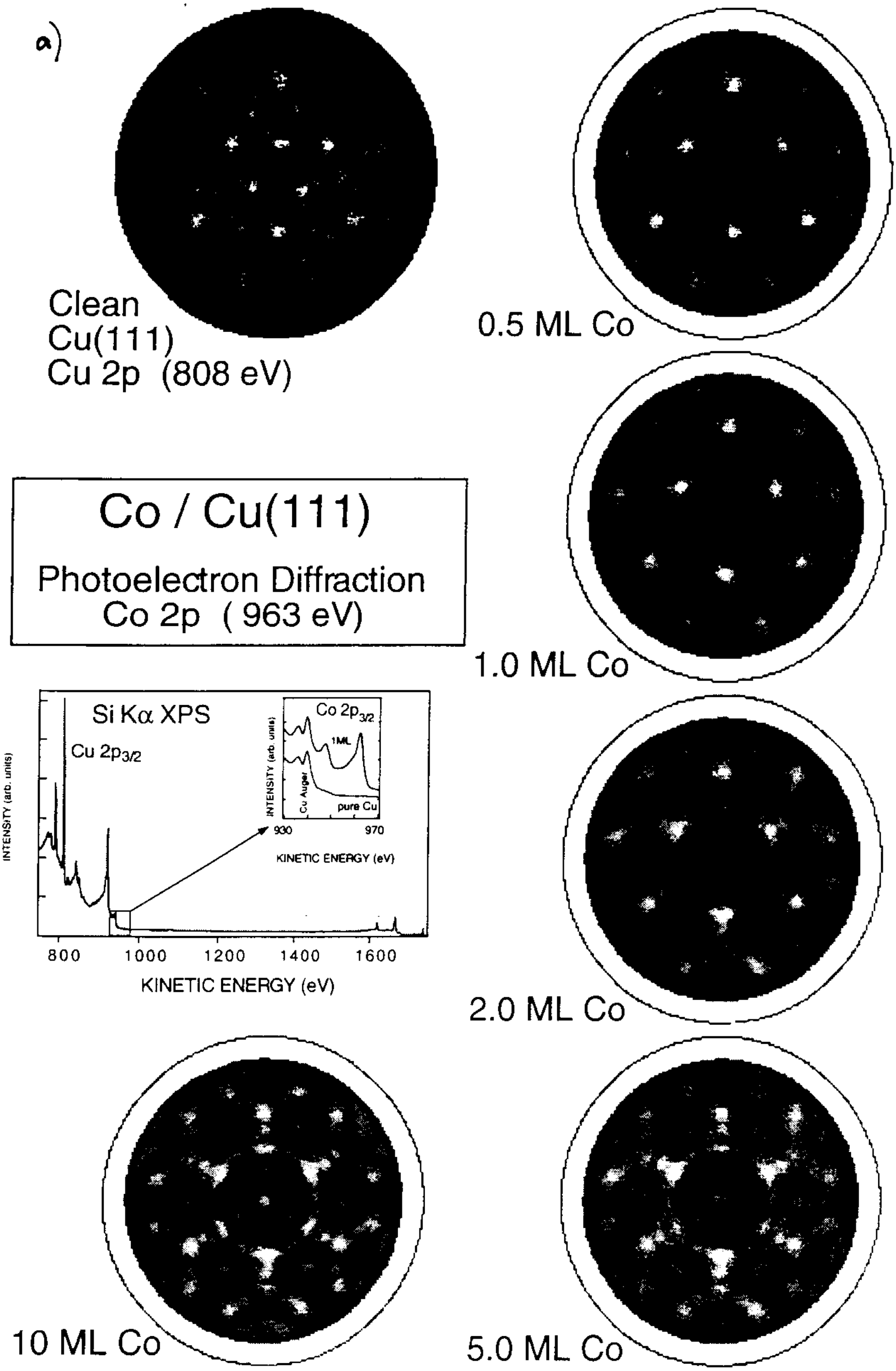
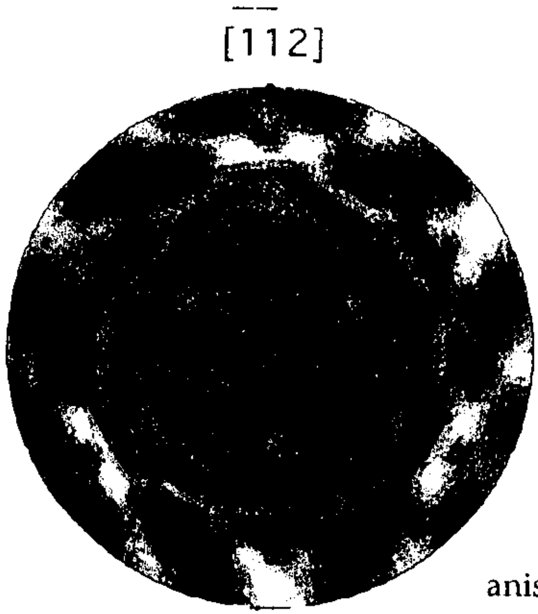


