

# Matrix elements: the effect of polarisation on ARPES spectra

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measurements;

# Topics

## 1. Short introduction:

- the matrix elements;
- selection rules;
- beyond selection rules.

## 2. Experimental results:

- non-magnetic materials: Cu(111) and Ag(100);
- demagnetised magnetic materials: Ni(111) and Fe(100);
- magnetic materials: Ni(111).

## 3. CMDAD from Ni(111)

## 4. Conclusions

# 1. Introduction: the matrix element

Photocurrent:  $I = \sum_i |\langle f | H_{el} | i \rangle|^2 A_i(\vec{k}, \omega) f(\omega)$  From the Fermi Golden Rule

Product of three factors:

1. **the spectral function**: decides the existence of a peak, its intrinsic intensity and width;
2. **the matrix element**: modulates intrinsic intensities according the geometric experimental constraints;
3. **the Fermi-Dirac distribution function**: tells the occupation probability as a function of both temperature and  $E_F$ .

# Semi-classical theory

A non-relativistic system obeys the “free” Schödinger equation:

$$H_0 \psi_0 = \left( \frac{p^2}{2m} + V(r) \right) \psi_0 = E \psi_0$$

The fields of the incident radiation is treated as classical:

$$\vec{B} = \vec{\nabla} \times \vec{A} \quad \vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t}$$

$$\Phi = 0, \vec{\nabla} \cdot \vec{A} = 0 \quad \text{Coulomb gauge}$$

The interaction with an electromagnetic external field is introduced adding the vector potential to the momentum to  $H_0$ :

$$H = \left( \frac{1}{2m} \left( \vec{p} + \frac{e}{c} \vec{A} \right)^2 + V(r) \right)$$

Expanding the square:

$$\left( \vec{p} + \frac{e}{c} \vec{A} \right)^2 = \frac{p^2}{2m} + \frac{e}{2mc} \vec{A} \cdot \vec{p} + \frac{e}{2mc} \vec{p} \cdot \vec{A} + \frac{e^2}{2mc^2} |\vec{A}|^2$$

Second order

Because of the gauge choice

# Semi-classical theory

To first order in  $\vec{A}$ :  $\langle f | H_{el} | i \rangle = \frac{e}{2mc} \langle f | \vec{A} \cdot \vec{p} | i \rangle$

$\vec{A}(\omega, t) = \vec{\sigma} e^{i(\omega t - \vec{q} \cdot \vec{r})}$  Plane wave form for  $\vec{A}$

$\vec{\sigma}$ : light polarisation (electric field),  $\vec{q}$  photon momentum

UV light (5-100eV):  $\lambda \gg r_0$ , exponential  $\sim 1$ : dipole approximation

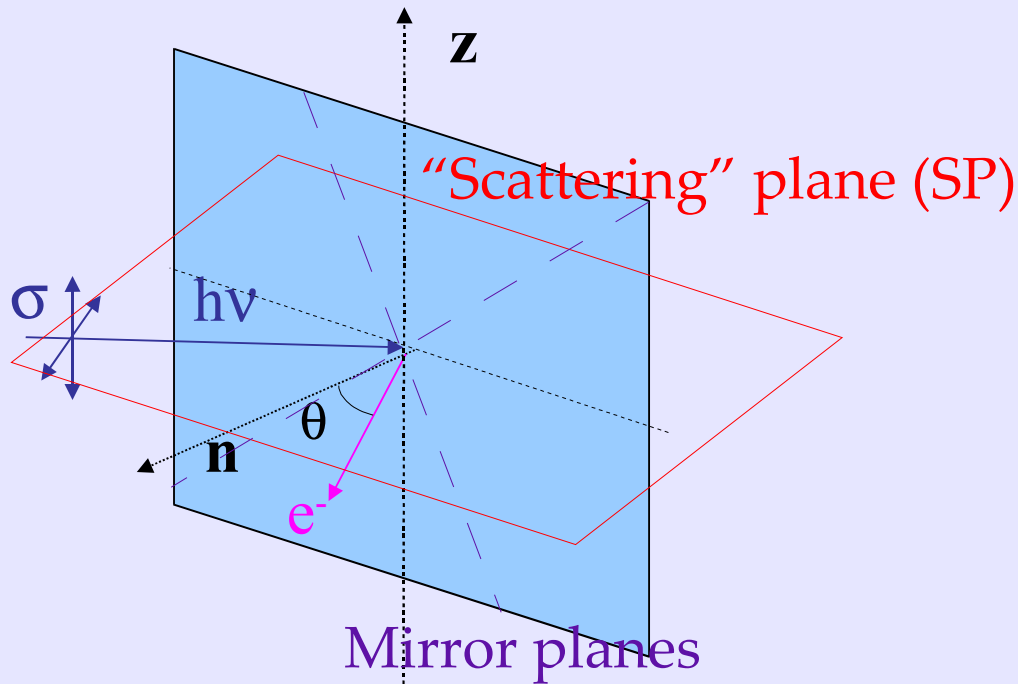


$$\langle f | H_{el} | i \rangle = \int \psi_f^\dagger (\vec{\sigma} \cdot \vec{p}) \psi_i dV$$

**Matrix element in the dipole approximation**

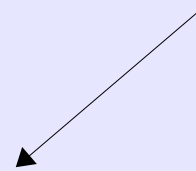
Quadrupolar matrix elements and surface emission are left out,  
*but they can play a role*

# Geometry: “scattering” and crystal planes



$\psi_i$  symmetries are fixed by the crystal lattice.

The  $\psi_f$  symmetry depends on the experiment geometry.



$\theta=0$ , normal emission:  $\psi_f$  must be centre-symmetric;

$\theta \neq 0$ , but sample a mirror plane coincides with the SP:

$\psi_f$  is mirror symmetric and  $\psi_i$  has to obey **selection rules**

$\theta \neq 0$  & no mirror planes coincide with the SP: **symmetry mixing**

# Parities from matrix elements

The symmetry of  $H_{el}$  is fixed by the polarisation vector reflection properties with respect to the scattering plane:

horizontal polarisation: even

vertical polarisation: odd

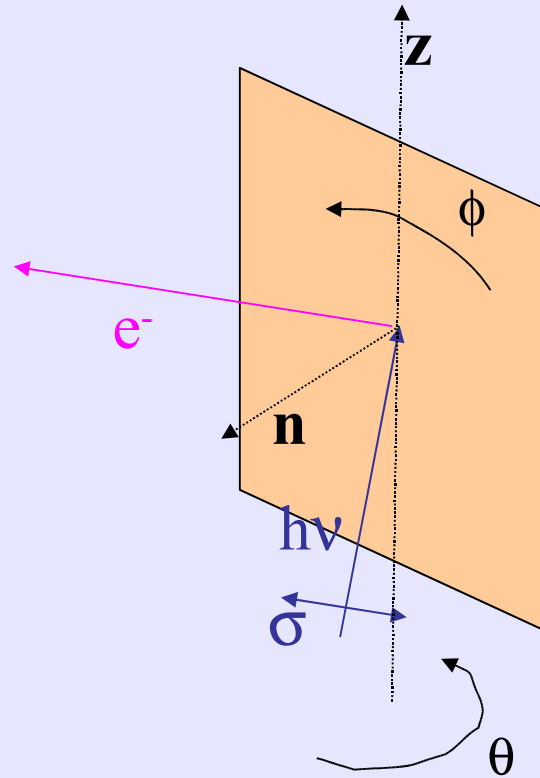
Assuming the final state as a free electron, it is invariant by reflection about the scattering plane: always even

Fixing the light polarisation and the emission direction automatically fixes the initial states contributing to the matrix elements.

Photoemission with different polarisation provides a direct measure of the ground state wavefunction parities.

# Beyond selection rules

The validity of selection rules is restricted to the high symmetry planes.



Azimuth rotation allows to map the whole reciprocal space. The intensities measured are the electron angular distributions (AD)



# Angular distributions of photoelectrons

Many AD can be measured depending on the light polarisation and sample magnetisation:

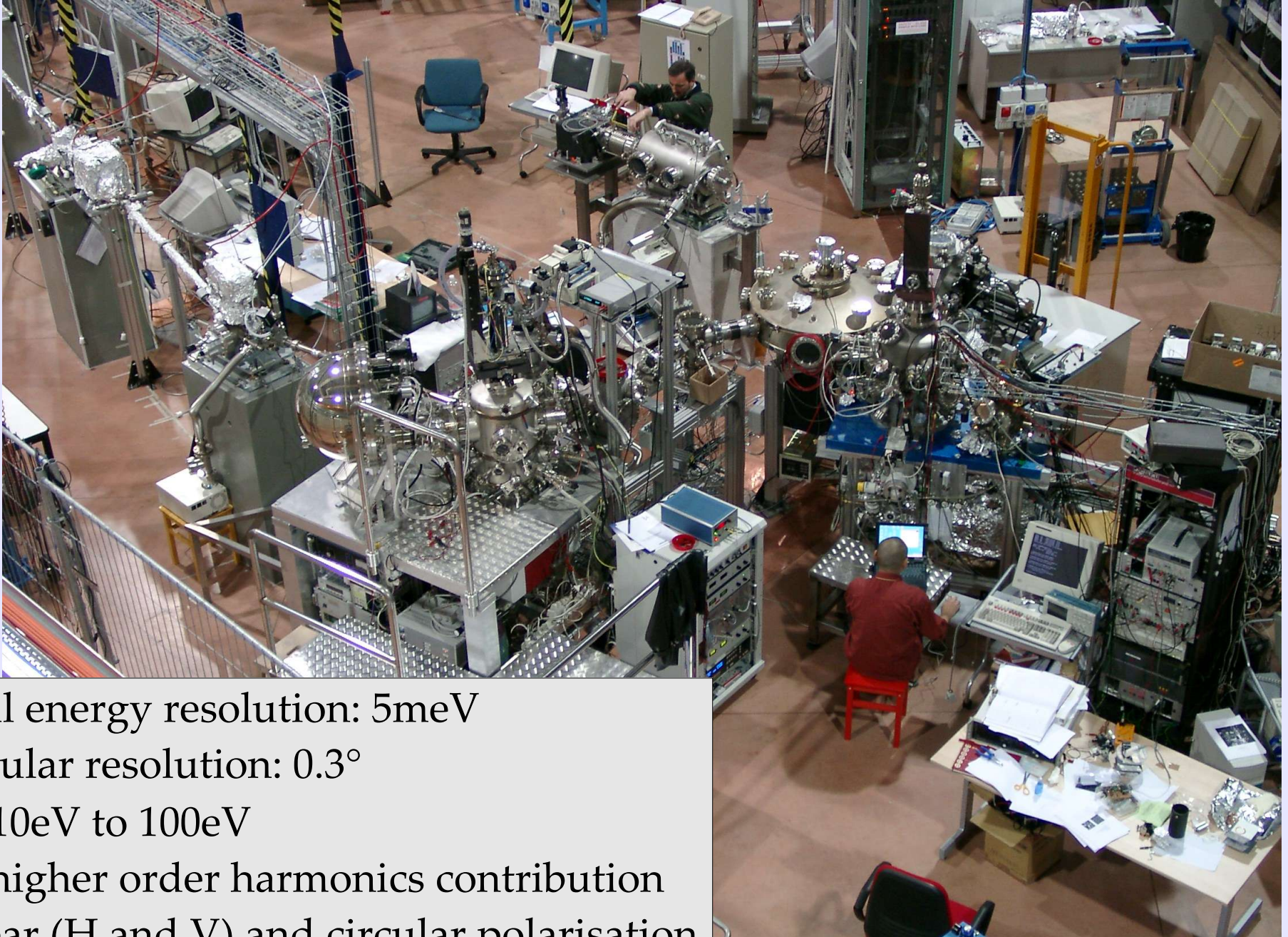
Linear Dichroism in the Angular Distribution (LDAD);  
Circular Dichroism in the Angular Distribution (CDAD);

Any material shows them: extensions of the selection rules

Magnetic Linear Dichroism in the Angular Distribution (MLDAD);  
Magnetic Circular Dichroism in the Angular Distribution (MCDAD);

