The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

2332

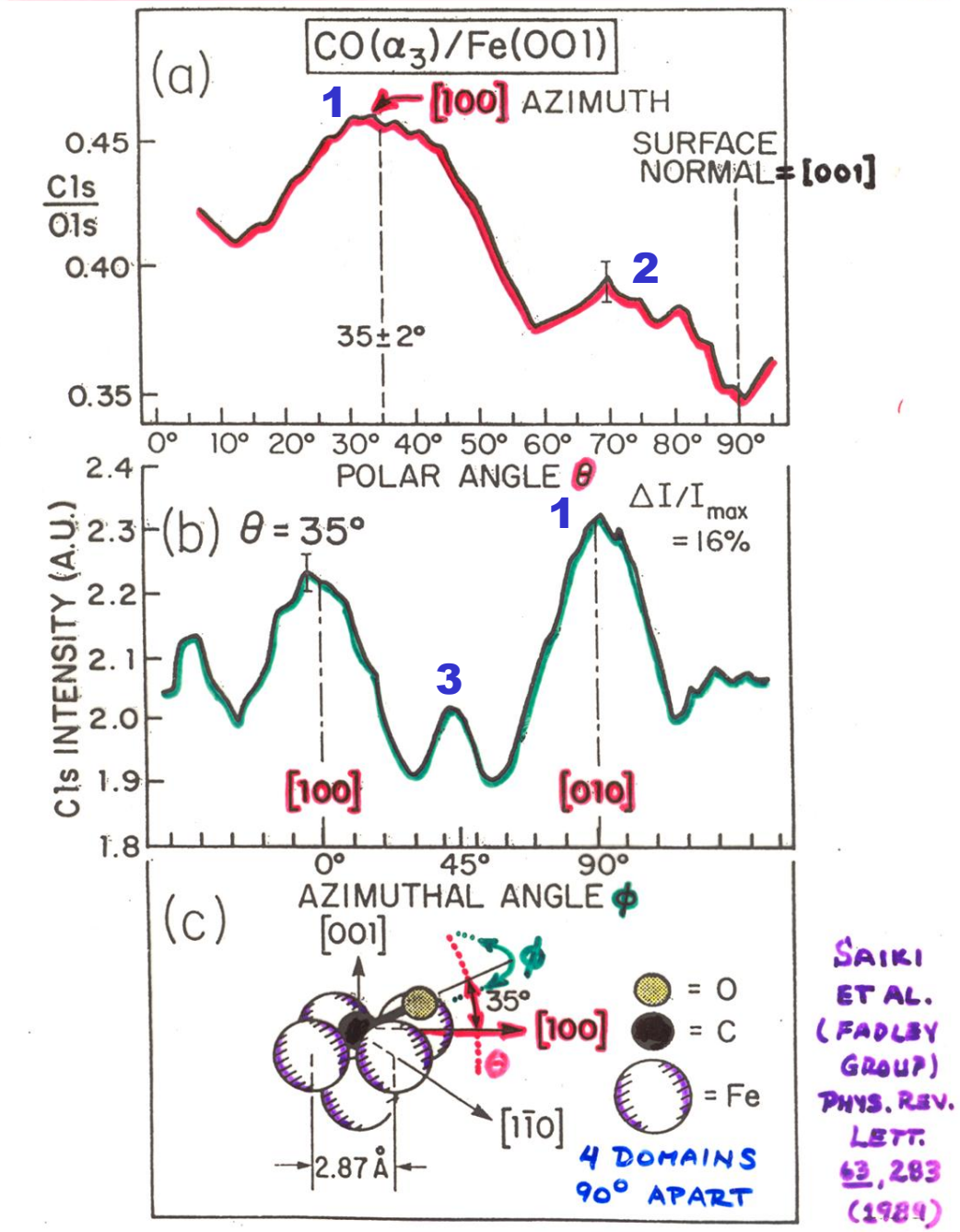
School on Synchrotron and FEL Based Methods and their Multi-Disciplinary Applications

19 - 30 March 2012

Additional information lecture 2

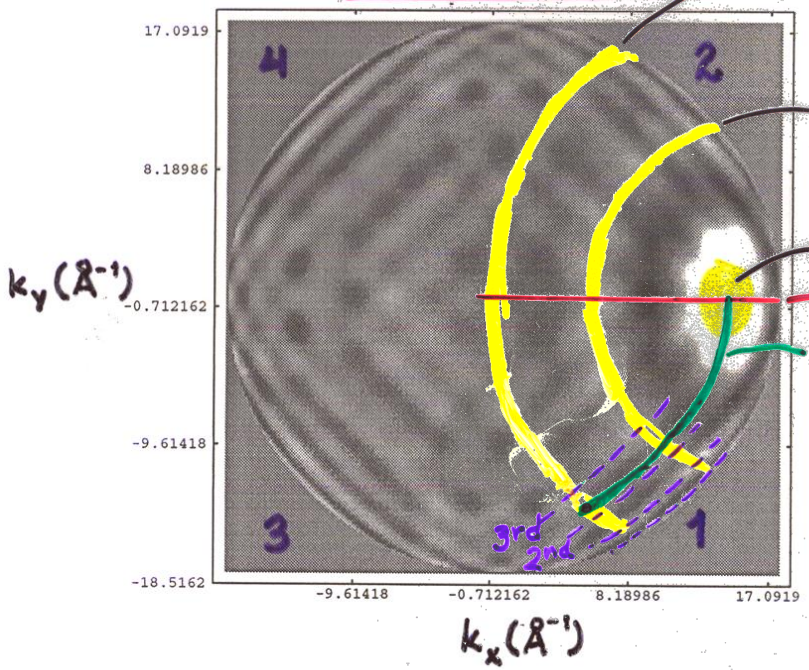
Charles S. Fadley
Univ. of California Davis & LBNL
USA