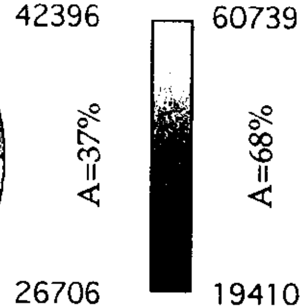
Fig. 2.1
Principle of the
XPD measurments
shown in this work

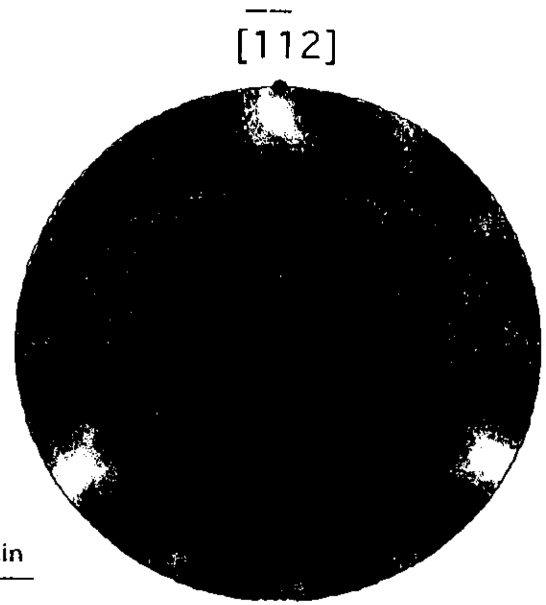
T5



a)
Clean
Cu(111)
Cu 2p (808 eV)
0.5 ML Co
Co / Cu(111)
Photoelectron Diffraction
Co 2p (963 eV)
1.0 ML Co
Si Kα XPS
Cu 2p3/2
INTENSITY (arb. units)
Co 2p3/2
1ML
Cu Auger
pure Cu
930
970
KINETIC ENERGY (eV)
800
1000
1200
1400
1600
KINETIC ENERGY (eV)
2.0 ML Co
10 ML Co
5.0 ML Co







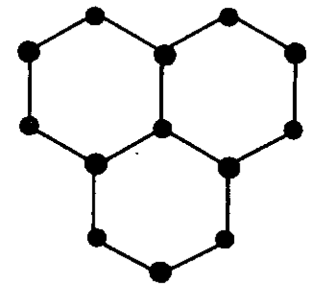
anisotropy $A = \frac{I_{max} - I_{min}}{I_{max}}$