Only detectable on magnetic materials in chiral geometries

# APE beamline



Total energy resolution: 5meV

Angular resolution: 0.3°

h $\nu$ : 10eV to 100eV

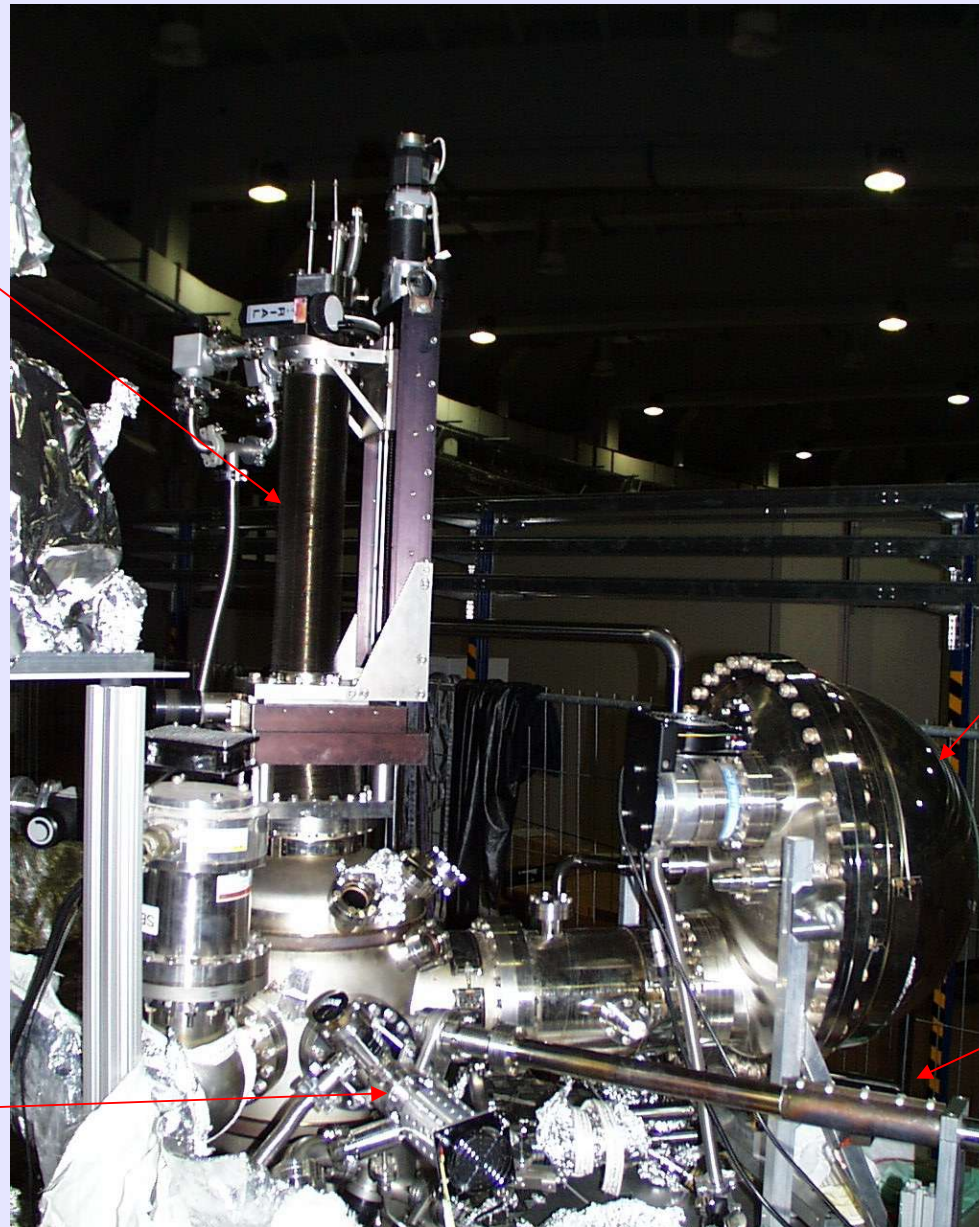
No higher order harmonics contribution

Linear (H and V) and circular polarisation



# APE-LE beamline endstation

Manipulator



Scienta SES 2002

Synchrotron beam

He Lamp

## 2. Experimental results: Cu(111)

The simplest material! The filled  $3d$  shell kills final-state effects

Since the low  $Z$ , relativistic corrections are very small

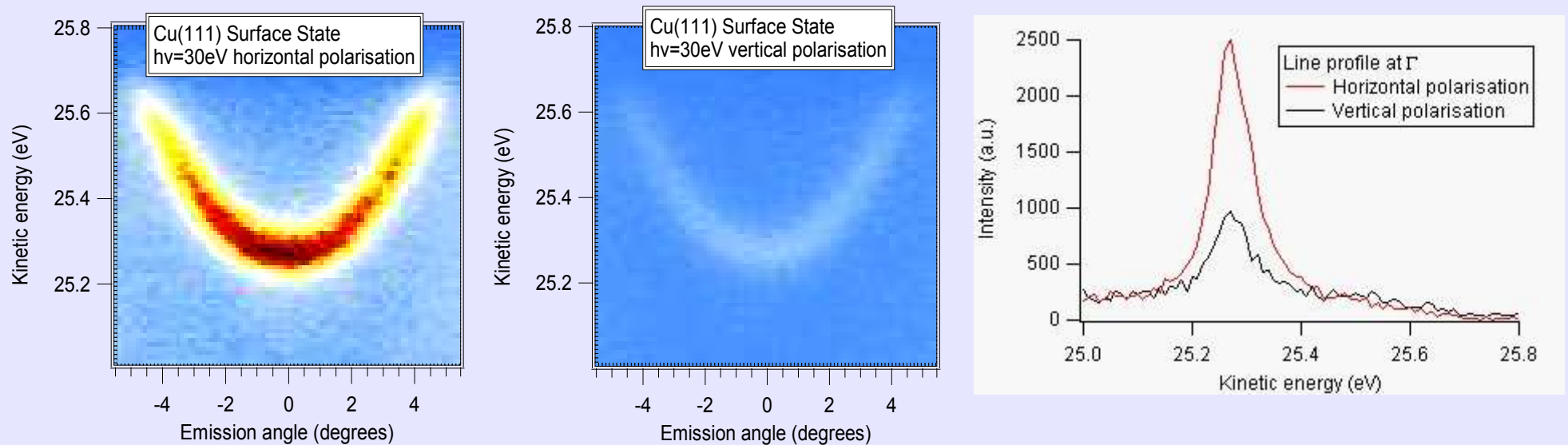
Nevertheless, matrix-elements effects are very strong

Surface state of Cu(111):

1. bidimensional electronic state (constant DOS);
2. parabolic dispersion law
3. binding energy at  $\Gamma$ :  $\sim 400\text{meV}$ .

The spectra have to be interpreted in terms of matrix element effects:  
all the other terms of the photocurrent are already determined

# Cu(111) surface state with linear light

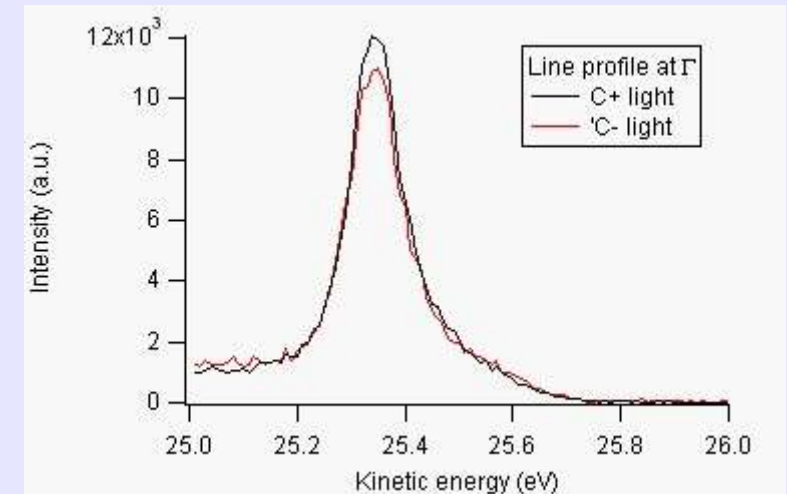
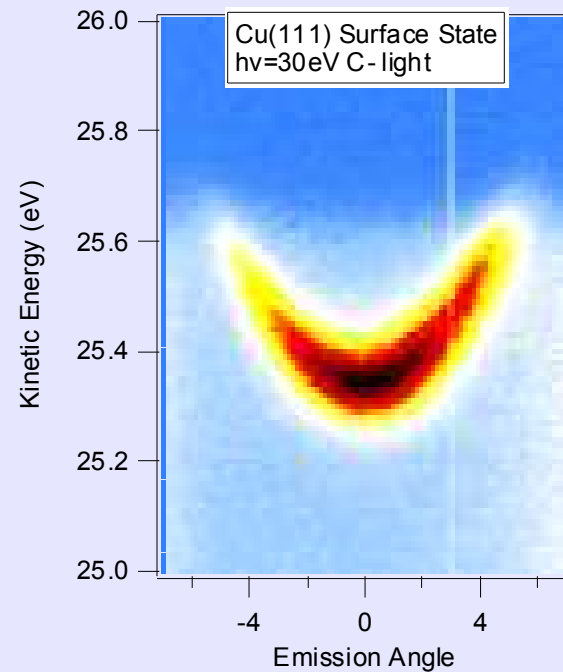
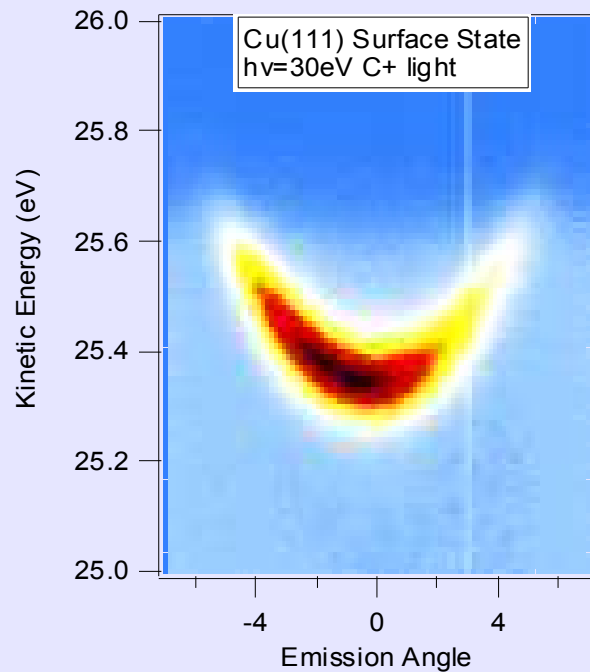


1. The binding energies are the same;
2. the widths are the same;
3. just the intensities change, coherently with  $\mathbf{k}$ ;

The horizontally polarised light picks up even states

The vertically polarised light picks up odd states

# Cu(111) surface state with circular light



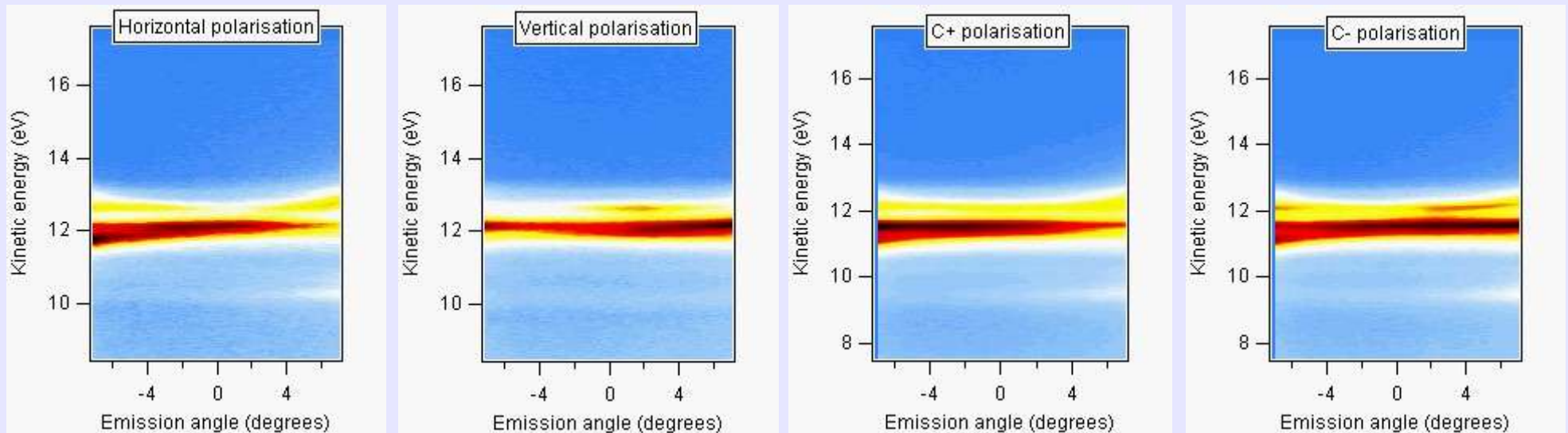
The intensities for C+ and C- are comparable