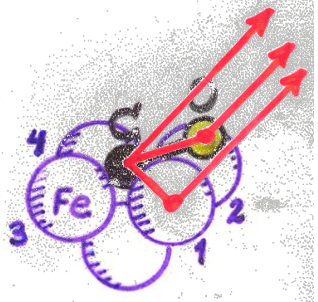
An illustrative example of x-ray photoelectron diffraction (XPD) and surface structure determination: CO on Fe(001)

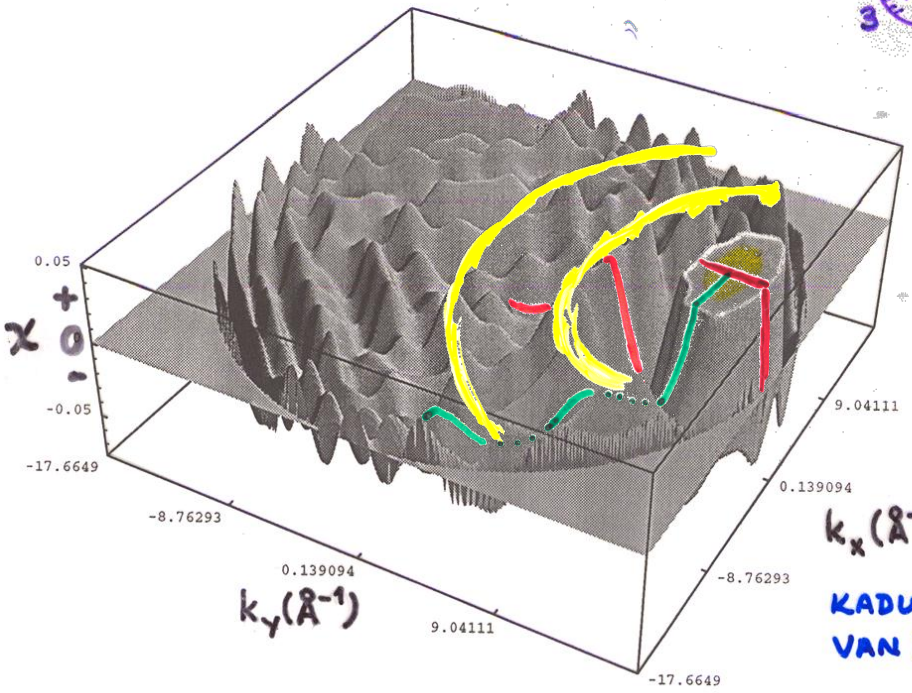


"Study of Surface Structures…"
Figure 9

CALCULATED 2π INTENSITY
$CO(\alpha_3)/Fe(001)$







KADUWELA, BUDGE, VAN HOVE, FADLEY

Online calculation of photoelectron diffraction patterns:

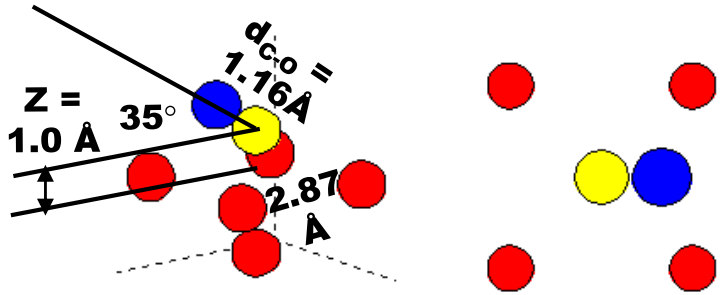
EDAC output for CO/Fe(001)

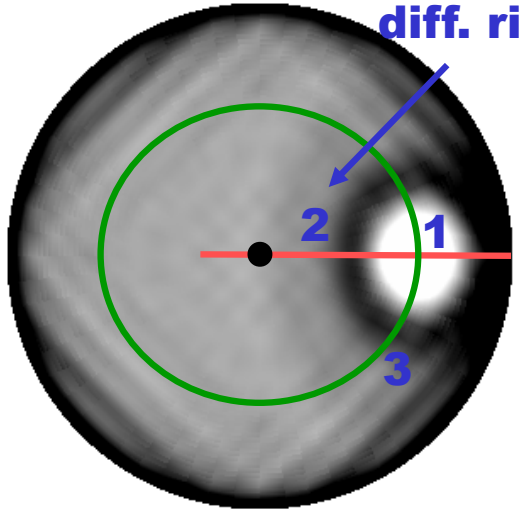
Click on the figure to download data.

http://csic.sw.ehu.es/jga/software/edac/a.html

Oxygen 1st order diff. ring

7 atoms:





Left: representation of the cluster rocking around a line parallel to the z direction and passing by the **emitter (yellow atom)**. The dashed lines stand for the xyz axes. **Right:** top view of the cluster, where the x/y direction (not plotted) runs along the horizontal/vertical screen direction. Different atomic species have been assigned the colors O, Fe.