h-BN/Ni(111): N1s 2π scan

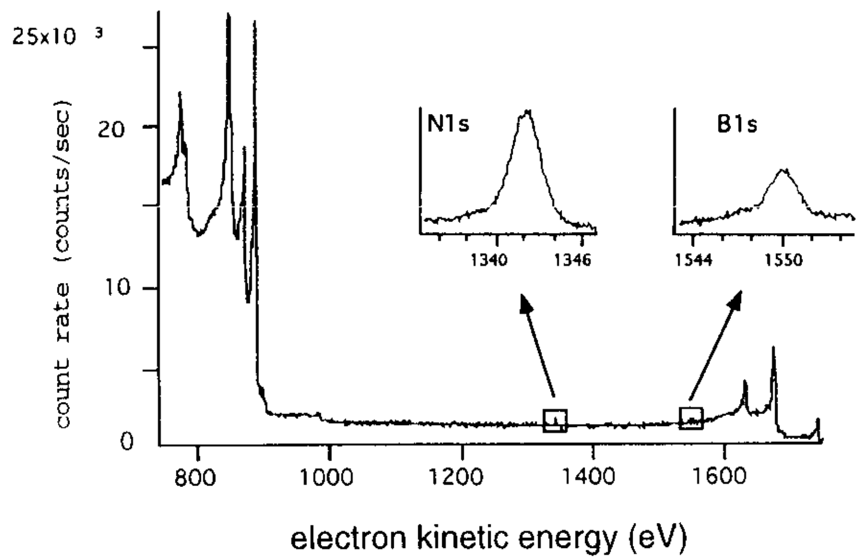
kin. Energy: 1341.9 eV, SiK α, t=23.8h

h-BN/Ni(111): B1s 2π scan

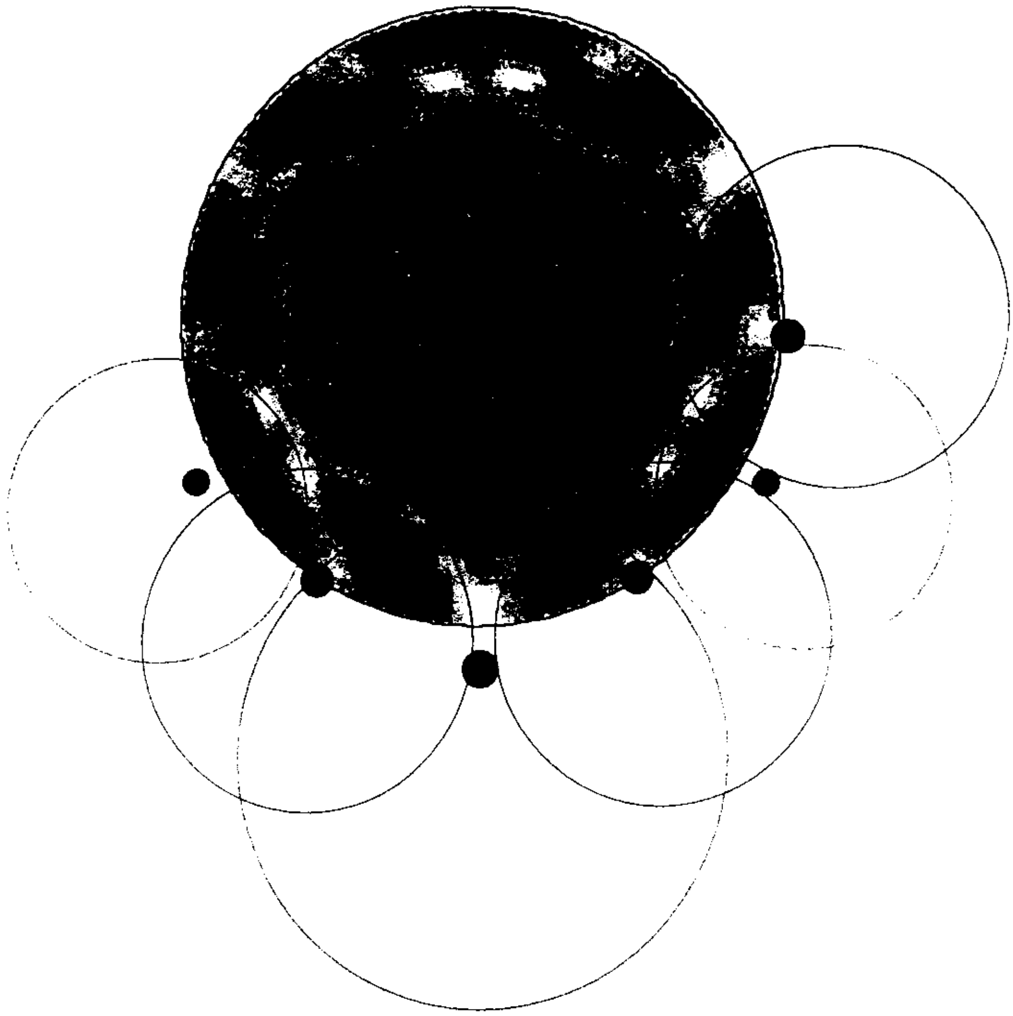
kin. Energy: 1549.8 eV, SiK α, t=37.8h

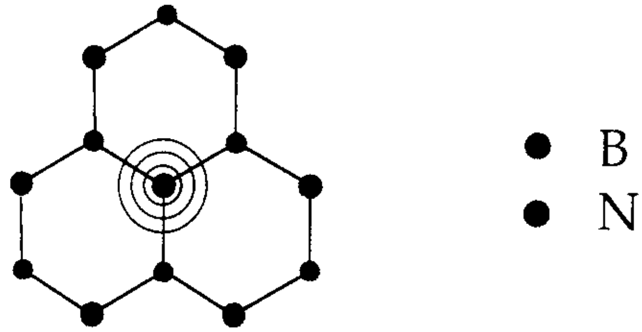