The spectral weight shifts from the left to the right of the  $\Gamma$  point



**CDAD**

# Ag(100) valence band at $\Gamma$



Valence band dispersion is more complex than that of a surface state

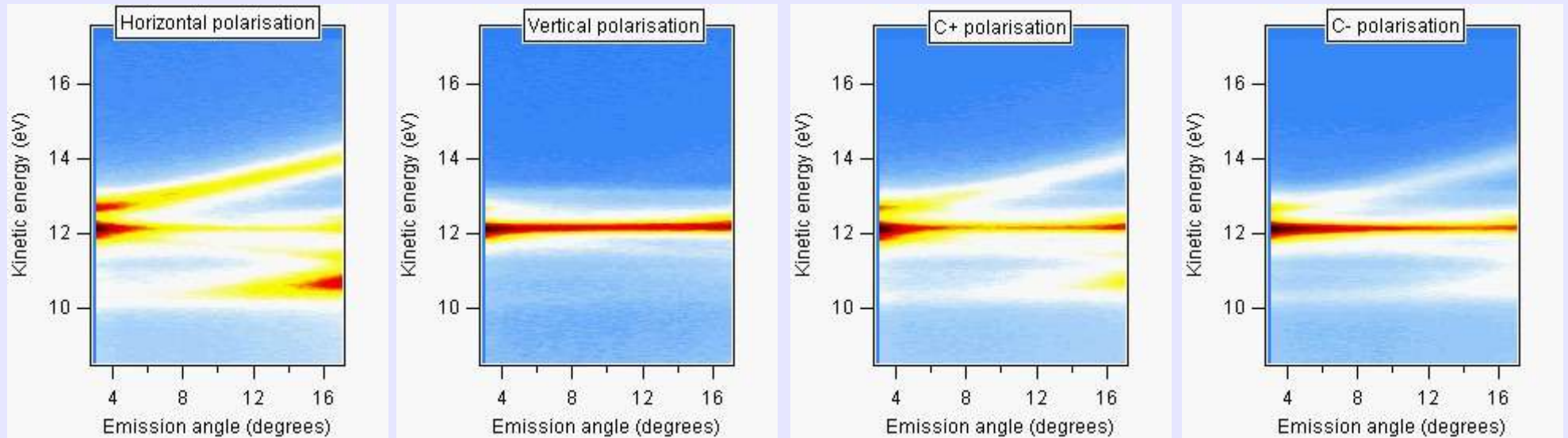
The *d* bands are not pure atomic *d* orbitals, but the intensity differences are caused by their different symmetries.

The intensity of one state is shifted by circular polarisation from the left to the right of the  $\Gamma$  point.

State symmetry close to Cu(111) surface state one



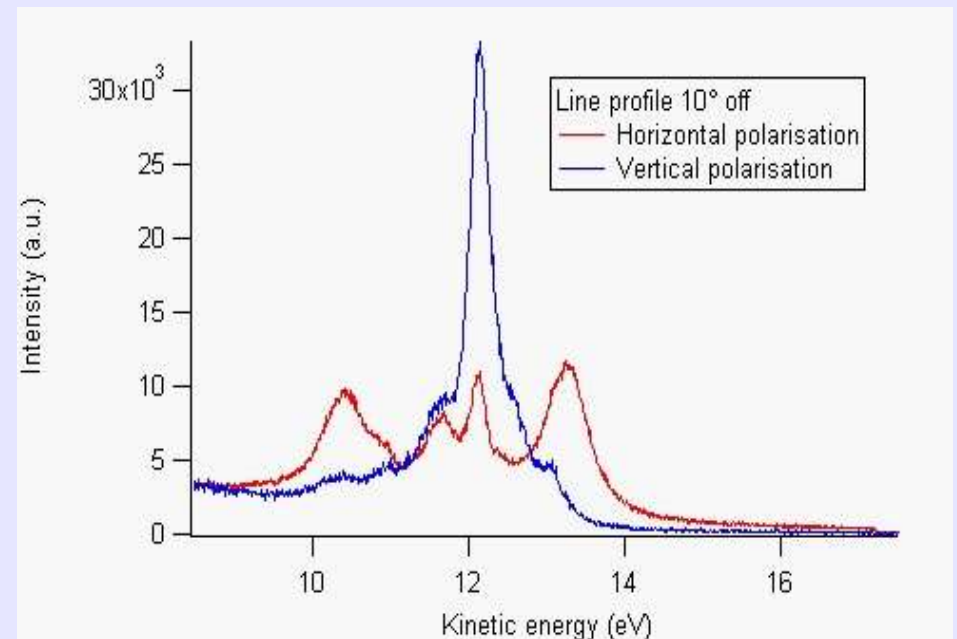
# Ag(100) valence band 10° off-normal



Horizontal light:  
four strong and one weak bands;

Vertical light:  
one strong and four weak bands;

Circular right and left:  
different intensity distribution





# Demagnetised Ni(111)

Ni, ferromagnetic under  $T_c=631\text{K}$

Its bands are flatter than those of Cu and Ag, evidence of correlations

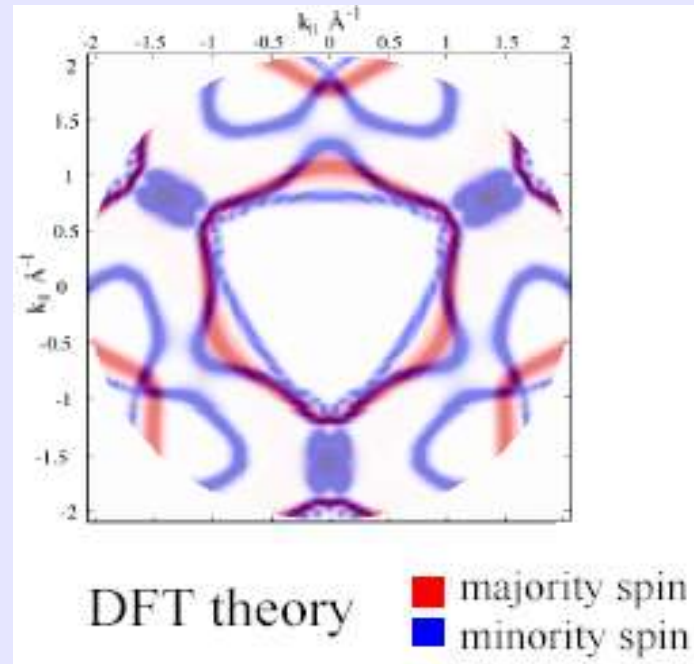
In PRB 58 1300 (1998), Ni Fermi surface and band dispersion measured as a function of the temperature

The majority and minority bands join together at  $T_c$ . Below it they are split by the exchange interaction

Ni should show magnetic dichroism upon magnetisation or polarisation change

Measurements of the valence band with different polarisations in the demagnetised state provide reference data

# Ni(111) Fermi surface

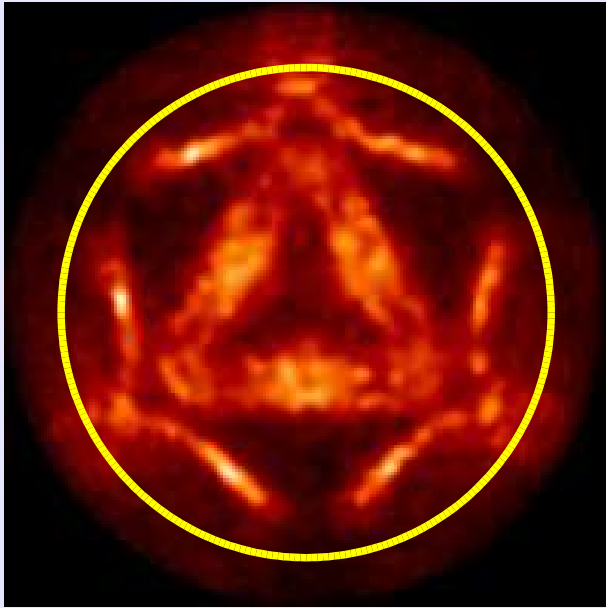


Measured with the He lamp

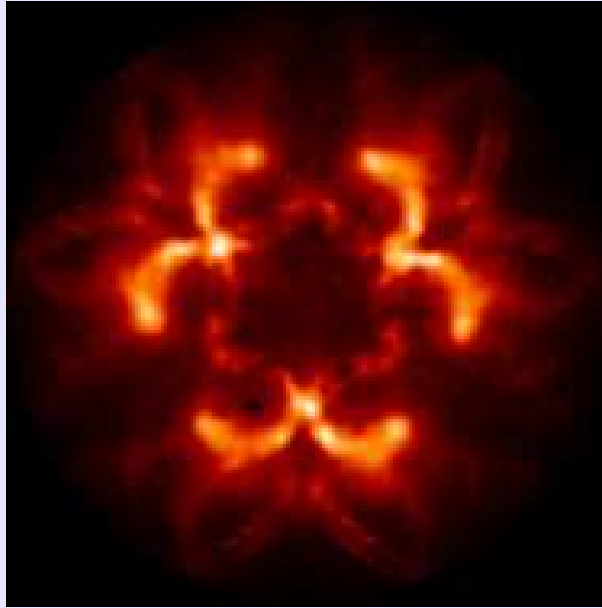
Ni minority *d* bands crosses  $E_F$  level. *sp* spin split states are present  $E_F$

Fixing the polar angle at  $78^\circ$  off normal and scanning azimuthally gives access to every band crossing  $E_F$ .

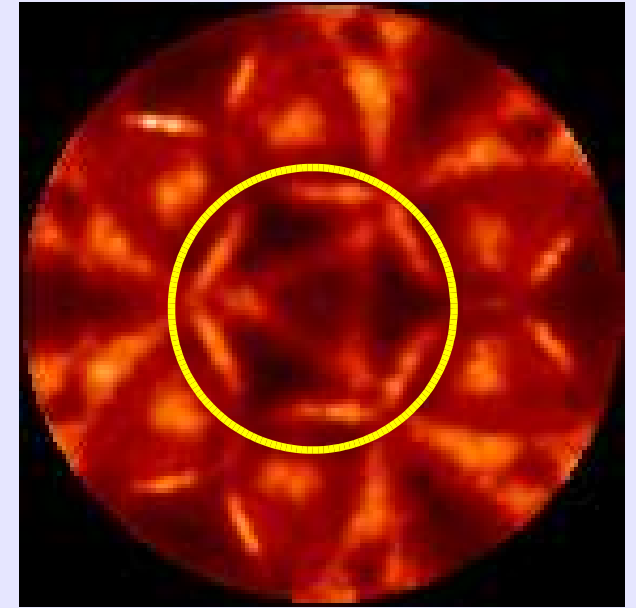
# Ni(111) Fermi surface



$h\nu=15\text{eV}$   
 $\theta_0=80^\circ$



$h\nu=30\text{eV}$   
 $\theta_0=60^\circ$



$h\nu=50\text{eV}$   
 $\theta_0=45^\circ$

The initial states energy is the same:  $E_F$ ; their k-vectors are different

The initial  $\phi$  angle is arbitrary

# Ni bands tomography with the He lamp

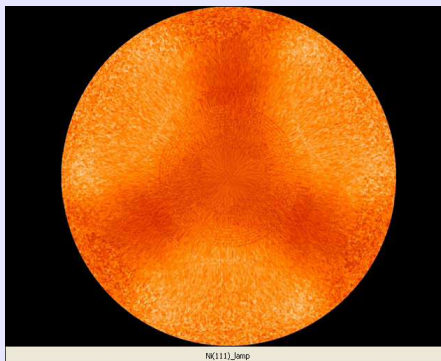
Bands tomography: extension of Fermi surface to deeply bound electrons