Polar scan of photoemission intensity (logarithmic scale). White/black regions correspond to high/low intensity. The orientation is the same as in the top-view of the cluster. The distance to the center of the figure is proportional to the polar angle θ. The polar angle range is (0.0, 89.0) (in degrees).

Parameters used in the calculation:

N=7 atoms
Iteration order=4
l_{max}=25
V_0=10.5 eV
Photoelecton energy=1202 eV
p-polarized light
z_0=1.435 Å
Recursion iteration method

X 4 domains rotated by 90°

Electron Diffraction in Atomic Clusters

for Core Level Photoelectron Diffraction Simulations

Created by F. Javier García de Abajo (CSIC and DIPC, San Sebastian, Spain)
in collaboration with M. A. Van Hove and C. S. Fadley (LBNL, Berkeley, and UCD, Davis, California)

This site allows performing on-line photoelectron diffraction calculations. Multiple scattering (MS) of the photoelectron is carried out for a cluster representing a solid or molecule. Select the corresponding parameters and click on the "Calculate" button below to perform the actual calculation and to produce a plot of the calculated data (a separate window pops out to display it). A numerical data table can be downloaded by clicking on the resulting plot. Click on the different parameter names in blue to see fuller explanations. Click on the "Preview Cluster" button to display the currently selected atomic cluster (but without performing a MS calculation) or the button "Download Cluster" to download the currently selected cluster. Notice that the scattering phase shifts and excitation radial matrix elements are calculated internally for each cluster configuration, so that the user does not have to provide them. Please, read the terms of use and the restrictions on input parameters before using this site for the first time.

Terms and conditions of use

Terms of use Restrictions on input parameters Password: ********
A password is only necessary for large computation times (click here for more details). Leave it blank otherwise.

Title (optional): CO/Fe(001)

Cluster definition

The cluster and the list of emitters are defined by a list of commands with the following format (click here or on the items of this list for further details):

atom symbol $x\ y\ z$ layer symbol $x\ y\ z\ a\ b\ \alpha_1\ \alpha_2$

surface symbol $x\ y\ z\ a$ type emitter $x\ y\ z$

Fill in the text box with these commands according to the cluster specifications that you need. Some examples are provided by clicking here (you may cut and paste them to this page and modify them further).

```
atom O 0.95 0 1.66
atom C 0 0 1.0
surface Fe 1.435 1.435 0 2.87 bcc100
emitter 0 0 1.0
end
```

The cluster consists of a maximum of [7] atoms. (Warning: a finite number of atoms generally introduces symmetry breaking.)

The size of the cluster is determined by the distance d_{max} = [10] Å and the reference point x_0 = [0] Å, y_0 = [0] Å, z_0 = [0] Å.

See cluster shape for more details.

Plot cluster on output? (•) Yes ( ) No

Cluster shape: (•) Parabolic ( ) Spherical

[Preview Cluster*] [Download Cluster*]

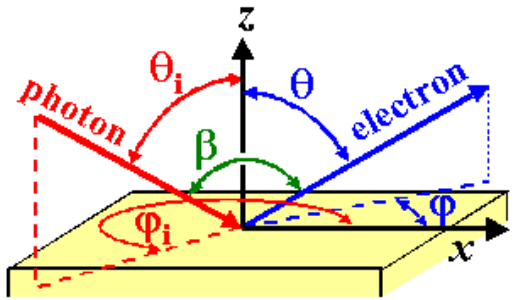
Geometry of beam and analyzer

Incoming beam parameters (see figure)

Polar angle θ_i = [0] degrees

Azimuthal angle φ_i = [0] degrees

Polarization:
(•) p-polarization
( ) s-polarization
( ) RCP
( ) LCP



Schematic representation of the geometry

Mobility of cluster beam, and sample (click here for details):
(•) Only the sample moves with constant β = [90] degrees
( ) Only the analyzer moves
( ) Both the sample and the analyzer move

Energy and angle scanning parameters (see figure above)

The following entries will select the range of photoelectron energies and angles of emission.

Energy scans for a given emission angle can be chosen by selecting more than one energy of emission and only one polar angle and one azimuthal angle (the value of each angle is then taken as the lower limit of the selected angular range, and the value of the upper limits are disregarded). In this case, the output is a 1D plot with the photoelectron intensity as a function of photoelectron energy.

Electron energy range: 1 equally-spaced value(s) of the electron energy from 1202 eV to 1202 eV

Polar angle: 50 equally-spaced value(s) of the polar angle θ from 0 degrees to 89 degrees

Azimuthal angle: 61 equally-spaced value(s) of the azimuthal angle φ from 0 degrees to 360 degrees

Type of 2D angular representation: ○ Linear scale ◉ Logarithmic scale

Type of azimuthal of polar angular representation: ◉ Cartesian ○ Polar

Photoelectron detector half-width acceptance angle = 0 degrees. The photoelectron intensities are angle-averaged over a cone with half aperture given by this parameter.