● B
● N



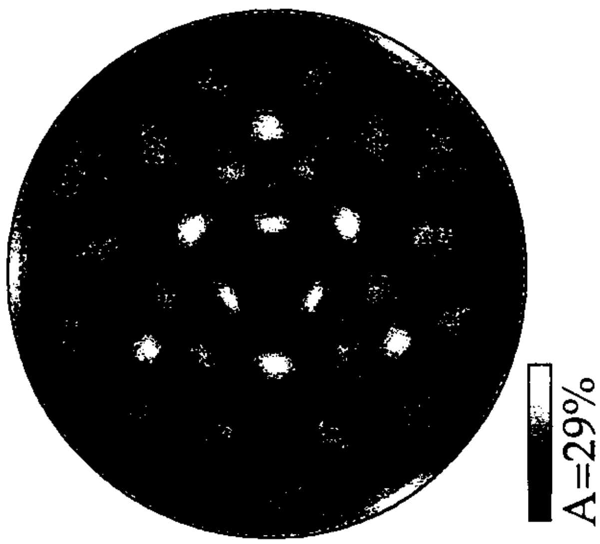
N 1s



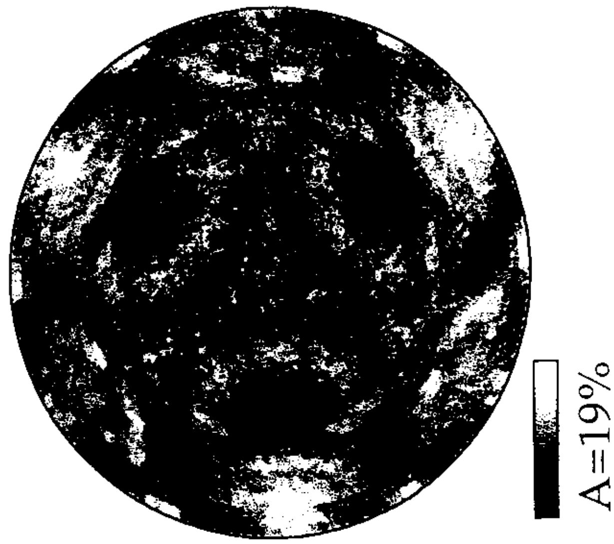


xpd measurements

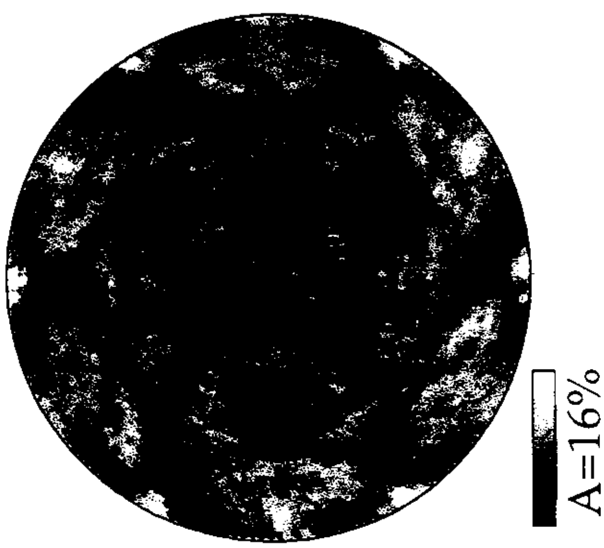
- oxygen dosage at room temperatur (10 L) or 470 K (10^2 - 10^5 L)
- measurements at 130 K