Helium lamp radiation features *no polarisation* and  $h\nu=21.22\text{eV}$

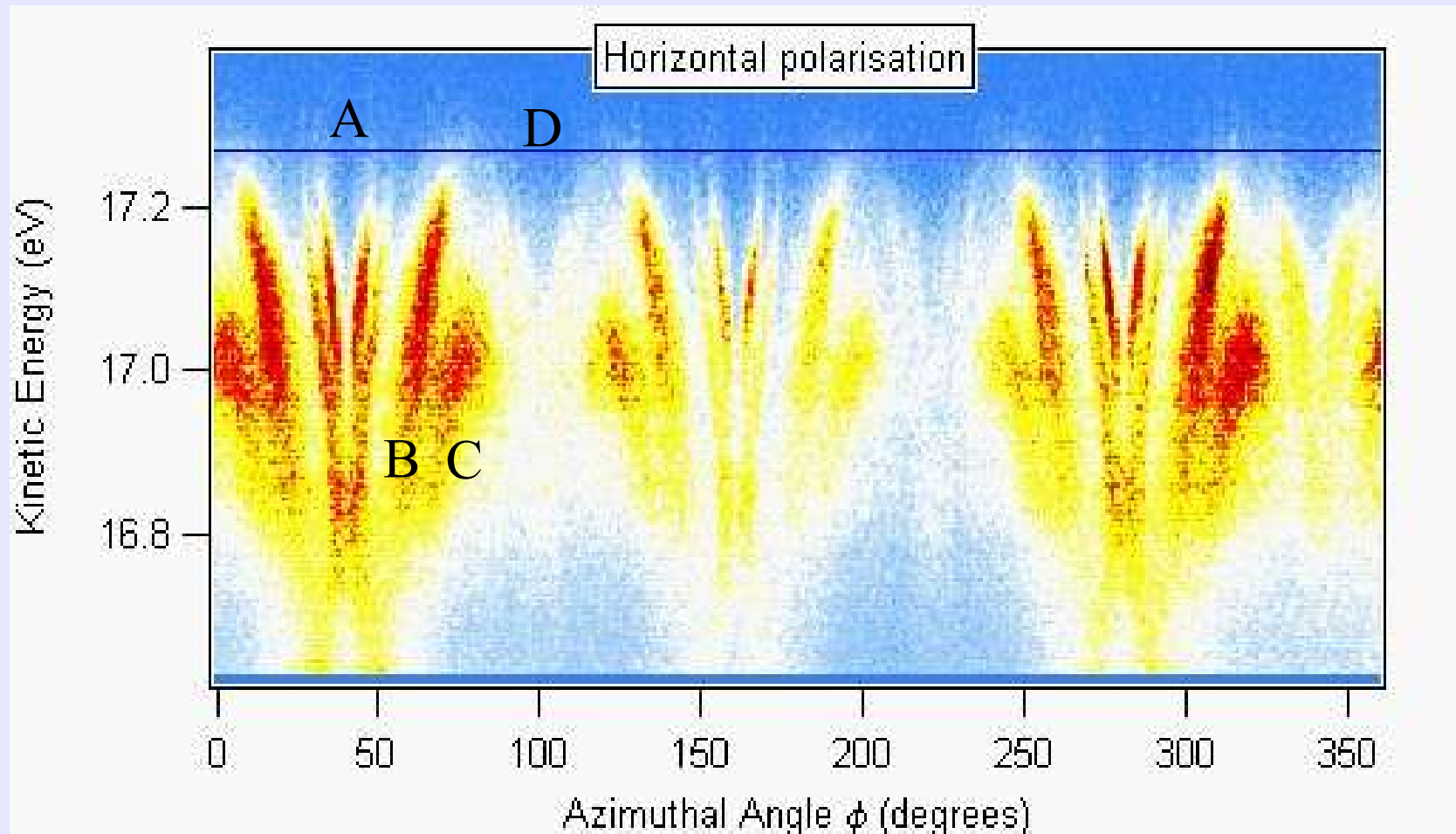
$E_{\text{K}}$  from 14.5eV to 17.1eV, total energy resolution  $\sim 100\text{meV}$ ,  $\Delta E=25\text{meV}$ ;

$\theta$  from 0 to  $79^\circ$  off normal,  $\Delta\theta=1^\circ$ ;

$\phi$  from 0 to  $120^\circ$ ,  $\Delta\phi=0.5^\circ$  independent of  $\theta$ ;

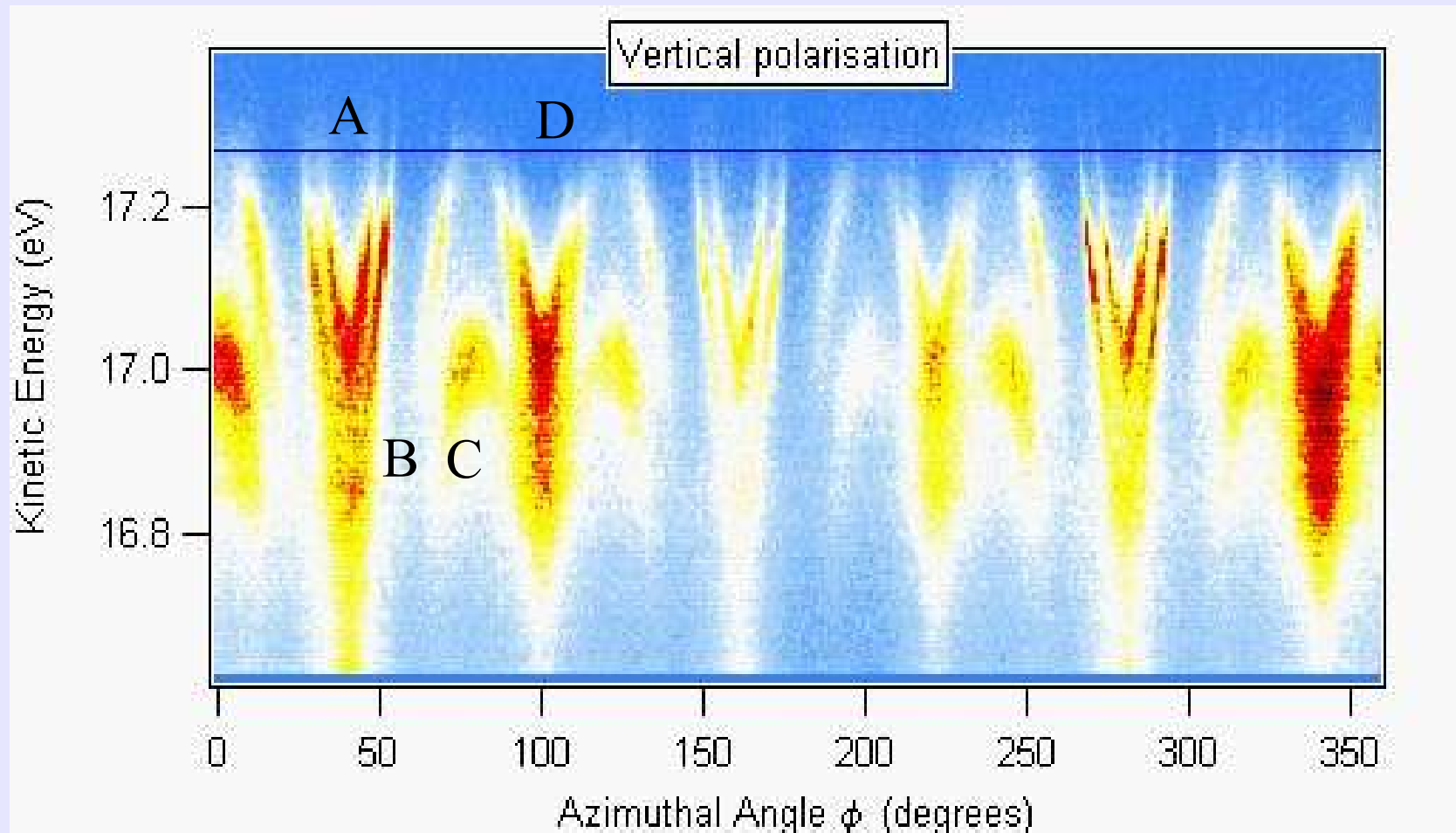


# 360°-azimuthal scan



78° off normal with  $h\nu=21.5\text{eV}$  horizontally polarised synchrotron light

# 360°-azimuthal scan



78° off normal with  $h\nu=21.5\text{eV}$  vertically polarised synchrotron light

# 360°-azimuthal scan

Feature A (*sp* states): the intensity of the majority states increases with respect to the minority ones (nearly unchanged);

Feature B (minority *d* band): intensity loss when the polarisation is turned;

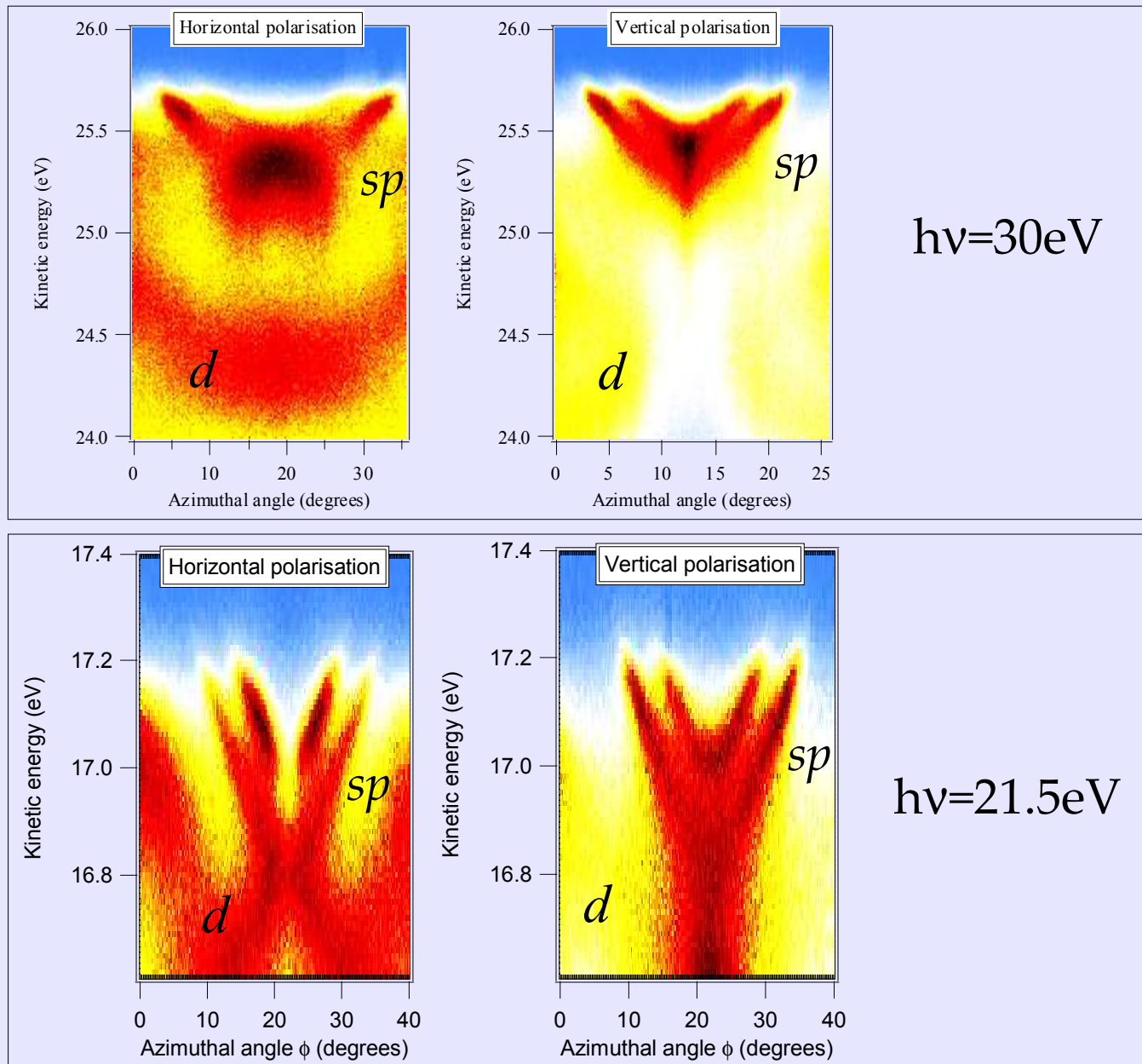
Feature C (majority *d* band): its intensity decreases, but not as strongly as feature B;

Feature D (“replica” *sp* states): strongly enhanced on polarisation change

Qualitative analysis:

1. the minority *d* bands are “purely” even;
2. the majority *d* band have a mixed character;
3. the “replica” states are odd, the “originals” have mixed symmetries