Multiple scattering parameters

Internal code parameters

Maximum orbital quantum number l_{max} = 25

Scattering order = 4

Iteration method: ○ Jacobi (regular MS) ◉ Recursion

Additional solid parameters

Inner potential V_0 = 12.4 eV

Electronic edge z_0 = 1.435 Å

8.1 eV from band struct. + work function = 4.3 eV = 12.4 eV

Inelastic mean free path: either choose a fixed value = 17.8 Å

or (if that last entry is <0) use the TPP-2M formula with parameters ρ = 8.91 g/cm^3, N_v = 10, E_p = 35.45 eV, and E_g = 0 eV

Temperature (K) = 300 and Debye emperature (K) = 450

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.)

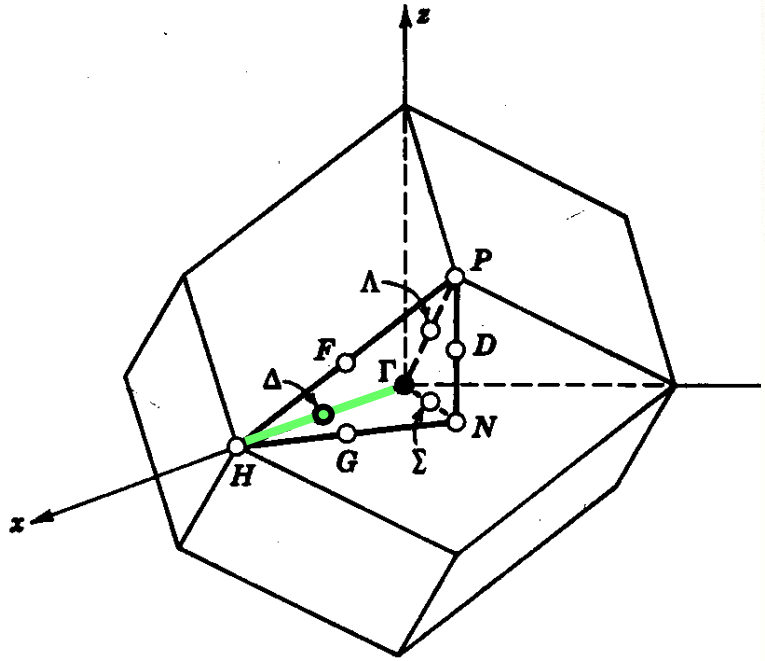
Atomic radius
= r_{MT}
= 0.5 n-n dist.

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

Density in g cm^{-3} (10^3kg m^{-3})
Concentration in 10^{22} cm^{-3} (10^{28} m^{-3})
Nearest-neighbor distance, in Å (10^{-10}m)