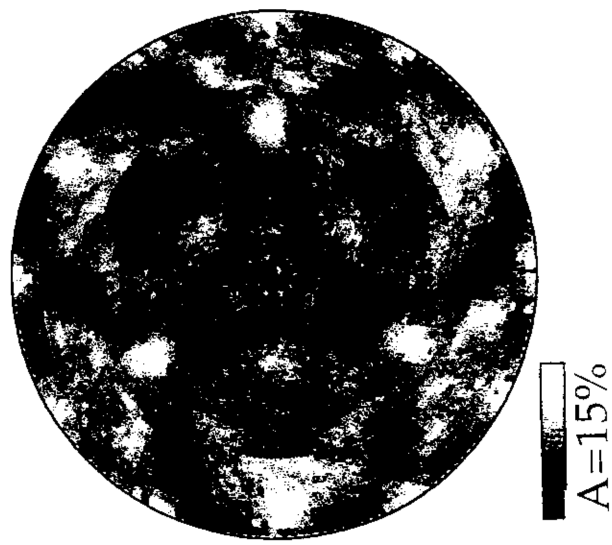
$Rh3d_{5/2}$ emission (E_{kin}=947 eV)



O1s emission (E_{kin}= 723 eV)
10 L O_2 at 300 K



O1s emission (E_{kin}= 723 eV)
10^3 L O_2 at 470 K

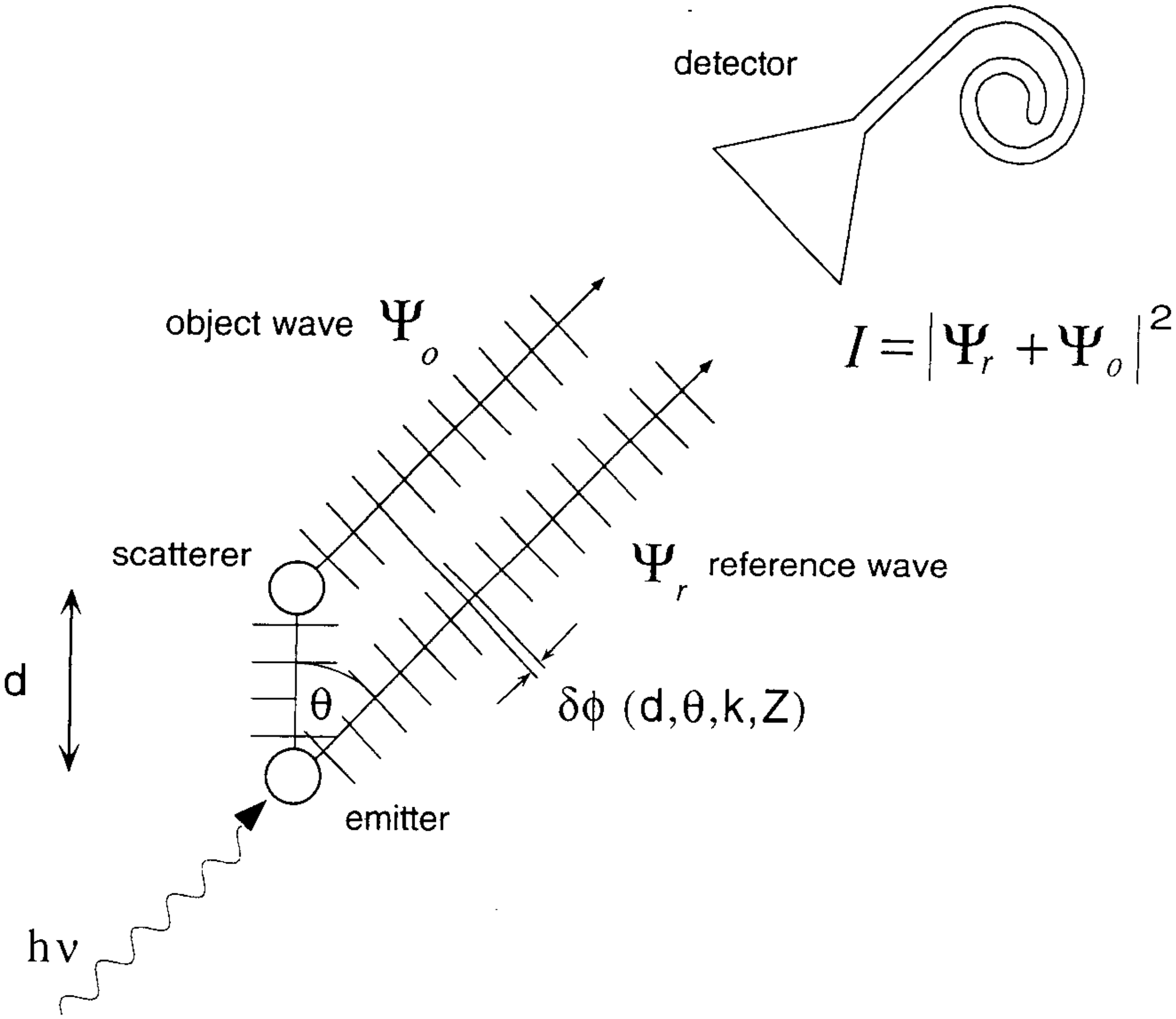


O1s emission (E_{kin}= 723 eV)
10^5 L O_2 at 470 K