# Zoom on the $sp$ states, linear polarisation



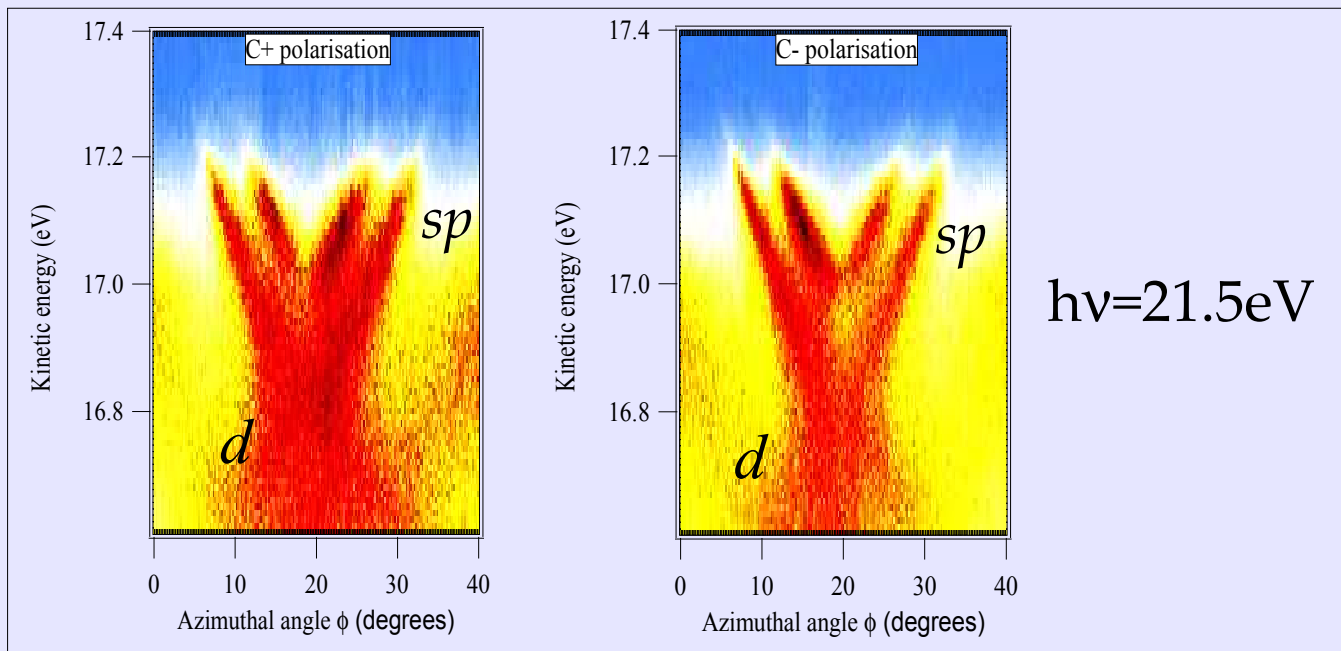
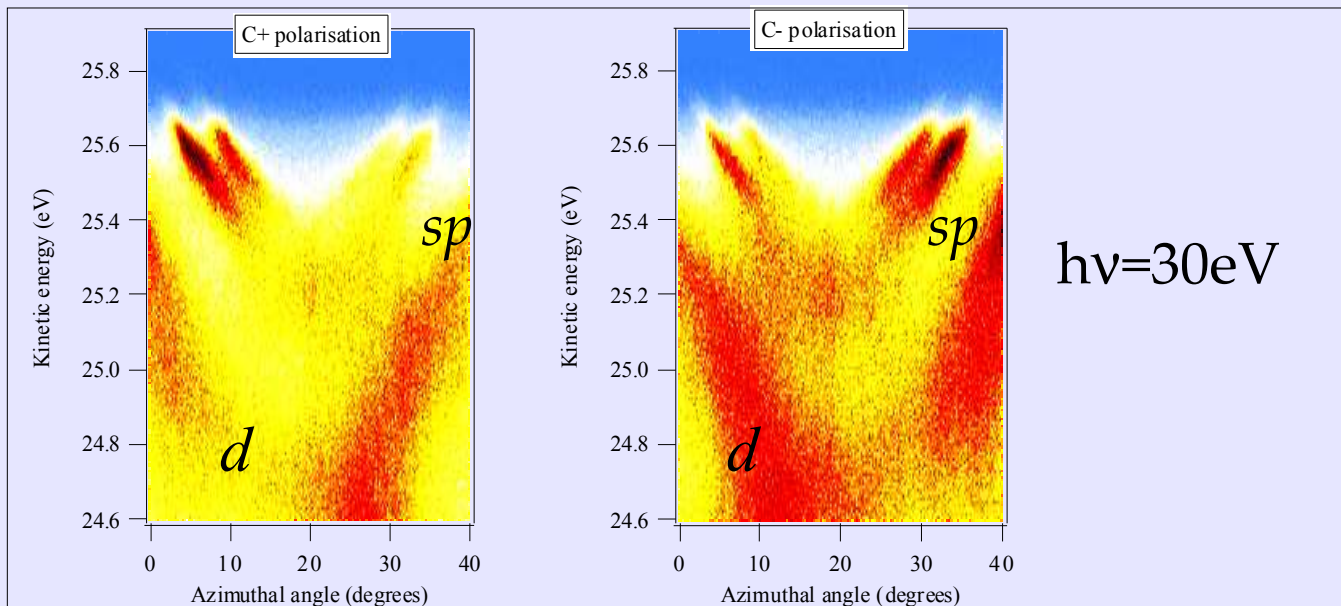


# Zoom on the $sp$ states, linear polarisation

At the centre of the images passes the  $(-1,-1,2)$  plane:

1. selection rules are valid only there;
2. reflection symmetry w.r.t. the reflection plane;
3. different behaviours of the intensity at the reflection plane for a change of the photon energy;
4. different photon polarisations and energies change the intensity ratios between minority and majority  $sp$  states
5. the free-electron final state is just an approximation

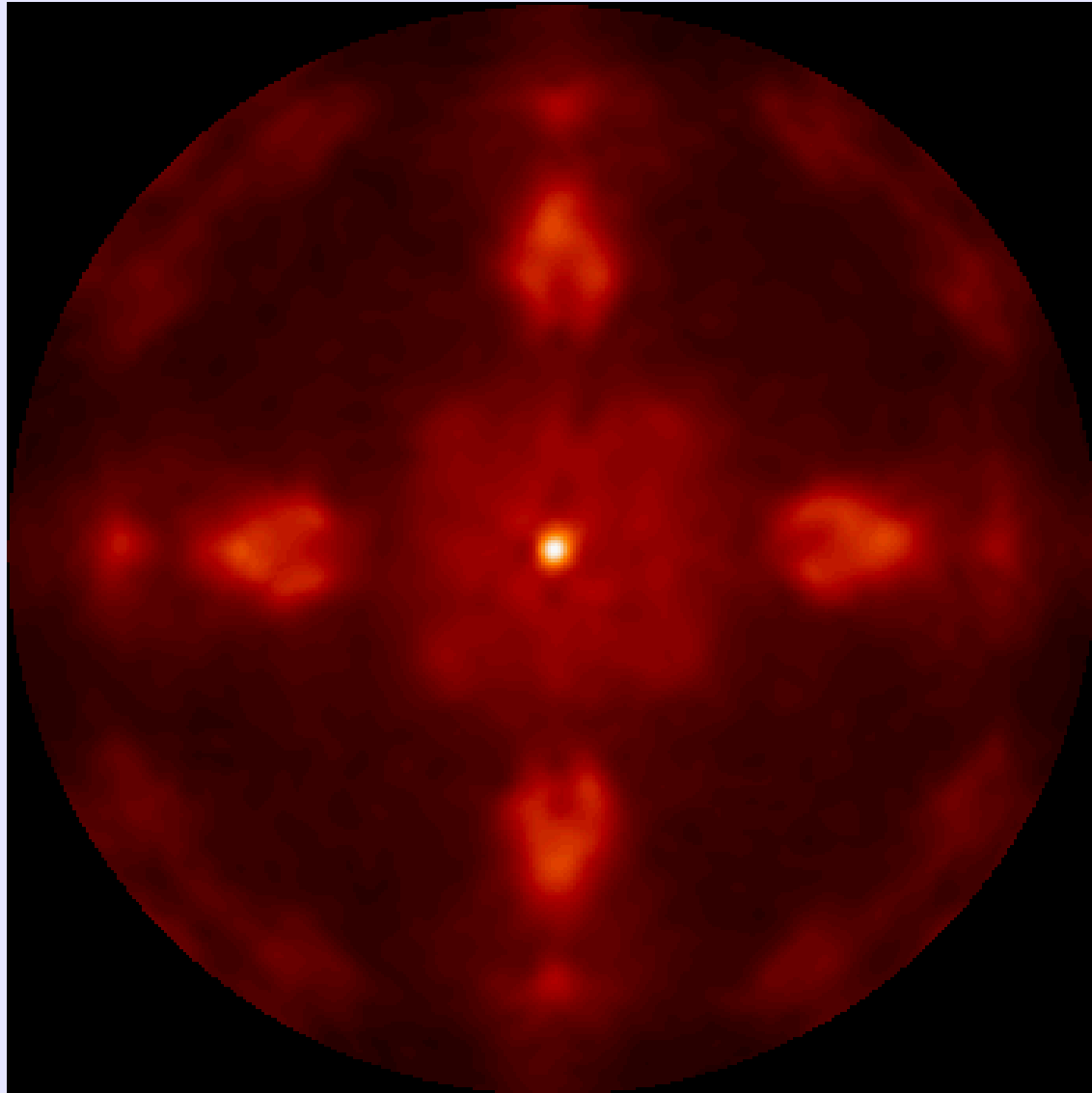
# Zoom on the $sp$ states, circular polarisation



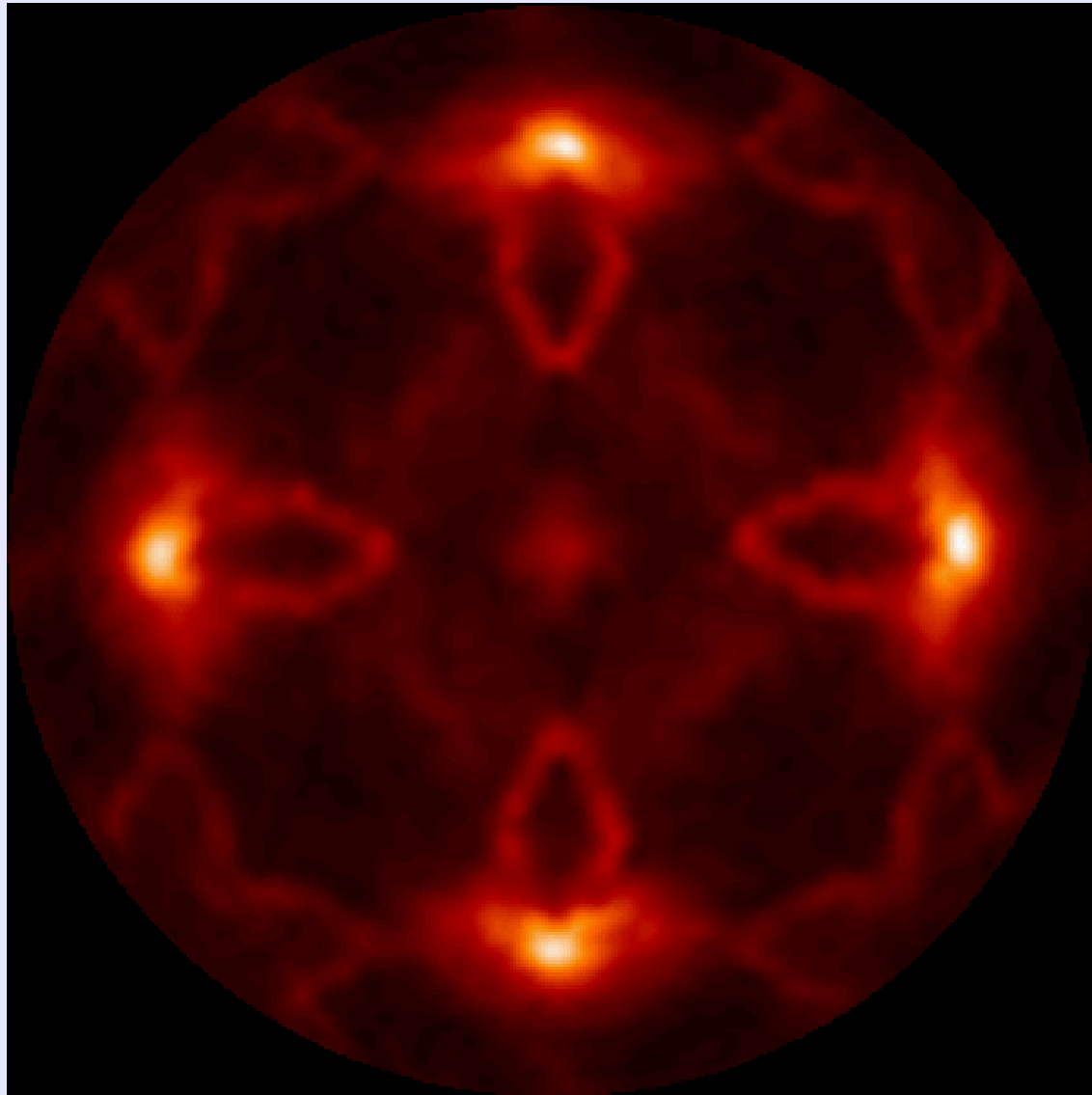
# Zoom on the $sp$ states, circular polarisation

