4) Quantitative diffraction

For MChem, Spring, 2009

Dr. Qiao Chen
(room 3R506)

http://www.sussex.ac.uk/Users/qc25/

University of Sussex
Today’s topic

- Quantitative LEED
- Surface x-ray diffraction
- Surface extended x-ray absorption fine structures
- X-ray photoelectron scattering
- Ion scattering
Glycine on Cu(110)

(3x2) lattice

3x2.55Å=7.65Å

2x3.61Å=7.22Å

How the molecules are arranged inside the unit cell?
Quantitative LEED analysis

What LEED can tell:

Unit cell size, surface symmetry

LEED can also tell:

Distance and bonding between adjacent atoms
You want to measure structure inside the unit cell.

Distance and bonding between adjacent atoms

The internal structure affects the diffraction intensity.

By scatter the electron with all atoms within the unit cell.

Can we measure it? Diffraction intensities

How? LEED I-V, Tensor-LEED, dynamic LEED
With multiple scattering in electron diffraction

Spot intensities contain information on structure within the unit cell

\[ I \sim |F|^2 \cdot |G|^2 \]

\[ |G|^2 = \text{structure factor or lattice factor} \]
contains shape and arrangement of repeat units (unit cells)
yields reciprocal lattice
determines location and shape of spots,
kinematic theory

\[ |F|^2 = \text{structure factor or form factor} \]
contains contribution from all atoms within the repeat unit,
includes multiple scattering, in-depth attenuation,
dynamic theory

Both \( F \) and \( G \) is a function of electron kinetic energy eV
Both F and G is a function of electron kinetic energy eV

Phase difference $d = a \sin(\theta) = n\lambda$

G is only related to the unit cell

F contains information of atomic structure within unit cell.
Multiple scattering data analysis

Dynamic LEED analysis: No direct deduction of structure from I-V-curves:

1. Guess structure model
2. Calculate I-V-curves compare with measured curves
3. Modify model
4. Check if improvement, if yes: proceed modifying in this direction, if no: modify in another direction or guess new model

Disadvantage:
Only for ordered structures
Much computer time
Not sensitive to H atom

But: very surface sensitive. One of very few methods for structure analysis of first few atomic layers (~1 nm).
LEED I-V study of Fe$_3$O$_4$ (111) thin film on Pt(111) 10nm thickness
3. X-ray diffraction: interaction with electron density

- **X-ray generation**: x-ray tubes or synchrotron radiation
- **Wavelength**: a few angstroms to 0.1 angstrom, comparable to lattice constants
- **X-rays can penetrate deep**: bulk structure
- **X-ray diffraction comes from the interference of the scattered x-ray due to the periodicity of the lattice**
How do we do on surface?  

- *The incident x-ray is fixed at a very small angle with respect to the sample surface*
- *The detector does 2θ scan*
- *Parallel x-ray beam is used*
- *Grazing incidence x-ray diffraction is usually used to study the surface of the sample*
What is grazing angle incidence?

Why we need grazing angle incidence?

1. In order to achieve total external reflection
2. In order to get surface information

Difficulty with grazing angle incidence:

X-ray spread out on the surface with large projection, signal is very weak
Diffraction intensity and surface contribution

Infinite lattice results in points in reciprocal space.

A single plane of atoms results in lines of intensity.

Surface is combination.
Surface x-ray diffraction data analysis

2.5 dimension system
Why x-ray diffraction?

- Non-destructive
- From atomic resolution to micrometer scales
- Better statistical information
- Probing buried objects and interfaces
- Versatile to different sample environments

Difficulty:
1. Deep penetration, Grazing angle incidence, sample moving
2. Intensity spread
3. Not sensitive to H atoms.

Pure kinematic scattering, no multiple scattering
Simple theory, more accuracy.
Using existing 3D x-ray diffraction calculation.
Surface x-ray diffraction study of the Rh(111)+(2x2)-3CO structure

Measured structure factors vs for different rods.
Continuous lines: hollow model
Dashed lines: bridge model

Hollow site

Bridge site
4. extended x-ray absorption fine structures (EXAFS)

EXAFS is part of the XAS process
Definition
In condensed matter or (multi-atomic gas molecules) the ejected photo-electron (wave) will be scattered by neighbouring atoms.

It is the interference between the outgoing electron and the back-scattered ones which leads to oscillations visible in the absorption spectrum above the edge. These can extend to up to 1000 eV past the edge. These oscillations are the EXAFS.
XAS

Bohr Atomic Model

edge: $K \quad L_{I} \quad L_{II} \quad L_{III}$

$^{2}P_{3/2}$  $^{2}P_{1/2}$  $^{2}S_{1/2}$  $^{2}S_{3/2}$

Multiple scattering

Single scattering
EXAFS Data processing

Advantage of EXAFS

EXAFS gives us information about
Distances between central and neighboring atoms.
The number of neighboring atoms.
The nature of neighboring atoms (their approximate atomic number)
Changes in central-atom coordination with changes in experimental conditions

The main advantage of EXAFS analysis over X-ray Crystallography is that structures can be studied in non-crystalline forms (including liquid and frozen solutions).
5. Photoelectron Diffraction

- X-ray diffraction
- Photoelectron diffraction (PhD)
- Extended X-ray Absorption Fine Structure (EXAFS)

Long range X-ray diffraction

Interference of many scattered photons

Short range PhD and EXAFS

Local scattering of electrons to nearest neighbor
Angle -Scanned X-ray Photoelectron Diffraction (XPD)

2π plot

modulations as a function of $\hat{k}$; $|\vec{k}| = \text{const.}$

Change the polar and azimuth angle

Elastic scattering!!!
A Note on “Short-Range Order”

EXAFS

XPD

LEED

<table>
<thead>
<tr>
<th>EXAFS</th>
<th>OK</th>
<th>OK</th>
<th>OK</th>
<th>OK</th>
<th>OK</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPD</td>
<td>OK</td>
<td>OK</td>
<td>OK</td>
<td>OK</td>
<td>NO</td>
</tr>
<tr>
<td>LEED</td>
<td>OK</td>
<td>OK</td>
<td>OK</td>
<td>NO</td>
<td>NO</td>
</tr>
</tbody>
</table>
Ion scattering: measuring elastically reflected ions

Ion scattering spectroscopy (ISS) is a **surface-sensitive analytical technique** used to characterize the chemical and structural makeup of materials. It involves directing a **stream of charged particles** known as **ions** at a **surface** and making observations of the positions, **velocities**, and **energies** of particles originating from that surface.

**Measuring:**
1. Angles
2. Intensities
3. Energies

**Advantage:**
1. Simple scattering theory
2. Only surface sensitive
3. H atom sensitive
Interactions with materials

(a) **x-rays**
- weak interaction
- single scattering
- kinematic theory

(b) **He atoms**
- strong repulsion
- single scattering
- kinematic theory

(c) **electrons**
- strong interaction
- multi scattering
- dynamic theory
Summary: quantitatively measuring surface structures

- Quantitative LEED
- Surface x-ray diffraction
- Surface extended x-ray absorption fine structures
- X-ray photoelectron scattering
- Ion scattering
- Comparison between EXAFS, XPD and LEED
- Comparison between X-ray, electron diffractions and ion scattering