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

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



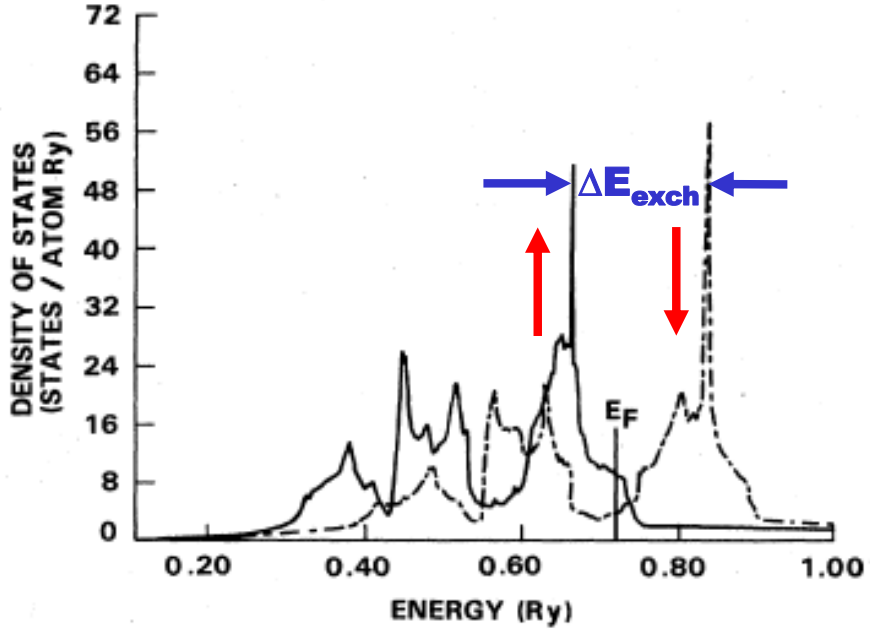
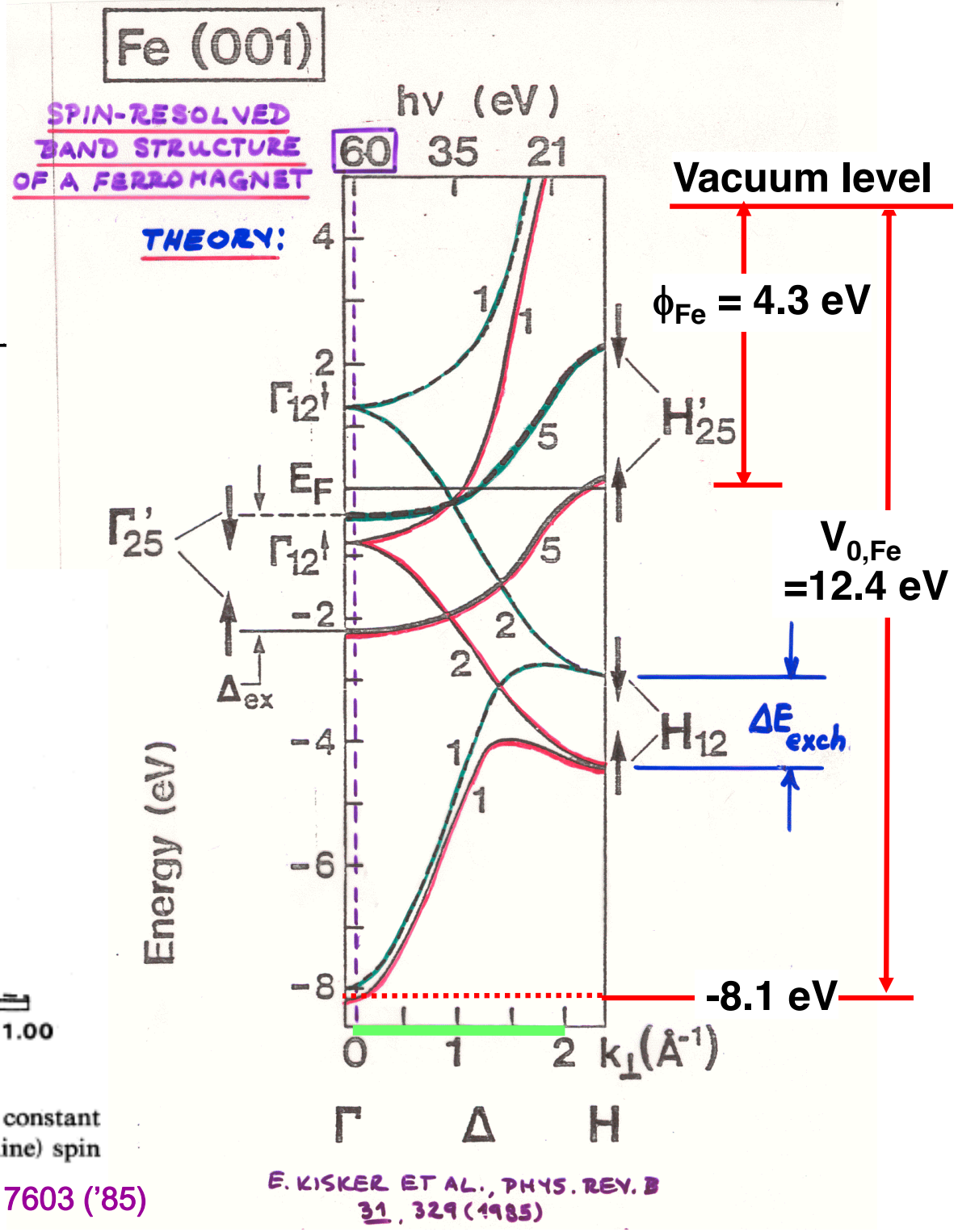


FIG. 4. Density of states at the equilibrium lattice constant of Fe for majority- (solid line) and minority- (broken line) spin states.

Hathaway et al., Phys. Rev. B 31, 7603 ('85)



Initial core-state quantum numbers

Radial matrix elements:

- (•) Automatic: core level (e.g. 1s, 2s, 2p, etc.) = 1s
- ( ) Manual: l_0=0, R_{l0+1}=1.0, δ_{l0+1}=0.0, R_{l0-1}=0.0, δ_{l0-1}=0.0

Calculate* | Download Input File** | Reset***

COMPUTATION TIME: the CPU time needed for the calculation using the default cluster and input parameters (use Reset to recover default input) is 1.24 seconds on a Pentium III @ 733 MHz. This gives a time scale to estimate the computation time for other input parameters, keeping in mind that it scales like $\sim (n_{scat} - 1)\, N^2\, (l_{max}+1)^3$, where N is the number of atoms in the cluster and n_{scat} is the scattering order. For reference, the default values are N=48, l_{max}=6, and n_{scat}=2, for which the above number is $7.9\ 10^5$.

IMPORTANT: READ THESE LINES BEFORE RUNNING THE CODE FOR THE FIRST TIME.

***The results will be plotted on a separate window.**

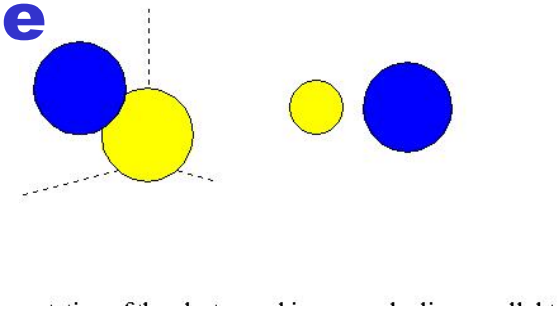
****The input file can be used to run the code locally, for which a copy of the code is needed. This can be obtained from F. Javier García de Abajo. An online version of the input-file manual is also available here.**

*****Reset all input values (including cluster specification) to the original settings.**

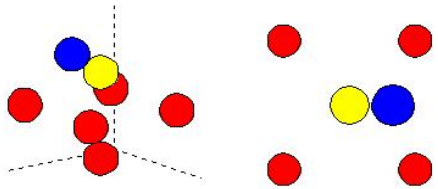
For comments/questions/suggestions, please contact F. Javier García de Abajo at jga@sw.ehu.es