1. circularly polarised light re-distributes the intensities to the left or to the right of the  $(-1,-1,2)$  plane according to its phase;
2. reflection symmetry is respected for binding energies, but not for intensities, **same behaviour of the Cu(111) surface state**;
3. the intensity re-distribution changes sign when the photon energy is changed;

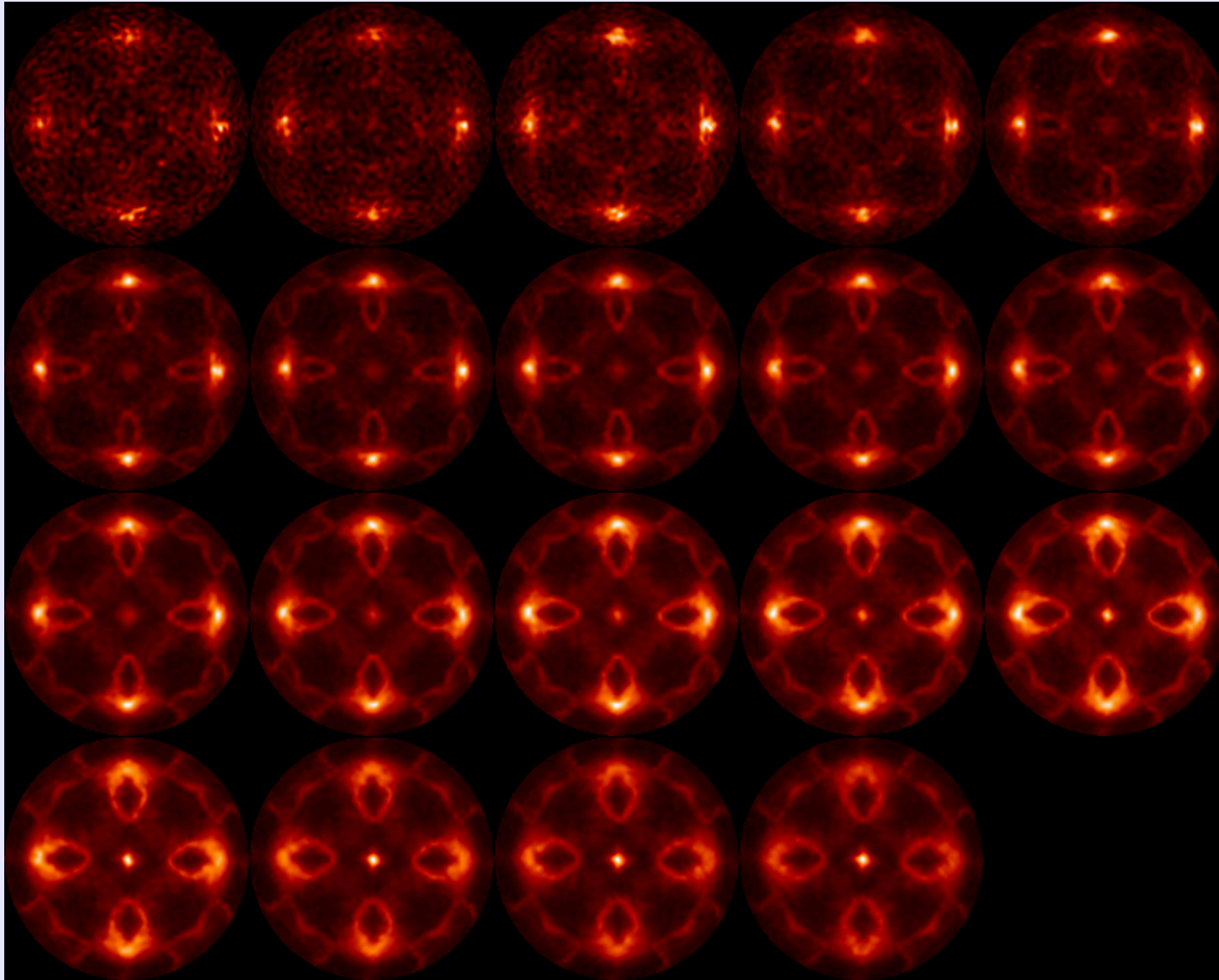
Fe(100) Fermi surface,  $h\nu=40\text{eV}$



Fe(100) Fermi surface,  $h\nu=50\text{eV}$



# Fe(100) Fermi surface, linear polarisation



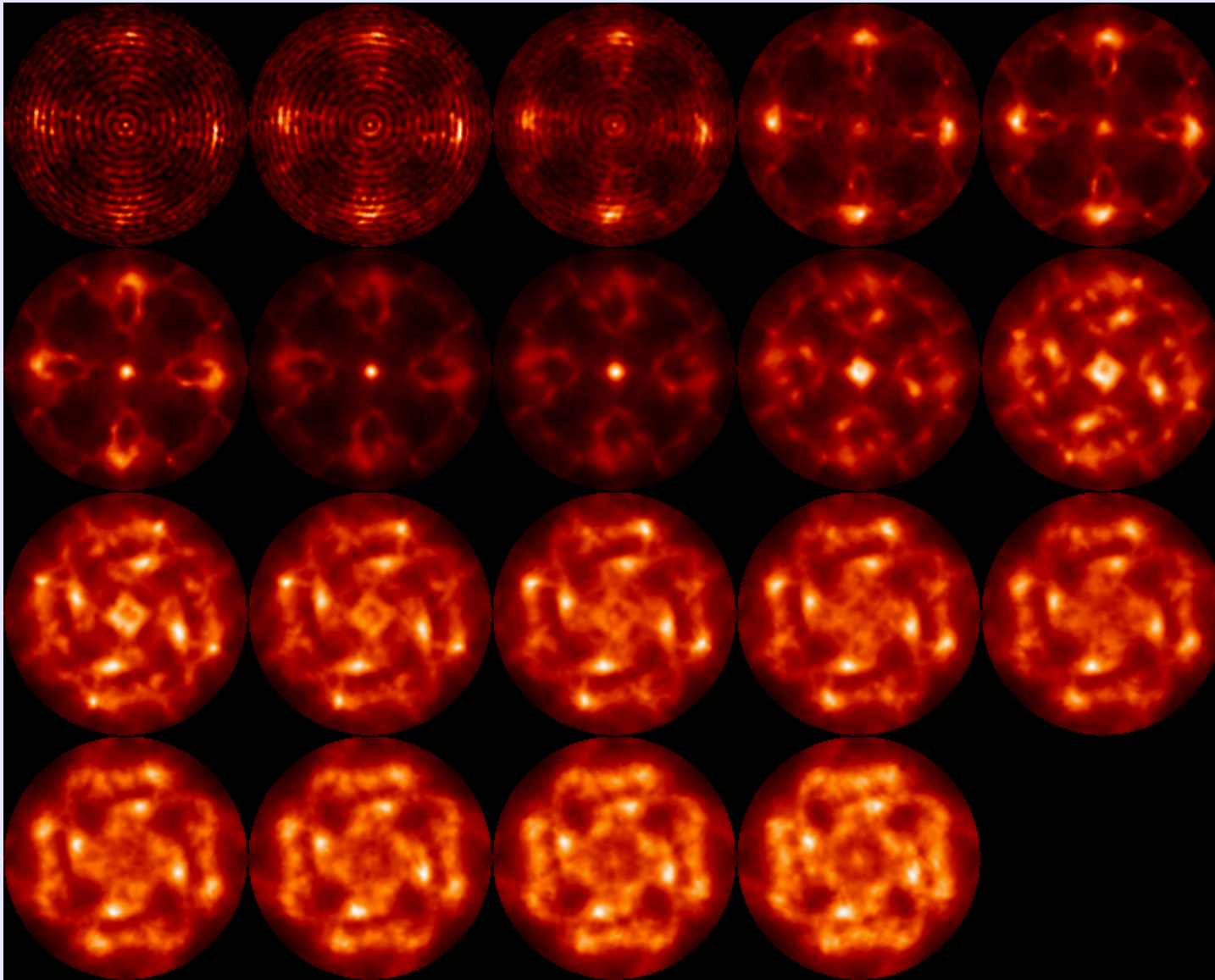
$h\nu=50\text{eV};$

19 images for  $0.8\text{eV};$

$\Delta E\sim 40\text{meV}$

$\Delta\theta=2^\circ$

# Fe(100) Fermi surface C+ polarisation



$h\nu=50\text{eV};$

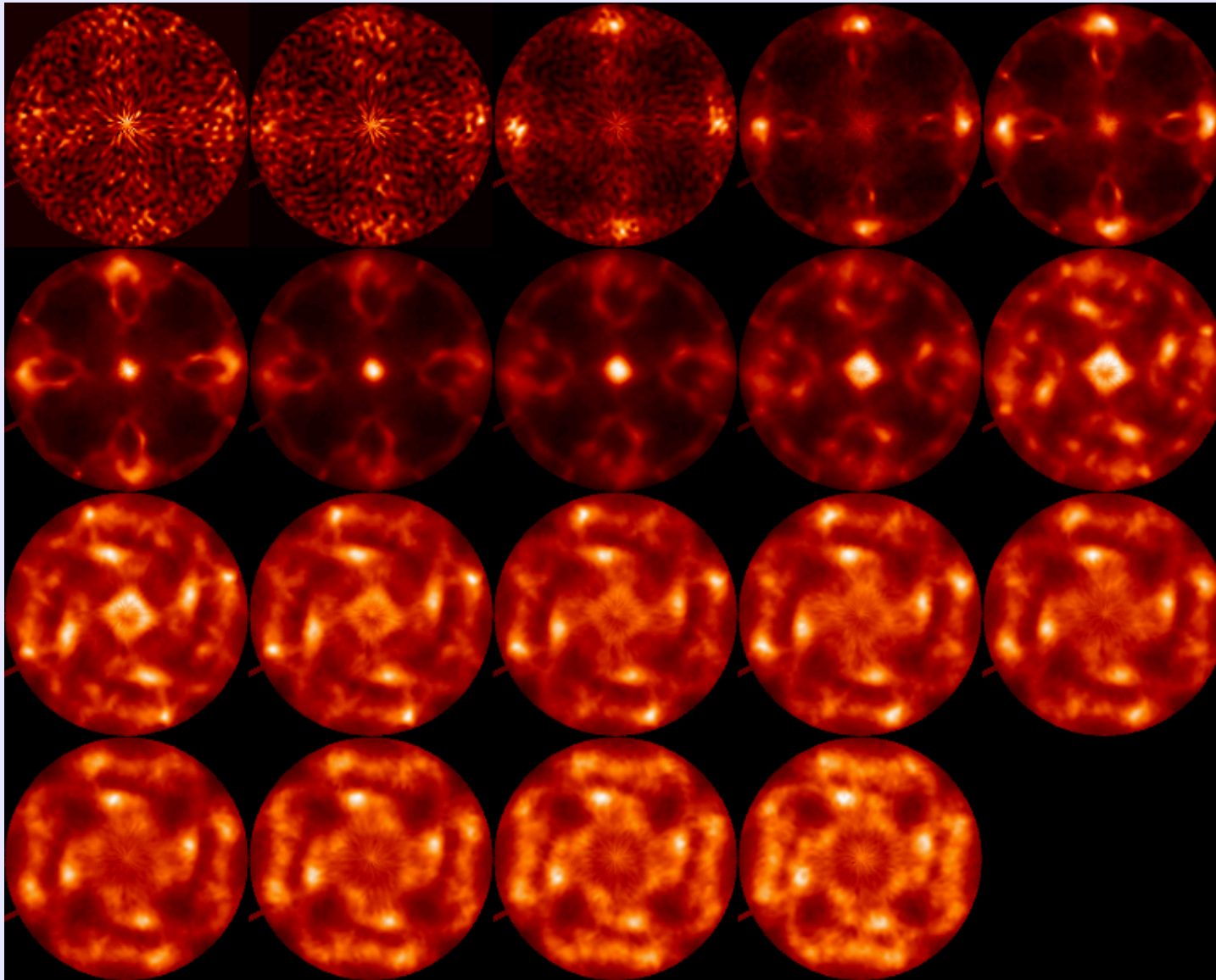
19 images for  $1.6\text{eV};$

$\Delta E\sim 80\text{meV}$

$\Delta\theta=2^\circ$



# Fe(100) Fermi surface C- polarisation



$h\nu=50\text{eV};$

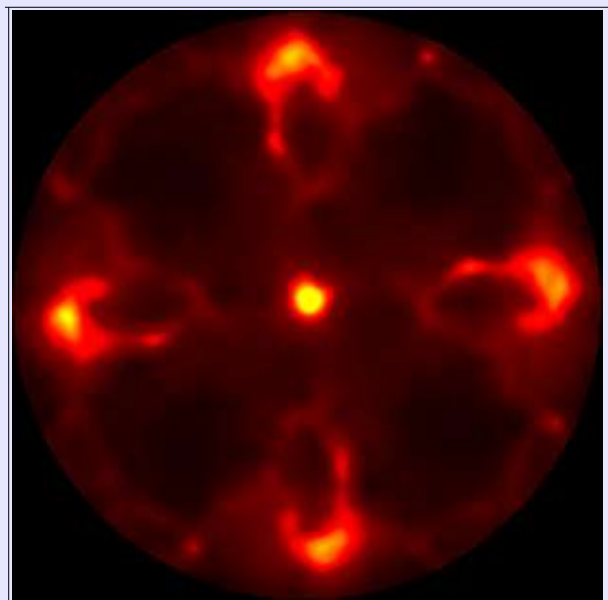
19 images for 1.6eV;