$$\text{anisotropy } A = \frac{I_{max} - I_{min}}{I_{max}}$$

Photoelectron Holography

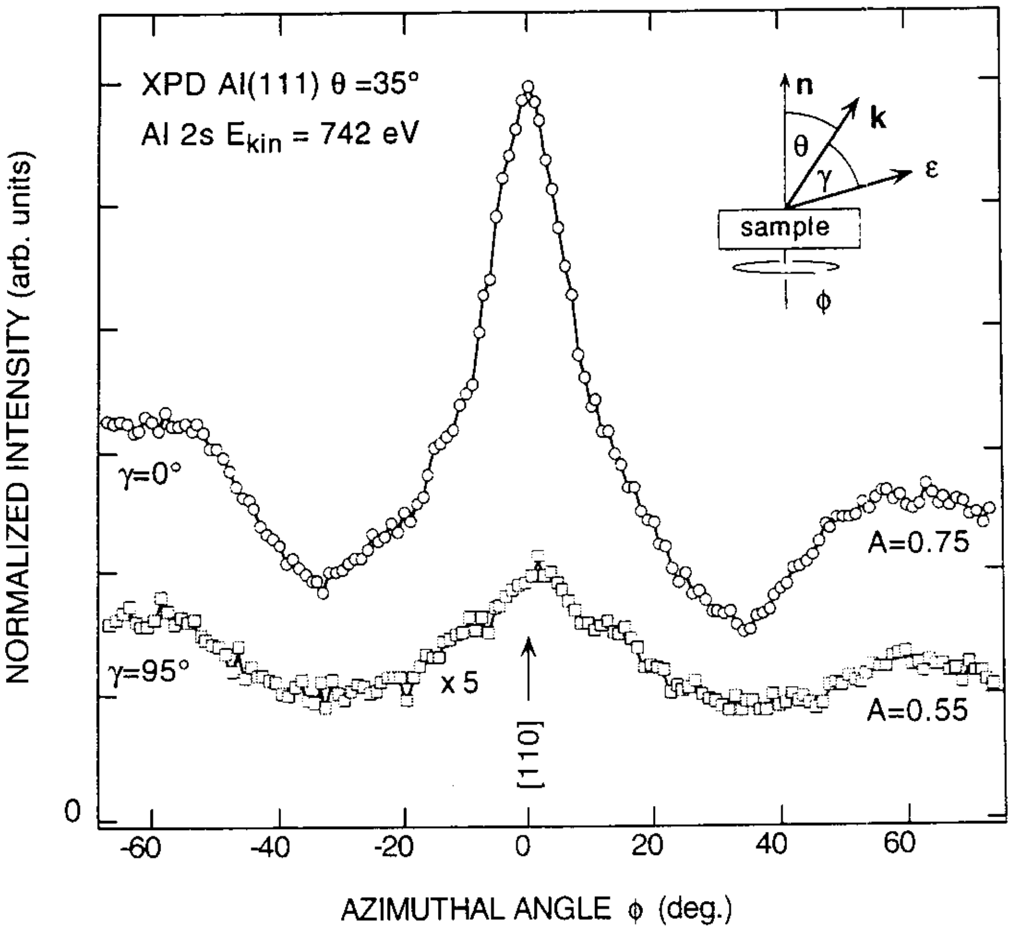
A. Szöke (1986)



phase condition for constructive interference:

$$kd\,(1 - \cos(\theta)) + \Delta\Phi(\theta,Z) = 2\pi n$$

Near Node Suppression of Forward Scattering



Data taken @ ALOISA, ELETTRA 0399