XAFS facility at Indus-2 and results

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Schematic view of Indus complex

Injection energy = 550 MeV

Indus-1
(450 MeV, 100 mA)
Total no. of beamline ports = 27

Ports for bending magnet beamlines = 22

12 Beamlines operational

- MCD/PES (BL-1)
- Soft X-ray (BL-3)
- Imaging (BL-4)
- ARPES/PEEM (BL-6)
- X-ray Lithography (BL-7)
- Dispersive EXAFS (BL-8)
- Scanning EXAFS (BL-9)
- EDXRD (BL-11)
- ADXRD (BL-12)
- GIXS (BL-13)
- XPES (BL-14)
- XRF-microprobe (BL-16)
- SWAXS (BL-18)
- Protein Crystallography (BL-21)
- X-ray Beam Diagnostic (BL-23)
- Visible Beam Diagnostic (BL-24)
View of Experimental Hall, Indus-2
XAFS TECHNIQUE

Spectroscopic tool which provides structural information about a sample by the analysis of its x-ray absorption spectrum, *does not require long range order.*

How?: Absorption Spectrum generated using tunable bright X-ray source: Two regions

XAFS is a type of diffraction pattern produced by the interference of outgoing and back scattered electron waves (in-situ LEED)

X-rays are absorbed by all matter by Photoelectric effect
X-ray Absorption Fine structure (XAFS) Technique

Information from XAFS

**XANES**

- Oxidation state
- Coordination chemistry (tetrahedral, octahedral) of the absorbing atom
- Orbital occupancy

**EXAFS**

- Radial distribution of atoms around the photoabsorber (bond distance, number and type of neighbours)

Application:

- Local structure in non-crystalline matter
- Local environment of an atomic impurity in a matrix of different atomic species
- Study of systems whose local properties differ from the average properties
- Detection of very small distortions of local structure

**Powerful tool for:** Magnetic materials, Materials Science (high Tc, CMR,..), Amorphous and liquid systems, Thin films and Surface Science.

\[
\chi(k) = S_0^2 \frac{N A(k)}{k R^2} e^{-2R} \sin(2k R + \phi(k) + \phi_c) e^{-2k^2 \sigma^2}
\]
Requirements of EXAFS experiment

- XAFS spectra consist of small variations in the absorption coefficient $\mu(E)$
- One requires S/N ratios better than $10^3$ in order to determine the spectra accurately enough in the region $\approx 600-1000$ eV
- An intense & tunable beam is required to obtain good data in reasonable time (minutes to hours); $10^{10}$ photons/sec or better (SR is must)
- Intensity of beam should not very much during scan
- Energy band width should be order of 1eV to resolve EXAFS features
- Beam at sample should be as small as possible: microns to mm size

Above requirements:
- impose significant demands on the design and quality of the mechanics and control system of beamline that is to be used for XAFS.

Requirements of Beamline

Experimental station:
- wide range of sample environments [ T, P, magnetic field, vacuum, “in situ”... ]
- Sample should be homogeneous in thickness & particle size

Resources:
Experimental geometry for XAFS measurements:

1. Energy Dispersive type

Suitable for:

- Sub-second data collection, but
  - Transmission only.
  - Long air path.
  - Energy range/resolution more limited than scanning techniques.

- Polychromatic beam
  \( \Delta E = 300 \text{ to } 1000 \text{eV} \)

2. Energy Scanning type

Suitable for:

- High resolution, fluorescence mode, thin film, dilute samples

Most of the Synchrotron Radiation facilities have both Dispersive & Scanning type EXAFS Beamlines to cater the needs of wide variety of samples.
XAFS Beamlines at Indus-2

• Energy Dispersive EXAFS BL( BL-08)
  • Open to users since March 2008

• Energy Scanning EXAFS BL (BL-09)
  • Open to users since Feb. 2013.

- K-edges of elements from
  
  Ti (4.966keV) to Mo(20000eV)

- L-edges:
  
  Rare earths and other high Z elements e.g. W, Pb...