$\Delta E\sim 80\text{meV}$

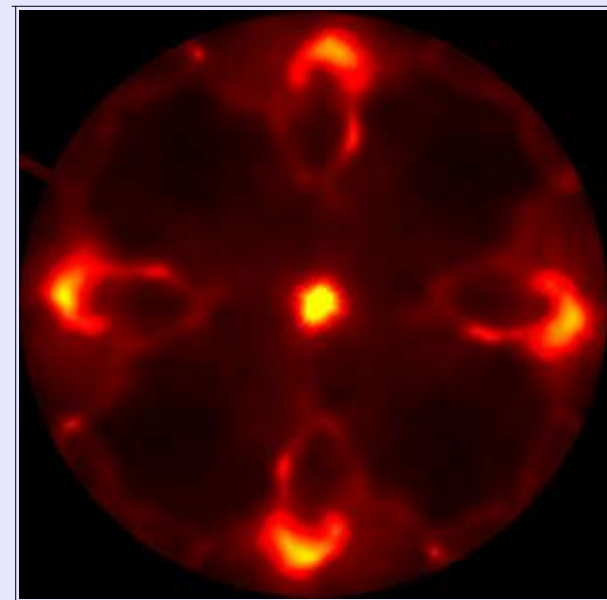
$\Delta\theta=2^\circ$



# Fe(100) test

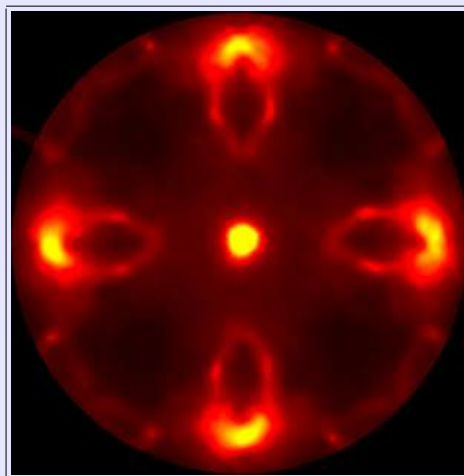


$\leftarrow C+$

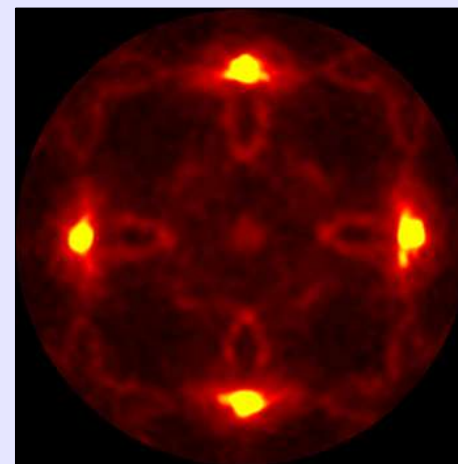


$C- \rightarrow$

$C+ + C-$



Linear horizontal



# Fe(100) Fermi surfaces

ALL the Fermi surface features depend on the light polarisation.

While the linear light scans are symmetric with respect to the centre, measurements with C+ and C- light are skew symmetric w.r.t. it

The behaviour is reversed when the light phase is reversed

C+ + C- data are similar to the horizontal light Fermi surface. This implies the vertical polarisation (Fe odd states) contribution is weak

# Partial conclusion

All what presented before was measured on both non magnetic and demagnetised materials

We think the phenomena here shown, to different extents, in ALL the materials, because **their origin is the symmetry of the ground state wavefunctions**

Magnetic Linear and Circular Dichroism in the Angular Distribution (MLDAD and MCDAD) from ferromagnetically ordered matter lies ON TOP of these effects

To avoid artifacts, spectra from magnetised samples must be compared to those from non-magnetised ones. This, in order to distinguish “structural” from “magnetic” effects

# 3. Ni(111): MCDAD from the *sp* bands

## Experimental

Dichroism from valence band states has been tried on Ni(111) because of our picture-frame crystal (prof. J. Osterwalder's). Because of its shape, the magnetic flux closes onto itself, eliminating the stray field.

The photoelectron trajectories are not affected by the magnetisation.

The surface preparation, requesting a 1000K annealing, allowed for the measures of the de-magnetised state before the magnetisation procedure.

Thanks to the chamber pressure  $3 \cdot 10^{-11}$  mbar, they are the same. Magnetisation has been obtained pulsing a 7-coils circuit with a 300A current for  $\sim 100 \mu\text{s}$ .

# MCDAD from the $sp$ bands

Core-level PES angular distribution is directly correlated to the magnetic state of matter. This is also true for valence ARPES dichroism in the angular distribution, but much less work has been dedicated to it.

Because of:

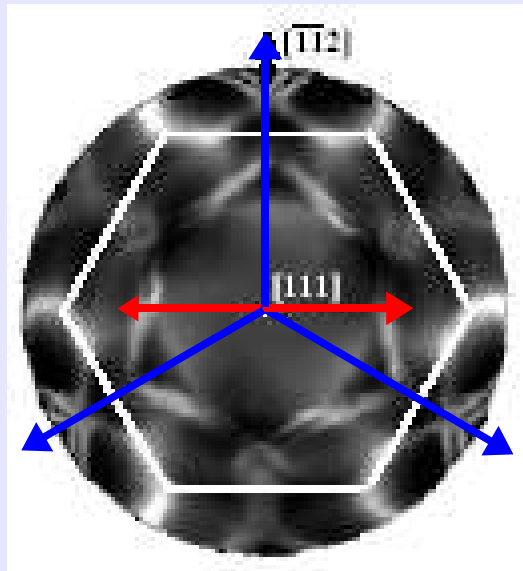
1. valence band state dispersion;
2. small spin-orbit coupling;
3. polarisation related selection rules;
4. role of core-hole effect

Anyway, magnetic dichroism should be based on the same principles:

1. there should be spin-orbit coupling in the ground state;
2.  $\vec{M}$ ,  $\vec{\sigma}$ ,  $\vec{k}$  should be in chiral geometries;
3. the magnetisation should be a well defined vector

# Magnetised Ni(111) $sp$ states

The surface is three-fold symmetric, the magnetisation is two-fold symmetric. The  $sp$  states extend over about 1/6 of the Fermi surface at high emission angles. Thus, there is not only one “chiral” geometry, but every angular configuration can give a dichroism.

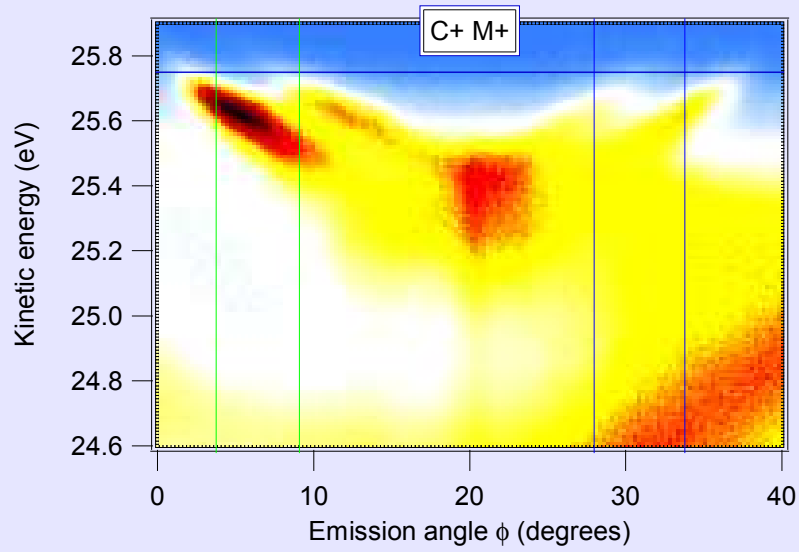


$\vec{M}$

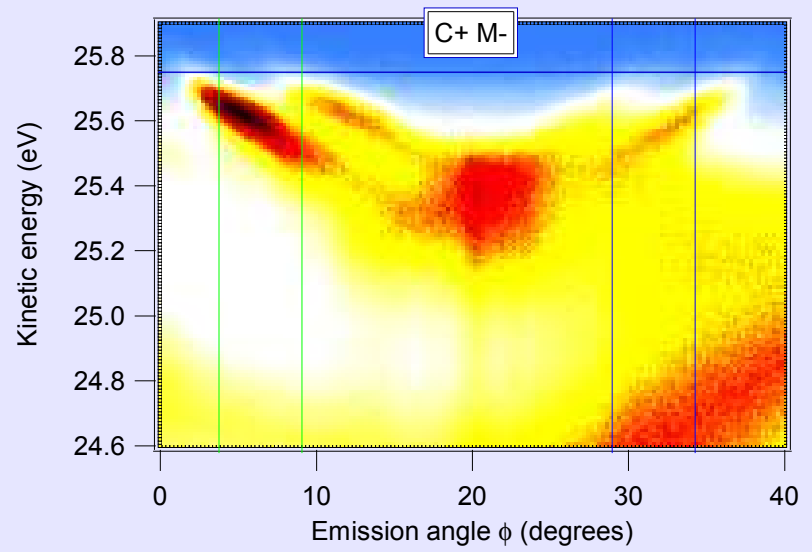
The  $(-1,-1,2)$  is a preferential direction for MCDAD.

Measurements taken along the other directions should result in a zero.

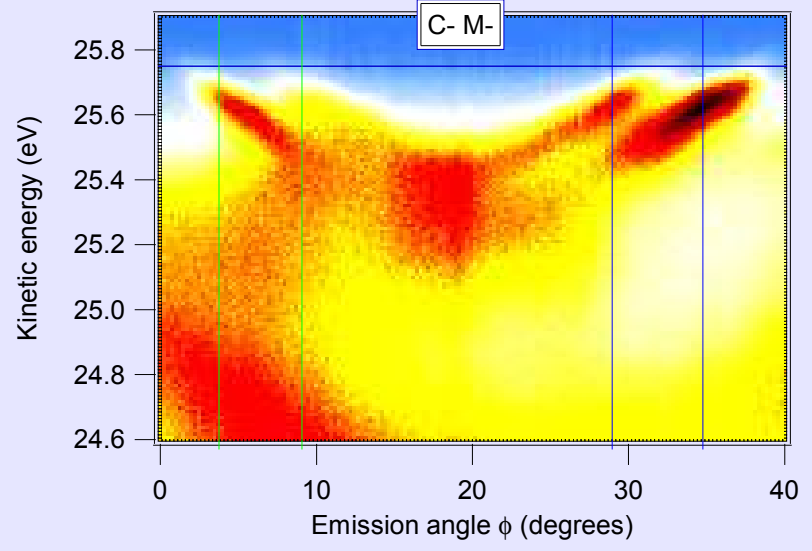
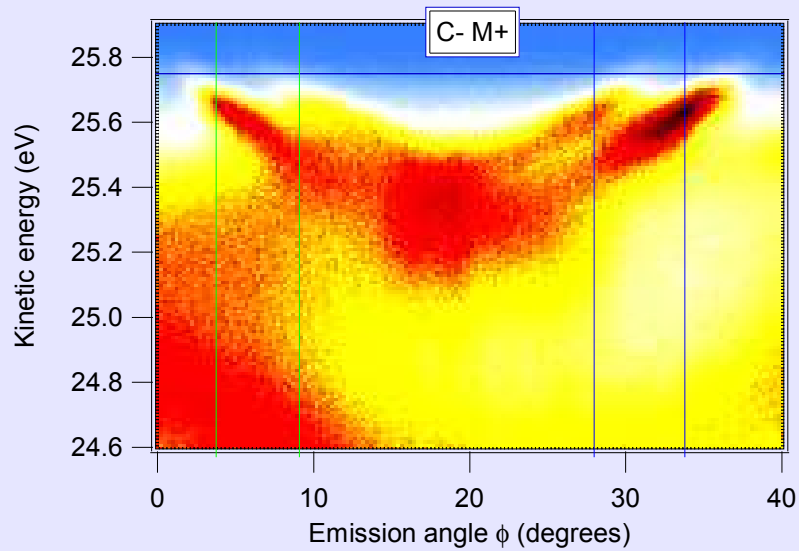
# MCDAD