CO/Fe(001)—Effect of CO height z above first Fe plane

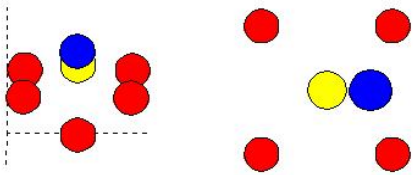
2 atoms: $Z = \infty$



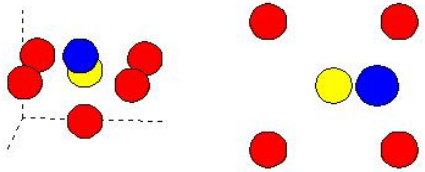
7 atoms: **1.0 Å**

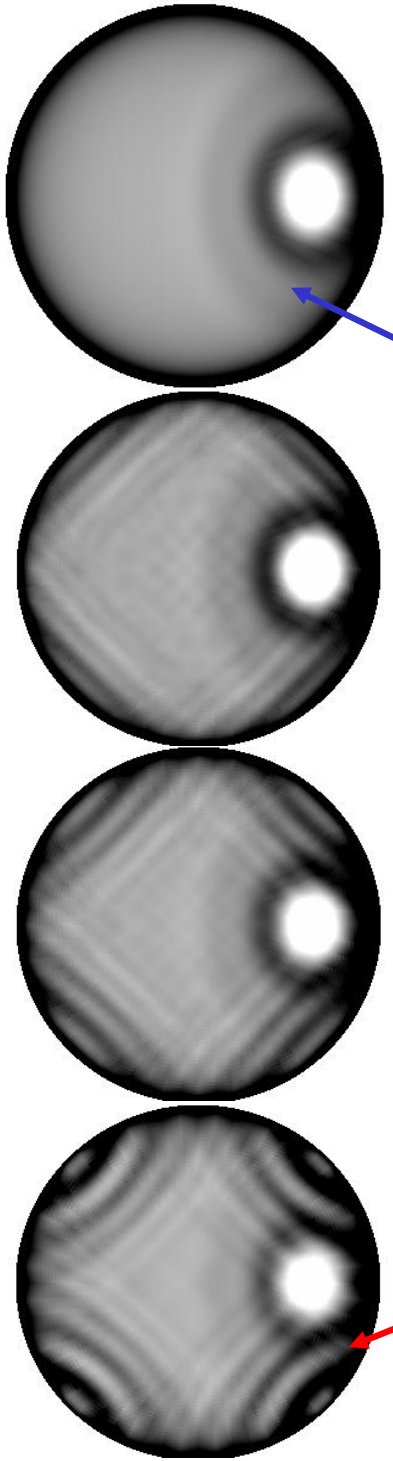


0.5 Å



0.0 Å

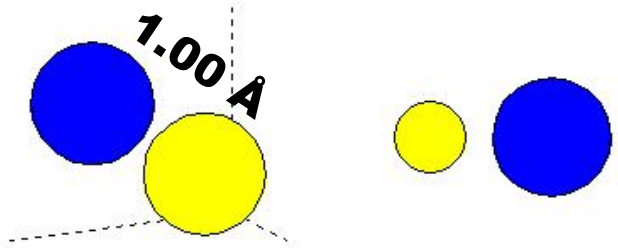


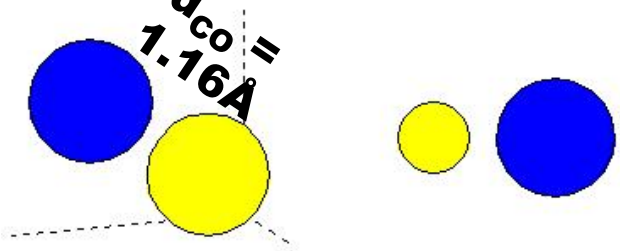


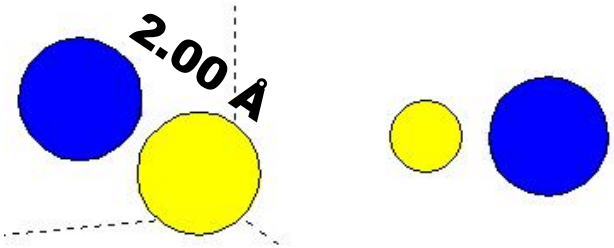