Beamlines are complex instruments, a interface between storage ring & sample that perform a variety of functions:

Safely transporting the X-rays to the experimental area; Preparing the beam for the experiment by precollimating, monochromating, focussing, and shuttering the beam using X-ray optics; performing precisely timed data acquisition that is synchronized to the motions of beamline optics.
Characteristics of Dispersive EXAFS (BL-8) at Indus-2

- Source: Bending magnet port BL-08
- Energy range: 5-20keV
- Resolution: $10^{-4}$ ($\Delta E/E$)
- Band pass: 300ev to 2000eV
- Flux: $10^{12}$ photons/sec/1000eV
- Polychromator: Si(111)
- Detector: CCD(2k x 2k ; pixel: 13.5x13.5 μm)
Optical Layout of DEXAFS Beamline at Indus-2

Top view

Source
Shielding Wall
Beam Aperture
Slit System
Pre-Mirror
Bent Crystal Polychromator
Slit System
Sample
Detector

BW-1

14,000 mm
18,000 mm
16,500 mm
15,000 mm

Used for horizontal focusing – cum – dispersion

Side view

S

BW-1

C

B

D

C


Used for vertical focusing – cum – higher harmonic rejection
Beam spot measured at sample position

Sample size can be as small as 500 microns.
Experimental station

Sample stage

Focused beam

Theta stage
Bender chamber

CCD

SR from BL

2 theta stage on
Pneumatic pad
View of ED-EXAFS BL inside the hutch at Indus-2
**Absorption Spectra of Mo Foil**

20 keV Setting

12.03.08@ 6 ma/2 GeV

**Complete Spectrum Taken In 1 Second**

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Mo & Nb absorption edge obtained at 20 keV setting

**Complete Spectrum Taken In 1 Second**

---

**Energy**

<table>
<thead>
<tr>
<th>Energy</th>
<th>20 keV</th>
<th>13 keV</th>
<th>11 keV</th>
<th>7 keV</th>
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</thead>
<tbody>
<tr>
<td>Resolution</td>
<td>$5 \times 10^3$</td>
<td>$7.5 \times 10^3$</td>
<td>$8.5 \times 10^3$</td>
<td>$\sim 10^4$</td>
</tr>
</tbody>
</table>

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Conclusion:

The present work is a comparative study of the XAFS spectra recorded at the BL-8 beamline with those recorded at three other well-known synchrotron EXAFS beamlines. For this study, two examples have been taken, one of copper metal (strong EXAFS oscillations case) and another of copper complex (weak EXAFS oscillations case). Theoretical models have been generated for both copper metal and the complex and fitted to their respective experimental EXAFS spectra to obtain the structural parameters. The structural parameters obtained by using BL-8 beamline have been found to be comparable to those obtained from other beamlines. Also, the results obtained from EXAFS data for the copper complex have been found to be comparable with the crystallographic results. Thus, it is seen that the spectra recorded at the BL-8 beamline
2. Energy Scanning EXAFS beamline (BL-9)
Energy Scanning Type EXAFS beamline

Source: Bending magnet

Target Specifications:

• Energy Range: 4 keV - 25 keV
• Resolution ($E/\Delta E$): $10^4$
Schematics of Optical layout of Scanning EXAFS beamline

Detectors:
Transmission Mode: 3 Ionization Chambers
Florescence Mode: Lytle/Vortex
Mechanical layout of Scanning EXAFS Beamline (BL-9)

BL length: ~37 meter from source point

Maintained at UHV
Scanning XAFS beamline

Sample environment: CCR He cryostat up to 10 K
High temperature cell up to 1000 K
Available detectors:
- Ionisation chambers (3 Nos) for transmission mode EXAFS
- Lytle & Vortex (SDD) Detectors for fluorescence mode
First result from BL-9

Beam at Front-end (at 16 meters from source point)

Observed on 22\textsuperscript{nd} Sept 2012
23:45 hrs

First absorption spectrum recorded
22nd Nov. 2012

![Graph of EXAFS Spectra of Cr\textsubscript{2}O\textsubscript{3}](image)
Data to illustrate the performance of Scanning EXAFS beamline

XAFS spectra of vanadium compounds in transmission mode

XAFS spectrum of \( \text{Y}_2\text{O}_3 \) thin film recorded in fluorescence mode

Data to illustrate the performance of Scanning EXAFS beamline

XAFS spectrum of ZnO nanomaterial recorded at 10K

Repeated EXAFS spectra of V metal foil
Examples of studies
EXAFS studies of doped ZrO$_2$ systems

Samples prepared at: Chem. Div., BARC; Applications: Intermediate temp. solid electrolytes

- Zirconia exhibits high anionic conductivity when doped with aliovalent cations which initiates the generation of oxygen ion vacancies for charge compensation.

- Yttria-stabilized zirconia (YSZ) typically at 8mol% yttria, is the most common material used in Solid Oxide Fuel Cells (SOFCs).

- Limitation
  Operate at relatively high temperatures of around 1100–1300K to achieve adequate ionic conduction. This has prompted the search for alternate materials with equivalent ionic conductivity at lower temperature.

Measurements were done on two sets of samples at the Zr K-edge, viz., (i) Zirconia doped with 11 mol% of Gd$^{3+}$, Nd$^{3+}$, La$^{3+}$, where the dopant cations are in the order of increasing ionic radii and (ii) zirconia doped with 7, 9, 11 and 13 mol% of Gd.

- Aim of the study

  To have insight into the mechanism of creation of oxygen vacancies and on their locations within the ZrO$_2$ matrix as a function of dopant ion size and Gd doping concentration, as there are contradictory information in the literature regarding the same.
**Variation of dopant cation size:**

- for larger size dopants (viz., Nd and La) the oxygen vacancies are created near the dopant site leaving the host sites unperturbed

- for smaller size dopant viz., Gd, oxygen vacancies are created near the host Zr site.

- Zr-Zr coordination also confirms that with increase in the size of the dopant cation the disorder near the host Zr cation is decreased.

- The above conclusion has been confirmed by ab-initio calculations for La-doped ZrO2 systems.
  
  (Acknowledgement: Dr. Aparna Chakrabarti, RRCAT, Indore)

- Since the Gd-doped samples have the minimum oxygen coordination, it can be concluded that Gd is most effective in generating oxygen vacancies.
**Variation in Gd concentration:**

- With increase in Gd concentration from 7% to 13%, the total oxygen coordination decreases significantly up to a doping level of 13% above which the oxygen coordination increases possibly due to clustering of Gd ions inside ZrO$_2$ lattice.

Later verified by Gd-edge EXAFS measurements

9-11% Gd doping is optimum for creation of vacancies near the Zr sites and hence for increasing its ionic conductivity

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Structural collapse of layered GaOOH nanorods by Eu ions

Samples prepared at: Chem. Div. BARC

- Used for the synthesis of Gallium oxide based luminescent materials and devices.
- To study changes in local environment around Ga in GaOOH nanorods brought about by the presence of lanthanide ions during its synthesis.

Measurements carried out at Ga K-edge on GaOOH: Eu (x%) x = 0, 0.5, 0.75, 1.0 & 3.0

XRD pattern of Undoped GaOOH

Gradual long range breakdown starting @ 1% Eu doping

EXAFS spectra do not show any local structure distortion

But disorder increases
There is no change in Ga-O bond length. Eu\(^{3+}\) do not replace Ga\(^{3+}\) as such.

However, the disorder increases appreciably even with the introduction of a small amount of Eu\(^{3+}\) (0.5\%) and reaches a maximum for 1\% Eu doping.

- Eu\(^{3+}\) ions/species get incorporated at the inter-layers of GaOOH wherein it preferentially interacts with OH groups to form Eu(OH)\(_3\) species.

- Formation of such hydroxide species destabilizes the layered structure of GaOOH.

<table>
<thead>
<tr>
<th></th>
<th>GaOOH</th>
<th>0.5Eu</th>
<th>0.75Eu</th>
<th>1.0Eu</th>
<th>3.0Eu</th>
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<tbody>
<tr>
<td>Ga-O1 (1.852 Å; 3)</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>R1</td>
<td>2.05</td>
<td>2.08</td>
<td>2.07</td>
<td>2.06</td>
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<tr>
<td>N1</td>
<td>3</td>
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<td>3</td>
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<tr>
<td>(\sigma^2_i)</td>
<td>0.0077</td>
<td>0.012</td>
<td>0.0135</td>
<td>0.017</td>
<td>0.011</td>
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<tr>
<td>Ga-O2 (1.975 Å; 3)</td>
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<tr>
<td>R2</td>
<td>2.18</td>
<td>2.22</td>
<td>2.20</td>
<td>2.19</td>
<td>2.20</td>
</tr>
<tr>
<td>N2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
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<tr>
<td>(\sigma^2_i)</td>
<td>0.006</td>
<td>0.0084</td>
<td>0.006</td>
<td>0.0081</td>
<td>0.005</td>
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<td>Ga-H (2.513 Å; 3)</td>
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<tr>
<td>R3</td>
<td>2.51</td>
<td>2.51</td>
<td>2.51</td>
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<tr>
<td>N3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>(\sigma^2_i)</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
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</table>

GaFeO$_3$ is a multiferroic system: demonstrates piezoelectricity and ferrimagnetism.

- Orthorhombic structure with two Ga sites (tetrahedral and octahedral) and two Fe sites (both octahedral)
- Ferrimagnetism occurs due to cationic site disorder and magnetic transition temperature is 200K

No structural change has been observed at magnetic transition temperature from XRD/Neutron Diffraction.

Low temperature X-ray Absorption Spectroscopy Study of GaFeO$_3$

*There is clear signature of change in bond lengths at the magnetic transition temperature of 200 K

EXAFS measurements clearly establishes the fact that magnetic transition in GFO system is related to cationic site disorder i.e. higher occupancy of Fe atoms in octahedral Ga sites.
A new Cu-grafted mesoporous material has been designed, which works as a heterogenous catalyst for converting different aryl halides with thiourea and benzyl bromide to produce aryl thioethers.

EXAFS measurements has unambiguously established that local structures around Cu atom in the reused catalyst remain unchanged after the catalytic reaction.

EXAFS to probe the Unexpected Adsorption-Coupled Reduction of U(VI) to U(V) and U(IV) on Borassus flabellifer-Based Adsorbents

Sample prepared: P. S. Padmaja et al., M. S. University of Baroda, Vadodara.

- Palm shell based absorbents (Biomaterial) prepared under different thermochemical condition is tested for their potential in absorption of uranium and absorption mechanism is understood using EXAFS technique.

- Normalized XANES spectra of different samples with standards UO2CO3 and UF4 samples indicate that uranium may simultaneously be present in different oxidation states.

- U-O axial and equatorial bond length found by EXAFS analysis are in good agreement with the XANES prediction.

- Fourier transforms show that the intensities of the first and second shell peaks, a function of coordination number and Debye-Waller factor vary for different samples which suggests the presence of mixed uranium species.

In-situ EXAFS study of ZnO nanoparticles in different gaseous environments

Size and shape dependent structural parameters of ZnO nanostructures have been investigated under different ambience of gases.

Applications: Gas sensors

This study aims at understanding the mechanism of absorption or desorption of gases in the nanocrystalline ZnO samples.

Samples with particle sizes varying from 5-100 nm were investigated at the Zn K-edge (9659 eV) in air, chlorine and hydrogen sulphide atmospheres.

The theoretical model assumed for fitting has 3 O atoms at 1.98 Å, 1 O atom at 1.99 Å and 6 Zn atoms at 3.21 Å.

The experimental versus $R$ spectra and the theoretical fits of the ZnO samples in air.

As the particle size decreases Zn-O bond lengths slightly increase in case of air-exposed sample giving an average value of the bulk and surface Zn-O bonds.

In Cl$_2$ atmosphere, Zn-O bond length slightly decreases possibly because O vacancies in the surface are filled up by Cl atoms.

For samples treated under H$_2$S atmosphere, on the other hand, Zn-O bond lengths do not show any change with decrease in particle size.

With particle size 20 nm and below the bond length and coordination number of the Zn-Zn shell decrease and the Debye-Waller factor increases significantly.

This implies drastic break down of the ZnO structure with reduced particle size below 20 nm.

Investigation into variations in local cationic environment in layered oxide series InGaO$_3$(ZnO)$_m$ (m=1-4)

- Layered oxides have distinct structure and electronic properties.
- Transparent conducting oxides combine both electrical conductivity and optical transparency in single material.
- Useful in solar cells, flat panel displays etc

Polyhedral representations of InGaO$_3$(ZnO)$_m$; XRD representation

EXAFS spectra for InGaO$_3$(ZnO)$_m$ at Zn K-edge, & Fourier transformed EXAFS spectra

**Problem:**
No clarity regarding the exact geometries of Zn or Ga

**Approach:**
EXAFS spectroscopic measurements at the Zn & Ga K-edges (TBP to Td)

Zn and Ga atoms are coordinated by 5 oxygen atoms for both m=1 and m=2 but for m=3 Zn and Ga atoms are surrounded by 4 oxygen atoms.

One of the apical Ga-O bond is found unexpectedly large (2.135 Å) for m=2 which is results of position of Ga in the equatorial triangle of the trigonal bipyramid.

There is no contribution of Ga-In shell in second peak since at higher m values the distance of the Ga-containing layer increase from the octahedral InO₂ layers.

Coordination of the Ga-Zn shell decreases and that of the Ga-Ga shell increases for m=3 sample compared to that of the m=2 sample.

<table>
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<tr>
<th>Paths</th>
<th>Parameters</th>
<th>m=1</th>
<th>m=2</th>
<th>m=3</th>
<th>m=4</th>
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<tbody>
<tr>
<td>Zn-O</td>
<td>R (Å)</td>
<td>1.91(±0.015)</td>
<td>1.91(±0.003)</td>
<td>1.89(±0.005)</td>
<td>1.91(±0.007)</td>
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<tr>
<td>N</td>
<td>3(±0.03)</td>
<td>3.78(±0.024)</td>
<td>2.85(±0.039)</td>
<td>3.0(±0.08)</td>
<td></td>
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<tr>
<td>σ²</td>
<td>0.006(±0.001)</td>
<td>0.006(±0.001)</td>
<td>0.006(±0.001)</td>
<td>0.007(±0.001)</td>
<td></td>
</tr>
<tr>
<td>Zn-O</td>
<td>R (Å)</td>
<td>2.34(±0.001)</td>
<td>2.38(±0.018)</td>
<td>2.24(±0.018)</td>
<td>2.21(±0.02)</td>
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<tr>
<td>N</td>
<td>2(±0.09)</td>
<td>0.91(±0.15)</td>
<td>1.37(±0.17)</td>
<td>0.96(±0.11)</td>
<td></td>
</tr>
<tr>
<td>σ²</td>
<td>0.009(±0.002)</td>
<td>0.005(±0.003)</td>
<td>0.01(±0.003)</td>
<td>0.003(±0.001)</td>
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<tr>
<td>Total O atoms</td>
<td>5</td>
<td>4.69</td>
<td>4.22</td>
<td>3.96</td>
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X-ray absorption spectroscopy of Sb doped Bi₂UO₆

Samples prepared at FCD, BARC

The BiO sheet resembles a fluorite structure where each Bi atom is coordinated by 4 in-plane oxygens (O₂ type) and three out of plane oxygens (O₃ type) which connects it to the UO₈ polyhedra.

- Sb doping does not alter the UO₈ polyhedra but Bi is substituted by Sb (similar ionic radius)
- The above result is consistent with the fact that Sb being more electronegative than Bi, Sb doping should increase effective positive charge at Bi sites.

XANES study

Absorption edge shifts due to change in oxidation state and also due to change in anionic species/chemical environment:

Effective Charge

High resolution XANES study:
Shift in absorption edge
(in collaboration with NPD, BARC)

D. Joseph, S. Basu, S.N. Jha and D. Bhattacharyya,
D. Joseph, A.K. Yadav, S.N.Jha and D.Bhattacharyya
<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>Journal/Book/Conference/Thesis/Other Details</th>
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<tr>
<td>3.</td>
<td>Origin of giant dielectric constant and magnetodielectric study in Ba(Fe0.5Nb0.5)O3 nanoceramics</td>
<td>Journal of alloy and comp. 591 (2014) 224.</td>
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<tr>
<td>8.</td>
<td>Investigations into variations in local cationic environment in layered oxide series InGaO$<em>{4m}$ZnO$</em>{1-m}$ (m = 1-4)</td>
<td>Dalton Transactions 43 (2014) 2120.</td>
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<td>17.</td>
<td>XPS, EXAFS, and FTIR As Tools To Probe the Unexpected Adsorption-Coupled Reduction of U(VI) to U(V) and U(IV) on Borassus fabellifer-Based Adsorbents</td>
<td>Langmuir 28 (2012) 16038.</td>
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<td>23.</td>
<td>On the method of calibration of the energy dispersive EXAFS beamline at Indus-2 and fitting theoretical model to the EXAFS spectrum</td>
<td>Sadhana (India) 36 (2011) 339.</td>
</tr>
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</table>
Summary

- XAFS is an extremely versatile technique for local structure probe.
- XAFS allows the determination of the oxidation state, the coordination motif of the probed element, the identity and the number of adjacent atoms and the absorber-ligand distances.
- Find applications in: Magnetic materials to Bioinorganic chemistry, catalysis, environmental science, physics, material science etc.
- Dispersive EXAFS beamline (BL-8) can be used for in-situ studies, kinetic catalysis etc.
- Scanning EXAFS beamline can be used for dilute samples and thin film samples in fluorescence mode/transmission mode.
- Sample environments available: 10K to 1000K

For booking beam time: register @ https://www.info-rrcat.ernet.in/beamline/

For details of beamline: http://www.cat.gov.in/technology/accel/srul/beamlines/exafs.html
Collaborators

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N.L. Mishra & group
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