1 2 3 4

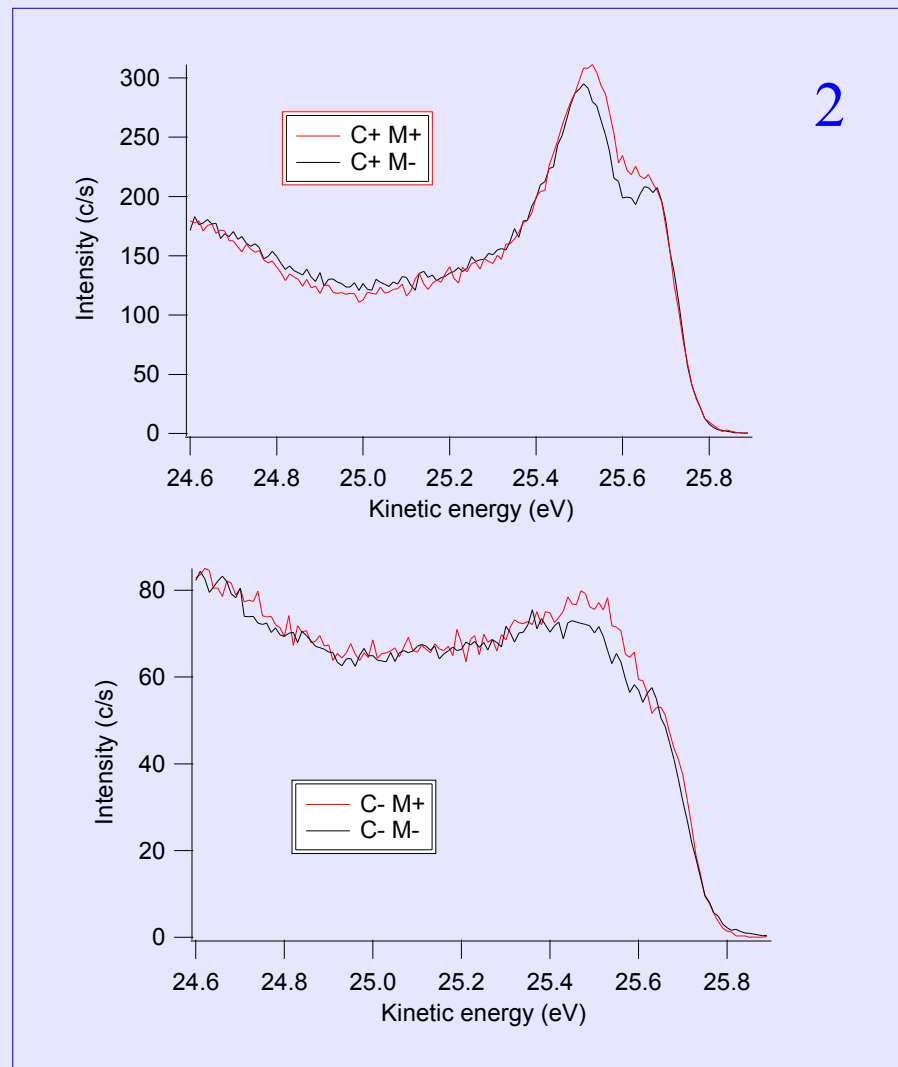
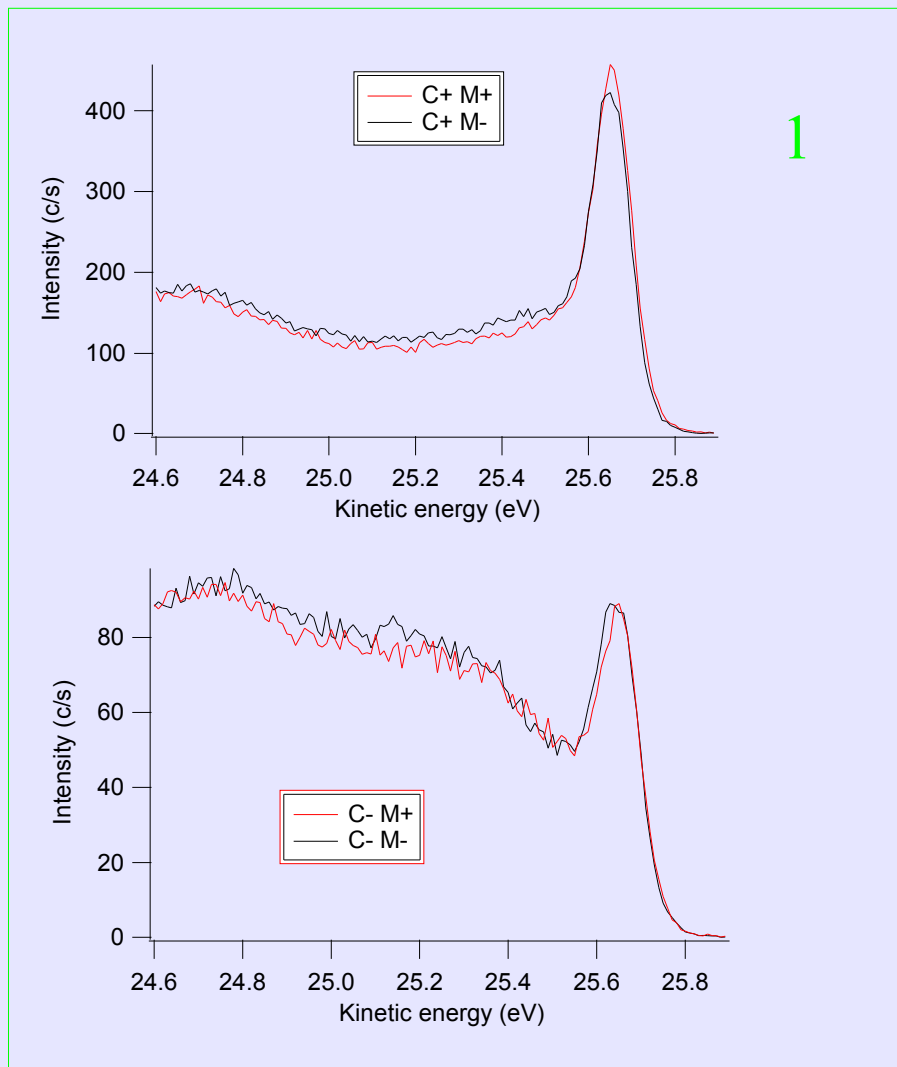


1 2 3 4



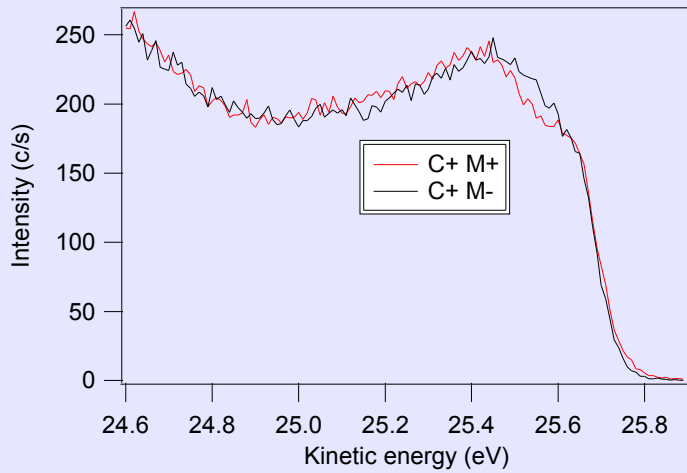
# MCDAD, 1 & 2

The MDC look almost the same, but the MCDAD it's in the “almost” ...

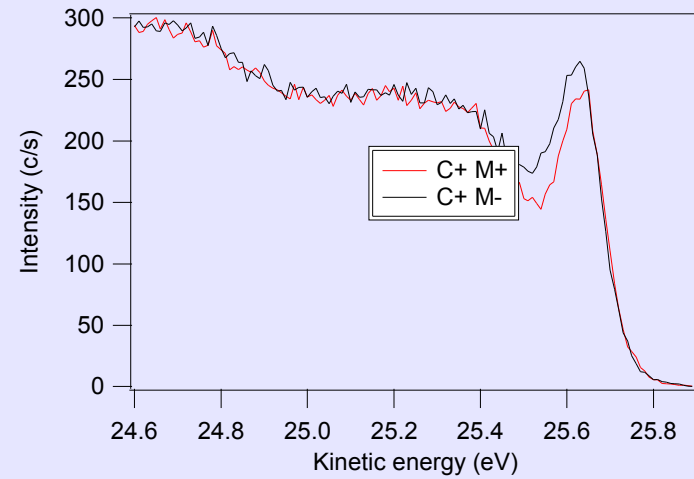




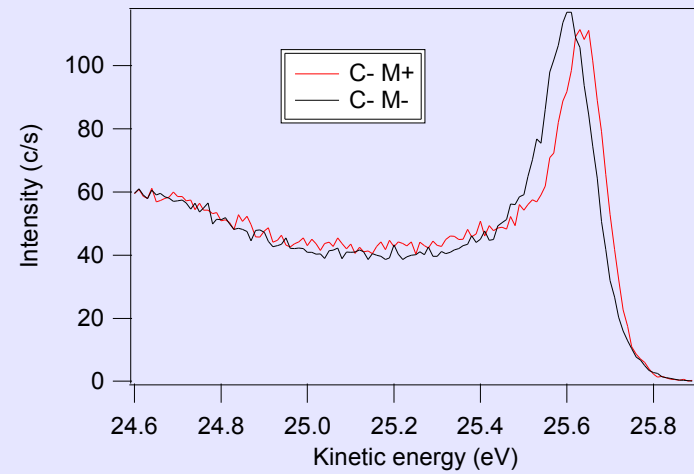
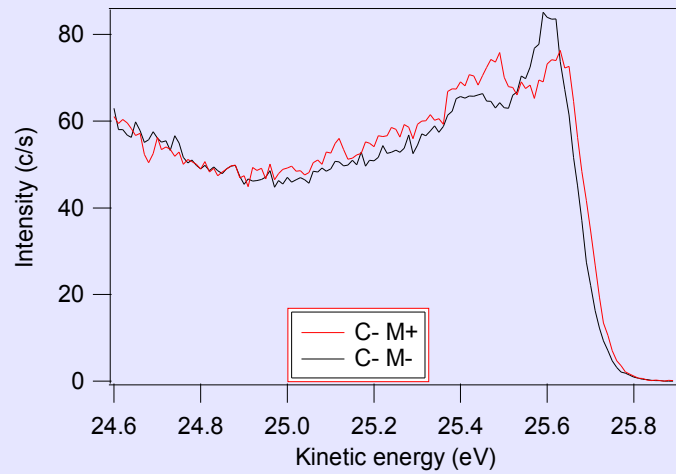
# MCDAD, 3 & 4



3



4



# MCDAD partial conclusion

The effects are not due to misalignments, to photon energy shifts or to the magnetic stray field

The dichroic signal strongly depends on the k-vector.

EDCs at 1 with C+ and at 4 with C- are different because the k-vectors are different.

The sum of the dichroisms at the other angular positions should be zero, once the magnetisation projections are taken into account.

The comparison of these data with calculation gives the k- dependent spin polarisation of Ni(111). Because of matrix elements it's not possible to determine it directly from the experimental data

# Conclusion

Our data say:

1. selection rules play a role, but only at the symmetry planes;
2. AD provides much richer information than ARPES in symmetric configuration;
3. the polarisation choice strongly affects the intensities;
4. this change does not depend on the feature one's looking for;
5. magnetic effects are subtle, but...
6. MCDAD can be “cleanly” measured in valence band by ARPES;

Rules of the thumb:

**Experimental conditions do matter!** Always ask for the parameters  
( $T$ ,  $h\nu$ ,  $\sigma$ ,  $\theta$ ,  $\phi$ ) at which the data have been collected

My opinion: ARPES data depend on the experimental details

# Work ahead

1. *ab initio* calculations of the electronic structure
2. calculations of the photocurrent by a one-step method
3. comparison between data and theory
4. magnetism: try to understand how much we get from the MCDAD experiment
5. ask for a complete theory for the MCDAD
6. apply the technique to other magnetic systems

*Thanks for your attention!!!*