Oxygen-1st order diff. ring

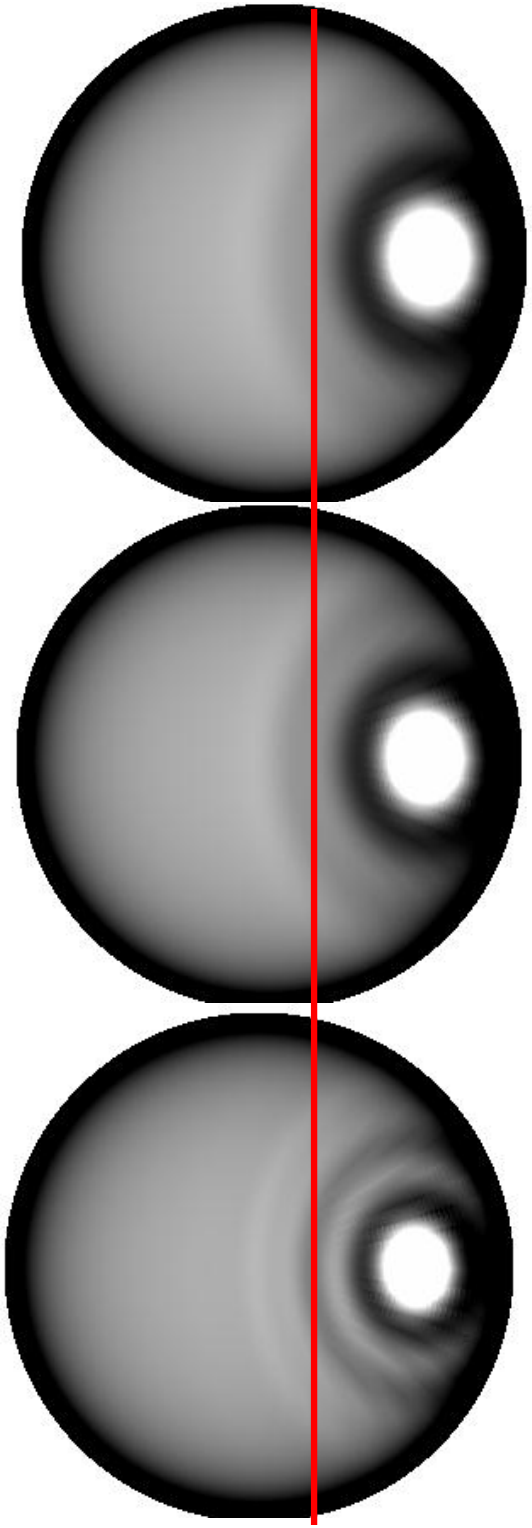
Iron-1st order diff. ring

CO/Fe(001)—Effect of CO bond dist.



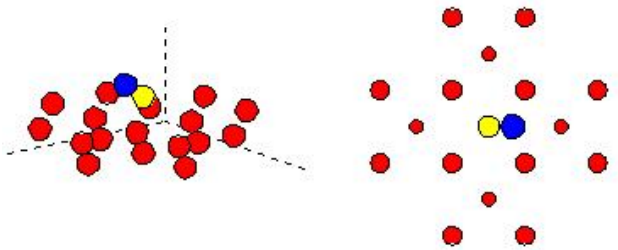


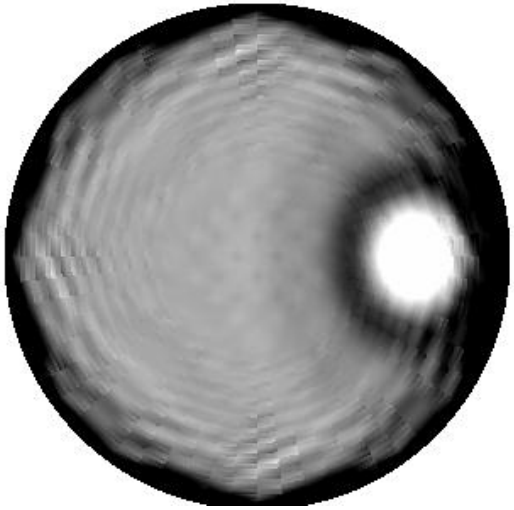




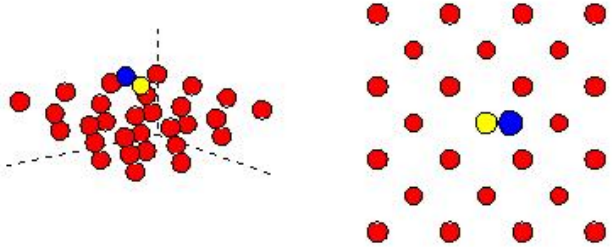
CO/Fe(001)—Effect of cluster size

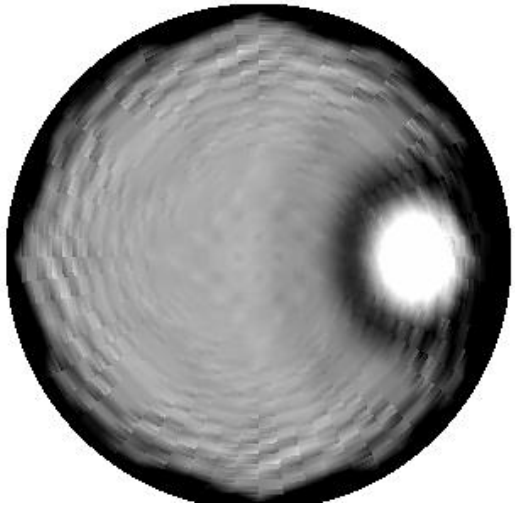
19 atoms:





31 atoms:

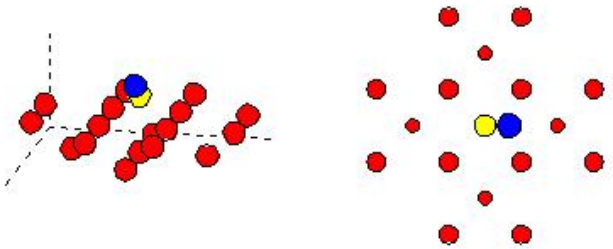


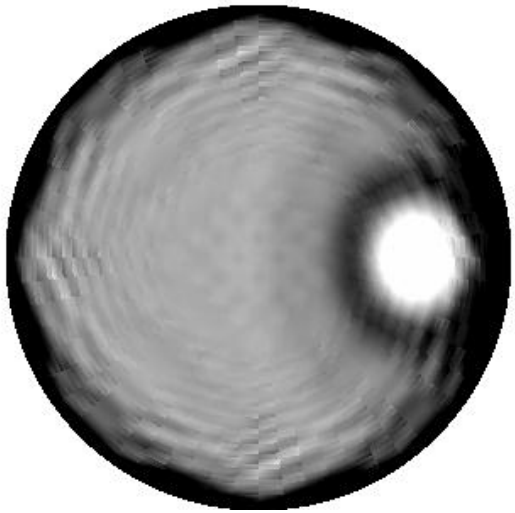


19 ≈ 31, AND SO “CONVERGED” AT 19 OR LESS

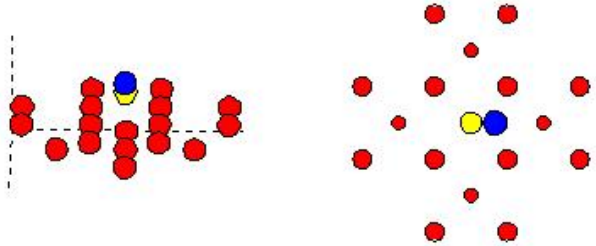
CO/Fe(001)—Effect of scattering order

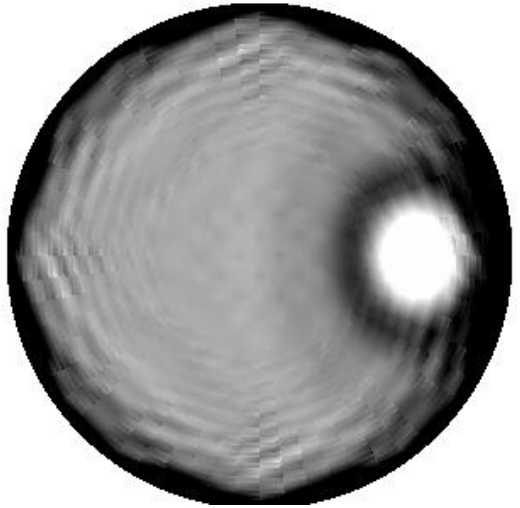
Single scattering:





Fourth order scattering:



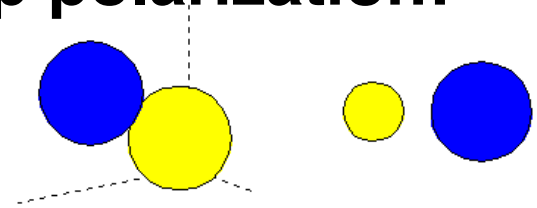


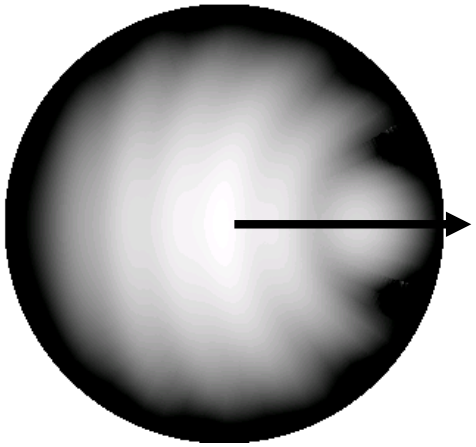
APPROX. CONVERGED AT SINGLE—FOR THIS PARTICULAR PROBLEM ONLY!

Effect of varying the polarization?: C 1s emission from CO

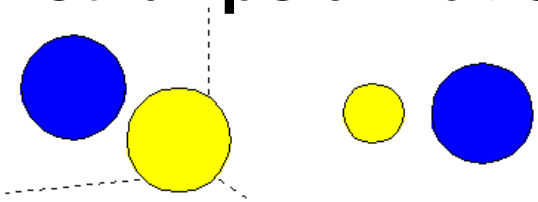
E_{kin} = 200 eV

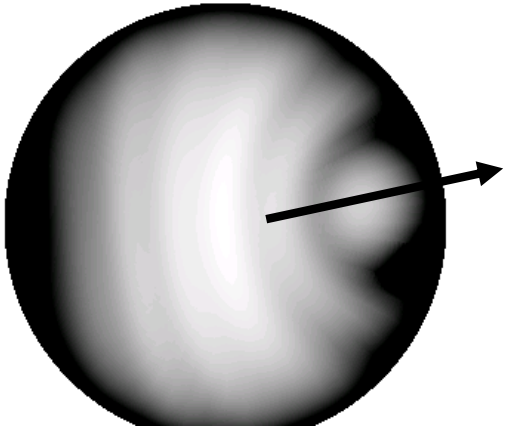
Linear p polarization:





Right circular polarization:





Circular dichroism in angular distributions (CDAD)—more later

Left circular polarization: