Inelastic x-ray scattering

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Outline - I

1) Introduction
   scattering kinematics
   generic excitation spectrum & information content
   some instrumental aspects

2) Resonant IXS
   “XAS beyond the core hole lifetime broadening”

3) X-ray Raman scattering
   “Soft x-ray XAS in the hard x-ray range”

4) IXS – phonons
Introduction I – scattering kinematics

- Energy transfer: \( E_f - E_i = \Delta E = 1 \text{ meV} \) – several keV

- Momentum transfer: \( \vec{k}_f - \vec{k}_i = \vec{Q} = 1 - 180 \text{ nm}^{-1} \)
Introduction II - schematic IXS spectrum

- quasieelastic
- phonon, magnons, orbitons
- valence electron excitations
- plasmon
- core-electron excitation
- Compton profile

Introduction III – overview 1

Phonons

Lattice dynamics
- elasticity
- thermodynamics
- phase stability
- e- -ph coupling

Magnons

Spin dynamics
- magnon dispersions
- exchange interactions
**Introduction IV – overview 2**

**Electron dynamics** $\varepsilon(q, \omega)$
- plasmons
- excitons
- orbitons

**Impulse distribution of electrons**
- chemical bonding
- local structures
**Introduction V – overview 3**

**X-ray Raman scattering**

**IXS from core electrons**
- electronic structure
- bulk sensitivity for low Z materials
- access to final states beyond the dipole limit

**Resonant IXS from core electrons**
- electronic structure
- reduced life time broadening
X-ray emission/fluorescence
- element selective
- valence selective
- spin selective
- ligand selective
Energy analysis of scattered X-rays
- $\Delta E/E = 10^{-4} - 10^{-8}$
- some solid angle

Rowland circle crystal spectrometer

$p = R_{\text{crystal}} \cdot \sin \theta_B$

$R_{\text{crys}} = 2 \cdot R_{\text{Rowl}}$
Introduction VIII – IXS at the ESRF

ID20: Electronic and magnetic excitations

ID26: XAS and emission spectroscopy

ID28: Phonons

ID32: soft X-ray IXS

ID15B: Compton: 30%
Incident photon energy is tuned through the 2p\(_{3/2}\) edge.

The radiative decay channel, following the filling of the 2p\(_{3/2}\) core hole, is monitored.
Resonant IXS from core electrons - II

“XAS beyond the core hole lifetime broadening”

- $E_{\text{scatt}}$ fixed, $E_{\text{inc}}$ tuned through absorption edge.
- Spectral sharpening by energy selection of emission channel.

Partial Fluorescence Yield X-ray Absorption Spectroscopy
or
High Energy Resolution Fluorescence Detected XAS

\[ 1/\Gamma_{PFY} = \sqrt{\frac{1}{\Gamma_{2p}^2} + \frac{1}{\Gamma_{4d}^2}} \]

Pt L\(_3\)-edge
\[ \Gamma_{L3} = 7 \text{ eV} \]
\[ \Gamma_{M4,5} = 1.9 \text{ eV} \]

Significant spectral sharpening !!!

RIXS from core electrons– Applications 1

CO oxidation over gold nano-particles by high energy resolution XANES

Conventional Emission Spectrometer

In-situ study

Incident photon energy is tuned through the oxygen K-edge

Soft X-rays $\Rightarrow$ (U)HV environment, surface sensitivity (?), experimental constraints

X-ray Raman scattering - II

Role of incident photon energy in XAS is played by the energy transfer in XRS

\[ E_{1s} + e_k = h\omega_1 \]

\[ E_{1s} + e_k = h\omega = h\omega_1 - h\omega_2 \]

Certain freedom in the choice of the incident photon energy

Hard X-rays => Bulk sensitivity; Access to buried layers
High pressure and/or temperature
pyrolytic graphite (1 mm) carbon K-edge: 284 eV 
Q = 50 nm⁻¹
borosilicate glass (130 µm)
oxygen K-edge: 540 eV
Q = 97 nm\(^{-1}\)
X-ray Raman scattering – Example 1

Microscopic structure of water at elevated P and T

Resistively heated diamond anvil cell

Direct tomography with chemical-bond contrast

Sample of carbon fibre-reinforced silicon carbide

3D map of the $sp^2$ chemical bonds (different colors represent different carbon bond orientations).

IXS from phonons - I

Relevance of phonons

Superconductivity

Thermal Conductivity

Phase stability

Sound velocities and elasticity
IXS from phonons - II

Vibrational spectroscopy: a short history

Infrared absorption - 1881
W. Abney and E. Festing, R. Phil. Trans. Roy. Soc. 172, 887 (1881)

Brillouin light scattering - 1922

Raman scattering – 1928
C. V. Raman and K. S. Krishnan, Nature 121, 501 (1928)

TDS: Phonon dispersion in Al – 1948
P. Olmer, Acta Cryst. 1 (1948) 57

INS: Phonon dispersion in Al – 1955

IXS: Phonon dispersion in Be – 1987

NIS: Phonon DOS in Fe – 1995
IXS from phonons - III

- Energy transfer:
  \[ E_f - E_i = E \quad (0.001 - 1 \text{ eV}) \]
- Momentum transfer:
  \[ \vec{k}_f - \vec{k}_i = \vec{Q} \quad (0.0001 - 100 \text{ nm}^{-1}) \]
Brockhouse (1955)

**Thermal neutrons:**

\[ E_i = 25 \text{ meV} \]
\[ k_i = 38.5 \text{ nm}^{-1} \]
\[ \Delta E/E = 0.01 - 0.1 \]

Burkel, Dorner and Peisl (1987)

**Hard X-rays:**

\[ E_i = 18 \text{ keV} \]
\[ k_i = 91.2 \text{ nm}^{-1} \]
\[ \Delta E/E \leq 1 \times 10^{-7} \]
IXS from phonons - V

IXS: Scattering kinematics

\[ (\vec{k}_f, E_f) \]
\[ (\vec{k}_i, E_i) \]
\[ Q, E \]
\[ d\Omega \]

\[
\begin{align*}
E &= E_i - E_f \\
|Q| &= 2|k_i| \sin(\theta)
\end{align*}
\]

momentum transfer is defined only by scattering angle
Interplay between structure and dynamics on $\approx$ nm length scale
Relaxations on the picosecond time scale
Excess of the VDOS (Boson peak)
Nature of sound propagation and attenuation

$Q = 4\pi/\lambda \cdot \sin(\theta)$
$\Delta E = E_i - E_f$

Disordered systems: Explore new $Q$-$\Delta E$ range
IXS from phonons - VII

Small sample volumes: \(10^{-4} \text{ – } 10^{-5} \text{ mm}^3\)

- (New) materials in very small quantities
- Very high pressures \(> 1\text{Mbar}\)
- Study of surface phenomena
IXS

\[ \frac{\partial^2 \sigma}{\partial E \partial \Omega} = r_0^2 \frac{k_1}{k_2} (\vec{e}_1 \cdot \vec{e}_2) f(Q)^2 S(\vec{Q}, E) \]

- no correlation between momentum- and energy transfer
- \( \Delta E/E = 10^{-7} \) to \( 10^{-8} \)
- Cross section \( \sim Z^2 \) (for small Q)
- Cross section is dominated by photoelectric absorption \( \sim \lambda^3 Z^4 \)
- no incoherent scattering
- small beams: 100 \( \mu \)m or smaller

INS

\[ \frac{\partial^2 \sigma}{\partial E \partial \Omega} = b^2 \frac{k_1}{k_2} S(\vec{Q}, E) \]

- strong correlation between momentum- and energy transfer
- \( \Delta E/E = 10^{-1} \) to \( 10^{-2} \)
- Cross section \( \sim b^2 \)
- Weak absorption => multiple scattering
- incoherent scattering contributions
- large beams: several cm
IXS from phonons - XI

Phonon dispersion and phonon density of states

- **single crystals**
  - triple axis: (very) time consuming
  - time of flight: not available for X-rays

- **polycrystalline materials**
  - reasonably time efficient
  - limited information content
Doping dependence in SmFeAsO$_{1-x}$F$_y$

M. Le Tacon et al.; Phys. Rev. B 80, 220504

e-ph coupling in $\alpha$-U

S. Raymond et al.; PRL 107, 136401
**IXS from phonons – functional materials**

**Piezoelectrics PbZr$_{1-x}$Ti$_x$O$_3**

J. Hlinka et al.; PRB 83, 040101(R)

**Skutterudites**

M.M. Koza et al.; PRB 84, 014306

**InN thin film lattice dynamics**

J. Serrano et al.; PRL 106, 205501
Sound velocities in Earth’s core

\[ V_p = 3.00 \rho - 6977 \]
\[ V_p = 1.82 \rho - 4169 \]
\[ V_p = 1.89 \rho - 8505 \]
\[ V_p = 0.94 \rho - 1466 \]
\[ V_c = 1.67 \rho - 3285 \]
\[ V_c = 1.07 \rho - 1392 \]

J. Badro et al.; Earth Plan. Science Lett. 98, 085501

Elastic anisotropy in Mg\textsubscript{83}Fe\textsubscript{0.17}O

D. Antonangeli et al.; Science 331, 64
Instrumentation for IXS - I

$\Delta E/E = 10^{-4}$ to $10^{-5}$

$\vec{Q} = \vec{K}_{\text{out}} - \vec{K}_{\text{in}}$

$R = 1$ or $2$ m

Si (Ge) $(333, 440, 551, \ldots)$ crystals

Bragg angles $\theta_B: 65^\circ - 90^\circ$

$\Delta E = 0.15$ – $2$ eV
Instrumentation for IXS - II

Crystal analysers

**Anodic Bonded Elastically Bent Analyzers**
- medium energy resolution
- Very thin wafers (Si)
- Curvature radius 1 and 2 m
- Energy compensation algorithm

**Diced Analyzers**
- very high energy resolution
- cube size 0.8 mm x 0.8 mm x 3 mm
- Curvature radius 1, 2, 6.5 m
- Energy compensation algorithm

In-house R&D: Roberto Verbeni et al; J. Synchrotron Rad. 16, 469 (2009)
Instrumentation for IXS - III

ID20 @ ESRF

spectrometers  monitoring  monochromators  focusing

lateral view
Instrumentation for IXS - IV

RIXS Spectrometer (ID20 - EH2)

Scan of both incident and scattered energy

5 bent or diced analysers
ΔE down to 25 meV
High flux and/or several q’s

1x5 Maxipix Detectors
55 μm pixel size
Energy compensation algorithm
Background removal
Instrumentation for IXS - V

X-ray Raman Spectrometer ID20 - EH3

Scan of incident energy

72 analysers
$\Delta E: 0.4 - 1.5$ eV

6x1 Maxipix Detectors
55 $\mu$m pixel size

3 moduli in the vert. plane
3 moduli in the horiz. plane

sample
KB mirrors
Instrumentation for IXS - VI

IXS set-up on ID28 at ESRF

Monochromator:
Si(n,n,n), $\theta_B = 89.98^\circ$
$n=7-13$
$\lambda_1$ tunable

Analyser:
Si(n,n,n), $\theta_B = 89.98^\circ$
$n=7-13$
$\lambda_2$ constant

$Q = \frac{4\pi}{\lambda \cdot \sin(\theta)}$

$\lambda = 2 \cdot d(T) \cdot \sin \theta_B$

$\frac{\Delta d}{d} = \frac{\Delta E}{E} = -\alpha(T) \cdot \Delta T$

$\alpha = 2.58 \cdot 10^{-6} \text{ 1/K at room temperature}$
**Instrumentation for IXS - VII**

**ID28 @ ESRF**

### 9- analyser crystal spectrometer

<table>
<thead>
<tr>
<th>Reflection</th>
<th>$E_{\text{inc}}$ [keV]</th>
<th>$\Delta E$ [meV]</th>
<th>Q range [nm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8 8 8)</td>
<td>15.816</td>
<td>6</td>
<td>2 - 73</td>
</tr>
<tr>
<td>(9 9 9)</td>
<td>17.794</td>
<td>3.0</td>
<td>1.5 - 82</td>
</tr>
<tr>
<td>(12 12 12)</td>
<td>23.725</td>
<td>1.3</td>
<td>0.7 - 100</td>
</tr>
</tbody>
</table>

Spot size on sample: 270 x 60 $\mu$m\(^2\) -> 14 x 8 $\mu$m\(^2\) (H x V, FWHM)
Further reading

• W. Schülke; *Electron dynamics by inelastic x-ray scattering*, Oxford University Press (2007)

• J.P. Rueff and A. Shukla; Rev. Mod. Physics 82, 847 (2010) *Inelastic x-ray scattering by electronic excitations under high pressure*

• L.J.P. Ament et al.; Rev. Mod. Physics 83, 705 (2011) *Resonant inelastic x-ray scattering studies of elementary excitations*
